



## Evaluation of antioxidant capacity in coffees marketed in Colombia: Relationship with the extent of non-enzymatic browning



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### ABSTRACT

Fifty-eight samples of commercial Colombian coffee with different characteristics (soluble, ground, decaffeinated, etc) were evaluated for antioxidant capacity (AC) (ABTS and FRAP), total soluble phenolics (TP), browning index (BI), color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$  and  $h^*$ ), HMF and furfural. The AC in Colombian coffees was very varied (164–1000, 100.8–885.9  $\mu\text{mol}$  of Trolox equiv/g and 12.5–127 mg gallic acid equiv/g, respectively for ABTS, FRAP and TP). AC, TP, BI, color, HMF and furfural values were higher ( $p < 0.05$ ) in soluble coffees than in ground ones, showing the lyophilized samples which showed the highest average values. Significant lineal correlations ( $p < 0.05$ ) were found between AC and color parameters, BI, HMF. No significant ( $p < 0.05$ ) differences in the AC between the different types of coffee were found. This work confirms the direct relationship between the rate of non-enzymatic browning and antioxidant capacity.

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### 1. Introduction

The coffee bean is an important product all over the world and its trade is increasing year after year. In Colombia, coffee is the flagship product of the economy with a production of  $7.2 \times 10^4$  tons per year, i.e. 11.4% of world market (Naranjo, Vélez, & Rojano, 2011). The coffee is widely consumed as a beverage all over the world and in Colombia can be found wide variety of coffees in trade, which can be classified according to the degree (light, medium, dark) and type of roasting (natural and torrefacto), soluble (lyophilized), ground, flavored, with designation of origin (DO), organics, decaffeinated and mixtures, among others (Colcafe, 2015; Juan Valdez, 2015).

Coffee is also known to be a rich source of compounds with potent antioxidant activity. The AC of coffee has been attributed to its content in polyphenols and melanoidins (Delgado-Andrade & Morales, 2005). During roasting process, the green coffee beans are subjected to temperatures between 200 and 250 °C depending on the degree of roasting. This process causes significant physico-chemical changes which involve thermal degradation of natural phenolic antioxidants, generation of flavors and brown-colored

compounds (melanoidins) products of the Maillard reaction (MR) (Liu & Kitts, 2011). Melanoidins are formed in the final stages of the MR, these compounds have been associated with important biological activities as antioxidants (Pastoriza & Rufián-Henares, 2014), chelating activity (Tagliazucchi, Verzelloni, & Conte, 2010) and antimicrobial (Rufián-Henares & Morales, 2008).

The AC of coffee can be influenced by several factors, such as the variety and origin of coffee (Parras, Martínez, Jimenez, & Murcia, 2007), the roasting degree (Nicoli, Anese, Manzocco, & Lerici, 1997), the type of roasting (natural or torrefacto), their blends (López-Galilea, de Peña, & Cid, 2007), and the technological parameters applied for coffee brew extraction. Several methods that have been used to evaluate the AC of coffee include FRAP, ABTS and the determination of TP (Borrelli, Visconti, Mennella, Anese, & Fogliano, 2002; Sánchez-González, Jiménez-Escrig, & Saura-Calixto, 2005).

The color is an important characteristic in roasted coffee that can be evaluated by the color parameters  $L^*$ ,  $a^*$  and  $b^*$  (Summa, de la Calle, Brohee, Stadler, & Anklam, 2007). During the roasting process of coffee beans, the lightness parameter  $L^*$  was negatively correlated to the roasting time at a given temperature, and a linear correlation between the reciprocal of lightness and roasting time was confirmed (Sacchetti, Di Mattia, Pittia, & Mastrocola, 2009). In fact, the radical scavenging capacity is a linear function of  $L^*$

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(Summa et al., 2007). The extent of browning is measured by the absorbance at 420 nm and is a useful end-point measurement for quantifying the yield of high molecular weight melanoidins (Wijewickreme, Kitts, & Durance, 1997). Brown color property while is useful indicator for the development of MR, is not directly correlated to the antioxidant potential of crude or fractionated MR products (MRPs) (Liu & Kitts, 2011).

5-Hydroxymethylfurfural (HMF) and furfural, are formed during heat processing of foods by acid-catalyzed dehydration of reducing sugars and MR (Antal, Mok, & Richards, 1990) and have been used for years as quality indicators of thermally processed food.

Although many studies have been conducted using different methods of extraction and preparation of samples for measurement of color, MRPs and AC in order to relate coffee AC and the degree of roasting, few studies have evaluated the AC and its relation to the degree of browning in commercial coffees of different types. Since the Colombian coffee is exported to more than 90 countries (Federación Nacional de Cafeteros de Colombia, 2011), the aim of this study was to evaluate the relation between the antioxidant activity and non-enzymatic browning degree, in order to know if the type (degree and type of roasting, soluble, ground, flavored, with designation of origin (DO), organics, decaffeinated and mixtures, etc.) of coffee can influence the parameters studied.

## 2. Materials and methods

### 2.1. Samples and reagents

Fifty-eight samples of commercial Colombian coffee with different characteristics (soluble, ground, flavored, with DO, decaffeinated and roasting degree (dark, medium, light) and type (natural or torrefacto)) were obtained in triplicate from three different local markets (Table 1).

2,2'-Azino-bis (3-ethylbenzenothiazoline-6-sulfonic acid) (ABTS), gallic acid and 2,4,6-Tri (2-pyridyl)-s-triazine (TPTZ) were purchased from Sigma-Aldrich Chemical (Oakville-Ontario, Canada). Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was obtained from MP Biomedicals (Illkirch-Graffenstaden, France), Folin-Ciocalteu reagent (2.0 N) and 2-furaldehyde from Merck (Darmstadt, Germany) and HMF from Alfa Aesar (MA, USA).

### 2.2. Antioxidant and total phenolics determination

#### 2.2.1. Sample preparation

Coffee extracts were used in this study. Extraction of antioxidant compounds was performed following the method described by Contreras-Calderón, Calderón-Jaimes, Guerra-Hernández, and García-Villanova (2011). 0.5 g of the sample were used to extraction. The extracts were stored at  $-18^{\circ}\text{C}$  in amber flasks. The extraction and measurements were made in triplicate.

#### 2.2.2. Measurement of ABTS

The ABTS assay was performed following Re et al. (1999). 100  $\mu\text{L}$  of test sample, diluted appropriately (1/100) with water were used for determination, and absorbance was measured at 730 nm (Varian Cary® 50 UV-vis Spectrophotometer). Aqueous solutions of Trolox (concentrations between 0 and 200  $\mu\text{M}$ ) were used for calibration. Results were expressed as micromoles of Trolox equivalents (TEs) per gram ( $\mu\text{mol}$  of TEs/g).

#### 2.2.3. FRAP assay

The FRAP assay was performed as previously described by Pulido, Bravo, and Saura-Calixto (2000). 30  $\mu\text{L}$  of test sample,

diluted appropriately (1/50) with water were used for determination, and absorbance was measured at 595 nm (Varian Cary® 50 UV-vis Spectrophotometer). Aqueous solutions of Trolox (concentrations between 0 and 500  $\mu\text{M}$ ) were used for calibration. Results were expressed as  $\mu\text{mol}$  of TEs/g.

#### 2.2.4. Total phenolics (TP)

The TP content was determined using the Folin-Ciocalteu assay (Rover & Brown, 2013). 100  $\mu\text{L}$  of test sample, diluted appropriately (1/10) with water were used for determination, and absorbance was measured at 725 nm against the blank (Varian Cary® 50 UV-vis Spectrophotometer). Aqueous solutions of gallic acid (concentration between 0 and 100 ppm) were used for calibration. Results were expressed as mg of gallic acid equivalents (GAEs) per g (mg of GAEs/g).

### 2.3. Color determination

Color was determined using an X-Rite 939 spectrodensitometer and calibrated with a white and black standard. 8 g of sample were placed in Petri dishes (9 cm diameter  $\times$  1.5 cm height) and color was recorded using the CIELab uniform color space at room temperature. Color determined by CIE (Commission Internationale l'Eclairage) classifies color in three dimensions;  $L^*$ , brightness,  $a^*$ , red to green color and  $b^*$ , yellow to blue color. Chroma ( $c^*$ ) and hue ( $h^*$ ) were also measured with spectrodensitometer. The results were expressed in accordance with the CIELAB system with reference to illuminant D65 and with a visual angle of  $0^{\circ}$  (Cortés, Esteve, & Frígola, 2008). The measurements were made in triplicate.

### 2.4. Browning index (BI)

Non-enzymatic browning index was determined with an absorbance measure at 420 nm (Meydav, Saguy, & Kopelman, 1977) with some modifications. Approximately 1.5 g of sample was added to 7 ml of deionized water and centrifuged at 4500 rpm during 10 min at room temperature, this process is repeated twice. The supernatants were clarified with 1500  $\mu\text{L}$  of Carrez I [15% potassium ferrocyanide (w/v)] and 1500  $\mu\text{L}$  of Carrez II [30% zinc acetate (w/v)] and water was added to make the final volume 25 ml. After filtering the mixture, the absorbance is measured at 420 nm. The extracts were made in triplicate.

### 2.5. Hydroxymethylfurfural (HMF) and furfural determination

Furanic compounds were determined in the obtained extracts for browning index, following a method described by Contreras-Calderón, Guerra-Hernández, and García-Villanova (2009) with some modifications. The supernatants were filtered through a 0.45  $\mu\text{m}$  filter and the samples were then analyzed with a Shimadzu HPLC system equipped with a LC-20 AD pump, a SIL-20A HT autosampler, and a SPD-M20A diode-array detector. 20  $\mu\text{L}$  of filtered solution were separated in a reversed-phase  $\text{C}_{18}$  column (LiChroCART 250-4 LiChrospher 100,  $250 \times 4.0$  mm, 5  $\mu\text{m}$ , Merck). HMF (between 0.01 and 120 mg/L) and furfural (between 0.01 and 3 mg/L) were quantified using the external standard method.

### 2.6. Statistical analysis

Multivariate statistics (including principal component analyses (PCA) and cluster analyses (CA)) were employed to quantitatively investigate relationships among the 58 samples of coffee with respect to the 9 indicators (3 related to antioxidant capacity and 6 related to non-enzymatic browning), variables were standardized before the analysis and principal components with

**Table 1**

Characteristics of commercial Colombian Coffees analyzed (according to the label).

| Coffees | Characteristics |               |               |             |          |    |          |
|---------|-----------------|---------------|---------------|-------------|----------|----|----------|
|         | Ground          |               |               |             |          |    |          |
|         | Toasting degree | Toasting type | Decaffeinated | Lyophilized | Flavored | DO | Organics |
| 1       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 2       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 3       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 4       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 5       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 6       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 7       | Dark            | Natural       | –             | –           | –        | –  | –        |
| 8       | Medium-Dark     | Natural       | –             | –           | –        | –  | –        |
| 9       | Medium-Dark     | Natural       | –             | –           | –        | –  | –        |
| 10      | Medium-Dark     | Natural       | –             | –           | –        | –  | X        |
| 11      | Medium-Dark     | Natural       | –             | –           | –        | –  | X        |
| 12      | Medium-Dark     | Natural       | –             | –           | –        | X  | –        |
| 13      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 14      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 15      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 16      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 17      | Medium          | Natural       | –             | –           | Vanilla  | –  | –        |
| 18      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 19      | Medium          | Natural       | –             | –           | Mocha    | –  | –        |
| 20      | Medium          | Natural       | –             | –           | –        | –  | X        |
| 21      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 22      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 23      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 24      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 25      | Medium          | Natural       | –             | –           | –        | –  | –        |
| 26      | Light           | Natural       | –             | –           | –        | –  | –        |
| 27      | Light           | Natural       | –             | –           | –        | –  | –        |
| 28      | Light           | Natural       | –             | –           | –        | –  | –        |
| 29      | –               | Natural       | X             | –           | –        | –  | –        |
| 30      | Medium-Dark     | Natural       | X             | –           | –        | –  | –        |
| 31      | –               | Natural       | –             | –           | –        | X  | –        |
| 32      | –               | Natural       | –             | –           | –        | X  | –        |
| 33      | –               | Natural       | –             | –           | Cinnamon | –  | –        |
| 34      | –               | Natural       | –             | –           | –        | X  | –        |
| 35      | –               | Natural       | –             | –           | –        | –  | –        |
| 36      | –               | Natural       | –             | –           | –        | –  | –        |
| 37      | –               | Natural       | –             | –           | –        | –  | –        |
| 38      | –               | Natural       | –             | –           | –        | X  | –        |
| 39      | –               | Natural       | –             | –           | –        | –  | X        |
| 40      | –               | Natural       | –             | –           | –        | X  | –        |
| 41      | –               | Natural       | –             | –           | –        | X  | –        |
| Soluble |                 |               |               |             |          |    |          |
| 42      | –               | Natural       | X             | –           | –        | –  | –        |
| 43      | –               | Natural       | X             | –           | –        | –  | –        |
| 44      | –               | Natural       | X             | –           | –        | –  | –        |
| 45      | –               | Natural       | X             | X           | –        | –  | –        |
| 46      | –               | Natural       | X             | –           | –        | –  | –        |
| 47      | –               | Torrefacto    | –             | –           | –        | –  | –        |
| 48      | –               | Natural       | –             | X           | Amaretto | –  | –        |
| 49      | –               | Natural       | –             | X           | –        | –  | X        |
| 50      | –               | Natural       | –             | X           | –        | –  | –        |
| 51      | –               | Natural       | –             | X           | Vanilla  | –  | –        |
| 52      | –               | Natural       | –             | X           | Caramel  | –  | –        |
| 53      | –               | Natural       | –             | X           | –        | –  | –        |
| 54      | Dark            | Natural       | –             | –           | –        | –  | –        |
| 55      | –               | Natural       | –             | –           | Caramel  | –  | –        |
| 56      | –               | Natural       | –             | –           | Vanilla  | –  | –        |
| 57      | –               | Natural       | –             | –           | –        | –  | –        |
| 58      | –               | Natural       | –             | –           | –        | –  | –        |

eigenvalues greater than one were selected. CA was made through k-means methods using square Euclidean distances. One-way ANOVA was applied to the results, differences between samples were established using LSD test with a level of significance of 95%. Correlations among variables were assessed by means of the Pearson's correlation test. All the statistical analyses were performed in Stat Graphics Centurion XVI®.

### 3. Results and discussion

#### 3.1. Antioxidant and TP determination

The precision of the entire procedure was carried out, including sample preparation and ABTS, FRAP and TP determinations. The study was carried out using sample 37 ( $n = 8$ ). The relative

standard deviations (RSD) were 14.13, 13.07 and 1.79, with mean values of 267.8, 239.6  $\mu\text{mol}$  of TEs/g and 28.54 mg of GAEs/g, with coefficients of variation (CV) of 5.28%, 5.45% and 6.26% by ABTS, FRAP and TP, respectively.

Coffees commercialized in Colombia showed a wide range of antioxidant capacity (Table 2). The AC evaluated by the three methods varied between 164–1000 (samples 40 and 42, respectively), 100.8–885.9  $\mu\text{mol}$  of TEs/g (samples 25 and 42,

respectively) and 12.5–127 mg of GAEs/g (samples 23 and 51, respectively) for ABTS, FRAP and TP, respectively. The highest antioxidant capacity was found in soluble samples with mean values of 652.9, 680.6  $\mu\text{mol}$  of TEs/g and 88.1 mg of GAEs/g, respectively for ABTS, FRAP and TP, compared with the ground coffee samples with mean values of 298.4, 281.05  $\mu\text{mol}$  of TEs/g and 31.91 mg of GAEs/g, respectively. Significant differences ( $p < 0.05$ ) between these two types of samples were found. This difference is due to the drying process in soluble coffee production, which consists of an evaporation or lyophilization step in which the soluble components are concentrated, including phenols with antioxidant potential (Mussatto, Machado, Martins, & Teixeira, 2011) as chlorogenic acid, caffeine and melanoidins (Vignoli, Bassoli, & Benassi, 2011).

The AC was also highly variable comparing within the same types of coffees, according to degree and type of roasted, decaffeinated, freeze-dried, organic, DO or flavored, where significant differences ( $p < 0.05$ ) were found between the majority of the samples. On the other hand, no significant ( $p > 0.05$ ) differences between the different types of coffees and roasting degree were found; so only mean values for ABTS are displayed in this section.

Depending on the roasting degree in ground coffees, the values ranged from 239.2–405.2, 100.8–468.4  $\mu\text{mol}$  of TEs/g and 12.5–49.1 mg of GAEs/g for ABTS, FRAP and TP, respectively, with mean values for ABTS of 299.3, 306.8, 292.4 and 329.5  $\mu\text{mol}$  of TEs/g for light, medium, medium-dark and dark, respectively, where dark coffees showed mean values slightly higher. These results are different to those reported by other authors (van der Werf, Marcic, Khalil, Sigrist, & Marchioni, 2014; Vignoli, Viegas, Bassoli, & de Benassi, 2014) who found that light and medium roasted coffee have higher antioxidant capacity than dark roasted coffees due to higher content of polyphenols, which are degraded with increasing the degree of roasting; however Vignoli et al. (2011) found no differences in antioxidant capacity in coffees with different roasting degrees.

In decaffeinated coffees, ABTS, FRAP and TP values ranged between 271.3–325.9, 307.3–359.9  $\mu\text{mol}$  of TEs/g and 36.1–37.3 mg of GAEs/g, respectively for ground coffees, and 459.7–1000, 668.9–885.9  $\mu\text{mol}$  of TEs/g and 56.5–115 mg of GAEs/g for soluble coffees, with mean values for ABTS of 298.6 and 696.7  $\mu\text{mol}$  of TEs/g for ground and soluble coffees, respectively. Lyophilized coffees showed values between 539.8–716.9, 509.3–828.5  $\mu\text{mol}$  of TEs/g and 82.9–127 mg of GAEs/g for ABTS, FRAP and TP, respectively, with a mean value for ABTS of 621.5  $\mu\text{mol}$  of TEs/g. In organic coffees, ABTS, FRAP and TP values varied between 286.8–353.4, 304.1–346.5  $\mu\text{mol}$  of TEs/g and 21.1–41.8 mg of GAEs/g, respectively in ground coffees, and 716.9, 828.5  $\mu\text{mol}$  of TEs/g and 97.4 mg of GAEs/g, respectively in the only organic lyophilized sample (49), which exhibit the highest AC of the lyophilized samples. The mean value for ABTS in organic ground coffees was 308.7  $\mu\text{mol}$  of TEs/g. In DO ground coffees (Table 2), AC ranged between 164.0–383.8, 100.8–308.5  $\mu\text{mol}$  of TEs/g and 14.3–34.2 mg of GAEs/g, respectively for ABTS, FRAP and TP, with a mean value for ABTS of 278.6  $\mu\text{mol}$  of TEs/g. In flavored coffees, the AC ranged between 273.2–408.2, 178.0–468.4  $\mu\text{mol}$  of TEs/g and 35.9–42.6 mg of GAEs/g, respectively for ABTS, FRAP and TP in ground samples, and between 550.6–710.7, 513.6–749.5  $\mu\text{mol}$  of TEs/g and 74.4–127 mg of GAEs/g, respectively in soluble samples, with mean values for ABTS of 360.1 and 637.9  $\mu\text{mol}$  of TEs/g for ground and soluble coffees, respectively. The only torrefacto coffee sample (47) had values of AC and TP in the range of the soluble samples. However Ludwig, Bravo, De Peña, and Cid (2013) found that the addition of sugar during the roasting process increases the AC of coffee, although also indicated that the degree of roast and other factors such as coffee variety, origin or also storage conditions influence the AC.

**Table 2**

The antioxidant capacity (ABTS and FRAP) and TP compound content of Colombian commercial coffees. Mean value  $\pm$  standard deviation ( $n = 3$ ).

| Coffees | ABTS ( $\mu\text{mol}$ TEs/g) | FRAP ( $\mu\text{mol}$ TEs/g) | TP (mg of GAEs/g) |
|---------|-------------------------------|-------------------------------|-------------------|
| Ground  |                               |                               |                   |
| 1       | 383.7 $\pm$ 18.3              | 384.6 $\pm$ 1.77              | 20.8 $\pm$ 1.29   |
| 2       | 293.7 $\pm$ 6.42              | 247.9 $\pm$ 26.4              | 41.0 $\pm$ 3.49   |
| 3       | 266.8 $\pm$ 17.9              | 226.2 $\pm$ 16.7              | 34.6 $\pm$ 1.10   |
| 4       | 346.1 $\pm$ 15.7              | 408.6 $\pm$ 11.4              | 38.1 $\pm$ 1.25   |
| 5       | 253.8 $\pm$ 18.9              | 390.4 $\pm$ 5.34              | 27.4 $\pm$ 1.58   |
| 6       | 240.6 $\pm$ 17.5              | 301.5 $\pm$ 32.0              | 32.0 $\pm$ 0.29   |
| 7       | 437.0 $\pm$ 41.9              | 425.3 $\pm$ 39.1              | 35.1 $\pm$ 0.47   |
| 8       | 260.7 $\pm$ 9.68              | 234.3 $\pm$ 13.3              | 37.8 $\pm$ 0.31   |
| 9       | 269.2 $\pm$ 15.0              | 307.2 $\pm$ 32.1              | 50.7 $\pm$ 2.29   |
| 10      | 286.8 $\pm$ 21.4              | 304.1 $\pm$ 32.7              | 21.1 $\pm$ 3.60   |
| 11      | 353.4 $\pm$ 41.1              | 346.5 $\pm$ 2.59              | 28.1 $\pm$ 3.93   |
| 12      | 321.2 $\pm$ 24.1              | 262.6 $\pm$ 1.29              | 18.4 $\pm$ 2.56   |
| 13      | 405.2 $\pm$ 28.2              | 279.5 $\pm$ 1.66              | 26.0 $\pm$ 1.95   |
| 14      | 330.0 $\pm$ 10.8              | 246.1 $\pm$ 12.0              | 36.8 $\pm$ 3.20   |
| 15      | 254.3 $\pm$ 13.6              | 237.1 $\pm$ 23.40             | 45.9 $\pm$ 0.68   |
| 16      | 340.8 $\pm$ 31.6              | 336.1 $\pm$ 32.4              | 36.3 $\pm$ 0.23   |
| 17      | 398.9 $\pm$ 45.1              | 445.5 $\pm$ 0.95              | 42.6 $\pm$ 6.54   |
| 18      | 239.3 $\pm$ 11.0              | 268.2 $\pm$ 21.3              | 34.9 $\pm$ 3.86   |
| 19      | 273.2 $\pm$ 14.0              | 178.0 $\pm$ 10.1              | 35.9 $\pm$ 4.16   |
| 20      | 290.6 $\pm$ 14.4              | 292.9 $\pm$ 14.5              | 41.8 $\pm$ 4.87   |
| 21      | 365.2 $\pm$ 22.6              | 214.8 $\pm$ 20.3              | 49.1 $\pm$ 3.75   |
| 22      | 267.5 $\pm$ 11.6              | 220.9 $\pm$ 7.20              | 32.2 $\pm$ 1.09   |
| 23      | 256.7 $\pm$ 4.26              | 283.5 $\pm$ 20.6              | 12.5 $\pm$ 1.95   |
| 24      | 265.0 $\pm$ 10.8              | 281.2 $\pm$ 1.63              | 13.0 $\pm$ 1.32   |
| 25      | 297.5 $\pm$ 29.5              | 100.8 $\pm$ 12.4              | 14.4 $\pm$ 1.24   |
| 26      | 320.7 $\pm$ 26.1              | 211.1 $\pm$ 16.4              | 33.5 $\pm$ 2.51   |
| 27      | 258.9 $\pm$ 10.8              | 346.2 $\pm$ 26.7              | 38.6 $\pm$ 4.51   |
| 28      | 318.1 $\pm$ 7.49              | 300.7 $\pm$ 11.3              | 36.1 $\pm$ 0.54   |
| 29      | 325.9 $\pm$ 23.3              | 359.9 $\pm$ 34.8              | 37.3 $\pm$ 3.02   |
| 30      | 271.3 $\pm$ 35.8              | 307.3 $\pm$ 25.9              | 36.1 $\pm$ 5.06   |
| 31      | 383.8 $\pm$ 28.4              | 308.5 $\pm$ 18.9              | 34.2 $\pm$ 4.73   |
| 32      | 252.8 $\pm$ 10.9              | 220.1 $\pm$ 12.4              | 32.3 $\pm$ 1.71   |
| 33      | 408.2 $\pm$ 12.9              | 468.4 $\pm$ 28.4              | 38.2 $\pm$ 3.92   |
| 34      | 237.8 $\pm$ 18.6              | 303.4 $\pm$ 39.2              | 34.1 $\pm$ 1.92   |
| 35      | 312.2 $\pm$ 2.58              | 185.9 $\pm$ 24.9              | 30.2 $\pm$ 3.38   |
| 36      | 256.3 $\pm$ 10.5              | 195.6 $\pm$ 11.3              | 24.9 $\pm$ 1.85   |
| 37      | 267.8 $\pm$ 14.1              | 239.6 $\pm$ 13.1              | 24.8 $\pm$ 3.63   |
| 38      | 235.3 $\pm$ 10.9              | 220.1 $\pm$ 8.25              | 14.3 $\pm$ 1.87   |
| 39      | 304.2 $\pm$ 8.01              | 329.9 $\pm$ 4.86              | 32.4 $\pm$ 2.15   |
| 40      | 164.0 $\pm$ 20.7              | 137.2 $\pm$ 1.68              | 28.8 $\pm$ 2.04   |
| 41      | 219.4 $\pm$ 7.72              | 165.5 $\pm$ 16.0              | 26.0 $\pm$ 1.12   |
| Soluble |                               |                               |                   |
| 42      | 1000 $\pm$ 32.8               | 885.9 $\pm$ 61.4              | 85.3 $\pm$ 9.04   |
| 43      | 728.2 $\pm$ 30.3              | 739.9 $\pm$ 57.4              | 82.6 $\pm$ 1.38   |
| 44      | 636.0 $\pm$ 18.2              | 850.6 $\pm$ 31.3              | 115 $\pm$ 18.5    |
| 45      | 635.0 $\pm$ 30.1              | 826.0 $\pm$ 35.6              | 103 $\pm$ 7.02    |
| 46      | 459.7 $\pm$ 24.4              | 668.9 $\pm$ 19.2              | 56.5 $\pm$ 2.95   |
| 47      | 723.4 $\pm$ 2.18              | 690.4 $\pm$ 77.3              | 58.7 $\pm$ 8.68   |
| 48      | 550.6 $\pm$ 17.6              | 572.3 $\pm$ 9.47              | 94.3 $\pm$ 7.58   |
| 49      | 716.9 $\pm$ 12.5              | 828.5 $\pm$ 33.0              | 97.4 $\pm$ 10.9   |
| 50      | 539.8 $\pm$ 22.3              | 509.3 $\pm$ 3.33              | 82.9 $\pm$ 3.47   |
| 51      | 594.1 $\pm$ 27.2              | 513.6 $\pm$ 10.2              | 127 $\pm$ 3.48    |
| 52      | 710.7 $\pm$ 11.3              | 639.4 $\pm$ 5.49              | 116 $\pm$ 5.96    |
| 53      | 630.2 $\pm$ 4.90              | 652.1 $\pm$ 5.99              | 87.3 $\pm$ 4.08   |
| 54      | 442.0 $\pm$ 2.00              | 352.2 $\pm$ 25.7              | 36.8 $\pm$ 0.10   |
| 55      | 660.6 $\pm$ 27.7              | 749.5 $\pm$ 5.47              | 74.4 $\pm$ 29.4   |
| 56      | 673.7 $\pm$ 28.0              | 732.8 $\pm$ 41.2              | 103 $\pm$ 4.41    |
| 57      | 725.3 $\pm$ 33.9              | 687.0 $\pm$ 17.8              | 91.5 $\pm$ 1.32   |
| 58      | 673.7 $\pm$ 34.5              | 671.4 $\pm$ 17.9              | 85.5 $\pm$ 0.34   |

Comparing the different coffees samples it is observed that the highest antioxidant capacity by both methods, ABTS and FRAP, was found in decaffeinated lyophilized soluble samples. This result is not consistent with the reports in literature, since it has been shown that caffeine is one of the main responsible for the antioxidant capacity of coffee (Vignoli et al., 2014, 2011), however, although caffeine has been widely studied from a pharmacological point of view, less attention has been paid to its AC that can be eclipsed by the Maillard reaction products and phenolic compounds (Ludwig et al., 2012). On the other hand, Rodrigues and Bragagnolo (2013) found higher contents of chlorogenic acid in decaffeinated coffees, which would explain the increased antioxidant capacity in these samples. In general, values of ABTS, FRAP and TP are similar to those reported by other authors for ground and instant coffees (Fonseca-García, Calderón-Jaimes, & Rivera, 2014; Ludwig et al., 2013).

The AC evaluated by the three methods (ABTS, FRAP and TP) showed a similar trend, with high and significant ( $p < 0.05$ ) direct correlation ( $r = 0.9242$ ,  $0.8348$  and  $0.8386$ ) to ABTS:FRAP, ABTS:TP and FRAP:TP, respectively (Table 4). These results are in agreement with those reported by other authors (Pérez-Martínez et al., 2010; Vignoli et al., 2014). It occurs because while the TP and FRAP assays only act by the mechanism of electron transfer (SET), the ABTS method acts by both SET and by hydrogen atom transfer (HAT) (Gülçin, 2012).

### 3.2. Color determination

The precision of the entire procedure was conducted with the sample 42 ( $n = 10$ ). The RSD for  $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$ , and  $h^*$  were 0.68, 0.14, 0.36, 0.39 and 0.22, with a mean values of 18.1, 5.59, 14.6, 15.6 and 69.0, with CV of 3.74%, 2.51% and 2.49%, 2.47% and 0.33%, respectively.

The color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $h^*$ ) also were highly variable (Table 3), with values ranging from 7.89–28.1, 2.73–8.40, 3.52–25.4, 4.45–26.7 and 52.2–73.3, respectively. Soluble coffees showed, in all cases, significantly higher mean values ( $p < 0.05$ ) ( $L^*$  (21.0),  $a^*$  (6.7),  $b^*$  (18.6),  $c^*$  (19.8),  $h^*$  (69.2)) than ground coffees ( $L^*$  (13.1),  $a^*$  (5.1),  $b^*$  (10.3),  $c^*$  (11.6),  $h^*$  (63.0)), i.e. soluble samples are lighter, reddish, and have a more intense yellow than ground samples. The higher values in color parameters of soluble coffees could be related to the concentration of soluble compounds as melanoidins (Vignoli et al., 2011). Similar results were found by Rodrigues and Bragagnolo (2013). However, it is noteworthy to mention that soluble coffees were lighter ( $L^*$ ) than ground coffees perhaps because of the presence of insoluble compounds in ground coffees providing dark pigments. It has been reported that melanoidins represent the 65% of color potential in high molecular weight fractions obtained from light roasted coffees and just 39% in dark roasted coffees (Nunes & Coimbra, 2007).

A comparison between ground coffees according to the roasting degree showed that samples with dark roasting have significant ( $p < 0.05$ ) lower values ( $L^*$  (11.0),  $a^*$  (4.1),  $b^*$  (7.5),  $c^*$  (8.6) and  $h^*$  (60.3)) than other ground coffees ( $L^*$  (13.5),  $a^*$  (5.3),  $b^*$  (11.0),  $c^*$  (12.2) and  $h^*$  (63.6)). Summa et al. (2007) found a decrease in color parameters ( $L^*$ ,  $a^*$  and  $b^*$ ), when intensity of roasting was increased, similar to those observed in this study. Furthermore Ludwig et al. (2013) found values significant higher ( $p < 0.05$ ) in  $a^*$  (red) and  $b^*$  (yellow) parameters in light roast coffee samples than in medium and dark roast coffee samples, finding significant correlations ( $p < 0.05$ ) between  $a^*:L^*$  and  $b^*:L^*$  ( $r = 0.786$  and  $0.912$ , respectively), similar to those found in the present research ( $r = 0.849$  and  $0.981$ , respectively for  $a^*:L^*$  and  $b^*:L^*$ ).

Lyophilized coffees ( $L^*$  (23.9),  $a^*$  (7.42),  $b^*$  (21.3),  $c^*$  (22.6) and  $h^*$  (69.9)) showed significant ( $p < 0.05$ ) higher values than the other soluble coffees ( $L^*$  (18.83),  $a^*$  (6.35),  $b^*$  (16.5),  $c^*$  (17.7)

and  $h^*$  (68.4)). These values in color parameters are similar to those reported by other authors (Ludwig et al., 2013; Vignoli et al., 2014). Sample 49 (organic lyophilized coffee) exhibited one of the highest color parameters, similar to those observed in AC where displayed the highest values, which is confirmed with a high and positive correlation between color parameters and AC (Table 4). A high and positive correlation ( $r = 0.9759$ ) was obtained between  $L^*$  and  $c^*$  in accordance with results obtained by Summa et al. (2007) ( $r = 0.9610$ ), what confirm that  $L^*$  is a useful indicator of the intensity thermal process.

### 3.3. Browning index (BI)

The precision of the method was performed including the preparation and analysis of samples. The study was conducted with the sample 57 ( $n = 10$ ). The RSD was 0.06, with a mean value of 1.52 and a CV of 4.03%.

Values of BI (Table 3) varied between 0.32 and 3.06, being significantly ( $p < 0.05$ ) more brown the soluble coffees than ground coffees, with mean values of 2.42 and 0.48, respectively, which could be due to the higher concentration of melanoidins in soluble coffees (Liu & Kitts, 2011; Pérez, Chávez, Medina, & Gámez, 2013). A wide range of BI was found in ground coffees (0.33–1.81) based on the roasting degree, however, only significant differences ( $p < 0.05$ ) were found between dark (0.39) and medium (0.55) ground coffees. On the other hand, Liu and Kitts (2011) did not found significant differences ( $p > 0.05$ ) in coffees roasted during 15 min at 210 and 240 °C. Comparing between the different types of coffee, it was observed that the most brownish samples were decaffeinated soluble (2.70), flavored (2.59) and lyophilized (2.52) coffees, however no significant differences ( $p > 0.05$ ) were found with the other samples. These results show the same trend than those found for AC.

Significant and positive correlations ( $p < 0.05$ ) were found between BI and both AC methods (Table 4) indicating that the greater the BI, the higher the AC in coffee. These results are in agreement with those of other authors (Liu & Kitts, 2011; Ludwig et al., 2013) who attribute the major part of the AC to the MR products, as melanoidins.

### 3.4. HMF and furfural

The precision of the method was carried out, including the preparation and analysis of samples. The study was conducted with the sample 57 ( $n = 10$ ). HMF and furfural recovery were 96.45% and 99.7%, respectively. The RSD were 25 and 0.2, with mean values of 648.4 and 25.19 mg/kg, with CV of 3.9% and 0.6% for HMF and furfural, respectively. The detection limit (LOD) (three times the signal-to-noise ratio) and quantification limit (LOQ) (ten times the signal-to-noise ratio) were 2.43 and 0.06 mg/kg and 8.10 and 0.20 mg/kg for HMF and furfural, respectively.

HMF and furfural contents ranged between 23.3–4112 and 18–135 mg/kg, respectively (Table 3). Soluble coffees showed a significant ( $p < 0.05$ ) higher HMF content than ground coffees (1333 Vs 102 mg/kg, respectively). However, furfural content did not present significant differences ( $p > 0.05$ ) between ground and soluble samples. Other authors found higher HMF and furfural contents in soluble coffees than in ground coffees (Arribas & Morales, 2010; Rodrigues & Bragagnolo, 2013).

According to the roasting degree, significantly higher HMF mean values ( $p < 0.05$ ) were found in light and medium roast ground coffees (162 and 140 mg/kg, respectively) than in medium-dark and dark ground coffees (75.4 and 27.0 mg/kg, respectively). Mean furfural contents were found to be significantly ( $p < 0.05$ ) higher in medium-dark, medium and light ground coffees (75.4, 61.0 and 65.0 mg/kg, respectively) than in dark

**Table 3**

HMF and furfural content, browning index (BI) and color parameters (L\*, a\*, b\*, c\*, h\*) of Colombian commercial coffees. Mean value ± standard deviation (n = 3).

| Coffees | HMF         | Furfural   | BI          | L           | a*         | b*          | c*          | h*          |
|---------|-------------|------------|-------------|-------------|------------|-------------|-------------|-------------|
| Ground  |             |            |             |             |            |             |             |             |
| 1       | 30.2 ± 0.80 | 22 ± 0.30  | 0.34 ± 0.04 | 12.9 ± 0.29 | 4.6 ± 0.10 | 9.70 ± 0.13 | 10.7 ± 0.15 | 64.4 ± 0.35 |
| 2       | 35.3 ± 1.10 | 21 ± 0.40  | 0.46 ± 0.03 | 11.1 ± 0.25 | 4.0 ± 0.03 | 7.30 ± 0.05 | 8.30 ± 0.05 | 61.0 ± 0.09 |
| 3       | 45.6 ± 0.50 | 32 ± 0.00  | 0.44 ± 0.03 | 10.9 ± 0.48 | 4.3 ± 0.12 | 7.20 ± 0.38 | 8.40 ± 0.38 | 59.2 ± 0.71 |
| 4       | 37.4 ± 0.20 | 21 ± 0.00  | 0.33 ± 0.01 | 11.8 ± 0.31 | 4.4 ± 0.09 | 8.80 ± 0.33 | 9.80 ± 0.33 | 63.6 ± 0.37 |
| 5       | 32.7 ± 0.30 | 33 ± 1.20  | 0.35 ± 0.00 | 7.90 ± 0.47 | 2.7 ± 0.07 | 3.50 ± 0.29 | 4.50 ± 0.26 | 52.2 ± 1.64 |
| 6       | 46.6 ± 0.90 | 28 ± 0.10  | 0.43 ± 0.07 | 10.2 ± 0.43 | 3.5 ± 0.03 | 5.90 ± 0.17 | 6.80 ± 0.16 | 59.6 ± 0.83 |
| 7       | 48.1 ± 0.70 | 29 ± 0.90  | 0.43 ± 0.01 | 12.5 ± 0.48 | 5.3 ± 0.12 | 10.0 ± 0.14 | 11.4 ± 0.17 | 62.1 ± 0.42 |
| 8       | 56.5 ± 1.60 | 42 ± 2.40  | 0.38 ± 0.02 | 12.8 ± 0.67 | 5.2 ± 0.13 | 10.2 ± 0.44 | 11.4 ± 0.45 | 59.9 ± 5.63 |
| 9       | 49.2 ± 0.10 | 32 ± 0.50  | 0.38 ± 0.01 | 12.7 ± 0.43 | 4.7 ± 0.12 | 8.60 ± 0.32 | 9.80 ± 0.34 | 61.2 ± 0.36 |
| 10      | 62.1 ± 2.20 | 47 ± 1.70  | 0.50 ± 0.03 | 12.3 ± 0.51 | 5.3 ± 0.05 | 10.2 ± 0.35 | 11.6 ± 0.34 | 62.8 ± 0.65 |
| 11      | 63.1 ± 1.10 | 41 ± 0.30  | 0.51 ± 0.02 | 15.2 ± 0.14 | 5.7 ± 0.02 | 11.9 ± 0.15 | 13.3 ± 0.14 | 64.3 ± 0.26 |
| 12      | 146 ± 4.40  | 67 ± 2.10  | 0.80 ± 0.01 | 14.7 ± 1.21 | 5.8 ± 0.27 | 11.4 ± 0.73 | 12.8 ± 0.77 | 63.2 ± 0.61 |
| 13      | 954 ± 11.0  | 34 ± 1.20  | 1.81 ± 0.01 | 15.7 ± 0.43 | 6.2 ± 0.09 | 13.9 ± 0.25 | 15.2 ± 0.25 | 66.1 ± 0.30 |
| 14      | 53.2 ± 1.90 | 45 ± 0.00  | 0.44 ± 0.06 | 13.7 ± 0.74 | 5.0 ± 0.10 | 10.3 ± 0.27 | 11.4 ± 0.28 | 64.2 ± 0.29 |
| 15      | 119 ± 2.60  | 71 ± 0.30  | 0.44 ± 0.04 | 13.4 ± 0.55 | 4.8 ± 0.02 | 10.7 ± 0.37 | 11.7 ± 0.34 | 65.6 ± 0.65 |
| 16      | 78.5 ± 1.30 | 50 ± 1.00  | 0.39 ± 0.00 | 14.5 ± 0.87 | 5.8 ± 0.14 | 12.4 ± 0.63 | 13.7 ± 0.63 | 64.9 ± 0.59 |
| 17      | 73.1 ± 1.00 | 41 ± 0.30  | 0.39 ± 0.01 | 13.8 ± 0.16 | 5.1 ± 0.06 | 11.4 ± 1.75 | 11.6 ± 0.42 | 64.1 ± 0.76 |
| 18      | 169 ± 6.20  | 71 ± 3.80  | 0.52 ± 0.01 | 14.4 ± 0.70 | 6.2 ± 0.13 | 14.1 ± 0.47 | 15.4 ± 0.48 | 66.4 ± 0.27 |
| 19      | 54.7 ± 0.30 | 135 ± 3.0  | 0.39 ± 0.02 | 13.9 ± 0.81 | 5.3 ± 0.19 | 10.9 ± 0.52 | 12.1 ± 0.55 | 64.2 ± 0.34 |
| 20      | 94.3 ± 2.50 | 60 ± 2.60  | 0.48 ± 0.00 | 12.2 ± 0.37 | 5.2 ± 0.10 | 9.80 ± 0.23 | 11.1 ± 0.24 | 62.0 ± 0.42 |
| 21      | 46.8 ± 1.00 | 28 ± 0.90  | 0.33 ± 0.01 | 11.0 ± 0.79 | 4.6 ± 0.13 | 8.80 ± 0.60 | 9.90 ± 0.58 | 62.1 ± 1.13 |
| 22      | 113 ± 0.40  | 70 ± 0.60  | 0.45 ± 0.01 | 12.9 ± 0.10 | 4.5 ± 0.02 | 8.60 ± 0.17 | 9.70 ± 0.15 | 62.2 ± 0.51 |
| 23      | 146 ± 5.30  | 77 ± 1.90  | 0.53 ± 0.02 | 11.7 ± 0.36 | 5.1 ± 0.03 | 9.90 ± 0.11 | 11.1 ± 0.09 | 62.7 ± 0.40 |
| 24      | 154 ± 5.30  | 70 ± 2.60  | 0.60 ± 0.12 | 13.5 ± 0.48 | 5.3 ± 0.11 | 10.7 ± 0.27 | 11.9 ± 0.29 | 63.6 ± 0.13 |
| 25      | 50.4 ± 1.20 | 40 ± 1.80  | 0.37 ± 0.02 | 11.2 ± 0.69 | 4.5 ± 0.09 | 8.10 ± 0.49 | 9.2 ± 0.47  | 61.0 ± 1.05 |
| 26      | 119 ± 1.60  | 56 ± 0.20  | 0.41 ± 0.03 | 15.9 ± 0.69 | 5.4 ± 0.05 | 12.3 ± 0.20 | 13.4 ± 0.20 | 66.3 ± 0.26 |
| 27      | 147 ± 3.20  | 68 ± 0.80  | 0.53 ± 0.03 | 13.2 ± 0.20 | 5.0 ± 0.03 | 9.80 ± 0.10 | 11.0 ± 0.07 | 62.8 ± 0.37 |
| 28      | 154 ± 4.40  | 72 ± 0.60  | 0.53 ± 0.03 | 15.3 ± 0.26 | 5.8 ± 0.07 | 12.4 ± 0.23 | 13.7 ± 0.24 | 64.8 ± 0.22 |
| 29      | 95.9 ± 0.40 | 49 ± 2.50  | 0.38 ± 0.02 | 15.5 ± 0.25 | 6.3 ± 0.02 | 13.9 ± 0.09 | 15.3 ± 0.08 | 65.5 ± 0.15 |
| 30      | 76.6 ± 0.90 | 51 ± 0.60  | 0.51 ± 0.01 | 10.4 ± 0.37 | 4.8 ± 0.02 | 8.30 ± 0.18 | 9.60 ± 0.15 | 59.8 ± 0.57 |
| 31      | 68.1 ± 1.60 | 52 ± 1.10  | 0.37 ± 0.01 | 10.4 ± 0.53 | 5.0 ± 0.14 | 9.00 ± 0.39 | 10.3 ± 0.41 | 60.9 ± 0.40 |
| 32      | 70.7 ± 2.20 | 53 ± 1.30  | 0.50 ± 0.03 | 15.4 ± 0.43 | 6.2 ± 0.08 | 13.3 ± 0.34 | 14.8 ± 0.33 | 65.1 ± 0.29 |
| 33      | 63.6 ± 0.80 | 47 ± 0.30  | 0.38 ± 0.03 | 13.3 ± 0.96 | 5.0 ± 0.16 | 10.4 ± 0.52 | 11.6 ± 0.54 | 64.2 ± 0.44 |
| 34      | 43.6 ± 0.50 | 33 ± 0.60  | 0.42 ± 0.01 | 12.7 ± 0.75 | 5.5 ± 0.15 | 11.1 ± 0.47 | 12.4 ± 0.49 | 63.6 ± 0.34 |
| 35      | 95.8 ± 2.80 | 58 ± 1.20  | 0.74 ± 0.05 | 13.2 ± 0.56 | 5.5 ± 0.10 | 10.5 ± 0.30 | 11.8 ± 0.30 | 62.5 ± 0.36 |
| 36      | 72.3 ± 2.00 | 41 ± 0.60  | 0.36 ± 0.00 | 12.2 ± 0.22 | 5.3 ± 0.01 | 10.6 ± 0.22 | 11.8 ± 0.20 | 63.6 ± 0.44 |
| 37      | 41.1 ± 0.50 | 32 ± 1.00  | 0.34 ± 0.03 | 15.5 ± 0.46 | 5.6 ± 0.09 | 12.9 ± 0.15 | 14.0 ± 0.17 | 66.3 ± 0.12 |
| 38      | 23.3 ± 0.00 | 18 ± 0.10  | 0.32 ± 0.00 | 10.1 ± 0.35 | 4.0 ± 0.07 | 6.50 ± 0.48 | 7.60 ± 0.43 | 58.5 ± 1.65 |
| 39      | 139 ± 0.20  | 68 ± 1.80  | 0.43 ± 0.01 | 17.5 ± 0.31 | 6.8 ± 0.15 | 15.4 ± 0.33 | 16.9 ± 0.31 | 65.9 ± 0.38 |
| 40      | 114 ± 0.40  | 80 ± 0.40  | 0.48 ± 0.01 | 14.2 ± 0.41 | 5.7 ± 0.07 | 12.3 ± 0.30 | 13.6 ± 0.29 | 65.3 ± 0.29 |
| 41      | 98.2 ± 3.00 | 64 ± 1.50  | 0.38 ± 0.00 | 15.6 ± 0.12 | 5.9 ± 0.05 | 12.9 ± 0.21 | 14.1 ± 0.21 | 65.4 ± 0.20 |
| Soluble |             |            |             |             |            |             |             |             |
| 42      | 847 ± 4.90  | 49 ± 0.70  | 2.82 ± 0.20 | 18.1 ± 0.68 | 5.6 ± 0.14 | 14.6 ± 0.36 | 15.6 ± 0.39 | 69.0 ± 0.22 |
| 43      | 1144 ± 0.40 | 37 ± 0.40  | 2.93 ± 0.14 | 14.3 ± 0.79 | 7.5 ± 0.18 | 14.3 ± 0.87 | 16.1 ± 0.84 | 62.3 ± 0.95 |
| 44      | 1756 ± 16.0 | 72 ± 2.00  | 2.66 ± 0.09 | 26.1 ± 0.64 | 7.1 ± 0.17 | 22.8 ± 0.70 | 23.9 ± 0.72 | 72.7 ± 0.19 |
| 45      | 1119 ± 42.0 | 43 ± 1.00  | 2.39 ± 0.11 | 26.1 ± 0.22 | 7.1 ± 0.05 | 23.5 ± 0.24 | 24.5 ± 0.22 | 73.3 ± 0.21 |
| 46      | 1196 ± 20.0 | 33 ± 0.70  | 2.71 ± 0.10 | 14.5 ± 0.28 | 7.6 ± 0.18 | 14.6 ± 0.29 | 16.4 ± 0.34 | 62.3 ± 0.10 |
| 47      | 654 ± 12.0  | 39 ± 1.40  | 0.38 ± 0.01 | 23.6 ± 0.23 | 6.6 ± 0.03 | 19.4 ± 0.19 | 20.5 ± 0.18 | 71.3 ± 0.18 |
| 48      | 1761 ± 132  | 84 ± 4.30  | 2.58 ± 0.04 | 28.1 ± 1.11 | 8.4 ± 0.21 | 25.4 ± 0.58 | 26.7 ± 0.61 | 71.7 ± 0.06 |
| 49      | 4112 ± 250  | 128 ± 3.00 | 2.52 ± 0.10 | 24.5 ± 0.14 | 7.3 ± 0.04 | 22.3 ± 0.26 | 23.4 ± 0.23 | 71.8 ± 0.28 |
| 50      | 1658 ± 111  | 108 ± 4.00 | 2.58 ± 0.14 | 26.5 ± 0.31 | 8.2 ± 0.09 | 24.4 ± 0.37 | 25.7 ± 0.38 | 71.5 ± 0.11 |
| 51      | 1906 ± 25.0 | 90 ± 16.30 | 2.57 ± 0.16 | 26.5 ± 0.27 | 8.1 ± 0.01 | 25.2 ± 0.16 | 26.5 ± 0.17 | 72.2 ± 0.14 |
| 52      | 1567 ± 17.0 | 96 ± 16.50 | 2.25 ± 0.01 | 13.0 ± 0.74 | 4.7 ± 0.13 | 8.90 ± 0.51 | 10.0 ± 0.51 | 62.0 ± 0.93 |
| 53      | 1753 ± 13.0 | 114 ± 3.90 | 2.49 ± 0.06 | 24.2 ± 0.58 | 7.9 ± 0.12 | 21.8 ± 0.36 | 23.2 ± 0.37 | 70.2 ± 0.11 |
| 54      | 32.1 ± 0.50 | 26 ± 0.90  | 0.71 ± 0.03 | 12.8 ± 0.37 | 4.8 ± 0.02 | 10.1 ± 0.25 | 11.2 ± 0.23 | 64.7 ± 0.52 |
| 55      | 717 ± 2.20  | 27 ± 0.40  | 2.58 ± 0.14 | 19.3 ± 0.43 | 5.9 ± 0.08 | 17.2 ± 0.21 | 18.2 ± 0.21 | 71.1 ± 0.16 |
| 56      | 1005 ± 5.20 | 41 ± 0.50  | 2.99 ± 0.21 | 20.6 ± 0.59 | 6.1 ± 0.09 | 17.4 ± 0.40 | 18.4 ± 0.41 | 70.6 ± 0.17 |
| 57      | 1278 ± 43.0 | 21 ± 1.20  | 2.92 ± 0.14 | 22.2 ± 0.27 | 6.6 ± 0.03 | 19.7 ± 0.07 | 20.8 ± 0.06 | 71.6 ± 0.10 |
| 58      | 158 ± 5.60  | 32 ± 0.90  | 3.06 ± 0.05 | 17.1 ± 0.29 | 5.9 ± 0.05 | 15.1 ± 0.10 | 16.2 ± 0.08 | 68.7 ± 0.30 |

**Table 4**

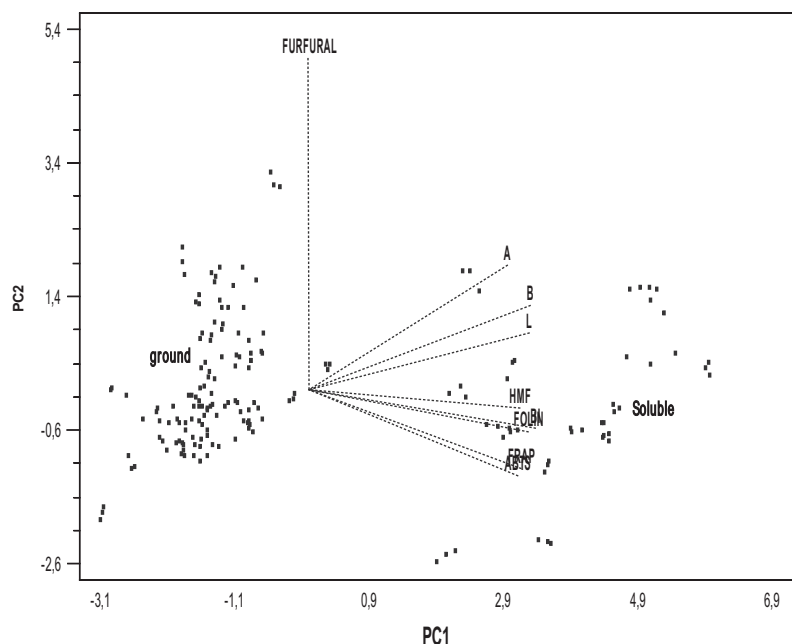
Pearson's correlation coefficients (r) between antioxidant capacity and TP, HMF, furfural, BI and color parameters in Colombian commercial coffees.

|      | FRAP    | TP      | HMF     | Furfural | BI      | L*      | a*      | b*      | c*      | h*      |
|------|---------|---------|---------|----------|---------|---------|---------|---------|---------|---------|
| ABTS | 0.9242* | 0.8348* | 0.6941* | 0.1238   | 0.8454* | 0.6666* | 0.5309* | 0.6483* | 0.6413* | 0.6522* |
| FRAP | –       | 0.8386* | 0.7155* | 0.1151   | 0.8405* | 0.6753* | 0.5452* | 0.6644* | 0.6575* | 0.6248* |

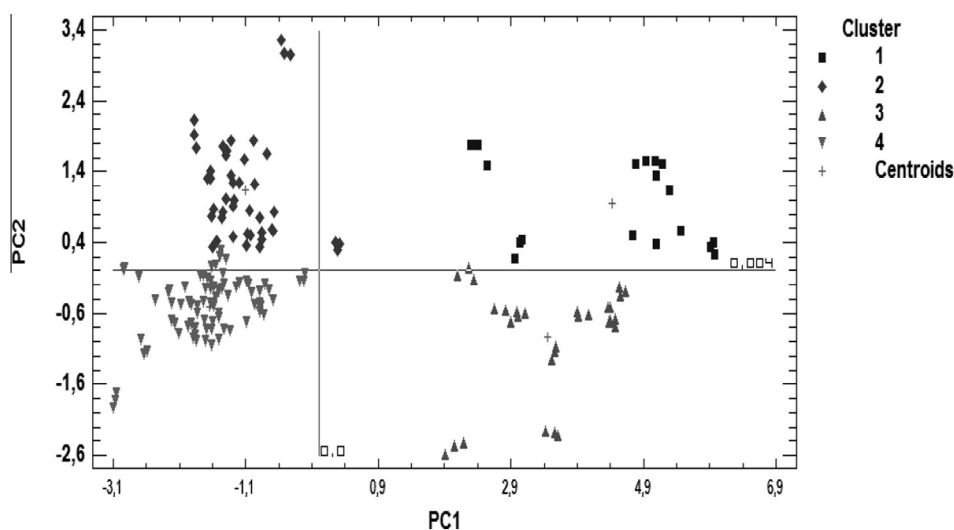
\* Significant at p &lt; 0.05.

ground coffees (27.0 mg/kg). Similar results were exhibited by Vignoli et al. (2014) who also found higher HMF and furfural contents in light roasted coffees due to the decrease of these com-

pounds as the degree of roasting is more intense. These authors found HMF and furfural contents up to 2300 and 300 mg/kg, respectively in ground Arabica coffees. Arribas and Morales



**Fig. 1.** Principal component analysis (PCA) of the Colombian commercial coffees according to the determinations of antioxidant capacity, total phenols, color and heat damage indicators.



**Fig. 2.** Clusters formed from Colombian coffee samples according to PC1 and PC2.

(2010) reported HMF contents of 110 and 625 mg/kg in natural ground coffees and in blend, respectively. These values are in accordance with those reported for ground natural coffees in the present study; however regarding blend coffees values were lower.

Lyophilized coffees displayed the higher ( $p < 0.05$ ) HMF and furfural contents (1982 and 94.7 mg/kg, respectively) regarding to soluble samples (972.8 and 37.7 mg/kg, respectively). Sample 49 showed the highest values for HMF and furfural contents. It is noteworthy to mention that sample 49 exhibited the highest values also for AC and color parameters; therefore it could be assumed that the lyophilization process could promote these results. It has been shown that higher roasting temperature, the HMF and F are degraded (Vignoli et al., 2014), so that during the lyophilization these compounds can be preserved, due to low process temperatures with respect to the high temperatures of a conventional

drying process. Significant differences ( $p < 0.05$ ) were found in HMF contents between DO and other ground coffees (130.0 Vs 221.4 mg/kg, respectively), however no significant differences ( $p > 0.05$ ) were found in furfural (52.4 Vs 49.5 mg/kg, respectively).

The results obtained in the present study are in agreement with those found in literature (Capuano & Fogliano, 2011; Vignoli et al., 2014). Variations can be explained by the different species and varieties used in the mixtures as well as the processing conditions, especially in the decaffeination and processing of soluble coffees (Rodrigues & Bragagnolo, 2013).

A positive and significant ( $p < 0.05$ ) correlation was found between AC and HMF contents (Table 4). However, no correlation was found between furfural and AC. The high correlation between HMF and AC can be explained for the AC of HMF, which is similar to that of 2,6-dibutyl-4-methylphenol and  $\alpha$ -tocopherol (Shinghara,

Macku, & Shibamoto, 1998). Flavored coffees did not show a trend or effect in AC, HMF and furfural content and other parameters in relation with other coffee samples.

### 3.5. Principal components analysis (PCA) and cluster analysis (CA)

In this study, two principal components (PCs) were obtained which explains 81.45% of total variance. Fig. 1 shows the biplot (PC2 vs. PC1) of coffee samples and variables. PC1 which explains 69.6% of the total variance, has influence of color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ), HMF, BI, and AC (FRAP, TP and ABTS), in addition there is a positive correlation between the mentioned variables, which implies a relation between AC, non-enzymatic browning and color. PC2 explains 11.87% of the variance which is mainly characterized by furfural content (Fig. 1); therefore, according to this analysis, furfural possibly is not related directly with AC, color development and other indicators of non-enzymatic browning. PCA clearly formed two groups of samples, namely in the right side of the Fig. 1 were placed soluble coffees and in the left side, ground coffees.

CA was performed based on the principal components analysis (PCA). Fig. 2 shows the distribution of samples inside the clusters according to PC1 and PC2, in which four clusters were formed. CA confirmed the clear separation between ground (Cluster II and IV) and soluble coffees (Cluster I and III), and coffees with high furfural content (Cluster I and II) and coffees with low furfural content (Cluster III and IV). Cluster I and III are mainly composed by soluble decaffeinated and lyophilized coffees, suggesting that these processes are not important variables in explaining the progress of non-enzymatic browning, color and AC. Cluster II and IV are formed mainly by coffee ground samples with light, medium and dark roasting degree, which leads to that the roasting degree possibly does not take an important role in the classification of samples according to the PCs used. Soluble coffees present higher values in color parameters, BI, HMF, and AC than ground coffees; furfural seems to be a variable which does not depend on the other variables.

## 4. Conclusions

Coffees commercialized in Colombia show a wide range of AC, HMF and furfural contents, color parameters and BI. AC has a positive and significant correlation with BI, HMF and color parameters what confirms the interdependency of these variables. Soluble coffees present significant higher AC, color parameters and BI than ground coffees due to the presence of soluble compounds as melanoidins and HMF. Lyophilized samples show the higher contents in HMF, AC, BI and color parameters. Except for the differences between soluble and ground coffees, no significant differences exist in AC regarding to degree of roasting, origin, organic, flavored, decaffeinated, lyophilized, and torrefacto coffee samples analyzed in the present study. Furfural is not related to any of the variables analyzed.

## Conflicts of interests

The authors declare that they have no conflict of interest.

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## References

- Antal, M. J., Mok, W. S. L., & Richards, G. N. (1990). Mechanism of formation of 5-(hydroxymethyl)-2-furfaldehyde from D-fructose and sucrose. *Carbohydrate Research*, 199, 91–109.
- Arribas, G., & Morales, F. J. (2010). Estimation of dietary intake of 5-hydroxymethylfurfural and related substances from coffee to Spanish population. *Food and Chemical Toxicology*, 48(2), 644–649.
- Borrelli, R. C., Visconti, A., Mennella, C., Anese, M., & Fogliano, V. (2002). Chemical characterization and antioxidant properties of coffee melanoidins. *Journal of Agricultural and Food Chemistry*, 50(22), 6527–6533.
- Capuano, E., & Fogliano, V. (2011). Acrylamide and 5-hydroxymethylfurfural (HMF): A review on metabolism, toxicity, occurrence in food and mitigation strategies. *LWT – Food Science and Technology*, 44(4), 793–810.
- Colcafe (2015). Marcas y productos Retrieved September 9, 2015. <<http://es.colcafe.com.co/es-ve/marcasyproductos/colombia/cafe/C3%A9tostado.aspx>>.
- Contreras-Calderón, J., Calderón-Jaimes, L., Guerra-Hernández, E., & García-Villanova, B. (2011). Antioxidant capacity, phenolic content and vitamin C in pulp, peel and seed from 24 exotic fruits from Colombia. *Food Research International*, 44(7), 2047–2053.
- Contreras-Calderón, J., Guerra-Hernández, E., & García-Villanova, B. (2009). Utility of some indicators related to the Maillard browning reaction during processing of infant formulas. *Food Chemistry*, 114(4), 1265–1270.
- Cortés, C., Esteve, M. J., & Frígola, A. (2008). Color of orange juice treated by High Intensity Pulsed Electric Fields during refrigerated storage and comparison with pasteurized juice. *Food Control*, 19(2), 151–158.
- Delgado-Andrade, C., & Morales, F. J. (2005). Unraveling the contribution of melanoidins to the antioxidant activity of coffee brews. *Journal of Agricultural and Food Chemistry*, 53(5), 1403–1407.
- Federación Nacional de Cafeteros de Colombia (2011). Sostenibilidad en acción 1927–2010 Retrieved December 2, 2015. <[https://www.federaciondecafeteros.org/static/files/informe\\_sostenibilidad\\_esp.pdf](https://www.federaciondecafeteros.org/static/files/informe_sostenibilidad_esp.pdf)>.
- Fonseca-García, L., Calderón-Jaimes, L. S., & Rivera, M. E. (2014). Capacidad antioxidante y contenido de fenoles totales en café y subproductos del café producido y comercializado en norte de Santander (Colombia). *Vitae*, 21(3), 228–236.
- Gülçin, İ. (2012). Antioxidant activity of food constituents: an overview. *Archives of Toxicology*, 86(3), 345–391.
- Juan Valdez (2015). Juan Valdez Café Retrieved September 9, 2015. <<http://www.juanvaldezcafe.com/es/colombia>>.
- Liu, Y., & Kitts, D. D. (2011). Confirmation that the Maillard reaction is the principle contributor to the antioxidant capacity of coffee brews. *Food Research International*, 44(8), 2418–2424.
- López-Galilea, I., de Peña, M. P., & Cid, C. (2007). Application of multivariate analysis to investigate potential antioxidants in conventional and torrefacto roasted coffee. *European Food Research and Technology*, 227(1), 141–149.
- Ludwig, I. A., Bravo, J., De Peña, M. P., & Cid, C. (2013). Effect of sugar addition (torrefacto) during roasting process on antioxidant capacity and phenolics of coffee. *LWT – Food Science and Technology*, 51(2), 553–559.
- Ludwig, I. A., Sanchez, L., Caemmerer, B., Kroh, L. W., De Peña, M. P., & Cid, C. (2012). Extraction of coffee antioxidants: Impact of brewing time and method. *Food Research International*, 48(1), 57–64.
- Meydavi, S., Saguy, I., & Kopelman, I. J. (1977). Browning determination in citrus products. *Journal of Agricultural and Food Chemistry*, 25(3), 602–604.
- Mussatto, S. I., Machado, E. M. S., Martins, S., & Teixeira, J. A. (2011). Production, composition, and application of coffee and its industrial residues. *Food and Bioprocess Technology*, 4(5), 661–672.
- Naranjo, M., Vélez, L. T., & Rojano, B. A. (2011). Actividad antioxidante de café colombiano de diferentes calidades. *Revista Cubana de Plantas Medicinales*, 16(2), 164–173.
- Nicoli, M. C., Anese, M., Manzocco, L., & Lerici, C. R. (1997). Antioxidant properties of coffee brews in relation to the roasting degree. *LWT – Food Science and Technology*, 30(3), 292–297.
- Nunes, F. M., & Coimbra, M. A. (2007). Melanoidins from coffee infusions. Fractionation, chemical characterization, and effect of the degree of roast. *Journal of Agricultural and Food Chemistry*, 55(10), 3967–3977.
- Parras, P., Martínez, M., Jiménez, A., & Murcia, M. (2017). Antioxidant capacity of coffees of several origins brewed following three different procedures. *Food Chemistry*, 102(3), 582–592.
- Pastoriza, S., & Rufián-Henares, J. A. (2014). Contribution of melanoidins to the antioxidant capacity of the Spanish diet. *Food Chemistry*, 164, 438–445.
- Pérez, L. M., Chávez, K., Medina, L. A., & Gámez, N. (2013). Compuestos fenólicos, melanoidinas y actividad antioxidante de café verde y procesado de las especies *Coffea arabica* y *Coffea canephora*. *Revista de Ciencias Biológicas Y de La Salud*, 15(1), 51–56.
- Pérez-Martínez, M., Caemmerer, B., De Peña, M. P., Cid, C., Kroh, L. W., Concepción, C., & Kroh, L. W. (2010). Influence of brewing method and acidity regulators on the antioxidant capacity of coffee brews. *Journal of Agricultural and Food Chemistry*, 58(5), 2958–2965.
- Pulido, R., Bravo, L., & Saura-Calixto, F. (2000). Antioxidant activity of dietary polyphenols as determined by a modified ferric reducing/antioxidant power assay. *Journal of Agricultural and Food Chemistry*, 48(8), 3396–3402.
- Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M., & Rice-Evans, C. (1999). Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biology & Medicine*, 26(9–10), 1231–1237.

- Rodrigues, N. P., & Bragagnolo, N. (2013). Identification and quantification of bioactive compounds in coffee brews by HPLC-DAD-MSn. *Journal of Food Composition and Analysis*, 32(2), 105–115.
- Rover, M. R., & Brown, R. C. (2013). Quantification of total phenols in bio-oil using the Folin-Ciocalteu method. *Journal of Analytical and Applied Pyrolysis*, 104, 366–371.
- Rufián-Henares, J. A., & Morales, F. J. (2008). Antimicrobial activity of melanoidins against *Escherichia coli* is mediated by a membrane-damage mechanism. *Journal of Agricultural and Food Chemistry*, 56(7), 2357–2362.
- Sacchetti, G., Di Mattia, C., Pittia, P., & Mastrocola, D. (2009). Effect of roasting degree, equivalent thermal effect and coffee type on the radical scavenging activity of coffee brews and their phenolic fraction. *Journal of Food Engineering*, 90(1), 74–80.
- Sánchez-González, I., Jiménez-Escrig, A., & Saura-Calixto, F. (2005). In vitro antioxidant activity of coffees brewed using different procedures (Italian, espresso and filter). *Food Chemistry*, 90(1–2), 133–139.
- Shinghara, A., Macku, C., & Shibamoto, T. (1998). Antioxidative activity of brewed coffee extracts. In T. Shibamoto, J. Terao, & T. Osawa (Eds.), *Functional foods for disease prevention II: Medicinal plants and other foods* (pp. 101–109). Washington: ACS symposium series.
- Summa, C. A., de la Calle, B., Brohee, M., Stadler, R. H., & Anklam, E. (2007). Impact of the roasting degree of coffee on the in vitro radical scavenging capacity and content of acrylamide. *LWT – Food Science and Technology*, 40(10), 1849–1854.
- Tagliazucchi, D., Verzelloni, E., & Conte, A. (2010). Effect of dietary melanoidins on lipid peroxidation during simulated gastric digestion: their possible role in the prevention of oxidative damage. *Journal of Agricultural and Food Chemistry*, 58(4), 2513–2519.
- van der Werf, R., Marcic, C., Khalil, A., Sigrist, S., & Marchioni, E. (2014). ABTS radical scavenging capacity in green and roasted coffee extracts. *LWT – Food Science and Technology*, 58(1), 77–85.
- Vignoli, J. A., Bassoli, D. G. G., & Benassi, M. T. T. (2011). Antioxidant activity, polyphenols, caffeine and melanoidins in soluble coffee: The influence of processing conditions and raw material. *Food Chemistry*, 124(3), 863–868.
- Vignoli, J. A., Viegas, M. C., Bassoli, D. G., & Benassi, M. de T. (2014). Roasting process affects differently the bioactive compounds and the antioxidant activity of arabica and robusta coffees. *Food Research International*, 61, 279–285.
- Wijewickreme, A. N., Kitts, D. D., & Durance, T. D. (1997). Reaction conditions influence the elementary composition and metal chelating affinity of nondialyzable model Maillard reaction products. *Journal of Agricultural and Food Chemistry*, 45(12), 4577–4583.