

Detection of adulterated coffee by fourier-transform infrared (FTIR) spectroscopy associated with sensory analysis

Yeison Barrios-Rodríguez¹ , Yenny Devia-Rodríguez² , Nelson Gutierrez-Guzmán² 

¹Pontificia Universidad Católica de Chile. Santiago de Chile, Chile

²Universidad Surcolombiana - Cesurcafe. Neiva, Colombia

Contact authors: yfbarrios@uc.cl; u20112106249@usco.edu.co; ngutierrezg@usco.edu.co

Received in October 8, 2021 and approved in June 30, 2022

ABSTRACT

Because of its huge economic value, coffee has been the target of adulteration worldwide. Given the successful application of spectroscopic methods in detecting adulterants, this study aimed to employ attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) to detect adulterants in roasted coffee samples and compare the results with that of sensory analysis. In this study, twelve coffee samples were intentionally adulterated with varying concentrations, i.e., 10%, 30%, and 50%, of corn, beans, sawdust, and coffee husk. These adulterated samples were compared with one unadulterated coffee sample and four roasted and ground commercially available coffee samples; spectral readings of caffeine and chlorogenic acid (CGA) standards were performed for reference. The sensory analysis was performed by 17 tasters who were trained by a Q-grader. The infrared (IR) spectra (FTIR) data were processed by multiplicative signal correction (MSC) and subjected to a principal component analysis (PCA), along with the results of the sensory analysis. The combination of sensory analysis and IR spectrum allowed to differentiate samples of adulterated coffee and unadulterated coffee by PCA, with an explanation of 79% variance. The results demonstrated that the wavenumbers associated with CGA and caffeine contribute significantly in distinguishing adulterated coffee samples.

Key words: Adulterants; coffee quality; chemometric; sensory analysis.

1 INTRODUCTION

Coffee is one of the most popular beverages in the world, leading to its large-scale commercialization. Because of this, it is of considerable importance to the economies of countries producing it. According to International Coffee Organization (International Coffee Organization - ICO, 2020a), world coffee production in 2020 was approximately 165 million bags, with a consumption of more than 165 million bags of 60 kg during the 2019–20 period (ICO, 2020b).

Due to its high commercial value, strategies for the assessment of coffee adulteration are of considerable importance (Sezer et al., 2018). Basically, coffee producers adopt adulteration to reduce costs and improve profits.

Perhaps the most detailed analysis on the evolution of the forms and methods of control in coffee adulteration, was made by Ferreira et al. (2021), who summarized the history of coffee adulterants and their control, starting in the 18th century. Adulteration not only deteriorates the sensory, physical, and chemical qualities of the product but also promotes the exploitation of consumers by violating product specifications and regulatory standards (Oliveira et al., 2009). Roasted and ground coffee is quite vulnerable to adulteration since it presents physical characteristics (particle size, texture, and color) that are easily reproduced by roasting and grinding a variety of biological materials, such as cereals, seeds, roots, and parchments (Reis; Franca; Oliveira, 2013b). The most common adulterants include coffee substitutes, such as chicory, malt, figs, cereals, caramel,

starch, maltodextrins, or glucose, as well as roasted or even unroasted coffee husk (Barbin et al., 2014).

The quality control of the coffee beverages is performed by trained or qualified tasters based on the following sensory characteristics: flavor, aroma, acidity, and body (Craig et al., 2018). However, since this human sensory evaluation can be markedly subjective and time-consuming (Murray; Delahunty; Baxter, 2001; Sano; Assad; Cunha, 2003), it would be advantageous in terms of quality to complement it with a type of chemical analysis. Traditionally, the strategies used to certify the chemical characteristics of coffee have been based on wet chemistry (Ribeiro; Salva; Ferreira, 2010). Studies have been carried out for the determination of adulterants in coffee, such as carbohydrates based on high-performance liquid chromatography (HPLC-UV-VIS) with post-column derivatization system (Pauli; Cristiano; Nixdorf, 2011), corn and coffee husk using nuclear magnetic resonance (NMR) with chemometric and high-performance anion-exchange chromatography/pulsed amperometric detection (HPAEC-PAD) (Milani et al., 2020; Garcia et al., 2009), and barley using solid-phase microextraction followed by gas chromatography-mass spectrometry (SPME-GC-MS) (Oliveira et al., 2009); Real-time PCR techniques for determination of cereals in commercial ground roast and soluble coffees (Ferreira et al., 2016). However, these methods are destructive, time-consuming, and sometimes expensive (Ribeiro; Salva; Ferreira, 2010). In the last recent years, the use of artificial intelligence to predict food adulteration (Nallan Chakravartula et al., 2022); as well as, the

electronics devices (i.e. electronic tongue) for the detection of coffee adulterations (Morais *et al.*, 2019).

Spectroscopy-based sensors have been reported as an alternative for the identification of adulterants (Negi; Pare; Meenatchi, 2021). Authors have also reported methods, such as laser-induced breakdown spectroscopy (LIBS) (Sezer *et al.*, 2018), diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) (Reis; Franca; Oliveira, 2013b), Fourier-transform infrared spectroscopy (FTIR) (Craig; Franca; Oliveira, 2011), photoacoustic spectroscopy (PAS) (Dias *et al.*, 2018), and FTIR-attenuated total reflectance (FTIR-ATR) (Barrios; Salas; Giron, 2020). The application of spectroscopy could be an attractive alternative to traditional analytical methods because of attributes like little sample preparation, rapid analysis, and the minimized use of hazardous solvents. On the other hand, since adulteration affects chemical compounds related to the quality of coffee, such as chlorogenic acids (CGA) and caffeine (minimally affected compounds in the processing of unadulterated coffee (Hameed *et al.*, 2018) the analysis of the spectrum regions influenced by these compounds could contribute to the authentication of coffee. In addition, studies analyzing the spectrum obtained by means of chemometric tools, such as principal component analysis (PCA), have demonstrated satisfactory results (Ebrahimi-Najafabadi *et al.*, 2012; Tavares *et al.*, 2016). The PCA is an exploratory technique that reduces the dimensionality of the data by projecting the samples in an orthogonal subspace built from linear combinations of the original variables, thereby facilitating the interpretation of multivariate datasets (Bro; Smilde, 2014).

The aim of this work was to employ attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) combined with chemometric tools to detect adulterants in roasted coffee samples and compare the results with that of sensory analysis.

2 MATERIAL AND METHODS

2.1 Reagents

The following reagents were used in the study: CGA primary reference standard 327-97-9, (3-Caffeoylquinic Acid) (Sigma-Aldrich, USA) and caffeine 99% (Sigma-Aldrich, USA).

2.2 Selection and preparation of samples

Arabica green coffee samples were acquired from the South Colombian Coffee Research Center in Neiva Colombia. The beans were manually sorted until non-defective coffee samples were obtained. In addition, four adulterants, i.e., corn (*Zea mays*), bean (*Nima calima*), sawdust, and coffee husk were purchased from local supermarkets. Batches (150 g) of coffee samples and adulterants were separately subjected to roasting

in a TC 150 R/G rotary Quantik drum roaster at a temperature of 190 °C. The degree of roasting of the adulterants was determined by measuring the luminosity (CIELAB L*) with a Konica Minolta CR-410 colorimeter, which was observed to be in the range of $18 > L^* < 21$. After roasting, the samples were finely grounded in a mill (Bunn G3, USA) to a particle size of 150–250 µm. Ground roasted coffee mixtures were prepared with increasing proportions, i.e., 10%, 30%, and 50% (w/w) of sawdust, coffee husk, beans, and corn as contaminants. Finally, to establish similarities with adulterated coffee samples, four commercially available roasted and ground coffee samples of different brands were included.

Therefore, a total of 21 samples were included for subsequent analyses, i.e., four commercially available coffee samples, one unadulterated coffee sample as control, four types of unmixed adulterants (coffee husk, sawdust, corn, and beans), and three samples each of coffee-sawdust, coffee-husk, coffee-corn, and coffee-bean mixtures at concentrations of 10%, 30%, and 50% (w/w).

2.3 FTIR analysis

In addition to the samples evaluated, caffeine and CGA standards were also analyzed in order to define wavenumbers associated with these compounds in the unadulterated coffee samples. The measurements of the medium IR spectrum of the samples (adulterated, unadulterated coffee, and standards of caffeine and CGA), at room temperature (20 ± 0.5 °C) and dry atmosphere, were performed in an Agilent Cary 630 FTIR spectrophotometer (Agilent, EEUU) with ATR sampling accessory. Approximately 1.0 g of sample powder was placed in the sampling accessory and pressed. The spectrum was obtained from the average of five readings and recorded from 650 to 4,000 cm^{-1} at a resolution of 8 cm^{-1} and 20 scans. The data were exported to excel format for further processing.

2.4 Sensory analysis

The sensory analysis was performed by 17 panelists, previously trained by a certified Q-grader professional. The preparation of the beverages (adulterated and unadulterated) was performed in accordance with the protocol described by Sanchez and Chambers (2015), using a ratio of 7.0 g of sample per 100 mL of water. The samples to be analyzed were prepared by fine grinding, using water filtered with activated carbon. The samples were prepared based on the V60 dripper method, with a water temperature of 93 ± 1 °C.

The attributes associated with coffee quality, such as aroma, color, sweetness, flavor, aftertaste, body, acidity, coffee flavor, bitterness, and scoring, were evaluated in 50 mL of the beverage; the evaluation was carried out on a hedonic scale from zero to ten, wherein, zero indicated the least acceptance and ten the highest approval.

2.5 Statistical analysis

The IR spectrum data were subjected to a polynomial fitting baseline correction method, with the “baselineSpectra” function of the ChemoSpec package of the R program and then were transformed by multiplicative signal correction (MSC). The information from the IR spectrum obtained from 650 to 1,800 cm^{-1} covers the fingerprint region of coffee samples. Principle component analysis (PCA) with the spectrum data was used to distinguish the four types of adulterants from the unadulterated coffee sample, which made it possible to identify the number of waves with the greatest influence.

The sensory data were expressed as mean \pm standard deviation (SD) for each of the samples. One-way analysis of variance (ANOVA) with a 95% confidence interval was performed.

The wavenumbers associated with caffeine and CGA and those with the greatest influence on adulterant discrimination were added as variables to the information obtained from the sensory analysis and a fresh PCA was performed. The analyses were performed using the statistical software R Core Team (2021) with the packages MDAtools and factoextra.

3 RESULTS

3.1 IR spectrum analysis of the adulterated and unadulterated coffee samples

The IR spectra corresponding to the unadulterated sample, commercially available ground coffee samples, and

the adulterated samples, i.e., coffee-sawdust, coffee-husk, coffee-corn, and coffee-bean, are presented in Figure 1. The results indicated a clear difference between the spectra of the adulterated coffee samples (2900–2800 cm^{-1}) and that of the unadulterated coffee sample (1800–650 cm^{-1}).

Analysis of the standard spectra of CGA and caffeine revealed two parallel peaks: one corresponding to the vibration of the O–H group attached to the benzene ring at 1,200–1,270 cm^{-1} and second due to C=O stretching at 1,600–1,700 cm^{-1} (Figure 2a) (Belay; Kim; Hwang, 2016). The bands identified at 809, 1,120, and 1,165 cm^{-1} from unadulterated roasted coffee are the characteristic bands of pure CGA isomers (Liang et al., 2016). For caffeine, the spectrum region between 1,600–1,700 cm^{-1} is taken for quantification (Abdalla, 2015). The peaks evidenced in this part of the spectrum are mainly due to the asymmetric and symmetric C=O stretching (Belay; Kim; Hwang, 2016). Pronounced peaks were observed at 1,700 and 1,650 cm^{-1} (Figure 2b); the latter was very close to 1,659 cm^{-1} (Gallignani et al., 2008; Garrigues et al., 2000; Singh et al., 1998), which along with 1,700 cm^{-1} are taken as reference for the quantification of caffeine (Ohnsmann et al., 2002). Also, the 1,549 cm^{-1} band was close to another reference band of caffeine, i.e., 1,554 cm^{-1} (Garrigues et al., 2000).

Figure 3 depicts the spectra of the adulterated coffee samples. A disproportion in the wavenumbers previously associated with compounds present in coffee was observed (caffeine and CGA) in the region 1,800–650 cm^{-1} .

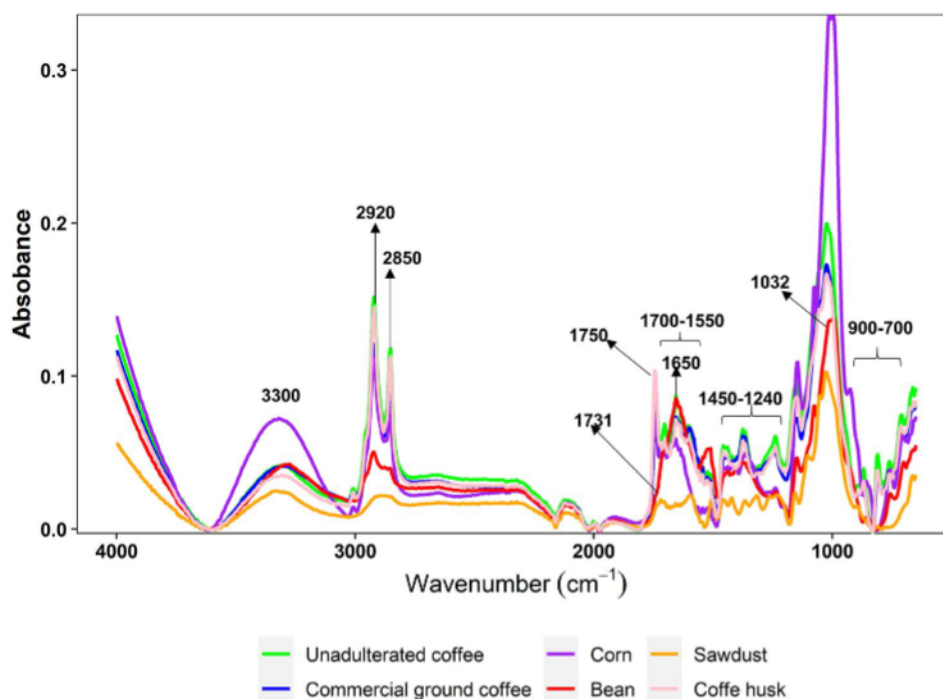


Figure 1: Wavenumber identification in the IR spectra associated with the vibration of functional groups of compounds present in the representative samples of unadulterated coffee, corn, beans, coffee husk, and sawdust.

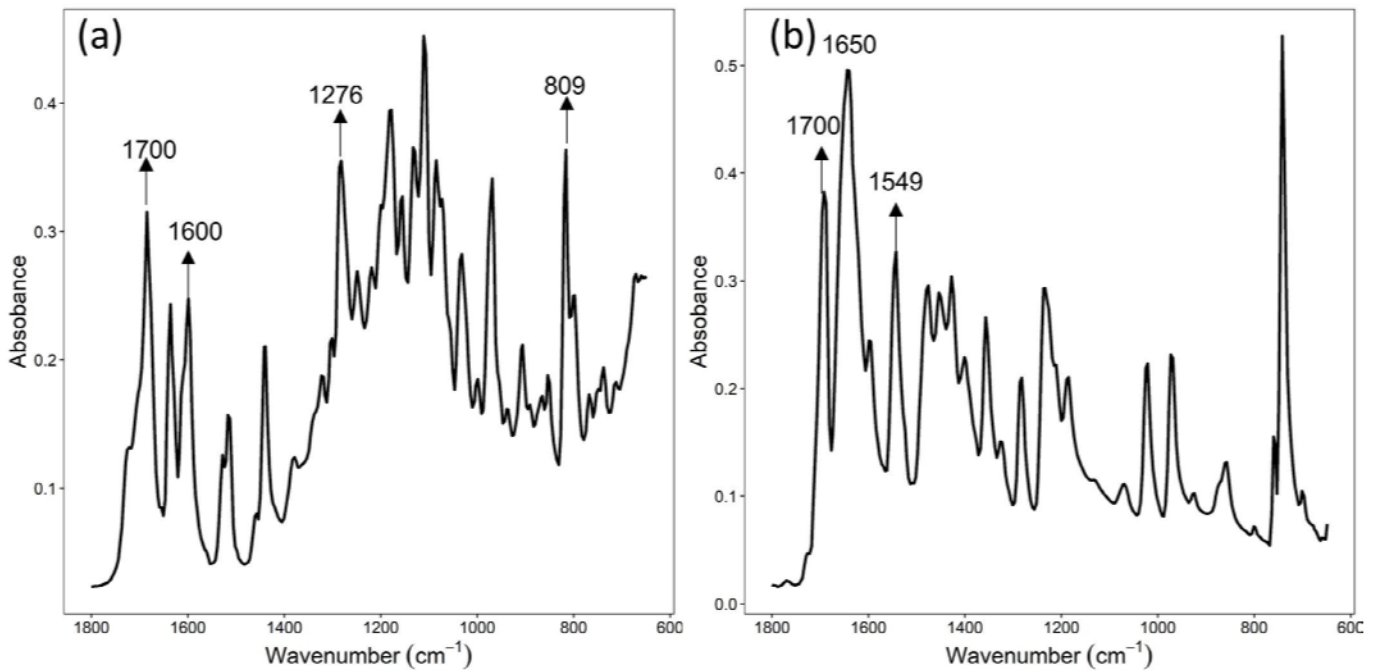


Figure 2: Infrared spectra of standard CGA (a) and caffeine (b) between 650-1,800 cm⁻¹.

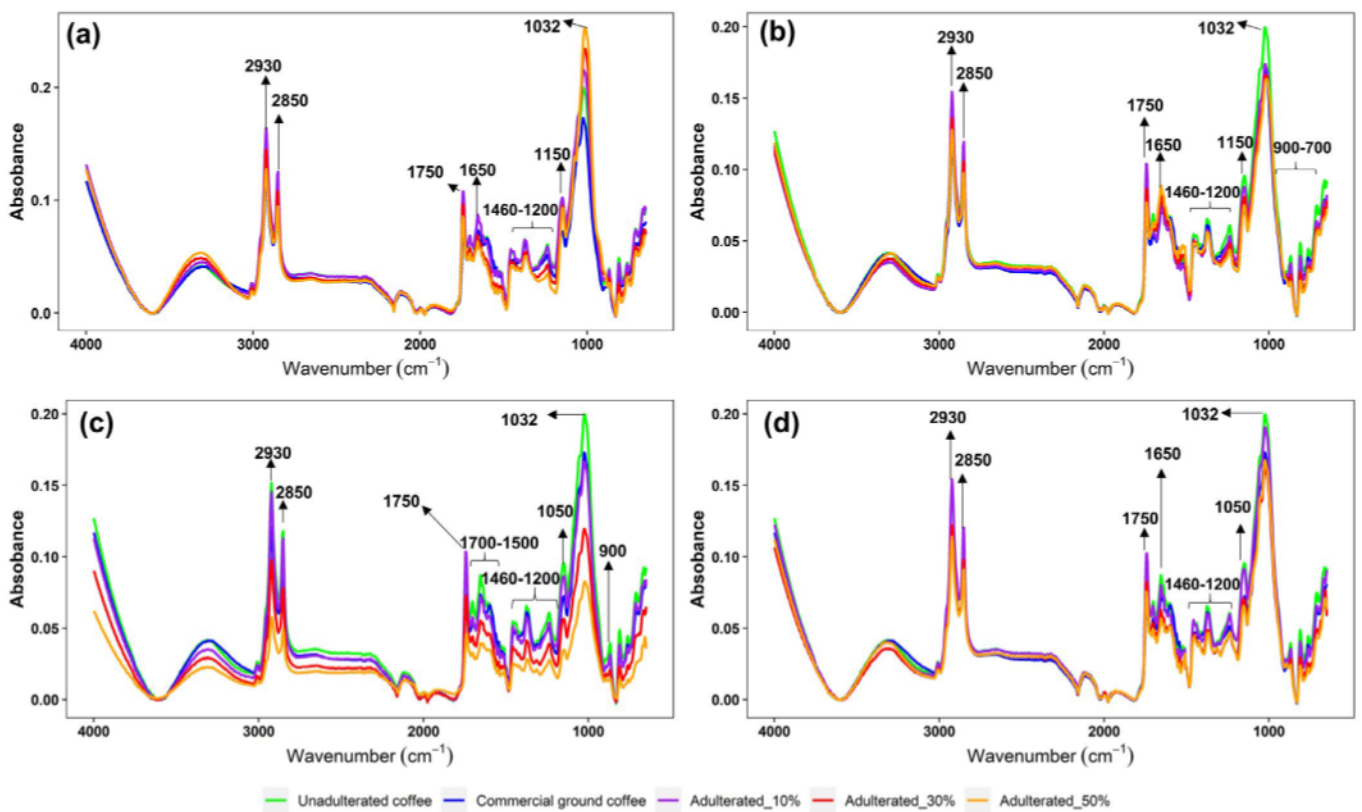


Figure 3: Effect of adulteration in wavenumber characteristics of the coffee IR spectrum. The infrared spectra correspond to samples of: Coffee-corn (a), coffee-bean (b), coffee-husk (c), and coffee-sawdust (d), in percentage portions (w/w) of 10%, 30%, and 50%.

After the superposition of IR spectra (Figure 3), the information between 1,800–1,650 cm^{-1} was utilized to evaluate the contribution of the wavenumbers in distinguishing the adulterated and unadulterated coffee samples by means of a PCA. Based on the PCA biplot with 82.9% explained variance (PC1 48.7% and PC2 34.1%), clear differentiation of coffee-corn, coffee-bean, and coffee-sawdust samples could be made from the unadulterated coffee sample; however, the coffee-husk sample presented a grouping very close to the unadulterated coffee sample (Figure 4). The lesser discrimination of the husk may be due to the similarities evident in the spectrum.

3.2 Effect of adulterants on the sensory properties of coffee and contribution to the FTIR-ATR analysis

Complementary to the FTIR analysis, a sensory analysis was performed to determine the effect of adulterants on the sensory attributes of coffee; the attributes exhibiting significant differences are shown in Figure 5. On average, a higher score was obtained for the attributes of unadulterated coffee samples. Also, a change in sensory attributes was observed with an increase in the concentration of adulterants, with a negative effect on acceptance for the samples adulterated with beans and corn. The commercially available ground coffee samples did not exhibit significant differences ($p < 0.05$) compared with the unadulterated coffee sample but presented a mean value equal to that of the samples with 10% adulterants in each of the sensory-quality attributes.

The scores indicated that all the coffee-bean samples, i.e., at 10%, 30%, and 50% concentrations, exhibited the highest differences compared with the unadulterated coffee sample, while the samples adulterated with corn, sawdust, and coffee husk presented differences only at the concentrations of 30% and 50%. This indicated that the greatest negative impact was observed at concentrations greater than or equal to 30% of the evaluated adulterants.

As evidenced by the sensory results of the panel of experts, a separate analysis was not decisive in differentiating between adulterated and unadulterated samples. Therefore, after analyzing the information of the IR spectrum, the wavenumbers related to compounds in coffee like caffeine (1,700, 1,650, and 1,549 cm^{-1}) and CGA (1,600, 1,276, and 809 cm^{-1}) (Figure 2) and those contributing highly (1,741, 1,532, 1,032, and 988 cm^{-1}) (Figure 4) to the separation of the adulterants by means of PCA were selected. In addition, sensory attributes that were statistically significant were included (Figure 6).

It is evident that the results obtained from the IR spectrum and sensory analysis taken together allow for the differentiation of the evaluated samples, with an explanation of 79.9% variance. The first dimension of PCA differentiates the adulterated samples, i.e., coffee-bean (10%, 30%, and 50%), coffee-sawdust (30% and 50%), and coffee-husk (30% and 50%), from the unadulterated coffee sample. The latter exhibited association with the sensory attributes of all adulterated samples at 10% concentration, while the coffee-bean samples had the strongest impact on the attributes

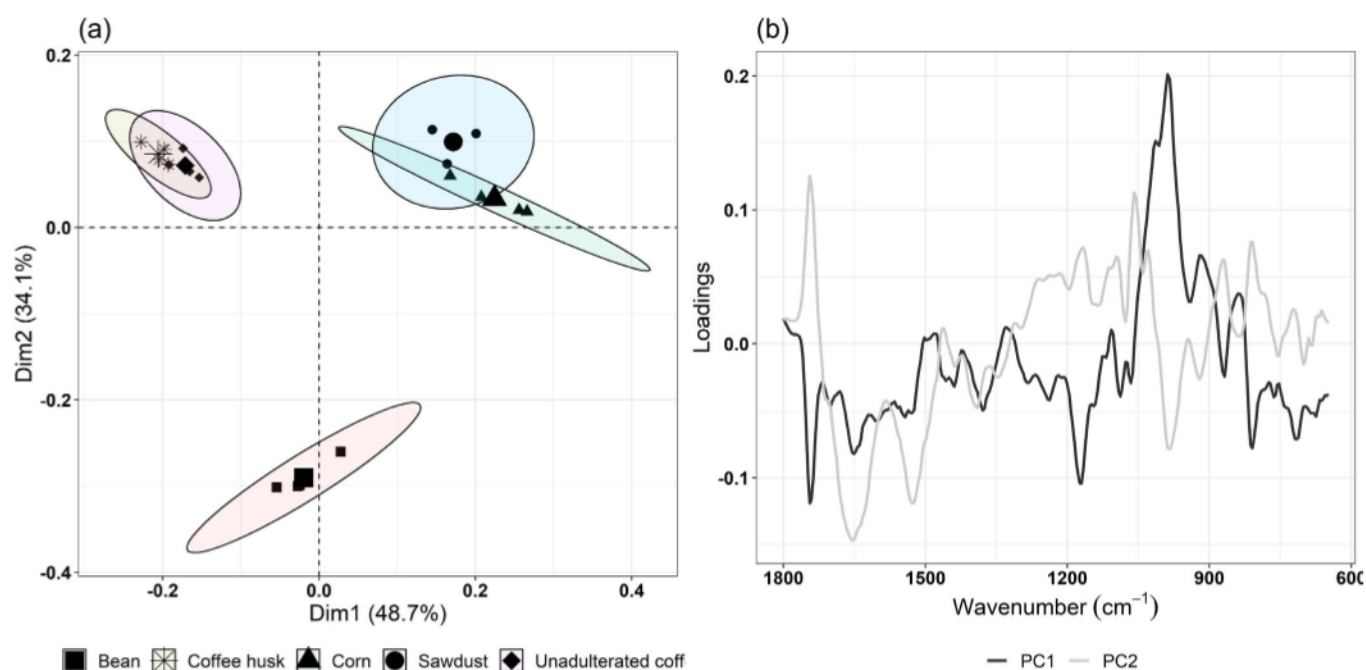


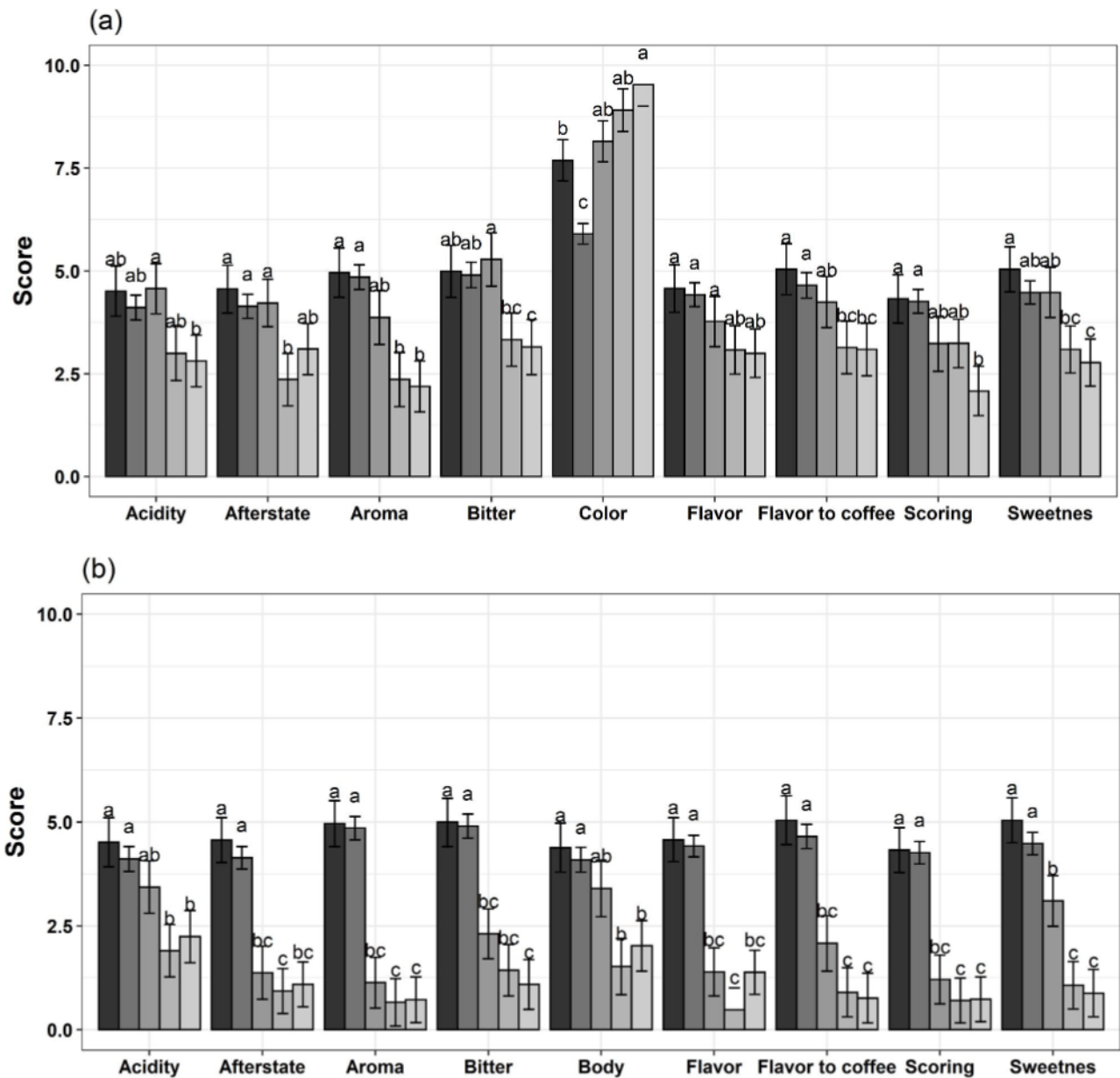
Figure 4: Principal component analysis (PCA) of the IR spectra in the range of 1,800–650 cm^{-1} ; (a) loads for PC1 and PC2 (b). The data were treated with baseline and multiplicative signal correction (MSC).

evaluated by the panelists. Additionally, the wavenumbers of 809 and 1,245 cm^{-1} , previously linked to the presence of CGA, presented a certain association with the samples of unadulterated coffee and those with 10% adulterants. The second dimension of PCA allowed for the classification of the samples adulterated with 30% and 50% corn, which was evidenced to be associated with the wavenumbers of 1,032 and 988 cm^{-1} contributed by the ether group in corn cellulose. The variables of the greatest contribution to the first dimension of PCA were the attributes of taste, flavor, aftertaste, body, overall score, sweetness, aroma, and acidity. In the second dimension, the greatest contribution

was made by the wavenumbers of 988, 1,275, 1,700, 1,600, 1,547, and 1,651 cm^{-1} , related to the possible presence of caffeine and CGA.

4 DISCUSSION

The IR spectrum (Figure 1) consisted of high-intensity wavenumbers of 2,924 cm^{-1} and 2,855 cm^{-1} corresponding to the symmetric and asymmetric vibrations of the C–H group, described for both caffeine and lipids in coffee (Paradkar; Irudayaraj, 2002). The vibrations were due to the modifications in alkenes, lipids, and olefins (Rojas *et al.*, 2020). Also, peaks



Continue...

Figure 5: Comparison of Tukey's mean for sensory-quality attributes for each of the evaluated coffee samples, including the adulterated coffee samples, i.e., coffee-corn (a), coffee-bean (b), coffee-husk (c), and coffee-sawdust (d).

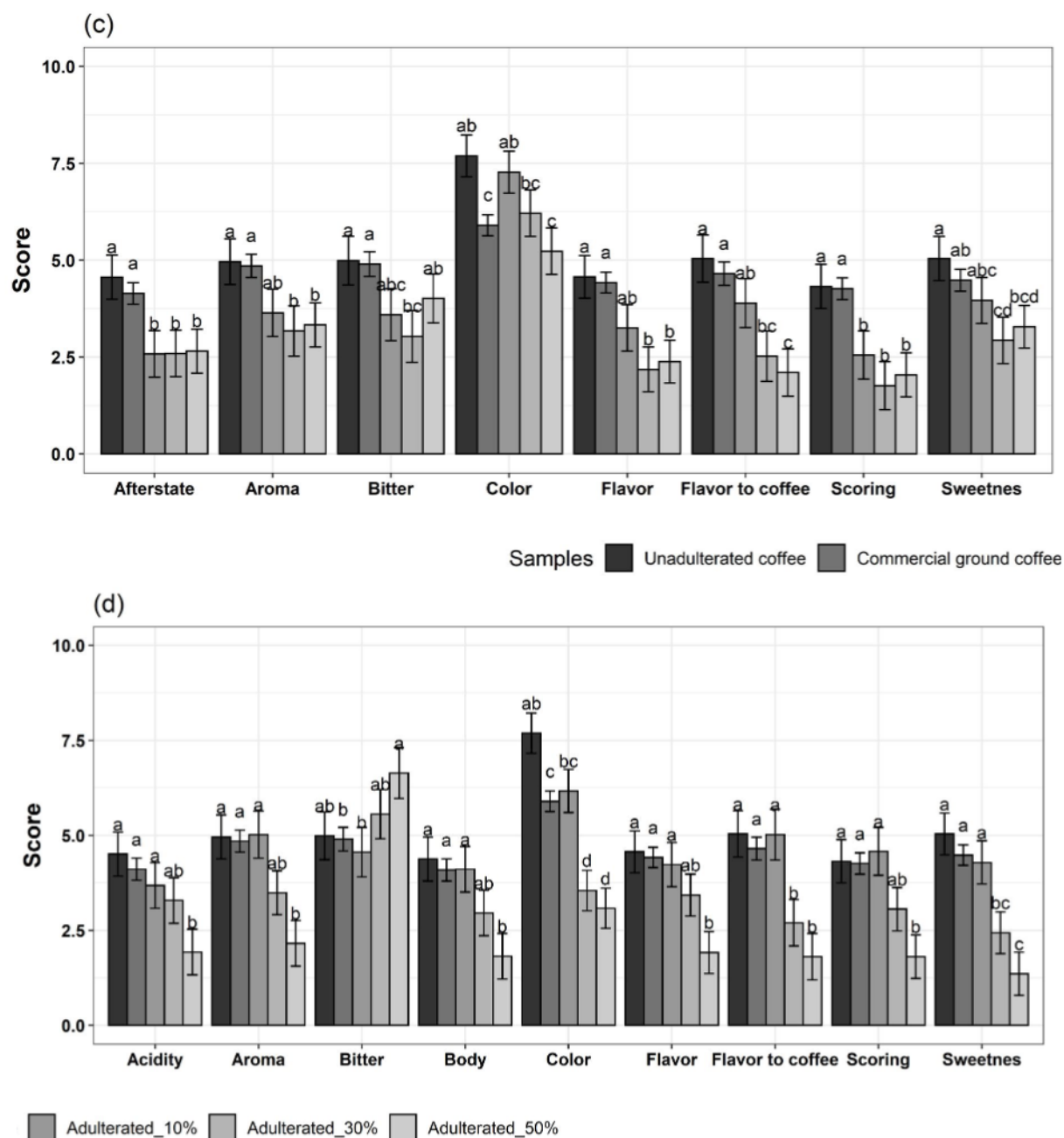


Figure 5: Continuation.

identified at 1,739 cm^{-1} and 1,650 cm^{-1} can be associated with the presence of compounds, such as lipids and caffeine (Gallignani et al., 2008; Reis; Franca; Oliveira, 2013a); the peaks corresponded to the vibration of carbonyl (CO) group in esters and that of C–H bond of the methyl group in caffeine (Bahamón; Parrado; Gutierrez, 2018; Barrios; Salas; Giron, 2020; Barrios; Gutierrez; Giron, 2020; Craig; Franca; Oliveira, 2011; Craig; Franca; Oliveira, 2012; Craig et al., 2018).

Likewise, the regions of 1,700–1,550 cm^{-1} , 1,600–1,300 cm^{-1} , and 1,450–1,240 cm^{-1} have been associated with compounds, such as caffeine, CGA, and trigonelline, respectively, in coffee (Craig; Franca; Oliveira, 2011; Reis;

Franca; Oliveira, 2013b, 2013a; Szafran et al., 2002). Due to the fact that these compounds are important for the flavor formation of coffee, the results of the IR spectra were checked for the presence of these compounds (Figure 2a–b). Previous research indicates that the molecules of CGA are mostly characterized by hydroxyl and carbonyl functional groups (Belay; Kim; Hwang, 2016).

In the overlapping spectra analysis (Figure 3a), a greater spectrum alteration between 1,400–1,200 cm^{-1} was observed in the region described for CGA in coffee, influenced by the low presence of absorbance peaks in this area for coffee-corn samples (Figure 1). Also, there was an

increase in the absorbance in the wavenumber $1,032\text{ cm}^{-1}$ with an increase in the percentage of adulteration. This may be due to the contribution of the cellulose ether group (Banerjee; Chattopadhyaya, 2017) or the presence of starch ($950\text{--}700\text{ cm}^{-1}$), lipids ($1,739\text{ cm}^{-1}$), and polysaccharides (993 cm^{-1}) in corn (Craig; Franca; Oliveira, 2011; Reis; Franca; Oliveira, 2013b), as is evidenced in the spectrum of corn (Figure 1). On the other hand, the 992 cm^{-1} peak had not been evident previously.

Similar effects were observed in the coffee-husk samples (Figure 3c). This region showed peaks in the IR spectrum (Figure 1) of the coffee-husk and coffee-corn samples, which were due to the skeletal vibration of the glycosidic bonds in the starch (Strubinger *et al.*, 2017). For the samples adulterated with beans (Figure 3b), an incidence in the wavenumbers $1,635\text{ cm}^{-1}$, $1,533\text{ cm}^{-1}$, and $1,245\text{ cm}^{-1}$ were evidenced, related to the amine groups (Alonso *et al.*, 2008; Plans *et al.*, 2013); the incidence was higher in beans due to their protein content. The effect on absorbance was observed at $1,032\text{ cm}^{-1}$, and the vibration can be associated with the contents of starch and lysine present in beans (Gordillo; García Salcedo; Mejía Morales, 2012).

The coffee-husk samples exhibited lower absorbance values in the spectrum as the percentage of adulteration

increased (Figure 3c); however, no strange peaks were present in the coffee spectrum. This may be because of the presence of some compounds, such as CGA, in low concentrations, which, as discussed above, have strong absorption at $1,450\text{ cm}^{-1}$ and $1,000\text{ cm}^{-1}$ (Strubinger *et al.*, 2017).

In the samples adulterated with sawdust (Figure 3d), an incidence of the adulterant was observed in the region between $1,700\text{--}1,032\text{ cm}^{-1}$. This can be attributed to the presence of chemical groups, such as cellulose, hemicellulose, and lignin. The differences found in the absorption bands, where a decrease in the absorbance values with an increasing percentage of sawdust was observed, can be explained by the low absorbance values presented by the coffee-sawdust samples compared with the unadulterated coffee samples (Figure 1). The wavenumbers of $2,920\text{ cm}^{-1}$, $2,850\text{ cm}^{-1}$, $1,731\text{ cm}^{-1}$, $1,600\text{ cm}^{-1}$, and $1,032\text{ cm}^{-1}$ were identified for the coffee-sawdust samples, as well as the peaks in the region of $1,450\text{--}1,350\text{ cm}^{-1}$. Previous studies have reported that $1,731\text{ cm}^{-1}$ can be assigned to a C=O stretch attributed to lignin aromatic groups (Bajpai, Bajpai; Rai, 2012). The region of $1,450\text{--}1,350\text{ cm}^{-1}$ has been assigned to the presence of C-H groups, and the signals of $2,900\text{--}2,880\text{ cm}^{-1}$ represent the symmetric and asymmetric vibrations of the CH_2 groups (Couto *et al.*, 2012).

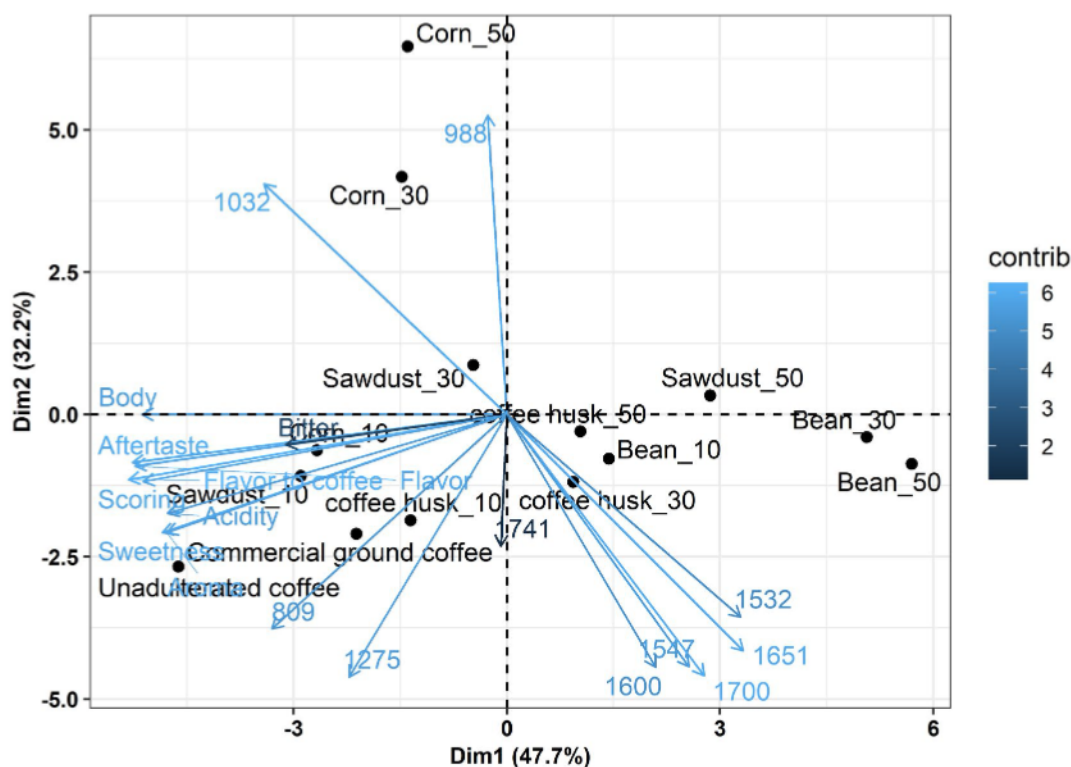


Figure 6: Correlation of the sensory attributes and wavenumbers of the IR spectrum related to the compounds of the evaluated samples based on the first two dimensions of PCA (PC1 47.7% and PC2 32.2%). The numbers refer to the concentrations of each of the adulterants.

The PCA results (Figure 4) indicated that it is feasible through the information obtained from the IR spectrum to distinguish the adulterated (coffee-corn, coffee-bean, coffee-sawdust, and coffee-husk) and unadulterated coffee samples, which is consistent with the results of Reis, Franca and Oliveira (2013a). Other authors have highlighted the potential usefulness of the FTIR-ATR technique combined with chemometrics for quality control in coffee, highlighting that it is a cost-effective, fast, easy to operate, and non-destructive technique (Barrios; Salas; Giron, 2020; Craig; Franca; Oliveira, 2012; Dias et al., 2018; Pauli; Cristiano; Nixdorf, 2011).

The results indicated that the wavenumbers of greatest contribution in the positive region of the PC1 are the region from 1,032–970 cm^{-1} with a central point at 988 cm^{-1} . While in the negative zone of the PC1, a great contribution of the peaks of 1,741 cm^{-1} and 1,650 cm^{-1} was observed. This last region, as it was previously discussed, is contributed by caffeine and was observed to be associated with the samples of unadulterated coffee; while the other region can be attributed to the contribution of the compounds of functional chemical groups of cellulose, hemicellulose, and lignin present in corn and sawdust. The PC2 was characterized by a strong contribution in the negative region of the peaks of 1,600–1,650 cm^{-1} , 1,520–1,560 cm^{-1} , and 1,000–900 cm^{-1} . The wavenumbers of 1,740–1,750 cm^{-1} have a high contribution to the positive region of the PC2. The above-mentioned results demonstrated that compounds, such as CGA and lipids, contribute to the differentiation of the coffee samples. The first regions were widely related to CGA and their isomers, while the 1,740 cm^{-1} region may be due to the contribution of carbonyl (CO) in the esters.

The sensory analysis results indicated that the addition of beans and corn had a greater adverse impact on the quality of coffee as compared to the addition of sawdust and coffee husk. This may be due to the fact that sawdust and coffee husk do not have compounds that significantly predominate, influence, or obscure the compounds responsible for coffee's own characteristics. For example, the major sawdust compounds, such as cellulose, lignin, and hemicellulose (Phonphuak; Chindaprasirt, 2015), can generate volatile compounds of interest at temperatures above 300 °C (Zhao; Jiang; Chen, 2017), i.e., temperatures far above that of this study. In the case of coffee husk, it shares some compounds similar to coffee but in a smaller proportion, such as CGA, caffeine, and trigonelline (Oliveira et al., 2018; Strubinger et al., 2017). The beans and corn have a higher content of carbohydrates and proteins, which are important precursors of flavors and aromatic compounds; this explains their greater impact on the sensory attributes of samples adulterated with these two types of grains.

5 CONCLUSIONS

The analysis of the IR spectrum with PCA allowed distinguishing the adulterated coffee samples (coffee-sawdust, coffee-husk, coffee-corn, and coffee-bean) from the unadulterated coffee sample. It was established that the greatest effects of the addition of adulterants in the IR spectrum of coffee were observed in the wavenumbers of 1,800–700 cm^{-1} , and it was more evident for the samples adulterated with beans and coffee husk. However, at the sensory level, a greater effect on the characteristics of coffee was evidenced by samples adulterated with beans and corn.

Based on sensory analysis and IR spectrum, it was possible to differentiate the samples with greater than 10% percentage of adulterants. In particular, the coffee-corn samples were classified far apart from other coffee samples in the PCA of the sensory analysis and IR spectrum. The wavenumbers associated with compounds in coffee, such as CGA and caffeine, made an important contribution to the differentiation of the adulterated samples. Therefore, this study could establish that the FTIR technique can be a feasible complement to sensory analysis in coffee authentication.

6 ACKNOWLEDGEMENTS

This work was supported by the South Colombian Coffee Research Center, CESURCAFÉ.

7 AUTHORS' CONTRIBUTION

YB-R wrote the manuscript and supervised the experiment, YD-R performed the experiment and co-work the manuscript, and NG-G supervised the experiment review and approved the final version of the work and conducted all statistical analyses.

8 REFERENCES

- ABDALLA, M. A. Determination of caffeine, the active ingredient in different coffee drinks and its characterization by FTIR/ATR and TGA/DTA. **International Journal of Engineering and Applied Sciences**, 2(12):85-89, 2015.
- ALONSO, A. et al. Habituation of bean (*Phaseolus vulgaris*) cell cultures to quinclorac and analysis of the subsequent cell wall modifications. **Annals of Botany**, 101(9):1329-1339, 2008.
- BAHAMÓN, A.; PARRADO, L.; GUTIÉRREZ, N. ATR-FTIR for discrimination of espresso and americano coffee pods. **Coffee Science**, 13(4):550-558, 2018.

- BAJPAI, S. K.; BAJPAI, M.; RAI, N. Sorptive removal of ciprofloxacin hydrochloride from simulated wastewater using sawdust: Kinetic study and effect of pH. **Water SA**, 38(5):673-682, 2012.
- BANERJEE, S.; CHATTOPADHYAYA, M. C. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. **Arabian Journal of Chemistry**, 10:S1629-S1638, 2017.
- BARBIN, D. F. et al. Application of infrared spectral techniques on quality and compositional attributes of coffee: An overview. **Food Research International**, 61:23-32, 2014.
- BARRIOS, Y.; GUTIERREZ, N.; GIRON, J. Effect of the postharvest processing method on the biochemical composition and sensory analysis of arabica coffee. **Engenharia Agrícola**, 40(2):177-183, 2020.
- BARRIOS, Y.; SALAS, K.; GIRÓN, J. Comparison of sensory attributes and chemical markers of the infrared spectrum between defective and non-defective Colombian coffee samples. **Coffee Science**, 15:e151659, 2020.
- BELAY, A.; KIM, H. K.; HWANG, Y. H. Binding of caffeine with caffeic acid and chlorogenic acid using fluorescence quenching, UV/vis and FTIR spectroscopic techniques. **Luminescence**, 31(2):565-572, 2016.
- BRO, R.; SMILDE, A. K. Principal component analysis. **Analytical Methods**, 6:2812-2831, 2014.
- COUTO, G. M. et al. Use of sawdust Eucalyptus sp. in the preparation of activated carbons. **Ciência e Agrotecnologia**, 36(1):69-77, 2012.
- CRAIG, A. P. et al. Mid infrared spectroscopy and chemometrics as tools for the classification of roasted coffees by cup quality. **Food Chemistry**, 245:1052-1061, 2018.
- CRAIG, A. P.; FRANCA, A. S.; OLIVEIRA, L. S. Discrimination between Immature and mature green coffees by attenuated total reflectance and diffuse reflectance fourier transform infrared spectroscopy. **Journal of Food Science**, 76(8):C1162-C1168, 2011.
- CRAIG, A. P.; FRANCA, A. S.; OLIVEIRA, L. S. Discrimination between defective and non-defective roasted coffees by diffuse reflectance infrared Fourier transform spectroscopy. **LWT-Food Science and Technology**, 47(2):505-511, 2012.
- DIAS, R. C. E. et al. Quantitative assessment of specific defects in roasted ground coffee via infrared-photoacoustic spectroscopy. **Food Chemistry**, 255:132-138, 2018.
- EBRAHIMI-NAJAFABADI, H. et al. Detection of addition of barley to coffee using near infrared spectroscopy and chemometric techniques. **Talanta**, 99:175-179, 2012.
- FERREIRA, T. et al. Three centuries on the science of coffee authenticity control. **Food Research International**, 149:110690, 2021.
- FERREIRA, T. et al. Using Real-Time PCR as a tool for monitoring the authenticity of commercial coffees. **Food chemistry**, 199:433-438, 2016.
- GALLIGNANI, M. et al. Determination of caffeine in coffee by means fourier transform infrared spectrometry. **Revista Tecnica de La Facultad de Ingenieria Universidad Del Zulia**, 31(2):159-168, 2008.
- GARCIA, L. M. Z. et al. Chemometric evaluation of adulteration profile in coffee due to corn and husk by determining carbohydrates using HPAEC-PAD. **Journal of Chromatographic Science**, 47(9):825-832, 2009.
- GARRIGUES, J. M. et al. Fourier transform infrared determination of caffeine in roasted coffee samples. Fresenius' **Journal of Analytical Chemistry**, 366(3):319-322, 2000.
- GORDILLO, F.; GARCÍA-SALCEDO, A.; MEJÍA-MORALES, C. Identificación de adulterantes soya, frijol y cebada en café tostado y molido utilizando EFA-IRTF. **Temas Agrarios**, 17(1), 2012.
- HAMEED, A. et al. Farm to consumer: factors affecting the organoleptic characteristics of coffee. II: Postharvest processing factors. **Comprehensive Reviews in Food Science and Food Safety**, 17(5):1184-1237, 2018.
- INTERNATIONAL COFFEE ORGANIZATION - ICO. **Crop year production by country**. 2020. Available in: <<https://ico.org/historical/1990%20onwards/PDF/1a-total-production.pdf>>. Access in: july, 15, 2020a.
- INTERNATIONAL COFFEE ORGANIZATION - ICO. **World Coffee consumption for 2019/2020**. 2020. Available in: <<http://www.ico.org/prices/new-consumption-table.pdf>>. Access in: july, 15, 2020b.
- LIANG, N. et al. Application of attenuated total reflectance-fourier transformed infrared (ATR-FTIR) spectroscopy to determine the chlorogenic acid isomer profile and antioxidant capacity of coffee beans. **Journal of Agricultural and Food Chemistry**, 64(3):681-689, 2016.

- MILANI, M. I. et al. Authentication of roasted and ground coffee samples containing multiple adulterants using NMR and a chemometric approach. **Food Control**, 112:107104, 2020.
- MORAIS, T. C. B. et al. A simple voltammetric electronic tongue for the analysis of coffee adulterations. **Food Chemistry**, 273:31-38, 2019.
- MURRAY, J. M.; DELAHUNTY, C. M.; BAXTER, I. A. Descriptive sensory analysis: Past, present and future. **Food Research International**, 34(6):461-471, 2001.
- NALLAN CHAKRAVARTULA, S. et al. Use of convolutional neural network (CNN) combined with FT-NIR spectroscopy to predict food adulteration: A case study on coffee. **Food Control**, 135:108816, 2022.
- NEGI, A.; PARE, A.; MEENATCHI, R. Emerging techniques for adulterant authentication in spices and spice products. **Food Control**, 127:108113, 2021.
- OHNSMANN, J. et al. Determination of caffeine in tea samples by fourier transform infrared spectrometry. **Analytical and Bioanalytical Chemistry**, 374(3):561-565, 2002.
- OLIVEIRA, F. C. et al. Characterization of coffee (*Coffea arabica*) husk lignin and degradation products obtained after oxygen and alkali addition. **Bioresource Technology**, 257:172-180, 2018.
- OLIVEIRA, R. C. et al. Evaluation of the potential of SPME-GC-MS and chemometrics to detect adulteration of ground roasted coffee with roasted barley. **Journal of Food Composition and Analysis**, 22(3):257-261, 2009.
- PARADKAR, M. M.; IRUDAYARAJ, J. Rapid determination of caffeine content in soft drinks using FTIR-ATR spectroscopy. **Food Chemistry**, 78(2):261-266, 2002.
- PAULI, E. D.; CRISTIANO, V.; NIXDORF, S. L. Method for determination of carbohydrates employed in the selection of adulterations in coffee. **Quimica Nova**, 34(4):689-694, 2011.
- PHONPHUAK, N.; CHINDAPRASIRT, P. Types of waste, properties, and durability of pore-forming waste-based fired masonry bricks. In: PACHECO-TORDAL, et al. **Eco-efficient masonry bricks and blocks: Design, properties and durability**. Amsterdam: Elsevier Science, v1, p. 103-127, 2015.
- PLANS, M. et al. Characterization of common beans (*Phaseolus vulgaris* L.) by infrared spectroscopy: Comparison of MIR, FT-NIR and dispersive NIR using portable and benchtop instruments. **Food Research International**, 54(2):1643-1651, 2013.
- R CORE TEAM. **R: A language and environment for statistical computing**. 2021. R Foundation for Statistical Computing, Vienna, Austria. Available in: <http://www.R-project.org/>. Access in: July 27, 2022.
- REIS, N.; FRANCA, A. S.; OLIVEIRA, L. S. Performance of diffuse reflectance infrared Fourier transform spectroscopy and chemometrics for detection of multiple adulterants in roasted and ground coffee. **LWT - Food Science and Technology**, 53(2):395-401, 2013a.
- REIS, N.; FRANCA, A. S.; OLIVEIRA, L. S. Quantitative evaluation of multiple adulterants in roasted coffee by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and chemometrics. **Talanta**, 115:563-568, 2013b.
- RIBEIRO, J. S.; SALVA, T. J.; FERREIRA, M. M. C. Chemometric studies for quality control of processed brazilian coffees using drifts. **Journal of Food Quality**, 33(2):212-227, 2010.
- ROJAS, M. et al. Roasting impact on the chemical and physical structure of Criollo cocoa variety (*Theobroma cacao* L.). **Journal of Food Process Engineering**, 43(6):e13400, 2020.
- SANCHEZ, K.; CHAMBERS, E. How does product preparation affect sensory properties? An example with coffee. **Journal of Sensory Studies**, 30(6):499-511, 2015.
- SANO, E. E.; ASSAD, E. D.; CUNHA, S. A. Quantifying adulteration in roast coffee powders by digital image processing. **Journal of Food Quality**, 26(2):123-134, 2003.
- SEZER, B. et al. Coffee arabica adulteration: Detection of wheat, corn and chickpea. **Food Chemistry**, 264:142-148, 2018.
- SINGH, B. R. et al. Determination of caffeine content in coffee using Fourier transform infra-red spectroscopy in combination with attenuated total reflectance technique: A bioanalytical chemistry experiment for biochemists. **Biochemical Education**, 26(3):243-247, 1998.
- STRUBINGER, A. et al. Valorization of waste from agro-industry using thermo-chemical treatments. **WIT Transactions on Ecology and the Environment**, 224(1):425-436, 2017.
- SZAFRAN, M. et al. Ab initio and DFT calculations of the structure and vibrational spectra of trigonelline. **Journal of Molecular Structure**, 614(1-3):97-108, 2002.

TAVARES, K. M. *et al.* Free tocopherols as chemical markers for Arabica coffee adulteration with maize and coffee by-products. **Food Control**, 70:31-324, 2016.

ZHAO, C.; JIANG, E.; CHEN, A. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. **Journal of the Energy Institute**, 90(6):902-913, 2017.