Separation between high and low quality coffees by FTIR-ATR
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ABSTRACT
The presence of defective coffee beans depreciates the quality of the coffee beverage consumed worldwide. The intrinsic defects (sour, black and immature beans) are the ones that, when roasted, contribute the most to the depreciation of the coffee beverage quality. Color sorting is the major procedure employed for separation of defective and non-defective coffee beans prior to roasting. However, such procedure is not efficient for separation of immature beans. Recent studies have shown that Fourier Transform Infrared Spectroscopy (FTIR) in combination with chemometric techniques have been successfully applied in the food industry for quality evaluation of food products. Thus, the objective of the present study was to evaluate the feasibility of employing FTIR for separation between high quality (non-defective) and low quality (defective) coffee beans. Defective (black, immature, light sour and dark sour) and non-defective Arabica coffee beans were manually separated. Ground coffee samples were then submitted to FTIR analysis employing an attenuated total reflectance (ATR) accessory. Multivariate statistical analysis (PCA and clusters) was performed in order to verify the possibility of discrimination between defective and non-defective coffee samples. The analysis was based on original spectral data and also on the first and second derivatives of the spectra. A clear separation between defective and non-defective coffee beans was observed, with the samples being distributed into three major groups: (i) non-defective, (ii) light sour and (iii) dark sour/black/immature. Such results indicate that FTIR analysis presents potential for the development of a fast and reliable analytical methodology for separation between high and low quality coffees.

Keywords: Spectroscopic methods; coffee; defective beans.

INTRODUCTION
The presence of defective coffee beans depreciates the quality of the coffee beverage consumed worldwide [1]. The intrinsic defects (sour, black and immature beans) are the ones that, when roasted, contribute the most to the depreciation of the coffee beverage quality. Colour sorting is the major procedure employed for separation of defective and non-defective coffee beans prior to roasting. In Brazil, manual sorting is usually employed for bean quality classification and electronic sorting is employed in farms and cooperatives of coffee producers for the actual removal of defective beans. In the electronic sorters, coffee beans pass, one by one, by an electronic eye or camera system, and depending on wavelength measurements, the bean is either allowed to pass or it is shot with a puff of air into a reject pile. However, such procedure is not efficient for separation of immature beans [2].

Recent studies have shown that some chemical parameters could be employed for separation between defective and non-defective green coffee beans of a given variety (Arabica or Robusta). Examples include levels of histamine [3] and ESI-MS profiles [4]. However, most of the employed instrumental techniques and analytical procedures are time demanding, expensive and involve a considerable amount of manual work. Recent studies have also shown that FTIR-based methods, in combination with chemometric techniques, can be successfully applied in the food industry, in association with food quality evaluation [5]. FTIR-based methods are fast, reliable, simple to perform and do not require sample pre-treatment. Such technique provides simple and reproducible means of handling food products with non-destructive analyses, with the sampling/analysis procedure usually taking less than 5 min.

There are a few studies that have focused on FTIR applied to coffee analysis, employing either roasted coffee or aqueous extracts (e.g. coffee beverage). The specific applications were separation between Arabica and
Robusta [6], adulteration of freeze-dried instant coffees by glucose, starch or chicory [7], evaluation of roasting conditions [8], geographical discrimination [9] and separation between decaffeinated and regular roasted coffees [10]. Thus, the objective of this work was to evaluate the potential of Fourier Transform Infrared (FTIR) spectroscopy in the characterization and separation of low quality (defective) and high quality (non-defective) coffee beans prior to roasting.

MATERIALS & METHODS

Arabica green coffee samples, acquired from Café Fino Grão (Belo Horizonte, MG), were comprised of coffee beans obtained from different cooperatives located in Minas Gerais State, Brazil, that were rejected by colour sorting machines. Black, sour (separated into light and dark coloured), immature and non-defective beans were manually picked to constitute separate sampling lots and ground to a particle diameter of 0.42 mm.

Colour measurements were performed using a tristimulus colorimeter (HunterLab Colorflex 45/0 Spectrophotometer, Hunter Laboratories, VA, USA), with standard illumination D65, and colorimetric normal observer angle of 10°, employing both whole and ground coffee samples. Colour measurements were performed thrice for each sample.

A Shimadzu IRAffinity-1 FTIR Spectrofotometer (Shimadzu, Japan) with a DLATGS (Deuterated Triglycine Sulfate Doped with L-Alanine) detector was used in the measurements that were all performed in a dry atmosphere at room temperature (20 ± 0.5 °C). A horizontal ATR sampling accessory (ATR-8200HAI) equipped with ZnSe cell was employed. In order to be able to obtain a constant sample mass, a small metal recipient 2.4 mm thick and presenting an aperture of the same size of the ATR accessory (79 mm long and 10 mm wide) was placed over the ZnSe ATR crystal. The ground coffee samples (2 g) were then placed inside the metal recipient and pressed with the machine's gripper in order to obtain the best possible contact with the crystal. All spectra were recorded within a range of 4000–700 cm$^{-1}$ with a 4 cm$^{-1}$ resolution and 20 scans. Spectra treatment consisted of baseline correction and normalization.

RESULTS & DISCUSSION

Average values of measured colour parameters for non-defective and defective coffee samples are shown in Table 1. Measurements were based on the CIE $L^*a^*b^*$ three dimensional Cartesian (xyz) colour space, represented by: Luminosity ($L^*$), ranging from 0 (black) to 100 (white); parameter $a^*$, representing the green–red color component; and parameter $b^*$, representing the blue–yellow component.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Whole beans</th>
<th>Ground beans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^*$</td>
<td>$a^*$</td>
</tr>
<tr>
<td>Non-defective</td>
<td>46.1±1.1$^a$</td>
<td>2.7±0.3$^c$</td>
</tr>
<tr>
<td>Immature</td>
<td>43.1±1.1$^b$</td>
<td>1.8±0.3$^d$</td>
</tr>
<tr>
<td>Sour (light)</td>
<td>37.1±2.1$^a$</td>
<td>6.5±1.0$^e$</td>
</tr>
<tr>
<td>Sour (dark)</td>
<td>29.6±1.0$^d$</td>
<td>3.7±0.4$^d$</td>
</tr>
<tr>
<td>Black</td>
<td>27.6±1.3$^d$</td>
<td>0.9±0.2$^c$</td>
</tr>
</tbody>
</table>

Average±Standard deviation. Average values followed by the same letter in the same column do not differ significantly by the Tukey test at 5% probability.

Results presented in Table 1 in terms of measurements performed on whole coffee beans, i.e., evaluation of the bean surface colour, show that black and dark sour beans presented lower luminosity values than non-defective, immature and light sour ones, indicating that this parameter can be successfully employed only to separate black and dark sour defects prior to roasting. It can also be observed that non-defective, immature and black beans presented higher values of hue angle in association with a greenish tone. Black and dark sour beans presented the lowest values of colour saturation. Colour measurements taken for ground samples represent an average colour of the material, taking into account both the surface and interior. Luminosity
values were higher for ground beans compared to whole ones, as a consequence of the fact that the bean
surface is darker than its core.

The results presented in Table 1 are corroborated by the score plots obtained for PCA analysis of colour
parameters of whole beans (see Figure 1). Data matrices for PCA analysis were assembled so that each row
corresponded to a sample and each column to a colour parameter. The first two principal components (PCs)
explained 66% and 32% of the data variance, respectively. Four distinct groups can be perceived, separated
by quadrant: light sour (positive PC1, positive PC2); dark sour (negative PC1, positive PC2); black (negative
PC1, negative PC2); non-defective and immature (positive PC1, negative PC2). The first component allowed
for separation between darker and lighter samples, being mostly affected by luminosity values. Separation
by the second component can be associated to black, immature and non-defective beans presenting a greenish
tone as opposed to the yellowish hue of sour beans. Such results indicate that even sorting systems that
employ bi-chromatic light measurements will not be able to separate immature and non-defective coffee
beans.

![Figure 1. PCA scores scatter plot of L*a*b* color parameters for whole coffee beans (PC1 vs. PC2). □ non-defective;
△ immature; ▲ sour (light); ▼ sour (dark); ▣ black.](image)

Typical FTIR spectra obtained for green coffee samples are shown in Figure 2. Although FTIR literature data
on coffee is only available for roasted samples, and thus a direct comparison cannot be done, a few
qualitative aspects of the spectra can be discussed. The two sharp bands that can be viewed in the 2800-3000
\( \text{cm}^{-1} \) range have also been reported for both Arabica and Robusta roasted coffee samples, but no
identification was attempted [6]. Nonetheless, studies of FTIR analysis of caffeine on soft drinks have also
reported two sharp peaks at 2829 and 2882 \( \text{cm}^{-1} \), with the later one being correlated with the asymmetric
stretching of C–H bonds of methyl (\(-\text{CH}_3\)) group in the caffeine molecule and the peak region being
successfully used to develop predictive models for quantitative analysis of caffeine [11]. The sharp band at
1743 \( \text{cm}^{-1} \) has been also observed on FTIR studies of roasted coffee [6, 8, 9] in association to carboxyl
(C=O) vibration in lipids [6] or to aliphatic esters [8]. Other bands that appear in the 1000 to 1500 \( \text{cm}^{-1} \) range
are probably associated to carbohydrates. The band at 1153 \( \text{cm}^{-1} \) falls within the absorption range reported
for chlorogenic acids [8].
PCA analysis of the ATR reflectance spectra, employing baseline correction and normalization is displayed in Figure 3. Analysis was based on a 54 x 1188 data matrix assembled so that each row corresponded to a sample and each column represented the spectra data at a given wavelength. The two first components accounted for 76% of the total sample variance. The first component provided separation of the evaluated samples into two major groups: non-defective/light sour (positive PC1) and black/dark sour/immature (negative PC1). Evaluation of the loadings plot (not shown) indicated that the spectral ranges that presented the highest influence on PC1 values in association with the black/dark sour/immature group were the following: 1482-1554, 1776-1797 and 3020-3100 cm\(^{-1}\). The only significant band that can be observed in the ATR spectra (Figure 2) in those ranges is the one at 1534 cm\(^{-1}\). It was also present in the spectra obtained by Lyman et al. [8] for aqueous extracts of roasted coffee, regardless of roasting conditions, although no identification was attempted. In the case of PCA based on the first-derivative of the spectra (not shown), the first and second principal components accounted for 28.6 and 12.6% of the total sample variance, respectively. No separation could be observed for the coffee samples. The results presented in Figure 3 confirm that separation between high (non-defective) and low quality (black, immature and dark sour) coffees can be accomplished by FTIR-ATR analysis. Although light sour beans could not be separated from non-defective ones, such separation could be easily performed by bi-chromatic colour sorting. Given that the main problem with color sorting is the separation of immature and non-defective beans, colour sorting could be employed as a first step to eliminate sour and black beans and thus FTIR-ATR could be employed for separation between immature and non-defective coffees.
CONCLUSION

The feasibility of employing FTIR as a methodology for the separation between low quality (defective) and high quality (non-defective) coffees was evaluated. PCA results based on normalized ATR-FTIR reflectance spectra indicated separation of the samples into two major groups: non-defective/light sour and black/dark sour/immature. The preliminary results obtained in the present study confirm that FTIR analysis presents potential for the development of an analytical methodology for separation between defective and non-defective coffee beans. Further studies will be conducted employing a larger set of samples in order to develop predictive models. The methodology will be also tested for roasted coffee samples.

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