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Fourier transform infrared spectroscopy and near infrared spectroscopy for the quantification of defects in roasted coffees

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ABSTRACT

The coffee strip-picking harvesting method, preferred in Brazil, results in high percentages of immature and overripe beans, as the fruits in a single tree branch do not reach ripeness at the same time. This practice, together with inappropriate processing and storage conditions, contribute to the production of high amounts of defective coffee beans in Brazil, which upon roasting will impart negative sensory aspects to the beverage. Therefore, the development of analytical methodologies that will enable the discrimination and quantification of defective and non-defective coffees after roasting is rather desirable. Given that infrared spectroscopy has been successfully applied to coffee analysis, the objective of this work was to evaluate and to compare the performances of Fourier transform infrared (FTIR) and near infrared (NIR) spectroscopies for the quantification of defective beans in roasted coffees. Defective and non-defective Arabica coffee beans were manually selected, roasted, ground and sieved. Mixtures of defective and non-defective roasted and ground coffees were produced and analyzed, with % defects ranging from 0% to 30%. FTIR and NIR spectra were recorded, respectively, within a range of 3100–800 cm^{-1} and 1200–2400 nm and submitted to mathematical processing. Quantitative models were developed by partial least squares regression (PLSR). Excellent predictive results were obtained indicating that defective coffees could be satisfactorily quantified. The correlation coefficients and the root mean squared errors of validation for the FTIR and NIR models developed to quantify the amount of defective roasted coffees mixed with non-defective ones were, respectively, as high as 0.891 and as low as 0.032, and as high as 0.953 and as low as 0.026. A comparison between the two techniques indicated that NIR provided more robust models.

1. Introduction

For every ten cups of coffee consumed in the world, approximately three come from beans produced in Brazil. In 2013, Brazil produced 45,152 million bags of coffee, which was almost twice the amount produced by the second largest producer, Vietnam (27,500 million bags) [1]. In order to achieve such a high number of coffee bags produced every year, the strip-picking harvesting practices are preferred in Brazil, and such practices usually result in coffees with high amounts of immature or unripe and overripe beans, as the coffee fruits in a single branch of the coffee plant do not reach ripeness at the same time. Furthermore, the harvest of fallen and fermented fruits in contact with the ground may also result in low quality beans. These practices, together with inappropriate processing and storage conditions contribute to the production of defective beans that comprise about 20% of the total coffee produced in Brazil [2–5]. Considered improper for exportation, defective beans are separated from non-defective ones by optical sorting machines prior to commercialization [3,4]. However, as these beans represent an investment in growing, harvesting and handling in the coffee production chain, coffee producers have adopted the practice of incorporating the separated beans into the Brazilian internal market in mixtures with non-defective ones, giving rise to a low-grade roasted and ground coffee [3].

Abbreviations: ATR, attenuated total reflectance; D, particle diameter; DLATGS, deuterated triglycine sulphate doped with L-alanine; FTIR, Fourier transform infrared spectroscopy; LV, latent variable; MSC, multiplicative scatter correction; NIR, near infrared; PLSR, partial least squares regression; RH, relative humidity; RMSEC, root mean square error of calibration; RMSECV, root mean square error of cross validation; RMSEP, root mean square error of prediction.

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Among the beans with irregular visual appearance, the most detrimental ones to the brew's flavor are immature, sour and black. Immature beans contribute to astringency, bitterness and metallic tastes. Sour beans are associated with 'overfermentation' caused by unfavorable conditions of temperature and humidity during processing, storage or transportation, being fermented by bacteria or xenophilic moulds. These beans impart sour, oniony and fermented taste and smell to the beverage. Black beans derive from beans that died within the cherry while still on the tree, from over-ripe cherries fallen on the ground or from beans that were attacked by fungi and other pests. This defect is generally regarded as giving a 'heavy' and 'ashy' flavor to the beverage and is considered the worst intrinsic defect [4,6].

Coelho et al. [7], studying the sensory impact of the inclusion of defective beans into coffees, observed that the transition of the cup quality from 'strictly soft' to 'hard' occurred after the addition of 19.5%, 16.4% and 14.3% of immature, sour or black beans, respectively. Puerta-Quintero [8] reported that 2.5% of immature beans mixed with non-defective ones was sufficient to promote rejection of 30% of samples by cuppers due to unpleasant tastes, while Bee and coworkers [4] reported that, in espresso coffee, the astringency and metallic tastes of immature beans can be perceived at quantities as low as 1%. In an attempt to identify the compounds that explain these effects, Toci and Farah [9] quantitatively determined 159 volatile compounds in defective and non-defective crude and roasted coffees. Defective beans presented a broader spectrum of volatile compounds than those presented by non-defective ones. Also, the volatile compounds identified in both defective and non-defective beans were present in higher concentrations in the latter, especially pyrazines, pyrroles and phenols.

In order to mask these detrimental flavors and/or aromas caused by the presence of defective beans, low-grade coffees are generally over roasted to a dark roasting degree. This procedure makes a suitable assessment of the quality of commercial coffees impractical, as the sensory analysis or cup-test still remains the ultimate tool to assess coffee quality. Aside from the undesirable sensory impact, studies suggest that the presence of defective beans may pose risks for human health due to the high incidence of ochratoxin A [10,11], which is only partially reduced during the roasting and extraction processes [12]. In the recent study by Taniwaki and coworkers [11], the presence of ochratoxigenic fungi and ochratoxin A in non-defective and in defective raw coffee beans was evaluated. The results indicated that all defective beans were infected with *Aspergillus carbonarius*, *A.* section *Nigri*, *A. westerdijkiae* or *A.* section *circumdati*, and highest ochratoxin A concentrations were observed in sour and black beans.

Good examples of rapid, reliable and promising fingerprint techniques that could be used to assess the overall coffee quality attributes are mid and near infrared spectroscopy. The mid infrared region (4000–400 cm^{-1}), with the corresponding spectroscopic method referred as Fourier transform infrared (FTIR), detects fundamental vibrations bands whereas the near infrared (NIR) spectrum (800–2500 nm) arises from the molecular absorptions of overtones and combinations of fundamental vibration bands in the mid infrared region [13,14]. A literature review clearly reveals that, among other applications [15], both FTIR and NIR can be effective for characterization and quantification of chemical attributes such as ash, lipids and caffeine content [16,17], for discrimination and quantification of arabica and robusta blends [18], for detection of adulterants [19–21] and for prediction of sensory properties and roasting degree [22,23]. In particular, previous works have shown that infrared spectroscopy is capable of discriminating non-defective from black, sour and immature defective beans in crude and roasted coffees [24–27].

Santos et al. [27] successfully developed a methodology based on NIR to quantify crude defective beans among non-defective ones which could enable the fast assessment of coffee grade. More recently, we have presented a comparative evaluation of the performances of FTIR and NIR for the qualitative discrimination of roasted defective and non-defective coffees, employing a novel statistical approach, Elastic Net [28]. The Elastic net models exhibited high percentages of correct classification. Furthermore, they provided insights on the characterization of the samples and on the visualization of discrete spectral bands associated with the correct classification of defective and non-defective coffees. The correct classification of non-defective coffees was associated to absorbance regions that are characteristic of carbohydrates (1138–1165 cm^{-1}, 1760–1871 nm) and lipids (1722–1759 cm^{-1}, 2810–2848 cm^{-1}, 2908–2920 cm^{-1}, 1680–1755 nm, 2132–2166 nm). Although the understanding of the chemical differences between high and low quality beans is scientifically relevant, in practice, commercial roasted coffees comprise a mixture of defective and non-defective beans. Therefore, the development of a methodology aiming to detect and quantify defective beans mixed with non-defective ones must be considered as a reliable analytical tool to regulate coffee quality.

In view of the aforementioned, the objective of this work was to further investigate the potential of FTIR and NIR spectroscopies to evaluate the quality of coffees based on the presence of defective beans. The major goals were to develop quantitative models based on partial least squares regression (PLSR) to predict the percentage of defective coffees in admixtures with non-defective ones and to compare the performance of FTIR and NIR techniques for this purpose.

2. Material and methods

2.1. Preparation of coffee samples and standard mixtures

Arabica green coffee samples were acquired from a roasting company located in Minas Gerais State, Brazil. Samples consisted of coffee beans harvested by strip-picking that were rejected by color sorting machines. The beans were manually sorted (by a professional trained and certified for green coffee classification) into five lots or sample classes: non-defective, immature, black, light sour and dark sour beans.

Samples of 25 g were taken from each lot and roasted in a convection oven (Model 4201D Nova Ética, SP, Brazil) at 235 °C. In our previous study [28], we showed that defective and non-defective coffees can be successfully discriminated based on their infrared spectra regardless of the roasting condition of the beans, which means that the variance due to beans quality is larger than the variance due to roasting degree. Therefore, in this study, all samples were roasted to a medium roasting degree similar to commercially available coffee samples. In order to achieve this roasting degree, each sample was roasted to a specific roasting time. Roasting times ranged from 10 to 15 min. Samples were then ground in a coffee grinder (Arbel, Brasil) and color evaluation was performed using a tristimulus colorimeter (HunterLab Colorflex 45/0 Spectrophotometer, Hunter Laboratories, VA, USA) with standard illumination D_{65} and colorimetric normal observer angle of 10°. Roasting degree was evaluated on ground samples by luminosity (L^*) measurements. Based on previous analysis of commercial coffees, a medium roasting degree was defined as $21 < L^* < 23.5$ [28]. Sequentially, samples were sieved. Fractions with 0.25 > particles diameter > 0.15 mm and 0.84 > particles diameter > 0.39 mm were employed for the FTIR and NIR experiments, respectively. The appropriate particle size ranges were chosen based on preliminary tests performed in previous studies [26,28], aiming at the conditions that provided the best quality spectra (higher intensity and lower noise interference).