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Performance of diffuse reflectance infrared Fourier transform spectroscopy and chemometrics for detection of multiple adulterants in roasted and ground coffee

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ABSTRACT

The quality of roasted and ground coffee is an important issue since it has been the target of fraudulent admixtures with a variety of cheaper materials, including spent coffee grounds, coffee husks and other roasted grains. Given the successful application of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for discrimination between roasted coffee, corn and coffee husks, the objective of this work was to confirm the potential of such technique for discrimination between pure roasted coffee and coffee samples adulterated with coffee husks, corn, barley and spent coffee grounds, regardless of roasting conditions. Principal Components Analysis (PCA) was employed for selection of target spectra regions responsible for group discrimination. Classification models were developed based on Linear Discriminant Analysis (LDA) and recognition and prediction abilities of these models were 100%, with the samples being separated into six groups: pure coffee, adulterated coffee (adulteration levels as low as 1 g/100 g), spent coffee grounds, coffee husks, corn and barley. Such results confirm that DRIFTS can be a valuable analytical tool for detection of adulteration in ground and roasted coffee.

1. Introduction

Intentional food adulteration can be defined as the unscrupulous act of corrupting a genuine food product for pecuniary profit by admixtures with cheaper products and materials which are difficult to detect by the consumers or by simple routine analytical techniques. High-priced commodities are usually targets for adulteration and roasted coffee, a leading commodity in international markets, is rather vulnerable to it. Ground roasted coffee presents physical characteristics (particle size, texture and color) that are easily reproduced by roasting and grinding a variety of biological materials (cereals, seeds, parchments, etc), thus, it has been the target of fraudulent admixtures with several materials, including lower quality coffees (Alves, Casal, Alves, & Oliveira, 2009; Craig, Franca, & Oliveira, 2012a) and a variety of spurious materials, such as twigs, coffee berry skin and parchment, spent coffee grounds, roasted barley, corn and other cheaper grains (Oliveira, Franca, & Augusti, 2009; Reis, Franca, & Oliveira, 2013). A few recent studies have established suitable parameters and markers for detection of coffee husks and roasted starchy grains in ground roasted coffee and instant or soluble coffee Garcia et al., 2009; Nogueira & Lago, 2009; Oliveira et al., 2009; Pauli, Cristiano, & Nixdorf, 2011). Although effective, the analytical methodologies employed are time demanding, expensive and laborious, and usually not appropriate for routine analysis.

The need for fast analytical methods in the field of food adulteration has prompted extensive research on spectroscopic methods, such as Fourier Transform Infrared Spectroscopy (FTIR), with reflectance-based methods being more commonly employed as routine methodologies for food analysis, given they present little or no requirements for sample pre-treatment (Rodriguez-Saona & Allendorf, 2011). Reflectance methods can be divided into Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS). Even though both techniques have been recently employed for coffee analysis, most of the ATR-based studies used liquid samples (Gallignani, Torres, Ayala, & Brunetto, 2008; Garrigues, Bouhsain, Garrigues, & De La Guardia, 2000; Lyman, Benck, Dell, Merle, & Murray-Wijelath, 2003; Wang, Fu, & Lim, 2011; Wang & Lim, 2012), and thus would require an extra extraction step in the analysis of roasted and ground coffee. However, ATR-FTIR can also be employed for analysis of solid samples

Abbreviations: ATR-FTIR, attenuated total reflectance Fourier transform infrared spectroscopy; DR, diffuse reflectance; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; DLATGS, deuterated triglycine sulfate doped with L-alanine; LDA, linear discriminant analysis; FTIR, Fourier transform infrared spectroscopy; PCA, principal components analysis; PR, pattern recognition.

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and our previous studies comparing ATR-FTIR and DRIFTS in the analysis of low and high quality coffees before roasting showed that, although both techniques were capable of discriminating between immature and mature coffees (Craig, Franca, & Oliveira, 2011), only DRIFTS could provide complete discrimination between non-defective (high quality) and defective (low quality) coffees (Craig, Franca, & Oliveira, 2012b).

The previously mentioned studies showed that DRIFTS presented a more effective performance than ATR-FTIR in the discrimination between crude coffees of different qualities. Furthermore, DRIFTS was also shown to be appropriate for the analysis of roasted coffees, providing satisfactory discrimination between Arabica and Robusta varieties (Kemsley, Ruault, & Wilson, 1995; Suchánek, Filipová, Volka, Delgadillo, & Davies, 1996), between regular and decaffeinated coffees (Ribeiro, Salva, & Ferreira, 2010) and between non-defective and defective coffees (Craig et al., 2012a). However, to the best of our knowledge, no attempts were reported in the literature on the use of this methodology for the analysis of adulteration of ground and roasted coffee samples, except for our preliminary study on the discrimination between roasted coffee, corn and coffee husks (Reis et al., 2013), in which the classification models developed were able to provide 100% discrimination between pure coffee, corn and coffee husks. The developed models were also able to discriminate between pure coffee and mixtures of coffee, corn and coffee husks, at adulteration levels of 10 g/100 g and above. Therefore, in the present study, we further evaluated this methodology by adding two more adulterants, i.e., spent coffee grounds and roasted barley, and decreasing the adulteration levels to 1 g/100 g, in order to confirm the potential of this technique for detection of multiple adulterants in roasted and ground coffee.

2. Materials and methods

2.1. Samples

Green Arabica coffee, barley and corn samples were acquired from local markets. Coffee husks were provided by Minas Gerais State Coffee Industry Union (Sindicafé-MG, Brazil). Spent coffee grounds were provided by a local soluble coffee industry (Café Brasília) and kept frozen ($T < -12$ °C) until further use.

Defrosted spent coffee grounds (three lots of 2 kg each) were washed with distilled water to remove impurities. Two 200 g samples were randomly selected from each lot and submitted to drying in a convection oven (Model 4201D Nova Ética, SP, Brazil) at 100 °C, for 5 h, to reduce their moisture content to that of ground roasted coffee (~5 g/100 g), providing a total of 30 samples (5 replicates). Coffee beans (50 g), coffee husks (30 g), barley (50 g) and corn samples (30 g) were submitted to roasting in the convection oven, at 200, 220, 240, 250 and 260 °C. After roasting, samples were ground ($0.15 < D < 0.5$ mm) and submitted to color evaluation. Color measurements were 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°. Measurements were based on the CIE $L^*a^*b^*$ three dimensional cartesian (xyz) color space represented by: Luminosity (L^*), ranging from 0 (black) to 100 (white) − z axis; parameter a^*, representing the green–red color component − x axis; and parameter b^*, representing the blue–yellow component − y axis. Previous studies have shown that roasting degree is dependent on the type of sample and on roasting temperature (Franca, Oliveira, Oliveira, Mancha Agresti, & Augusti, 2009; Oliveira et al., 2009; Reis et al., 2013). Therefore, roasting conditions were established for each specific type of sample. Roasting degrees were defined according to luminosity (L^*) measurements similar to commercially available coffee samples, corresponding to light ($23.5 < L^* < 25.0$), medium ($21.0 < L^* < 23.5$) and dark ($19.0 < L^* < 21.0$) roasts. Notice that only L^* (luminosity) values were employed for establishment of roasting degrees, because previous studies have shown that this parameter is the most relevant in terms of color differences for roasted coffee (Mendonça, Franca, & Oliveira, 2009). Average data of color measurements for coffee and each adulterant and the corresponding roasting times and temperatures are displayed in Table 1. As shown in Table 1, each sample was submitted to three different roasting temperatures and three different roasting degrees for each temperature, resulting in nine roasting conditions. Roastings were performed in five replicates, so 45 samples were obtained for each lot and a total of 180 samples representing pure coffee and each roasted contaminant. Pure coffee and adulterants were intentionally mixed, at adulteration levels ranging from 1 to 66 g/100 g (see Table 2), providing a total of 20 samples at different adulteration levels (five replicates each).

Table 1
Color measurements, roasting parameters and conditions.

Roasting temperature	Luminosity values (Roasting time)		
	Light roast	Medium roast	Dark roast
	Coffee		
200 °C	24.28 ± 0.02 (40 min)	21.48 ± 0.08 (70 min)	19.62 ± 0.37 (90 min)
220 °C	23.18 ± 0.12 (20 min)	21.51 ± 0.01 (22 min)	19.96 ± 0.13 (25 min)
240 °C	25.17 ± 0.04 (11 min)	22.01 ± 0.33 (13 min)	19.89 ± 0.08 (15 min)
	Coffee husks		
200 °C	22.22 ± 0.05 (20 min)	21.66 ± 0.15 (30 min)	20.16 ± 0.12 (50 min)
220 °C	23.00 ± 0.06 (10 min)	20.41 ± 0.30 (13 min)	19.88 ± 0.13 (15 min)
240 °C	25.16 ± 0.04 (6 min)	21.34 ± 0.17 (7 min)	20.47 ± 0.06 (9 min)
	Corn		
240 °C	24.45 ± 0.21 (30 min)	22.01 ± 0.33 (35 min)	19.89 ± 0.08 (40 min)
250 °C	24.63 ± 0.26 (15 min)	22.17 ± 0.08 (17 min)	19.33 ± 0.07 (19 min)
260 °C	22.25 ± 0.06 (11 min)	21.10 ± 0.16 (12 min)	19.26 ± 0.10 (13 min)
	Barley		
250 °C	22.91 ± 0.05 (28 min)	22.01 ± 0.09 (30 min)	20.54 ± 0.04 (32 min)
265 °C	23.19 ± 0.02 (16 min)	21.03 ± 0.04 (17 min)	19.22 ± 0.04 (17.5 min)
270 °C	25.07 ± 0.07 (14 min)	23.88 ± 0.04 (14.5 min)	20.37 ± 0.33 (15 min)
–	Spent coffee grounds		
–	19.15 ± 0.4 (Lot 1)	19.77 ± 0.19 (Lot 2)	20.11 ± 0.34 (Lot 3)
–	Reference (commercial coffee)		
–	$23.5 < L^* < 25.0$	$21.0 < L^* < 23.5$	$19.0 < L^* < 21.0$