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Quantitative evaluation of multiple adulterants in roasted coffee by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and chemometrics

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ABSTRACT

The current study presents an application of Diffuse Reflectance Infrared Fourier Transform Spectroscopy for detection and quantification of fraudulent addition of commonly employed adulterants (spent coffee grounds, coffee husks, roasted corn and roasted barley) to roasted and ground coffee. Roasted coffee samples were intentionally blended with the adulterants (pure and mixed), with total adulteration levels ranging from 1% to 66% w/w. Partial Least Squares Regression (PLS) was used to relate the processed spectra to the mass fraction of adulterants and the model obtained provided reliable predictions of adulterations at levels as low as 1% w/w. A robust methodology was implemented that included the detection of outliers. High correlation coefficients (0.99 for calibration; 0.98 for validation) coupled with low degrees of error (1.23% for calibration; 2.67% for validation) confirmed that DRIFTS can be a valuable analytical tool for detection and quantification of adulteration in ground, roasted coffee.

1. Introduction

Coffee is one of the most widely traded food products and the world's second largest industrial commodity [1]. Such highly-priced commodities are usually a target for adulteration, and ground, roasted coffee, whose appearance can easily be reproduced by roasting and grinding a variety of materials, is rather vulnerable to this type of adulteration [2]. The major adulterants of coffee include by-products of coffee processing such as coffee husks, parchment, spent coffee grounds, cheaper grains (barley, corn, soybean, maize and others), and lower quality coffees [1–5]. Some recent studies have targeted the detection of coffee husks and roasted grains in ground, roasted coffee and instant or soluble coffees [2,6–9]. Although effective, the methods employed (gas chromatography–mass spectrometry, high performance liquid chromatography, high performance anion-exchange chromatography with pulsed amperometric detection, and solid phase microextraction) were time demanding, expensive, laborious, and, in most cases, not appropriate for routine analysis.

Over the last decades, the need for new and rapid analytical methods in the field of food adulteration has prompted extensive research on spectroscopic methods, such as near infrared spectroscopy (NIRS), Raman spectroscopy (RS) and Fourier Transform Infrared (FTIR) spectroscopy [10–12]. Recent applications of such methods to coffee quality analysis include discrimination between Arabica and Robusta species [13,14], discrimination between high and low quality coffees [4,15–17] and discrimination between pure and adulterated coffee samples [1,5]. Ebrahimi-Najafabadi et al. [1] employed NIRS for the identification and quantification of the fraudulent addition of barley to ground, roasted coffee samples. The authors employed different species of coffee (pure Arabica, Robusta and mixtures), with different degrees of roast, and four types of barley at adulteration levels ranging from 2% to 20% w/w of barley. Genetic algorithms were used to determine the spectral regions that would be most useful for identifying the adulteration of coffee with barley. The models presented excellent predictive abilities, with quite low root mean square errors for both calibration (1.4%) and validation (0.8%) sets. The feasibility of applying

Abbreviations: DR, diffuse reflectance; DRIFTS, Diffuse Reflectance Infrared Fourier Transform Spectroscopy; DLATGS, Deuterated Triglycine Sulfate Doped with L-Alanine; LDA, Linear Discriminant Analysis; MSC, multiple scatter correction; NIRS, near infrared spectroscopy; FTIR, Fourier Transform Infrared Spectroscopy; PLS, Partial Least Squares Regression; RMSEC, root mean square error for calibration; RMSECV, root mean square error for cross validation; RMSEP, root mean square error for validation; RS, Raman spectroscopy; SNV, standard normal variates.

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Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) for detection of adulteration of coffee was established in a recent study [5]. Two different types of adulterants (roasted coffee husks and roasted corn) were mixed with roasted Arabica coffee under different roasting conditions (light, medium and dark roasts and roasting temperatures ranging from 200 to 260 °C). Linear Discriminant Analysis (LDA) was employed to construct classification models that were able to discriminate between pure coffee and mixtures of coffee, corn and coffee husks. Such models were able to provide complete discrimination (100% recognition and prediction) between pure coffee and adulterated coffee samples at adulteration levels of 10% and above.

It is clear from these studies that spectroscopic techniques offer promise for the detection of adulteration in ground, roasted coffee. However, in the aforementioned studies, only one or two types of adulterants were evaluated, and, the models are only applicable for these specific adulterants. A larger variety of adulterants should be employed when attempting to quantify the adulteration levels to obtain more representative and, therefore, more widely applicable models. In the present study, we sought to confirm the potential of DRIFTS for the detection of multiple adulterants in ground, roasted coffee. The adulterants were coffee by-products (roasted coffee husks and spent coffee grounds) and roasted grains (corn and barley). A Partial Least Squares Regression (PLS) was employed to construct models for the prediction of the levels of adulteration in coffee samples.

2. Experimental

2.1. Samples

Green Arabica coffee (*Coffea arabica*), barley and corn samples were acquired from local markets. Coffee husks (residue obtained after dehulling dried coffee beans) were provided by the Minas Gerais State Coffee Industry Union (Sindicato da Indústria de Café do Estado de Minas Gerais, Brazil). Spent coffee grounds were provided by a local soluble coffee manufacturer (Café Brasília, Minas Gerais, Brazil) and kept frozen (−12 °C) until needed.

Spent coffee grounds (three lots of 2 kg each) were defrosted (18 h at 25 °C) and washed with distilled water to remove impurities. Three 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 the moisture content to that of ground roasted coffee (~5 g/100 g). Coffee beans (50 g), coffee husks (30 g), barley (50 g) and corn samples (30 g) were submitted to roasting in a convection oven (Model 4201D Nova Ética, São Paulo, Brazil) at 200, 220, 240, 250 and 260 °C. The samples were ground ($D < 0.85$ mm) after roasting and submitted to color evaluation. Color measurements were performed using a tristimulus colorimeter (HunterLab Colorflex 45/0 Spectrophotometer, Hunter Laboratories, VA, USA) with standard D_{65} illumination and normal colorimetric 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 [2,5,18] have shown that the degree of roast will be dependent on the type of sample and on the roasting temperature. Preliminary tests showed that it would take higher temperatures (over 240 °C or 250 °C) to roast corn and barley, whereas coffee husks required milder processing conditions (temperatures equal to or below 240 °C). Therefore, roasting conditions were established for each type of sample according to the results of luminosity (L^*) measurements. Previous studies have shown that L^* can be employed as a reference of roasting degree, given that darker roasts will result in coffees with smaller values of luminosity [5,18]. Degrees of roasting were then defined by comparison with commercially available coffee samples ($19.0 < L^* < 25.0$) as light ($23.5 < L^* < 25.0$), medium ($21.0 < L^* < 23.5$) and dark ($19.0 < L^* < 21.0$) roasts.

2.2. FTIR analysis

A Shimadzu IRAffinity-1 FTIR Spectrophotometer (Shimadzu, Japan) with a Deuterated Triglycine Sulfate Doped with L-Alanine (DLATGS) detector was used for the measurements that were all performed in a dry, controlled atmosphere at room temperature (20 ± 0.5 °C). Diffuse reflectance (DR) measurements were performed in diffuse reflection mode with a Shimadzu sampling accessory (DRS8000A). Each sample was mixed with KBr, and 23 mg of this mixture was placed inside the sample port. Pure KBr was employed as the reference material (background spectrum). All spectra were recorded within a range of 4000–400 cm^{-1} with 4 cm^{-1} resolution and 20 scans, and submitted to subtraction of background (pure KBr spectra). They were also truncated to 2500 data points in the range from 3200 to 700 cm^{-1} to eliminate noise present in the upper and lower ends of the spectra. Preliminary tests were performed to evaluate the effect of particle size ($0.39\ mm < D < 0.5\ mm$; $0.25\ mm < D < 0.39\ mm$; $0.15\ mm < D < 0.25\ mm$; and $D < 0.15$ mm) and sample/KBr mass ratio (1%, 5%, 10%, 20% and 50%) on the quality of the spectra. The conditions that provided the best quality spectra (higher intensity and lower noise interference) were $D < 0.15$ mm and 10% sample/KBr mass ratio.

2.3. Data analysis

PLS was employed for quantification of adulterants (pure or mixed) in roasted coffee samples using the DR spectra as chemical descriptors, with adulteration levels ranging from 1% to 66% in mass (see Table 1). To reduce the effect of noise, remove redundant information and enhance sample-to-sample differences, the following data pre-processing (pretreatment) techniques were evaluated: (1) no additional processing (raw data), (2) mean centering, (3) absorbance normalization, (4) absorbance normalization followed by mean centering, (5) area normalization, (6) area normalization followed by mean centering, (7) first

Table 1
Mass composition of adulterated coffee samples.

Sample	Adulteration level	Mass fraction (%)				
		Coffee	Spent coffee grounds	Coffee husks	Barley	Corn
1	66	33.3		33.3		33.3
2	50	50		50		
3	50	50				50
4	40	60	10	10	10	10
5	40	60		20		20
6	40	60	20		20	
7	20	80	5	5	5	5
8	20	80		10		10
9	20	80	10		10	
10	10	90		5		5
11	10	90	5		5	
12	10	90	3.33	3.33		3.33
13	10	90	10			
14	10	90		10		
15	10	90			10	
16	10	90				10
17	1	99	1			
18	1	99		1		
19	1	99			1	
20	1	99				1