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Feasibility Study on Chemometric Discrimination of Roasted Arabica Coffees by Solvent Extraction and Fourier Transform Infrared Spectroscopy

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Supporting Information

ABSTRACT: In this feasibility study, Fourier transform infrared (FTIR) spectroscopy and chemometric analysis were adopted to discriminate coffees from different geographical origins and of different roasting degrees. Roasted coffee grounds were extracted using two methods: (1) solvent alone (dichloromethane, ethyl acetate, hexane, acetone, ethanol, or acetic acid) and (2) coextraction using a mixture of equal volume of the solvent and water. Experiment results showed that the coextraction method resulted in cleaner extract and provided a greater amount of spectral information, which was important for sample discrimination. Principal component analysis of infrared spectra of ethyl acetate extracts for dark and medium roast coffees showed separated clusters according to their geographical origins and roast degrees. Classification models based on soft independent modeling of class analogy analysis were used to classify different coffee samples. Coffees from four different countries, which were roasted to dark, were 100% correctly classified when ethyl acetate was used as a solvent. The FTIR-chemometric technique developed here may serve as a rapid tool for discriminating geographical origin of roasted coffees. Future studies involving green coffee beans and the use of larger sample size are needed to further validate the robustness of this technique.

KEYWORDS: solvent extraction, FTIR, coffee, discrimination, chemometrics

INTRODUCTION

Coffee is one of the most popular beverages in the world due to its unique aroma, taste, and stimulating effects of caffeine. The quality of brewed coffee is affected by many parameters. Depending on the species (Arabica, Robusta, or Liberica) and method used to process the coffee cherries (dry vs wet), the overall quality and chemical composition of coffee bean can vary considerably. By and large, the Arabica coffees have more pronounced and finer flavor profiles that are considered better quality and, accordingly, command a higher price than the Robusta and Liberica coffees.[1] The composition of the soil and its fertilization, the altitude and weather of the plantation, and the final cultivation and drying methods used will all affect the green bean quality.[2] Roasting, the final processing step before grinding and brewing, ultimately determines the organoleptic properties of the coffee beverage. During the roasting process, the reactions that occur in the coffee bean are complex and strongly dependent on the time−temperature profile used.[4,30]

Grading of whole coffee beans (green or roasted) is relatively easy as compared to ground coffee due to the presence of visual clues in the former (size, shape, defect, etc.). By contrast, these indicators are absent for ground coffees; therefore, sample discrimination can be difficult. Often time, sensory evaluation and cupping are needed.[5] Analytical methods have been successfully used for compositional analysis of coffee, including mineral contents,[5,6] volatile compounds,[7] chlorogenic acids,[8] fatty acids,[9] and amino acid enantiomers.[10]

Fourier transform infrared (FTIR) spectroscopy is a rapid and nondestructive technique that has been used for investigating covalent bond vibration in coffee. This method has been used to determine the caffeine content in roasted coffee,[11,12] to discriminate coffee varieties,[11,13,14] and to detect adulteration in instant coffees.[15] Because of the complexity of FTIR spectral data, chemometric analysis [e.g., principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA)] is often used to reduce the dimensionality of spectral data to aid the extraction of useful information, identification of natural data trends, and classification of unknown samples.[16] Chemometric analysis has been successfully applied to analyze FTIR spectral data of coffee, for instance in the chemical discrimination of Arabica and Robusta coffees,[17] quality control and authentication of instant coffees,[18] and adulteration detection of freeze-dried instant coffees.[15]

In this study, we employed attenuated total reflectance (ATR)-FTIR to analyze coffee extracts prepared using six organic solvents (dichloromethane, ethyl acetate, hexane, acetone, ethanol, and acetic acid). Our objective was to investigate the feasibility of using infrared spectra of these extracts, in conjunction with PCA and SIMCA, to discriminate four Arabica ground coffees from different origins (Colombia, Costa Rica, Ethiopia, and Kenya) that had been roasted to two roast degrees (medium or dark).

MATERIALS AND METHODS

Chemicals. Hexane was purchased from Sigma-Aldrich Ltd. (St. Louis, MO). Dichloromethane, ethyl acetate, acetone, and acetic

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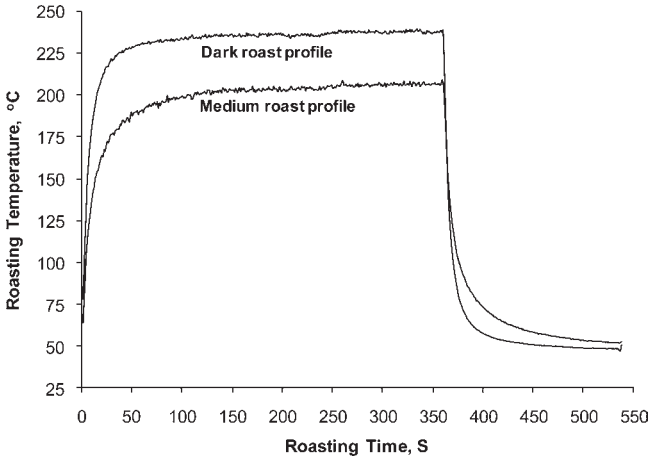

Figure 1. Air temperature (in roast chamber) profiles of the fluidized bed hot air coffee roaster.

acid were purchased from Fisher Scientific (Ottawa, Canada). Ethanol was purchased from Greenfield Ethanol Inc. (Brampton, Canada).

Coffee Beans and Roasting Conditions. Wet-processed green coffee beans (Arabica variety) from Colombia, Costa Rica, Kenya, and Ethiopia were purchased from Green Beanery (Toronto, Canada). Green coffee beans (45 g) were roasted in a fluidized bed hot air roaster (Fresh Roast SR 500, Fresh Beans Inc., Park City, UT). Two isothermal roasting programs were used for preparing dark and medium roast coffees (Figure 1). The roasted beans were stored in hermetic glass bottles in the dark at 15 °C before grinding.

Degree of Roast as Determined by Color Measurements. Roasted coffee beans were milled into powder using an electric burr grinder (Bodum Antigua, Bodum, Inc., Copenhagen, Denmark) at the medium grind setting. The color of the ground coffee was measured in the L^*, a^*, b^* system using a Konica Minolta CM-3500d spectrophotometer (Konica Minolta Sensing, Inc., Osaka, Japan) in the reflectance mode. Before analysis, the instrument was calibrated on a white standard tile. Measurements were taken in triplicate.

Solvent Extraction of Ground Coffee. After grinding, coffee grounds were extracted with dichloromethane, ethyl acetate, hexane, acetone, ethanol, or acetic acid, following two extraction procedures. In the first procedure (method #1), 0.2500 g of ground coffee was accurately weighed into a glass vial, and 1 mL of deionized water was added to wet the sample. The glass vial was shaken for 1 min with an IKA-VIBRAX-VXR vibrator (Janke & Kunkel, Inc., Staufen, Germany) at the 200 dial setting; 1 mL of organic solvent was added, and the mixture was shaken for an additional 5 min. The organic phase was then transferred to another vial and allowed to rest for 10 min before ATR-FTIR analysis. In the second procedure (method #2), a similar procedure was used except that water was not added prior to solvent extraction. All extractions were performed in triplicate.

ATR-FTIR Analysis. The coffee extract was scanned using an FTIR spectrometer (IR Prestige-21; Shimadzu Corp., Tokyo, Japan) equipped with a deuterated triglycine sulfate detector and a KBr beam splitter. A MIRacle ATR accessory equipped with a diamond crystal (Pike Technologies, Madison, WI) was used for sampling. The background spectrum was collected using an empty ATR cell. Before scanning, a drop of extract (6 μL) was placed onto the ATR crystal, and the solvent was allowed to evaporate. The time required for the solvent to evaporate was determined by monitoring the spectrum until the solvent bands were no longer detectable. The time taken for this to occur was noted and applied to all extracts prepared using a given solvent. By removing the background absorbance interference from the solvent, the sensitivity of the chemometric analysis was improved considerably. To collect the IR spectrum, samples were scanned from 600 to 4000 cm^{-1} at 4 cm^{-1} resolution, and 20 scans were averaged to give the final spectrum. For each extract, three FTIR spectra replicates were scanned. Between samples, the ATR crystal was carefully cleaned with 95% (v/v) aqueous ethanol solution and dried with lint-free tissue paper. The spectral baseline was examined to ensure that no residue from the previous sample was retained on the crystal. All spectra were recorded at room temperature (23 ± 0.5 °C).

Table 1. L^* Value of Roasted Ground Arabica Coffee Beans

roast degree	coffee bean sample	lightness (L^*)
dark	Colombian	19.83 ± 0.05
	Costa Rican	19.61 ± 0.18
	Ethiopian	19.46 ± 0.21
	Kenyan	19.72 ± 0.06
medium	Colombian	25.21 ± 0.16
	Costa Rican	25.35 ± 0.29
	Ethiopian	25.64 ± 0.06
	Kenyan	25.28 ± 0.09

Data Analysis. Statistical comparison of color values of ground coffee samples was conducted based on Tukey pairwise comparisons using R software (www.r-project.org). For chemometric analysis, FTIR spectra were exported as ASCII format, organized in Excel spreadsheets, and then analyzed using Pirouette v.4.0 software (Woodinville, WA). During PCA, second derivative and mean-center were applied to FTIR spectra to reduce baseline variation and enhance spectral features. Nine spectra (three extracts for each coffee and three replicate spectra for each extract) for each coffee were divided into two groups: Six spectra from the first two extracts were used to calibrate the SIMCA model, while the remaining three spectra from the third extract were used for validation to evaluate the prediction accuracy of the calibrated SIMCA model. The optimum number of PCs in each class was selected on the basis of the lowest number of PCs giving minimum value of variance.

RESULTS AND DISCUSSION

Color Analysis. Ground coffee samples from different geographical regions could not be distinguished readily by visual inspection. The L^* (lightness) values of ground coffee beans from different geographic regions (Colombia, Costa Rica, Ethiopia, and Kenya) were similar among medium roast or dark roast samples (Table 1). Tukey pairwise comparison analysis confirmed that differences in L^* values were not significant between ground samples for dark or medium roasted beans, implying that samples from the same degree of roast exhibited the same lightness.

ATR-FTIR Analysis. Selected FTIR spectra of solvent extracts obtained by methods #1 (with water) and #2 (no water) are shown in Figure 2. The 3100 to 2750 cm^{-1} region in the majority of spectra (except acetic acid, acetone, and ethanol extracts obtained with extraction method #1) were typical for the fatty acid moiety of lipids due to asymmetrical C−H stretching (2920 cm^{-1}), symmetrical C−H stretching (2850 cm^{-1}), and methylene asymmetrical stretching (weak shoulder at 2954 cm^{-1}).[19] In the presence of water, the absorbance around 3676−3028 cm^{-1} for acetic acid, acetone, and ethanol extracts can be attributed to the O−H stretching band. The 1800−800 cm^{-1} region contained absorbance bands due to C═O (ester, aldehydes, and ketones) stretching, C−H (methylene) bending (scissoring), C−O (esters and alcohol), and CH_2

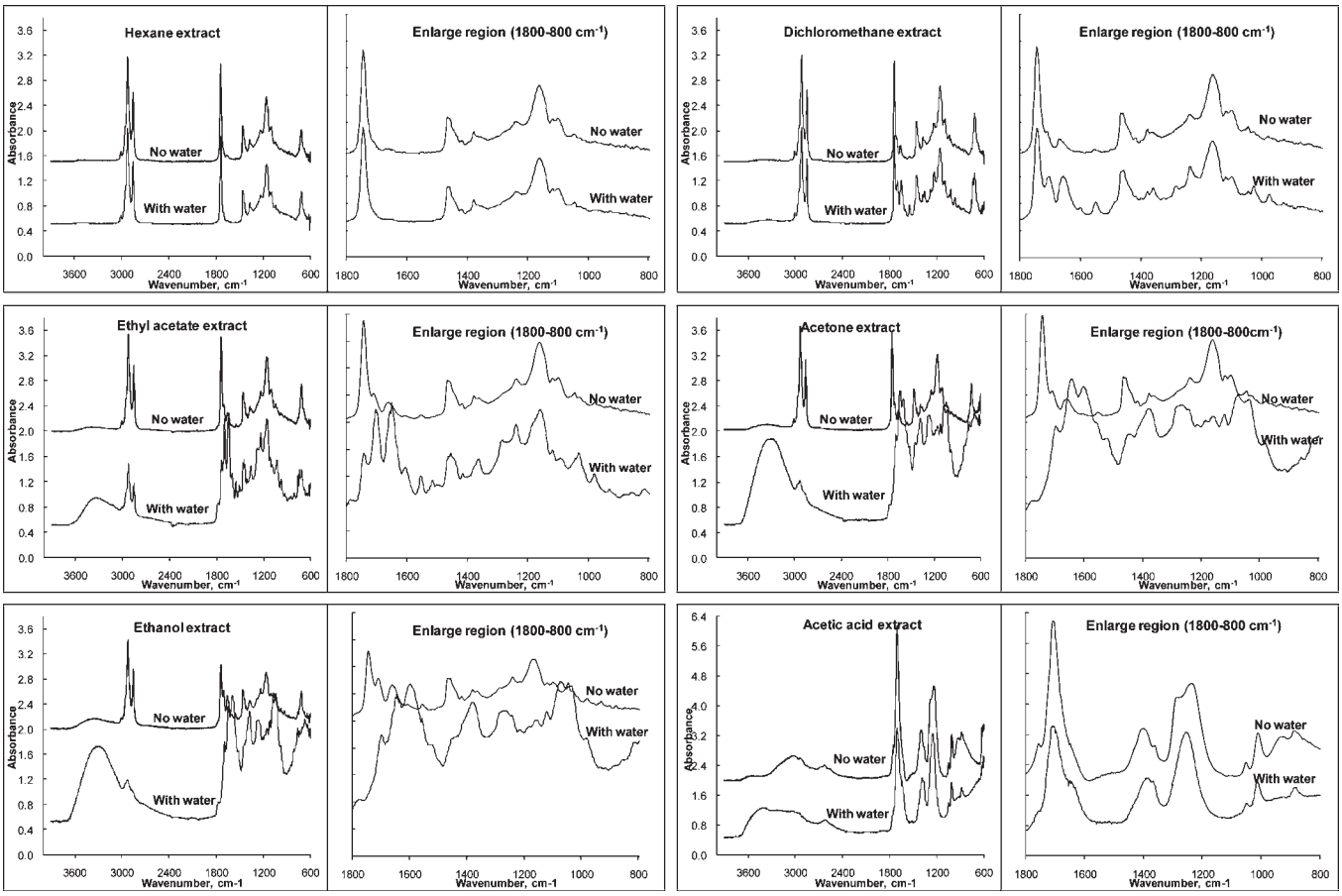

Figure 2. FTIR spectra of coffee extracts obtained with hexane, dichloromethane, ethyl acetate, acetone, ethanol, or acetic acid using method #1 (with water) and method #2 (no water).

stretching/bending.[19] These regions contained fingerprint information that may be important for discriminating coffee samples from different origins.

Spectra from method #1 were relatively more complex than those from method #2, especially when dichloromethane and ethyl acetate were used as solvents. For instance, the dichloromethane extracts prepared from method #1 had many additional peaks that were absent for those prepared from method #2, including 1487 (C═C, C−H deformation), 1398 (CH_3 symmetric deformation), 1323 (symmetric vibrations of COO− groups), and 1284 cm^{-1} (amide III band components of proteins).[20] In terms of band shape and intensity, different spectral features were observed in the 1720−1203 and 1064−940 cm^{-1} regions. With method #1, water-induced swelling of the coffee particles might have facilitated the extraction of additional compounds. A similar enhancement in spectral features was observed for ethyl acetate coffee extracts. For the hexane and acetic acid extracts, minimal spectral differences were observed between methods #1 and #2. The IR spectra of the hexane extracts were similar to lipid,[21] indicating that lipids may be the main components extracted. Overall absorbance values were considerably stronger for the acetone and ethanol extracts probably due to the contribution from water present in the extracts. The spectra of acetic acid extracts and pure acetic acid were similar (data not shown), indicating that acetic acid is not an effective solvent for coffee extraction. On the basis of the evaporation time data and FTIR spectral features observed, dichloromethane, hexane, ethyl acetate, and acetone extracts obtained via method #1 were selected for subsequent analyses.

PCA Analysis of Solvent Extracts of Coffee Beans. FTIR spectra of the organic solvent extracts (method #1) are highly complex. Although variances between spectra exist, the differences are subtle, and data interpretation was difficult (data not shown; see Figure S1 in the Supporting Information). To extract relevant information from the data, PCA was employed to reduce the dimensionality of the IR spectra and facilitate the visualization of the inherent structure of the data set (Figures 3 and 4).

For the medium roast samples, FTIR data for dichloromethane and ethyl acetate extracts appeared as separated clusters in PCA score plots, which corresponded to the four countries of origin (Figure 3, row A); however, cluster patterns were less discernible for hexane and acetone extracts. For the dark roast samples, the PCA score plots showed clear distinctive groupings corresponding to the four countries of origin (Figure 4, row A). Overall, separation distances between clusters were greater for the dark roast samples than for the medium roast counterparts, implying that the IR-active components that were distinctive to the bean origin tended to develop when the beans were roasted to a darker degree. It is well-known that the aroma characteristic of coffee is strongly dependent on the time−temperature profile applied during the roasting process.[30] The greater cluster separation for dark roast samples observed in the current study may be due to a larger number of country-specific aroma compounds produced in the dark roasted coffee.[22]

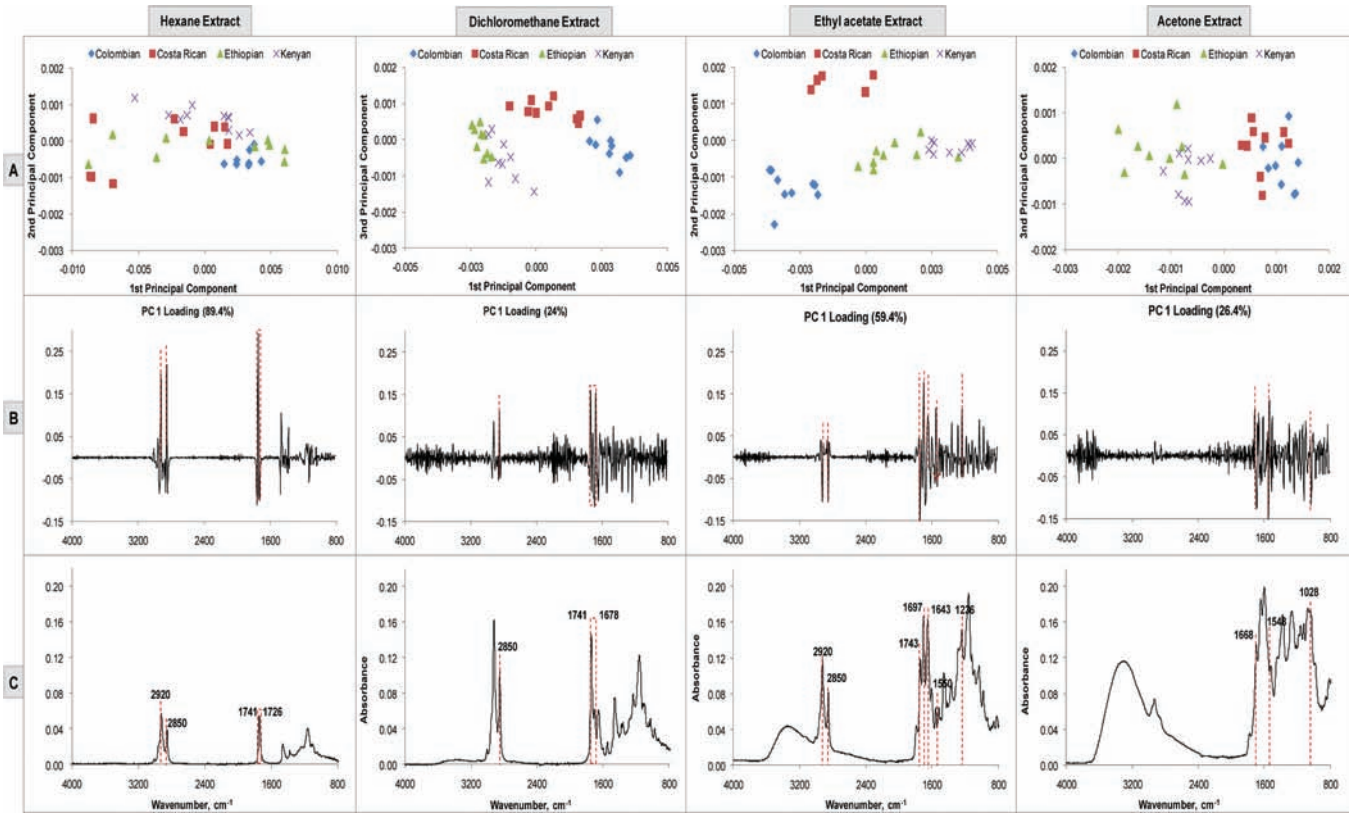

Figure 3. PCA of FTIR data for hexane, dichloromethane, ethyl acetate, and acetone extracts of medium roast coffee. Row A: Two factor score plots. Row B: Loading plots of PC1. Row C: Corresponding FTIR raw spectra.

The different clustering behaviors observed for extracts prepared from different solvents could be attributed to the different polarities of the solvents used. The polarity indices for hexane, dichloromethane, ethyl acetate, and acetone are 0.1, 3.1, 4.4, and 5.1, respectively.[22] Thus, hexane is nonpolar and extracts only nonpolar compounds from the coffee. On the other hand, acetone is relatively more polar and tends to extract polar compounds. For dichloromethane and ethyl acetate, both polar and nonpolar compounds are extracted. The polarity effect can be observed in the original spectra (Figures 3 and 4, row C). The spectral region from 3676−3028 cm^{-1} is mainly due to the O−H stretching band from water. As shown, the absorbance intensity in this region progressively became stronger for hexane, dichloromethane, ethyl acetate, and acetone in ascending order. This result is consistent with the polarity for these solvents.

To further investigate regions of spectra that contribute to the variance of samples, the loading plots for a corresponding PC were inspected. Here, we focused on PC1 since it explained the maximum variance existing in the data set (Figures 3 and 4, row B). The percent variance accounted by PC1 was also indicated on each loading plot. Regions of each spectrum with a relatively large loading score (>0.1) were highlighted as red dotted lines. As shown, the loading plots for hexane extracts were markedly different than those of the other three solvent extracts, due to the nonpolar nature of hexane. The loading plots of hexane extracts for medium and dark roasts were similar, except that absorbance at region 1741−1726 cm^{-1}, which is due to C═O stretching band mode of fatty acid esters, was higher and wider in the medium roast as compared with the dark roast coffee.[23]

For dichloromethane extracts, the most prominent difference in loading plots for dark and medium roast coffees was in the region of 2920−2850 cm^{-1}, which can be attributed to CH_2 asymmetrical stretching vibrations of hydrocarbon methyl groups.[24] The medium roast coffees exhibited significant loading score around this region but negligible for dark roast coffees. A similar trend was observed for the region around 1741−1678 cm^{-1} The minimal changes observed for these spectral regions for the dark roast samples could be caused by a decrease in protein and lipids due to the Maillard reaction and pyrolytic cleavage, respectively.[25,26]

For ethyl acetate extracts, loading plots for medium and dark roast coffees were comparable, indicating that the compounds extracted by ethyl acetate from medium and dark roast coffees were similar, although subtle differences did exist. The main regions that contribute to the differences between samples are 1743−1741, 1647−1643, and 1697 cm^{-1}. The band at 1697 cm^{-1} is due to isolated carbonyl stretching of C═O bonds, and the band at 1647 cm^{-1} is due to conjugated carbonyl stretching of C═O bonds of caffeine compounds.[27] Garrigues et al.[12] and Ohnsmann et al.[13] also utilized absorbance at 1659 and 1704 cm^{-1} to determine the caffeine content in coffee and tea, respectively. In these cited studies, the C═O bands investigated shifted to higher frequencies due to the different solvent used (i.e., chloroform). On the basis of this information, it is hypothesized that the separated clusters observed were partly caused by the different caffeine contents of among the various coffee samples.

Other important vibration bands that contributed to the separated clusters for dichromethane extracts were at 1705 (C═O stretching vibrations of ketones), 1655 (C═O stretching of caffeine

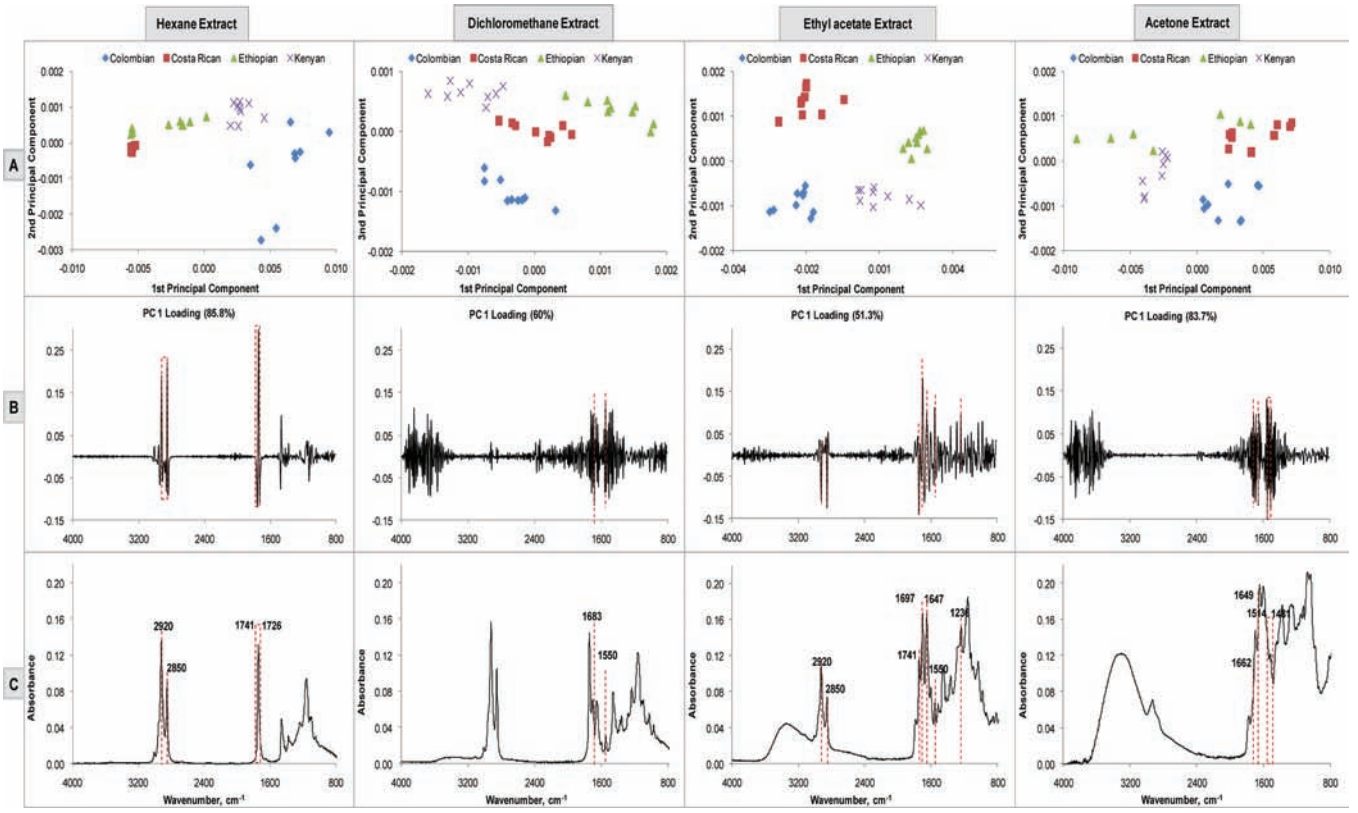

Figure 4. PCA of FTIR data for hexane, dichloromethane, ethyl acetate, and acetone extracts of dark roast coffee. Row A: Two factor score plots. Row B: Loading plots of PC1. Row C: Corresponding FTIR raw spectra.

compounds), 1599 (−NH group), and 1548 cm^{-1} (N−H bending of peptide groups). These bands were also detected in ethyl acetate and acetone extracts with some shifts (1701, 1651, 1604, and 1552 cm^{-1} for ethyl acetate; 1699, 1647, 1599, and 1558 cm^{-1} for acetone).[28,29] For hexane extracts, the most prominent spectral difference between the medium and dark roast coffees is that the latter showed a stronger overall absorbance, implying that more lipids (1600−1700 cm^{-1}) and fatty acid esters (1700−1800 cm^{-1}) were being extracted from the dark roast coffee.

PCA Analysis for Coffees According to Degree of Roast. Roasting results in many physical changes and chemical reactions in the coffee beans. Depending on the extent of the roast, which is time−temperature dependent, the quality and sensory properties of the resulting coffees can vary considerably. Medium roast coffee has a more full-bodied flavor, a balance of taste and aroma, and carries citrus taste. In comparison, dark roast coffee has a heavier sweet taste, with a lingering aftertaste of chocolate.[3,30]

The FTIR spectra of dichloromethane and ethyl acetate extracts were analyzed for dark and medium roast coffees. The two-component score plots for these extracts show well-separated clusters corresponding to dark (right clusters) and medium (left clusters) roast samples for each coffee variety (Figure 5 for ethyl acetate extract; see the Supporting Information for dichloromethane extract). The loading plots for dichloromethane extracts showed that all coffee samples, except the Columbian coffee, exhibited strong loading scores at 2920, 2850, and 1743 cm^{-1} due to CH_2 asymmetrical stretching of methyl groups, C−H symmetrical stretching of methyl groups, and C═O stretching of aliphatic esters.[21,31] For the Colombian coffee, the bands that correspond to significant loading scores at 1550, 1510, and 1481 cm^{-1} can be attributed to N−H bending of peptide groups, C═N stretching of amino groups, and benzene absorption bands, respectively.[29,32,33]

For ethyl acetate extracts, the loading plots (Figure 5, row B) revealed that spectral regions that contributed to cluster separation were mainly at 2850−2920 cm^{-1} due to CH_2 asymmetrical stretching and C−H symmetrical stretching of methyl groups[21] as well as 1650−1750 cm^{-1} due to C═O stretching vibrations and C═N stretching.[34] For coffee, this region has been assigned to a number of important compounds, including aromatic acids (1700−1680 cm^{-1}), aliphatic acids (1714−1705 cm^{-1}), ketones (1725−1705 cm^{-1}), aldehydes (1739−1724 cm^{-1}), and aliphatic esters (1755−1740 cm^{-1}).[35−37] Absorbance in the 2850−2920 cm^{-1} region was mainly due to lipids.[21]

Overall, roasting coffee from a medium to a dark degree causes increases in esters/lactones (1788 cm^{-1}), aldehydes/ketones (1739−1722 cm^{-1}), ketones (1725−1705 cm^{-1}), aromatic acids (1700−1680 cm^{-1}), and aliphatic acids (1714−1705 cm^{-1}) but a decrease in caffeine content (1700−1692 and 1647−1641 cm^{-1}).[20,30,31] Others have also observed decreases in the amount of lipids (around 1736, 1740, 1745, and 1750 cm^{-1}), polysaccharides and hemicelluloses (1739 cm^{-1}), esters (1751−1740 cm^{-1}), and lipids/proteins (2935−2847 cm^{-1}).[20,30,31]

SIMCA Analysis. Following the successful application of PCA techniques to discriminate selected coffee samples according to their geographical origin and degree of roast, SIMCA classification was employed to predict the origin and degree of roast for unknown samples.

Table 2 shows the results of the prediction performance for coffee from different origins based on SIMCA models at the 5% significance level. Except for the dichloromethane extract for the

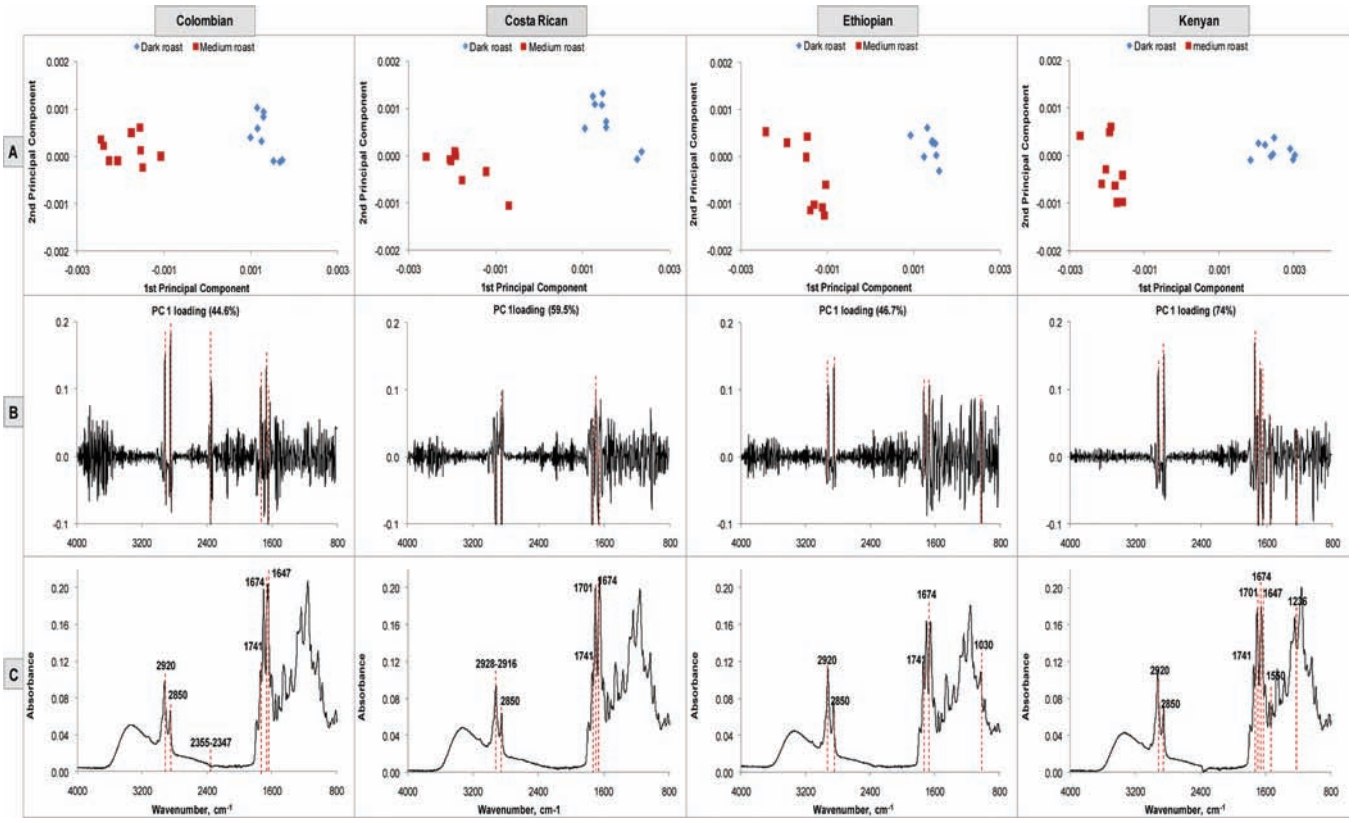

Figure 5. PCA of FTIR data for ethyl acetate extracts of coffee (from the same origin) with two degrees of roast. Row A: Two factor score plots. Row B: Loading plots of PC1. Row C: Corresponding FTIR raw spectra.

Table 2. SIMCA Classification Results for Coffees from Different Geographic Origins

		country of origin correct classification (%)			
solvents	roast degree	Colombia	Costa Rica	Ethiopia	Kenya
dichloromethane	dark	100	100	100	100
	medium	100	100	33	100
ethyl acetate	dark	100	100	100	100
	medium	100	100	100	100

Table 3. SIMCA Classification Results for Coffees According to Degree of Roast

		roast degree correct classification (%)	
solvents	origin	dark	medium
dichloromethane	Colombia	100	100
	Costa Rica	100	100
	Ethiopia	100	100
	Kenya	100	100
ethyl acetate	Colombia	100	67
	Costa Rica	100	100
	Ethiopia	100	100
	Kenya	100	100

Ethiopian medium roast sample, all other samples were correctly assigned to the country of origin during model validation. Similar validation results were obtained for the prediction degree of roast within each coffee (Table 3). Overall, ethyl acetate is a more optimal solvent for the discrimination of coffee origins and roasting degrees. Ethyl acetate is also a common solvent used for decaffeinating coffee and tea leaves.[38,39]

In summary, the solvent extraction and chemometric analysis methodologies presented in this study may be useful for the coffee industry as a rapid and reasonably accurate tool to classify roasted coffee according to origin and degree of roast. Future investigations involving more coffee varieties and bigger sample size are necessary to further improve the model robustness. By correlating the chemometric results with sensory data, potentially the methods may be useful for routine quality evaluation, which complement sensorial and cupping procedures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Typical FTIR spectra of dichloromethane extracts for dark roast coffee beans from various regions and PCA and spectral data of dichloromethane extracts for dark and medium roast coffees. This material is available free of charge via the Internet at http://pubs.acs.org.

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