Mid-Infrared Spectroscopic Analysis on Brewed Coffee Characteristics

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ABSTRACT

We developed a mid-infrared (MIR) spectroscopic evaluation method of brewed coffee, whose quality and taste highly depend on the properties such as the geographical origin and the roasting, grinding, blending and extraction conditions, using an FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. The objective and stable method to evaluate the brewed coffee characteristics is desirable, since the determination of coffee process conditions and the grasp of the characteristics of coffee varieties are very empirical in coffee manufacturing. Then we studied the influences of the coffee varieties and the roasting degree on the MIR spectral characteristics of brewed coffee and examined to determine the caffeine and chlorogenic acid contents in brewed coffee using the FT-IR/ATR method. Arabica (Colombia, Brazil and Guatemala) and Robusta (Indonesia) coffees roasted to City were prepared as the sample. Indonesian coffees roasted to Full City were also used. All roasted beans were ground to a standard cupping grind and brewed by adding hot water. As the results, the differences between the second derivatives of the ATR spectra of the brewed Arabica and Robusta coffees were observed around the several peaks. In addition, the brewed coffee from the Brazil variety had the different spectral features from those of the other Arabica coffees. Moreover, the roasting conditions of the Indonesian beans reflected the spectral features of the brewed coffee. Furthermore, the caffeine and chlorogenic acid contents in brewed coffee would be determined by the spectroscopic method as well as those in the aqueous solutions.

KEYWORDS
coffee, mid-infrared spectroscopy, quality evaluation

INTRODUCTION

Coffee is one of the most popular foods in the world. A huge amount of brewed coffee is manufactured, and very long time has passed since the start of the manufacturing. But the coffee process is empirically controlled based on the information provided by the cup tasters and the manufacturing experts, and the process control could be generally due to the expertise accumulated in each coffee manufacturing company. Additionally, the brewed coffee is produced through the many complicated operations such as roasting, grinding, blending and extraction. Furthermore, the coffee beans as the inventory of the brewed coffee are miscellaneous and are highly reflected by the varieties and geographical origins. So the objective and stable method to evaluate the brewed coffee characteristics is desirable for the process control, because the brewed coffee is not only the final product but also gustoish liquid food tasted by us. In order to get a good grasp of the brewed coffee characteristics for the process control, it is very important that not only the contents of the main components but also their molecular structures are nondestructively and simultaneously monitored in real time. Then, application of spectroscopy, especially in mid-infrared (MIR) region, to the above measurement is desirable as a high potential implement.

Suchanek *et al.* (1996) reported that the green coffee could be quantitatively analyzed by MIR spectroscopy, and Kemsely *et al*. (1995) and Briandet *et al.* (1996) studied how to discriminate Arabica and Robusta varieties using MIR spectroscopic analysis of the roasted coffee beans and instant coffee, respectively. The caffeine content in the roasted coffee beans could be quantified using the MIR information related to $CHCl_3$ and NH_3 groups (Garrigues *et al.*, 2000). As the above, the MIR analysis on the coffee beans and instant coffee has been performed, but the development of the MIR spectroscopic evaluation method of the brewed coffee in liquid condition is not reported. Incidentally, in parallel developments of a Fourier transform infrared (FT-IR) spectrometers and attenuated total reflection (ATR) techniques (Harrick, 1967; Mirabella and Harrick, 1985), the FT-IR/ATR spectroscopic method provides substantial potential as a quantitative tool for liquids based on the molecular structure and on the interactions between the molecule and its environments. In addition, the report by Paradkar and Irudayaraj (2002) suggested the possibility of the FT-IR/ATR spectroscopic determination of caffeine in the brewed coffee with chemometrics.

The objective of this study is to develop a simple, rapid and accurate method evaluating the brewed coffee by MIR spectroscopy. We then studied the influences of the coffee varieties and the geographical origins of the coffee beans and of the roasting degree on the MIR spectral characteristics of the brewed coffee and examined to determine the caffeine and chlorogenic acid contents in brewed coffee using the FT-IR/ATR method, after determination of the brewing conditions for the MIR spectroscopic analysis.

MATERIALS AND METHOD

Coffee Samples

Arabica (Colombia, Brazil and Guatemala) and Robusta (Indonesia) coffees roasted to City were prepared as the sample. Indonesian coffees roasted to Full City (Clarke, 1987) were also used. All roasted beans were ground to a standard cupping grind. All coffee powders ground to a standard cupping grind were brewed by two methods; a method adding hot water and a coffee brewer method.

150 mL of boiled water was poured in to a 200-mL beaker containing 10, 15, 20 or 25 g of the coffee powders. After agitation for 2 min using a magnetic stirrer, the boiled water of the same volume as the evaporated water during the agitation was again added into the beaker. The mixture was poured onto a filter (No.1 filter; Toyo Roshi Kaisha, Ltd., Tokyo, Japan), and 120 mL of the solution passed through the filter was kept at 298 K in a water bath.

All coffee powders were also brewed using an automatic coffee brewer (NC-1103; Matsushita Electric Industrial Co., Ltd., Osaka, Japan). 1350, 675, 540 or 337.5 mL of distilled water to 75 g of the coffee powder was prepared, and the brewed coffee was made according to the manual attached to the coffee brewer. The brewed coffee was cooled with iced water for 270 s and was also kept at 298 K in the water bath.

Additionally, the brewed coffee samples added caffeine or chlorogenic acid (Special Grade; Wako Pure Chemical Industries, Osaka, Japan) and their aqueous solutions were used. The reagent was dissolved into the brewed coffee, which was extracted using 25 g of the coffee powder to 150 g of water using the above method adding hot water, kept at 333 K for the easy dissolution. The amounts of the dissolved caffeine and chlorogenic acid were varied.

Mid-Infrared Spectral Measurement

A Magna 750 FT-IR spectrometer (Nicolet Instrument Corp.) equipped with a KBr beamsplitter and a deuterated triglycine sulfate KBr detector was used to collect the spectra. The MIR spectra were obtained from 4000 to 800 cm^{-1} with a horizontal ATR sampling accessory with a diamond internal reflection element on a zinc selenide crystal (Applied System, DuraSampleIR). Sixty-four scans of symmetrical interferograms at 4 cm^{-1} resolutions were added for each spectrum. The instrument was allowed to purge for several minutes prior to the acquisition of spectra in order to minimize the spectral contribution due to atmospheric water vapor. The ATR spectra and Brix values of the solutions were measured at 298 K. The spectral measurements were carried out thrice for each sample.

RESULTS AND DISCUSSION

Determination of Extraction Conditions for Spectral Measurement

Figure 1(a) displays the influences of amount of the Brazilian coffee powder to the fixed water volume on the stability of the second derivative spectra calculated by using the Savitzky-Golay method (Savitzky and Golay, 1964) with thirteen points. The each spectrum represented Figure 1(a) is the

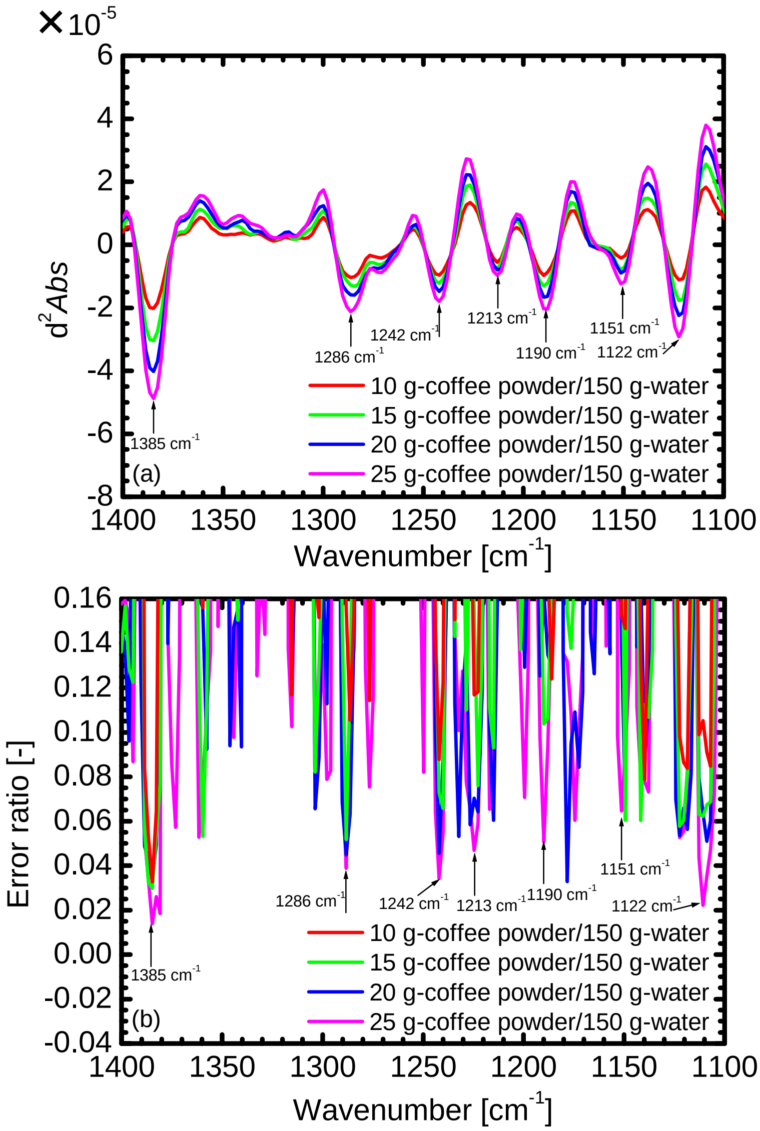

Figure 1. Influences of ratio of amount of coffee (Brazil) powder to water on the stability of MIR spectral characteristics of brewed coffee. (a) second derivative spectra; (b) ratio of standard deviation to average.

average of the three spectra. The negative peaks characterizing the Brazilian coffee were observed around 1385, 1286, 1242, 1213, 1190, 1151 and 1122 cm^{-1}. The peak values of the second derivative spectra decreased with increase in the amount of the coffee powder at the brewing. In addition, the excellent correlations between the second derivative values at the above wavenumbers and the Brix values treated as an index of the coffee concentration. These results meant that the above peaks indicated in Figure 1(a) closely related to the coffee components.

The ordinate of Figure 1(b) is the error ratio of the standard deviation of the three spectra to the average for brewed coffee. The ratio spectra show the low values close to zero around the wavenumbers of the peaks characterizing the brewed coffee (Figure 1(a)) and decreased with increase in the amount of the coffee powder at the brewing. The experiments of the method using the coffee brewer showed the results similar to those for the method adding hot water. Hence, Figures 1(a) and (b) suggested that the most stable spectrum could be obtained under the brewing conditions of the 25 g-coffee powder to 150 g-boiled water.

The comparison of the error ratio of the standard deviation of the three spectra to the average for brewed coffee between the two brewing methods is indicated in Figure 2. Almost over the finger print region, the ratio spectrum for the brewing method adding hot water behaves lower than that for the other. Especially at the wavenumbers around 1385, 1286, 1242, 1190 and 1151 cm^{-1} characterizing the Brazilian coffee, the results were very significant. From the viewpoint of collecting the stable MIR spectral information for the coffee analysis, Figure 2 experimentally represents that the brewing method adding hot water are more useful than the other. We then used the spectra of the coffee brewed by the method adding hot water under the conditions of the 25 g-coffee powder to 150 g-boiled water in the further discussion of the MIR spectroscopic characteristics.

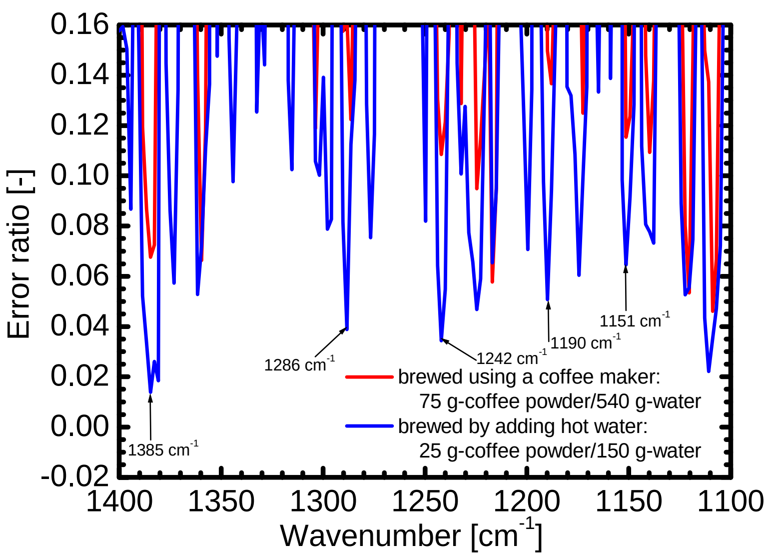

Figure 2. Comparison of error ratio for MIR spectra of brewed coffee (Brazil) between the two coffee brewing methods.

Quantitative Mid-Infrared Spectral Analysis of Brewed Coffee

We studied the spectral feature changes of the brewed coffee (Brazil) in addition of caffeine or chlorogenic acid, which is one of the most important components of the brewed coffee and closely related to the quality and taste, and the results are respectively displayed in Figures 3(a) and (b). The peaks characterizing caffeine at the wavenumbers around 1367, 1336, 1290, 1242 and 1190 cm^{-1}

decreased with the increase in the amount of the addition of caffeine into the brewed coffee (Figure 3 (a)), although the Brazilian coffee spectra also indicated at the same wavenumbers as some of the above caffeine peaks (Figure 1(a)). But the small peak around 1213 cm^{-1} that was found for the caffeine aqueous solution (data not shown) was negligible because of the peak based on the coffee components. On the other hand, at the wavenumbers around 1284, 1271, 1190, 1161 and 1122 cm^{-1}, the peaks decreased with the increase in the amount of the addition of chlorogenic acid into the brewed coffee (Figure 3(b)). Thus, Figures 1(a) and 3 experimentally express that we could get the MIR information about caffeine and chlorogenic acid in the brewed coffee that is the very complicated system. Conversely, we could analyze the brewed coffee characteristics other than caffeine and chlorogenic acid using the MIR spectroscopic information such as around 1385 and 1151 cm^{-1} as shown in Figure 1(a).

Based on the above discussion, we made calibration curves for caffeine and chlorogenic acid in the brewed coffee for quantitative analysis of the MIR spectroscopic information. We then analyze the

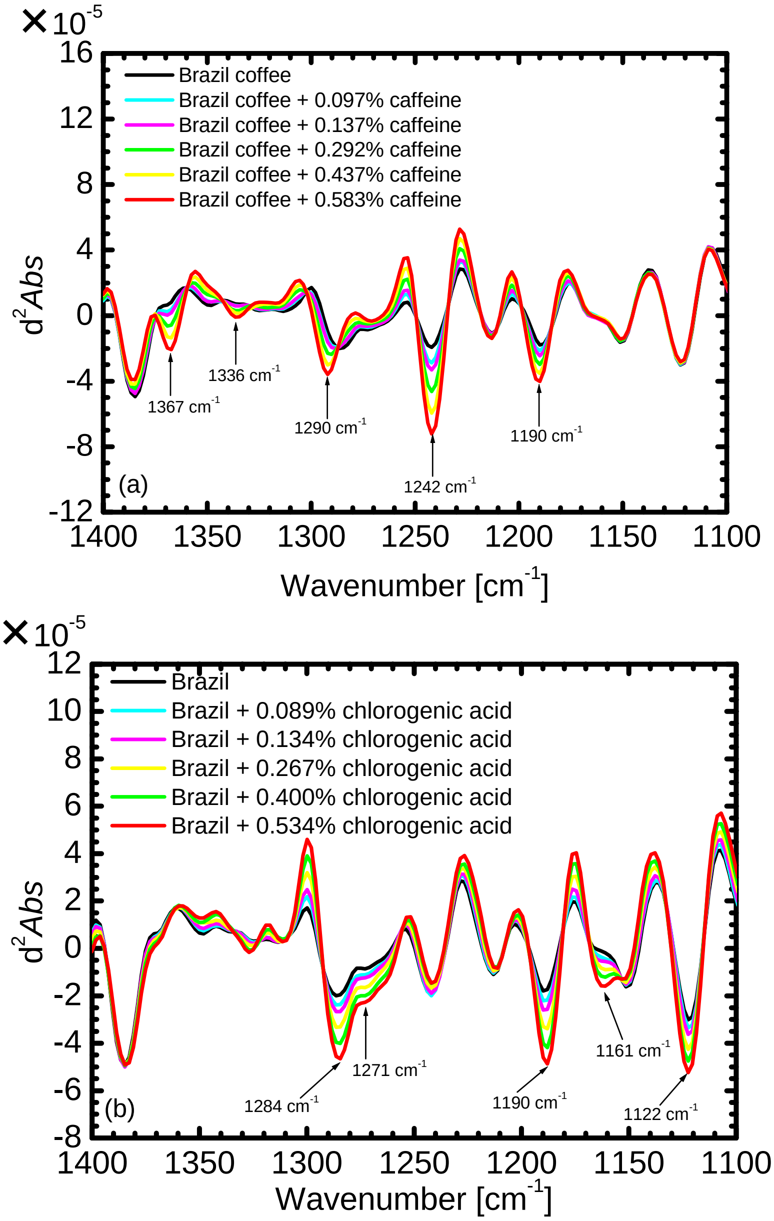

Figure 3. Influences of addition of caffeine or chlorogenic acid into brewed coffee (Brazil) on the MIR spectral characteristics. (a) caffeine; (b) chlorogenic acid.

relation between the concentrations and the second derivative values around 1242 and 1122 cm^{-1} respectively for caffeine and chlorogenic acid, since the peaks around the above wavenumbers were very stable in the brewed coffee as shown in Figure 3. Figure 4 displays the calibration curves for the both caffeine aqueous solution and the Brazilian coffee added caffeine, and the parameters obtained by performing the linear regression analysis are summarized in Table 1 as same as those for the chlorogenic acid solutions.

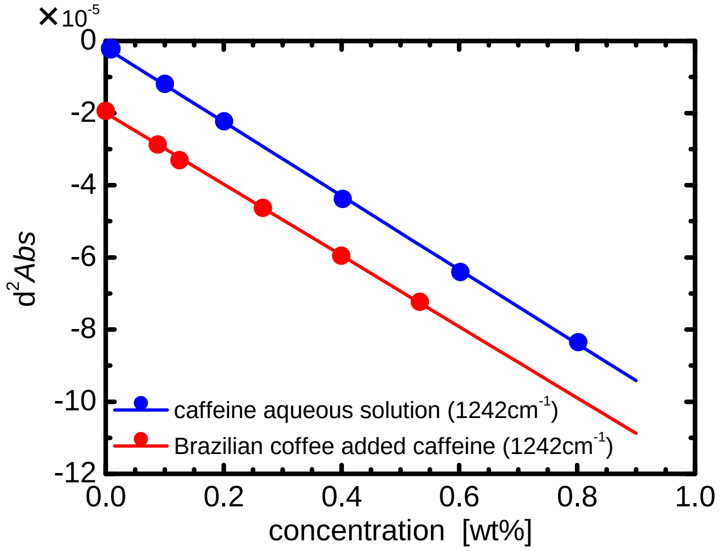

Figure 4. Comparison of error ratio for MIR spectra of brewed coffee (Brazil) between the two coffee brewing methods.

Table 1. Fitting parameters and correlation coefficients of calibration curves.

reagents	wavenumber [cm^{-1}]	solvent	slope [$wt\%^{-1}$]	intercept [wt%]	correlation coefficient [-]
caffeine	1242	brewed coffee	$1.003x10^{-4}$	$1.939x10^{-5}$	0.999
	1242	pure water	$1.047x10^{-4}$	$0.066x10^{-5}$	0.999
chlorogenic acid	1122	brewed coffee	$3.685x10^{-5}$	$3.014x10^{-5}$	0.998
	1120	pure water	$4.925x10^{-5}$	$0.121x10^{-5}$	0.998

For the both reagents, the fitting results of the slope values for the brewed coffee were roughly equal to those for the aqueous solution, but the fitting results of the intercept values for the brewed coffee were quite bigger than those for the aqueous solution. These spectroscopically mean that the interactions between the reagents and the other components in the brewed coffee were almost negligible. Additionally, the differences of the intercept values between the brewed coffee and the aqueous solutions would be due to the existence of the coffee components other than caffeine and chlorogenic acid or not. Consequently, using the MIR spectroscopic information, we could quantify the caffeine and chlorogenic acid contents in the brewed coffee as the very complicated system and might analyze the quality as the liquid food.

Mid-Infrared Spectral Identification of Brewed Coffee Characteristics

We tried to qualitatively identify the important properties of the brewed coffee closely related to the quality, such as the geographical origin, varieties and the roasting degree, using the MIR spectroscopic information. Figure 5 shows the spectra of all kinds of the brewed coffee measured in this study. The spectra of the Indonesian brewed coffee as the Robusta variety have a characterizing peak around 1369 cm^{-1}, and the peaks around 1385 and 1242 cm^{-1} for the Indonesian brewed coffee respectively show the higher and lower values than those for the Colombian, Brazilian and Guatemalan brewed coffee as the Arabica varieties. It is then easy to find out the differences of the spectral features of the Indonesian coffee from the others. In addition, around 1385, 1369, 1292, 1286, 1190 and 1151 cm^{-1}, the differences of the spectral features of the Indonesian coffee between the City roast and Full City roast were observed. Furthermore, focusing our attention on the peak around 1385 cm^{-1} not due to caffeine and chlorogenic acid, we would identify the Brazilian coffee among the Arabica varieties. Hence, these spectral characteristics of the brewed coffee would be acceptable to identify the varieties and geographical origins of the beans and were reflected by the roasting conditions of the Indonesian beans.

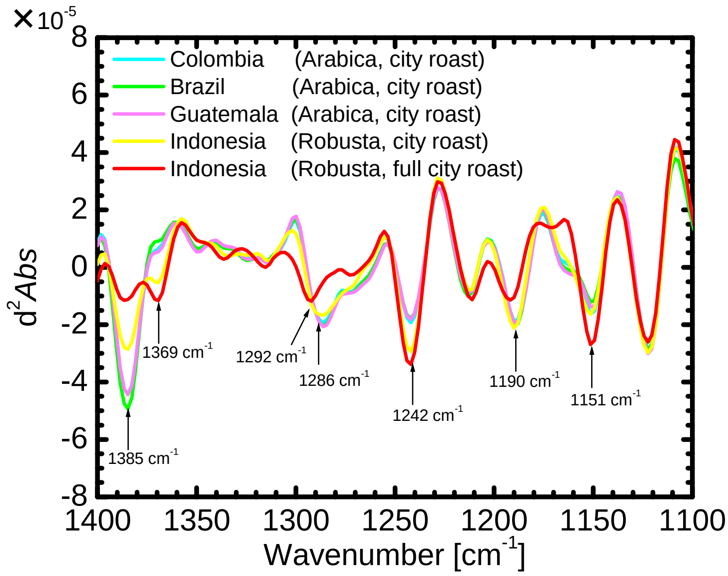

Figure 5. Influences of varieties, geographical origins and roasting degree of coffee beans on MIR spectral characteristics of brewed coffee.

CONCLUSIONS

We studied the MIR spectroscopic information of the brewed coffee. Findings of this study may be summarized as follows.

1. For collecting the stable MIR spectral information for the brewed coffee analysis, the brewing method adding hot water under the conditions of the 25 g-coffee powder to 150 g-boiled water was the most useful among all brewing conditions tested in this study.

2. Using the MIR spectroscopic information, we could quantify the caffeine and chlorogenic acid contents in the brewed coffee as the very complicated system and might analyze the quality as the liquid food.

3. It would be possible to identify the varieties and geographical origins of the beans by the MIR spectroscopic analysis of the brewed coffee, and the roasting conditions of the Indonesian beans reflected the spectral features of the brewed coffee.

Therefore, this study represents as the very important step in developments of the MIR spectroscopic evaluation of the brewed coffee characteristics for determination of coffee process conditions and of the characteristics of the coffee varieties and geographical origins, which are very empirical in coffee manufacturing. The acceptance and implementation of the FT-IR method by the food industry requires that the method is pre-programmed and made user friendly. Furthermore, it is desirable that the quantitative MIR spectroscopic method of the ionic dissociative mixtures (Nakanishi *et al.*, 2003, Pan *et al.*, 2003, 2004) would be applied to the analysis of the brewed coffee, since the acidity gives a good account of the very important factor for the taste of the brewed coffee. In addition, the influences of temperature on the MIR spectral information should be considered.

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