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FTIR-ATR Analysis of Brewed Coffee: Effect of Roasting Conditions

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FTIR-ATR was used to study the effect of roasting conditions on the flavor of brewed coffee using Guatemala Antigua coffee beans. The 1800−1680 cm^{-1} carbonyl region for vinyl esters/lactones, esters, aldehydes, ketones, and acids was found to provide a flavor-print of the brewed coffee. A study of light, medium, and dark roasts indicated that when the rate of heating to the onset of the first and second cracks was kept constant, the types of carbonyl compounds formed were similar, varying only in their concentration. This difference in concentration is apparently due to the additional heating of the coffee bean beyond the second crack. When the heating rate to the onset of the first and second crack was varied, both the types and concentration of the carbonyl compounds formed during roasting were affected. Thus, heating rates of green coffee beans to the onset of the first and second cracks are important determinants of the basic taste and aroma of brewed coffee.

KEYWORDS: Coffee; Guatemala Antigua; roasting conditions; FTIR-ATR; flavor

INTRODUCTION

The aroma and taste of coffee as well as its stimulating properties have made it one of the most popular beverages worldwide. The complex blending of aroma (from volatile compounds sensed in the nose) and taste (from volatile and nonvolatile compounds sensed in the mouth) gives brewed coffee its distinctive flavor. This flavor is dependent on a number of factors such as the species of coffee bean (arabica or robusta), the geographical growing conditions (including type of soil and altitude), whether the fruit was wet or dry processed, the age of the bean, and the roasting conditions.

Unroasted coffee has been described as having an herb-like green bean aroma. Typically, coffee is roasted by heating the green coffee beans at a controlled rate from room temperature to about 220 °C over about a 12-min period. Since charring of the beans begins at about 230 °C, only the darkest Italian and French roasts are taken to about 240 °C. During the roasting process, many chemical reactions occur simultaneously inside the bean (*1*−*4*). The chemical processes that occur in the first portion of the heating cycle appear to be primarily hydrolytic reactions involving the simple saccharides present in the green beans, giving rise to glucose, fructose, mannose, and galactose. Cellulose, the polysaccharide making up the structure of the coffee bean, also begins to hydrolyze in the mildly acidic environment of the bean, increasing the concentration of glucose and reducing the toughness of the bean structure. As the temperature exceeds 100 °C, water that is not strongly bonded to organic molecules begins to vaporize. When the vapor pressure is sufficient (at 120 °C the vapor pressure is about 30 psi), some of the weakened cellulose walls begin to crack, giving rise to the first crack sound from the roaster as the coffee beans, which act like miniature pressure cookers, let off excess pressure.

As the temperature continues to rise, a number of ring opening reactions of sugars with amino acids (Maillard reactions) begin to occur. The aldosamine and ketosamine compounds formed in these initial reactions can cyclize or can further react with other compounds (and then cyclize). As the temperature rises toward 160 °C, another reaction (Strecker Degradation) begins. These reactions involve the condensation of dicarbonyl compounds (formed from the oxidation of activated sugar molecules) with amino acids. These initial linear condensation products degrade, giving off CO_2, to form aminoketones and aldehydes, which can then cyclize. By whichever reaction mechanism these compounds are formed, the syntheses primarily involve sugar molecules (of which there are likely five basic types plus dicarbonyl) reacting with the various free amino acids (17 of which have been identified in the green coffee bean). Thus, a large variety of organoleptic compounds are formed via the Maillard and Strecker Degradation reactions.

Increased amounts of fatty acids also begin to form at these elevated temperatures by hydrolysis of the lipids. Since the free fatty acids are surfactants, they help blend less soluble molecules into the water phase of the coffee, thus improving the overall

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taste. However, since some lipids are unsaturated, they can oxidize (both in roasting and in storage) and adversely affect the taste of coffee.

The continuing hydrolysis of the cellulose as the temperature rises above 160 °C makes the beans weaker and more brittle. The second crack sound occurs when the pressure of the CO_2 being formed in the Strecker degradation exceeds the strength of the cellulosic walls of the bean and is released. One consequence of this loss of CO_2 is that excess sugar molecules begin to oxidize (or caramelize), producing noncyclic aldehydes, ketones, and acids. As the temperature continues to rise, thermal degradation of many organic molecules begins. For example, pyruvic acid is formed and can further degrade to acetaldehyde, caffeic acids can oxidize to form hydroxybenzaldehydes (an aromas in apricots), and the quinic acids may lose water and form phenolic acids, which can give a bitter taste to coffee. Caffeine is relatively stable under these conditions and thus remains effectively unchanged.

The formation of this complex mixture of organoleptic compounds gives brewed coffee its distinctive aroma and taste (*1*, *2*, *4*, *5*). While early research on coffee in the 1920s identified about 29 compounds in coffee, more modern analytical techniques using gas chromatography (GC) and thin-layer chromatography have identified over 800 compounds in the roasted coffee bean (*2*). Attempts to determine the major compounds responsible for the flavor of brewed coffee have utilized GC to separate and identify the volatiles in brewed coffee as well as in the headspace above brewed coffee. While some compounds were detected by both techniques, each method detected compounds that the other did not, thus indicating the complexity of assessing coffee flavor.

While these techniques are useful in identifying specific compounds in coffee, it was of interest to determine whether Fourier transform infrared (FTIR) spectroscopy using attenuated total reflection (ATR) techniques could be used to characterize the mixture of both volatile and nonvolatile compounds that constitute the flavor of brewed coffee. In this paper, we present the results of our FTIR-ATR study on the effect of roasting conditions (such as light, medium, and dark roasting) on coffee brewed from Guatemala Antigua arabica coffee beans.

MATERIALS AND METHODS

Roasting of Coffee Beans. Guatemala Antigua green coffee beans (85 g per roast) were roasted in a Probat Twin Roaster (Probat BRZ-2, Probat Burns Inc., Memphis, TN) under various roasting conditions to study the effect of roast conditions on brewed coffee. In the first set, beans were roasted under conditions to achieve light, medium, and dark roasts. Roasting times to the onset of the first and second cracks for each roast were kept constant at 8.5 and 11 min, respectively. The light-roasted beans were removed immediately after the onset of the second crack and cooled; the medium-roasted beans were removed 1 min after the onset of the second crack and cooled; the dark-roasted beans were removed 2 min after the onset of the second crack and cooled.

In the second set, the beans were roasted under conditions (known as sweated and baked) in which the heating times to the first and second cracks were varied. Timings to the onset of the first crack and second crack for the sweated and baked roasting were 4.5, 6.5 min and 11.0, 18 min, respectively. The roasted beans were removed 0.5 min after the onset of the second crack and cooled.

Each type of roast resulted in beans that were uniform in color, with the exception of the sweat-roasted beans.

Brewing of Coffee. All roasted beans were ground to a standard cupping grind (similar to that of a French press grind). Coffee was brewed by adding six ounces of hot (98 °C) filtered water to seven grams of ground coffee in a tasting cup and allowing the mixture to steep for 4.25 min. The crust floating on the top of each cup was then broken and the coffee aroma noted. Samples (approximately 25 mL) of each coffee were placed in 120 mL polypropylene screw capped jars and refrigerated until analyzed. A sample of the filtered water used in brewing the coffee was also placed in a 120 mL polypropylene screw capped jar and refrigerated. The various roasts were then tasted by the cuppers (see **Table 1**).

Table 1. Taste and Aroma Comments of Brewed Coffee from Various Roasts[a]

type of roast	cupper's perception[b]
light	light snappy acidity, drier finish, citrus-like flavor
medium	slightly heavier citrus flavor with a good balance of taste and aroma
dark	heavier sweet taste with a lingering sweet or chocolate aftertaste
sweated	grassy, sour, underdeveloped taste and aroma
baked	flat, woody, low acidity

[a] Guatemala Antigua green coffee beans were used in all the roastings. [b] Reference 13.

FTIR Analyses. Samples of brewed coffee were analyzed using a Digilab (Randolph, MA) FTS-40A Fourier transform infrared spectrometer with a liquid nitrogen cooled mercury−cadmium-telluride (MCT) detector and a Prism Liquid ATR cell (Harrick Scientific, Ossining, NY) with a 45° ZnSe crystal ($\theta = 45°$). Spectra were obtained from 4000 to 700 cm^{-1}, using 128 scans at a resolution of 4 and Norton-Beer medium apodization. The spectrum of the filtered water used to brew the coffee, obtained on the same Prism Liquid ATR cell, was used for subtraction. Water subtraction, deconvolution ($\gamma = 1$, smoothing $= 0$), and second derivatives were done using the GRAMS/386 program (ThermoGalactic, Salem, NH).

RESULTS AND DISCUSSION

FTIR spectroscopy, having a constant high-resolution and high-energy throughput over the entire spectral region and a good signal-to-noise ratio, allows the spectroscopist to distinguish weaker bands and shoulders in the spectra. In addition, the subtractive capabilities of the instrument in the absorbance mode allows the absorption bands of coffee compounds, whose spectra are obtained as aqueous solutions, to be studied without the interference of overlapping water bands. A small band at 2120 cm^{-1}, which occurs due to a combination of water vibrations (*6*, *7*), can be used for the water subtraction since organic materials usually do not absorb at this wavelength.

ATR techniques have been used to identify differences between aqueous solutions of reconstituted freeze-dried arabica and robusta coffee (*8*). These studies focused on the differences in the chlorogenic acid and caffeine content of the coffees and utilized their respective absorptions at 1300−1150 cm^{-1} and 1650−1600 cm^{-1}. However, the fingerprint region of the spectra (1600−1000 cm^{-1}), while unique for each organic molecule, is a complex region of C−H, C−O, C−N, and P−O vibrations and difficult to analyze. This is further complicated by the presence of over 800 compounds ranging from simple linear and branched structures to complex cyclic and heterocyclic structures. However, in this complex mixture, as well as in the 22 compounds reported to be important roast coffee flavor compounds (*2*), are large numbers of ketone, aldehyde, ester, and acid compounds (*1*, *4*, *5*). The presence of a carbonyl group often confers organoleptic qualities to compounds by affecting the aroma and taste centers in the nose and mouth. For example, aldehydes usually exhibit sharp odors, ranging from woody to cucumber, to cooked fruit, to nuts. Ketone odors are less sharp than aldehydes but exhibit many of these same odors. Esters often exhibit softer, more fruity aromas. Acids can exhibit aromas ranging from vinegar to chocolate, to burnt caramel,

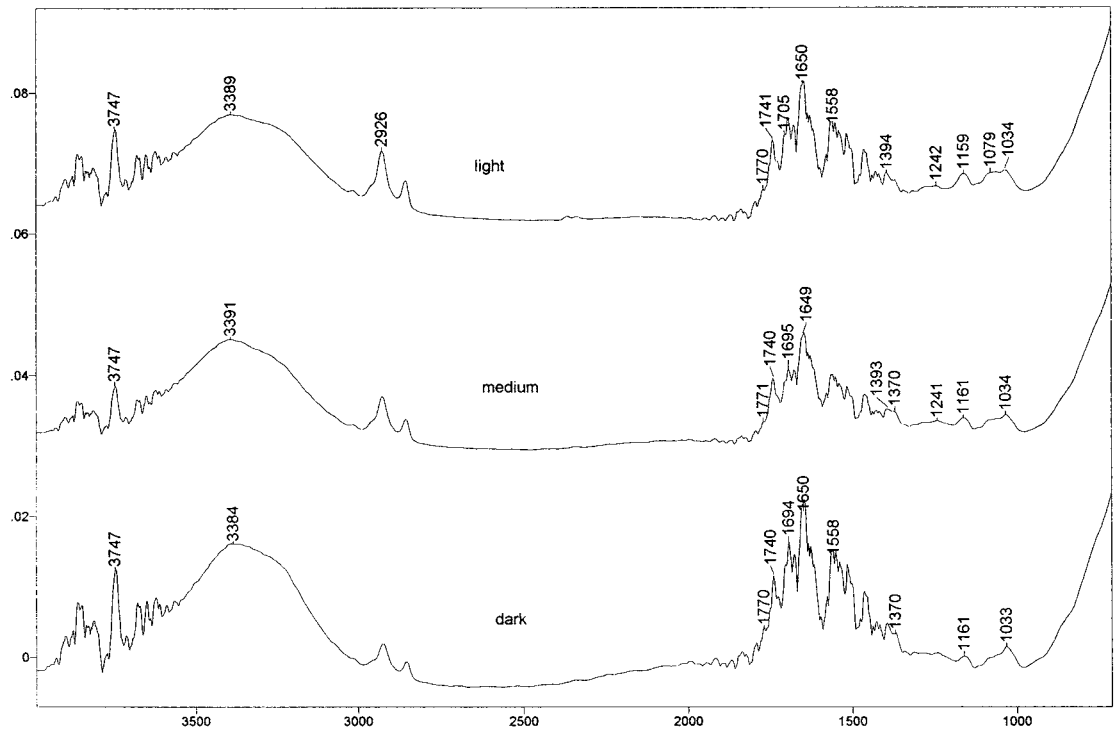

Figure 1. Water-subtracted spectra of coffee brewed from light-, medium-, and dark-roasted Guatemala Antigua coffee beans [absorbance/wavenumber (cm^{-1})].

but some have no odor. However, acids can contribute to the perceived brightness in taste (*9*). Thus, it would appear that the type and concentration of carbonyl compounds in the roasted coffee bean contribute significantly to the differing flavors of brewed coffee. Therefore, it was of interest in this study to examine the 1800−1680 cm^{-1} carbonyl absorption region of the spectra. General band assignments, based on general literature (*10*, *11*) and published spectra (*12*) of a number of known compounds of coffee, are as follows: aromatic acids (1700−1680 cm^{-1}), aliphatic acids (1714−1705 cm^{-1}), ketones (1725−1705 cm^{-1}), aldehydes (1739−1724 cm^{-1}), aliphatic esters (1755−1740 cm^{-1}), and vinyl ester and lactones (1780−1762 cm^{-1}).

Comparison of Light, Medium, and Dark Roasts. Since the heating rates of the light, medium, and dark roasts of the Guatemala Antigua coffee beans are the same up to the onset of the second crack, the major differences that occur in the organoleptic compounds result from chemical reactions that occur during or after the second crack. In light-roasted coffee, the reactions were essentially stopped after the onset of the second crack by immediately removing and cooling the hot beans. With the medium and dark roasts, the reactions were allowed to continue for an additional one and two minutes, respectively, beyond the onset of the second crack before the beans were removed and cooled.

The water-subtracted spectra of coffee brewed from these three roasts are shown in **Figure 1**. While spectra of all three roasts are rather similar, there are subtle differences. For example, the fingerprint region (1600−1000 cm^{-1}) of the spectra is unique for each organic molecule. Of greater interest for this study is the 1800−1680 cm^{-1} carbonyl absorption region of the spectra (**Figure 2**). This region indicates the differences in the types and concentrations of lactone, ester, aldehyde, ketone, and acid compounds in these roasts.

The exact number of carbonyl compounds may not be fully identifiable from this portion of the spectra since several compounds may have similar carbonyl absorption frequencies.

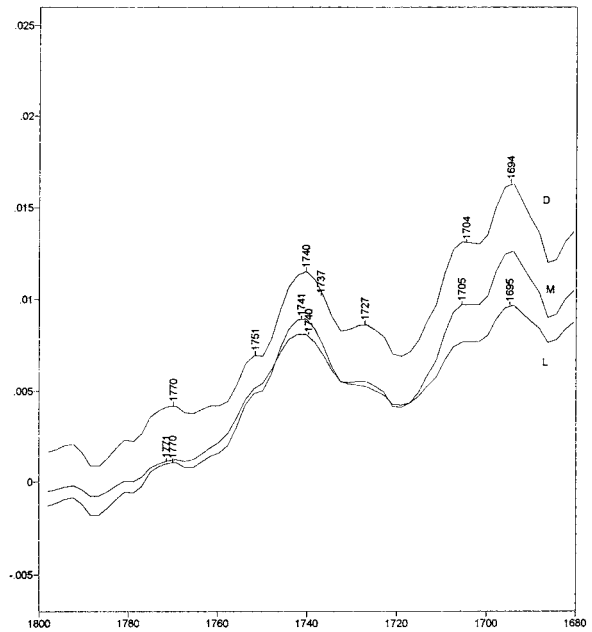

Figure 2. The expanded 1800–1660 cm^{-1} carbonyl region of the spectra in **Figure 1** [absorbance/wavenumber (cm^{-1})].

However, the deconvoluted spectra and the second derivatives of the spectra indicate that at least 26 different carbonyl compounds make up this 1800−1680 cm^{-1} absorption region. More interestingly, since the deconvoluted spectra and second derivatives of the spectra of the three roasts have identical band positions, the same compounds appear to be present in each roast. The relative concentration of these various carbonyl materials (based on the curve-fit band areas and assuming that the absorptivities of the various carbonyl bands are similar) is shown in **Figure 3**. Thus, the differences in the flavor of coffee brewed from the light, medium, and dark roasts (see **Table 1**)

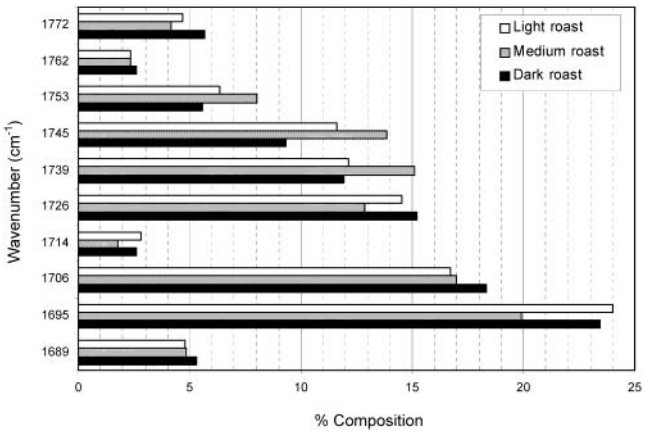

Figure 3. Bar graph showing relative concentrations of selected carbonyl compounds in coffee brewed from light-, medium-, and dark-roasted beans (from curve-fit areas).

appear to be related to differences in the relative concentrations of similar carbonyl compounds rather than from differences in the types of carbonyl compounds.

In going from a light roast to a medium roast, the major changes in concentration appear to be increases in ester (at 1754−1744 cm^{-1}) and aldehyde (at 1741−1738 cm^{-1} and 1729−1723 cm^{-1}) compounds, and decreases in the aldehyde or ketone (around 1726 cm^{-1}), ketone (around 1714 cm^{-1}), acid (around 1695 cm^{-1}), and vinyl ester and/or lactone (around 1772 cm^{-1}) compounds. These changes in the ester, aldehyde, ketone, and acid flavor compounds appear to give medium-roasted coffee a more full-bodied flavor, an improved balance of taste and aroma, and a more pronounced citrus taste compared to light-roasted coffee. The relative decrease in the acid compounds is consistent with a decrease in the brightness of the taste. The flavor qualities of the light roast and medium roast might suggest that the decrease in compounds whose carbonyl absorption are in the 1792−1962 cm^{-1} region are lactones rather than the more pungent unsaturated esters. It is interesting to note that a standard roast (medium) of Guatemala Antigua beans using a commercial roaster (Probat G45, 20 Kg roast size) gave spectra comparable to the small roaster except for a slight increase in acidic compounds.

In going from the medium roast to the dark roast, again there are major changes in the concentration of the carbonyl compounds resulting from the additional minute of heating. There are increases in the amounts of unsaturated ester/lactone (at 1772−1762 cm^{-1}), aldehyde/ketone (around 1726 cm^{-1}), ketone (around 1714 cm^{-1}), and acid (at 1706−1689 cm^{-1}) compounds. There are also decreases in the amount of ester (at 1755−1740 cm^{-1}) and aldehyde (around 1739 cm^{-1}) compounds. These changes in concentrations are consistent with the cuppers' comments of a heavier, sweet taste, with a lingering aftertaste of chocolate. Caramelization of sugar from this additional minute of heating of the dark roast may also contribute to an increase in sweetness.

Comparison of Sweated and Baked Roasts. Two additional roasting treatments of the green coffee beans were examined. In the sweated process, the heating rate is increased (i.e., 4.5 min. to the onset of the first crack and 6.5 min to the onset of the second crack compared to 8.5 and 11 min for the medium roast) while in the baked process the heating rate is decreased (11 min to the onset of the first crack and 18 min to the onset of the second crack). While the final temperature of the beans is approximately the same as in the medium roast, the differing times at the various reaction temperatures should affect the

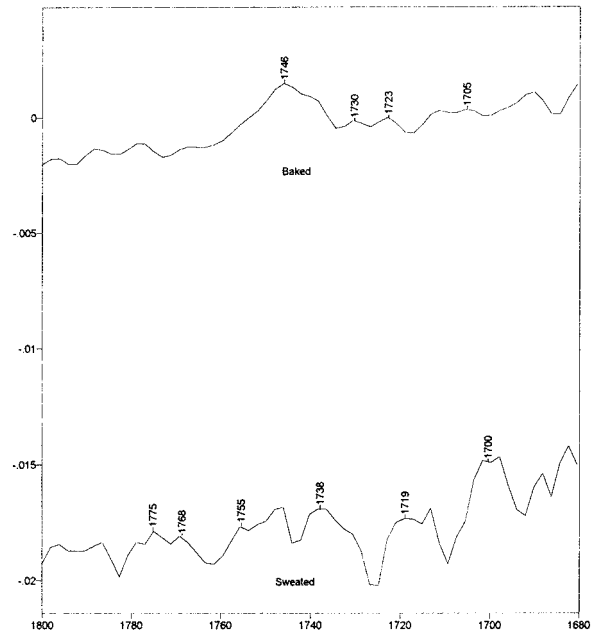

Figure 4. The expanded 1790–1680 cm^{-1} carbonyl region of the water-subtracted, deconvoluted spectra of coffee brewed from sweated and baked Guatemala Antiqua coffee beans [absorbance/wavenumber (cm^{-1})].

extent of the hydrolytic, Maillard, and Strecker Degradation reactions and, thus, the overall chemical composition of coffee. In addition, the observation that the sweated-roasted beans were nonuniform in color suggests that the actual reaction temperature in each bean varies in this process, thus complicating even further the various reaction sequences. The resulting effect on the flavor of coffee brewed from these two roasts was striking. The cuppers' perception (**Table 1**) was that the sweated-roasted coffee was sour, grassy, and underdeveloped; the baked-roasted coffee was flat, woody, with low brightness or acidity.

The expanded 1800−1660 cm^{-1} carbonyl region of the water-subtracted, deconvoluted spectra of coffee brewed from sweated and baked beans is shown in **Figure 4**. Again, the exact number of carbonyl compounds may not be fully identifiable from this portion of the spectra since some compounds may have similar carbonyl absorption frequencies. However, the deconvoluted spectra and second derivatives of the spectra of the sweated beans indicate that at least 26 different carbonyl compounds make up this 1800−1680 cm^{-1} absorption region. Even with shorter and variable reaction times (due to the apparent uneven heating of each bean), some of the same compounds are formed in the sweated roast as were formed in the medium roast. These are the esters absorbing at 1755−1746 cm^{-1}, the aldehydes absorbing at 1738 cm^{-1}, the ketone/aldehydes absorbing at 1712 cm^{-1}, and the acids absorbing at 1689 cm^{-1}. However, there are new compounds in the sweated beans indicated by five new absorption bands at 1776 and 1768 cm^{-1} (lactones/vinyl esters), 1730 and 1719 cm^{-1} (aldehydes), and 1700 cm^{-1} (acids).

The relative composition (based on the curve fit band areas and assuming that the absorptivities of the various carbonyl bands are similar) is shown in **Figure 5**. Compared to the medium-roasted coffee, there is an overall concentration imbalance of the lactones, esters, aldehydes, and ketones (compounds which contribute to the medium-roasted coffee's fruity aroma and body) in the coffee brewed from the sweated roast. Also, there are new types of the lactones/unsaturated esters, aldehydes, and acids in the sweated coffee. These new components could be responsible for the pungent, grassy smell and sour flavor of this coffee.

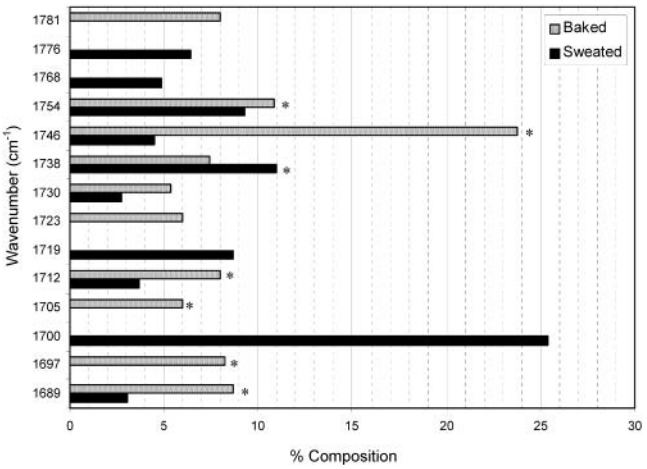

Figure 5. Bar graph showing relative concentrations of selected carbonyl compounds in coffee brewed from sweated and baked coffee beans (from curve-fit areas). The asterisk indicates carbonyl absorptions that were also found in coffee brewed from medium-roasted Guatemala Antiqua coffee beans.

In contrast, the deconvoluted spectra and second derivatives of the spectra of baked coffee indicate that at least 22 different carbonyl compounds make up this 1800−1680 cm^{-1} absorption region. With the longer reaction times, more of the compounds that were present in the medium-roasted beans are present in the baked beans (see **Figure 5**). These are the esters at 1755−1748 cm^{-1}, the aldehydes at 1738 cm^{-1}, the ketones at 1712 cm^{-1}, and the acids at 1705, 1697, and 1689 cm^{-1}. Again, there is an overall concentration imbalance of these lactones, esters, aldehydes, and ketones which contributed to the medium-roasted coffee's fruity flavor. In addition, there are new compounds in the baked-roasted beans as indicated by three new absorption bands at 1781 cm^{-1} (lactones/vinyl esters), 1730 cm^{-1} (aldehydes), and 1723 cm^{-1} (ketones). These new components could be responsible for the woody flavor of this coffee.

Of interest are these eight new absorption bands that appear in these two coffee roasts that were not present in the medium-roasted coffee. One absorption band, 1730 cm^{-1} (aldehyde), is common to both the sweated and baked coffees. However, four of the absorption bands are present only in the sweated coffee (1776 and 1768 cm^{-1} (vinyl ester/lactone), 1719 cm^{-1} (ketone), and 1700 cm^{-1} (acid) and two absorption bands are present only in the baked coffee (1781 cm^{-1} (vinyl ester/lactone), and 1723 cm^{-1} (aldehyde/ketone). This would suggest that the sour, grassy flavor could be related to the bands that were only in the sweated coffee, while the woody flavor could be related to the bands that were only in the baked coffee.

Thus, our studies show that FTIR-ATR spectra of brewed coffee can be used to determine the effect of roasting conditions on the molecular composition of the brewed coffee. The 1800−1680 cm^{-1} carbonyl region of the spectra provides a flavorprint which appears to be consistent with the taste and aroma perceived by coffee cuppers. The composition of these carbonyl compounds (vinyl esters/lactones, esters, aldehydes, ketones, and acids) in the brewed coffee appears to be dependent upon the heating rate of the green beans to the onset of the first and second cracks. If the heating rate is kept constant (as in the light, medium, and dark roasts), the types of the carbonyl compounds formed are similar and only vary in their relative concentration, apparently due to the amount of heating beyond the onset of the second crack. When the rate of heating to the onset of the first and second cracks is changed, such as in the sweated process or baked process, both the types and concentration of the carbonyl compounds that are formed can vary.

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