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Effect of Roasting Conditions on the Polycyclic Aromatic Hydrocarbon Content in Ground *Arabica* Coffee and Coffee Brew

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Roasting is a critical process in coffee production as it enables the development of flavor and aroma. At the same time, roasting may lead to the formation of nondesirable compounds, such as polycyclic aromatic hydrocarbons (PAHs). In this study, *Arabica* green coffee beans from Cuba were roasted under controlled conditions to monitor PAH formation during the roasting process. Roasting was performed in a pilot spouted bed roaster, with the inlet air temperature varying from 180 to 260 °C, using both dark (20 min) and light (5 min) roasting conditions. Several PAHs were determined in both roasted coffee samples and green coffee samples. Also, coffee brews, obtained using an electric coffee maker, were analyzed for final estimation of PAH transfer coefficients to the infusion. Formation of phenanthrene, anthracene, and benzo[*a*]anthracene in coffee beans was observed at temperatures above 220 °C, whereas formation of pyrene and chrysene required 260 °C. Low levels of benzo[*g*,*h*,*i*]perylene were also noted for dark roasting under 260 °C, with simultaneous partial degradation of three-cycle PAHs, suggesting that transformation of low molecular PAHs to high molecular PAHs occurs as the roasting degree is increased. The PAH transfer to the infusion was quite moderate (<35%), with a slightly lower extractability for dark-roasted coffee as compared to light-roasted coffee.

KEYWORDS: *Arabica*; coffee; fluidization; polycyclic aromatic hydrocarbons; roasting

INTRODUCTION

Roasting is a crucial step for the production of coffee, as it enables the development of color, aroma, and flavor, which are essential for the characterization of the coffee quality. Both the temperature and time conditions of the roasting step need to be optimized and controlled to achieve maximum aroma and flavor development. In practice, the roasting conditions differ depending on the coffee quality expected and the type of roaster used.

Chemical reactions are known to be responsible for the development of aroma and flavor during the roasting step, such as the Maillard reaction, which involves the reaction of the free amino group of an amino acid, a peptide, or even a protein with the carbonyl group of a reducing sugar during heating. This is the first step of a succession of reactions, most of them leading to the formation of aroma compounds (such as pyrroles) as well as melanoidins, compounds with possible antioxidant properties (*1*). Yet, at the same time, the formation of toxic compounds may not be excluded, and some of them could be mutagenic. Hence, the heating at 250 °C of trigonelline (*N*-methylpyridinium-3-carboxylate), a natural component of green coffee beans, leads to mutagenic compounds, with probably heterocyclic amines as well as mutagens of other types (*2*).

Very recently acrylamide, a suspected carcinogen and mutagen compound also formed during the Maillard reaction, has been reported in coffee samples. It is formed at the beginning of the roasting step. A lower acrylamide content was observed in dark-roasted coffee as compared to medium-roasted coffee, which could be attributed to either evaporation or degradation of acrylamide during higher processing temperatures or longer processing times (*3*–*5*). This observation was confirmed by results showing that the acrylamide level in coffee showed a maximum during roasting, with a rapid appearance, and then an exponential degradation during heating at either 200 or 225 °C (*6*). A similar trend has been recently observed for 5-hydroxymethyl-2-furfural, another Maillard product, with a rapid formation and subsequent degradation during the roasting of coffee at 240 °C (*7*).

The presence of polycyclic aromatic hydrocarbons (PAHs) in coffee samples has also been reported and may be attributed to either contamination of the initial green beans or formation

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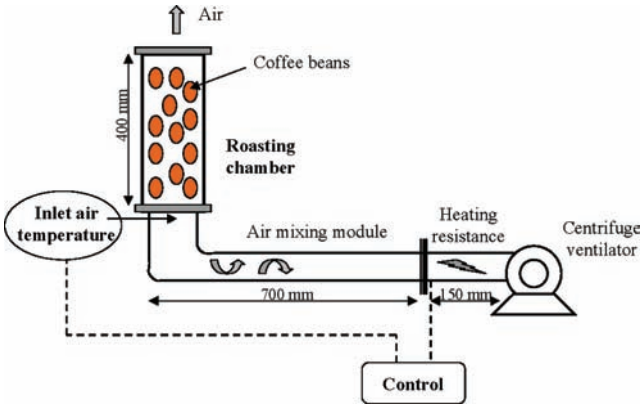

Figure 1. Schema of the pilot spouted bed roaster used in this study.

of these compounds during the roasting step (*8–14*). Thus, roasting conditions should be controlled to avoid their formation due to their suspected carcinogenic and mutagenic properties. Therefore, the present work was undertaken to study the influence of roasting conditions on the PAH content of coffee samples. To avoid variations in PAH concentrations related to the coffee origin, only *Arabica* samples from Cuba were considered. Both ground coffee and coffee brew were analyzed in this study.

MATERIALS AND METHODS

Most experiments were done in triplicate, enabling mean values and relative standard deviations (RSDs) to be determined.

Reagents and Chemicals. The reagents were all used in the form purchased without additional purification or alteration. A PAH mix solution was used (Supelco, Saint-Quentin Fallavier, France) containing the 16 EPA PAHs (10 mg L^{-1} in acetonitrile) with purities above 96% as indicated: naphthalene (97.7%), acenaphthylene (99.9%), acenaphthene (99.9%), fluorene (98.6%), phenanthrene (99.9%), anthracene (99.8%), fluoranthene (98.2%), pyrene (96.6%), benzo[*a*]anthracene (97.9%), chrysene (98.7%), benzo[*b*]fluoranthene (99.9%), benzo[*k*]fluoranthene (99.5%), benzo[*a*]pyrene (99.9%), dibenzo[*a,h*]anthracene (99.6%), benzo[*g,h,i*]perylene (99.1%), and indeno[1,2,3-*c,d*]pyrene (99.9%). HPLC-grade solvents were used, supplied by either Carlo-Erba (i.e., acetonitrile, methanol, anhydrous ethanol, tetrahydrofuran, cyclohexane) or Prolabo (i.e., acetone, dichloromethane, hexane). Deionized water was produced with a Milli-Q system from Millipore (Saint-Quentin-en-Yvelines, France). Anhydrous sodium sulfate was supplied by Merck (for analysis grade) and potassium hydroxide (KOH) by Prolabo (Rectapur grade). Stock standard solutions were prepared by diluting the PAH solutions in an appropriate volume of tetrahydrofuran to obtain the desired concentrations in the range of 5–500 μg L^{-1}. All solutions were stored at 4 °C in the dark for up to 5 weeks.

Coffee Roasting. Green coffee beans (*Arabica*) were of Cuban origin. Two lots (A and B) were obtained from Coffea (Le Havre, France). Green beans (100 g) were roasted in a pilot spouted bed roaster as indicated in **Figure 1** (coffee beans were manually placed in the chamber before roasting). Roasting was carried out for either 5 or 20 min and at different temperatures, ranging from 180 to 260 °C for the inlet air temperature as indicated in **Table 1**. The roasted beans were kept in the dark in closed polyethylene flasks before being submitted to the sample treatment procedure recently developed and validated for the determination of the 11 PAHs reported in **Table 2** (*12*).

Extraction and Cleanup of Ground Coffee Samples. Prior to their extraction, coffee beans were ground using a coffee grinder (Prep'Line 850, power of 180 W, Seb, France). Ground coffee samples were then extracted using a pressurized liquid extraction system (ASE 100, Dionex), with hexane/acetone 50:50 (v/v) under 150 °C as already detailed (*12*). The obtained extract was then concentrated to a few milliliters using a rotary evaporator and finally to dryness under a gentle stream of nitrogen, before being submitted to alkaline saponification and cyclohexane extraction as already reported (*12*). The final extract was then concentrated to a few milliliters using a rotary evaporator and finally to near 2 mL under a gentle stream of nitrogen.

Table 1. Roasting Conditions Tested in This Study

expt	replicates (*n*)	*Arabica* green coffee lot	inlet air temp (°C)	outlet air temp (°C)	mean roasting chamber temp (°C)	roasting time (min)
1	3	A	180	170.4	175.2	5
2	3	A	180	170.4	175.2	20
3	3	A	200	188.8	194.4	5
4	3	A	200	188.8	194.4	20
5	3	A	220	207.1	213.5	5
6	3	A	220	207.1	213.5	20
7	3	B	240	225.3	232.6	5
7 bis	1	A	240	225.3	232.6	5
8	3	B	240	225.3	232.6	20
9	3	B	250	234.4	242.1	5
10	3	B	250	234.4	242.1	20
10 bis	1	A	250	234.4	242.1	20
11	3	A	260	243.5	251.6	5
12	3	A	260	243.5	251.6	20

Table 2. Toxicity Equivalent Factors (TEF) for the 11 PAHs Determined in This Study

compound	abbreviation	no. of cycles	IARC[a] group	TEF[b]
phenanthrene	Phen	3	3	0.001
anthracene	Anthr	3	3	0.01
fluoranthene	F	4	3	0.01
pyrene	Pyr	4	3	0.01
benzo[*a*]anthracene	B[a]A	4	2A	0.1
chrysene	Chrys	4	3	0.01
benzo[*b*]fluoranthene	B[b]F	5	2B	0.1
benzo[*k*]fluoranthene	B[k]F	5	2B	0.1
benzo[*a*]pyrene	B[a]P	5	2A	1
dibenzo[*a,h*]anthracene	DB[ah]A	5	2A	1
benzo[*g,h,i*]perylene	B[ghi]P	6	3	0.01

[a] International Agency for Research on Cancer (IARC): group 2A, probable human carcinogen; group 2B, possible human carcinogen; group 3, not classifiable for human carcinogenicity. [b] From the French Food Safety Agency (AFSSA).

The saponified extracts were cleaned up using solid-phase extraction on disposable silica cartridges (Supelclean LC-Si, 1 g, supplied by Supelco, Saint-Quentin Fallavier, France). A Visiprep vacuum manifold system (Supelco) was used. Cartridges were conditioned with 5 mL of cyclohexane and PAHs eluted with 4 × 5 mL of cyclohexane. After evaporation to dryness under a gentle stream of nitrogen, the dry residue was redissolved in 0.4 mL of tetrahydrofuran (THF) before further analysis.

Coffee Brew Preparation. The coffee brew samples were obtained using an electric coffee maker equipped with a paper filter. In all cases, 50 g of ground roasted coffee was treated by passing 300 mL of Milli-Q water as performed in another study (*11*).

Extraction and Cleanup of Coffee Brew Samples. Fifty milliliters of coffee brew was taken and submitted to alkaline saponification to eliminate interferent compounds that hinder PAH analysis (*14*, *15*). Hence, 2.8 g of KOH was added to the coffee brew sample, and saponification was performed under reflux for 30 min. After cooling, 25 mL of an ethanolic solution of KOH (at 1 mol L^{-1}) and 100 mL of cyclohexane were added, and the mixture was heated under reflux for 30 min. After cooling, the cyclohexane phase was kept and mixed (for 5 min) with 100 mL of water. Then the two phases were kept overnight for efficient decantation. In the case of emulsions, 25 mL of ethanol was added to favor the phase separation. The aqueous phase was discarded, and the organic layer again extracted twice with 100 mL of water. Then, anhydrous sodium sulfate was added to dry the organic layer and then removed from the liquid extract by filtration. The final extract was then concentrated to a few milliliters using a rotary

Table 3. Mean PAH Concentrations (with RSDs) and Toxicity Equivalents (TEQ) in Green Coffees as well as in Ground Coffees Roasted for 20 min under Different Inlet Air Temperatures[a]

	Arabica lot A											*Arabica* lot B					
	0 °C (green coffee)		180 °C		200 °C		220 °C		250 °C	260 °C		0 °C (green coffee)		240 °C		250 °C	
	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1}))	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)
Phen	**8.89**	*9.72*	**13.27**	*9.01*	**7.45**	*5.69*	**14.60**	*2.92*	**46.87**	**17.37**	*5.26*	**4.60**	*7.59*	**18.08**	*5.45*	**44.95**	*14.48*
Anthr	**0.68**	*7.49*	**0.90**	*2.89*	**1.01**	*17.35*	**1.08**	*8.60*	**1.90**	**2.17**	*14.85*	**0.45**	*13.86*	**1.91**	*3.18*	**1.95**	*4.57*
F	**6.85**	*3.90*	**13.09**	*3.86*	**4.99**	*3.98*	**4.34**	*12.67*	**11.48**	**17.54**	*11.03*	**6.91**	*8.98*	**4.69**	*2.07*	**11.50**	*11.64*
Pyr	**3.27**	*15.14*	**6.07**	*10.27*	**3.47**	*19.59*	**2.60**	*15.22*	**5.87**	**53.05**	*11.47*	**2.63**	*5.91*	**2.29**	*15.40*	**6.06**	*11.30*
B[a]A	**0.20**	*41.52*	**0.16**	*11.43*	**0.54**	*32.17*	**1.40**	*18.69*	**6.52**	**12.67**	*9.42*	**traces**	-----	**3.68**	*9.80*	**6.52**	*13.49*
Chrys	**0.45**	*9.75*	**1.13**	*2.09*	**2.21**	*19.31*	**1.84**	*6.40*	**1.29**	**12.82**	*13.43*	**0.43**	*16.91*	**1.47**	*13.38*	**1.54**	*30.35*
B[b]F	**0.27**	*13.36*	**0.31**	*6.62*	**0.14**	*21.87*	**0.16**	*20.17*	**0.20**	**nd**		**0.20**	*28.30*	**0.20**	*20.23*	**0.29**	*7.19*
B[k]F	**traces**		**traces**		**nd**		**traces**		**traces**	**traces**		**traces**		**traces**		**traces**	
B[a]P	**traces**		**traces**		**traces**		**traces**		**nd**	**nd**		**traces**		**0.20**	*0.09*	**0.21**	*6.10*
DB[ah]A	**nd**		**nd**		**nd**		**nd**		**nd**	**nd**		**nd**		**nd**		**nd**	
B[ghi]P	**nd**		**nd**		**nd**		**nd**		**nd**	**1.71**	*36.49*	**nd**		**nd**		**nd**	
Σ11 PAHs	**20.61**		**34.93**		**19.81**		**26.02**		**74.13**	**117.33**		**15.22**		**32.52**		**73.02**	
TEQ (11 PAHs)	**0.17**		**0.27**		**0.19**		**0.27**		**0.92**	**2.16**		**0.13**		**0.71**		**1.15**	

[a] nd, not detected; traces, compound detected at levels below the limit of detection of the method.

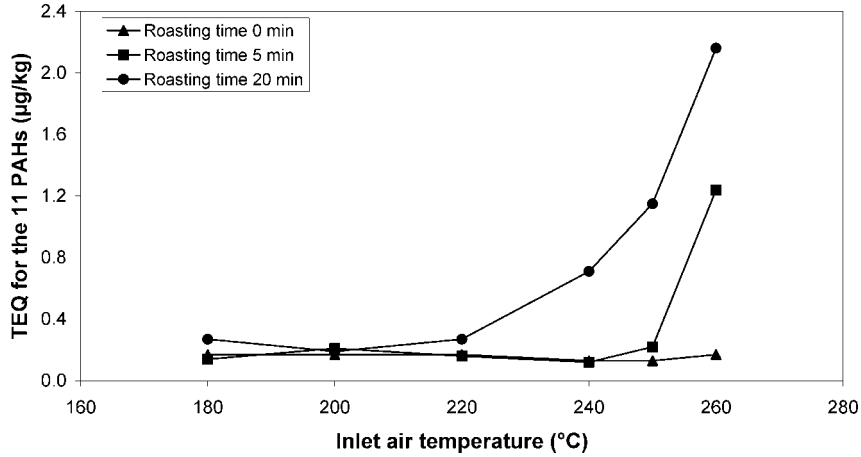

Figure 2. Effect of roasting conditions (both temperature and time) on the mean toxicity equivalent for the 11 PAHs analyzed in ground coffee.

evaporator and finally to near 1 mL under a gentle stream of nitrogen, before further cleanup on solid-phase extraction on disposable silica cartridges as already reported for ground coffee samples.

PAH Analysis. Extracts were analyzed using HPLC coupled to a fluorometric detector (FD). The HPLC system consisted of a Varian 9010 high-pressure gradient pump, a Rheodyne model 7125 injection valve equipped with a 20 μL loop, a Thermo Separation Science fluorometric detector (FL3000), and a computer. Data analysis was performed using the TurboChrom TC4 Navigator. A Supelcosil LC-PAH column (250 × 4.6 mm i.d., C_{18}-silica, 5 μm particle size, Supelco) was used, along with a precolumn (containing C_{18}-silica). Separation was performed using the following gradient: acetonitrile/water (60:40, v/v) for 5 min, followed by a 25 min ramp to 100% acetonitrile, this solvent being further maintained for 15 min. The total flow rate was 1.5 mL min^{-1}. The analytical column was placed in an oven (Waters Column Heater Module connected to a Waters Temperature Control Module) and its temperature regulated at 35 °C, enabling stability of the retention times. Detection was performed at selected excitation and emission wavelengths, programmed as follows: 0–9.6 min, 220/340 nm; 9.6–16.5 min, 230/410 nm; 16.5–20.0 min, 280/380 nm; 20.0–27.3 min, 250/420 nm; 27.3–40.0 min, 286/420 nm. External calibration was performed using standard solutions of PAHs in THF in the range of 5–500 or 5–50 μg L^{-1} depending on the PAH concentrations in the samples. Identification of PAHs was based on peak retention times, by comparison with standards analyzed daily. Confirmation of the presence of suspected PAHs in coffee samples was achieved using HPLC coupled with a diode array UV–visible detector (HPLC-DAD) as well as gas chromatography coupled to mass spectrometry (GC-MS) as already reported (*12*).

RESULTS AND DISCUSSION

The effect of the roasting step conditions on PAH contents of ground coffee samples was investigated under different temperature and time conditions, based on previous studies (*16*). The roasting time was fixed at either 5 or 20 min, to simulate light or dark roasting. The temperature was fixed between 180 and 260 °C for the inlet air of the roaster, to simulate low roasting as well as strong roasting conditions (see **Table 1**). Besides roasted coffee beans, green coffee beans were also analyzed to take into account the possible PAH contamination of the beans, thus avoiding an overestimation of the PAH content that could be formed upon chemical reactions during the roasting step. Also, two different green coffee lots from the same origin (Cuba) were tested, as their initial PAH contents may differ. Finally, coffee brew samples were prepared from most of the ground roasted coffee samples and also analyzed to estimate PAH transfer coefficients from ground coffee to the infusion.

Effect of Temperature for Dark Roasting (20 min). The mean PAH contents estimated for the ground roasted coffee as

Table 4. Mean PAH Concentrations (with RSDs), Transfer Coefficients (Ct), and Toxicity Equivalents (TEQ) in Coffee Brews Prepared from Ground Coffees Roasted for 20 min under Different Inlet Air Temperatures[a]

	Arabica lot A									*Arabica* lot B					
	200 °C			220 °C			260 °C			240 °C			250 °C		
	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)
Phen	**0.21**	*2.64*	***11.3***	**0.42**	*2.92*	***11.5***	**0.45**	*1.06*	***10.4***	**0.26**	*20.7*	***5.7***	**0.17**	*17.24*	***1.5***
Anthr	**traces**			**traces**			**0.019**	*12.9*	***3.5***	**traces**			**traces**		
F	**0.22**	*3.15*	***17.6***	**0.16**	*12.67*	***14.7***	**0.79**	*13.2*	***18.0***	**0.27**	*0.26*	***23.0***	**0.34**	*16.01*	***11.8***
Pyr	**0.12**	*1.54*	***13.8***	**0.093**	*15.22*	***14.3***	**0.37**	*12.65*	***2.8***	**0.078**	*1.89*	***13.6***	**0.15**	*4.7*	***9.9***
B[a]A	**traces**		***5.7***	**0.014**	*18.69*	***4.0***	**0.02**	*13.65*	***0.6***	**traces**			**traces**		
Chrys	**0.048**	*20.6*	***8.7***	**0.027**	*6.40*	***5.9***	**0.087**	*10.58*	***2.7***	**0.020**	*1.7*	***5.4***	**0.021**	*2.11*	***5.5***
B[b]F	**0.14**	*20.1*	***3.5***	**traces**			**nd**			**traces**			**traces**		
B[k]F	**traces**			**traces**			**traces**			**traces**			**traces**		
B[a]P	**traces**			**traces**			**nd**			**nd**			**traces**		
DB[ah]A	**nd**			**nd**			**nd**			**nd**			**nd**		
B[ghi]P	**nd**			**nd**			**nd**			**nd**			**nd**		
Σ11 PAHs	**0.738**			**0.714**			**1.736**			**0.628**			**0.681**		
TEQ (11 PAHs)	**0.018**			**0.005**			**0.015**			**0.004**			**0.005**		

[a] nd, not detected; traces, compound detected at levels below the limit of detection of the method.

Table 5. Mean PAH Concentrations (with RSDs) and Toxicity Equivalents (TEQ) in Green Coffees as well as in Ground Coffees Roasted for 5 min under Different Inlet Air Temperatures[a]

	Arabica lot A											*Arabica* lot B					
	0 °C (green coffee)		180 °C		200 °C		220 °C		240 °C	260 °C		0 °C (green coffee)		240 °C		250 °C	
	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)	concn (μg kg^{-1})	RSD (%)
Phen	**8.89**	*9.72*	**7.36**	*8.51*	**6.05**	*1.99*	**6.51**	*14.08*	**9.26**	**8.39**	*17.14*	**4.60**	*7.59*	**4.71**	*10.84*	**11.02**	*16.53*
Anthr	**0.68**	*7.49*	**0.81**	*9.95*	**0.68**	*9.65*	**0.74**	*18.05*	**1.19**	**1.80**	*7.21*	**0.45**	*13.86*	**0.56**	*4.28*	**0.89**	*15.57*
F	**6.85**	*3.90*	**4.71**	*3.30*	**6.86**	*11.95*	**7.50**	*18.22*	**7.27**	**10.98**	*10.08*	**6.91**	*8.98*	**3.12**	*11.13*	**4.61**	*16.15*
Pyr	**3.27**	*15.14*	**3.45**	*2.49*	**3.57**	*5.57*	**3.63**	*14.91*	**4.43**	**6.60**	*15.83*	**2.63**	*5.91*	**1.28**	*3.15*	**1.83**	*25.18*
B[a]A	**0.20**	*41.52*	**0.17**	*13.71*	**0.75**	*26.33*	**nd**	*24.45*	**1.33**	**3.86**	*13.80*	**traces**		**0.40**	*16.67*	**1.06**	*5.89*
Chrys	**0.45**	*9.75*	**0.69**	*16.93*	**1.85**	*2.46*	**1.73**	*24.38*	**1.85**	**1.58**	*20.0*	**0.43**	*16.91*	**0.33**	*27.35*	**0.63**	*34.03*
B[b]F	**0.27**	*13.36*	**0.20**	*10.45*	**traces**		**0.18**	*47.06*	**nd**	**0.43**	*21.03*	**0.20**	*28.30*	**0.20**	*64.91*	**0.20**	*101.73*
B[k]F	**traces**		**traces**		**nd**		**nd**		**traces**	**0.17**	*14.85*	**traces**		**traces**		**traces**	
B[a]P	**traces**		**traces**		**traces**		**traces**		**traces**	**0.20**	*31.63*	**traces**		**traces**		**nd**	
DB[ah]A	**nd**		**nd**		**nd**		**nd**		**nd**	**0.37**	*31.65*	**nd**		**nd**		**nd**	
B[ghi]P	**nd**		**nd**		**nd**		**nd**		**nd**	**0.78**	*24.13*	**nd**		**nd**		**nd**	
Σ 11 PAHs	**20.61**		**17.39**		**19.76**		**20.29**		**25.33**	**35.16**		**15.22**		**10.60**		**20.24**	
TEQ (11 PAHs)	**0.17**		**0.14**		**0.21**		**0.16**		**0.29**	**1.24**		**0.13**		**0.12**		**0.22**	

[a] nd, not detected; traces, compound detected at levels below the limit of detection of the method.

well as the green coffee samples are presented in **Table 3**. First, it is interesting to note that the two green coffee lots considered present similar PAH contents as well as distributions, with a slightly lower phenanthrene content of lot B as compared to lot A. With regard to individual PAHs in roasted coffee samples, the most abundant compounds were phenanthrene, fluoranthene, and pyrene whatever the temperatures considered, with concentrations in the range of 3–50 μg kg^{-1}, allowing confirmation of their presence by HPLC-UV-DAD. Due its lack of sensitivity, this analytical system failed in confirming the identity of other suspected PAHs determined in the samples, which required the use of GC-MS/MS analysis. Concentrations of the three major PAHs (phenanthrene, fluoranthene, and pyrene) were found to increase with temperatures, especially at 250 and 260 °C. Significant concentrations of benzo[*a*]anthracene and chrysene were also observed for strong roasting conditions (i.e., 260 °C), with concentrations near 13 μg kg^{-1} for both compounds. Interestingly, the most highly toxic compounds, benzo[*a*]pyrene and dibenzo[*a,h*]anthracene, were either not detected or found only at very low levels under strong roasting. Indeed, the benzo[*a*]pyrene levels obtained in the roasted coffee samples (i.e., around 0.20 μg kg^{-1} at 240 and 250 °C) are in good agreement with previously published data for several roasted coffees that vary from below 0.1–0.7 μg kg^{-1} to possible levels up to 2 μg kg^{-1} in over-roasted coffees (*9, 10, 17*).

Considering the sum of the 11 PAHs in ground coffee samples, concentrations were rather constant up to 240 °C, with values in the range from 15 to 35 μg kg^{-1}. A significant increase was observed at 250 °C, which was even more pronounced under 260 °C, with respective concentrations near 75 and 115 μg kg^{-1}. These values are in agreement with our previous study, reporting values of around 60 μg kg^{-1} for commercial *Arabica* roasted coffee from Colombia (*12*). A similar trend was found for the toxicity equivalent (TEQ), with values near 0.15–0.70 μg kg^{-1}

Table 6. Mean PAH Concentrations (with RSDs), Transfer Coefficients (Ct), and Toxicity Equivalents (TEQ) in Coffee Brews Prepared from Ground Coffees Roasted for 5 min under Different Inlet Air Temperatures[a]

	Arabica lot A									*Arabica* lot B					
	200 °C			220 °C			260 °C			240 °C			250 °C		
	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)	concn (μg L^{-1})	RSD (%)	Ct (%)
Phen	**0.21**	*6.20*	***13.9***	**0.49**	*13.47*	***30.1***	**0.49**	*6.62*	***23.4***	**0.33**	*1.45*	***28.6***	**0.42**	*13.29*	***15.3***
Anthr	**traces**			**traces**			**traces**			**traces**			**traces**		
F	**0.39**	*2.36*	***22.7***	**0.44**	*2.22*	***23.5***	**0.76**	*6.37*	***27.7***	**0.17**	*1.06*	***22.6***	**0.35**	*0.24*	***30.4***
Pyr	**0.16**	*3.25*	***17.9***	**0.18**	*3.55*	***19.8***	**0.29**	*5.81*	***17.6***	**0.062**	*1.22*	***19.4***	**0.13**	*0.94*	***28.4***
B[a]A	**0.031**	*3.83*	***16.6***	**traces**			**0.15**	*2.11*	***15.5***	**0.025**	*3.09*	***24.3***	**0.082**	*5.49*	***30.9***
Chrys	**0.087**	*3.11*	***18.8***	**0.14**	*6.14*	***32.4***	**0.11**	*3.47*	***27.9***	**0.024**	*3.49*	***29.6***	**0.046**	*4.17*	***29.2***
B[b]F	**traces**			**traces**			**traces**			**traces**			**traces**		
B[k]F	**traces**			**traces**			**traces**			**traces**			**traces**		
B[a]P	**nd**			**nd**			**traces**			**nd**			**nd**		
DB[ah]A	**nd**			**nd**			**nd**			**nd**			**nd**		
B[ghi]P	**nd**			**nd**			**nd**			**nd**			**nd**		
Σ 11 PAHs	**0.878**			**1.25**			**1.80**			**0.611**			**1.03**		
TEQ (11 PAHs)	**0.01**			**0.008**			**0.027**			**0.005**			**0.014**		

[a] nd, not detected; traces, compound detected at levels below the limit of detection of the method.

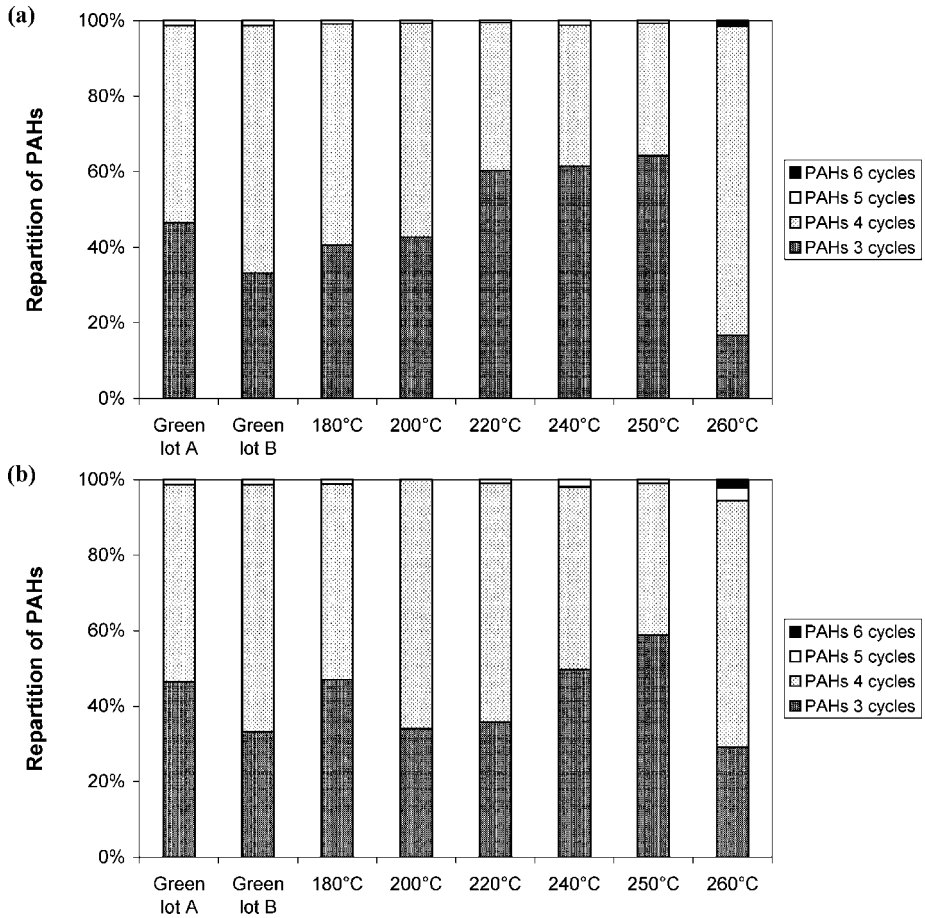

Figure 3. Repartition of the 11 PAHs analyzed in ground coffee according to the number of cycles in their molecules: (**a**) roasting for 20 min; (**b**) roasting for 5 min.

up to 240 °C, increasing to around 1.15 and 2.16 μg kg^{-1} under 250 and 260 °C, respectively, as shown in **Figure 2**.

Results for coffee brew samples are presented in **Table 4**. Similarly as for ground coffee, phenanthrene, fluoranthene, and pyrene were the main PAHs, with concentrations ranging from 0.078 to 0.79 μg L^{-1}. For the latter two compounds, an increase in brew levels was noticeable for coffee roasted under 260 °C. Chrysene was also present (0.020–0.087 μg L^{-1}), as well as benzo[*a*]anthracene at low levels. Traces of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*a*]pyrene were also observed. The TEQ values in all of the samples remained very low, in the range of 0.004–0.018 μg L^{-1}. Transfer coefficients varied greatly, between 0.6 and 23%, depending on the PAH and the coffee samples.

Effect of Temperature for Light Roasting (5 min). Under the same conditions, the two green coffee lots were roasted

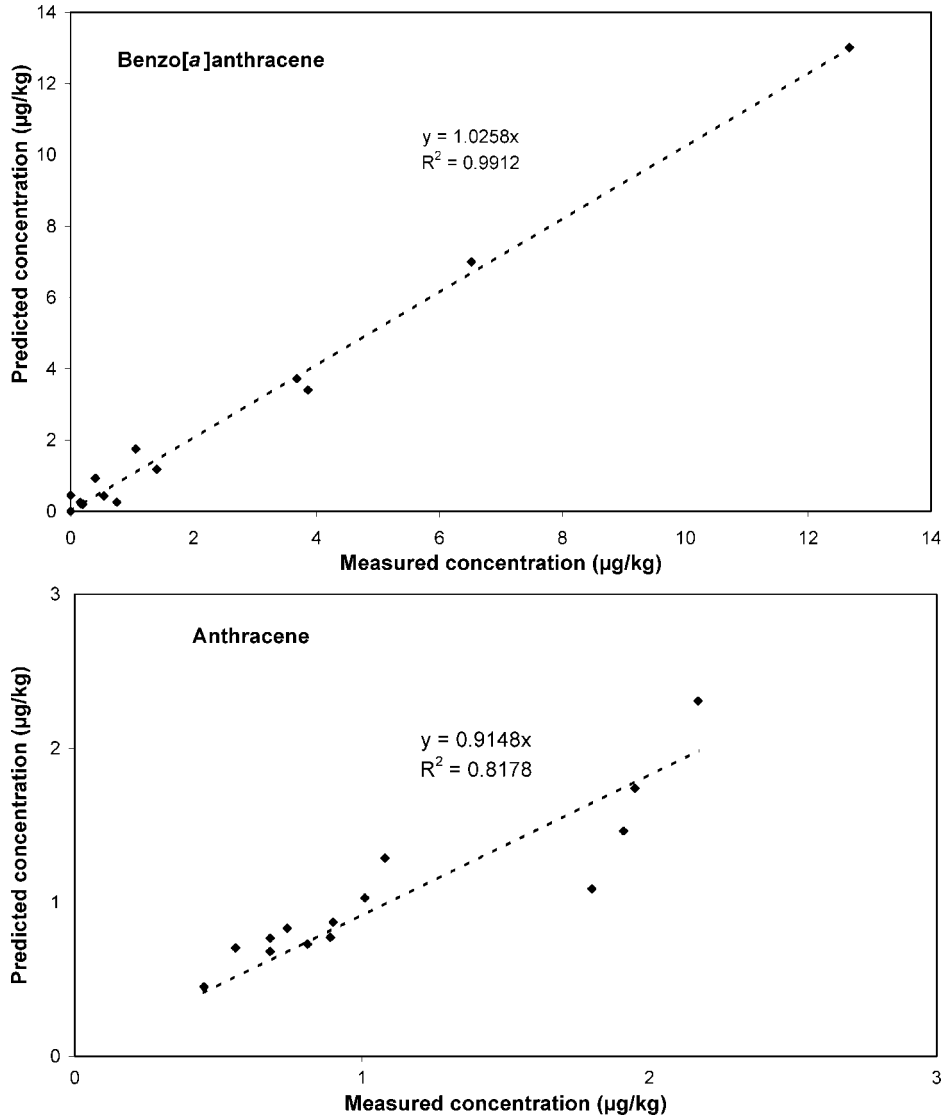

Figure 4. Comparison of measured and predicted concentrations for benzo[*a*]anthracene and anthracene in ground roasted coffee samples, using a simple kinetic model based on an overall apparent zero-order reaction rate and the Arrhenius law.

during 5 min. The PAH contents estimated for the ground coffee samples are presented in **Table 5**. The trends were similar to those previously observed, yet with a less pronounced effect due to the shorter roasting time. Hence, phenanthrene, fluoranthene, and pyrene remained the major compounds in all of the coffee samples, but with concentrations lower than under dark roasting conditions (in the range of 2–11 μg kg^{-1}). Concentration of phenanthrene faced a maximum under 250 °C, whereas fluoranthene and pyrene presented rather constant concentrations, except under 260 °C where an increase was noticed. Again, the most toxic compounds, benzo[*a*]pyrene and dibenzo[*a*,*h*]anthracene, were not detected or found at trace levels, except at 260 °C where noticeable concentrations were observed (0.20 and 0.37 μg kg^{-1}, respectively). The total mean contents for the 11 PAHs determined in ground coffees remained quite constant until 240 °C (range of 10–20 μg kg^{-1}) and then slightly increased to near 35 μg kg^{-1} under 260 °C.

PAH concentrations estimated for coffee brews are given in **Table 6**. On the whole, results were quite similar to those observed for coffee brews previously prepared from ground dark-roasted coffee samples, except that transfer coefficients were noticeably higher (13.9–32.4%).

DISCUSSION

Our results give evidence of the formation of some PAHs during strong roasting conditions, as well as the formation and subsequent decrease of other PAHs. Thus, formation of phenanthrene, anthracene, and benzo[*a*]anthracene is noticeable at temperatures above 220 °C. Whereas the content of the latter two increases at elevated temperatures, a maximum is observed for phenanthrene at 250 °C, possibly due its degradation under strong roasting conditions to form larger PAHs, such as pyrene and chrysene, the formation of which is observed only at 260 °C. Consequently, we can assume that low molecular PAHs may be formed under light-roasting conditions and then be degraded under stronger conditions, leading to high molecular PAHs. To test this assumption we considered the repartition of three-, four-, five- and six-cycle compounds among the 11 PAHs analyzed. Results are illustrated in **Figure 3**. It can be seen that compounds with four rings were dominant in green coffees as well as coffees roasted up to 200 °C, with fraction near 50–65%, followed by three-ring compounds with fraction in the range of 35–45%. In these samples, five-cycle PAHs accounted for 0–1.3%, and six-cycle compounds were not detected or present only at trace levels. Formation of three-cycle PAHs was noted when roasting under 220–250 °C for 20 min, followed by their

subsequent partial degradation at 260 °C, with simultaneous appearance of the six-cycle compound benzo[*g*,*h*,*i*]perylene at low concentration (1.71 μg kg^{-1}). Therefore, results seem to indicate possible transformation of low molecular PAHs to high molecular PAHs as the roasting degree is increased.

As for anthracene and benzo[*a*]anthracene, increasing formation was observed when the temperature was elevated for each roasting time considered, a simple kinetic model was considered for these PAHs, based on an overall apparent zero-order reaction rate:

$$[\mathrm{PAH}]^{T,t} = k^T t + [\mathrm{PAH}]_0$$

where $[\mathrm{PAH}]^{T,t}$ (μg kg^{-1}) is the content of PAH in ground coffee roasted under the temperature T for a given time t, $[\mathrm{PAH}]_0$ (μg kg^{-1}) the measured content at time zero (i.e., in green coffee), k^T (μg kg^{-1} min^{-1}) the overall kinetic rate constant at temperature T, and t the roasting time (min). According to the Arrhenius law, k^T depends on temperature as

$$k^T = k^0 \exp(-E_a/RT)$$

where E_a is the activation energy of the reaction (J mol^{-1}), R the universal gas constant (8.3145 J mol^{-1} K^{-1}), T the temperature (K), and k^0 a constant.

On the basis of our data, apparent activation energies were estimated as 140.4 and 53.8 kJ mol^{-1} for benzo[*a*]anthracene and anthracene, respectively. Using this simple kinetic model, satisfactory correlations between predicted and measured concentrations in ground roasted coffee samples could be obtained for these two PAHs, especially benzo[*a*]anthracene as shown in **Figure 4**. However, this simple model was not able to predict the complex behavior of the other compounds. In the near future we intend to study in detail the effect of roasting time on PAH content of coffee beans, with a view of better modeling the formation of some PAHs during the roasting step. Besides, further experiments should be conducted on model compounds that are possible precursors of PAHs in coffee beans, to better understand the chemical reactions responsible for the PAH formation during the roasting process of coffee. Hence, chlorogenic acid is considered as a possible precursor, because a previous study reported the formation of PAHs during the pyrolysis of chlorogenic acid, even at moderate temperatures (i.e., 250 °C) (*18*). Trigonelline is also suspected, as its roasting has been reported to form unknown compounds with mutagenic activity (*2*). However, other coffee components may lead to PAH formation upon strong heating, such as lipids, amino acids, carbohydrates, and sterols. Consequently, PAH formation is expected to proceed through several complex pathways in coffee beans.

With regard to the PAH contents of coffee brews prepared from these several roasted coffee samples, they remained very low, which was expected due to the hydrophobic character of PAHs. The observed transfer coefficients were variable, and no correlation could be drawn with either the water solubility, the octanol–water partition coefficient, or the roasting temperature. However, the slightly lower values observed for ground dark-roasted coffees may be explained by the formation of oil droplets in such samples, with a subsequently lower PAH extractability during the brewing process as recently observed for heterocyclic amines in coffee (*19*).

In conclusion, phenanthrene, fluoranthene, and pyrene were the major PAHs in the *Arabica* coffee samples analyzed in this study. Even though theey were present in green coffee beans, their contents increased during the roasting process under elevated temperatures (250–260 °C), up to 15–50 μg kg^{-1}. Strong roasting conditions led to significant levels of chrysene and benzo[*a*]anthracene (near 13 μg kg^{-1}), whereas low levels of anthracene, benzo[*b*]fluoranthene, and benzo[*a*]pyrene were also noted in several samples. In the case of anthracene and benzo[*a*]anthracene, a simple kinetic model was proposed with satisfactory correlations between measured and predicted concentrations in ground roasted coffee samples. Transfer coefficients to the infusion always remained below 35% for all of these compounds whatever the roasting conditions, leading to low values of the toxicity equivalent in coffee brews.

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