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Occurrence of Acrylamide in Coffee

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ABSTRACT

Acrylamide is incompatible with acids, bases, oxidizing agents, iron, and iron salts. Researchers know there is relationship between dietary intake of acrylamide and the risk of developing cancer and in large amounts can cause cancer and reproductive problems. AA is a chemical compound that forms naturally in a wide variety of foods when they are cooked, including coffee, chocolate, almonds, french fries, crackers, potato chips, cereal, bread and even some fruits and vegetables. Estimates for the proportion in the diet coming from the consumption of coffee range from twenty to forty percent; however roasted coffee also contains a range of anti-cancer compounds and antioxidants. Most acrylamide are accumulated during the final stages of baking, grilling or frying processes as the moisture content of the food falls and the surface temperature rises (120 °C or higher), with the exception of coffee where levels fall considerably at later stages of the roasting process. Therefore, the degree of roasting will be a key factor in acrylamide content, with light roasted coffee attaining significantly higher amounts when compared with dark roasted counterparts. In a general way, acrylamide levels in ground coffee (both Arabica and robusta) significantly decreased with increased roasting period and very high levels of acrylamide were detected in the lightest roasted coffee.
Keywords: *Arabica, Espresso, Roasting, Robusta, Temperature*

INTRODUCTION

Acrylamide*(AA)* is a chemical compound that forms naturally in a wide variety of foods when they are cooked, including coffee, chocolate, almonds, french fries, crackers, potato chips, cereal, bread and even some fruits and vegetables. Importantly, it presents experimental results generated under laboratory model conditions, as well as under actual food processing conditions in high levels in fried, baked, grilled, toasted or microwaved carbohydrate-rich foods covering different food categories(Granby and Fagt, 2004). Most acrylamide are accumulated during the final stages of baking, grilling or frying processes as the moisture content of the food falls and the surface temperature rises (120 °C or higher), with the exception of coffee where levels fall considerably at later stages of the roasting process. Coffee roasting process takes place at quite high temperatures and induces several visible changes in color, texture, density and size (Oliveira *et al.*, 2005). Coffee roasting has divided into three phases (Kristina, 2011). The initial is a drying phase when the moisture is eliminated from the coffee beans, keeping the bean temperature at around 100^0C. This phase lasts only a few seconds since the green coffee beans contain no more than 12 % of humidity. The second phase is the actual roasting step. In this phase at~170^0C complex exothermic pyrolytic reactions take place. Large quantities of CO2, water and volatile substances are released. Sugar and minor lipid degradation reactions also take place at the temperatures close to 180-200^0C. Also the beans lose up to 8 % in dry weight, mainly because of the loss in sugars taking place in the Maillard reaction and pyrolysis (Oosterveld *et al.*, 2003). The third phase is the cooling phase. The beans are rapidly cooled using cold air or water as a cooling agent. Due to the use of roasted coffee beans in making coffee, the probability of significant levels of acrylamide being present was considered to be high and the chemistry of coffee roasting is complex (Şenyuva and Gökmen, 2005). Acrylamide formation starts rapidly at the beginning of the roasting process and it decreases shortly after reaching a maximum level, probably due to physical and chemical losses (Bagdonaite *et al.*, 2008). Therefore, the degree of roasting will be a key factor in acrylamide content, with light roasted coffee attaining significantly higher amounts when compared with dark roasted counterparts

(Bagdonaite *et al.,* 2008). Moreover, when comparing the two coffee species of higher economical importance, namely Coffeaarabica and Coffeacanephora increased levels of acrylamide are described for the latter (Bagdonaite *et al.,* 2008). As a result, the reported levels for roasted coffee beans vary widely, usually within the range of 35-540 µg/kg of coffee (Summa *et al.,* 2007).

Acrylamide is highly soluble in water and, thus, easily transferred from the coffee powder to the beverage (brew) (Andrzejewski *et al.,* 2004). The chemical composition of coffee brew is highly dependent on several factors, including the amount of coffee used to prepare the blend, their degree of roasting, as well as the coffee/water ratio used, which depends on cultural and personal preferences (Alves *et al.,*2007). Among all coffee brews, espresso is highly appreciated in Europe, and its consumption is increasing worldwide. This brew is prepared by a special brewing technique in which a limited amount (20-50 mL) of hot water under high pressure (9 ± 2 atm, 90 ± 5 ^{0}C) is percolated in a very short time (30 ± 5 s) through a ground coffee cake (6.5 ± 1.5 g). The result is a concentrated and intensely flavored brew covered by a dense foam layer, which should be tasted at the exact moment of extraction (Alves *et al.,* 2007). It was observed, that coffee beverages show some antioxidant properties (Borrelli *et al.,* 2004).

Formation of Acrylamide

sparagine is an amino acid which is a building block of proteins, found in many vegetables, with higher concentrations in different types of potatoes. Acrylamide (Fig 1) is the result of a thermal Maillard pathway(Mottram *et al.,* 2002). The formation of acrylamide results from reactions between *asparagine* (a hydrophilic amino acid) and *reducing sugars* (glucose and fructose) as on (Fig 2). The carbon backbone and amide nitrogen of acrylamide originate from asparagine was provided by the use of stable isotope- labeled asparagine (Zyzak *et al.,* 2003). The Maillard pathway leading from asparagine to acrylamide is complex and may involve very different intermediates. *Acrolein*and its oxidized product *acrylic acid* react with ammonia to produce acrylamide (Becalski *et al.,* 2003). In certain conditions, acrolein together with asparagines may lead to the formation of acrylamide (Yasuhara *et al.,* 2003).

Fig1. *Acrylamide structure*

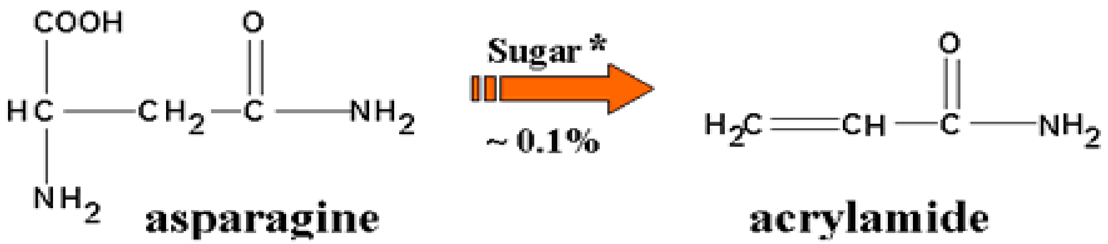


Fig2. *Formation of acrylamide*

Acrylamide Occurrence in Coffee

Performance of Method for Acrylamide

A total of 1 g of coffee was weighed into a 10 ml centrifuge tube and the sample was spiked with acrylamide (50, 100, 250 and 500 ng/ g of acrylamide, and 50 and 100 n/g of 13 C3-labelled acrylamide) to determine the percentage recovery of the method at this stage. The sample was suspended in 5ml of methanol and extracted for 2min in a vortex mixer. The suspension was centrifuged at 5000 rpm for 10 min. Since acrylamide is highly soluble in water (215.5 g/100ml), the sample preparation was usually started by extracting the food samples with water enough for a proper swelling in most of the methods based on liquid chromatography (LC) coupled to tandem mass spectrometric (MS) detection system (*Roach et al.,* 2003). The initial attempts of analysing coffee samples for acrylamide which started with extraction with water resulted in undesirable results during LC-MS analyses due to interfering co-extractives. Co-detection of acrylamide and interferences in coffee extract was confirmed by analysing the purity of co-eluted peaks in scan mode. Number of peaks were observed both before and after the acrylamide peak in the ion profiles monitored for coffee extracts during LCMS- MS analysis, despite two solid-phase extraction(SPE) cartridges clean-up steps (Andrzejewski *et al.*, 2004). The significant loss of the analyte and ion suppression effect leading to a low response of acrylamide were also encountered after a two-step extract clean-up approach with Isolute Multimode and cation-exchange cartridges for coffee (Delatour *et al.*, 2004). The recovery of acrylamide was determined by analysing each of the spiked samples four times for levels ranging from 50-500 ng/g. Recovery samples were prepared by spiking ground filter coffee containing an acrylamide level of 49.0±1.0 ng/g (Şenyuva and Gökmen, 2005). The mean percentage recoveries exceeded 99% for all spiking levels for coffee (Table 1).

Table1. *Percentage recoveries of acrylamide from ground filter coffee for different spiking*

Spiking level, ng/g	Recovery, %	
	AA	
50	98.8	
100	100.0	
250	100.0	
500	101.5	

Source: Şenyuva and Gökmen, 2005

Effect of Roasting on Concentration of Acrylamide

Influence of Degree of Roasting

When coffee beans are subjected to the high temperatures of roasting, innumerous chemical reactions occur as well as physical modifications that might influence the extraction of some compounds to the brew (Illy and Viani, 2005). In order to observe the influence of the degree of roasting on the acrylamide content and extractability, four green coffee samples (two arabicas, Brazil and Honduras, and two robustas, Uganda and Ivory Coast) were roasted at three different roasting degrees [(8-11 min, 210^{0}C), (light, medium and dark)]. Organic roast loss and colors achieved are summarized in Table 2, together with the results for acrylamide. The total acrylamide content was calculated for 6.5 g of ground coffee and the acrylamide extractability obtained by the following formula: espresso content/cake content x 100. In a general way, acrylamide levels in ground coffee (both Arabica and robusta) significantly decreased ($p < 0.05$) with increased roasting period, for each individual sample. In fact, very high levels of acrylamide were detected in the lightest roasted coffee samples, with maximum of 1240 and 2190 µg/kg, for Arabica and Robusta, respectively (Alves *et al.*, 2009). Taeymans *et al.*(2004) reported that levels of about 2000 µg/kg were observed at the early stages in the process of coffee beans roasting. Moreover, the amount present in dark roasts (Table 2) corresponds only to 15% and 23% of that present in light roasts, for Arabica and Robusta, respectively. Therefore, considering all the samples together, mean loss of about 80% occurred from the light roast to the dark one. Taeymans *et al.*(2004), based on experiments with isotope-labelled acrylamide, reported that more than 95% of the total acrylamide generated by roasting is further degraded during the process and is no longer found in the final product. Comparing the two coffee species analyzed (Table 2), the average acrylamide contents of the compound were always significantly higher ($p < 0.05$) for robusta ground coffee, in all roasting stages.

Table2. *Acrylamide contents and extractability in espresso coffees at different roast degrees*

Sample	Roast degree	ORL (%)	Color	Ground coffee (µg /kg)	µg /L	µg/EC (30 mL)	Extraction (%)
Arabica				Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.
Brazil	Light	7	200	782.78 ± 33.71 a	135.6 ± 5.7 a	4.07 ± 0.17 a	79.9 ± 0.1 a
	Medium	10	138	183.37 ± 8.35 b	32.8 ± 0.3 b	0.99 ± 0.01 b	82.7 ± 2.9 a
	Dark	13	119	131.79 ± 5.75 c	22.8 ± 1.3 c	0.68 ± 0.04 c	79.7 ± 1.1 a
Honduras	Light	6	200	1243.14 ± 67.34 a	216.0 ± 11.0 a	6.48 ± 0.33 a	80.2 ± 0.3 a
	Medium	9	130	279.26 ± 4.09 b	50.8 ± 1.2 b	1.52 ± 0.04 b	84.0 ± 3.3 a

	Dark	12	112	185.54 ± 1.24 c	33.8 ± 0.5 c	1.01 ± 0.01 c	84.1 ± 1.7 a
Robusta							
Uganda	Light	7	200	1384.50 ± 69.02 a	236.6 ± 0.5 a	7.10 ± 0.01 a	79.0 ± 3.8 a
	Medium	11	122	454.85 ± 2.67 b	73.5 ± 1.4 b	2.20 ± 0.04 b	74.6 ± 1.0 a
	Dark	13	97	383.46 ± 18.93 c	68.5 ± 2.1 b	2.05 ± 0.06 b	82.6 ± 6.5 a
Ivory Coast	Light	6	200	2191.18 ± 20.37 a	390.0 ± 16.6 a	11.70 ± 0.50 a	82.1 ± 4.3 a
	Medium	10	131	564.06 ± 25.05 b	97.3 ± 3.9 b	2.92 ± 0.12 b	79.6 ± 0.3 a
	Dark	13	110	441.91 ± 6.44 c	72.8 ± 1.7 c	2.18 ± 0.05 c	76.0 ± 0.6 a

ORL, organic roast loss; EC, espresso coffee; SD., standard deviation

Data followed by different letters within each column, for each geographical origin, are significantly different according to Student's t-tests at $p < 0.05$.

Source: *Alves et al., 2009*

The results obtained for espresso coffees follow a similar profile (Table 2): significant decreases ($p < 0.05$) of acrylamide were observed during roasting; pure robusta espressos contained approximately double amounts of acrylamide of arabica, for all degrees of roasting; and mean decreases of 30% and 20%, for arabica and robusta, respectively, were found when comparing medium roasted ECs with dark roasted counterparts (Alves *et al., 2009*). Thus, ECs prepared from dark roasted commercial blends might have about 25% less acrylamide than medium roasted brews. Concerning the extraction efficacy of acrylamide, no significant differences ($p > 0.05$) were found between different degrees of roasting in each sample analysed. Also, no differences ($p > 0.05$) existed when arabica and robusta groups were compared. Therefore, although coffee species and degree of roasting influence the acrylamide content of the brew they do not affect acrylamide extractability (mean extraction of 80%, in a standard espresso of 30 mL).

Coffee Roasting in a Laboratory Roaster on Acrylamide

Four different types of coffee were used for roasting in a laboratory roaster experiment to observe the acrylamide amount. The coffee types were collected from Cameroon Robusta, Santos Brazil Arabica, Colombian Excelso Arabica and Uganda Organico Biocoffee Arabica. Cameroon Robusta and Santos Brazil Arabica were roasted for 360s, 450s, 720s and 870 at temperature of 250^{0}C. Both Colombian Excelso and Uganda Organico Biocoffee were roasted for 450 second of 80 g of each coffee green bean was taken to the laboratory roaster. Formation of acrylamide in 4 different types of coffee roasted in a laboratory roaster roasting 450s is usually used for common drinking coffee. During roasting the coffee the temperature in a laboratory roaster is high, but normally not above 250^{0}c. There was significant difference of acrylamide concentration in different coffee beans roasted in a laboratory roaster. Cameroon Robusta showed a significantly larger amount of acrylamide formed during roasting (Kristina, 2011) while in other types of coffee beans of Arabica, both washed and unwashed concentration of acrylamide detected was 7.6 (Santos Brazil) to 10.5 (Colombian Excelso) times less. Furthermore, Cameroon Robusta coffee beans roasted 360 and720 second had a higher acrylamide concentration compared to Santos Brazil (Kristina, 2011).

Coffee Heated in a Thermostatic Oven

Cameroon Robusta coffee beans were used for thermostatic oven heating and 10.0 g of beans were roasted in an oven at 180, 200, 220^{0}C for 1, 3 and 5 minutes and at 220, 240, 260^{0}C for 5, 10 or 15 minutes. The glass dishes were preheated in an oven for 10 minutes before roasting of the coffee. After roasting the samples were immediately put on ice for 15 minutes. The cooled coffee was ground in a coffee grinder and the samples were prepared for ion exclusion with UV detection chromatographic analysis. The highest concentration of acrylamide in beans was detected roasted at 240^{0}C for 5 minutes (Table 3). Also in coffee beans, roasted at 220 and 260^{0}C for 5 minutes higher amounts of acrylamide detected than in those roasted at 10 or 15 minutes. With the increase of roasting time the acrylamide decrease at all temperatures (Kristina, 2011). Acrylamide is formed in coffee beans heated at temperatures between 220 and 260. The largest acrylamide amount forms during the first five minutes and lower temperature (220). Heating at higher temperatures and for longer (5, 10 minutes) time acrylamide concentration in the coffee beans is decreasing. The acrylamide formation and elimination processes are faster at higher temperatures than at lower ones (Kristina, 2011).

Table3. *AA in Cameroon Robusta, heated in thermostatic oven, ng/g. for 5, 10 and 15 minute*

Temperature	Time, min		
	5	10	15
220	463	250	0
	488	158	0
240		191	
		107	
		110	
260	239	0	0

Source: *Kristina, 2011*

When coffee beans were roasted at temperature of 180, 200 and 220^{0}C for 1, 3 and 5 minutes (Table 4) the highest acrylamide amount was detected in beans, heated to 220^{0}C for 5 minutes. With the increase of the roasting time at all temperatures (180, 200, 220) there was an increase of acrylamide formation. At higher temperatures (220^{0}C) this increase was more rapid. It was observed the acrylamide increase in the samples, roasted for longer time. It seems that the highest acrylamide amount forms in the first 5 minutes of coffee roasting and later it decreases (Kristina, 2011). It seems that acrylamide is formed in coffee during the first 5 heating minutes. The higher the temperature and the longer the time of the roasting process, the faster acrylamide degradation can be observed in the coffee (Kristina, 2011). The acrylamide formation and elimination processes are faster at higher temperatures than at lower ones. Both time and temperature have significant for the formation of acrylamide (Kristina, 2011).

Table4. *Acrylamide in Cameroon Robusta, heated in thermostatic oven, ng/g.1, 2 and 3 minute*

Temperature	Time, min		
	1	3	5
180	31.5	28.5	39.7
200	n.d.	41.7	42.9
220	29.4	40.2	122

n.d. = not detected

Source: *Kristina, 2011*

Standard Coffee Roasting Condition

The analyzed 19 coffees from different parts of the world, roasted under standard roasting conditions (240^{0}C for 7 minutes), shows significant difference between Robusta and Arabica coffees (Table 5). The results showed no big difference in acrylamide amount formed in Arabica coffees, whereas acrylamide amounts in Robusta coffees were higher than in all tested Arabica's. The growth area of coffee beans did not have a significant influence in acrylamide formation (Kristina, 2011). Coffee beans from Asia had lower acrylamide amounts in dry-processed and semi-washed beans, whereas washed Arabica beans and especially monsooned ones had higher acrylamide amounts. Indonesian coffees had similar acrylamide content, even if coffees were processed by different methods. Also in Robusta dry-processed coffee beans had lower acrylamide amount than in washed ones.

Table5. *Coffee roasted under standard conditions*

Coffee	AA, ng/g
Robusta Indian Parchment	653
Robusta Vietnam	762
Indian MonsoonedAspinwalls Malabar AA	575
Indian Plantation A	401
Indonesian Sumatra Lintong	301
Indonesian Sulawesi Kalossi	306
Tanzania Arabica	354
Ethiopian SidamoYirgamo Grade 2	425
Zambia AA	331
Kenya washed	531

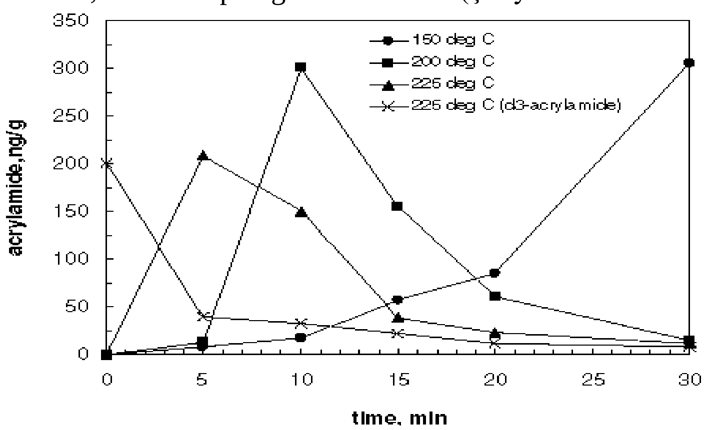
Kenya A/A	299
Nicaragua Talia Extra	433
Guatemala SHB	374
Mexico Maragogype	363
Mexico Altura	380
Costa Rica Tarazzu	310
Honduras	307
Papua New Guinea Sigri C	352
Java WIB1 Jampit Gr1	357

Source: *Kristina, 2011*

Neither place of origin nor processing method has significant influence on the acrylamide formation. The medium roasted coffee has the highest amount of acrylamide and it can be reduced by roasting the coffee beans to a darker color, allowing the coffee to roast for longer time. After the extraction, clean-up and analysis methods were established, the following could be concluded. Arabica and Robusta coffee beans differ in acrylamide amounts formed. Coffee roasted in a laboratory roaster to common degrees for consumer, as well as in the thermostatic oven under standard roasting conditions Robusta showed to have the highest amounts of acrylamide (Kristina, 2011). It seems that asparagine is a limiting factor for acrylamide formation in coffee, because Robusta coffees also contain higher amounts of asparagine than Arabica's. Highest AA in coffee is formed at the very beginning of roasting process. After five minutes of roasting at temperatures higher than 220^{0}C the amount of acrylamide is decreasing with increasing the roasting time. Furthermore, AA forms in lower amounts at higher temperatures because of the faster elimination process(Kristina, 2011). However, acrylamide formation is connected to a heating temperature value: the higher the heating temperature, the shorter time is needed to achieve a maximum acrylamide concentration in the mixture. Furthermore, in the asparagine and glucose mixtures both 3-aminopropionamide and acrylamide can be formed already in the mixtures heated to 130 (Kristina, 2011).

Effect of Heat Treatment on Acrylamide and Colour

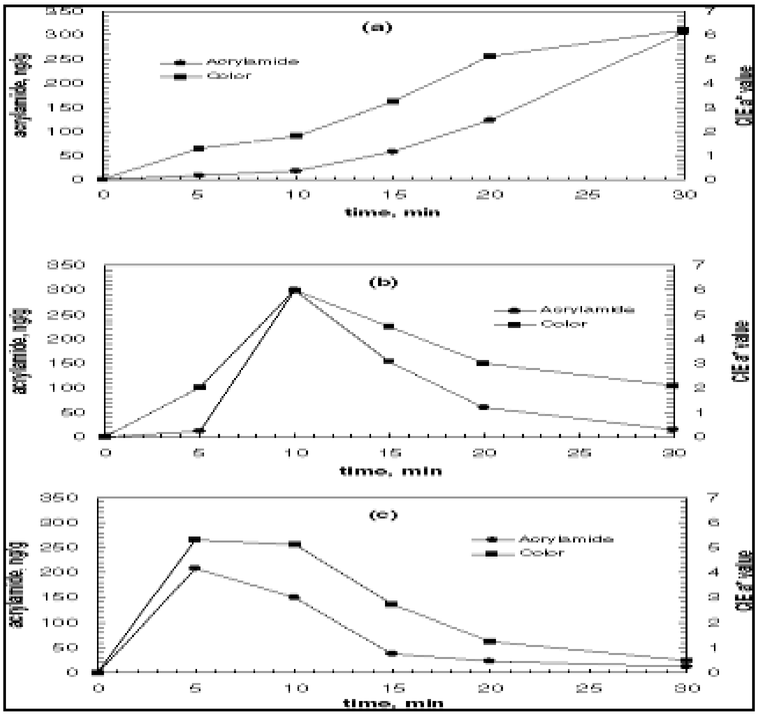
In order to determine the effects of heating on the amounts of acrylamide in relation to colour green coffee was roasted at three temperatures of 150, 200 and 225^{0}C for up to 30min. The amount of acrylamide measured increased rapidly at the onset of roasting, reaching an apparent maximum, and then decreasing exponentially as the rate of degradation exceeded the rate of formation at 200 and 225^{0}C. However, the amount of acrylamide measured continued to increase during roasting at 150^{0}C. As shown in figure 3, experiments with deuterium labeled acrylamide spiked to green coffee prior to roasting confirmed the exponential degradation during heating at 225^{0}C. The acrylamide level was reduced by a factor of approximately 20 at the end of 30 min of roasting at 200 and 225^{0}C, compared to the highest level recorded. As noted by other findings (Taeymans *et al.*, 2004), the results obtained in this study also revealed that the darker coloured coffee may contain much lower amounts of acrylamide than light coloured coffee (Şenyuva and Gökmen, 2005).



Source: *Şenyuva and Gökmen, 2005*

Fig3. *Acrylamide formation during roasting of green coffee at different temperatures*

Based on CIE (Commission Internationale de l'Eclairage) colour space, L* indicates lightness and a* and b* indicate color directions. +a* and -a* are the red and the green directions, + b* and -b* are the yellow and the blue directions, respectively. Changes in the CIE L*a*b* colour values of coffee were also monitored during roasting. Although CIE L* and b* values decreased exponentially with time, CIE a* values measured increased rapidly at the onset of roasting, reaching an apparent maximum, and then decreasing exponentially at 200 and 225^{0}C, but reached to a maximum with continuous increase at 150^{0}C. The changes in the amounts of acrylamide and CIE a* values followed almost the same pattern, as shown in figure 4.



Source: *Şenyuva and Gökmen, 2005*

Fig4. *Changes in the amount of acrylamide and CIE a* value in coffee during heating at (a) 150°C, (b) 200°C, (c) 225°C.*

These results recommend that there is a significant correlation between the amount of acrylamide and the CIE a* value of roasted coffee (Şenyuva and Gökmen, 2005). Since similar correlations were obtained between the amount of acrylamide and CIE a* value during roasting at all temperatures studied, it was concluded that the correlation between acrylamide and CIE a* value is independent of temperature. Acrylamide concentrations of a variety of roasted coffee samples were determined roughly using this function. The difference between the predicted and measured acrylamide concentrations was ranged from 1-59% for roasted coffees of different origin, as well as for a commercial gold type instant coffee (Table 6).

Table6. *Measured and predicted AA in ground roasted coffee by logarithmic correlation model*

Roasted coffee	Measured		Predicted	
	AA, ng/g	CIE a* colour	AA, ng/g	Difference, %
Mexico	18	2.22	24	33
Irish coffee	14	2.20	22	59
Tanzanian peaberry	15	2.17	23	54
Colombian supremo	22	2.11	22	1
Guatemala	18	2.30	25	40
Colombian decaf	15	2.14	22	50
Indonesian sumatra	28	2.59	31	10
Ethiopian mocha	21	2.48	29	36
Jacobs monarch	338	5.94	318	6

Source: *Şenyuva and Gökmen, 2005*

Acrylamide in Commercial Coffee Samples

A total of 20 coffee samples from four groups were analysed for their acrylamide contents. Samples were randomly selected from coffee shops and supermarkets, therefore, may not representative of coffee supply. This is to stress that results cannot provide guidance in consumers' choice between different products and brands within certain coffee types. The results are a general guide to acrylamide concentrations in a selected segment of coffee supply. The acrylamide level was an average of 19 ng/g in roasted ground coffee different origins. The acrylamide levels of Turkish type coffee was slightly higher and averaged as 46 ng/g. Gold type instant coffees were found to contain significantly higher amounts of acrylamide (Table 7). Andrzejewski *et al.*(2004) have reported the average acrylamide levels ranging from 45 to 374ng/g in 31 ground coffee types.

Table7. *AA level of commercial coffee samples*

Coffee sample	AA, ng/g
Turkish coffees (n=5)	29-75
Filter coffee (n=1)	50
Instant coffees (n=3)	42-338
Roasted ground coffees (n=11)	
Irish coffee	14
Mexico	18
Costa Rica S.H.B.	29
Tanzanian peaberry	15
Colombian supremo	22
Colombian decaffeinated	15
Guatemala	18
Yemen mocha	12
Indonesian sumatra	28
Ethiopian mocha	21
Kenya	18

Source: *Şenyuva and Gökmen, 2005*

Effect of Caffeinated and Decaffeinated Coffee Samples on Amount of Acrylamide

The acrylamide contents of caffeinated Espresso coffee (30 mL), prepared from commercial coffee blends, were highly variable, as can be observed in Table 8. The results are in accordance with those previously reported for standard espressos: 10.7-48.7 μg/L (Soares *et al.*, 2006). Although average levels obtained for decaffeinated ECs were lower, when compared with caffeinated samples (Table 8), the differences between both groups were not statistically significant ($p > 0.05$), suggesting that decaffeination process does not significantly affect acrylamide precursors in green coffee beans (Alves *et al.*, 2009).

Table8. *AA in caffeinated and decaffeinated espresso coffee*

Commercial samples	μg /L	μg /EC (30 mL)
	Mean	Mean
Caffeinated	41.9 a	1.26 a
Decaffeinated	33.2 a	1.00 a
Servings*	42.3 a	1.27 a

*EC, espresso coffee; *, caffeinated samples; Data followed by the same letters within each column are not significantly different according to ANOVA ($p > 0.05$)*

Source: *Alves et al., 2009*

Servings are individual doses of ground coffee (about 6-7 g) coated with a paper layer, commercially available and produced to make an EC in a rapid, simple, and clean way, in adapted machines. No significant differences ($p > 0.05$) were found when comparing the espressos prepared from servings with regular and decaffeinated ECs (Alves *et al., 2009*). The great variability found in samples tested (Table 8), with some espressos containing twice the acrylamide amount than others, can be justified by consideration of several factors.

Influence of Coffee Species on Amount of Acrylamide

The influence of each coffee species (Arabica and Robusta) on the acrylamide content of EC were shown on Table 9. Samples were medium roasted (210^{0}C, 10 min), by a standard procedure, the organic roast loss was different within each species, as a consequence of the beans intrinsic characteristics. Significantly higher amounts ($p < 0.001$) of acrylamide were found in Robusta samples, with levels per cup (30 mL) ranging between 1.71 and 2.92 µg and Arabica coffee, the levels were half lower, varying from 0.87 and 1.52 µg/EC (Alves *et al.*, 2009). Lantz *et al.*(2006) reported average levels of 378 and 251µg/kg, for Robusta and Arabica medium roasted coffees, respectively. This difference associated with an increased content of asparagine amount in Robusta raw beans (Bagdonaite *et al.*, 2008), in comparison with Arabica beans. Arabica and Robusta coffees, the two main species used to prepare brews, have different chemical and sensory properties. The quality of the beverage is usually dependent on the proportion of both in the blend, Arabica being considered a higher value product. Table 9 indicates the minimum and maximum levels of acrylamide that can be found in EC prepared with medium roasted coffee beans. Although subjected to a different postharvest treatment, no significant ($p > 0.05$) differences were found between the dry-processed sample from Brazil and other wet-processed Arabicas (Alves *et al.*, 2009).

Table9. *Acrylamide contents in espresso coffees of medium roasted beans*

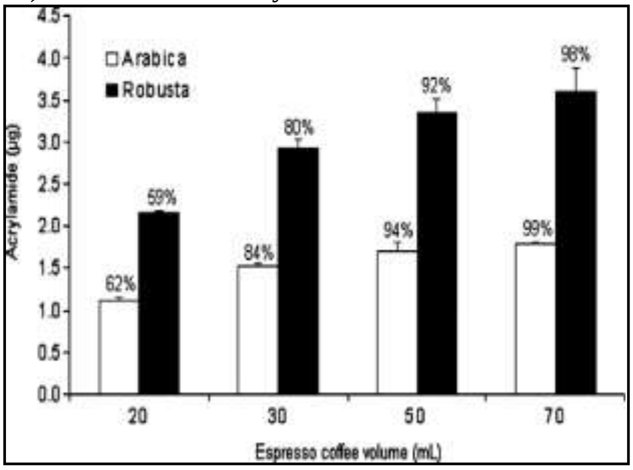
Coffee species	Geographical origin	% ORL	Color	µg/L Mean ± S.D.	µg /EC(30 mL) Mean ± S.D.
	Hawaii	5	132	29.1 ± 0.8	0.87 ± 0.02
	Costa Rica	11	127	38.0 ± 0.3	1.14 ± 0.01
	Jamaica	11	126	33.3 ± 0.2	1.00 ± 0.01
	Colombia	7	122	32.7 ± 0.2	0.98 ± 0.01
Arabica	Ethiopia	12	128	44.6 ± 1.5	1.34 ± 0.04
	Honduras (1)	9	123	49.4 ± 0.5	1.48 ± 0.01
	Honduras (2)	9	130	50.8 ± 1.2	1.52 ± 0.04
	Brazil	10	138	32.8 ± 0.3	0.99 ± 0.01
	Total mean (n = 8)	9	128	38.8 ± 8.4 a	1.16 ± 0.25 a
	India (1)	10	118	56.9 ± 1.4	1.71 ± 0.04
	India (2)	11	133	84.1 ± 3.4	2.52 ± 0.10
	Uganda (1)	9	122	75.5 ± 0.8	2.27 ± 0.02
	Uganda (2)	11	122	73.5 ± 1.4	2.20 ± 0.04
Robusta	Cameroon (1)	16	124	80.5 ± 1.5	2.41 ± 0.05
	Cameroon (2)	12	132	89.4 ± 3.7	2.68 ± 0.11
	Ivory Coast	10	131	97.3 ± 3.9	2.92 ± 0.12
	Indonesia	9	125	58.0 ± 0.2	1.74 ± 0.01
	Total mean (n = 8)	11	126	76.9 ± 14.2 b	2.31 ± 0.43 b

ORL, organic roast loss; EC, espresso coffee; S.D., standard deviation; Data followed by different letters within each column are significantly different according to ANOVA at $p < 0.001$.

Source: *Alves et al., 2009*

Influence of Espresso Coffee Volume on Amount of Acrylamide

Espresso coffee (EC) brewing is incompletely extracts acrylamide from ground coffee, unlike other coffee brews due to the short contact time with water (Lantz *et al.*, 2006). Therefore it is interest to see the technological parameters affecting acrylamide extraction into the espresso brew. Mean EC volume, usually consumed, is around 30-40 m L. Percolation was described by Lantz *et al.*(2006) as the only brewing procedure that incompletely extracted acrylamide from ground coffee when compared with other coffee brews, due to the short contact time between coffee and water. In order to study the influence of the water volume on the amount of acrylamide of espresso, two coffee samples (one Arabica and one Robusta) were used to prepare ECs of different lengths (20, 30, 50 and 70 mL). Arabica cake under test (6.5 g) contained 1.82 ± 0.03 µg of acrylamide, while Robusta contained 3.67 ± 0.03 µg (Fig. 5). Behavior of acrylamide extraction was very similar in both coffee species, showing that an increase in the water volume that percolates through the coffee cake is responsible for a higher extraction of the compound. The extraction percentage variation according to the brew volume was also very similar: from 59% to98%, for robusta, and from 62% to 99%, for arabica. The final content of acrylamide increases with volume (Fig. 5), brew concentration (ng/mL) simultaneously decreases, as expected, due to reduction in coffee/water ratio: from 108.2 ± 1.5 to 50.1 ± 3.9 µg/L, for Robusta ECs, and from 56.3 ± 1.3 to 24.2 ± 0.3 µg/L, for arabica.



Source: *Alves et al., 2009*

Fig5. *Influence of volume on espresso coffee acrylamide content; Percentages on each bar represent acrylamide extractability*

Comparisono of Espresso Coffee with Other Coffee Brews on Amount of Acrylamide

The highly water-soluble AA is easily extracted from the ground coffee to liquid phase of the beverage (Andrzejewski *et al.,* 2004). Some studies reporting acrylamide levels in common coffee beverages (as plunger pot and filtered coffee) have already been published, reporting values between 2 and 25 µg/L. The acrylamide concentrations reported in this study, for standard espressos (30 mL), are higher than those reported by other authors for other coffee brews. Indeed, considering all caffeinated samples the mean acrylamide concentration was 40 ± 9 µg/L. Moreover, acrylamide levels of medium roasted ECs could vary between 38 ± 8 and 77 ± 14 µg/L, when Robusta percentage in blend ranges from 0% to 100%, respectively. These high concentrations (compared with other beverages) depend essentially on the coffee/water ratio used to prepare the brew, factor that varies with consumers' preferences and geographical habits: 20 g/L in USA (Andrzejewski *et al.,* 2004) and 40 g/L in Northern Europe (Granby and Fagt, 2004), while in Portuguese espressos may range from 325 (''ristretto") to 93 g/L (''lungo") (Alves *et al.,* 2007). Considering the final acrylamide content per cup, it will obviously depend on the ingested amount of beverage. While EC is, generally, a very short beverage, higher volumes per cup of other coffee beverages are usually consumed. For example, a cup of filter coffee may achieve 200 mL, because it is considered a light brew (Alves *et al.*, 2007).

Method of Coffee Product Preparation on Amount of Acrylamide

Randomly selected 26 coffee samples products were collected from supermarkets. The acrylamide analysis was conducted. The result shows the acrylamide levels ranged from 11.4 to 36.2 µg/L in ground roasted coffee analyzed as "espresso", 47.4 to 95.2 µg/ L for instant coffee and 200.8 to 229.4 µg/L for coffee blends with cereals (Table 10). Soluble "cappuccino" contained 6.4 µg/L (Soares *et al.,* 2006). Considering that 6 g of ground coffee extracted with ~30 mL water are used to prepare an "espresso", the concentration of AA per cup is therefore 0.32 to 1.46 µg/30 mL. To prepare a cup of instant coffee the usual measure is 2 g per individual portion making 0.47 to 0.95 µg per 30 mL. Considering that coffee blends with cereals were prepared as soluble coffee (2 g/ 30 mL cup) the concentration of AA per cup is therefore 2.01 to 2.09 µg per 30 mL cup. "Cappuccino" as analysed is a soluble mixture of coffee, milk powder, cocoa and sugar and each individual dose correspond to 14 g, resulting in an acrylamide concentration of 0.45 µg per 30 mL cup. These results highlight the fact that the addition of cereal products to coffee increased the amount of AA. This in agreement with studies (Yusà *et al.*, 2006) reporting that cereal products form substantial amounts. The quantity of AA found in coffee products is dependent on the coffee processing and preparation method (Soares *et al.*, 2006).

Table10. *Acrylamide levels in different coffee products*

Samples	n	Acrylamide µg/ L			Acrylamide / 30 mL cup		
		Min	Mean	Max	Min	Mean	Max
"Espresso"	18	11.4	21	36.2	0.32	0.62	1.46
Soluble coffee	5	47.4	72.4	95.2	0.47	0.72	0.95
Coffee blends with cereals	2	200.8	215.2	229.4	2.01	2.15	2.29
Cappuccino	1	-	6.4	-	-	0.45	-

Source: *Soares et al., 2006*

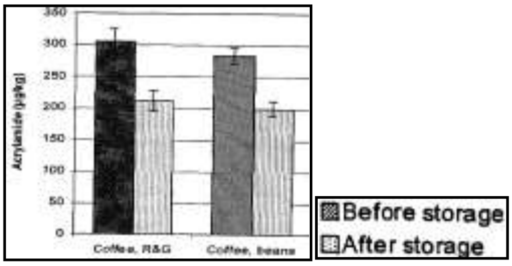
Effect of Storage on Stability of Acrylamide in Roasted Coffee Products

To examine AA stability vacuum packed several original 250g of ground coffee were stored at 10-12^{0}C of the same production batch. 10 randomly selected packs in duplicate homogeneity were analyzed, the average AA concentration was 305µg/Kg, and the standard deviation was 21µg/Kg. Ten unopened vacuum packages were then stored for 3 months and analysed again. Significantly lower amounts were found for all packages (Hoenicke and Gatermann, 2005). Average acrylamide concentration was 210µg/Kg and the standard deviation was 13µg/Kg, indicating a significant and uniform decrease of acrylamide over time even when vacuum-packaged (Fig. 6) (Hoenicke and Gatermann, 2005).In order to check the stability of AA in roasted coffee beans, the same examination with whole beans packaged in 500g original packages were performed. A significant decrease of acrylamide levels was determined similar to that in the ground coffee (Fig. 6) (Hoenicke andGatermann , 2005). Average AA concentrations were 285$\pm$ 12µg/Kg before and 200 $\pm$ 8µg/Kg after storage. The 40-65% reduction of acrylamide were revealed for re-analysed of selected samples was after 6 month storage. No AA degradation was determined for frozen coffee stored at -40^{0}C. In the other case strong decrease of acrylamide levels in ground coffee that was stored at room temperature in its original containers but opened once (Andrzejewski *et al.*, 2004). AA seems to be stable both in soluble coffee (spry-dried coffee extracts and in coffee substitutes (spray- dried extracts) over 3 months of storage (Table 11). For coffee substitutes, no significant decrease of acrylamide occurred even after 1 year of storage. AA losses occur over time both in vacuum-packed ground coffee and in coffee beans, due to a result of reactions with coffee-typical constituents (Hoenicke and Gatermann, 2005). It can be supposed that these substances are present in coffee beans but are less (or not) available in the extract or in the spray-dried extract. In agreement with this Andrzejeweski *et al.* (2004) proved that acrylamide is quite stable in brewed coffee, even over 5 hrs of heating.

Table11. *Average acrylamide level (µg/Kg) and recoveries (%) determined before and after a respective storage time (month) of different coffee products*

Product types	Storage time	Before	After storage	Recovery
Coffee, roasted & ground	3	305	210	70
Coffee, beans	3	285	200	71
Coffee, soluble	3	840	850	101
Coffee substitute	12	1300	1200	92

Source: *Hoenicke andGatermann, 2005*



Source: *Hoenicke and Gatermann, 2005*

Fig6. *Average acrylamide levels and standareddevations(n=10) of vacuum- packaged roasted and ground (R&G) coffee and packaged coffee beans determined before and after 3 months storage at 10^0- 12^{0}C*

CONCLUSION

Arabica and Robusta coffee beans differ in acrylamide amounts formed. Coffee roasted in a laboratory roaster to common degrees for consumer; as well as in the thermostatic oven under standard roasting conditions, Robusta showed to have the highest amounts of acrylamide than the Arabica coffee. Furthermore, acrylamide forms in lower amounts at higher temperatures because of the faster elimination process. The quantity of acrylamide found in coffee products is dependent on the coffee processing and preparation method. The AA content of roasted and brew coffee differs mainly with the coffee species, degree of roasting, blending amount (ratio on coffee species) and storage conditions. The presented review has highlighted that acrylamide is a potential threat to the human health as it is a precursor to carcinogenic compounds. Looking for coffee varieties for low acrylamide content and method of post-harvest processing are suggested as a future research line.

REFERENCES

[1] Alves, R. C., Casal, S., & Oliveira, B. P. P. (2007). Factors influencing the norharman and harman contents in espresso coffee. Journal of Agricultural and Food Chemistry, 55, 1832–1838

[2] Andrzejewski, D., Roach, J. A., Gay, M. L., & Musser, S. M., 2004.Analysis of coffee for the presence of acrylamide by LC–MS/MS. Journal of Agricultural and Food Chemistry, 52, 1996-2002

[3] Bagdonaite, K., Derler, K., & Murkovic, M. (2008). Determination of acrylamide during roasting of coffee. Journal of Agricultural and Food Chemistry, 56, 6081–6086

[4] Becalski A, Lau BP-Y, Lewis D, Seaman SW. (2003). Acrylamide in foods: Occurrence, sources, and modeling. Journal of Agricultural and Food Chemistry 51:802–808

[5] Borrelli R.C., Esposito F., Napolitano A., Ritieni A., Fogliano V., (2004). Characterization of a new potential functional ingredient: coffee silverskin. J. Agric.Food Chem. 52, 1338-1343

[6] Delatour T, Perisset A, Goldmann T, Riediker S, Stadler RH. (2004).Improved sample preparation to determine acrylamide in difficult matrixes such as chocolate powder, cocoa, and coffee by liquid chromatography tandem mass spectroscopy. Journal of Agricultural and Food Chemistry 52:4625–4631

[7] Granby K., and Fagt S., (2004).Analysis of acrylamide in coffee and dietary exposure to acrylamide from coffee.AnalyticaChimicaActa, 520, 177-182.

[8] Hoenicke, K., &Gatermann, R. (2005).Studies on the stability of acrylamide in food during storage. Journal of AOAC International, 88, 268–273.

[9] Illy, A., &Viani, R. (2005). Espresso coffee: The science of quality. London, UK: Academic Press.

[10] Kristina Bagdonaite (2011),Formation of Acrylamide during Roasting of Coffee http: \\www.foodscience.tugraz

[11] Lantz, I., Ternité, R., Wilkens, J., Hoenicke, K., Guenther, H., & van der Stegen, G. H. (2006).Studies on acrylamide levels in roasting, storage and brewing of coffee. Molecular Nutrition and Food Research, 50, 1039–1046.

[12] Mottram, D. S., B. L. Wedzicha, and A. T. Dodson.(2002). Acrylamide is formed in the Maillard reaction. *Nature* 419:448–449

[13] Oliveira S.D., Franca A.S., Gl´oria M.B.A., Borges M.L.A., (2005).The effect of roasting on the presence of bioactive amines in coffees of different qualities. Food Chem. 90, 287-291.

[14] Oosterveld A., Voragen A.G.J., Schols H.A., (2003). Effect of roasting on the carbohydrate composition of Coffeaarabica beans.Carbohydr. Pol. 54, 183-192

[15] Roach JA, Andrzejewski D, Gay ML, Nortrup D, Musser SM. (2003). Rugged LC-MS/MS survey analysis for acrylamide in foods. Journal of Agricultural and Food Chemistry 51:7547–7554.

[16] Senyuva, H. Z., &Gökmen, V., 2005. Study of acrylamide in coffee using an improved liquid chromatography mass spectrometry method: Investigation of colour changes and acrylamide formation in coffee during roasting. Food Additives and Contaminants, 22, 214–220.

[17] Soares Dias, Cristina; Cunha, Sara and Fernandes, José (2006), Determination of acrylamide in coffee and coffee products by GC-MS using an improved SPE clean-up, Internet document accessed on May 2011. http://mc.manuscriptcentral.com

[18] Summa, C. A., de la Calle, B., Brohee, M., Stadler, R. H., &Anklam, E. (2007). Impact of the roasting degree of coffee on the in vitro radical scavenging capacity and content of acrylamide. LWT – Food Science and Technology, 40, 1849–1854

[19] Taeymans, D., Wood, J., Ashby, P., Blank, I., Studer, A., Stadler, R. H., 2004. A review of acrylamide: An industry perspective on research, analysis, formation, and control. Critical Reviews in Food Science and Nutrition, 44, 323-347.

[20] Yasuhara, A., Y. Tanaka, M. Henel, and T. Shibamoto. (2003). Gas chromatographic investigation of acrylamide formation in browning model systems.*J Agric Food Chem* 51:3999–4003

[21] Yusà V, Quintás G, Pardo O, Martí P, Pastor A. (2006). Determination of acrylamide in foods by pressurized fluid extraction and liquid chromatography-tandem mass spectrometry used for a survey of Spanish cereal-based foods. Food Additives and Contaminants 23:237-244.

[22] Zyzak, D. V., R. A. Sanders, M. Stojanovic, D. H. Tallmadge, B. L. Eberhart, D. K. Ewald, D. C. Gruber, T. R. Morsch, M. A. Strothers, G. P. Rizzi, and M. D. Villagran. (2003). Acrylamide formation mechanism in heated foods.*J Agric Food Chem*51:4782–4787

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