COFFEES AND INDUSTRIAL BLENDS AROMA PROFILE DISCRIMINATION ACCORDING TO THE CHROMATIC VALUE

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ABSTRACT: Different polymeric phases have been used in order to perform roasted coffee aroma analysis although not in a systematic way. Variations in the type of SPME polymer and sample composition make experimental results interpretation difficult and may hinder coffee blend differentiation. In the present work, static headspace solid phase microextraction using carboxen/ polydimethylsiloxane polymeric fibre (HS-SPME(CAR/PDMS)) followed by gas chromatography-mass spectrometry (GC-MS), revealed the best analytical performance to characterize the aroma profile of coffees and industrial blends with different chromatic values (64.9, 70.6, 75.3, 86.1 and 89.6). The most relevant classes of aroma compounds founded were pyrroles, ketones, pyrazines, furans, phenolics, pyridines, alcohols and acids, independent of the degree of roasting. By combining the analytical methodology with principal component analysis (HS-SPME (CAR/PDMS)/GC-MS/PCA), important aroma compounds such as 2-furancarboxaldehyde, 2-furanmethanol and acetic acid, allows to discriminate the different degrees of roasting, from light (chromatic value 89.6) to dark (chromatic value 64.9) roast. The proposed analytical approach may help to build aroma profile databases to allow a better evaluation of coffee blend quality, and in controlling the industrial roasting processes.

Index terms: Roasting degree; chromatic value; carboxen polydimethylsiloxane polymeric fibre, gas chromatography, mass spectrometry.

DISCRIMINAÇÃO DO PERFIL AROMÁTICO DE CAFÉS E MISTURAS INDUSTRIAIS DE ACORDO COM O VALOR CROMÁTICO

RESUMO: *Diferentes fases poliméricas têm sido utilizadas, a fim de realizar-se a análise do aroma do café torrado, embora isso não tenha sido feito de forma sistemática. Variações no tipo de polímero de SPME, bem como na composição da amostra tornam a interpretação dos resultados experimentais difícil o que pode inclusive interferir em tentativas de diferenciação de diferentes misturas de café. No presente trabalho, a microextração de fase sólida para análise estática de "espaço-de-cabeça", utilizando o polímero carboxen/polidimetilsiloxano (HS-SPME (CAR/PDMS)), associada a cromatografia gasosa acoplada a espectrometria de massa (GC-MS), revelou o melhor desempenho analítico na caracterização do perfil aromático de cafés e misturas industriais, com diferentes valores cromáticos (64,9, 70,6, 75,3, 86,1 e 89,6). As classes de compostos aromáticos mais importantes identificadas nos cafés foram: pirróis, cetonas, pirazinas, furanos, fenóis, piridinas, álcoois e ácidos, independentemente do grau de torra. Ao combinar a metodologia analítica com a análise de componentes principais (HS-SPME (CAR/PDMS)/GC-MS/PCA), verificou-se que os compostos aromáticos furancarboxaldeído, 2-furanmethanol e ácido acético permitem discriminar os diferentes graus de torrefação. A abordagem proposta neste estudo pode ajudar a construir bases de dados de perfis aromáticos de uma maneira mais robusta, permitindo uma melhor avaliação da qualidade de misturas de café e melhor controle do processo industrial de torração.*

Termos para indexação: *Grau de torra, valor cromático, polímero carboxen polidimetilsiloxano, cromatografia gasosa, espectrometria de massa.*

1 INTRODUCTION

Commercial available roasted coffees derive from two species, *i.e. Coffea arabica* and *Coffea canephora* that are cultivated in all continents except Europe. Usually, consumers buy coffee blends composed by a mixing of these two species of coffee. Different mixtures originate different blends whose aroma and flavour can be quite distinct and exquisite (MENDES et al., 2001).

Arabica coffee is usually used in blends for the aroma effect whereas robusta is used for taste and body (CORREIA, 1990). Nevertheless, if the type of coffee is an important factor determining blend

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quality, other characteristics such as origin and roasting conditions may also affect the final product quality. To obtain a good cup of coffee, roasting is a very important step in order to develop specific organoleptic properties, *i.e.* flavour, aroma and colour (HERNANDÉZ et al., 2007). During this process, pyrolitic reactions take place leading to the formation of volatile and semi-volatile aroma compounds responsible for the sensory qualities of roasted coffee (GROSCH, 2001; HERNANDÉZ et al., 2007). Therefore, roasting temperature affects the volatiles profile by favouring different reactions and product removal pathways at different processing conditions (FRANCA et al., 2009). Industrially, the degree of roast is evaluated by measuring roasted ground beans light reflectance and by visual inspection of the colour of the beans. The value obtained by light reflectance is often designated as the "chromatic value" of the roasted coffee, as it is related to the degree of roast and ultimately with the final colour of the roasted beans (MENDOZA; DEJMEK; AGUILERA, 2006).

The offer of commercial *gourmet* blends has increased largely over the last years since the greater quality of these products demands a higher degree of quality control. There is a major concern in maintaining the aroma characteristics of those blends over time. To manage this, coffee industry has to rely on analytical methods that are reproducible and more efficient on general aroma compounds profile determination. Solid-phase microextraction in the static headspace mode combined with gas chromatography coupled to mass spectrometry (HS-SPME/GC-MS) has been largely accepted for the determination of aroma compounds in many food stuffs such as fruits (FERREIRA; PERESTRELO; CÂMARA, 2009), beverages (ALVES; NASCIMENTO; NOGUEIRA, 2005; CÂMARA et al., 2007), sauces (HARMON, 2002) and coffee (AKIYAMA et al., 2005; AKIYAMA; IWABUCHI; TANAKA, 2003; ROBERTS; POLLIEN; MILO, 2000; ROCHA et al., 2003; SANZ et al., 2001). HS-SPME is a reproducible and precise methodology although the optimization concerning the selection of the most suitable fibre coating polarity as well as the most important experimental parameters, which are known to influence the sampling performance of the system under study are required (PAWLISZYN, 1997).

In the case of HS-SPME application on roasted coffee samples, several methodologies are reported in literature that demonstrate the best conditions for the enrichment of the aroma compounds (AKIYAMA et al., 2005; AKIYAMA; IWABUCHI; TANAKA, 2003; FRANCA et al., 2009; ROBERTS; POLLIEN; MILO, 2000; ROCHA et al., 2003; SANZ et al., 2001). Important coffee aroma compounds have been identified by the former authors by applying this methodology, *e.g.* pyridine, the pyrazines 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine and 2-ethyl-5-methylpyrazine, the furans 2-furancarboxaldehyde, 2-furanmethanol and 5-methyl-furfural, the phenolics 2-methoxyphenol (guaiacol), 2-methoxy-4-vinylphenol (vinylguaicol) and 4-ethyl-2-methoxyphenol, the pyrroles 1H-pyrrole-2-carboxaldehyde and 1-(1-H-pyrrol-2-il)-ethanone, as well as maltol and acetic acid. Nonetheless, few studies have showed how SPME fibres performance may change with the degree of roast and which fibre is more convenient to evaluate the aroma independently of the roasting degree.

Recently, Franca et al. (2009) have introduced this concept by assaying at laboratory scale a preliminary evaluation of the effect of roasting temperature on coffee aroma compounds using the HS/GC-MS approach. However, the aroma compounds of roasted coffee obtained at an industrial quality control laboratory, according to in-house quality control methods, were never characterized in relation to different chromatic values.

The aim of this work was to develop a methodology adapted to quality control on different chromatic values of coffee and blends at industrial laboratories in order to promote the aroma profile characterization and differentiation. The discrimination of the aroma compounds found at different roasting levels has been evaluated through Kruskal-Wallis one-way analysis of variance and multivariate data analysis.

2 EXPERIMENTAL

2.1. Samples

Different roasting bean colour samples were prepared with commercial arabica Brazilian green coffee (crude) (crop 2005-2006) at Novadelta S.A. industrial installation (Campo Maior, Portugal). The

green coffee was roasted in Novadelta's quality control laboratory using a Probat (Germany) roaster and each degree of roast was prepared with 300 g of green coffee. The roaster was allowed to cool between the different roasts. The chromatic values of grinded roasted coffee samples were determined using a Colour Reflectance Meter (Dr. Lange, Germany). The in-house chromatic values practice for the coffee analysed was from 73 to 83.

The aroma profiles achieved in the roasted samples characterized by chromatic values were 64.9 (dark roast), 70.6, 75.3, 86.9 and 89.6 (light roast). Dr. Lange chromatic values are lower when roasting is heavier and higher for lighter roasting degrees (GONZÁLEZ-MIRET et al., 2007). The roasting degrees and experimental roasting conditions are summarized in Table 1. One batch for each treatment was obtained. Samples were grinded in an industrial grinder at a degree of grinding 13 (Mahlkoning, Germany) at Novadelta and immediately transferred to 20 mL vials for transportation and kept at -20 ºC until analysis.

2.2. HS-SPME assays

A manual SPME device and fibres coated with polydimethylsiloxane (PDMS; 100 mm), Carboxen-PDMS (CAR/PDMS; 75 mm) and PDMS-divinylbenzene (PDMS/DVB; 65 mm) polymeric phases were supplied from Supelco Inc. (Bellefonte, PA, USA). Two grams of grounded coffee sample were placed into 20 mL vials sealed with caps having PTFE-faced silicone septa (Supelco) using a manual crimper and placed in a water bath maintained at 60 ºC. For sampling, the SPME fibre was inserted into the HS during 60 min at 60 ºC, according to other authors (CHEN et al., 2007; ROCHA et al., 2003; ZAMBONIN et al., 2005). Subsequently, the SPME device was introduced in the injector port for GC-MS analysis and was allowed to remain in the inlet for 10 minutes. Blank runs using empty vials instead of sample were done in order to control for possible memory effects.

2.3. GC-MS analysis

GC-MS analysis was performed on an Agilent 6890 series gas chromatograph interfaced to an Agilent 5973 *N* mass selective detector (Agilent Technologies, Little Falls, DE, USA). A vaporization injector was used in the splitless mode (2 min) at 270 ºC using a fused silica capillary column, 30 m ´ 0.32 mm ID 0.25 mm film thickness (HP-5MS; 5% diphenyl 95% dimethyl polydimethylsiloxane, Agilent Technologies). The oven temperature program was 40 ºC for 1 min, 40-150 ºC at 3 ºC/min, 150 ºC for 15 min, 150-250 ºC at 5 ºC/min and 250 ºC for 5 min according to Zambonin et al. (2005). Helium was used as carrier gas at 35 cm sec^{-1}. Electron ionisation mass spectra in the range 40-400 Da was recorded at 70 eV. The quadrupole, source and transfer line temperatures were maintained at 150, 230 and 280 ºC, respectively, and a turbo molecular pump (10^{-5} torr) was used. All data were recorded using a MS ChemStation (G1701CA; Rev C.00.00; Agilent Technologies). Volatile compounds were tentatively identified by comparing their mass spectra with the Wiley´s library spectral data bank (G1035B; Rev D.02.00; Agilent Technologies) and retention index (RI) using C_{10}-C_{24} *n*-alkanes, as well as by comparison with Adams database (ADAMS, 2001). All samples having different chromatic values were analysed in triplicate by HS-SPME. For semi-quantification purposes, the average of abundances (n=3) of each identified compound was accepted whenever the standard deviation was lower than 5 %.

TABLE 1 – Experimental roasting conditions for different chromatic values.

Chromatic value	Roasting final temperature (ºC)	Roasting time (min)
89.6	175	8.8
86.1	185	9.5
75.3	190	10.0
70.6	190	10.5
64.9	195	11.0

2.4. Statistic analysis

Kruskal-Wallis one-way analysis of variance was performed according to VassarStats (Vassar College, USA). For principal component analysis (PCA), the average abundances of the aroma compounds obtained by HS-SPME(CAR/PDMS)/GC-MS assays were standardized and used as variables for object description (chromatic values), and performed with Statistica 8.0 software (Statsoft, USA).

3 RESULTS AND DISCUSSION

3.1. Aroma characterization according to the chromatic values

From the onset, SPME fibers were selected according to the best response to the volatile aroma compounds expected to be found in the HS of roasted coffee samples. In a first approach, the PDMS fiber was found to present good sensitivity and stability among the set of the tested fibers, namely under repeated assays. Nevertheless, since aroma compounds in roasted coffee also include targets with a great prominence of polar characteristics, other fibres such as CAR/PDMS and PDMS/DVB were also tested. Therefore, to select the best polymeric coating, HS-SPME assays on arabica coffee samples from Brazil were carried out under a temperature of 60 ºC for 60 minutes (ROCHA et al., 2003; SANZ et al., 2001). Figure 1 shows the main differences on the average abundances of several chemical classes observed by using three fibre types (PDMS/DVB (a), PDMS (b) and CAR/PDMS (c)) obtained by HS-SPME/GC-MS analysis on roasting coffee samples having different chromatic values.

From the obtained data it is possible to observe that the HS-SPME(CAR/PDMS)/GC-MS assays show a much higher average of abundances in what relates to pyrazines, furans, pyridines, acids and ketones (Figure 1.c), the most relevant classes of aroma compounds usually founded in roasted coffee aroma. The statistical comparisons in between the abundances variance obtained by each fiber for the different chromatic value were performed through *F*-test in order to evaluate if it was possible to apply the parametric single-factor ANOVA. Nevertheless, this was not possible as there was no difference between variances (BRÖHAN et al., 2009). As a

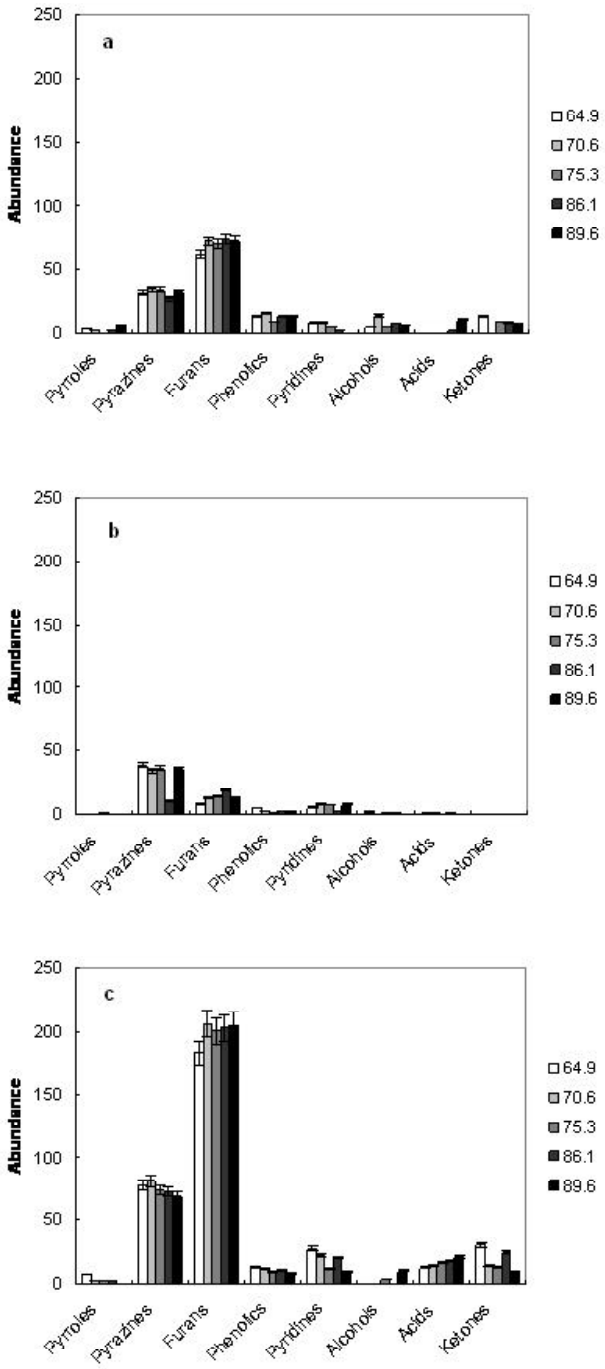

FIGURE 1 – Average abundances ($\times 10^7$) of chemical classes of aroma compounds obtained by HS-SPME/GC-MS using PDMS/DVB (a), PDMS (b) and CAR/PDMS (c) fibres on roasting coffee samples having different chromatic values.

consequence, the one-way comparison of abundances variance was done through the Kruskal-Wallis test for the most relevant chemical classes corresponding to each chromatic value, *i.e.* pyrazines, furans, pyridines, acids and ketones (Figure 1). Therefore, for the different chromatic levels assayed, the abundances difference among the three fibres tested were quite significant ($p < 0.05$) and we can prove that CAR/PDMS fiber is the most effective, under similar experimental conditions. Pyridines were identified by Franca et al. (2009), as being characteristic of samples submitted to a dark roast; similarly, these compounds had a higher influence on our sample discrimination, as it will be shown in the subsequent multivariate data analysis. Equivalent results were also obtained by other authors (AKIYAMA; IWABUCHI; TANAKA, 2003), where CAR/PDMS fibre showed much better response for compounds such as 2-methylfuran, 2- and 3-methylbutanals, 1-methyl-1H-pyrrole and 1H-pyrrole, although with lower level of 2-methoxyphenol, 4-ethenyl-2-methoxyphenol and 4-hydroxy-2,5-dimethyl-3(*2H)*-furanone, in relation to the other two fibre types (PDMS and PDMS/DVB). These authors also state that PDMS is the fibre coating with the lowest sensitivity to analyse typical aroma compounds from coffee matrices, which is also agreement with our data. Table 2 summarizes the aroma compounds and the average composition founded by HS-SPME(CAR/PDMS)/GC-MS methodology in Brazilian roasted coffee samples having different chromatic values.

The volatile fraction of roasted coffee can be grouped in the following chemical classes, namely, pyrroles, ketones, pyrazines, furans, phenolics, pyridines, alcohols and acids, where the compounds achieved in the HS had already been reported in the literature (AKIYAMA et al., 2005; AKIYAMA; IWABUCHI; TANAKA, 2003; AMASTALDEN; LEITE; MENEZES, 2001; BICCHI et al., 1997; BUFFO; CARDELLI-FREIRE, 2004; GONZÁLEZ-RIOS et al., 2007; GROSCH, 2001; HUANG et al., 2007; ISHIKAWA et al., 2004; ROCHA et al., 2003; SANZ et al., 2001; YERETZIAN et al., 2002; ZAMBONIN et al., 2005), which are known to coming from the Maillard reactions and Strecker's degradations. The flavour development during roasting depends on the time-temperature processing in which the beans are conditioned (YERETZIAN et al., 2002). Thus, a chromatic value of 64.9 showed lower peak abundance for furans that are usually associated with caramel and spicy sensory notes (AKIYAMA; IWABUCHI; TANAKA, 2003; BERLITZ; GROSCH; SCHIEBERLE, 2004; CZERNY; MAYER; GROSCH, 1999). In the case of coffee with a chromatic value of 89.6 (the lightest roast degree studied), pyrazines, ketones, pyridine and phenolics appeared in lower abundance (Figure 1c). When the degree of roast is lighter some of these aroma compounds are not formed. For higher chromatic values, a lower level of these compounds, which are known to be formed in final roasting stages, combined with a higher abundance of organic acids usually produces a brew with accentuated acidity but with a very poor aroma. With a more intensive roast, pyrazines are formed and the well-known nutty-roast smell of roasted coffee will be developed (BERLITZ; GROSCH; SCHIEBERLE, 2004). The data obtained show that a different aroma profile will developed, depending on the time-temperature of the roasting process. So, the HS-SPME(CAR/PDMS)/GC-MS analytical approach proved to have a good performance for the characterization of aroma profiles from coffee samples independently of the chromatic value they exhibit.

3.2. Profile discrimination of roasted coffees

As stated in the previous section, HS-SPME(CAR/PDMS)/GC-MS methodology applied to coffee samples having different chromatic values, revealed different aroma profiles. From the data obtained (Table 2), the ANOVA (Kruskal-Wallis) test allowed to confirm the significance of these differences ($p < 0.005$) for the chemical classes of pyrroles, phenolics, pyridines and acids. Subsequently, PCA was performed to verify the discrimination in between different degrees of roast based on the average abundance of the aroma compounds obtained by the HS-SPME(CAR/PDMS)/GC-MS assays.

Figure 2 depicts the PCA from the average abundances of 1H-pyrrole-2-carboxaldehyde, 2,5-dimethylpyrazine, 2-furancarboxaldehyde, 2-furanmethanol, 5-methyl-2-furancarboxaldehyde, pyridine, 1,3-butanediol, maltol and acetic acid. All these compounds are known to play a key role in the discrimination of the final aroma of roasted coffee.

TABLE 2 – Aroma compounds and average composition found in Brazilian coffees with different chromatic values obtained by HS-SPME(CAR/PDMS)/GC-MS.

		%[1]				
		Chromatic value				
Compound	RI[2]	**64.9**	**70.6**	**75.3**	**86.1**	**89.6**
Pyrroles						
1H-pyrrole-2-carboxaldehyde	1166	1.3				
1-(2-furanylmethyl)-1H-pyrrol	1162	1.0	0.8	0.7	0.8	
Total pyrroles		2.3	0.8	0.7	0.8	
Ketones						
1-(1H-pyrrol-2-yl)-ethanone	1047	3.6			2.8	2.8
3-hydroxy-2-methyl-4H-pyran-4-one	1094	5.6	4.1	4.0		
1-(6-methyl-2-pyrazinyl)-1-ethanone	1095				4.5	
Total ketones		9.1	4.1	4.0	7.3	2.8
Pyrazines						
2-methylpyrazine	813	5.4	5.8	5.4	5.5	
2,5-dimethylpyrazine	885	16.5	16.9	15.5	16.5	19.0
3-ethyl-2,5-dimethylpyrazine	1052	1.5	1.7	1.4		1.8
Total pyrazines		23.4	24.4	22.3	22.0	20.8
Furans						
2-furancarboxaldehyde	820	11.4	15.9	15.8	17.2	18.4
2-furanmethanol	848	20.3	19.8	20.5	18.9	18.4
5-methyl-2-furancarboxaldehyde	937	15.6	19.7	18.1	19.2	18.8
2-furanmethanol, acetate	966	8.0	6.9	6.0	6.0	6.2
Total furans		55.3	62.2	60.5	61.3	61.9
Phenolic compounds						
2-methoxyphenol	1063	2.4	2.2	1.5	1.8	1.9
4-ethyl-2-methoxyphenol	1264	0.5		0.4		
2-methoxy-4-vinylphenol	1300	1.1	1.2	1.1	1.5	0.6
Total phenolic compounds		4.0	3.4	2.9	3.3	2.5
Pyridines						
pyridine	772	8.3	6.7	3.4	6.2	2.7
Total pyridine		8.3	6.7	3.4	6.2	2.7

Continue...

TABLE 2 – Continuation....

		% [1]				
		Chromatic value				
Compound	RI [2]	**64.9**	**70.6**	**75.3**	**86.1**	**89.6**
Alcohols						
1,3-butanediol	801			1.2		
maltol	1094					3.0
Total alcohols				1.2		3.0
Acids						
acetic acid	744	3.8	4.4	4.9	5.3	6.3
Total acid		3.8	4.4	4.9	5.3	6.3

[1]Relative to the optimum chromatic value (75.3); [2]retention index relative to C_{10}-C_{24} *n*-alkenes.

The first two PCs presenting, respectively, eigenvalues of 5.36 and 2.23, which explain 77.9 % of the variability among the chromatic variance (Figure 2). An enough differentiation between the lightest and darkest degrees of roasting was obtained based on the first component, where the light roast (chromatic value 89.6) was negative and the dark roast (chromatic value 64.9) was positive. The variables that influenced PC1 were 2-furancarboxaldehyde, 2-furanmethanol and acetic acid. On the other hand, in the case of PC2, 1H-pyrrole-2-carboxaldehyde, 2,5-dimethylpyrazine and 1,3-butanediol seems to have the greater contribution. The chromatic value 75.3, *i.e*. the optimum roasting degree according to the industrial practice, presents an intermediate behaviour according to PC1 and discriminated from the other roasted samples in relation to PC2. A lower abundance of phenolics and pyridine (Table 2) seems to contribute for the discrimination between chromatic value 86.1 and the other roasted samples.

The above mentioned volatile constituents are relevant coffee aroma compounds produced at different stages of the roasting process. To obtain different chromatic values of the same coffee it is necessary to vary the time of the roasting process. In result, we obtain higher chromatic values rich in aroma compounds characteristic of the initial stages of roasting, and with lower concentration of compounds that would be produced it the later stages of the roasting process (*e.g.* pyridines). In the case of the lower chromatic values, the inverse is observed. According to Yeretzian et al. (2002), there are two distinct phases in the roasting process, initially starting with an endothermic drying phase followed by a second exothermic phase with massive formation of volatile compounds. During this stage, a strong change occurs in the aroma composition over time. This author's demonstrated a highest level of 'pyrrol' at dark and very dark degrees of roast, which may explain our data and the importance of this particular chemical class for the discrimination of chromatic values observed. In what relates to our highest chromatic value (89.6), corresponding to the lightest degree of roast, acids and alcohols played a major role discriminating those from other chromatic values. Several authors have also reported a higher abundance of compounds of these chemical families in arabica coffees when the roasting is lighter (RODRIGUES et al., 2007; YERETZIAN et al., 2002). This observation may explain the importance of the total abundance of these types of compounds in the discrimination of our highest chromatic values from all other roasting degree.

Our data shows that different coffees could be discriminated based on HS-SPME(CAR/PDMS)/GC-MS/PCA methodology independently of the roasted degree, which may be used in roasted coffee routine quality control. It may help to build aroma profile databases to a better evaluation of coffee blends quality, development of high quality gourmet blends and in controlling the industrial roasting processes. The described methodology may eventually be applied to other foodstuff matrices in order to develop a narrower control of their production and quality at industry.

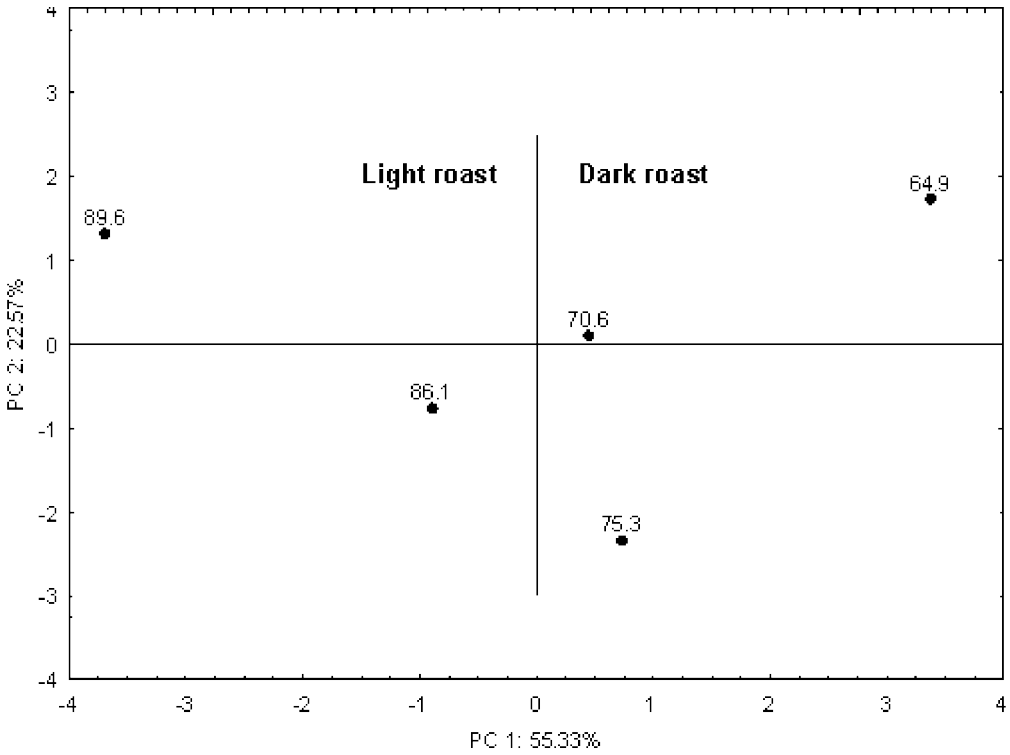

FIGURE 2 – PCA scores scatter plot of the sum of average abundances of the chemical classes from roasted coffees having different chromatic values, obtained by HS-SPME(CAR/PDMS)/GC-MS analysis.

4 CONCLUSION

Carboxen polydimethylsiloxane polymeric fibre revealed the best analytical performance to characterize the aroma profile of coffees and industrial blends with different chromatic values by HS-SPME/GC-MS.

The most relevant classes of aroma compounds founded were pyrroles, ketones, pyrazines, furans, phenolics, pyridines, alcohols and acids, independently of the roasting degree.

When combining the analytical methodology with PCA (HS-SPME(CAR/PDMS)/GC-MS/PCA), the first two PCs presenting, respectively, eigenvalues of 5.36 and 2.23, explaining 77.9 % of the chromatic variance.

From the data obtained, important aroma compounds, *i.e.* 2-furancarboxaldehyde, 2-furanmethanol and acetic acid, discriminating the different chromatic values involved; from light (chromatic value 89.6) to dark (chromatic value 64.9) roast.

The proposed analytical approach may help to build aroma profile databases for a better evaluation of coffee blends quality, and in controlling the industrial roasting processes in food industry.

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