

A Further Tool To Monitor the Coffee Roasting Process: Aroma Composition and Chemical Indices

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S Supporting Information

ABSTRACT: Coffee quality is strictly related to its flavor and aroma developed during the roasting process, that, in their turn, depend on variety and origin, harvest and postharvest practices, and the time, temperature, and degree of roasting. This study investigates the possibility of combining chemical (aroma components) and physical (color) parameters through chemometric approaches to monitor the roasting process, degree of roasting, and aroma formation by analyzing a suitable number of coffee samples from different varieties and blends. In particular, a correlation between the aroma composition of roasted coffee obtained by HS-SPME-GC-MS and degree of roasting, defined by the color, has been researched. The results showed that aroma components are linearly correlated to coffee color with a correlation factor of 0.9387. The study continued looking for chemical indices: 11 indices were found to be linearly correlated to the color resulting from the roasting process, the most effective of them being the 5-methylfurfural/2-acetylfuran ratio (index).

KEYWORDS: coffee, roasting process, color, chemometrics, aroma composition, HS-SPME-GC-MS, chemical indices

■ INTRODUCTION

Aroma strongly influences coffee organoleptic properties and, as a consequence, its appeal. Coffee aroma is developed during the roasting process, and its composition strongly depends on species, variety, and origin of the crude beans as well as on operative conditions, mainly temperature and time. Monitoring of the roasting process is therefore an unavoidable task to obtain the desired aroma and taste at an industrial level and/or to keep coffee quality constant. The coffee roasting process is in general characterized through the degree of roasting, which includes several chemical and physical properties, the best known of them being the external color of the beans, the loss of weight during the roasting process, the change in chemical composition, and the developed sensory characteristics.¹ These parameters can all be adopted individually or in combination to define the degree of roasting, but, at present, a universally accepted parameter(s) or method(s) to measure it is not available.

Several indirect markers to monitor and determine the degree of roasting have also been proposed including free amino acids,² alkylpyrazines,³ chlorogenic acids,⁴ and the chlorogenic acid/caffeine ratio.⁵ Other approaches involve the analysis of coffee roasting exhaust gases by both cryotrapping–GC⁶ or direct laser–mass spectrometry⁷ and monitoring 2-furfuryl alcohol and hydroxyl-2-propanone by GC–selective odorant measurement by multisensor array (GC-SOMMSA).⁸ In general, however, the most adopted indicator to control the degree of roasting in industry is color determination by ground bean light reflectance, or, even, still today, visual inspection, even though dry matter loss has been considered to provide a more reliable evaluation of degree of roasting also in in-plant determination.¹ Despite its widespread adoption, this approach is not free from criticisms because some authors showed coffee beans presenting the same average color value although they

were of different quality and/or roasted to a different degree.^{5,6,9} The question is in any case still open because, for instance, at the end of a study about coffee roasting degree assessment, Franca et al. concluded that color and weight loss are not fully reliable and temperature must also be considered.⁹ In contrast, in a study about the influence of the time–temperature conditions on aroma formation during coffee roasting, Baggenstoss et al. found that attaining the same coffee bean color under different roasting time–temperature conditions does not necessarily imply equivalent coffee aroma and physical properties.¹⁰ However, in industry, where constant quality of green coffee is processed with the same time–temperature conditions and the same roasting plant, color is a simple and fast approach to monitor the degree of roast.

It is well-known that the nature and abundance of most coffee aroma components are directly related to the chemical reactions to which sugars and free amino acids are submitted during roasting (e.g., Maillard reactions and Strecker degradation) and that their formation and abundance strongly depend on the roasting conditions. Flament, Reineccius, and Shibamoto reviewed in-depth the chemical reactions leading to roasted coffee flavor components.^{11–13} Several flavor components have been demonstrated to be effective markers of specific coffee characteristics, for instance, the ratios 2-methylfuran/2-butanone, methanethiol/hexanal, and 2-furfurylthiol/hexanal, which were found to be useful indicators of staling as well as for the aroma freshness of coffee brew.¹⁴ In the above-mentioned study, Baggenstoss et al. investigated the development of 16 key aroma compounds in a commercial

Received: July 23, 2012

Revised: October 18, 2012

Accepted: October 19, 2012

Published: October 19, 2012

Table 1. Coffee Samples and Colors Measured by Ground Bean Light Reflectance

sample ^a	color	roasting degree	sample ^a	color	roasting degree	sample ^a	color	roasting degree
A1	61	light	R1	61	light	B1	59	light
A2	51	medium	R2	50	medium	B2	49	medium
A3	40	dark	R3	40	dark	B3	39	dark
A4	62	light	R4	62	light	B4	60	light
A5	51	medium	R5	49	medium	B5	51	medium
A6	39	dark	R6	40	dark	B6	40	dark
A7	62	light	R7	59	light	B7	58	light
A8	50	medium	R8	51	medium	B8	49	medium
A9	41	dark	R9	38	dark	B9	38	dark
A10	59	light	R10	58	light	B10	60	light
A11	49	medium	R11	50	medium	B11	49	medium
A12	40	dark	R12	40	dark	B12	38	dark
A13	59	light	R13	60	light	B13	61	light
A14	49	medium	R14	50	medium	B14	51	medium
A15	40	dark	R15	41	dark	B15	42	dark
A16	61	light	R16	62	light	B16	62	light
A17	51	medium	R17	50	medium	B17	49	medium
A18	42	dark	R18	40	dark	B18	39	dark
A19 ^b	57	light	R19 ^b	57	light	B19 ^b	58	light
A20 ^b	48	medium	R20 ^b	48	medium	B20 ^b	35	dark
A21 ^b	61	light	R21 ^b	52	medium	B21 ^b	48	medium
A22 ^b	53	medium	R22	46	medium	B22 ^b	39	dark
A23 ^b	47	medium	R23 ^b	52	medium	B23 ^b	52	medium
A24 ^b	38	dark				B24 ^b	50	medium
A25 ^b	40	dark						
A26	46	medium						
A27 ^b	49	medium						

^aA, Arabica; R, Robusta; B, blend. ^bSamples used as external test set.

coffee sample submitted to different roasting conditions but resulting in the same color.¹⁰ Very recently, Wieland et al. investigated the possibility of establishing a predictive model to control online the roasting coffee process and to achieve a target roasting degree.¹⁵

The present study aims to investigate whether it is possible to find marker(s) or component ratios whose abundance can directly be related to the color determined by ground bean light reflectance. Samples of Arabica and Robusta coffees and their blends were roasted to a light, medium, or dark degree of roasting under standardized conditions, and their resulting color was carefully determined. The headspace of the resulting roasted coffees was analyzed with HS-SPME combined with GC-MS with the aim to correlate chemometrically the resulting analytical profiles to their colors and find components or indices determined from their ratios in a direct relationship to the measured colors.

MATERIALS AND METHODS

Chemicals. Furan, 2-methylfuran, 2-methylbutanal, 3-methylbutanal, 2,5-dimethylfuran, 2,3-butanedione, 2,3-hexanedione, 1-methylpyrrole, pyridine, pyrazine, methylpyrazine, 3-hydroxy-2-butanone, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, ethylpyrazine, 2,3-dimethylpyrazine, 1-hydroxy-2-butanone, 3-ethylpyridine, 2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, trimethylpyrazine, 2-ethyl-3-methylpyrazine, 2-propylpyrazine, acetic acid, furfural, 2-acetylfuran, furfuryl acetate, 1-methyl-2-carboxaldehyde pyrrole, furfuryl alcohol, 1-furfurylpyrrole, guaiacol, 2-acetylpyrrole, and 2-carboxaldehyde pyrrole were purchased from Sigma-Aldrich (Milan, Italy) and were used to identify coffee markers.

Reagents and Matrices. A total of 74 samples of 100% Arabica (27 samples), 100% Robusta (23 samples), and different 50/50 blends

of them (24 samples) roasted at three different degrees (light, medium, and dark) in a Probat-Werke von Gimborn Maschinenfabrik GmbH roaster model BRZ 2 (Emmerich, Germany) were kindly supplied by Lavazza over a period of 12 months. A mixture of α -thujone and β -thujone (puriss. $\geq 99.0\%$ GC) and dibutylphthalate (DBP) were purchased from Sigma-Aldrich. Table 1 reports the list of coffee samples together with the measured colors and their roasting degree. The color of each sample was carefully measured by ground bean light reflectance with a single-beam Neuhaus Neotec Color Test II instrument (Ganderkese, Germany) at a wavelength of 900 nm on 25–30 g of ground coffee.

Sample Preparation and SPME Fiber Standardization. HS-SPME Sampling. Five hundred milligrams of ground and roasted coffee and 5 μ L of a 2.0 mg/mL solution of α - and β -thujone in dibutylphthalate, used as internal standard, were sampled by HS-SPME with a CAR/PDMS/DVB fused silica fiber (2 cm –50/30 μ m) for 40 min at 50 °C. The analyses were run in triplicate.

SPME device and CAR/PDMS/DVB fused silica fibers from different lots were supplied by Supelco (Bellefonte, PA, USA). Before use, all fibers were conditioned as recommended by the manufacturer and tested to evaluate the consistency of their performance versus a reference roasted Arabica coffee sample selected among those available in the authors' laboratory and stored at –18 °C immediately after roasting. In addition, fiber extraction reliability was evaluated and compared by a full evaporation HS-SPME sampling of the vapor phase from a standard solution of α - and β -thujone (5 μ L of a 2.0 mg/mL solution in DBP) and of 1 μ L of a 5 mg/mL peppermint essential oil solution in DBP. This EO was chosen to extend the performance evaluation to analytes with different chemical properties (volatility and polarity). Normalized peak areas collected from the entire set of analyses (5 replicates per sample) and from all fibers (F1, F2, and F3) were submitted to an analysis of variance (ANOVA). Only fibers that passed the ANOVA test were chosen. Once the equivalence of SPME devices had been established, a verification protocol was defined if additional fibers were necessary during the extended time interval of

Table 2. Selected Components Together with Their Retention Times, Retention Indices, Target Ions and Qualifiers, Dark/Light Area Ratios, and Their Trend with Roasting^a

ID	compound	ret time	ident ^b	I^T_{CW}	I^T_{OVI}	target ion	Q_1	Q_2	DV	dark/light area ratios			trend with roasting
										Arabica	Robusta	blend 50/50	
1	furan	3.73	RF	837	500	68	39	58	R	2.1	1.6	1.5	↑
2	2-methylfuran	4.48	RF	873	586	82	81	53	R	2.8	2.2	2.1	↑
3	2-methylbutanal	5.09	RF	903	641	86	57	41		1.0	1.0	1.1	=
4	3-methylbutanal	5.09	RF	904	635	86	71	57					
5	2,5-dimethylfuran	5.85	RF	938	691	96	95	81		2.4	1.9	2.1	↑
6	2,3-butanedione	6.31	RF	960	555	86	57	43	V, R	1.2	1.3	1.2	=
7	2,3-pentanedione	8.49	tentative	1043	668	100	57	43	V, R	0.5	0.6	0.6	↓
8	2-vinylfuran	9.00	tentative	1059		94	65	66		1.3	1.2	1.3	=
9	2,3-hexanedione	10.87	RF	1117	756	43	71	43		1.3	1.4	1.4	↑
10	1-methylpyrrole	11.17	RF	1124	715	81	80	66	V, R	1.8	1.5	1.7	↑
11	2-vinyl-5-methylfuran	11.79	tentative	1139		108	107	79	V	1.1	1.1	1.1	=
12	pyridine	12.61	RF	1165	720	79	52	39	V, R	2.0	1.7	2.0	↑
13	pyrazine	13.85	RF	1195	709	80	53	70	R	1.4	1.3	1.4	↑
14	methylpyrazine	16.08	RF	1249	802	94	67	53		1.0	0.9	1.0	=
15	3-hydroxy-2-butanone	16.84	RF	1265	681	88	73	45		1.0	0.9	1.2	=
16	1-hydroxy-2-propanone	17.41	tentative	1278	626	74	43	41		0.5	0.8	0.7	=
17	2,5-dimethylpyrazine	18.45	RF	1306	893	108	81	42		0.8	0.8	0.8	=
18	2,6-dimethylpyrazine	18.74	RF	1313	889	108	81	42		0.9	0.8	0.9	=
19	ethylpyrazine	19.01	RF	1318	895	107	108	80		0.9	0.9	0.9	=
20	2,3-dimethylpyrazine	19.45	RF	1329	904	108	67	93		1.1	1.1	1.1	=
21	1-hydroxy-2-butanone	20.57	RF	1353	732	88	57	42		0.5	0.8	0.6	↓
22	3-ethylpyridine	20.85	RF	1364	934	107	92	79	R	3.0	2.3	2.6	↑
23	2-ethyl-6-methylpyrazine	21.22	RF	1371	977	121	122	94		0.8	0.8	0.8	=
24	2-ethyl-5-methylpyrazine	21.46	RF	1376	981	121	122	94		0.8	0.8	0.8	=
25	trimethylpyrazine	21.96	RF	1389	984	122	81	42		0.8	0.8	0.9	=
26	2-ethyl-3-methylpyrazine	22.00	RF	1391	985	121	122	80		0.9	0.8	0.9	=
27	2-propylpyrazine	22.59	RF	1402	985	94	107	122	V	1.3	1.2	1.3	=
28	2-ethyl-3,6-dimethylpyrazine	23.77	tentative	1427	1059	135	136	108		0.8	0.8	0.8	=
29	acetic acid	23.79	RF	1432	547	60	43	45		0.4	0.7	0.5	↓
30	furfural	24.44	RF	1443	801	96	95	39	V, R	0.3	0.5	0.4	↓
31	1-acetoxy-2-propanone	24.57	tentative	1448	825	43	86	116		1.0	1.0	1.0	=
32	2-acetylfuran	26.11	RF	1483	882	95	110	39	V	1.0	1.2	1.1	=
33	furfuryl acetate	27.63	RF	1521	963	81	98	140		1.7	1.5	1.5	↑
34	5-methylfurfural	28.86	tentative	1551	933	110	109	81	V, R	0.4	0.5	0.5	↓
35	1-methyl-2-carboxaldehyde pyrrole	30.66	RF	1596	974	109	108	80		0.9	0.8	0.9	=
36	furfuryl alcohol	32.36	RF	1640	823	98	81	69		1.2	1.1	1.1	=
37	1-furfurylpyrrole	38.58	RF	1805	1152	81	147	53	V, R	1.4	1.2	1.2	=
38	guaiacol	39.54	RF	1832	1064	109	124	81	V, R	3.1	2.5	2.6	↑
39	2-acetylpyrrole	43.26	RF	1941	1030	94	109	66	V, R	1.5	1.3	1.3	=
40	2-carboxaldehyde pyrrole	44.97	RF	1991	976	95	94	66		0.8	0.8	0.7	=
41	<i>p</i> -vinylguaiacol	50.47	tentative	2163	1289	150	135	107		1.5	1.4	1.3	↑

^aItalic, key aroma compounds; bold, significant variables for PCA discrimination of degree of roasting (R) or variety (V); ret time, retention time (min); I^T , linear retention index; Q_1 and Q_2 , qualifiers; DV, discriminating variable. ^bMarkers were identified on the basis of their linear retention indices and MS-EI spectra compared with those of authentic standards (indicated with RF) or tentatively identified through their MS-EI fragmentation patterns and retention indices (tentative).

this study. New devices should be submitted to the whole testing routine by analyzing reference coffee sample stored at $-18\text{ }^\circ\text{C}$. Absolute peak area values for target compounds should fall within a 10% variability (expressed as RSD%) as established during the method performance verification.

Analysis Conditions. Analyses were carried out with an MPS-2 multipurpose sampler (Gerstel, Mülheim a/d Ruhr, Germany) installed on an Agilent 7890A GC unit coupled to an Agilent 5975C MSD (Agilent, Little Falls, DE, USA).

GC-MS method, chromatographic conditions: injector temperature, $230\text{ }^\circ\text{C}$; injection mode, split; ratio, 1/10; carrier gas, helium; flow rate, 1 mL/min; fiber desorption time and reconditioning, 5 min;

column, Megawax 20 M ($d_f = 0.20\text{ }\mu\text{m}$, $d_c = 0.20\text{ mm}$, length = 50 m) (Mega, Legnano (Milan), Italy); temperature program, from $40\text{ }^\circ\text{C}$ (1 min) to $230\text{ }^\circ\text{C}$ at $3\text{ }^\circ\text{C}/\text{min}$, then to $250\text{ }^\circ\text{C}$ (5 min) at $10\text{ }^\circ\text{C}/\text{min}$.

MSD conditions: ionization mode, EI (70 eV); scan range, 35–350 amu; ion source temperature, $230\text{ }^\circ\text{C}$; quadrupole temperature, $150\text{ }^\circ\text{C}$; transfer line temperature, $250\text{ }^\circ\text{C}$.

Identification of Volatile Compounds. The volatile compounds of the headspace of coffee were identified by comparing their calculated linear retention indices and their mass spectra to those of authentic samples or, tentatively, to those collected in homemade or commercial libraries (Wiley Mass Spectral Data) or reported in the literature.

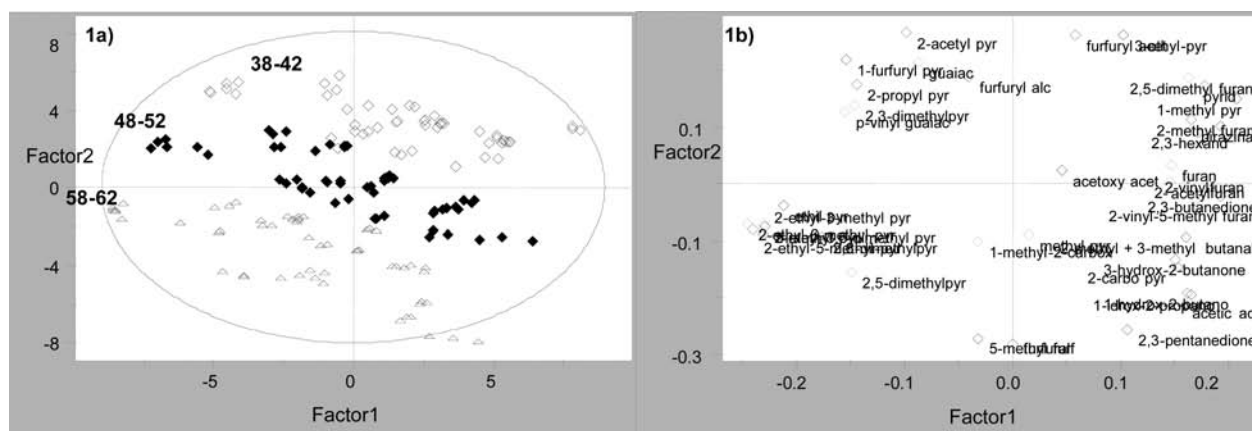


Figure 1. Scores plot (a) and loadings plot (b) on the first two principal components using all profile components ($n = 41$; explained variance, 58.93; preprocessing, autoscale) from HS-SPME-GC-MS patterns of the training set coffee samples. Categories: light roasting (open triangle; color 58–62), medium roasting (solid diamond; color 48–52), dark roasting (open diamond; color 38–42).

Data Elaboration. Data collection was performed with Enhanced ChemStation software (MSD ChemStation version E.02.01.1177, Agilent Technologies 1989–2005) and chemometric elaborations were run with Pirouette (Comprehensive Chemometrics Modeling Software version 4.0, 2009) from Infometrix Inc. and XLstat (version 7.5.1), copyright 1995–2005 Addinsoft. Unsupervised PCA was used to visualize sample groups in particular versus color and/or varieties, and regression tools were used to correlate HS-SPME-GC-MS volatile profile to color. Samples were divided in a training set of 56 samples (6 samples for each variety (Arabica A1–A18 and Robusta R1–R18) and their 50/50 blend (B1–B18) at three different degrees of roasting (light, medium, and dark)) and in an external test set of 18 samples (8 Arabica A19–A27, 4 Robusta R19–R23, and 6 blends B19–B24) of different origin and at different roasting degrees; for sample reference see Table 1.

Repeatability and Intermediate Precision of the Method. Because of the extended period of time in which the samples had to be analyzed, in agreement with the *EURACHEM/CITAC Guide*,¹⁸ precision was used to evaluate the method performance: intraday repeatability and intermediate precision were measured on a 3 week validation, that is, 1 week validation every month during 3 months. In this period, sources of variability that may affect results dispersion (method procedure, laboratory, operator, and instrumentation) remained unaltered.

Repeatability was determined by analyzing a standard 50/50 Arabica/Robusta coffee blend and an external standard stock solution (ESTD) (5 μ L of a 2 mg/L α - and β -thujone solution in DBP) over 1 week in the same laboratory, with the same instrument and operator. Repeatability is here expressed as relative standard deviation percent (RSD%) on normalized peak areas for groups of coffee target analytes and as absolute peak areas for ESTD in each validation week; intermediate precision was referred to the same samples and analytes but monitored over the 3 months of validation.

RESULTS AND DISCUSSION

This section is divided into two parts: the first one concerns possible correlations between degree of roasting and aroma profile obtained by HS-SPME-GC-MS determined with multivariate statistical analysis (i.e., principal component analysis (PCA)), and the second (strictly related to the previous one) concerns the possibility of establishing a direct relationship between specific markers or indices deriving from their ratios and the colors of the investigated coffee samples.

Reliability and robustness of the method were evaluated in terms of repeatability and intermediate precision (see Table 1S in the Supporting Information). Intraday repeatability within each week of validation was very good, with RSD% ranging

from 1.4% for furfuryl acetate to 10.1% for pyridine. Intermediate precision over 3 months showed highly satisfactory RSD% values, too, for both coffee volatiles and ESTD, ranging from 1.3% for 2,6-dimethylpyrazine to 10.1% for furfural and about 10–11% for thujones. Data were then submitted to the ANOVA to evaluate the comparability of intraweek and interweek peak areas (quantitative descriptor). The one-way ANOVA on the five sample replicates per week (15 analytical runs), collected over the 3 weeks, for the target compounds and for ESTDs (α - and β -thujone) revealed that the null hypothesis “there is no difference between absolute peak areas values measured in different weeks” could be accepted for every compound with $p \leq 0.05$.

Chemometric Analysis of HS-SPME-GC-MS Profile of the Investigated Samples. Seventy-four samples consisting of 100% Arabica and 100% Robusta coffees and of mixtures of them, each roasted at three different degrees (light, medium, and dark) under standardized conditions, were submitted to color determination and to headspace analysis by HS-SPME-GC-MS under the conditions reported above. The color range for each degree of roasting was determined for all samples (Table 1) of the training set (56) and resulted to be 38–42 for dark, 48–52 for medium, and 58–62 for the light coffees. Forty-one compounds, for which area could reliably be measured in all analyzed samples, were chosen in the HS-SPME-GC-MS profiles and used for PCA statistical elaboration. Table 2 reports the list of selected components together with their target ions and retention indices. Only seven of these compounds belonged to the set of coffee key aroma compounds as defined by Blank et al. and Czerny et al.^{16,17} The areas of the 41 selected components from HS-SPME-GC-MS analyses were normalized to the internal standard and submitted to PCA. The score plot of the first two principal components (PCs) showed a satisfactory separation of the coffee samples in terms of roasting degree (Figure 1a). Because of the collinearity of some variables, the set of data was then processed to select those mostly contributing to discrimination. The Fisher weight ratio algorithm was then applied to choose those variables that mathematically maximized the variances among the categories (i.e., degree of roasting). Variables were thus reduced from 41 to 16, and the following PCA gave an effective discrimination of the coffee samples submitted to light, medium, and dark roasting processes with an explained variance of the first two PCs accounting for 80.69% and in agreement

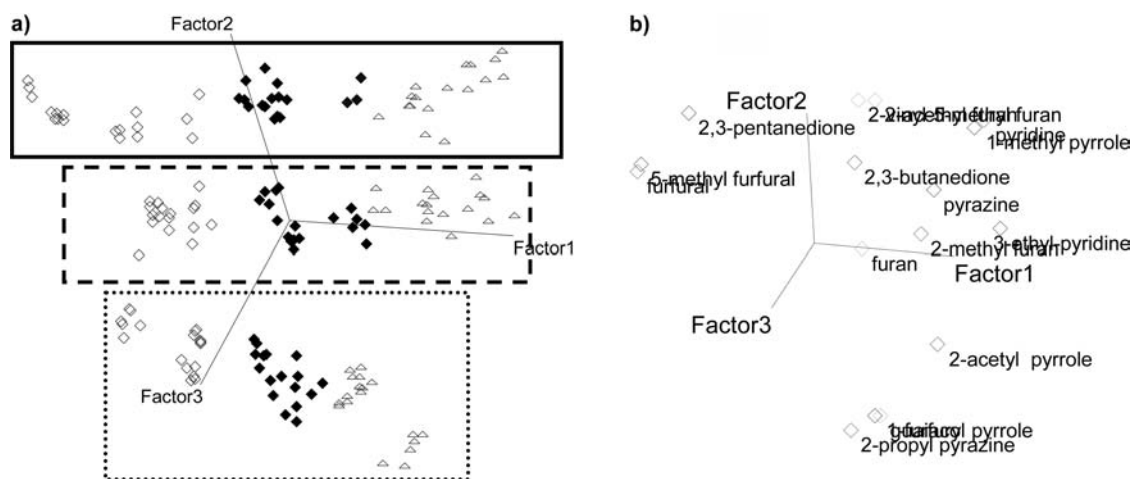


Figure 2. Scores plot (a) and loadings plot (b) on the first three PCs on the variables selected by the Fisher algorithm ($n = 16$; explained variance, 90.68%; preprocessing, autoscale) from the HS-SPME-GC-MS patterns of the training set coffee samples. Categories: light roasting (open triangle; color 58–62), medium roasting (solid diamond; color 48–52), dark roasting (open diamond; color 38–42). Robusta in dotted line, blend 50/50 in dashed line, and Arabica in solid line.

Table 3. Estimation of the Color of the Test Set through the Equation Calculated by MLR and by the Unique Correlation Equation of the 5-Methylfurfural/2-Acetylfuran Index on the Training Set Samples

sample	measured color	prediction on MLR between normalized area markers and color				prediction by 5-methylfurfural/2-acetylfuran index	
		pred (color)	SD on pred	inferior limit 95% (means)	superior limit 95% (means)	pred (color)	Δ
A19	57	56.70	0.88	54.92	58.49	59	2
A20	48	47.22	0.95	45.29	49.15	49	1
A21	61	60.79	1.10	58.55	63.04	60	-1
A22	53	54.53	0.87	52.75	56.30	55	2
A23	47	46.77	1.31	44.11	49.43	48	1
A24	38	38.06	0.75	36.53	39.60	37	-1
A25	40	40.95	0.70	39.52	42.38	40	0
A27	49	47.71	0.87	45.94	49.48	47	-2
R19	57	57.31	0.92	55.44	59.17	59	2
R20	48	47.87	1.11	45.60	50.13	46	-2
R21	52	52.99	1.07	50.82	55.17	50	-2
R23	52	51.76	0.99	49.73	53.78	53	1
B19	58	56.69	0.77	55.12	58.25	60	2
B20	35	36.13	0.91	35.23	37.04	35	0
B21	48	47.02	0.75	45.48	48.56	46	-2
B22	39	41.19	0.80	39.56	42.83	39	0
B23	52	50.24	0.77	48.66	51.82	53	1
B24	50	52.16	0.69	50.75	53.56	52	2

with the average colors. Moreover, when the second and third PCs were considered, the distinction of the samples as a function of variety and blend, and within them, of the different degrees of roasting with an explained variance of 90.68% (Figure 2a) was obtained. The loadings plots reported in Figures 1b and 2b indicate the variables that influence sample discrimination in terms of degree of roasting and variety on the first three PCs. These variables can mainly be divided into three subgroups: (i) mainly discriminative for roasting, furan (1), 2-methylfuran (2), 2,3-butanedione (6), 2,3-pentanedione (7), pyridine (12), 3-ethylpyridine (22), furfural (30), 5-methylfurfural (34), and guaiacol (38); (ii) mainly discriminative for varieties, 2-vinyl-5-methylfuran (11), 2-propylpyrazine (27), and 2-acetylfuran (32); (iii) discriminative for both roasting and varieties, although to different extents, 2,3-butanedione (6), 2,3-pentanedione (7), 1-methylpyrrole (10), pyridine (12),

furfural (30), 5-methylfurfural (34), 1-furfurylpyrrole (37), guaiacol (38), and acetylpyrrole (39).

These experiments enabled us to visualize a possible correlation between degree of roasting and a selected group of discriminating variables. The possibility to correlate “directly” the analytical data to the degree of roasting through the coffee color was then investigated by applying a multiple linear regression (MLR) approach. The results showed a good linear relationship between the color and the analytical set of data resulting in a correlation factor (r) of 0.9387. The applied model also fitted very well when the 18 samples of the test set were processed as is clearly shown in Table 3, where estimated and measured color values are reported together with the residual in prediction and confidence interval values. The MLR results confirmed that the 16 components of the aroma volatile

Table 4. Roasting Indices Identified for the Training Set (Arabica, Robusta, and Blend 50/50), Their Ranges, Averages, and RSD% Together with the Degree of Roasting and Color Range

no.	index	roast	color	Arabica			Robusta			blend 50/50		
				range	av	RSD%	range	av	RSD%	range	av	RSD%
1	pyridine/5-methylfurfural	light	58–62	826–1144	935	14.2	676–1053	849	17.4	845–1215	1032	13.1
		medium	48–52	1669–2023	1887	10.5	1391–1587	1477	4.5	1541–2173	1952	12.9
		dark	38–42	3307–4959	4333	13.2	2266–3089	2719	11.8	3046–5346	4411	17.9
2	pyridine/furfural	light	58–62	755–1612	1065	31.2	800–1395	1110	21.6	1141–1621	1331	14.1
		medium	48–52	2087–3594	2749	19.2	1832–2382	2042	9.4	2113–3480	2878	19.6
		dark	38–42	5496–7879	6541	11.7	2729–3919	3535	14.7	3997–7451	6298	20.8
3	2-methylfuran/2,3-pentanedione	light	58–62	1006–1505	1248	15.0	1945–3246	2579	20.4	1582–2836	1908	24.4
		medium	48–52	2247–3734	2772	18.4	3386–6898	4942	23.8	3115–5016	3836	18.8
		dark	38–42	5109–9141	6243	24.8	7360–10962	8960	14.0	5931–8729	7424	15.1
4	2,5-dimethylfuran/2,3-pentanedione	light	58–62	181–311	234	22.8	333–517	452	15.9	290–404	342	12.8
		medium	48–52	461–682	519	15.9	678–984	858	13.5	534–861	697	15.9
		dark	38–42	905–1305	1062	14.3	1268–1549	1392	9.2	999–1566	1273	14.9
5	2-methylfuran/furfural	light	58–62	64–92	79	14.0						
		medium	48–52	199–286	238	13.1						
		dark	38–42	425–914	641	27.1						
6	5-methylfurfural/2-acetylfuran	light	58–62	3500–4014	3751	5.2	3178–4041	3641	9.1	3187–3797	3553	6.6
		medium	48–52	2383–2843	2651	7.1	2367–2607	2524	3.3	2303–2818	2455	8.1
		dark	38–42	1433–1761	1571	7.2	1522–1885	1665	7.6	1325–1864	1513	12.9
7	2,3-pentanedione/2,3-butanedione	light	58–62	1186–1575	1396	9.9						
		medium	48–52	845–1075	959	9.6						
		dark	38–42	533–673	619	9.9						
8	guaiaicol/2-ethyl-3,6-dimethylpyrazine	light	58–62				427–646	532	16.7	314–425	362	11.9
		medium	48–52				911–1039	983	4.8	540–748	673	13.0
		dark	38–42				1407–1768	1621	8.4	884–1301	1151	12.7
9	pyridine/methylpyrazine	light	58–62	769–996	859	10.7	474–604	536	10.0	734–894	792	7.3
		medium	48–52	1134–1363	1232	6.9	717–756	735	2.2	1010–1195	1103	7.2
		dark	38–42	1626–1839	1760	4.3	907–1035	982	4.6	1321–1733	1603	9.6
10	pyridine/2,6-dimethylpyrazine	light	58–62	1557–1835	1690	6.4	844–1143	971	14.2	1236–1750	1508	12.7
		medium	48–52	2350–2799	2586	6.2	1250–1508	1389	7.0	2059–2297	2203	4.3
		dark	38–42	3199–4548	3947	11.0	1794–2125	1935	6.5	2978–3712	3371	7.0
11	pyridine/2,5-dimethylpyrazine	light	58–62	1632–2001	1793	8.6	913–1270	1052	15.1	1348–1894	1621	11.9
		medium	48–52	2667–3160	2882	6.9	1425–1638	1552	5.4	2255–2612	2472	5.2
		dark	38–42	3735–5084	4513	9.7	2098–2467	2239	6.8	3311–4311	3881	8.5
12	furfuryl acetate/2-ethyl-3,6-dimethylpyrazine	light	58–62	1898–2763	2351	16.9	1423–2000	1718	13.5	1938–2661	2266	10.9
		medium	48–52	3065–4386	3690	13.3	2387–2531	2480	2.3	2831–3586	3259	8.6
		dark	38–42	4486–5321	4964	6.0	2933–3232	3096	4.1	3690–4556	4247	8.3
13	pyridine/ethylpyrazine	light	58–62	3441–4067	3792	6.6	1676–2189	1905	12.9	2649–3682	3196	12.8
		medium	48–52	5193–6035	5703	5.9	2426–3036	2701	8.2	4323–4855	4589	4.6
		dark	38–42	6859–9879	8488	11.4	3403–4023	3732	6.4	6247–7622	6946	6.3
14	pyridine/2-ethyl-6-methylpyrazine	light	58–62	2632–3223	2942	8.4	1265–1747	1512	16.2	2017–3148	2529	16.6
		medium	48–52	4333–5279	4742	7.5	1997–2677	2204	12.3	3565–4361	3790	8.1
		dark	38–42	5736–9283	7303	15.6	2797–3455	3124	9.1	5724–6321	5906	3.7

Table 5. Experimentally Measured and Estimated Color Values Calculated with the Correlation Equations of the 13 Indices of Roasting Identified for Arabica Test Set Samples

no.	index	color values determined by the correlation equations of the indices of roasting identified for Arabica								
		A19	A20	A21	A22	A23	A24	A25	A26	A27
1	pyridine/5-methylfurfural	61	58	62	60	50	45	50	58	57
2	pyridine/furfural	61	57	62	61	49	44	48	58	56
3	2-methylfuran/2,3-pentanedione	58	47	61	56	45	17	31	48	44
4	2,5-dimethylfuran/2,3-pentanedione	59	47	62	57	46	17	31	48	43
5	2-methylfuran/furfural	59	55	61	58	47	33	40	54	52
6	5-methylfurfural/2-acetylfuran	58	48	59	55	48	38	40	48	47
7	2,3-pentanedione/2,3-butanedione	50	40	51	47	41	34	36	42	40
8	pyridine/methylpyrazine	59	49	67	57	46	36	41	54	52
9	pyridine/2,6-dimethylpyrazine	59	51	66	58	46	42	46	57	55
10	pyridine/2,5-dimethylpyrazine	59	51	66	58	45	39	44	55	54
11	furfuryl acetate/2-ethyl-3,6-dimethylpyrazine	42	17	53	35	41	15	22	34	32
12	pyridine/ethylpyrazine	58	50	66	57	45	39	44	55	53
13	pyridine/2-ethyl-6-methylpyrazine	57	48	64	54	43	39	44	54	53
6	5-methylfurfural/2-acetylfuran ^b	59 ^b	49 ^b	60 ^b	55 ^b	48 ^b	37 ^b	40 ^b	48 ^b	47 ^b
	experimentally measured color values	57	48	61	53	47	38	40	46	49

^b color determined by the unique equation built through the index 6 for all samples of the training set.

profile are directly connectable to the color and, as a consequence, to the degree of roasting.

Identification of Headspace Markers and/or Indices of the Degree of Roasting and Possible Correlation with the Roasted Coffee Color Value. This section explores the possibility of identifying headspace component(s) whose variation of abundance can directly be related to a physical property such as the color of the corresponding sample, to monitor the roasting process or, better, to measure the degree of roasting. The first step investigated the “answers” of the selected components characterizing the volatile fraction of coffee analyzed by HS-SPME-GC-MS to the different roasting conditions. The average dark/light area ratios of the target ion of each selected component of the training set were therefore measured. The resulting area ratios showed to be repeatable because the RSD% calculated for each component within the same variety was always below 20% (data not reported). These results indicated that the selected components can arbitrarily be classified into three main groups: (i) those whose abundance increase with roasting, that is, whose area ratios increase within the range fixed between 1.4 and 3.1; (ii) those whose area ratios tend to stay unvaried with ratios between 0.7 and 1.3; and (iii) those whose area ratios decrease with ratios between 0.3 and 0.6. Table 2 lists the trend of each component with roasting and the related light/dark ratios with Arabica, Robusta, and their 50/50 blend.

The next step implied the search for roasting indices with the aim of making the results more robust. Roasting indices are ratios of components that can be useful to find reliable relationships with color values. The mutual area ratios of the selected components for each variety were calculated through a routine carried out with a specific visual basic Excel macro. The resulting ratios were multiplied by a factor 1000 to facilitate data handling, and those ratios with a variation of at least 100 units between the degrees of roasting were arbitrarily considered as possible indices. In detail, 13 indices for Arabica, 12 for Robusta, and 12 for their 50/50 blend deriving from the ratio between 16 components as evidenced by PCA were found. Table 4 reports the three groups of indices for Arabica, Robusta, and their 50/50 blend with their average values and

RSD%. In this case, too, the resulting indices showed a good repeatability with RSD% mostly below 20%. Eleven indices are in common between Arabica and Robusta; the 2-methylfuran/furfural and 2,3-pentanedione/2,3-butanedione indices are specific for Arabica, and the guaiacol/2-ethyl-3,6-dimethylpyrazine index is specific for Robusta. The 50/50 blend indices were the same as those of the Robusta variety.

These indices have been assumed as indicative of the degree of roasting of the training set samples and, as already done with the single variables, the possibility to correlate linearly their average value to the degree of roasting expressed as color value was investigated for each sample within each variety or blend. Very good correlation coefficients were found (r always >0.93) for all indices identified for Arabica, Robusta, and 50/50 blend (see Table 2S in the Support Information). The color values were first predicted through an internal validation for each sample of the training set using the correlation equations obtained above and then compared to those determined experimentally via ground bean light reflectance. As expected, the results for the samples of the training set all fell within the limit acceptance (± 2 color units) in general adopted by industry. The equations were then applied to the test set consisting of 18 samples of different origins, varieties, and blends at different roasting degrees. The results to evaluate the index ability to predict color values are here discussed in detail for the nine Arabica samples of the test set. Table 5 reports the list of the color values calculated with the correlation equations of the 13 indices for Arabica and those experimentally measured. The results on the 11 indices common to all varieties and blends evidence that the 5-methylfurfural/2-acetylfuran index gave the lowest difference between experimental and estimated color values (Δ color), that is, within the limit of usual acceptance (± 2 color units) (Table 5 in bold). Similar consideration can be done for Robusta and blend samples: in these cases, too, the 5-methylfurfural/2-acetylfuran index gave the best Δ colors for all samples. The above results were obtained with equations specific for Arabica, Robusta, and their blend; a new unique correlation equation including all varieties was recalculated using experimental color values and 5-methylfurfural/2-acetylfuran ratios of all samples of the training

set. The reliability of the unique equation was tested by predicting the estimated color value of each sample of the test set with its experimental 5-methylfurfural/2-acetylfuran index. The results showed a good confidence and were within the acceptable limit as is shown in Table 5 for Arabica (in italic) and for all samples of the test set in Table 3. The very high value of the correlation coefficient of this equation ($r = 0.9989$) is further evidence of the reliability of the 5-methylfurfural/2-acetylfuran index as a marker of the degree of roast. 5-Methylfurfural is reported in the literature to be formed during Maillard reactions.^{19–21}

In conclusion, this study involving several coffee varieties and blends shows that the chemical profile of the coffee volatile fraction can chemometrically be related to the color obtained with the roasting process and that the 5-methylfurfural/2-acetylfuran index is linearly correlated to the color obtained with different roasting conditions.

The results here reported are a further confirmation that aroma composition can successfully be used to monitor the roasting process and that, in perspective, chemical and physical data can be associated to evaluate the behavior of different coffees when new blends have to be developed, to obtain a standardized aroma and to follow its formation.

In addition, the identified indices are further chemical data to define the degree of roasting of coffee in a complementary combination with the physical parameters and, in particular, color. The reported method is reliable and easy to automate and handle, in particular for industry where, in general, the quality of the processed green coffee and blend composition are constant as well as the roasting plant and time–temperature conditions.¹⁰ Conversely, it is more time-consuming than the methods to measure physical parameters, although analysis time is not critical, referring this method to controls carried out on the final product. Speed of analysis competitive to the physical methods can be achieved only by nonseparative approaches (i.e., HS-SPME-MS), by adopting the MS profile as chemical parameter.²²

■ ASSOCIATED CONTENT

● Supporting Information

Table 1S, data of repeatability and intermediate precision over 3 months of validation of a group of target coffee analytes and thujone's solution (ESTD); Table 2S, correlation equations and coefficients of the indices of roasting identified for Arabica, Robusta, and blend 50/50 obtained versus the average colors of the training set samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

The results here reported are part of the ITACA project of the POR-FESR "Competitività regionale e occupazione" 2007/2013, Asse 1, Misura I.1.1, "Piattaforme innovative" of the Piedmont Region (Italy), for which the authors are indebted.

Notes

The authors declare no competing financial interest.

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