

Kinetics of volatile organic compounds (VOCs) released by roasted Coffee during the first ten days after processing

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All relevant data are within the paper and its Supporting Information files.

Competing Interests:

The authors declare no competing interests.

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Abstract: The quality of coffee is linked to the aroma created by the chemical reactions that occur during the roasting process. While it is generally thought that roasted coffee is a stable product with a relatively long shelf-life, little information is available on the evolution (kinetic) of the volatile organic compounds (VOCs) in the days immediately following the process. The aim of this study is to determine the evolution of VOCs released by coffee beans, on samples of *Coffea arabica* (three different origins) and *Coffea canephora* (1 single origin), by using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) 24 hours after roasting, and for the next 9 days. Results confirmed the differences already highlighted in previous studies between the VOCs spectra of the two species. There were also significant differences in the intensity of emissions for the different origins of *Coffea arabica*, with the highest VOCs amount over time always detected in the Honduras Arabica samples. The involved detected protonated ions were grouped into three classes: compounds (ppbv) present with decreasing quantity; weakly increasing; almost constant trend; or always increasing. A complex dynamic emerged for the different protonated ions over time, which not only affects the mass spectra of the different species but also influences the configuration of the mass spectra of the different geographical zones of production.

1. Introduction

Two species contribute to the production of roasted beans, *Coffea arabica* (commercially known as Arabica) and *Coffea canephora* var.

Robusta (commercially known as Robusta). These two species are characterized by different economic value, with Arabica having the higher costs, due to both the different aromatic properties and the higher production costs. The two species are distinguishable by aromatic profiles (Gloess *et al.*, 2014; Yener *et al.*, 2014; Colzi *et al.*, 2017), and our previous work (Colzi *et al.*, 2017) demonstrated that the Proton Transfer Reaction - Time of Flight - Mass Spectrometry (PTR-ToF-MS) can be successfully used to distinguish between the aromatic profiles of these two species in each step of the processing chain (green beans, roasted beans, ground coffee, brews).

Little known are the changes in volatile organic compounds (VOCs) detected through headspace analyses, that could be used to recognize the genetic origin of the coffee stock and, within the same species, the geographical provenience as macro zone of production.

The quality of coffee is linked to the particular aroma created by the chemical reactions that occur during the roasting process (Maillard reaction). In addition to the roasting conditions, the quality of the product also depends on the genetic origin of the raw material. Roasted coffee is generally considered a stable product with a relatively long shelf-life. Nevertheless, little is known about the possible changes in the days immediately following the roasting process, which could alter the complex kinetics of VOCs determining the coffee aroma and therefore its value. Indeed, evidence indicates that chemical changes can still occur following the roasting process (Nicoli *et al.*, 2009), affecting the aroma of the brews. Confirming this, coffee made from freshly ground beans was found to have a stronger aroma, less bitterness and was preferred by expert panelist when compared with beans stored for 1 or 2 weeks (Ross *et al.*, 2006).

The present study has two goals: 1) to define the VOCs emission in coffee beans of different species and origins in the first days after roasting; 2) to ascertain if differences in the VOCs kinetics depend on the physical parameters of the roasted bean, such as porosity and the surface; 3) to explore the variation of the VOCs *spectra* emitted over time as a way to improve the possibility of distinguishing the different species and, within them, the origins of the different stocks.

2. Materials and Methods

Coffee samples

Coffee was sampled from medium-dark roasted

beans of 3 certified commercial stocks of *C. arabica* having different origin (Honduras, India, and Nicaragua) and from one of *C. canephora* var. Robusta (Congo). All just roasted coffee samples were provided by Caffè Magnelli S.r.l. (Florence, Italy) and stored in laminate packaging in the dark at room temperature (21-23°C) before the analysis. Mass spectrometry analyses were thus performed on 120 samples, subdivided in 90 *C. arabica* and 30 *C. canephora*.

VOCs analysis

VOC measurements on roasted beans were performed by using a commercial PTR-ToF 8000 model, from Ionicon Analytik GmbH (Innsbruck, Austria). The analyses were carried out starting approximately 25 hours after roasting, and proceeded for the next 9 days, with 24-hour intervals. Three 5 g samples were taken each day from the different coffee stocks for the analyses. The analyses were performed following the methodology reported by Colzi *et al.* (2017). Each sample was put into a 0.75 l glass container plugged with a cover in which two Teflon tubes are inserted, respectively connected to a zero-air generator (Peak Scientific, Glasgow, Scotland) and to the PTR-ToF-MS. Before each analysis, the jar was cleaned for 60 seconds with free VOCs air and after was incubated for 60 s. The measurement was carried out for 60 seconds using a dynamic headspace flushing flow rate of 0.75 l per minute (lpm). Since, the "temperature" is critical for the release of VOCs, the analysis was performed in a climatized room (22°C, 90% RH). The raw data were acquired by the TOFDAQ Viewer® software (Tofwerk AG, Thun, Switzerland) and subsequently VOCs were converted in ppbv using the formula described by Lindinger *et al.* (1998) and constant values for the reaction rate coefficient ($k_R=2.109 \text{ cm}^3 \text{ s}^{-1}$) to calculate concentration for each VOC (Cappellin *et al.*, 2011).

All detected compounds were tentatively identified by comparing the measured protonated ions with those reported in the extensive literature regarding the composition of VOCs released from coffee and in other previous PTR-MS studies (Colzi *et al.*, 2017; Flament and Bessière-Thomas, 2002; Gloess *et al.*, 2014; Lindinger *et al.*, 2008; López *et al.*, 2016; Maeztu *et al.*, 2001; Mondello *et al.*, 2005; Romano *et al.*, 2014; Yener *et al.*, 2014; Yeretziyan *et al.*, 2002).

Statistical data analysis

One-way analyses of variance (ANOVA) was per-

formed to compare the total VOCs content in 4 coffee stocks over 10 days; the separation of means was calculated by the Fisher's least significant difference (LSD) test. Computations were performed by Statgraphics Centurion XV v. 15.0.04.

On 90 Arabica and 30 Robusta samples, a multivariate partial least square-discriminant analysis (PLS-DA) was applied, as supervised classification method, on the spectral data ($n = 129$) obtained from a total of 120 coffee samples taken from 4 different stocks (Arabica Honduras, Arabica India, Arabica Nicaragua, and Robusta Congo), to determine whether it is possible to distinguish the genetic and geographical origin of the samples based on the VOC profiles. For a more detailed description of the method, see (Colzi *et al.*, 2017; Taiti *et al.*, 2017). Data were pre-processed by a logarithmic transformation ($\log+1$). The statistical analysis was performed by PLS-Toolbox v. 8.0.2 (Eigenvector Research Inc., West Eaglerock Drive, Wenatchee, WA) for MATLAB® R2015b (Mathworks Inc., Natick, MA, USA).

To monitor VOC trend in real-time in each coffee batch over the 10 days after roasting, a Batch Statistical Process Control (BSPC) was performed after logarithmic transformation ($\log+1$) on spectral (PTR-ToF-MS) data of the 120 samples. BSPC is the analysis of process data as a function of both correlation among the measured variables and correlation in time (also known as the "batch trajectory"). In this analysis the "measured variables" were 54 protonated ion signals selected on a total of 129 as tentatively identified in previous studies (Maeztu *et al.*, 2001; Flament and Bessi re-Thomas, 2002; Yeretian *et al.*, 2002; Mondello *et al.*, 2005; Lindinger *et al.*, 2008; Gloess *et al.*, 2014; Romano *et al.*, 2014; Yener *et al.*, 2014; L pez *et al.*, 2016; Colzi *et al.*, 2017), while the "time" was represented by the 10 days of surveys. The VOCs data were subdivided into 4 "batches" (experiments) (Arabica Honduras, Arabica India, Arabica Nicaragua, and Robusta Congo) that were subsequently subdivided into "Steps" (10 steps = 10 days). A summary Principal Component analysis (PCA) was then applied, after mean centering, summarizing the change in measured variables over the batch progress based on the "mean" as a reference statistic, sufficiently sensitive to the trajectory profile, to capture the trends in the trajectories of the variables.

As unsupervised classification method a hierarchical clustering (Ward method, Euclidean distance) was performed on the data expressed as percentage of the highest value of each protonated ions, related to

the 90 Arabica samples, which represent all the samples unequivocally related to the same species. Computations were performed by XLSTAT 2014.5.03 software.

3. Results and Discussion

Figure 1 shows the amount of the VOCs emitted from the 4 stocks during the 10 days of testing, and the related trend curves (2nd grade polynomials: for Arabica Honduras $y = -61.937x^2 + 656.19x + 4604$; for Arabica India $y = -95.22x^2 + 1126x + 455.4$; for Arabica Nicaragua $y = -108.42x^2 + 1250.8x + 1382.7$; for Robusta Congo $y = -7.1514x^2 + 111.47x + 1705.4$). The compared samples of the 4 batches were strongly differentiated both for amounts of emitted VOCs and for trends (Table 1). The Robusta (Congo) recorded the lowest emissions, that did not statistically change during the considered time period. By contrast, the comparison between the Arabica samples highlighted key differences between the 3 batches. Coffee samples from Honduras were very rich in VOCs. The Nicaraguan samples had a less intense emission, and quantitatively increased only until the 5th day. Although the amount of VOC emitted resulted lower compared with the Nicaraguan samples, the Arabica samples of Indian origin had a similar VOC emission trend with a peak on the 5th day after roasting (Fig. 1) (Table 1).

The data represented in figure 1 were explored through two different methods of multivariate analysis: a PLS-DA (Fig. 2), and a PCA applied to the results of a batch process (Fig. 3). These approaches allow to highlight the two different aspects related to the fac-

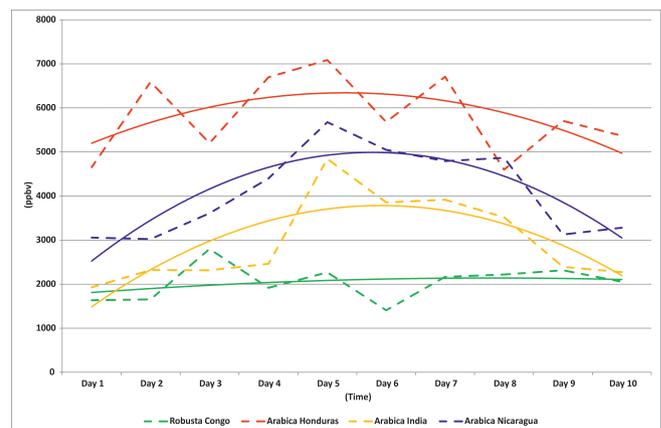


Fig. 1 - Total VOCs emission (ppbv) in the different Coffee stocks over the time (dotted line) and related trend curves (whole line).

Table 1 - Trend of total VOCs emission (ppbv) in 4 coffee batches over 10 days

Time	Total VOCs (ppbv)				Average *
	Arabica Honduras	Arabica India	Arabica Nicaragua	Robusta Congo	
Day 1	4654.6 ± 340.3	1928.8 ± 353.9	3055.9 ± 125.0	1634.7 ± 249.7	2818.5 ± 1261.3 a
Day 2	6588.9 ± 516.63	2321.3 ± 392.1	3023.0 ± 465.0	1653.1 ± 267.0	3396.5 ± 2022.5 ab
Day 3	5200.3 ± 92.8	2315.7 ± 5.19	3609.9 ± 250.3	2797.1 ± 123.0	3480.8 ± 1150.8 ab
Day 4	6694.6 ± 2105.3	2461.9 ± 756.2	4398.1 ± 931.3	1916.7 ± 491.7	3867.8 ± 2223.7 abc
Day 5	7087.2 ± 2509.9	4844.2 ± 314.3	5677.0 ± 912.4	2267.03 ± 197.3	4968.8 ± 2162.8 c
Day 6	5680.3 ± 1146.0	3856.5 ± 449.9	5048.2 ± 906.3	1408.3 ± 148.6	3998.4 ± 1826.5 abc
Day 7	6706.1 ± 576.0	3915.7 ± 1614.9	4792.3 ± 747.9	2166.0 ± 684.7	4395.0 ± 1907.6 bc
Day 8	4600.6 ± 522.9	3517.5 ± 481.2	4867.8 ± 632.7	2218.1 ± 355.4	3801.0 ± 1173.7 abc
Day 9	5704.1 ± 1286.2	2393.8 ± 681.6	3127.7 ± 890.6	2315.0 ± 586.2	3385.2 ± 1630.0 ab
Day 10	5368.0 ± 862.5	2271.3 ± 646.7	3281.8 ± 934.5	2055.4 ± 459.3	3244.1 ± 1510.8 ab
Average *	5828.5 ± 1345.7 d	2982.7 ± 1102.6 b	4088.2 ± 1126.8 c	2043.1 ± 513.0 a	3735.6 ± 1764.0

Average ± S.D.

*Different lower case letters within a row or a column indicate difference by the LSD test at the 95.0% confidence level (p=0.05).

tors influencing the process: 1) species and origins (PLS-DA applied to 120 coffee samples based on 129 detected signals), and 2) the processes that develop over time expressed as coefficients of 54 selected variables with PC1 during the 10 days of surveys after roasting (PCA applied to a BSPPC).

The score plot from PLS-DA shown in figure 2 confirmed that VOC analysis using the PTR-ToF-MS technique can indeed be used to distinguish Robusta from Arabica samples. Furthermore we found that the evaluation of the whole spectrum of VOC emission during 10 days of surveys can also be used to determine within the same species, albeit with some overlapping, the different origins (Fig. 2).

In the figure 3, where the dynamics of the single 54 tentatively identified protonated ions related to VOCs found in the Arabica samples of the three different origins are reported, a downward shift of the VOCs pool on the 4th day is observed (Fig. 3, red cir-

cle) while, in general, a progressive slight decrease and compression of the VOCs complex can be seen in the time, up to the 10th day.

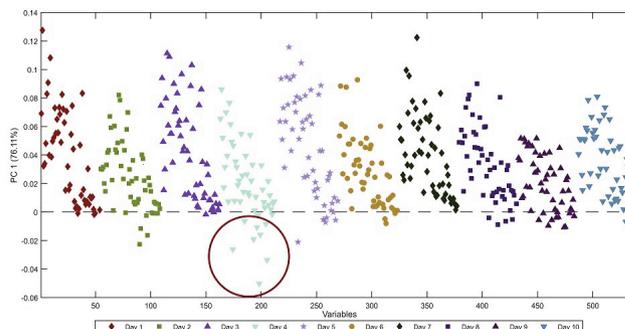


Fig. 3 - Score plot from a PCA applied to a BSPPC, showing the dynamic over the 10 days of surveys evidenced by the VOCs complex (54 protonated ion signals tentatively identified) related to 120 Coffee samples. Outlier samples were highlighted by a red circle.

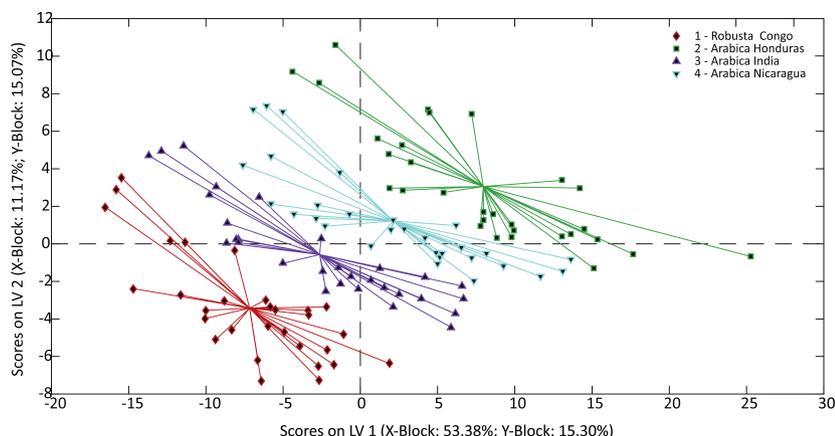


Fig. 2 - Score plot of PLS-DA model and summary statistics for the 4 Coffee stocks samples based on 129 protonated m/z.

Statistics	Robusta Congo	Arabica Honduras	Arabica India	Arabica Nicaragua
LVs	5	5	5	5
SE (Cal)	1.000	1.000	0.846	1.000
SP (Cal)	0.987	1.000	0.908	0.961
SE (CV)	0.962	0.917	0.654	0.923
SP (CV)	0.961	0.974	0.803	0.895
SE (P)	1.000	1.000	0.750	0.750
SP (P)	1.000	1.000	0.786	1.000
Class. error (Cal)	0.006	0.000	0.122	0.019
Class. error (CV)	0.038	0.054	0.271	0.091
Class. error (P)	0.000	0.000	0.232	0.125
RMSEC	0.186	0.159	0.300	0.254
RMSECV	0.246	0.246	0.402	0.343
RMSEP	0.251	0.154	0.365	0.263

In the dendrogram obtained by the hierarchical classification of the three Arabica stocks (90 samples) based on 54 protonated ions, two main clusters (A and B) were identified and, within the cluster B, a further division into two subgroups of compounds (B1 and B2) emerged (Fig. 4). Each group was characterized by a particular trend in the 10 days of the test. Cluster A combined compounds characterized by a decreasing trend over time. On the other hand, cluster B grouped compounds with increasing trend (B1), or compounds at first increasing and then decreasing their amount over the time, in slightly different way (B2).

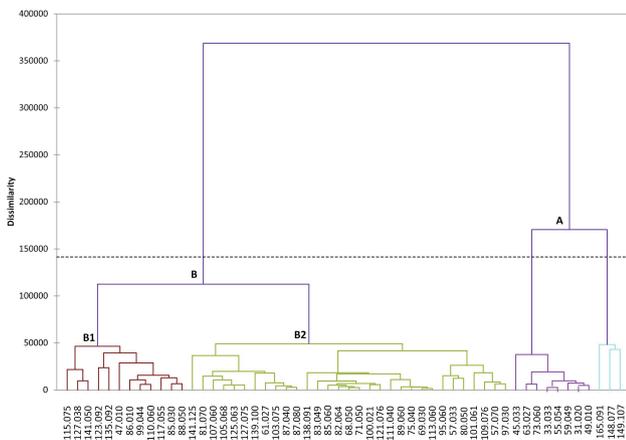


Fig. 4 - Dendrogram from cluster analysis of 90 Arabica sample based on 54 selected protonated m/z .

Figure 5 shows the trends, for the three Arabica stocks, of three protonated ions chosen as representative of the groups emerged by the dendrogram reported in figure 4. In particular, mass $m/z = 45.030$, representative of the group A, was always decreasing, while mass $m/z = 99.040$ (B1) showed an upward trend and mass $m/z = 82.060$ (B2) initially increased

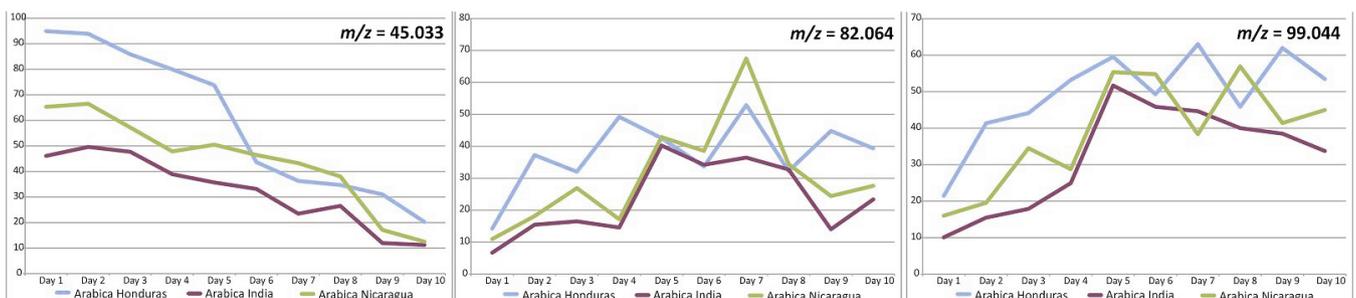


Fig. 5 - Trend of $m/z = 45.030$, $m/z = 99.040$, and $m/z = 82.060$, representative of group A, subgroup B1, and subgroup B2, respectively. Average values for each of the 4 stocks from normalized data.

and and then decreased to finally stabilize on intermediate values.

4. Conclusions

Roasted coffee beans are considered resistant to spoiling phenomena, and as such are marketed, or considered for subsequent treatments. Nevertheless, little is known about the possible changes in the days immediately following the roasting process, which can determine complex variations in the kinetics of VOC emission within the different species and of different origins. The data set collected in this work highlights that samples of Arabica and those coming from Honduras production area have the highest level of VOC emissions and the greater dynamism in the kinetics of change. These changes in the VOC kinetics in the 10 days following the roasting process found within the Arabica samples also improved the separation of the samples based on their geographical origin.

The Arabica species samples hierarchical classification applied to the 54 selected protonated ions related to VOCs and/or fragment of VOCs allowed to pool them together, independently of the chemical family they belong to, in relation to their kinetics over time.

Three groups of VOCs were highlighted from the dendrogram (Fig. 4). The first, which clustered together those that decrease over time. On the other hand, the second and third group respectively combined VOCs that either had an upward trend but then stabilized over time, or those that constantly increased.

The analysis of the VOCs highlighted dynamics that changed over time. This was associated with the simultaneous presence of VOC whose amount

in the *spectrum* decreased while others tended to increase. The combined resulting variability determined changes of coffee aromas in the 10 days immediately following the roasting.

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