Extraction kinetics of coffee aroma compounds using a semi-automatic machine: On-line analysis by PTR-ToF-MS

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ABSTRACT

The hot-water extraction process used to make an espresso coffee is affected by a large number of factors. A proper understanding of how these factors impact the profile of the final cup is important to the quality of an espresso coffee. This work examines the effect of water temperature and pressure on the extraction kinetics of volatile organic compounds (VOCs) in coffee. This was achieved by on-line monitoring of the volatiles directly from the coffee flow, using proton-transfer-reaction time-of-flight mass-spectrometry (PTR-ToF-MS). Using hierarchical cluster analysis (HCA), tentatively identified compounds were grouped into 5 families according to their time–intensity profiles. VOCs grouped into each family had similar physicochemical properties while polarity was found to be one of the main forces driving VOC extraction kinetics. The effect of pressure was studied by extracting espresso coffees at 7, 9 and 11 bar. A pressure of 11 bar resulted in an increased extraction of volatiles over the entire extraction time (25 s). To study the effect of temperature, espresso coffees were extracted at 82, 92 and 96 °C. An increase in temperature produced a significant increase in the extraction of VOCs, especially during the last part of the extraction. The effect of temperature on extractability was more pronounced for the less polar compounds.

1. Introduction

Coffee is one of the most widely consumed beverages [1]. The beverage is made from coffee beans that are first harvested and processed, then roasted and ground before finally being extracted. Each and every single transformation step, from the seed to the cup, must be mastered and performed with great care in order to deliver the best quality in the cup [2–9]. Here, we focused on the last and crucial transformation step, the extraction – more specifically, espresso coffee extraction using a semi-automatic coffee machine.

During extraction, soluble compounds are dissolved and, depending on the extraction technique, non-soluble compounds are washed away with the extraction water, ending up in the extract as dissolved or suspended solids [10–15]. Many different extraction techniques have been introduced over the past centuries, which vary according to factors such as geography, culture and social context, as well as personal preferences; these different factors can

result in vastly different flavor profiles in the extract. Of all coffee brewing methods, espresso brewing is among the most popular techniques.

Starting with whole roasted coffee beans, the preparation of the "perfect" espresso is as much a science as an art. It is the result of the interplay between several parameters that must be carefully controlled. These parameters include the particle size distribution of the ground coffee, the water-to-coffee ratio, the final volume of the brew in the cup and the temperature and pressure of the extracting water. An espresso is defined as a 25–35 ml beverage prepared from 7 to 9 g of coffee, through which clean, 92–95 °C water has been forced at 9–10 atmospheres of pressure, and where the grind of the coffee is such that the brewing 'flow' time is approximately 20–30 s [11].

An increase in the extraction temperature, for example, leads to higher quantities of non-volatiles (i.e. total solids, caffeine, lipids) as well as higher quantities of some volatiles, such as pyrazines, in the final cup [16–18]. This may result in over-extraction and a coffee cup with negative flavor notes, such as woody, burnt or acrid flavors. Increasing pressure up to 11 bar also resulted in coffees with higher odor intensity and lower consumer acceptance than coffees

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extracted at 7 or 9 bar [19]. In these previous studies, the authors focused on the composition and sensorial attributes of the final cup in order to assess the impact of water temperature and pressure on espresso preparation. In a complementary line of research, some scientists have been exploring the extraction kinetics of the volatiles that contribute to the aroma of coffee. Two main methods have been previously used to determine the extraction kinetics of coffee volatiles: off-line analysis of fractions using GC–MS [20] and on-line analysis of the volatiles released by the coffee flow using Proton Transfer Reaction Time of Flight Mass Spectrometry (PTR-ToF-MS) [21,22]. In both cases, the methods were applied to single-serve capsule systems in which both temperature and pressure were kept constant. The objective of the research presented here was to investigate the effect of temperature and pressure on the extraction kinetics of coffee aroma compounds by applying on-line analysis by PTR-ToF-MS. We focused on 46 VOCs in particular and explored the link between extraction kinetics and their physicochemical properties.

2. Materials and methods

2.1. Coffee extraction

The yellow bourbon variety of *Coffea Arabica* L. from Mogiana, Brazil (Roaster: Kaffeepur, Switzerland, "Yellow Sun"), roasted to a medium roast degree of 95 Pt (Colorette 3b, Probat, Germany), was used for all of the extraction experiments. The coffee was frozen two weeks after roasting and defrosted 12 h prior to the experiments to ensure a constant and equal freshness of the coffee for all of the experiments. Less than one month elapsed from roasting to extraction. The beans were ground using a Compak K10 grinder (Barcelona, Spain) using position 47 on a scale from 0 (fine ground, Turkish coffee) to 60 (coarse ground, French Press pot). 18 g of the ground coffee were weighed into a double porta-filter basket, tapered by hand and extracted for 25 s using a semi-automatic coffee machine (Dalla Corte Mini, Dalla Corte, Italy). The water used for the extractions was commercially available Volvic mineral water (total mineralization 130 mg/L; HCO_3^-: 71 mg/L; SO_4^{2-}: 8.1 mg/L; Na^+: 11.6 mg/L; Ca^{2+}: 11.5 mg/L; Mg^{2+}: 8 mg/L). Extractions were performed with five different combinations of water pressure and temperature, one within the recommendations provided by the Specialty Coffee Association of America (center point conditions) and the others with values that exceed or were lower than recommended: (9 bar/92 °C: center point; 7 bar/92 °C; 11 bar/92 °C; 9 bar/82 °C; and 9 bar/96 °C). Although all the coffees were prepared by an experienced barista, variations resulting from the manual preparation process were expected. To reduce this variability, we performed 8 extractions for each set of conditions and selected the 5 replicates for which the final weight of the extract was closest to 30 g, ending up with coffee weights in the range of 31.5 g ± 2 g.

2.2. Sampling setup

Volatiles were sampled using a previously used setup [22], with certain modifications (Fig. 1). The extracted coffee flowed into a custom built system that was heated to 96 °C to avoid condensation. Volatiles were drawn out using a vacuum pump and diluted 10-fold with dry compressed air to reduce their concentration to the dynamic range of the PTR-ToF-MS being used.

2.3. PTR-ToF-MS

A commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was used for all measurements. The diluted sample was introduced via a 90 °C heated sampling line into
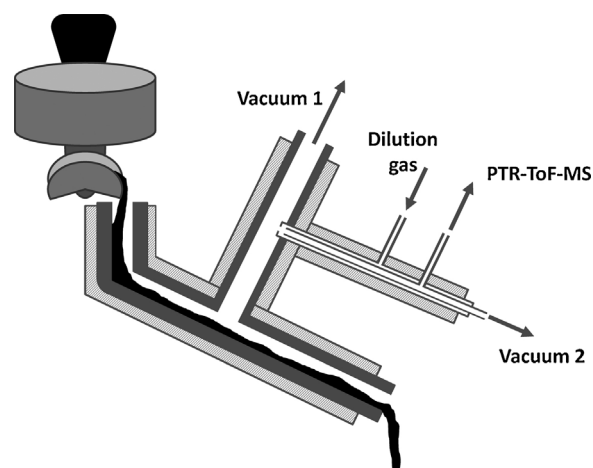

Fig. 1. Setup used for the online monitoring of volatiles during coffee extraction.

the drift tube operated at 2.3 mbar, 90 °C and 600 V drift tube voltage, resulting in an E/N value (electric field strength/gas number density) of 140 Townsend (Td, 1 Td = 10^{-17} cm^2/V s). PTR-ToF-MS data were recorded by TOFDAQ v.183 data acquisition software (Tofwerk AG, Thun, Switzerland). Mass spectra were recorded in the mass-to-charge (m/z) range of 0–300 with one mass-spectrum recorded every 2 s.

2.4. Data processing

Dead time correction, mass calibration, peak extraction and integration were performed using PTR-TOF DATA Analyzer software (v4.17) [23]. Duty cycle corrected signals were normalized to 10^6 H_3O^+ primary ions and the concentration in parts per billion by volume (ppbv) was estimated using 2×10^{-9} cm^3 s^{-1} as a reaction rate constant coefficient [24].

More than 500 mass peaks were detected in the range 0–300 m/z. Ions not related to the sample (O_2^+, NO^+ and water clusters) were eliminated, the background was subtracted and a concentration threshold of 1 ppb was set for further peak selection. This resulted in a reduction to 120 mass peaks that were present in all of the samples. From these peaks, 46 compounds (Table 1) were tentatively identified by comparing them to the literature [25,26].

2.5. Statistical analysis

The areas under the time–intensity curves were calculated for the 120 mass traces of each of the five replicates of the five different extraction conditions. Principal Component Analysis (PCA) was performed using mean centered and scaled areas. Analysis of Variance (ANOVA) was applied to assess the effect of the different extraction variables on the total area of the selected compounds using Tukey's Honest Significant Difference (HSD) post hoc test ($p < 0.01$). In order to identify compounds with similar dynamic behavior, first the time–intensity profiles of all the 120 m/z were normalized to their maximum intensity before performing self-organizing tree algorithm (SOTA). Subsequently the same SOTA analysis was performed on only the tentatively identified 46 VOCs. In addition the normalized time–intensity profiles of the 46 tentatively identified compounds were subjected to Hierarchical Cluster Analysis (HCA) using Ward's minimum variance method and half-squared Euclidean distances. All analyses were performed and all graphs were created using existing packages (clValid, multcomp, and ggplot2) and scripts developed in R [27].

Table 1
List of tentatively identified mass peaks, assigned sum formula and physic-chemical properties. Compounds are grouped in families according to the results obtained from Hierarchical Cluster Analysis (HCA).

Compound number	Measured m/z	Theoretical m/z	Sum formula	Tentative identification	Boiling point/°C	log K_{aw}	Vapor pressure/ KPa at 25 °C	Water solubility/g L^{-1}	log K_{ow}
Family A									
1	31.019	31.018	CH_3O^+	Formaldehyde	−19	−4.861	518	400	0.35
2	33.034	33.033	CH_5O^+	Methanol	65	−3.730	16.9	1000	−0.77
3	45.034	45.033	$C_2H_5O^+$	Acetaldehyde	20	−2.564	120	1000	−0.34
4	59.047	59.049	$C_3H_7O^+$	Acetone	56	−2.790	30.9	1000	−0.24
				Propanal	48	−2.523	42.3	306	0.59
5	61.029	61.028	$C_2H_5O_2^+$	Acetic acid	118	−5.388	2.09	1000	−0.17
6	75.045	75.044	$C_3H_7O_2^+$	Propanoic acid	141	−4.740	0.471	1000	0.33
				Ethyl acetate	77	−2.261	12.4	80	0.73
7	87.046	87.044	$C_4H_7O_2^+$	2,3-Butanedione	88	−3.265	7.57	200	−1.34
				Butyrolactone	204	−5.667	0.060	1000	−0.64
Family B									
8	47.014	47.013	$CH_3O_2^+$	Formic acid	101	−5.166	7.01	1000	−0.54
9	57.036	57.033	$C_3H_5O^+$	2-Propenal	53	−2.302	36.5	212	−0.01
10	71.051	71.049	$C_4H_7O^+$	2-Methylpropenal	68	−2.023	20.7	50	0.74
				3-Buten-2-one	81	−2.721	12.2	60.63	0.41
11	85.066	85.065	$C_5H_9O^+$	Methylbutenal	117	−2.444	2.39	25	1.15
12	89.061	89.060	$C_4H_9O_2^+$	Methylpropanoate	80	−2.148	11.2	62.4	0.84
13	101.061	101.060	$C_5H_9O_2^+$	Pentanedione	138	−4.017	0.495	166	0.4
				γ-Valerolactone	192	−2.255	0.073	93.81	0.11
Family C									
14	55.057	55.054	$C_4H_7^+$	1,3-Butadiene	−4	0.478	281	0.735	1.99
15	63.03	63.026	$C_2H_7S^+$	Dimethyl sulfide	37	−1.182	66.9	22	0.92
16	73.064	73.065	$C_4H_9O^+$	Butyraldehyde	75	−2.328	14.8	71	0.88
				2-Methylpropanal	65	−2.133	23.1	89	0.74
				Butanone	80	−2.633	12.1	223	0.29
Family D									
17	68.051	68.049	$C_4H_6N^+$	Pyrrole	130	−3.133	1.11	45	0.75
18	69.036	69.033	$C_4H_5O^+$	Furan	31	−0.656	80.0	10	1.34
19	70.041	70.040	$C_2H_4N_3^+$	Triazole	203	−4.212	0.080	240	−0.29
20	82.064	82.065	$C_5H_8N^+$	Methylpyrrole	112	−3.388	2.85	10	1.21
21	95.062	95.060	$C_5H_7N_2^+$	Methylpyrazine	135	−4.046	1.29	80	0.21
22	97.031	97.028	$C_5H_5O_2^+$	Furfural	162	−3.861	0.295	77	0.41
23	99.046	99.044	$C_5H_7O_2^+$	Furfuryl alcohol	171	−5.493	0.081	1000	0.28
24	103.077	103.075	$C_5H_{11}O_2^+$	Hydroxypentanone	179	−3.255	0.033	48.868	0.2
				1-Methyl-2-butanoic acid	177	−4.468	0.065	45	1.18
25	109.078	109.076	$C_6H_9N_2^+$	Dimethylpyrazine	156	−3.838	0.365	38.16	0.54
				Ethylpyrazine	153	−3.999	0.476	28.41	0.69
26	111.046	111.044	$C_6H_7O_2^+$	Acetylfuran	175	−3.398	0.126	39.1	0.52
				5-Methylfurfural	187	−3.218	0.091	29.11	0.67
27	113.062	113.060	$C_6H_9O_2^+$	5-Methylfurfuryl alcohol	191	−5.010	0.017	49.18	0.99
28	115.075	115.075	$C_6H_{11}O_2^+$	4-Methyltetrahydro-2H-pyran-2-one	213	−2.131	0.025	32.19	0.6
29	117.057	117.055	$C_5H_9O_3^+$	2-Oxopropyl acetate	171	−4.467	0.199	151.9	−0.19
30	131.073	131.070	$C_6H_{11}O_3^+$	Ethyl acetoacetate	181	−4.309	0.104	110	0.25
Family E									
31	80.052	80.049	$C_5H_6N^+$	Pyridine	115	−3.347	2.77	1000	0.65
32	87.082	87.080	$C_5H_{11}O^+$	Methylbutanal	94	−2.187	1.39	10	1.23
33	105.068	105.070	$C_8H_9^+$	Vinylbenzene	145	−0.949	0.853	0.310	2.95
34	107.06	107.060	$C_6H_7N_2^+$	Ethenylpyrazine	167	−4.121	0.240	21.38	0.84
35	110.064	110.060	$C_6H_8NO^+$	2-Acetylpyrrole	220	−6.171	0.004	17.59	0.93
36	121.075	121.076	$C_7H_9N_2^+$	Ethenylmethyl-pyrazine	188	−3.762	0.072	7.284	1.33
37	123.093	123.092	$C_7H_{11}N_2^+$	2-Ethyl-5-methylpyrazine	169	−3.715	0.081	1.903	1.53
				Trimethylpyrazine	171	−3.795	0.193	15.21	0.95
38	125.063	125.060	$C_7H_9O_2^+$	Guaiacol	205	−4.309	0.014	18.7	1.32
				Methylbenzenediol	241	−8.580	4.6×10^{-4}	16.48	1.58
39	127.075	127.075	$C_7H_{11}O_2^+$	Ethylbenzenediol	265	−8.456	1.0×10^{-4}	5.52	2.07
				Ethylcyclopentanedione	225	−5.081	0.017	104.8	−0.05
40	135.091	135.092	$C_8H_{11}N_2^+$	5-Methyl-6,7-dihydro-5H-cyclopentapyrazine	201	−3.948	0.019	2.416	1.83
41	138.087	138.091	$C_8H_{12}NO^+$	2-Acetyl-1-ethylpyrrole	209	−4.718	0.022	3.716	1.6
				3-Acetyl-2,4-dimethylpyrrole	247	−6.085	3.1×10^{-4}	3.327	1.65
42	148.077	148.076	$C_9H_{10}NO^+$	1-Furfurylpyrrole	292	−3.195	0.011	0.568	2.5
43	149.112	149.107	$C_9H_{13}N_2^+$	Dihydro-dimethyl cyclopentapyrazine	237	−3.985	0.004	0.557	2.51
44	165.093	165.091	$C_{10}H_{13}O_2^+$	Allylguaiacol	264	−5.706	3.1×10^{-4}	0.305	2.73
Separate compounds									
45	57.072	57.070	$C_4H_9^+$	1-Butene	−1	0.978	300	0.2	2.4
46	83.051	83.049	$C_5H_7O^+$	Methylfuran	65	−0.615	20.8	3	1.85

3. Results and discussion

3.1. Dynamics of extraction

During the 25 s coffee extraction, the intensity over time of the volatile compounds in the coffee was monitored and analyzed in detail for the 46 tentatively identified compounds. The focus was put on these 46 compounds, in contrast to the complete list of 120 compounds, as this allowed to link the identified VOC to their physical properties. Hierarchical Clustering Analysis (HCA) was firstly applied to the normalized time–intensity profiles of the center point experiment (9 bar/92 °C) resulting in the classification of 44 compounds into five different families that shared similar time–intensity profiles (Table 1 and Fig. 2). Two compounds did not fit into any of the five main families: 1-butene ($C_4H_9^+$) and methylfuran ($C_5H_7O^+$). In the case of 1-butene, the intensity showed an irregular profile during extraction, with high standard deviation between the replicates. The m/z attributed to 1-butene (57.073) has also been reported as an alcohol fragment [28]. This suggests m/z 57.073 does not correspond only to 1-butene but rather to a superposition of ion intensities from additional compounds and/or fragments with the same mass-to-charge ratio, which interfered with the 1-butene signal. In the case of methylfuran, the signal rose to its maximum value at 4–6 s and then remained constant until the end of the extraction process. This behavior was not observed for any other compound. It should also be noted that the time–intensity profiles recorded for methylfuran did not show any significant differences for any of the extraction conditions analyzed.

HCA was subsequently applied to the time–intensity profiles of all the extraction conditions together, to check if the VOC families observed for the center point were independent of the extraction conditions. Essentially the same five families were reproduced when considering all conditions, although a few compounds clustered differently for the lowest pressure and the highest temperature conditions, relative to the center pint extraction: (i) for extraction at 7 bar, three compounds from family D (methylpyrazine, furfural and acetol acetate) were classified as members of family B; (ii) for extraction at 96 °C, all three compounds from family C (butadiene, dimethylsulfide and methylpropanal) appeared in family B, and four compounds from family E (ethenyl pyrazine, pyridine, acetylpyrrole and ethylbencenediol) appeared in family D.

Clustering was performed only on the 46 tentatively identified compounds. In order to confirm that those compounds are representative of all the measured m/z, we used the Self Organizing Tree Algorithm (SOTA) on a data set composed of the 3000 intensity profiles recorded (5 brewing conditions × 5 replicates × 120 m/z). Six clusters were obtained of which five were identical to the main

families and a sixth one containing only 49 profiles corresponding to mass traces that did not fit with the other families (Supplementary material 1). This corroborates the robustness of the five main families of volatile, and of their corresponding classification according to different extraction dynamics during espresso brewing.

Fig. 2 shows the time–intensity profiles of the center point experiment for each of the five families. Time zero corresponds to the moment at which the pump of the coffee machine started to run, however, coffee did not start to flow out of the portafilter until 5–6 s later. After 25 s, the pump was stopped and 1 s later the coffee flow also stopped. This figure shows the distinguishing features found between the different families.

Family A was characterized by a fast rise in intensity 6 s after the coffee machine started to pump water, reaching maximum intensity at 10 s. From that point until the end of the extraction, this family exhibited the fastest decrease in intensity of all of the families, with final values lower than 40% of the maximum intensity. Independent of the extraction conditions, the same seven compounds were always clustered into this family.

Family B's profile was similar to that of A during the first 10 s, after which and in contrast to compounds of family A the intensity did not change (i.e. decrease) significantly, resulting in a plateau of maximum intensity until second 16. At this point it started to decrease, before finally reaching 60–70% of the maximum of the intensity at the end of the extraction process.

Family C exhibited a local maximum in intensity (visible as a peak shoulder) at 4 s. This shoulder was also present in the other families, although much less pronounced. From that point on, the intensity rose rapidly until it reached a maximum at 10 s, after which the profile was almost identical to family B, with a plateau until 16 s and a subsequent decrease. This high similarity in profiles, in particular for the second half of the extraction time, meant that families B and C were clustered together for the extraction at 96 °C. Despite not being separated by HCA at the highest extraction temperature, the profiles for family C could still be visually differentiated by the characteristic shoulder at 4 s.

In **Family D**, the intensity started to rise after 6 s and reached a maximum at between 14 and 16 s. After that, the intensity decreased to 70–80% of the maximum. For extraction at 7 bar, three compounds from this family were grouped together with those in family B. As will be discussed in Section 3.2, extraction at 7 bar showed a slower increase in intensity and lower maximum intensities than the center point experiment (9 bar/92 °C) for compounds belonging to family B, making the profiles of this family more similar to those of D and hence affecting the classification into families.

Family E showed the slowest increase in intensity from 6 s to a maximum at 20 s. The intensity decreased slightly from the maximum until the end of the extraction, with values that were approximately 80–95% of the maximum intensity. When the extraction was performed at the highest temperature, the characteristic decrease in intensity during the last part of the extraction was not observed for some compounds in family D. In fact the intensity increased until the end of the extraction for some compounds in family E (Fig. 5). This effect resulted in similar profiles to family D, meaning that four compounds from family E were grouped with those of family D for the 96 °C extraction.

3.2. Classification of families

The extraction of aroma compounds from the coffee beans by water is mainly driven by polarity [20]. For the 46 compounds that were tentatively identified, values for log K_{ow} (partition coefficient between octanol and water), log K_{aw} (partition coefficient between air and water), water solubility, boiling point and vapor pressure are provided in Table 1. Apart from a few exceptions, water solubility decreases and log K_{ow} increases as one moves from family A
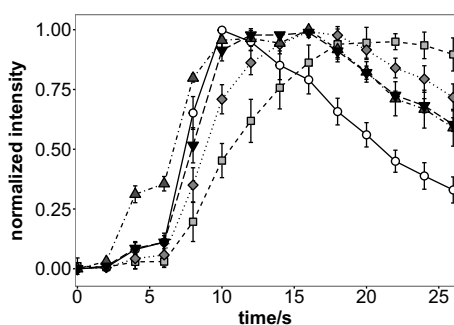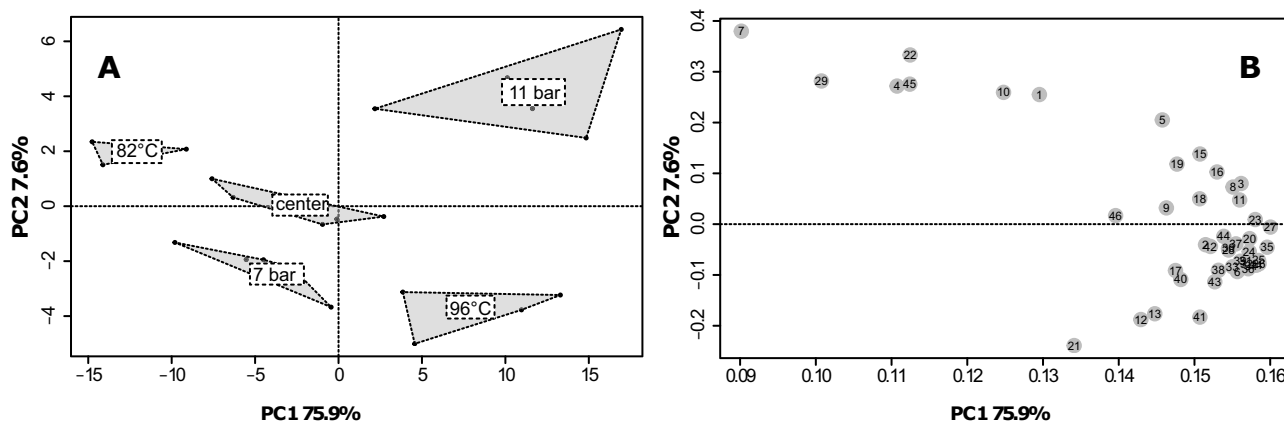

Fig. 2. Normalized time–intensity profiles of the different families of compounds extracted at 92 °C and 9 bar. Lines represent the mean and the error bars represent the standard deviation of all the compounds in family A (●), B (▼), C (▲), D (◆), E (■).

Fig. 3. Score-plot (A) and loading-plot (B) of the first two components detected in the PCA, performed on the area under the time–intensity profiles for the 120 *m/z*. Data points on the score plot represent the five different extractions performed for each set of conditions. Numbers on the loading plot correspond to the compound list in Table 1. Non-identified compounds have been omitted from the loading plot for the purposes of clarity. A plot showing the loadings of all 120 *m/z* can be found in the supplementary materials.

to E, indicating that the most polar compounds belong to family A and the least polar ones to family E. Compounds in family A – with water solubility of between 80 and 1000 g L^{-1} and log K_{ow} between 1.34 and 0.73 – were extracted quickly, within the first seconds of extraction, and their concentration levels decreased significantly at the later stage of the extraction. Polarity and water solubility of the compounds in family B are slightly lower than in family A, meaning that the intensity also increased quickly at the beginning, but their extraction lasted longer. In family C, the compounds have a lower water solubility (0.7–223 g L^{-1}) and lower polarity (log K_{ow} 0.29–1.99) than those of families A and B. This would imply that these compounds are extracted more slowly from the coffee bed. However, their intensity did increase rapidly during the first 6 s. This fast increase in signal can be attributed to the high volatility of the compounds in this family (vapor pressure: 12–281 KPa and log K_{aw}: −2.64 to 0.48) that favored their release to the gas phase. This could also explain the characteristic shoulder at 4 s, time at which the coffee had not started to flow, but the coffee powder had already been wetted by hot water and, as a consequence, compounds were released to the gas phase. Families D and E contain the least polar, water soluble and volatile compounds. Therefore compound transfer from the ground coffee particles to water was slow, with an important fraction of these compounds still being extracted after 25 s.

Grouping of dynamic data into families can also be used to improve compound identification. Generally, tentative identification of compounds using PTR-ToF-MS and other direct mass spectrometry techniques is performed by assigning a sum formula to the measured mass and comparing it with compounds previously reported in the literature. However, this can potentially lead to errors in compound assignment. When clustering all the compounds according to their dynamic behavior, it is expected that compounds in the same group will have similar physico-chemical characteristics and those which differ might have been miss-identified. In Table 1, some compounds can be singled out as possibly having been miss-identified. For example, compound number 6 (C$_3$H$_7$O$_2$$^+$) has been reported in the coffee literature as both propanoic acid and ethyl acetate. The polarity and water solubility of ethyl acetate are lower than those of the other compounds in family A, suggesting that the measured compound was most probably propanoic acid. Another potential miss-assignment is compound 31 (C$_5$H$_6$N$^+$), which was reported as pyridine and clustered in family E. However, the physicochemical characteristics of pyridine are closer to those of family A or B than to those of family E, indicating we may have detected a fragment of a less polar compound containing a pyridine ring instead of pyridine itself.

3.3. Factors affecting extraction

To evaluate the impact of temperature and pressure on the extraction, a PCA was performed using the total area under the time–intensity curves of the selected 120 mass traces (Fig. 3). The first two principal components explained 82.5% of the total variability in the data, and the graphical representation of the scores for these two components allowed differentiation into five different groups corresponding to the different conditions used for extraction (Fig. 3A). More information can be drawn from the loading plot (Fig. 3B). Loadings for the 46 tentatively identified compounds were all positive for PC1, indicating an increase in total area under the curve for higher temperatures and pressures. For PC2, 18 tentatively identified compounds had positive scores and are related to high pressure extraction. All but four of the compounds (18, 19, 22, 29) belong to the most polar groups A, B or C. Compounds with negative scores for PC2 belonged to families D and E, together with compounds number 2, 6, 12, 13 and 14 from the other families. Negative PC2 scores are related to an increased area under the curve for higher extraction temperatures, indicating that increases in temperature had a greater effect on the less polar compounds.

To obtain additional information on how pressure and temperature affected the extraction, the respective time–intensity profiles and the time evolution of the area under the curve were compared for one compound from each family (Fig. 4 for pressure and Fig. 5 for temperature effect). As discussed in the Section 3.1, the grouping of the different time–intensity profiles hardly varied between the different extraction parameters and so we, therefore, assumed that one compound would be representative of the whole family.

3.3.1. Effect of pressure

The time–intensity profiles of family A showed no significant differences based on extraction pressure for the representative compounds (Fig. 4). For C$_5$H$_9$O$^+$ and C$_4$H$_9$O$^+$, representatives of families B and C respectively, extraction at 7 bar resulted in lower intensities, but only during the middle phase of the extraction (8–16 s). The highest effect of pressure on the time–intensity profiles was observed for families D and E, where there were no differences between 7 and 9 bar. However, extraction at 11 bar resulted in significantly higher intensities during the last 10 s of extraction. Since the differences in intensities at each point in time were small, but could accumulate and have high impact in the final cup, we also calculated and plotted the total area under the curve up to each point in time (second column Fig. 4). Boxplots showed no significant differences between 7 and 9 bar for any of the families, but extraction at 11 bar always resulted in significantly higher
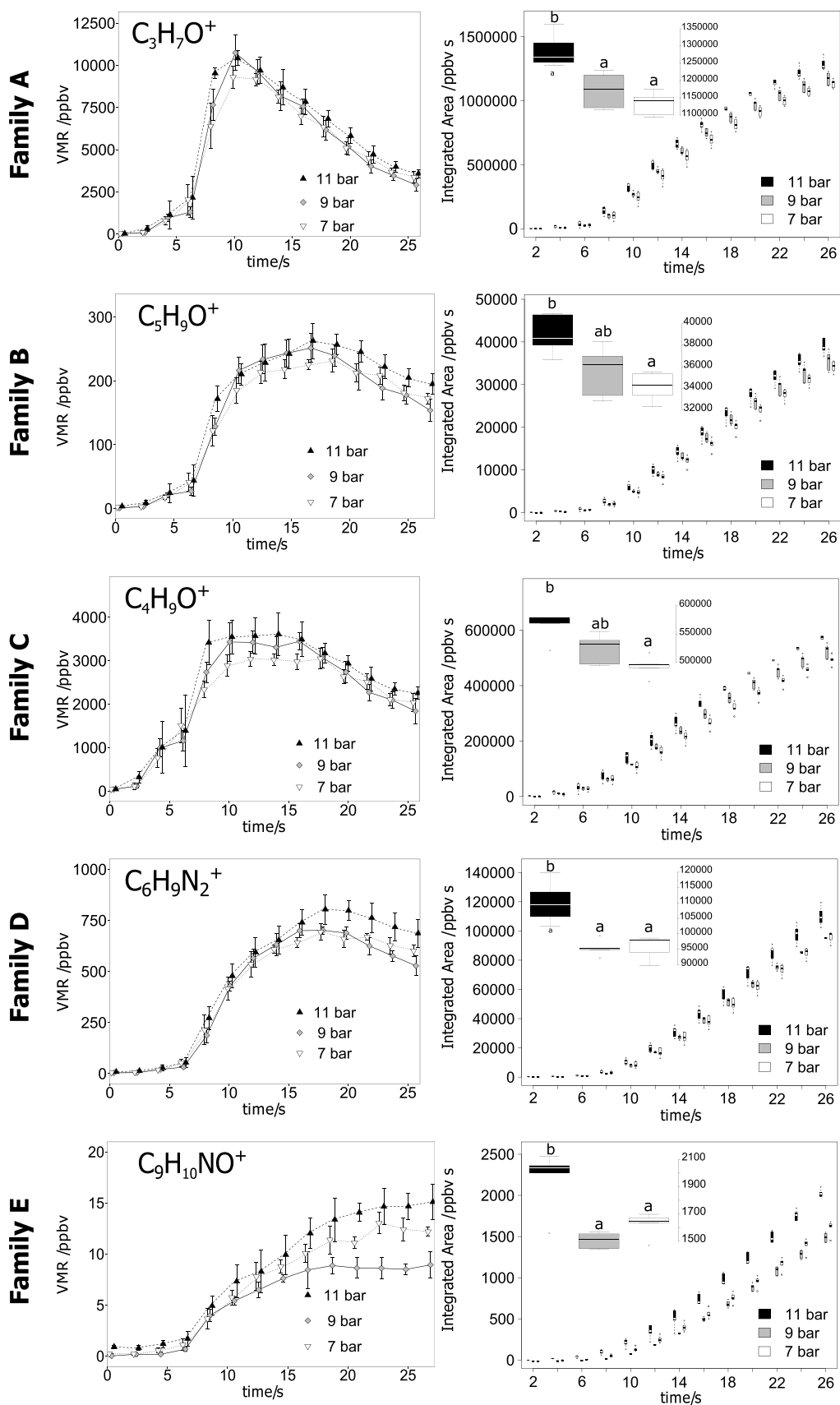
Fig. 4. Time–intensity profiles of compounds chosen as single representatives of each family during coffee extraction at three different pressures. Points represent the mean and the error bars represent the standard deviation of the replicates. Boxplots represent the area under the curve at that point in time and the insert in the left corner is a magnification of the last point (26 s), with letters representing measurements that differ significantly for the different extraction parameters (Tukey's test, $p < 0.01$).
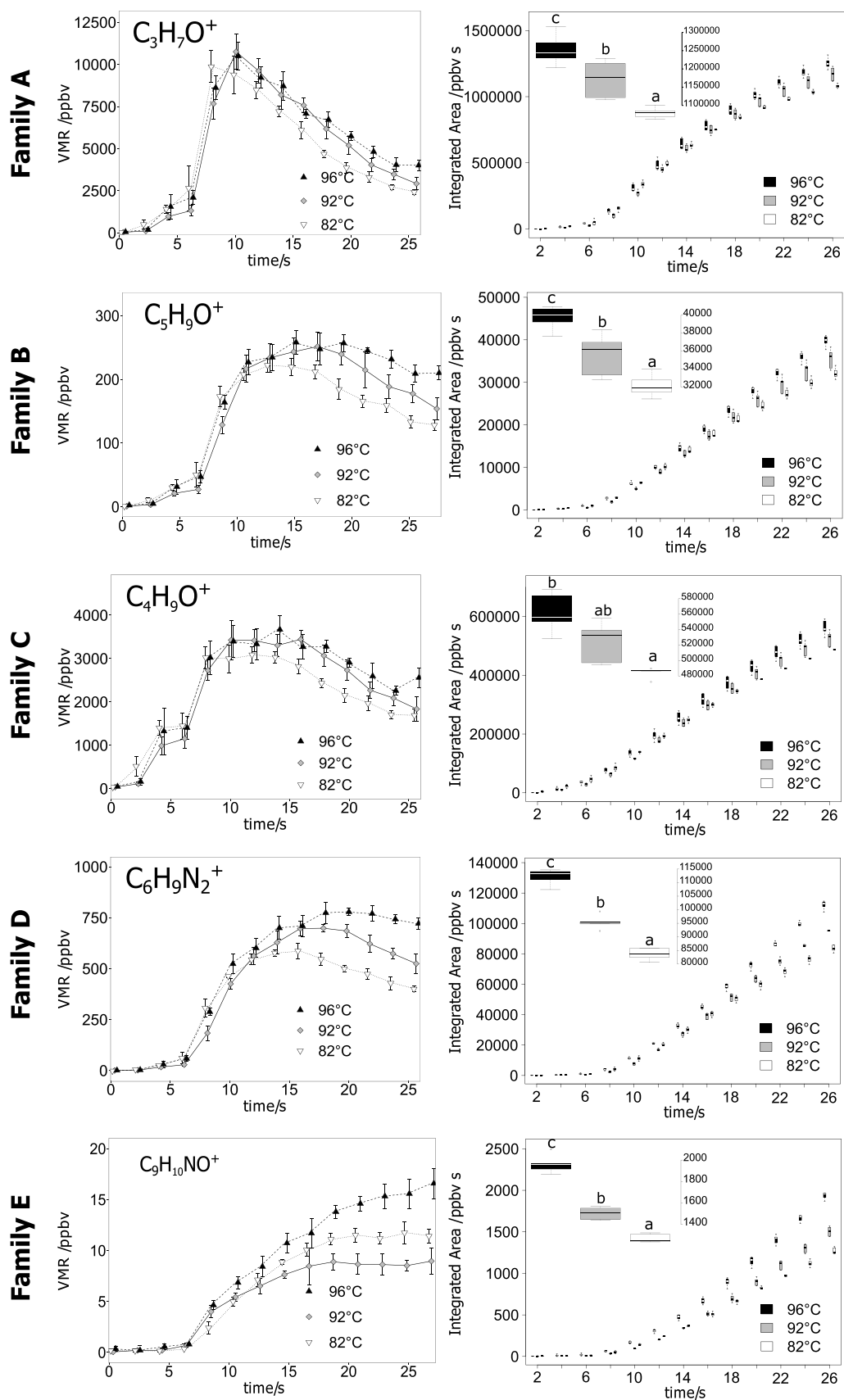
Fig. 5. Time–intensity profiles of one representative compound of each family during coffee extraction at three different temperatures. Points represent the mean and the error bars represent the standard deviation of the replicates. Boxplots represent the area under the curve at that point in time and the insert in the left corner is a magnification of the last point (26 s) with letters representing measurements that differ significantly for the different extraction parameters (Tukey's test, p < 0.01).

concentrations over the entire extraction time, compared to the extraction at 7 bar.

Pressure is the driving force required to produce a flow of water through the compacted coffee cake, assisting the extraction of compounds trapped inside the coffee particle structure, and also helping to transfer solid particles and oil droplets from the ground beans to the cup [15]. Some authors have reported an increase in chlorogenic acids, lipids, coffee oil, diterpenes and aroma compounds when increasing pressure from 7 to 9 bar [19,29] although no differences in caffeine or total solids were observed. A further pressure increase to 11 bar had either no effect or produced a decrease in the above compounds. The negative effect on extraction efficiency of high pressures has been attributed to a decrease in flow [19,29]. In our case, the extraction at 11 bar did not significantly change the average flow of the coffee. This might be the reason why the extraction efficiency of aroma compounds did not decrease and extraction at 11 bar resulted in the highest intensity of volatile compounds. This general increase in concentrations of volatile compounds at 11 bar also correlates with the highest ranking for odor intensity reported by Andueza et al. when extracting at this pressure [19].

3.3.2. Effect of temperature

Increases in temperature resulted in an increase in the measured intensity of VOCs, as shown on the time–intensity profiles (Fig. 5). This was especially visible in the second half of the extraction ($t > 14$ s); however, the effect was different for each compound family.

For family A, no significant difference was observed between extractions at 92 and 96 °C, but the extraction at 82 °C resulted in lower intensities. Boxplots of the evolution of the area under the curve showed differences at the two extreme temperatures (82 °C and 96 °C) after 20 s of extraction, with all three temperatures resulting in significantly different areas under the curve at the end of the extraction. Family C displayed similar behavior, but there was only a statistical difference between 82 °C and 96 °C at the end of the extraction. For family B, differences were evident on the time–intensity profiles after 16 s, although only in the last 2 s of the extraction was the area under the curve significantly different for all three temperatures.

The greatest effect of temperature was observed for families D and E. Significant differences in the area under the curve for the two extreme temperatures appeared earlier than for the other families (starting at 16 and 12 s for family D and E, respectively), and increased with increasing extraction time. In the case of dimethylpyrazine, the representative of family D, we observed that at 96 °C the intensity reached a maximum at 16 s and then remained constant until the end of the extraction, while for the other extraction temperatures the intensity started to decrease once the maximum had been reached. In the case of the representative compound of family E (furfurylpyrrole), the increase of extraction efficiency at 96 °C was even more evident. The time–intensity curve increased until the end of the extraction, suggesting that the maximum had not been reached within the extraction time of 25 s.

In general, an increase in water temperature results in higher water solubility for some compounds. The use of water at high temperatures for brewing espressos has been related to increases in extraction yield, caffeine, diterpenes, coffee oil and lipids [15–17,29]. The more efficient extraction of coffee oil and lipids at higher extraction temperatures may, in turn, favor the extraction of more lipophilic compounds. This could explain the greater effect of temperature on the extraction of volatiles from families D and E, which contain lower polarity compounds.

4. Conclusions

On-line PTR-ToF-MS analysis of volatile coffee compounds released from the coffee flow during extraction has revealed itself to be a very powerful approach for studying the kinetics of coffee aroma extraction for various pressure and temperature parameters using a semi-automatic coffee machine. The time–intensity profiles showed large differences in the extraction kinetics between different volatile compounds and allowed compounds to be grouped into five families with similar physicochemical characteristics. It was shown that the polarity of the volatile compounds was the main driving force for their extraction. Extraction profiles of the aroma compounds changed with the different brewing parameters used: increases in both pressure and temperature resulted in higher extraction of VOCs, with the least polar compounds being the most affected, mainly impacting the aroma balance in the last stage of the extraction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2016.02.015.

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