

Influence of Foam Structure on the Release Kinetics of Volatiles from Espresso Coffee Prior to Consumption

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ABSTRACT: The relationship between the physical structure of espresso coffee foam, called crema, and the above-the-cup aroma release was studied. Espresso coffee samples were produced using the *Nespresso* extraction system. The samples were extracted with water with different levels of mineral content, which resulted in liquid phases with similar volatile profiles but foams with different structure properties. The structure parameters foam volume, foam drainage, and lamella film thickness at the foam surface were quantified using computer-assisted microscopic image analysis and a digital caliper. The above-the-cup volatile concentration was measured online by using PTR-MS and headspace sampling. A correlation study was done between crema structure parameters and above-the-cup volatile concentration. In the first 2.5 min after the start of the coffee extraction, the presence of foam induced an increase of concentration of selected volatile markers, independently if the crema was of high or low stability. At times longer than 2.5 min, the aroma marker concentration depends on both the stability of the crema and the volatility of the specific aroma compounds. Mechanisms of above-the-cup volatile release involved gas bubble stability, evaporation, and diffusion. It was concluded that after the initial aroma burst (during the first 2–3 min after the beginning of extraction), for the present sample space a crema of high stability provides a stronger aroma barrier over several minutes.

KEYWORDS: espresso coffee, crema, above-the-cup volatile release, foam structure

INTRODUCTION

The term *aroma* refers to perceptions of volatiles in the atmosphere through the olfactory system. It is related to volatile organic compounds (VOCs) that reach the olfactory epithelium in the upper part of the nose. During food consumption, the VOCs released to the headspace can enter the consumer's nose, leading to an aroma impression even before the start of eating or drinking. Whereas in total more than 800 VOCs have been identified in coffee aroma, several studies^{1–4} have shown that only fewer than 50 of them can be considered as impact aroma compounds.

Espresso coffee is the beverage prepared by short percolation (30 ± 5 s) of hot water (90 ± 5 °C) at high pressure (above 7 bar) through a layer of roasted and ground coffee (6.5 ± 1.5 g). The extraction results in a polyphasic colloidal system. A foam layer of small bubbles is formed on top of the aqueous solution with dispersed fine coffee particles and microscopic oil droplets.^{5,6} On the physicochemical point of view, the espresso coffee foam, called crema, is a dynamic biphasic colloidal system. It is composed of gas bubbles framed by liquid films called lamella. The gas phase of the crema consists of air, water vapor from the percolation process, carbon dioxide formed in the Maillard reaction during coffee roasting and present in the roasted and ground coffee grain asperities, and volatile aroma compounds that are released from the liquid into the gas phase. Several factors affect the formation of the crema. The carbon dioxide formed during the Maillard reaction and the pressure applied during the extrac-

tion are the two main factors.^{7,8} In the *Nespresso* system used in current study the pressure during the extraction is determined not only through the particle size and the packing of the coffee but also through the membrane of the *Nespresso* capsule that provides a back-pressure before rupture. The somewhat elastic aluminum membrane ruptures upon swelling when the pressure inside the capsule becomes high enough.

When gas is dispersed in water, the increase in interfacial area increases the free energy of the system. According to the thermodynamic dictum, all systems strive to reach a state of global energy minimum. Liquid foams are not stable, but collapse by separating into two phases to minimize the interfacial area and the system's free energy. This instability makes foams very difficult to study. Most foams owe their existence to the presence of surface active molecular compounds, which decelerate foam destabilization by reducing the surface energy and by stabilizing the lamella films against rupture.^{9,10} The destabilization of espresso coffee foam has been ascribed to the mechanism of drainage,⁷ meaning that the liquid between the bubbles drains to the bulk. The lamella films become thin and eventually rupture. This leads to bubble coalescence and, in the case of exposed films, to foam collapse,

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including the release of entrapped gas and a loss of foam structure. Thus, the lamella films are of crucial importance for foam stability. Their thickness is reduced not only by drainage but also by evaporation, considering the temperature of espresso coffee.^{7,9–12}

Besides the roasted and ground coffee, the second most important ingredient of espresso coffee is water. It constitutes >95% of the beverage.⁶ Calcium and magnesium ions in the water have been found to decrease foam stability as already claimed by Navarini and Rivetti.¹³ The mechanism can be explained by a change in ion content, respectively by the interaction between the cations and protein/polysaccharide complexes, leading to a destabilization of the foaming mechanism.^{6,9}

The crema of espresso coffee is highly appreciated by consumers for its sensory properties, notably its appearance prior to consumption. Once in the mouth it contributes to the creaminess and smoothness of the drinking experience. Crema is traditionally believed to act as an aroma-sealing lid that traps the volatilized compounds and doses their emission into the atmosphere.^{6,7,14} In the current contribution, we propose that the crema structure affects and supports volatile release.

Given the importance of aroma in coffee consumption and the consumers' appreciation of crema, the objective of this work was to investigate the influence of the physical structure of espresso coffee foam on headspace volatile release. Several parameters of crema structure were analyzed with regard to their impact on volatile release above the cup.

MATERIALS AND METHODS

Materials. Two different blends of commercial *Nespresso* capsules were used: blend A (A) (lot 92333786PD 17:49 B) and blend B (B) (lot MOUON-13 07:39 A). Both types of capsules contained pure *Arabica* coffee. The main sensory attributes for blend A are roasted and cocoa notes; blend B has roasted and fruity notes. For coffee extraction commercial bottled waters of different mineral contents were used: Acqua Panna (Pan) (lot L9245087701) for its medium–low mineralization (calcium, 32.9 mg/L; magnesium, 6.5 mg/L) and Contrex (Con) (lot 92473019N6) for its high mineralization (calcium, 468.0 mg/L; magnesium, 74.5 mg/L). For all extractions a commercial *Nespresso* machine C190 Plus was used.

Foam Structure Analysis Methods. The elapsed time before the start of foam structure analysis and the elapsed time before the start of the volatile release analysis methods was synchronized. The starting point of all measurements, $t = 0$ min, was set as being 1 min after the start of coffee extraction.

Foam Volume. Foam volume was determined using a digital caliper (Garant IP65-CI50, Hoffmann Group, Munich, Germany). Measurements were carried out in a commercial *Nespresso* glass cup (Essenza espresso cup ref 3301/2/B). The distance from the top of the cup to a certain fill level was linked to the respective fill volume by doing a calibration with distilled water of 20 °C. Volumes were plotted against filling heights, and a third-order polynomial was fitted as calibration curve. For foam volume analysis, 40 g of coffee beverage was extracted into the cup. The distance from the top of the cup to the foam surface and from the top of the cup to the liquid surface was measured with the digital caliper. Corresponding filling volumes were calculated using the third-order polynomial fit. The foam volume was calculated as the difference of the two volumes. The measurement was done at $t = 0$ min and at $t = 5$ min (equaling 1 and 6 min after the start of coffee extraction). Ten repetitions were done for each sample. Averages and standard deviations were calculated.

Foam Drainage. Foam drainage was determined using computer-assisted microscopic image analysis. An amount of 25 g of coffee beverage

was extracted into a plastic vessel. The plastic vessel had a transparent and plane side wall, which allows a cross-sectional view of the crema and the liquid volume beneath the crema. The plastic vessel was placed into a dark chamber facing a digital microscopy camera (Infinity Y2-1C, Lumenera Corp., Ottawa, Canada). Microscopic images were taken every 15 s, starting at $t = 0$ min (1 min after the start of coffee extraction). In total 40 images were taken. The microscopic images were analyzed using the image processing software Colibri developed in-house. For each picture, the area (level) of the liquid underneath the foam was calculated. Data were normalized by equating the area at $t = 0$ min to 100%. This allowed a relative comparison between the drainage kinetics of the different samples. Triplicates were done for each sample. Averages and standard deviations were calculated for each data point.

Foam Surface Area Fraction. The quality of the foam surface was analyzed using computer-assisted microscopic image analysis. An amount of 40 g of coffee beverage was extracted into a commercial *Nespresso* porcelain cup and placed into a dark chamber under a digital microscopy camera (Infinity Y2-1C, Lumenera Corp.) and a luminous ring (Schott S40-55, Schott AG, Mainz, Germany). Five samples were extracted and analyzed for each of the four investigated coffee beverages. For each of the five samples, a series of 20 microscopic images of the complete illuminated foam surface was taken at intervals of 30 s starting at $t = 0$ min (1 min after the start of coffee extraction). Positioning of the camera and coffee sample remained the same throughout the measurements. The microscopic images were analyzed using the image processing software Colibri (noncommercialized in-house development). Each color image was transformed into a black/white image. For each black/white image the area fraction was calculated as the ratio between the area of white parts of the crema surface in the transformed image and the total area of the crema surface. Averages and standard deviations have been calculated from the five repetitions for each time point and for each coffee beverage.

Volatile Release Analysis Methods. The above-the-cup aroma intensity of the samples was measured online by proton transfer reaction mass spectrometry (PTR-MS). The setup consisted of a headspace sampling oven linked to a proton transfer reaction mass spectrometer. Identification of the chemical compounds contributing to the ion trace markers monitored by PTR-MS was done. The VOCs were identified by using Tenax trapping and gas chromatography (GC) with simultaneous and parallel detection by PTR-MS and time-of-flight mass spectrometry (TOF-MS). The volatile release analysis methods used for this work were described in detail by Lindinger et al.^{15–17}

Online Headspace Volatile Release. A double-jacketed, water-heated sample cell (glass vial) was placed inside an oven at a temperature of 100 °C with active air circulation. A water bath at a temperature of 50 °C was connected to the sample cell to keep the sample at constant temperature. The sample cell was connected to the fix-installed top of the cell by a clamp and sealed by a silicone O-ring. Three tubes were installed in the cover of the cell. The first tube was supplied by the preheated purge gas, the second provided a thermocouple to measure the sample temperature, and through the third one the sample gas was pushed out of the vial. Before analysis by PTR-MS, the sample gas was diluted with dry air. Two flow controllers provided the dilution gas and the purge gas, keeping the dilution ratio constant. Only a small fraction of sample gas (40 standard cubic centimeters per minute (sccm)) was used for analysis by PTR-MS (high-sensitivity PTR-MS, Ionicon Analytik GmbH, Innsbruck, Austria). The major part was removed through an exhaust line. Dry synthetic air was used as purge gas and dilution gas. The flow rate of the purge gas was maintained at 300 sccm, the one of the dilution gas at 3000 sccm.

To analyze the impact of crema, volatile release was measured for each of the four beverages with crema (wc) and without crema (woc). For the preparation of a sample without crema, a glass funnel covered with two paper filters (KIMTECH Science precision wipes, Kimberly-Clark Corp., Dallas, TX) was put on the sample cell and 40 g of coffee brew

was extracted and filtered. On average, a residue of 3 g of crema mixed with coffee was held back, and 37 g of coffee brew was collected into the sample cell. The elapsed time from the start of the extraction to the end of filtration (45 s) and then to connection of the sample cell to the headspace sampling oven (15 s) was maintained constant at 60 s. To prepare a sample with crema, the coffee was directly extracted into the sample cell. On average, 40 g coffee brew was collected. As for the coffee preparation without crema, the sample cell was connected to the oven setup 60 s after the start of the coffee extraction. Therefore the time delay (45 s) caused by filtering in the case of extraction without crema did not influence the comparability of the measurements.

The concentration (parts per billion) in the gas phase of 58 selected ion traces was obtained during 10 consecutive minutes after connection of the sample cell. The 58 ion traces chosen showed to be the most discriminating over the mass range m/z 20–160 for coffee headspace analysis. For each analysis three individual headspace release measurements were done. Between consecutive measurements, the sample cell was equilibrated in the oven setup for 30 min. Ion trace release profiles were obtained by calculating average concentrations and standard deviations for each data point (each 12.4 s).

Identification of Volatile Organic Compounds. To analyze the chemical compounds contributing to the ion traces monitored by PTR-MS, entrapment on Tenax traps was used. Tenax traps were desorbed with an automatic thermodesorption unit (ATD), which was connected to a GC column. Tenax traps were desorbed at 300 °C for 10 min on the ATD unit (ATD Turbo Matrix 350, PerkinElmer Inc., Boston, MA) and purged with a helium flow of 20 sccm to the ATD trap. The volatile compounds were cryofocused at –30 °C for 10 min, desorbed at 320 °C for 3 min, and injected into the GC (Agilent 6890N series GC, Agilent Technologies Inc., Santa Clara, CA) at 200 °C. A 60 m DB-Wax column (J&W scientific Inc., Folsom, CA) with an internal diameter of 0.32 mm and a film thickness of 0.5 μ m was used. The temperature was kept at 20 °C for 5 min, increased at a rate of 4 °C/min to 240 °C, and maintained for 10 min. Helium at 3 sccm was used as flow carrier gas. After thermodesorption and GC separation, the eluent was split (1:1) to two detectors that were supplied parallel and simultaneously: TOF-MS (Pegasus III TOF-MS, LECO Corp., St. Joseph, MI) for identification based on the fragmentation patterns and PTR-MS (high-sensitivity PTR-MS, Ionicon Analytik GmbH) to identify the ion trace found online and to semiquantify contribution compounds by their GC peaks for a selected ion corresponding to the same ion trace in the online mode. To allow a proper coupling of GC with PTR-MS, the effluent gas of the GC column had to be mixed with moist air prior to splitting. As the mobility of ions depends on the buffer gas and its humidity, these parameters had to be kept constant to obtain the same PTR-MS fragmentation pattern. In the online mode dry synthetic air was used as buffer gas for the humid headspace sample. The gas from the GC column in the offline mode was dry helium. To compensate for this, the PTR-MS reaction chamber was fed by two inlets in the offline mode. One came from the GC column carrying the dry helium. The other one came from the PTR-MS headspace oven setup, where the sample cell was filled with 100 mL of purified water to mimic the humidity of the headspace sample gas in the online mode.

The identification of the chemical compounds contributing to the ion traces monitored by PTR-MS was done by comparing GC relative retention times (RI) and fragmentation patterns detected by TOF-MS to commercial and internal databases (Wiley Registry of Mass Spectral Data, 9th edition, Wiley, European Distribution Centre, PO22 9NQ UK; FMD, internal Flavor Molecules Database).

RESULTS AND DISCUSSION

Physical Foam Structure. *Foam Volume.* Foam volumes of the four espresso coffee samples were determined with a digital

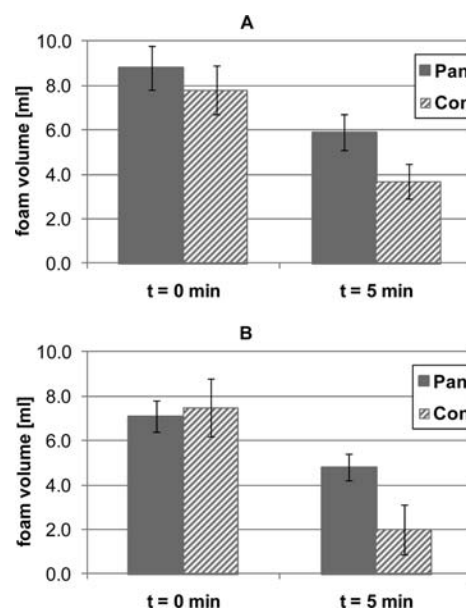


Figure 1. Foam volumes of espresso coffees prepared from blends A and B, both using Acqua Panna (Pan) and Contrex (Con) at $t = 0$ min and at $t = 5$ min (equaling 1 and 6 min after the start of coffee extraction) (averages and standard deviations of 10 repetitions shown).

caliper. Results are shown in Figure 1. A t test (two-sided, unpaired, $\alpha_{\text{risk}} = 0.01$) was applied to check for significant differences. The risk level $\alpha_{\text{risk}} = 0.01$ was the threshold level we fixed to confirm the significance of a difference. The p values produced from the t tests were compared to α_{risk} . If the observed p value was below α_{risk} we concluded that the difference was significant.

The initial foam volumes ($t = 0$ min) are not significantly different between the beverages prepared with Acqua Panna and those prepared with Contrex. At $t = 5$ min, the foam volumes of espresso coffees prepared using different waters show significant differences. Higher foam volumes were measured for the espresso coffees prepared with Acqua Panna than for those prepared with Contrex. For both types of coffee capsules, the foam of espresso coffees prepared with medium–low mineralized Acqua Panna shows higher stability in volume than the foam of the corresponding espresso coffees prepared with the highly mineralized Contrex.

Foam Drainage. The amount of liquid draining from the espresso coffee foam was obtained by measuring the increase of the area-projected volume of liquid phase underneath the foam. Data were normalized by equating the area of liquid phase present at $t = 0$ min (equals 1 min after the start of coffee extraction) to 100%. Figure 2 shows averages and standard deviations obtained of triplicates for the four espresso coffee samples. The espresso coffees prepared with Contrex show a higher increase of the area of liquid underneath the foam than the corresponding beverages prepared with Acqua Panna. This observation applies to each data point within the study period of 10 min. For both types of coffee capsules, blends A and B, more liquid drains out of the foams of espresso coffees prepared with Contrex than of the foams of espresso coffees prepared with Acqua Panna.

Foam Surface Area Fraction. Figure 3 shows average area fractions and standard deviations obtained of five measurement repetitions for each of the four different espresso coffee beverages. All four espresso coffee samples show the same area fraction of

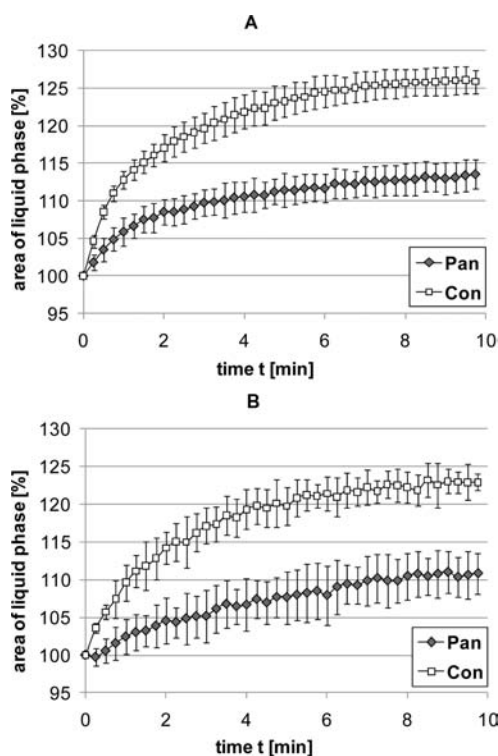


Figure 2. Increase of area projected volume of liquid phase underneath espresso coffee foam starting at $t = 0$ min (equals 1 min after the start of coffee extraction) for blends A and B, both prepared with Acqua Panna (Pan) and Contrex (Con) (averages and standard deviations of triplicates shown).

approximately 0.6 at $t = 0$ min. The temporal evolution of the area fraction shows clear differences between the beverages prepared with Acqua Panna and those prepared with Contrex. At elapsed times >6 min after the start of the coffee extraction, the area fractions of both espresso coffees prepared with Acqua Panna remain at higher values compared to those of the espresso coffees prepared with Contrex. Consequently, the kinetics of the area fraction depends on water ion content. The area fraction indicates the intensity of light reflected by the crema surface. The visual perception “white” in the black/white images results from reflected light. According to basic electromagnetic theory, the capacity to reflect light depends on the thickness of the lamella films located at the foam surface.¹⁰ Thus, the results of the area fraction can be interpreted as follows: All four espresso coffees show approximately the same value for the area fraction at $t = 0$ min, meaning that the initial film thickness of the lamella films located at the top of the crema does not differ considerably between samples. The faster decrease of the area fraction for espressos prepared with water of higher mineral level compared to espressos prepared with water of lower mineral level indicates a more pronounced thinning of the lamella films located at the foam surface.

Generally, a decrease in foam volume can be assigned to phase segregation, implying the loss of gas into the surrounding air and the loss of fluid into the liquid bulk due to drainage. The latter implicates thinning of the lamella films, which in turn leads to film rupture and foam collapse, including a loss of entrapped gas and a loss in foam volume.^{7,9,10} Thus, the observations on foam volume, foam drainage, and foam surface quality support each

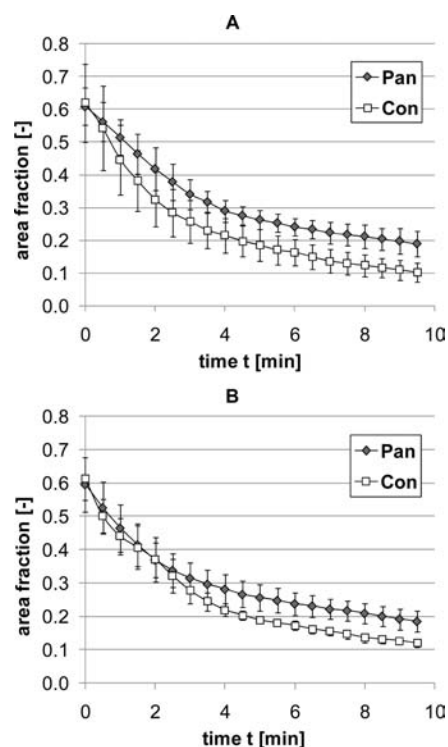


Figure 3. Area fraction (calculated by dividing the area of white parts of the crema surface in the black/white images by the total area of the crema surface) starting at $t = 0$ min (equals 1 min after the start of coffee extraction) for blends A and B, both prepared with Acqua Panna (Pan) and Contrex (Con) (averages and standard deviations of five repetitions shown).

other and demonstrate that the foams of espresso coffees prepared with water of high mineralization show a lower stability than the foams of the corresponding espresso coffees prepared with water of low to medium mineralization.

A possible explanation for the lower stability measured for espresso coffees prepared with water of high mineral content is the potential disturbing effect of the ions on the interactions between the foaming fractions. Surfactant molecules can bind to proteins and polysaccharides, forming surfactant–biopolymer complexes, which may have functional characteristics different from those of the individual components. The interaction can be based on different mechanisms, whereby the most important are electrostatic and hydrophobic interactions. These have a strong influence on physicochemical properties of the system, which, in the case of espresso coffee, are directly linked to the physical crema structure. It is possible that the ions of the high mineralized water disturb these electrostatic interactions of surfactant–biopolymer complexes and change the stability of the surface physical network.^{8,19}

Volatile Release above the Cup. The headspace volatile release was measured online using PTR-MS. Each of the 58 monitored ion traces shows its own release pattern. Within the framework of this study, some markers were selected for further investigation and discussion. Three selection criteria were applied: First, the signal-to-noise ratio of the ion trace release profile should be >10 .¹⁸ Second, the selected markers should represent potential coffee aroma compounds. This selection criterion was applied by using an internal database (FMD, internal Flavor Molecules Database). However, compounds such as 2-furfurylthiol,

3-mercapto-3-methylbutylformate, methional, β -damascenone, and Furanol known to have a high aroma impact are not covered by the markers, because they are present in coffee headspace at concentrations too low to be detectable by online techniques.^{1–4}

Third, ion traces associated with acetic acid were excluded, as this molecule showed disturbing effects due to interaction of the molecule with the tubing system of the headspace sampling setup. By applying these three selection criteria, 8 of 58 ion traces were chosen for further analysis for blend A (m/z 45, 59, 69, 73, 75, 81, 87, and 95), and 7 of 58 ion traces (m/z 45, 59, 69, 73, 75, 81, and 87) were chosen for blend B.

Figures 4 and 5 exemplarily show the release profiles of m/z 45, 59, and 81 for blends A and B, prepared with Contrex and Acqua Panna, both with crema (wc) and without crema (woc).

Table 1 shows the chemical components contributing to m/z 45, 59, and 81. Each marker represents several chemical compounds. Thus, the release profiles need to be considered as the superposition of release profiles of all contributing compounds.

The three markers m/z 45, 59, and 81 represent volatiles with both very high and very low volatilities. The other investigated markers are similar to or between the extremes represented by these three marker characteristics.

Within the first 2.5 min after the start of the coffee extraction, the presence of crema generally resulted in an above-the-cup volatile concentration significantly higher than that of the liquid coffee phase without crema. This was shown for both coffee blends and for all investigated release patterns. After this initial burst, the impact of crema is more differentiated. Depending on the investigated group of chemical compounds and on the type of water used, the crema on top of the liquid coffee phase can either act as long-term enhancer of the volatile release above cup or have no effect or act as a long-term barrier of volatile release. These findings demonstrate that the concept of crema being an aroma-sealing lid^{7,14} cannot be generalized. When the impacts of foams with different stability patterns starting at $t = 2.5$ min are compared, it can be observed within the given sample space that the volatile concentration above the cup is higher for espresso coffees prepared with water with high mineral content (here: Contrex). For the corresponding liquid coffee phases without crema, no considerable influence of the type of water used for coffee preparation could be evidenced. With regard to this finding, it is suggested that espresso coffees with a crema of lower stability provide higher above-the-cup volatile concentrations at longer times after the extraction (>2.5 min). To confirm this preliminary conclusion, the data of physical foam structure and volatile release were used for a statistical correlation study.

Correlation of Physical Foam Structure and Above the Cup Volatile Release. For espresso coffee samples prepared with crema (A Pan wc, A Con wc, B Pan wc, and B Con wc), a normalized principal component analysis (PCA) was done considering the markers m/z 45, 59, 69, 73, 75, 81, and 87. Variables (i.e., markers) are represented as lines. The smaller the angle between two variables, the better is the correlation. Individuals (i.e., coffee samples) are represented as dots. When a coffee sample is positioned at large distance from the center (reference) and close (orthogonal projection) to the vector of a marker, the coffee sample has a high value for this marker. In addition, the data obtained for the structure parameters foam volume (FoamVol), foam drainage (FoamDrain), and foam surface area fraction (FoamSAF) are added as supplementary variables (i.e., these variables are added a posteriori on the PCA map).

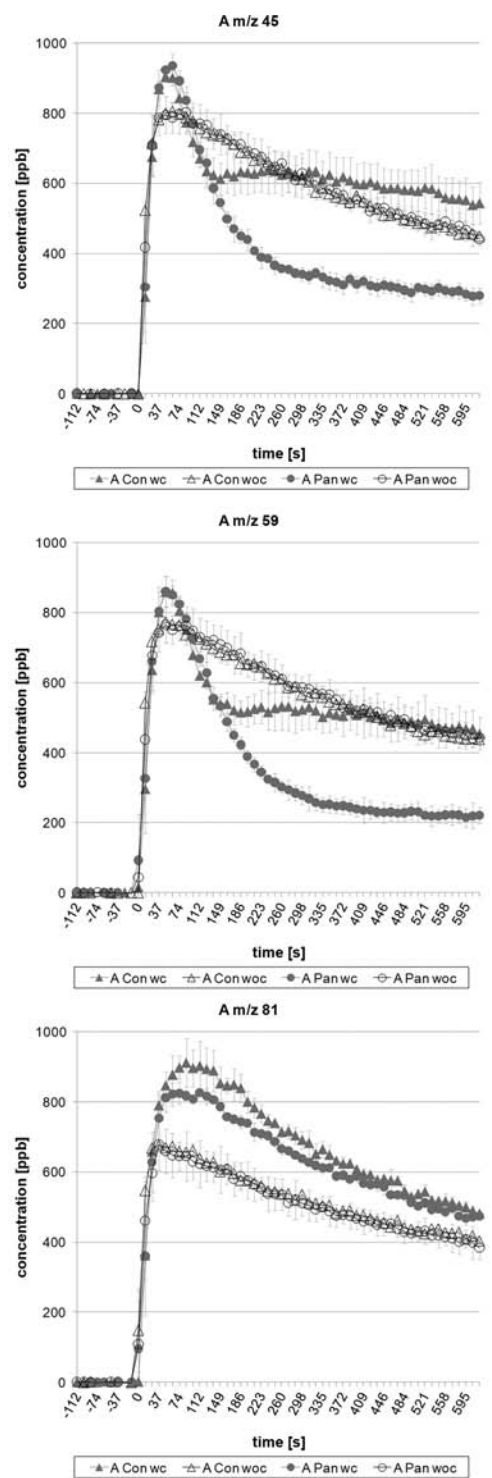


Figure 4. Volatile release profiles of PTR-MS ion traces m/z 45, 59, and 81 for samples prepared from blend A with Contrex (Con) and Acqua Panna (Pan), both with crema (wc) and without crema (woc) ($t = 0$ min equals 1 min after starting coffee extraction) (averages and standard deviations of triplicates).

Three different PCAs were done. The first one using data obtained at t burst, the time corresponding to the highest aroma release intensity, which occurs around 45 s after the start of the headspace release measurements (Figure 6). The second PCA was

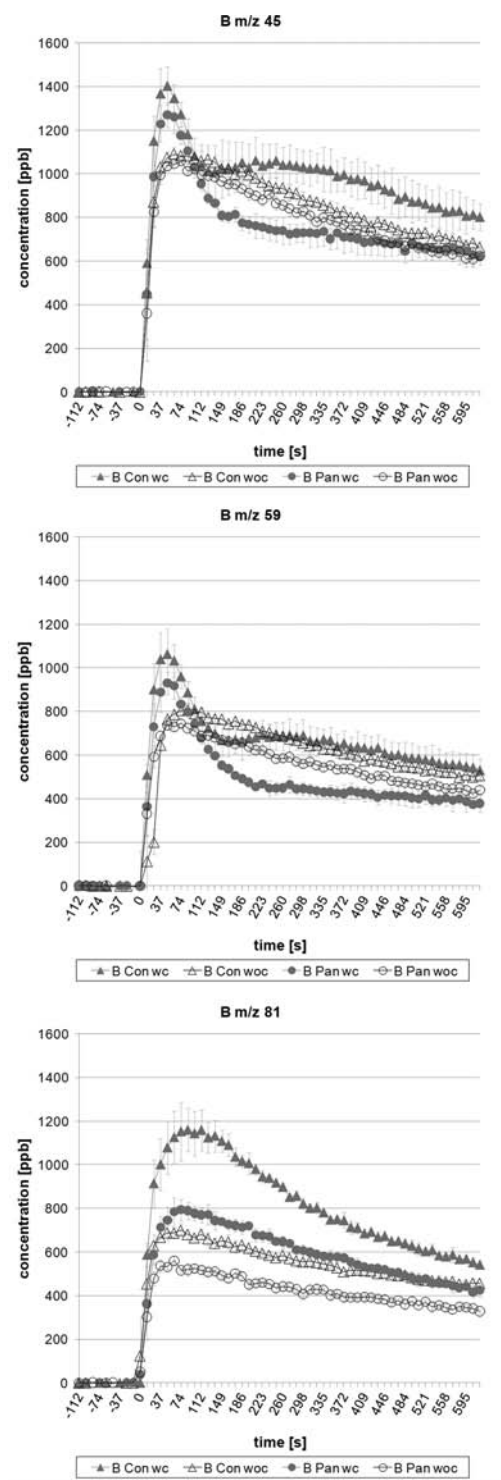


Figure 5. Volatile release profiles of PTR-MS ion traces m/z 45, 59, and 81 for samples prepared from blend B with Contrex (Con) and Acqua Panna (Pan), both with crema (wc) and without crema (woc) ($t = 0$ min equals 1 min after the start of coffee extraction) (averages and standard deviations of triplicates).

done on data obtained at $t = 5$ min, equaling 6 min after the start of the coffee extraction (Figure 7). The third PCA was done on the calculated differences between the data obtained at t burst and the data obtained at $t = 5$ min (t burst $- t = 5$ min) (Figure 8).

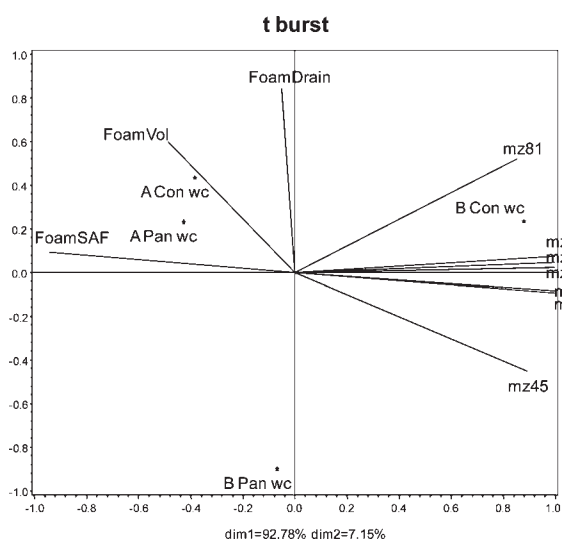
The PCA at t burst (Figure 6) shows that the essential information is reflected by the first principal component (93%, horizontal axis). It is almost one-dimensional. The volatile release of all seven markers is highly negatively correlated with the foam surface area fraction. From the results of the PCA for this time point it can be concluded that the thinner the lamella films located at the foam surface, the higher is this initial aroma burst. There is no correlation with the foam drainage or the foam volume at this short time after extraction. It cannot be observed either that foams of different stabilities cause different initial above-the-cup aroma intensities. Therefore, we suggest that the rupture of the thin exposed lamella films leads to bubble collapse and release of entrapped gas.^{7,9,10} Thus, the initial burst could be explained as follows: The VOCs entrapped in the gas phase of the foam bubbles are released into the headspace as the bubbles at the crema surface explode due to rupture of thin exposed lamella films. Thinning of films at the top of foams is caused either by evaporation of the liquid phase or through gravity-driven drainage.¹⁰ As no correlation with foam drainage was shown and considering the temperature of freshly brewed coffee, we concluded that evaporation is a major influencing phenomenon here. At the high exchange surface area of the crema, volatiles will evaporate from the liquid phase to the gas phase above the cup and will thus be available for perception. Rate-limiting effects are unlikely for the liquid phase, because the liquid is exposed to natural convection. Consequently, in the presence of crema the mechanisms of volatile release are lamella rupture and evaporation. The high exchange surface area of crema allows a burst of both high and low volatile aroma compounds. In the absence of crema the mechanism of volatile release is purely driven by evaporation at the liquid-gas interface.

The PCA of data obtained 6 min after the start of the coffee extraction ($t = 5$ min) (Figure 7) is almost one-dimensional, too, but shows correlations other than the PCA at t burst. The volatile release is strongly negatively correlated with the foam volume and negatively correlated with the foam surface area fraction. It can be concluded that the thinner the lamella films at the foam surface and the lower the foam volume, the higher is the volatile concentration above the cup. Large foam drainage can also be considered as contributor to a high above-the-cup aroma intensity because the corresponding vector in the PCA has a small angle with most marker vectors. A low foam volume, thin lamella films at the foam surface, and drainage of the liquid out of the foam into the bulk are all indicators for foam destabilization.^{9,10,12} Accordingly, for all coffee samples, the PCA for $t = 5$ min reveals that the volatile release of espresso prepared with the highly mineralized water (Contrex) is globally higher than the volatile release of espresso prepared with low mineralized water (Acqua Panna). Thus, this PCA confirms the assumption that was already made on the basis of the results of the foam structure analysis and the volatile release analysis. After the initial aroma burst, a crema of low stability gives higher above-the-cup volatile concentrations than a crema of high stability in the present sample space. This can be explained to a large extent by the fact that foam bubbles rupture due to thin lamella films and release the trapped volatiles into the surrounding air. For a more stable crema the VOCs remain trapped in the gas bubbles for a longer time. For the initial aroma burst it was suggested that evaporation leads to thinning of lamella films. From the correlation observed between above-the-cup volatile concentration and foam destabilization for the situation after the initial aroma burst, the thinning of lamella films can be attributed to drainage.

Table 1. Chemical Compositions of the PTR-MS Ion Traces^a m/z 45, 59, and 81 Obtained by GC-MS Coupling¹⁶ for Blends A and B, Both Prepared with Acqua Panna and Contrex^b

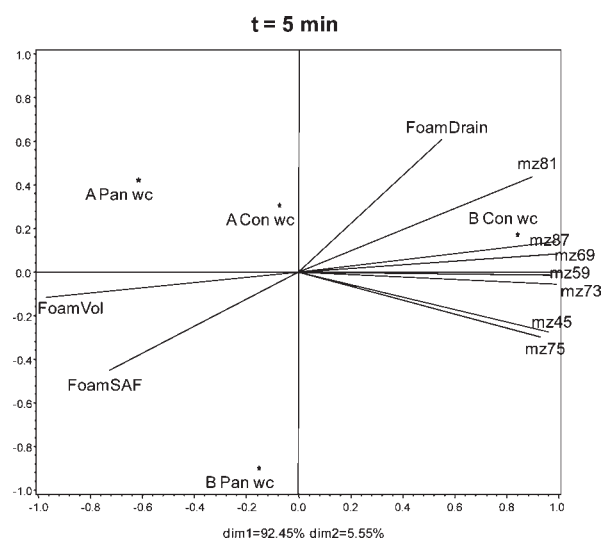
| m/z 45 (fruity, green, malty notes) | | m/z 59 (buttery, green notes) | | m/z 81 (roasted notes) | |
|---------------------------------------|-------------------------------|---------------------------------|-------------------------------|--------------------------|-------------------------------|
| compound | $K_{\text{air}/\text{water}}$ | compound | $K_{\text{air}/\text{water}}$ | compound | $K_{\text{air}/\text{water}}$ |
| acetaldehyde | 1.63×10^{-2} | acetone | n/a | 2-furanmethanol | 1.19×10^{-4} |
| 2-methylbutanal | 8.36×10^{-2} | 2,3-butanedione | 5.98×10^{-3} | 2-furfuryl formate | n/a |
| 3-methylbutanal | 7.91×10^{-2} | propanal | 1.80×10^{-2} | 2-furfuryl acetate | 6.12×10^{-3} |
| 2-methyltetrahydrofuran-3-one | n/a | | | pyridine | n/a |
| | | | | pyrazine | n/a |

^a Tentatively identified using commercial and internal databases. ^b Sensory descriptors (internal data bases) of odorant compounds identified in the chemical composition of PTR-MS ion traces were assigned directly to the corresponding masses. Air/liquid partition coefficients $K_{\text{air}/\text{water}}$ (without unit) were measured by stripping with pure air an aqueous solution containing individually the dissolved chemical compounds at mg/L levels. Depletion of VOC's relative concentration in the gas phase measured at 60 °C by PTR-MS allowed determination of partition coefficients.²⁰

**Figure 6.** PCA of foam structure parameters and volatile release of selected markers (vectors) for t burst (105 s after the start of coffee extraction) for the four different espresso coffee samples with crema (points).

In a third PCA, differences in the volatile release profiles between t burst and $t = 5$ min were correlated to differences in the foam structure between t burst and $t = 5$ min. The PCA for the difference $Diff$ (Figure 8) illustrates that the decrease of volatile concentration of markers m/z 73, 87, 45, and 59 is positively correlated with the decrease of foam drainage and negatively correlated with the decrease of foam surface area fraction.

For these markers, the decrease in volatile release is stronger for the espresso coffees prepared with Acqua Panna than for the espresso coffees prepared with Contrex. Correspondingly, for a more stable crema with less drainage and thicker lamella films, we observed a stronger decrease in volatile release with respect to its maximum level of intensity. However, for three other groups of chemical compounds (markers m/z 81, 69, and 75), the PCA indicates a much weaker correlation between foam stability and volatile release as compared to the four markers mentioned above. The decrease of the volatile release for the markers m/z 81 and 69 tends to correlate strongly with the decrease in foam volume, whereby it has to be considered that m/z 75 is only weakly represented in this PCA. It is suggested that the different correlations of the markers are related to the volatility of the

**Figure 7.** PCA of foam structure parameters and volatile release of selected markers (vectors) for $t = 5$ min (6 min after the start of coffee extraction) for the four different espresso coffee samples with crema (points).

different compounds (Table 1). The low-volatile compounds are less present in the gaseous phase of the crema, and thus their concentration above the cup is less correlated to the destabilization process of the crema.

Four effects are proposed to take place depending on the volatility of the aromas and the stability of the crema: For high-volatile compounds ($K = 10^{-3} - 10^{-2}$) and a crema of low stability, the crema acts as an enhancer for aroma release. High volatiles are abundant in the gas phase of the foam bubbles and released upon their rupture. Examples for this effect are the release patterns of Contrex m/z 45 and Contrex m/z 59. For low-volatile compounds ($K = 10^{-4} - 10^{-3}$) and a crema of low stability, the creation of new interface upon bubble rupture increases the diffusion of low-volatile aromas. The release pattern of Contrex m/z 81 shows this behavior. For high-volatile compounds and a crema of high stability, the crema acts as a barrier that entraps volatiles. Acqua Panna m/z 45 and Acqua Panna m/z 59 are examples for this effect. For low-volatile aromas and a crema of high stability, the aromas will be released from the interface through a diffusion process, as, for example, shown by the release pattern of Panna m/z 81.

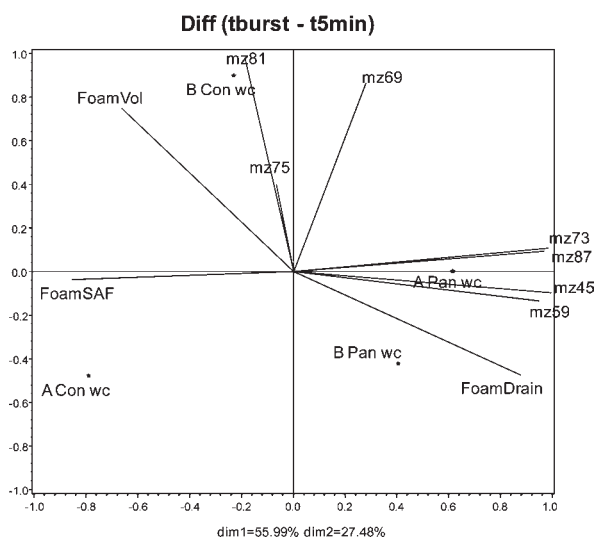


Figure 8. PCA of foam structure parameters and volatile release of selected markers (vectors) for the difference Diff (values for t burst – values for $t = 5$ min) for the four different espresso coffee samples with crema (points).

Conclusion. These results show for the first time the influence of crema stability properties on the volatile release profiles above the cup. In summary, during the first 2.5 min after the start of the espresso coffee extraction, the presence of crema provides a volatile burst above the cup, no matter if the crema is of high or low stability. Six minutes after the start of the extraction, a crema of low stability gives higher above-the-cup volatile concentrations than a crema of high stability. After the initial aroma burst, a crema of low stability provides a more long-lasting high above-the-cup aroma intensity.

It is still an open question whether these release kinetics and their differences can be perceived by a consumer or not, and beyond, which kinetics would then be the most liked. It should be kept in mind that in an average consumption behavior the first sip would occur during the burst of the aromas above the cup (during the first 2.5 min), and most probably the cup is fully consumed after 5 min. To provide a sensory validation, time-resolved sensory studies and consumer preference studies are required.

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ABBREVIATIONS USED

VOCs, volatile organic compounds; A, blend A; B, blend B; Pan, Acqua Panna; Con, Contrex; PTR-MS, proton transfer reaction mass spectrometry; GC, gas chromatography; TOF-MS, time-of-flight mass spectrometry; sccm, standard cubic centimeters per minute; ppb, parts per billion; ATD, automatic thermodesorption; wc, with crema; woc, without crema; PCA, principal component analysis; RI, retention index (time); FoamVol, foam volume; FoamDrain, foam drainage; FoamSAF, foam surface area fraction; α_{risk} , risk level of significance used in the t test.

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