Release Kinetics of Volatile Organic Compounds from Roasted and Ground Coffee: Online Measurements by PTR-MS and Mathematical Modeling

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The present work shows the possibilities and limitations in modeling release kinetics of volatile organic compounds (VOCs) from roasted and ground coffee by applying physical and empirical models such as the diffusion and Weibull models. The release kinetics of VOCs were measured online by proton transfer reaction–mass spectrometry (PTR-MS). Compounds were identified by GC-MS, and the contribution of the individual compounds to different mass fragments was elucidated by GC/PTR-MS. Coffee samples roasted to different roasting degrees and ground to different particle sizes were studied under dry and wet stripping conditions. To investigate the accuracy of modeling the VOC release kinetics recorded using PTR-MS, online kinetics were compared with kinetics reconstituted from purge and trap samplings. Results showed that uncertainties in ion intensities due to the presence of isobaric species may prevent the development of a robust mathematical model. Of the 20 identified compounds, 5 were affected to a lower extent as their contribution to specific m/z intensity varied by <15% over the stripping time. The kinetics of these compounds were fitted using physical and statistical models, respectively, the diffusion and Weibull models, which helped to identify the underlying release mechanisms. For dry stripping, the diffusion model allowed a good representation of the release kinetics, whereas for wet stripping conditions, release patterns were very complex and almost specific for each compound analyzed. In the case of prewetted coffee, varying particle size (∼400–1200 μm) had no significant effect on the VOC release rate, whereas for dry coffee, the release was faster for smaller particles. The absence of particle size effect in wet coffee was attributed to the increase of opened porosity and compound diffusivity by solubilization and matrix relaxation. To conclude, the accurate modeling of VOC release kinetics from coffee allowed small variations in compound release to be discriminated. Furthermore, it evidenced the different aroma compositions that may be obtained depending on the time when VOCs are recovered.

KEYWORDS: VOCs; coffee; PTR-MS; release; kinetics; modeling

INTRODUCTION

For the production of soluble coffee, aroma recovery efficiency is one of the most important factors besides the optimal selection of raw material coffee. Optimizing aroma recovery by modulating stripping parameters such as roasting degree, ground particle size, or coffee prewetting is important for obtaining maximal recovery on the one hand and a balanced aroma compound composition on the other hand. The objective of this study is to investigate the feasibility of modeling the release kinetics of volatile organic compounds (VOCs) from

roasted and ground coffee under stripping conditions depending on the stripping parameters. Being able to apply a model for calculating the variations in compound balance and quantity depending on those parameters would allow prediction of variations in aroma perception of the final product.

Empirical models are frequently used when information on the mass transfer mechanisms and equilibrium relationships is missing. In case they fit well the data, links between the model parameters and different mass transfer mechanisms might be provided. Examples of the release of VOCs from a food system being modeled using empirical or mechanistic models can be found in several publications (*1–4*).

Conventional analytical techniques used to sample VOCs released in the headspace (HS) of food generally include (1)

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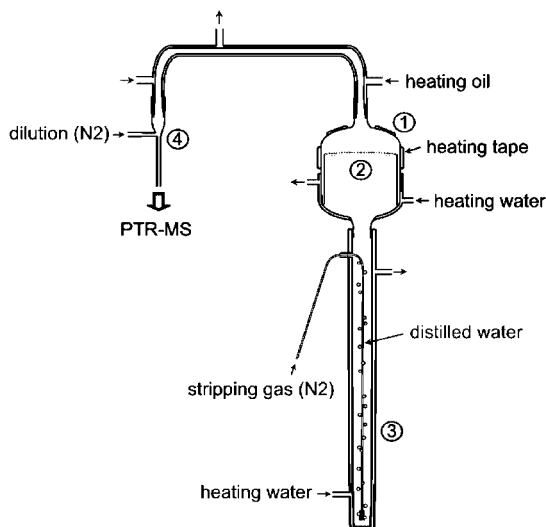† Nestlé Product Technology Center.
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Figure 1. System for coffee VOC stripping using water-saturated nitrogen (1, double-jacketed glass stripping cell with temperature controllers; 2, ~50 μm stainless steel mesh maintaining the coffee bed in the cell; 3, water column for generating vapor-saturated nitrogen; 4, sampling port for the PTR-MS).

recovery of VOCs on a physical support (trapping, enrichment), (2) desorption and separation by gas chromatography, and (3) identification (by MS or other analyzers) and quantification using molecular standards (5, 6). Methods using aroma trapping with gas chromatography (GC) were used by Haesselbarth and Ullrich (7) to monitor aroma release kinetics above the cup of coffee brew. On a series of Tenax/Carboxen traps placed directly

above the cup of coffee, the authors trapped the released headspace for 3–20 s (depending on the desired time resolution). After 2–3 min, the intensity of the very volatile compounds was decreased to a few percent, whereas the less volatile compounds decreased to values between 20 and 50%, thus leading to a drastically modified aroma balance with time. A non-time-resolved aroma analysis performed in closed systems would give integral quantities of aroma compounds and not reflect these important differences.

Due to the unavoidable sample preparation time (trapping, preconcentration, separation, etc.), during which unstable compounds may undergo some degradation, and due to the low resolution in time, conventional HS-GC analysis presents evident limitations, and fast online methods are more and more used to monitor aroma release (8). These important advantages have to be contrasted with a potential drawback of online MS techniques. The absence of chemical separation implies that, at any measurement cycle, we obtain the spectrum of the superposition of all compounds' spectra (termed "fingerprint"). Depending on the complexity of the analyzed mixture, compound identification (and quantification) can sometimes be difficult or impossible.

However, several methods were developed to allow the direct analysis of the components in the headspace without separation (9–14). PTR-MS was introduced in 1993 by W. Lindinger and co-workers (14). Numerous applications in medical, environmental, and food areas are reported in the literature (15, 16). PTR-MS is based on chemical ionization by proton transfer reaction with H_3O^+ using a drift tube as a reaction chamber followed by a quadrupole mass spectrometer for ion separation. A detailed description of the PTR-MS technique is published (16–19). An important advantage of
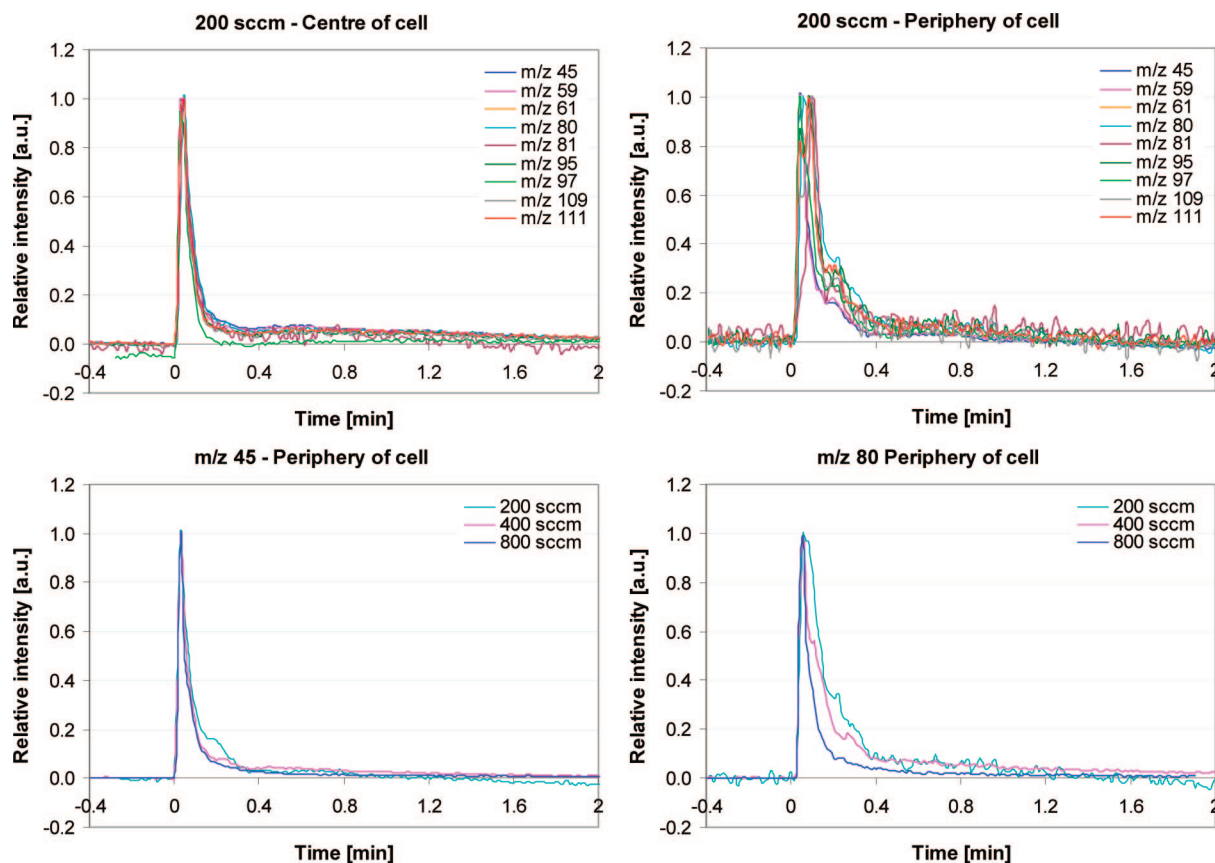

Figure 2. Response of the stripping system to a pulse-shaped injection of volatile compounds at the center and at the periphery of the cell, for various dry gas flow rates (similar results with dry or water-saturated nitrogen): *m/z* 45, acetaldehyde; *m/z* 59, acetone; *m/z* 61, acetic acid; *m/z* 80, pyridine; *m/z* 81, furfuryl alcohol; *m/z* 95, methylpyrazine; *m/z* 97, furfural; *m/z* 109, dimethylpyrazine; *m/z* 111, methylfurfural.
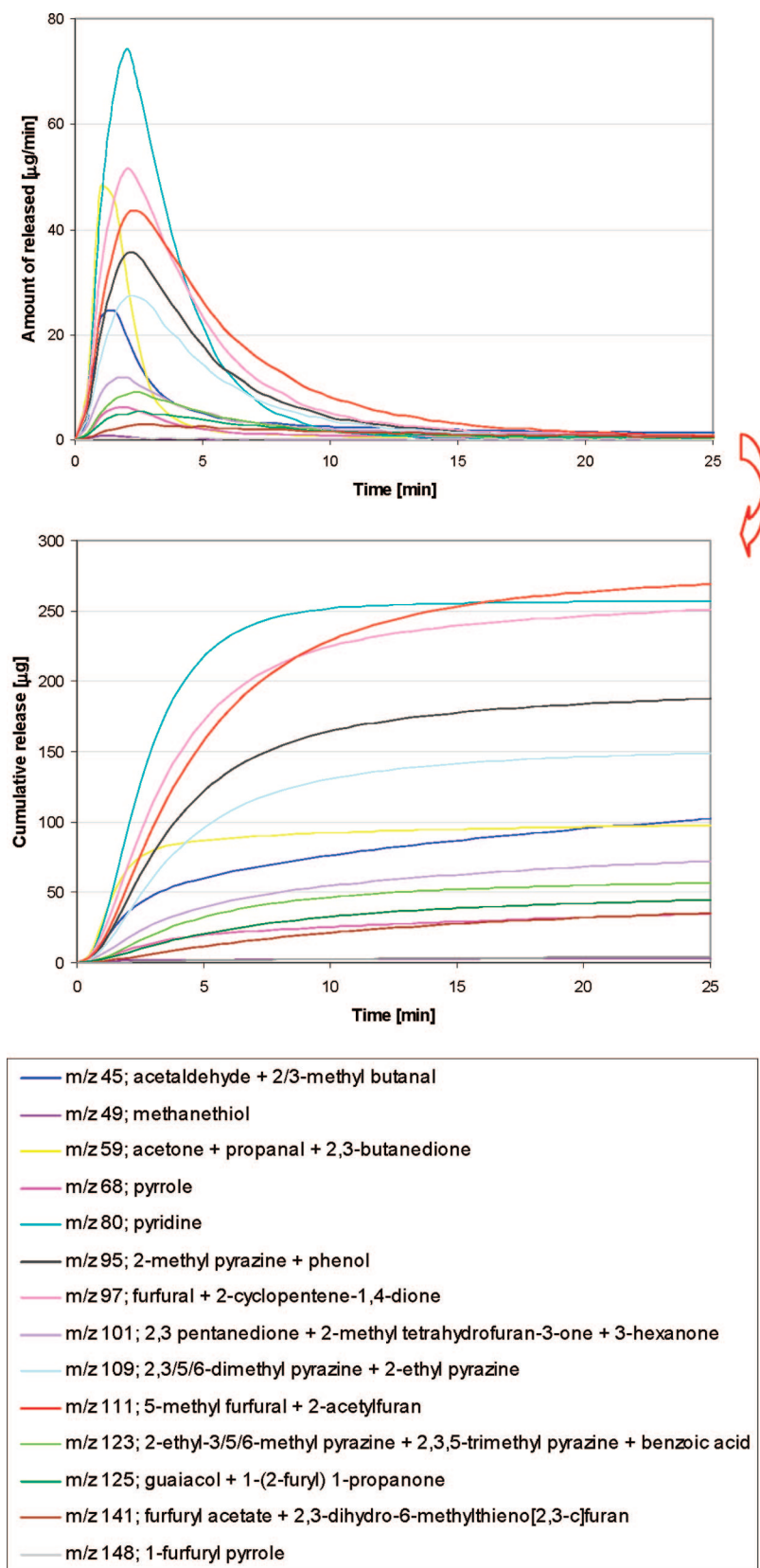
Figure 3. Instantaneous and cumulative release of VOCs from roasted and ground Colombian coffee (wet stripping conditions). Mentioned compounds represent the major contribution to the specific ion trace (>95%).

applying chemical ionization instead of electron impact ionization or charge transfer reaction (i.e., from Xe^+) is the soft ionization. Many of the proton transfer processes are nondissociative, so that only one product ion occurs for each neutral compound. Nevertheless, most aroma compounds are less stable when ionized within the reaction chamber of PTR-MS and suffer on fragmentation. Parent and fragment ions (isobaric ions) from different compounds can overlap in PTR-MS spectra and prevent a clear identification of VOCs in a complex mixture. The combination of VOC separation by GC followed by simulta-
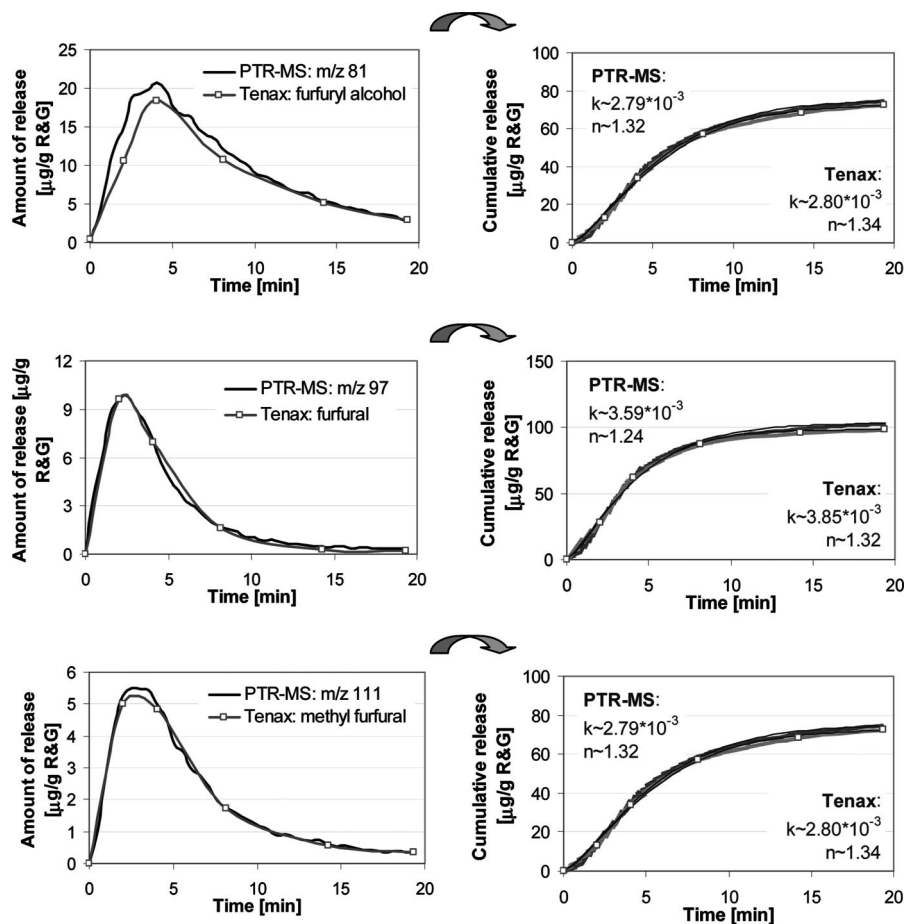
Figure 4. Effect of varying contribution to a specific *m/z* ion abundance on the shape of release kinetics: examples for release kinetics of furfuryl alcohol and furfural from roasted and ground (R&G) coffee CTN 100, 1100 μm particles, stripped with water-saturated N_2.

neous and parallel detection of the GC effluent by PTR-MS and EI-MS was introduced in refs 20 and 21. The coupling of PTR-MS with GC-MS allowed a clear interpretation of the complex PTR-MS spectra. Lindinger et al. (21) applied the technique to the HS of coffee in the first few minutes following beverage preparation. Although some *m/z* ion signals consisted of a superposition of ions originating from different compounds, a series of ion traces was nearly pure (>86% of participation in a *m/z* ion signal). Hence, in the online PTR-MS measurement of the coffee HS, the ion traces at *m/z* 68, 75, 80, and 95 were assigned to pyrrole, methyl acetate, pyridine, and 2-methylpyrazine, respectively. However, the assignment was valid only for a specific time window, and the relative concentrations of the identified molecules may change over time. For example, it was observed that 2-methylbutanal had a decreasing contribution to the PTR-MS ion trace *m/z* 87, whereas compounds such as 2,3-butanedione and γ-butyrolactone showed an increasing contribution with time.

Coffee aroma belongs to the most challenging systems to be analyzed by online HS techniques as more than 900 different VOCs have been identified in coffee (22, 23), including compounds found in green and roasted coffee, from different botanical origins. Using PTR-MS, coffee HS was analyzed under various conditions, during roasting (13, 24, 25), upon solubilization of soluble/brew coffee (15, 26), or above the cup (27). In the last study, Yeretzian et al. proposed a tentative assignment and rough quantification of 64 compounds from the HS of coffee brew. Several analyses of coffee have shown that the differences in aroma perception are not so much caused by the presence or absence of different odorants but mostly by variations in their

relative concentrationd (28–31). Thus, accurate measurement and modeling of release kinetics of coffee aroma compounds is very relevant to understand variations of aroma perception.

In terms of modeling, the model of Fickian diffusion in a sphere was used by many authors: for solid–liquid extraction (32–35) and carbon dioxide degassing (36). The analytical solution to Fick's diffusion in a sphere was developed by Crank (37)

$$\frac{C_t}{C_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[\frac{-D_{app}n^2\pi^2 t}{R^2}\right] \quad (1)$$

where C_t is the total amount of diffusing substance that has left the sphere at time t (g), C_∞ is the quantity corresponding to C_t after infinite time (g), D_{app} is the apparent diffusion coefficient (m²/s), n is the number of composite spheres, and R is the radius of the sphere (m).

Weibull's model was recently applied in many biological systems for the modeling of release or absorption processes (2–4). This model has two parameters: the scale parameter k, which represents the process rate constant (s⁻¹), and the shape parameter n (dimensionless). The higher k is, the faster the process is at the beginning of the release. If $n = 1$, Weibull's model reduces to classical first-order kinetics. When $n > 1$, the sigmoid shape of the Weibull function indicates that a complex mechanism governs the release process.

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-(kt)^n\right] \quad (2)$$

where M_t and M_∞ are the total amount (g) of substance transferred, respectively, at time t (s) and at infinite time.

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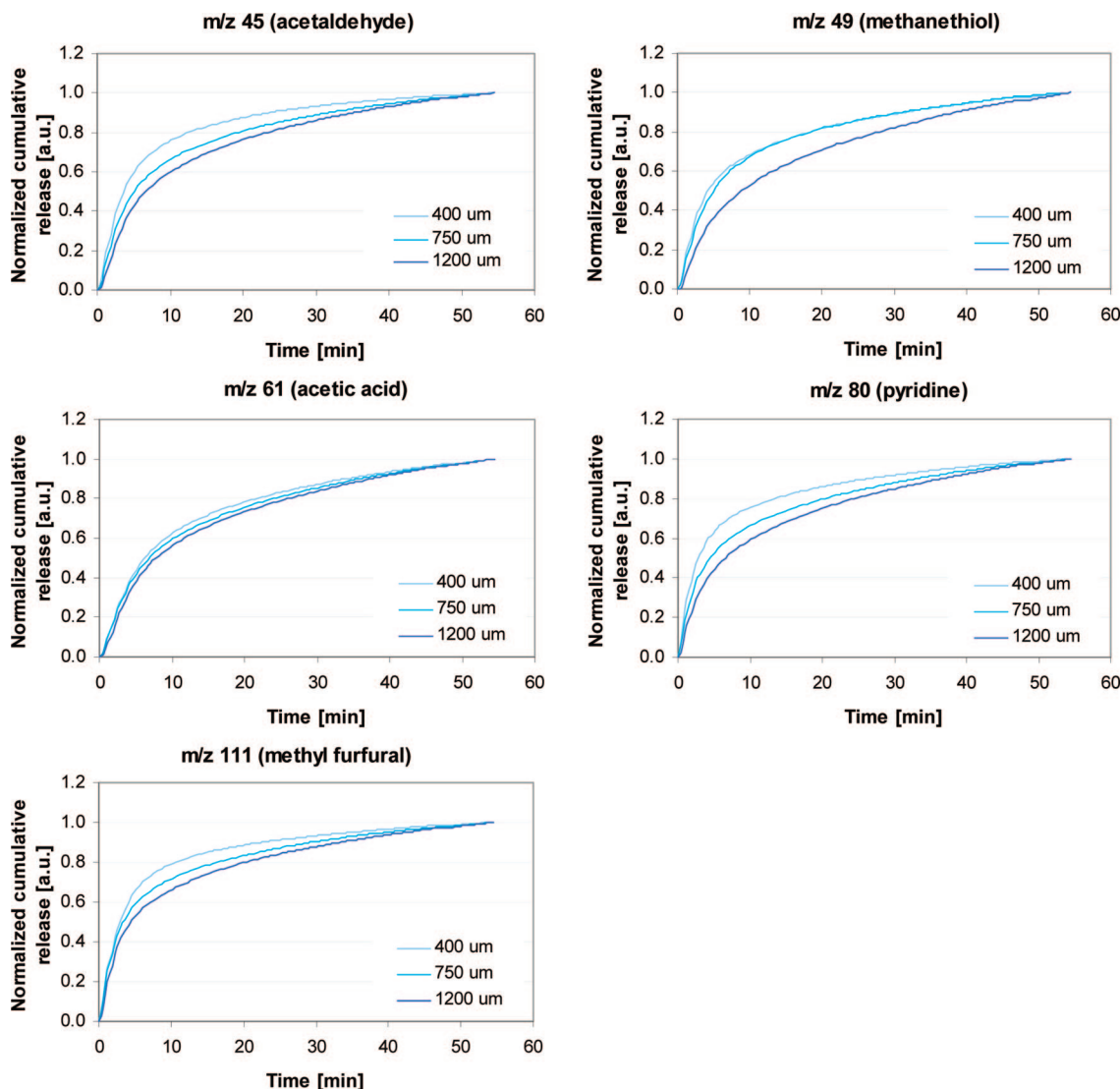*J. Agric. Food Chem.,* Vol. 55, No. 25, 2007 **10121**

Figure 5. Effect of particle size on the release kinetics of VOCs from coffee under dry stripping conditions: normalized curves (normalization based on total amount recovered between 0 and 55 min).

Marabi et al. (*4*) used Weibull's function to simulate rehydration of air-dried and freeze-dried carrots. The authors derived values of the shape parameter *n* for various mechanisms of water uptake by comparing Weibull's model with other theoretical approaches, that is, Fickian diffusion, external resistance model, and relaxation. For spheres, cylinders, and slabs, values for diffusion were 0.67, 0.72, and 0.81, respectively; for external resistance, values were 1.0, 0.98, and 0.97, respectively; and for relaxation, values were 1.21, 1.32, and 1.60, respectively. The authors concluded that Weibull's function could be used for differentiating various mechanisms of water uptake. A similar approach was used by Papadopoulou et al. (*2*) to describe the release of drugs from dissolved tablets. The Fickian diffusion process was identified when $n < 0.75$, whereas a combined mechanism (Fickian and case II transport) was associated with *n* values in the range of $0.75 < n < 1$. Finally, Garcia-Pascual et al. (*3*) used Weibull's model to study the effect of temperature in the rehydration kinetics of mushrooms and found a Weibull shape parameter *n* in the range of values of mass transfer processes at which the internal resistance prevails: ranging between 0.54 and 0.64. To conclude, although Weibull's function has been developed empirically, the results of recent studies provide a link between the model parameters and different release mechanisms in various system geometries.

Accurate modeling of VOC release kinetics is possible using time-resolved measurement techniques such as PTR-MS. However, the identification of each species and its contribution to a given ion trace intensity is key to achieving accurate prediction of single-compound kinetics. In the investigation of the feasibility of modeling the release kinetics of VOCs from roasted and ground coffee measured online using PTR-MS, the presence of isobaric species and its effect on the measurements of single compounds are first determined. Then, Fickian diffusion and Weibull's models are tested to study the underlying release mechanisms.

EXPERIMENTAL PROCEDURES

Coffee Samples. Colombian Arabica green beans (Nestlé) were roasted in a fluidized bed hot air roaster (Neuhaus Neotec) to light, medium, and dark roast degrees at 236 °C for 380, 550, and 900 s, respectively. Roasting degree was characterized by a color test number (CTN) by color measurement (Colortest II, Neuhaus Neotec) of the coffee powder with 850 ± 50 μm average particle size. CTN values of the three aforementioned roasting degrees were 100, 80, and 60 ± 2, respectively. The roasted beans were ground using a disk grinder (Ditting KFA 903) to a defined particle mean volume diameter.

Right after grinding and sampling, 5 g of roasted and ground coffee was placed in a 200 mL glass vessel (65 mm diameter) and wetted
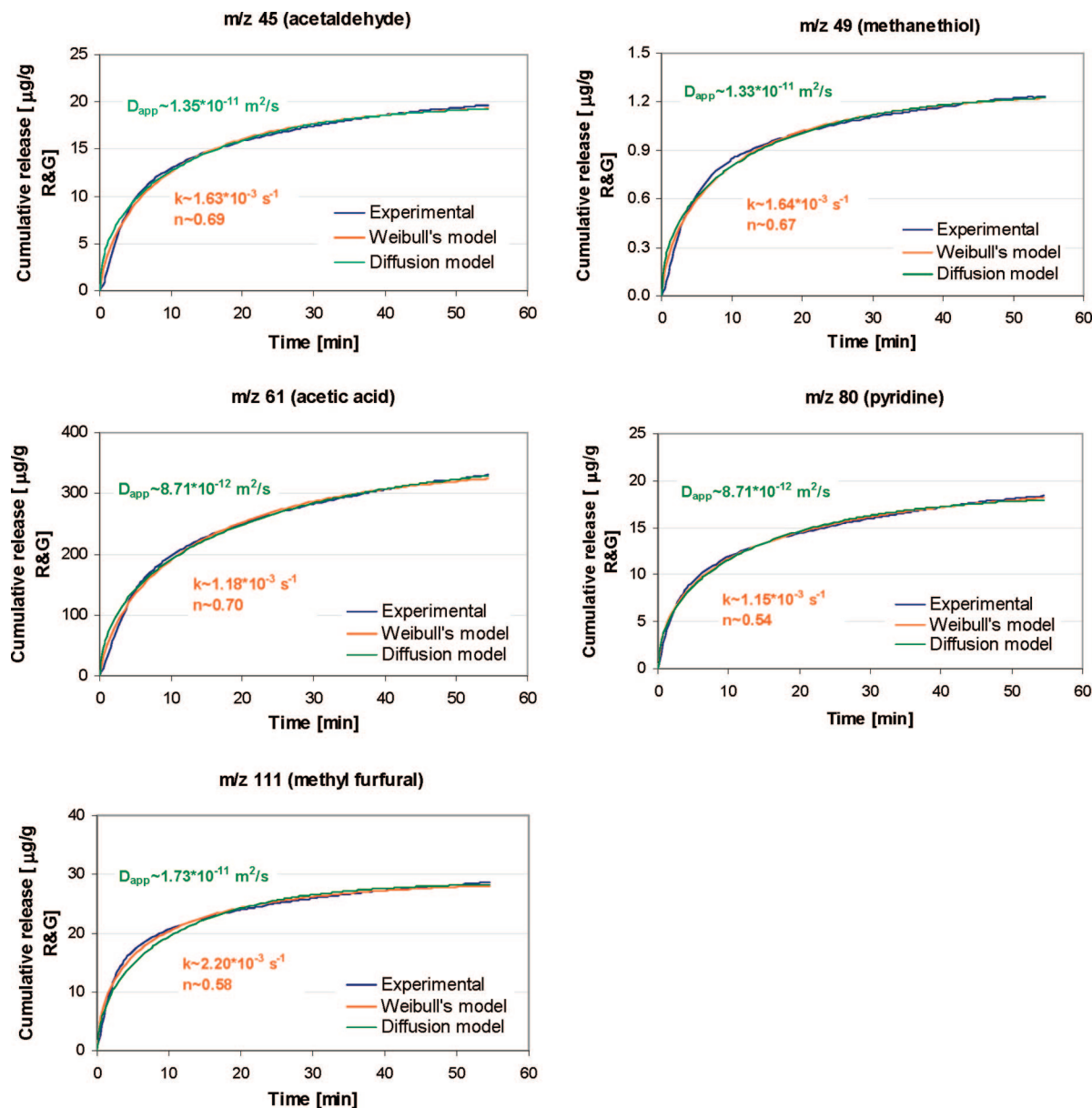
Figure 6. Experimental release kinetics of VOCs from 750 μm coffee particles under dry stripping conditions and predicted kinetics using the diffusion and Weibull models.

according to the following standardized procedure: Distilled water (arbitrarily 5 mL) at 90 ± 2 °C was added manually using a graduated glass pipet and the sample stirred for 30 s with a stainless steel coffee spoon. Wetting homogeneity was evaluated by weighing 20−50 mg of particles from six different parts of the sample. The water content of the particles was then determined gravimetrically by oven-drying.

These controls showed that the chosen wetting procedure provided a homogeneous water distribution in the particles, with a relative standard deviation (RSD) of <5%. The extent of coffee wetting is expressed as water content. The definition of water content (percent w/w) is as follows: 100 × mass of added water to the material (g)/ total mass of material (g).

Stripping System. The stripping system used to measure aroma release kinetics is similar to the system developed by Pollien et al. (*38*) for the measurement of air−coffee partition coefficients. **Figure 1** provides a schematic representation of the setup.

Coffee was placed 2 min after the beginning of the wetting procedure on a mesh inside the stripping cell by opening the upper part of the cell, and release kinetics were recorded for ~60 min under stripping. In the case of dry roasted and ground coffee (no application of the wetting procedure), a delay of 2 min was kept between sampling and stripping. Two stripping procedures were used:

(1) Dry roasted and ground coffee was stripped with 740 sccm of dry nitrogen at 90 °C. These conditions are referred to as "dry stripping conditions".

(2) Coffee was prewetted to a 50% w/w water content and stripped with 740 sccm of water-saturated nitrogen at 90 °C. These conditions are referred to as "wet stripping conditions".

As the stripping cell is not a perfect cylinder, gas velocity at the periphery or at the center of the cell could affect measured kinetics. To validate the accuracy of the online stripping system, the effect of the gas velocity variation within the cell on measured kinetics was determined. To this effect a test gas was manually injected via a piece of GC-column glass capillary at different places within the stripping cell, and response patterns were recorded by PTR-MS. **Figure 2** shows kinetics patterns for several compounds, after injection at the center or at the periphery of the cell. Results indicated that the transfer delay was independent from the place of injection but slightly increased when the gas flow rate decreased. However, we concluded that the effects of such delays (<30 s) do not significantly alter the shape of measured release kinetics during coffee stripping and thus were neglected in this study.

PTR-MS. Before the gas leaving the stripping cell was introduced into the online gas analyzer, two dilution steps were necessary to avoid
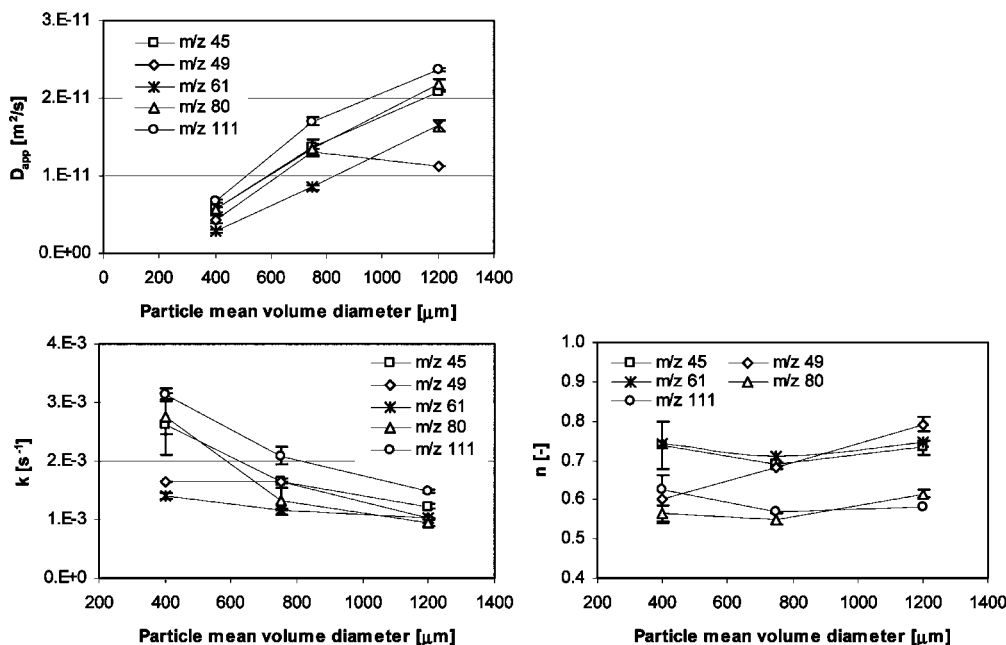
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Figure 7. Effect of particle size on the rate constants D_{app} (diffusion model) and k and n (Weibull's model) for acetaldehyde (m/z 45), methanethiol (m/z 49), acetic acid (m/z 61), pyridine (m/z 80), and methylfurfural (m/z 111), dry stripping conditions.

saturating the instrument. The gas coming from the stripping cell was first diluted and cooled by the addition of 6000 sccm of nitrogen at room temperature (to avoid condensation on cold spots along the lines heated at 80 °C and saturation of the mass spectrometer). A second dilution step was adapted according to the gas concentration (e.g., dilution factor of 5/6 or 2/3 in the case of dry stripping and wet stripping conditions, respectively). Finally, ca. 40 sccm of this diluted gas was introduced into the drift tube of the high-sensitivity PTR-MS HS (Ionicon Analytik).

As transfer line to the inlet system of the PTR-MS a quartz glass coated steel tube (inert surface) was used to avoid memory effects and catalytical reactions (Silcosteel tubings; Horst).

The online PTR-MS was used in scan mode to monitor the ion traces from m/z 21 to m/z 170 with a dwell time of 0.2 s per mass. The parameters of the drift tube were set as follows: drift voltage, 600 V; temperature, 80 °C; pressure, 2 mbar.

Mass specific transmission values (quadrupole transmission) were measured according to the specifications of the supplier (*39*). Background and transmission corrected spectra were averaged over three sample replicates, and the RSD of the ion intensity was calculated at each acquisition point of the kinetics (i.e., every 30 s). For the various compounds considered, RSD values were <20%. These variations are in accordance with those reported in other studies of aroma release from coffee. In the study by Haesselbarth and Ullrich (*7*), who used traps to monitor aroma release above a cup of coffee, most of the compounds were measured with a repeatability of >10% RSD. Conversely, very water-soluble compounds were determined with poor repeatability of >50% RSD.

The quantified released amount of compounds corresponding to a specific ion trace was calculated using the following equation. The equation takes into account the specific physical conditions in the reaction and detection chambers. A full description of the quantification model is given by Pollien et al. (*40*).

$$C_{VOC} = \frac{(Int_{MH^+}/Trans_{MH^+})P_s T_{drift} F m_M}{(Int_{H_3O^+}/Trans_{H_3O^+})P_{drift} T_s N t_{drift} k} \times \frac{1}{frag} \quad (3)$$

where C_{VOC} is the release rate (g/min) of VOCs corresponding to ion trace MH^+; Int_{MH^+} and $Int_{H_3O^+}$ are the PTR-MS signal intensities of the protonated ion and primary ion, respectively (counts per second); $Trans_{MH^+}$ and $Trans_{H_3O^+}$ are the mass specific transmissions of the protonated ion and primary ion, respectively (dimensionless); Ps is the

standard pressure (1.013 bar); T_{drift} is the drift tube temperature (K); F is the flow rate taking into account the purge and the dilution gas flow (sccm); m_M is the molecular mass of VOC (g/mol); P_{drift} is the drift tube pressure (0.002 bar); T_s is the standard temperature (273.15 K); N is Avogadro's number (6.0220×10^{-23} mol^{-1}); t_{drift} is the reaction time (105×10^{-6} s); k is the reaction rate coefficient of the VOC with H_3O^+ ($\sim 2 \times 10^{-9}$ cm^3/s); and frag is the ratio of contributing fragment if MH^+ is a fragment of the observed VOC.

The relative contribution of different compounds corresponding to a specific m/z value was quantified during the stripping process, using the PTR-MS/GC-MS coupling as reported by Lindinger et al. (*21*). The following methodology was used:

Coffee was stripped under various conditions (CTN 60 or 100, ground to 400 or 1100 μm particles, dry or wet stripping conditions).

The sample HS was trapped on Tenax tubes by connecting traps at subsequent time intervals to the exhaust line of the release setup. Compounds were trapped for 50 s at 1.5, 3.5, 7.5, and 13.5 min after stripping started (at 19.5 min of stripping, concentrations trapped were too low to be analyzed). The trapping flow rate was set to 50 sccm.

The trapped volatiles were thermally desorbed using an automatic thermal desorber (ATD 400, Perkin-Elmer), cryofocused and injected into the DB-Wax capillary GC column (60 m × 0.53 mm, film thickness = 1 μm) (J&W Scientific). The column was kept at 20 °C for 1 min, then heated to 220 °C with a 4 °C/min ramp, and finally kept at this temperature for 10 min. The column outlet was split into the MS and the PTR-MS for the simultaneous analysis of the eluted compounds.

Identification was performed by EI fragmentation pattern recognition (GC-EI-MS data) using the Wiley database and by comparison of the observed retention time with that of the injected standard compound.

The GC/PTR-MS spectrum allowed determination of the relative contributions of different compounds with identical m/z values and therefore to interpret the online monitored release. For each mass, the relative intensity of the different eluted peaks was determined. Peaks with signal/noise ratio lower than 10 were not considered.

Modeling of Aroma Release Kinetics. VOC release kinetics was analyzed by converting the curves of released amount into cumulative release versus time, as shown in **Figure 3**. The cumulative release profiles were then fitted with the diffusion and Weibull models using Excel macros, and the parameters k and n and the apparent diffusion coefficient D_{app} were quantified. Weibull's model was already presented

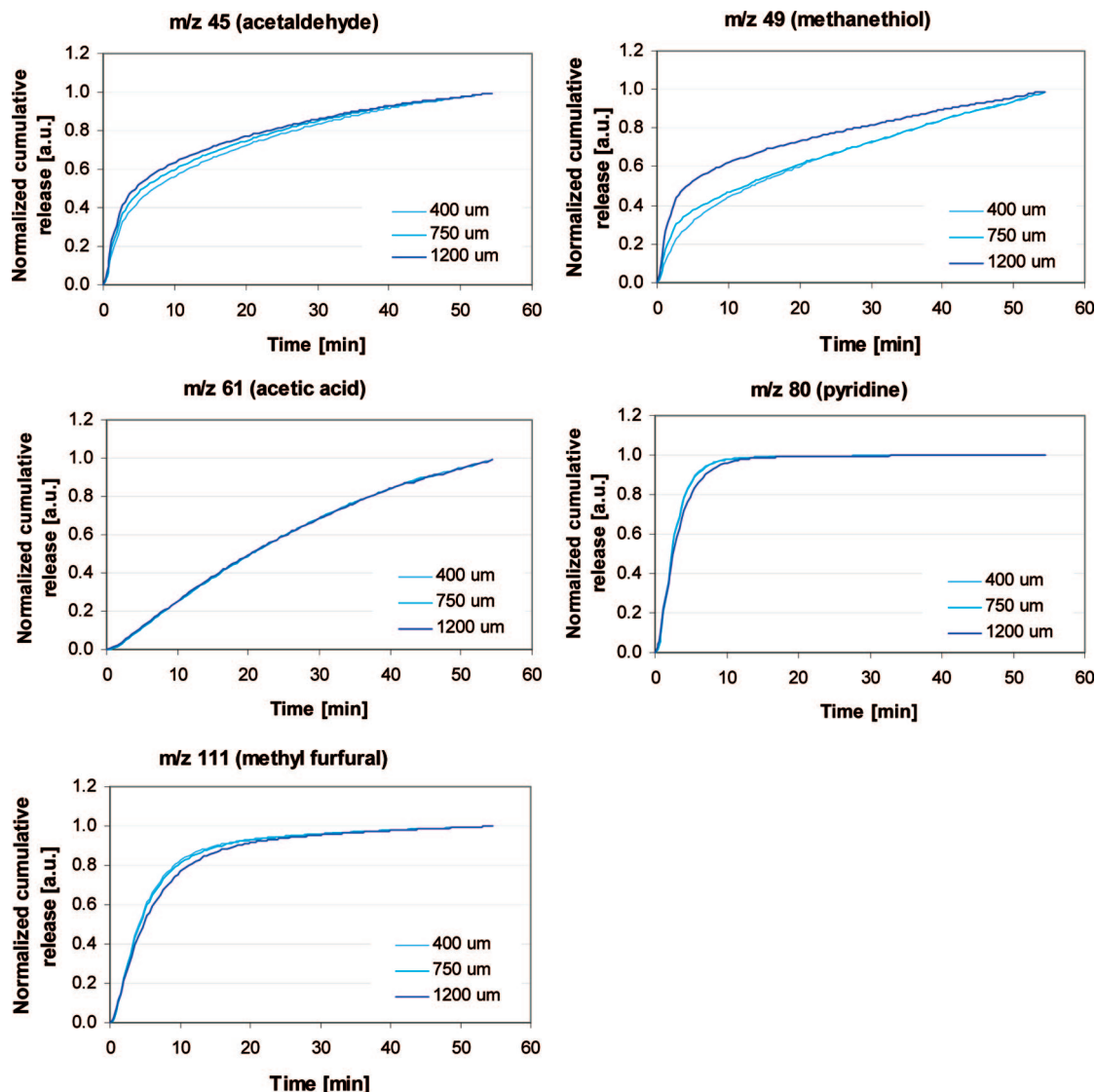**10124** *J. Agric. Food Chem.,* Vol. 55, No. 25, 2007

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Figure 8. Effect of particle size on the release kinetics of VOCs from coffee under wet stripping conditions: normalized curves (normalization based on total amount recovered between 0 and 55 min).

in the introduction. The diffusion model used is the model of non-steady-state diffusion in a sphere with surface evaporation (*37*):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6B_i \exp(-\beta_n^2 D_{app} t/R^2)}{\beta_n^2 [\beta_n^2 + B_i(B_i - 1)]} \qquad (4)$$

β_n are the positive roots of $\beta \cot \beta + B_i - 1 = 0$ and $Bi = R(k'K_{aw})/D$. M_t and M_∞ are the total amounts of diffusing substance that have left the sphere at time *t* and at infinite time, respectively (g); *n* is the number of composite spheres (chosen to be 200); D_{app} is the apparent diffusion coefficient (m²/s); *R* is the radius of the sphere (m); Bi is the Biot number; k' is the external mass transfer coefficient (m/s); and K_{aw} is the partition coefficient between gaseous and aqueous phases [(kg/m³)$_{air}$/(kg/m³)$_{water}$].

Using the rate coefficient estimates, the residual between theoretical and experimental concentrations was minimized iteratively, using the least-squares method. Each set of release kinetics is presented after normalization (time 55 min taken as the maximum) to allow a better comparison of the kinetics and to see the effect of the studied parameters.

RESULTS AND DISCUSSION

Isobaric Ions and Kinetics Determination. The contribution of ions from different molecules to a specific ion trace (*m/z* value) (isobaric ions) can make it difficult to determine the

release kinetics of individual VOCs with PTR-MS. We measured the change in the relative concentration of molecules of a specific *m/z* value during the stripping process, using Tenax traps and the GC/PTR-MS coupling system. Examples of the relative contribution of compounds to a specific *m/z* intensity are reported in **Figure 4**. Each graph shows the kinetics of the released superposition of compounds with a specific *m/z* value measured by online PTR-MS and the release kinetics of the single compounds contributing to the specific *m/z* value, as determined via Tenax trapping using offline GC/PTR-MS. For example, the contribution of furfural to *m/z* 97 varied by 35% over a stripping time of 19 min. Comparing Weibull's parameters *k* and *n* determined from the online PTR-MS data and from the trapping measurements, we found variations of 7 and 6%, respectively. For methylfurfural, the contribution of the compound to the *m/z* 111 varied by 11% and Weibull's parameters varied by <2%.

To conclude, we found five compounds for which the contribution to a specific ion trace during the stripping process varied by <15%, for various stripping conditions. These compounds were acetaldehyde (*m/z* 45), methanethiol (*m/z* 49), acetic acid (*m/z* 61), pyridine (*m/z* 80), and methylfurfural (*m/z* 111). A variation of <15% was estimated not to affect

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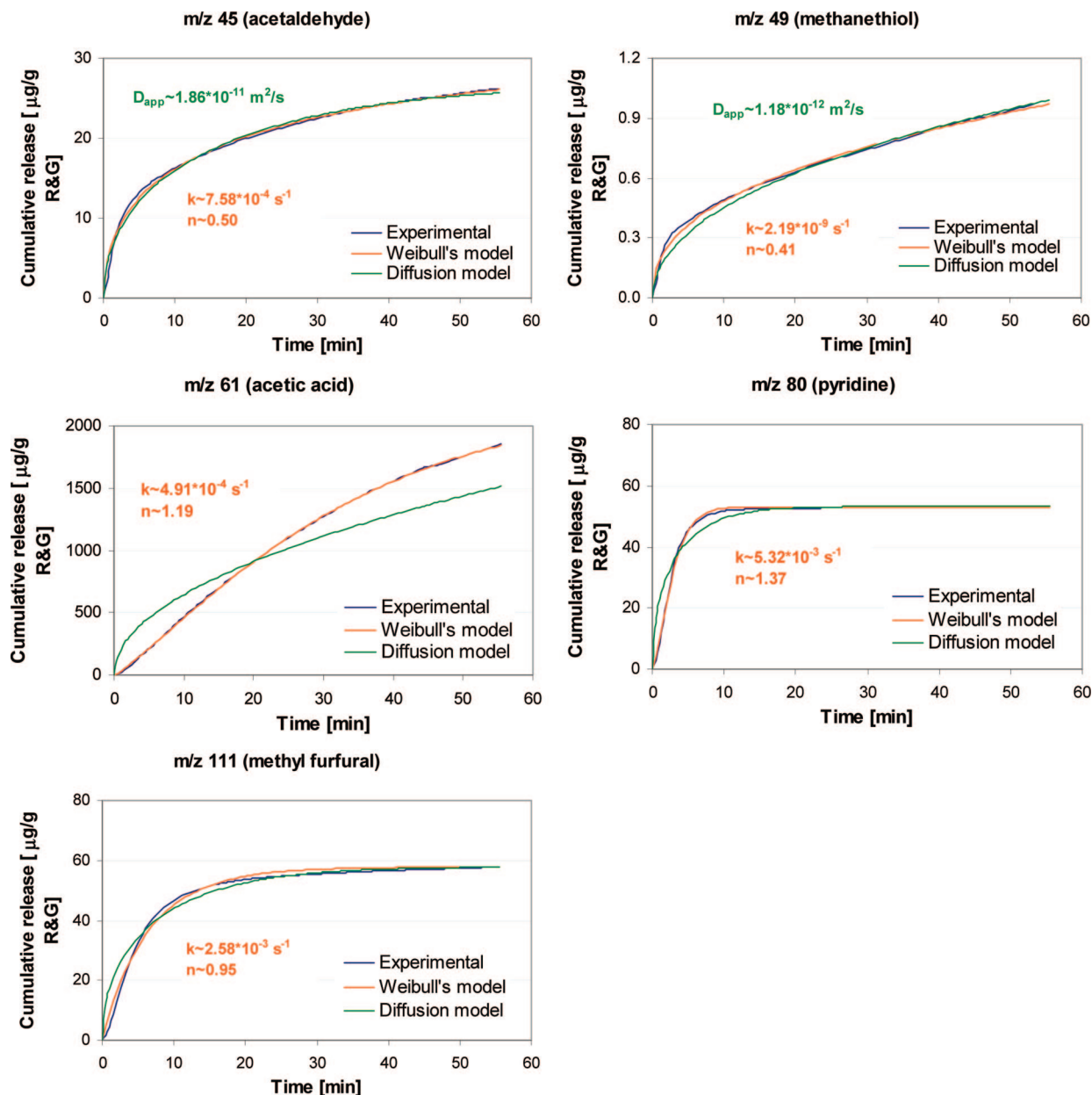J. Agric. Food Chem., Vol. 55, No. 25, 2007   **10125**

Figure 9. Experimental release kinetics of VOCs from 750 μm coffee particles under wet stripping conditions and predicted kinetics using the diffusion and Weibull models.

significantly the shape of the kinetics. The results reported here essentially concern online release kinetics of these five compounds and their dependence on coffee particle size at dry and wet stripping conditions. Applying GC/PTR-MS to measure release kinetics (trapping measurements) is not restricted to these five compounds but much less accurate. However, it still showed the possibility to obtain enough information to apply the models (data partially shown in **Figure 4**). In the case of more dynamic release processes where an offline technique is not applicable, a new development in online high mass resolution mass spectrometry would be necessary to distinguish between superposing compounds to a specific m/z value as described before. Nevertheless, there will be no possibility to distinguish between isomers.

Application: Effect of Coffee Particle Size on VOC Release. *Dry Stripping Conditions.* **Figure 5** presents different release kinetics from coffee under dry stripping conditions, changing the particle sizes. Results showed that release kinetics were faster at smaller particle size. This may be due to the higher

open porosity of smaller coffee particles as shown previously from pycnometric measurements (*41*). Results are in accordance with findings from the work by Grosch (*42*), who concluded that the evaporation of odorants is 8 times more efficient from ground coffee than from whole beans.

Measured release kinetics (**Figure 5**) were fitted using the diffusion and Weibull models. The results for 750 μm particle size are presented in **Figure 6** and show a relatively good fit for both models. The evolution of Weibull's parameters k and n and the apparent diffusion coefficient D_{app} as a function of particle size is shown in **Figure 7** and confirms that VOC release is significantly faster at lower particle size (higher k value). The good quality of the fit by the diffusion model suggests that intraparticle diffusion is the limiting transfer mechanism. Furthermore, a value of Weibull's shape parameter n of 0.6–0.7 has been assigned to diffusion mechanisms by various authors (*2–4*).

According to the diffusion theory for an ideal spherical particle, the diffusion coefficient D_{app} should be independent
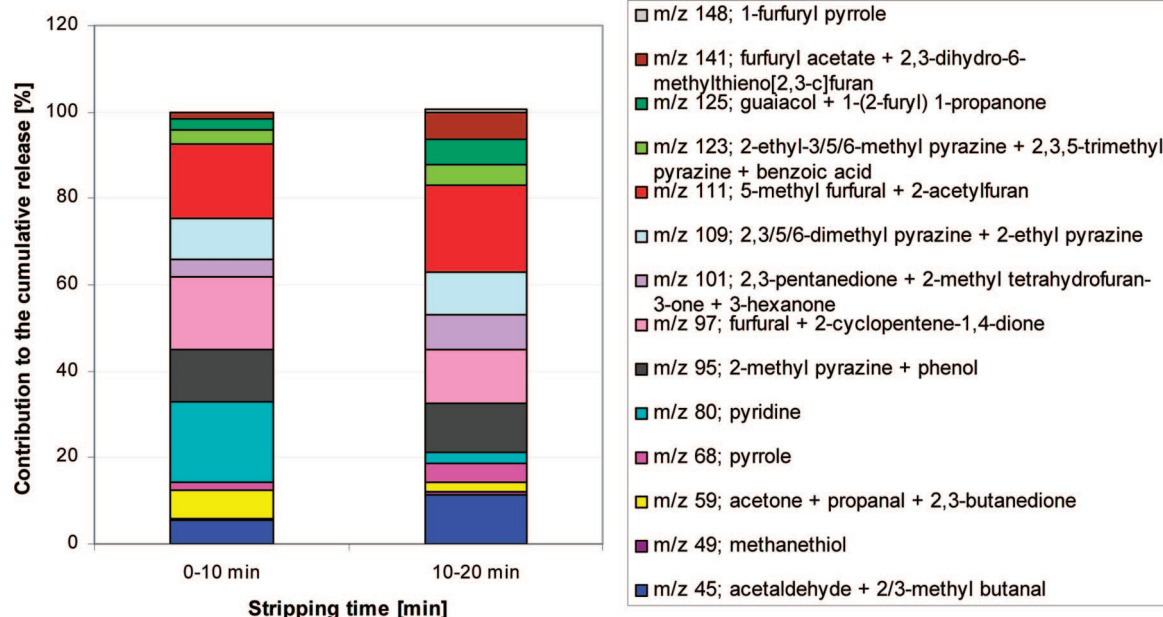
Figure 10. Relative concentration of aroma compounds from coffee during two different stripping windows: 0–10 and 10–20 min (wet stripping conditions).

of particle size, whereas, in our study, the coefficient is higher for larger particles (**Figure 7**). Results from the work of Anderson et al. (*43*) showed the same discrepancies. Carbon dioxide had higher diffusivity at larger coffee particle size, which was tentatively explained by the tighter packing of smaller particles, reducing gas circulation through the particle bed. Thus, difference in diffusivities may occur due to differences in packing tightness. Another plausible explanation, however, is that the particle radius may not be the relevant dimension characterizing the diffusion path length.

To summarize, internal mass transport was found to be the limiting factor when dry stripping conditions were applied. This finding was also validated by the fact that the amount recovered was higher for lower particle size (results not shown), even though the gas flow rate (and the external mass transfer) remained the same.

Wet Stripping Conditions. Contrary to dry stripping conditions, in the case of wetted coffee there was no significant effect of particle size on VOC release kinetics, as shown in **Figure 8** (except for methanethiol, release was faster for larger particles), and Weibull's parameters did not vary significantly. Two complementary phenomena may be involved that oppose the expected size effect (i.e., slower rate for larger particles):

Wetting led to a decrease in closed porosity and an increase in matrix mobility, as was confirmed in previous studies (*41, 44*). Consequently, the real characteristic length of the diffusion path is most likely smaller than the effective particle size.

For wetted coffee at small particle size, particle aggregation occurs, decreasing the gas accessibility and diffusivity. Aggregation results in an increase in the apparent size of the particles. This phenomenon has already been discussed for small particle size when porosity is measured by He pycnometry (*44*).

For wet stripping conditions, the diffusion model was not able to fit accurately the release kinetics (**Figure 9**). Furthermore, for wet coffee, the parameter n was higher for acetic acid, pyridine, and methylfurfural ($\sim$1.2, 1.4, and 1.0, respectively) than for acetaldehyde and methanethiol ($\sim$0.3–0.6). Values of $0.75 < n < 1$ have been attributed to "Fickian diffusion associated with case II of transport" or to significant "external

resistance", whereas values of $n > 1$ have been attributed to "relaxation" (*4, 45*).

(1) The hypothesis of high external resistance for methylfurfural is relevant as the compound presents a low K_{aw} value ($\sim$4.1 $\times$ 10^{-3} (g/L)$_a$/(g/L)$_w$, versus 4.0 $\times$ 10^{-2}, 6.1 $\times$ 10^{-1}, 1.9 $\times$ 10^{-4}, and 1.0 $\times$ 10^{-2} (g/L)$_a$/(g/L)$_w$ for acetaldehyde, methanethiol, acetic acid, and pyridine, respectively).

(2) For acetic acid and pyridine, chemical interactions can explain the observed behavior and the high values of n:

(a) Pyridine. The protonation of pyridine at coffee pH is expected to affect its release kinetics. It is known that pyridine is a weak base, and the nonvolatile protonated form of the compound (pyridinium ion) becomes dominant at pH < pK_A $\sim$ 5.3. Due to its high buffering effect, the pH of solutions containing 5−30% roasted and ground coffee does not vary significantly: pH $\sim$5.0–5.3. Using the acid–base relationship, the ratio [pyridine]/[pyridinium ion] can be calculated. At pH 5, $\sim$60% of the pyridine is in nonvolatile protonated form, which partially explains the fact that the release kinetics of pyridine quickly reached a plateau.

The following scenario for pyridine release can then be proposed: (1) In dry coffee, pyridine is trapped in the closed cells (or pores). (2) During wetting, it escapes quickly due to the increase in matrix open porosity. (3) At the same time, the pH is greatly decreased and the protonation of pyridine inhibits its further release. The remaining free pyridine diffuses out of the particles at a very low rate, that is, over a much longer time period than our experimental time window.
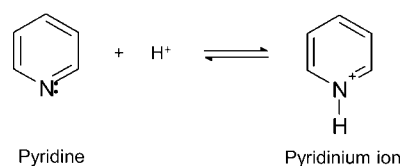
(b) Acetic Acid. A double effect accounts for the slow release of acetic acid from wetted coffee: dissociation of the compound (p$K_A \sim$ 4.75) and high solubility. At pH $\sim$5, the ratio [acetate]/[acetic acid] is $\sim$1.78, meaning that the nonvolatile form of

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the compound is dominant. High solubility of acetic acid in water is reflected in its low K_{aw} value.

To conclude, chemical interactions of acetic acid and pyridine with water may explain the different release patterns observed, whereas for dry coffee all compounds exhibited a similar behavior.

Impact of Release Kinetics on Coffee Aroma Composition. Depending on the time when aroma is recovered during the stripping process, different aroma compositions may be obtained. As an example, if we consider the release kinetics reported in **Figure 3**, coffee stripped from time 0 to 10 min should present an aroma mass balance different from that of the fraction recovered between 10 and 20 min (**Figure 10**). The first fraction contains more acetone, pyridine, and furfural, which are compounds with "almond and fishy" notes, and the second fraction, more acetaldehyde, furfuryl acetate, 2,3-pentanedione, and methylfurfural, which have "phenolic, roasty, and buttery" notes. The sensory characteristics of these two aroma fractions are likely to be different as well. Indeed, it is known that our perception of aroma depends on both the amount and the pattern of volatiles sensed at the olfactory epithelium (*28–31*). This illustrates the importance of understanding the mechanisms that govern the compounds' release kinetics. An interesting extension of this work would be the analysis of the aroma sensory profile during the stripping time and a comparison with the physico-chemical study based on the compounds' release kinetics.

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