JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Tongue Pressure and Oral Conditions Affect Volatile Release from Liquid Systems in a Model Mouth

O. Benjamin,*[,†,‡,§] P. Silcock,[‡] J. Beauchamp,[§] A. Buettner,[§] and D. W. Everett[†,‡]

[†]Riddet Institute, Massey University, Palmerston North 4442, New Zealand

[‡]Department of Food Science, University of Otago, Dunedin 9054, New Zealand

[§]Department of Sensory Analytics, Fraunhofer Institute for Process Engineering and Packaging IVV, 85354 Freising, Germany

ABSTRACT: The release of volatile organic compounds (VOCs) into the mouth cavity is an integral part of the way flavor is perceived. An *in vitro* model mouth with an artificial tongue was developed to measure the dynamic release of VOCs from liquid model systems [e.g., aqueous solution, oil, and oil-in-water (O/W) emulsions] under oral conditions. The release of seven selected VOCs was affected by the different polarity and vapor pressure of the compounds and their affinity to the liquid system media. Different tongue pressure patterns were applied to the liquid systems, and the release of VOCs was monitored in real time using proton transfer reaction−mass spectrometry. The release was significantly more intense for longer tongue pressure duration and was influenced by the tongue altering the sample surface area and the distribution of the VOCs. The role of saliva (artificial versus human) and the sample temperature had a significant effect on VOC release. Saliva containing mucin and a higher sample temperature enhanced the release.

KEYWORDS: *Volatile release, tongue pressure, PTR−MS, model mouth, saliva, sample temperature*

INTRODUCTION

The perception of flavor during food consumption depends upon the nature of the food composition, including the concentration of constituent volatile organic compounds (VOCs). This perception varies between individuals, depending upon different oral-processing behaviors and mouth physiology.[1] There is a positive relationship between the released amount of VOCs in the oral and nasal cavities and sensorial perception. Chewing and swallowing events control the velum palatinum (soft palate) barrier between the oral and nasal cavities; the so-called "swallow breath" then allows for a pulse of air from the lungs to carry VOCs to the olfactory receptors.[2] The distinctive retronasal perception, associated with this exhalation pulse, is mainly seen during the first expiration after swallowing.[3,4] To a lesser degree, *in vivo* experiments with solid and semi-solid food have also shown that movements of the jaw and tongue are capable of slightly opening the velum to allow for VOCs to be carried into the nasal cavity without the swallowing event occurring.[5]

The tongue has a crucial role in manipulating, transporting, and lubricating the bolus with saliva through the different phases of oral processing. The tongue propels the bolus from the oral cavity to the pharynx by applying pressure against the palate. Recent studies on tongue pressure during swallowing have shown substantial interindividual variance while maintaining a consistent pattern over time for each individual.[6] Both positive and negative pressures are generated, depending upon the location on the tongue and the time sequence during swallowing.[7] Direct contact between the tongue and the bolus raises the question of whether the pressure pattern of the tongue may also have an impact on VOC release. Tongue movements have been found to affect sensorial perception of texture, taste, and odor of semi-solid foods by breaking the food down and redistributing with saliva over a large surface area.[8,9] Each individual has their own flavor release and perception signature, but whether this is related to tongue movement and pressure pattern among other physiological factors is not clear.

Saliva in general is an aqueous mixture of salts and proteins, the main roles of which are lubricating the food to form a bolus, buffering the oral pH, and providing an antibacterial action.[10] Saliva varies within and between subjects according to flow rate and composition. These, in turn, differ according to various parameters including age, food stimulation, and degree of food hydration. As a consequence, the intensity release of VOCs in the mouth during mastication is affected by the presence of saliva. In some cases, the intensity is lower because of dilution and interactions with saliva components (e.g., mucin proteins and enzymes), whereas the release can also be increased when saliva salts cause a salting-out effect of VOCs from the aqueous phase, especially those that are hydrophilic.[11,12]

A novel *in vitro* model mouth using an artificial tongue was designed in our group to evaluate VOC release from liquid and semi-solid foods.[13] The model is capable of generating accurate and consistent human-like tongue pressure patterns using an artificial computer-controlled tongue. The release of selected VOCs from the model was monitored dynamically by high-sensitivity proton transfer reaction−mass spectrometry (PTR−MS). The objective of the study was to measure the effect of tongue pressure patterns on VOC release using this model mouth system. The impact of other oral parameters, such as saliva composition and temperature, on the VOC release were also examined for three model systems: an aqueous solution, oil, and an oil-in-water (O/W) emulsion.

Received: July 3, 2012
Revised: September 4, 2012
Accepted: September 10, 2012
Published: September 10, 2012

dx.doi.org/10.1021/jf3028232 | *J. Agric. Food Chem.* 2012, 60, 9918−9927

Table 1. Physiochemical Characteristics[a] of VOCs and Their Release Parameters from Aqueous Solution under Average Swallowing Tongue Pressures[b]

VOC	m/z	log $P^{a,c}$	vapor pressure[a] (mmHg) at 25 °C	I_{start} ($\times 10^3$, ncps)	I_{max} ($\times 10^3$, ncps)	t_{max} (s)	peak duration (s)
1-butanol	57	0.88	6.70	17.3 ± 2.2 ab	26 ± 5 c	3.1 ± 1.0 c	9.8 ± 0.9 d
2-butanone	73	0.29	90.60	58 ± 9 d	68 ± 14 e	1.3 ± 0.7 a	3.6 ± 1.2 a
ethyl butanoate	89	1.73	13.94	73 ± 8 e	27 ± 9 c	1.1 ± 0.3 a	3.6 ± 1.0 a
trans-4-heptenal	95	2.17	3.64	50 ± 6 c	55 ± 15 d	1.2 ± 0.3 a	3.9 ± 1.2 a
benzaldehyde	107	1.48	1.27	22 ± 4 b	33 ± 6 c	1.9 ± 0.2 b	7.1 ± 1.5 c
2-octanone	129	2.37	1.35	22.3 ± 3.0 b	16.5 ± 3.8 b	1.8 ± 0.1 b	5.7 ± 1.4 b
ethyl hexanoate	145	2.83	1.56	13 ± 5 a	4.8 ± 1.4 a	1.5 ± 0.3 ab	4.6 ± 1.1 ab
CV (%)				13.7	24.4	24.6	24.1

[a]From the Syracuse Research Corporation.[45] [b]Mean swallowing pressure was defined as 25 kPa with 0.4 s duration. Values with different letters within a column differ significantly ($p < 0.05$). Standard deviations are provided ($n \geq 4$). VOC, volatile organic compound; m/z, product ion mass/charge ratio (listed as predominant product ions monitored via PTR−MS; see the text); I_{start}, signal intensity at the start of measurements; I_{max}, maximum signal intensity; t_{max}, time to I_{max}; ncps, normalized counts per second (i.e. PTR−MS signal intensity; see the text); and CV, coefficient of variance. [c]Partition coefficient between octanol and water.

MATERIALS AND METHODS

Materials and Sample Preparations. Seven VOCs with different physicochemical characteristics were used (Table 1): 2-butanone and 2-octanone (Sigma-Aldrich, Steinheim, Germany), ethyl butanoate and benzaldehyde (Fluka, Steinheim, Germany), and 1-butanol, ethylhexanoate, and *trans*-4-heptenal (Aldrich, Steinheim, Germany). The purity of all VOCs was at least 95%. Stock solutions of dissolved VOCs [1% (v/v) in propylene glycol] were stored at −18 °C.

Three liquid model systems, 5 mM phosphate buffer at pH 7 (referred to as the aqueous solution), oil, and O/W emulsion, were prepared using deionized water, mono- and disodium phosphate salts, soy oil, and Tween 20 emulsifier (polyoxyethylene sorbitan monolaurate) purchased from Sigma-Aldrich (Steinheim, Germany). The emulsion solution was prepared from a warmed mixture of soy oil and Tween 20 solution [5% (w/w) oil and 1% (w/w) Tween 20 at 50 °C and pH 7.0], followed by two homogenization stages. A coarse emulsion was initially prepared using a benchtop homogenizer (Ultra Turrax T25, IKA, Wilmington, NC) at 470 g for 30 s. The second stage used a microfluidizer homogenizer (Microfluidics Corporation, Newton, MA) at 43 MPa for 10−12 strokes to prepare a fine emulsion (<0.5 μm). Sodium azide, as an antimicrobial agent, was added to the emulsion solution (0.02%, w/w). A mixture of the seven VOCs (each at 0.004%, v/v) was added to all prepared model systems and mixed by vortexing. The samples were stored at 4 °C for a maximum of 1 week prior to analysis.

Artificial and Human Saliva Preparation. Artificial saliva with comparable properties to human saliva (e.g., salt content, ionic strength, buffer capacity, and pH) was prepared on the basis of a suggested composition from a dental study.[14] The following compounds were dissolved in deionized water: 0.125 g/L NaCl, 0.964 g/L KCl, 0.654 g/L KH_2PO_4, 0.2 g/L urea, and 0.631 g/L $NaHCO_3$. Calcium ions were excluded from the saliva to avoid the formation of insoluble aggregates with phosphate ions. NaCl was added in place of the calcium ions to achieve the same final ionic strength (I = 29.8 mM) in saliva. Porcine gastric mucin (1%, w/w, Sigma-Aldrich, Steinheim, Germany) was used to simulate human salivary mucin proteins with similar saliva viscosity and the absence of a sediment. Porcine mucin was found to be a suitable substitute for human oral salivary mucin with a similar effect on the partitioning of VOCs to the headspace.[11] The saliva were stored at 4 °C for a maximum of 1 week prior to analysis. The artificial saliva pH was adjusted to pH 7.0 with 1 M HCl on the day of the analysis.

As a comparison to the artificial saliva, 5 mL of human saliva from 10 healthy volunteers from Fraunhofer IVV (five males and five females, aged 20−30 years) was collected on the morning of the same day of the VOC release analysis and mixed together to form a single pool. The volunteers were asked to rinse their mouth and to avoid any food consumption before providing samples to minimize any variation in saliva composition (referred as unstimulated saliva). The saliva viscosity was measured (Bohlin Instruments, CVO 100, Malvern, Worcestershire, U.K.) using a 60 mm 2° cone plate at 100 s^{-1} shear rate. The plate and the samples were warmed to 37 °C.

Sample Preparation in the Model Mouth. The samples were introduced into a model mouth containing an artificial glass tongue recently developed by our group.[13] The tongue pressure was calculated from the measured force divided by the ratio of the load cell area and the contact area of the tongue with the glass bottom of the model mouth. The model mouth temperature was maintained at 37 °C using circulated water within a glass jacket. A simple and consistent sampling method was used for all of the samples, as described below. Prewarmed saliva (1 mL, 37 °C) was added to the model mouth before introducing the sample. The samples (5 mL, ∼23 °C) were injected to the model mouth using a polytetrafluoroethylene (PTFE) syringe through a PTFE-faced septa to minimize the risk of carryover of VOCs. Other sample serving temperatures were also used to represent the temperatures used when serving chilled (4 °C) and hot (60 °C) beverages. Additional saliva was added at a flow rate of 1.4 mL min^{-1} for 2 min to mimic stimulated saliva flow during consumption.[15] On the same sample, the model tongue carried out a minimum of three mastication times, and this procedure was repeated in three replicate samples. The tongue was controlled by LabChart software (version 7.2, ADInstruments, Castle Hill, New South Wales, Australia) using a pulsed mathematical movement pattern to apply a range of pressures (0, 12, 32, and 65 kPa) for a constant duration (0.4 s) or a range of durations (0.2, 0.4, 0.7, and 3 s) at a constant pressure (25 kPa). The effect of the initial position of the tongue and movement direction was tested (forward, 3.5, 7.0, 14.0, and 17.5 mm; backward, 0, 3.5, and 7.0 mm, above the bottom of the model mouth) using a constant tongue pressure and duration (25 kPa and 0.4 s). For the remainder of the trials, the starting tongue position was 5 mm above the sample surface and 17.5 mm above the bottom of the model mouth. One set of conditions for tongue pressure, duration, and position was used for comparison between the sample systems and saliva types to closely mimic the average positive human tongue pressure pattern during swallowing (25 kPa, 0.4 s, and 3.5 mm), as described in our previous study.[13] This measurement set was carried out over 4 min in total, for which the first 2 min included seven mastication strokes. A delay of 30 s between each stroke was programmed to provide for a clear peak for the VOC release. Cleaning between analyses proceeded by rinsing the model mouth, including the tongue, with water containing a detergent solution [Mucasol 1% (v/v), BrandTech Scientific, Inc., Essex, CT] and, subsequently, only with clean water until the mouth was free of detergent, as monitored by PTR−MS via a detergent-specific VOC signal intensity (i.e., the mouth was deemed free of detergent once this signal had returned to background levels).

Dynamic Headspace Analysis. The detection of VOC release from the model mouth was carried out by high-sensitivity PTR−MS (Ionicon Analytik GmbH, Innsbruck, Austria). All measurements were carried out under drift tube conditions with a drift pressure of 2.2

mbar, chamber temperature of 60 °C, and voltage of 600 V, which resulted in an electric field strength (E) to buffer gas density (N) ratio (E/N) of 138 Td (Td = Townsend; 1 Td = 10^{-17} V cm^2). Zero air (i.e., air free of VOCs) generated by a gas calibration unit (GCU; Ionimed Analytik GmbH, Innsbruck, Austria)[16] was introduced to the model mouth at 1000 mL min^{-1} and was drawn into the PTR−MS through a heated 0.04 in. inner diameter and $^1/_{16}$ in. outer diameter Silcosteel capillary transfer line (Restek Co., Bellefonte, PA) at 80 °C at a flow rate of 280 mL min^{-1}. Selected VOCs were measured at the following mass/charge ratios (m/z) based on their fragmentation patterns at the given instrument settings, as determined in preliminary assessments of pure compounds (values in parentheses indicate percent abundance of the total VOC signal): 1-butanol, m/z 57 (54%); 2-butanone, m/z 73 (93%); ethyl butanoate, m/z 89 (57%); *trans*-4-heptenal, m/z 95 (52%); benzaldehyde, m/z 107 (84%); 2-octanone, m/z 129 (82%); and ethyl hexanoate, m/z 145 (66%). Two primary ions (H_3O^+ and the $H_2OH_3O^+$ water cluster, measured via their ^{18}O isotopologues at m/z 21 and 39, respectively) were also measured to assess potential changes in the PTR−MS operating conditions and cluster ion formation and allow for normalization between data sets. The fragmentation pattern of each VOC was initially determined in a single compound aqueous solution for overlapping signals. During the sample analysis run, the VOCs were monitored in multiple ion detection mode for the selected VOC fragments using a dwell time of 50 ms. The VOC signals were additionally measured before a sample was introduced into the model mouth to provide a background spectra for data correction (see below). Measurements of sets of samples were carried out on the same day to achieve close similarity for the operating conditions of the PTR−MS and model mouth.

Data Processing and Statistical Analysis. The VOC raw counts per second (cps) data signals were normalized to the sum of 10^6 primary ions (m/z 21 + 39) and 2.2 mbar drift pressure, yielding normalized counts per second (ncps). Mean ncps values of the background signal per m/z were subtracted from the VOC profile data to filter out potential interference signals from within the system. The I_{start} value was the signal 35 s after sample addition, and immediately prior to mastication, the maximum intensity signal for each mastication peak (I_{max}), peak duration, i.e. time to maximum intensity from the baseline (t_{max}), and the area under the release curve (AUC, also referred as total VOC release) were calculated using R package software (R-2.1.2, http://www.r-project.org). The results from the model mouth VOC release under different tongue operating conditions and different liquid systems were analyzed by multivariate analysis of variance (MANOVA) and a post-hoc Fisher test to determine least significant differences (LSDs; $p < 0.05$). The linear regression correlations were defined by Pearson's product coefficient (r). Statistica 8.0 software (StatSoft, Tulsa, OK) was used for the analysis.

RESULTS AND DISCUSSION

Volatile Release from Aqueous Solution in the Model Mouth. The dynamic release of seven VOCs in the model mouth system was evaluated at 37 °C at an air flow rate of 1000 mL min^{-1} and with simulated representative human tongue swallowing pressure of 25 kPa for a duration of 0.4 s.[7] The VOC release parameters (I_{start}, I_{max}, t_{max}, and peak duration) and physiochemical properties are reported in Table 1. The model mouth system can be considered to be a consistent tool for *in vitro* measurement of rapid VOC release because of the relatively low coefficient of variance (CV < 25%). Significant effects ($p < 0.05$) were observed for all of the release parameters. However, within each release parameter, not all of the VOCs were significantly different from each other. The results imply that the VOC physiochemical properties, such as the vapor pressure (P) and the compound activity coefficient (γ), proportionally affect the partition coefficient (K) between the compound concentration in the air and in the liquid sample.[17] The results in Table 1 show that a more intense initial release (I_{start}) was observed for VOCs with a combination of high vapor pressure and low compatibility with water (high γ or log P). These VOCs have previously been shown to have high K values above aqueous solutions.[18,19] For example, 2-butanone, the most volatile compound in the group (P = 90.6 mmHg), and the lipophilic volatile ethyl butanoate (P = 13.94; log P = 1.73) yielded higher values for I_{start} compared to the hydrophilic 1-butanol (log P = 0.88) or ethyl hexanoate with low volatility (P = 1.56). The results can be better explained by considering the release of VOCs in a non-equilibrium situation, as occurs in the mouth. This dynamic state in the model mouth was created by the mastication movement and the fast rate of air flow depleting the VOCs from the liquid−gas interface. The following equation models the dynamic release from liquids:[20]

$$\frac{dc_a(t)}{dt} = \frac{h_d A_{as}}{V_a}\left[c_s(t) - \frac{c_a(t)}{K}\right] \quad (1)$$

where the compound concentration in the air (dC_a/dt) is governed by the depletion rate from the sample (C_s), influenced by the compound mass-transfer coefficient through the sample to the interface (h_d), the partition coefficient (K), and the sample surface area (A_{as}). The data show that VOCs with high peak signals ($I_{max} > 50 \times 10^3$ ncps) after mastication, such as *trans*-4-heptenal and 2-butanone, quickly regenerated the interface after depletion. These compounds also had short t_{max} and peak duration, about 1.2 and 3.5 s, respectively. VOCs that had the highest degree of depletion had high K values and low mass-transfer coefficients.[17] In contrast, the hydrophilic compounds, 1-butanol and benzaldehyde, had lower I_{max} and longer peak duration because of their affinity with water. The release during liquid consumption is known to be strongly controlled by diffusion through the gas−liquid interface as a function of VOC volatility and affinity to the medium.[21]

Tongue Mastication Effect. The effect of the artificial tongue movement pattern during mastication of aqueous solutions on the release behavior of different VOCs was monitored online using PTR−MS (Figures 1−3). The tongue movement effect is shown in the schematic illustration of Figure 4. The magnitudes of tongue pressure and duration were selected from an *in vivo* range of tongue pressure patterns,[22] except for the pressure of 65 kPa and duration of 3.0 s, which are outside the normal range but were selected to clarify the effect of the tongue pressure pattern on the release. MANOVA showed an overall significant difference for the effect of the tongue pressure [$F(18\,294) = 3.694$; $p < 0.05$] and tongue pressure duration [$F(18\,271) = 7.185$; $p < 0.05$]. The only significant difference for the tongue pressure was observed when the tongue did not touch the chamber bottom (pressure = 0 kPa). In this case, the more volatile compounds, 2-butanone, 2-octanone, and *trans*-4-heptenal, exhibited higher values for I_{max} than at other pressures (Figure 1A). Apparently, applying an increasing pressure between the tongue and the chamber bottom did not cause any significant change for the I_{max} value ($p > 0.05$). In contrast, pressure duration did affect the peak intensity of the VOCs with an increase of more than 40% in I_{max} as the duration increased from 0.4 to 3.0 s (Figure 1B). The highest increase was measured for benzaldehyde with 188%, followed by 2-octanone and *trans*-4-heptenal at around 160%. The release of these compounds was influenced favorably by the physiochemical properties, as explained previously. The results for both experiments suggest that the

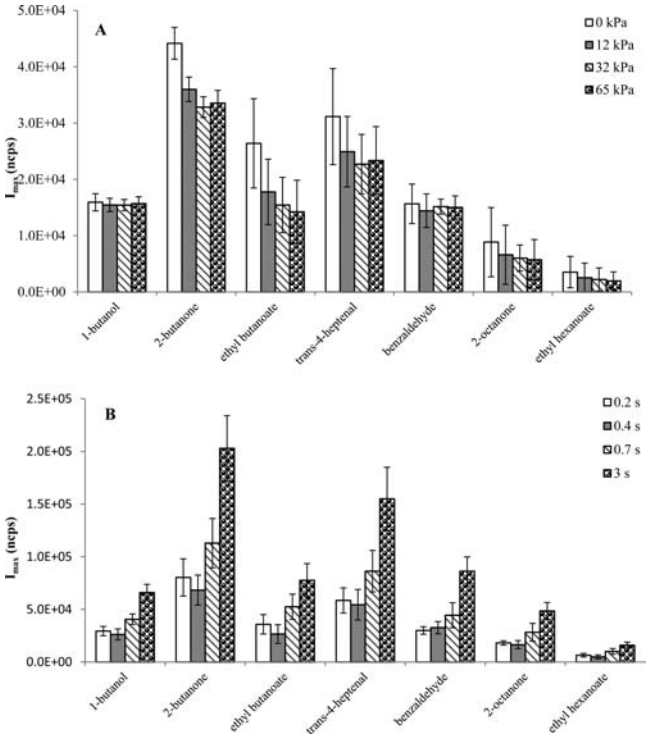

Figure 1. Mean ($n \geq 9$) I_{max} for selected VOCs released from aqueous solution under different (A) tongue pressures and (B) stroke durations. Error bars represent standard deviations, and LSD values were determined for each VOC.

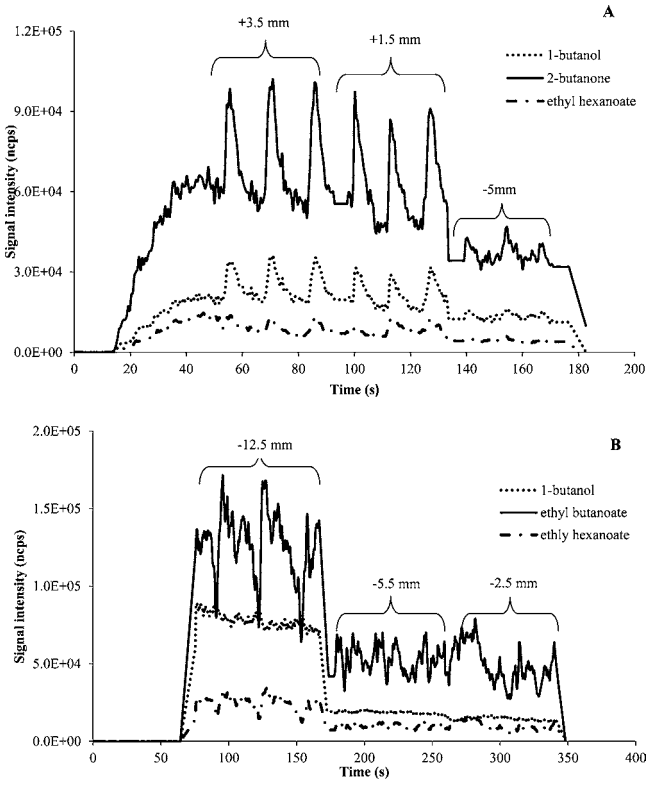

Figure 2. Release curves for three selected VOCs (1-butanol, ethyl butanoate, and ethyl hexanoate) masticated by the tongue in (A) downward and (B) upward directions and different initial tongue positions from the aqueous solution surface [plus (+) position relates to above the surface, and minus (−) position relates to below the surface]. The tongue pressure and duration were constant at 25 kPa and 0.4 s, respectively. The curves were modified in the sections between mastication length positions to create a continuous profile.

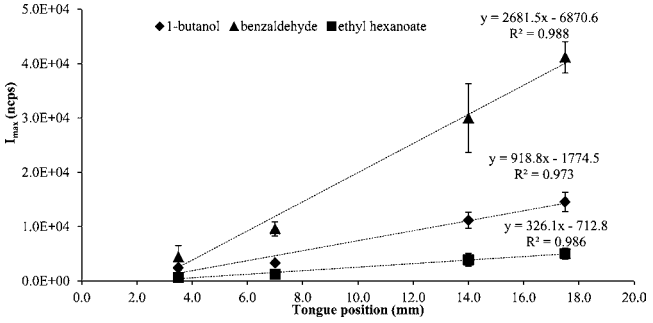

Figure 3. Linear regression curves for three released VOCs (1-butanol, benzaldehyde, and ethyl hexanoate) from an aqueous solution masticated by the tongue in different initial positions above the bottom of the model mouth.

tongue created turbulence on and below the aqueous solution surface area after mastication (images A−C of Figure 4). Mastication agitated the liquid, whereby increasing the mass-transfer coefficient of each VOC to a rapidly formed interfacial layer according to the penetration theory.[20] The signal peaks in Figure 2A clearly show how a burst of VOCs was released after every tongue stroke. The effect of mastication or stirring on the release of volatile compounds in a model mouth system has been reported in other studies as well.[23,24] The explanation for the differences in the I_{max} for the pressure and duration is based on the specific dynamic changes that occur in the model mouth. When no pressure was applied, the tongue reached full stroke without touching the chamber bottom. The small gap remaining between the tip of the tongue and the chamber bottom allowed for more liquid to pass through and mix on both sides of the spherical tongue. The longer the duration of the tongue inside the liquid, the more inner turbulence occurred, allowing for more VOCs to accumulate at the interface over time (with a smaller interfacial surface area). After retraction of the tongue, a new and larger surface area was created for the sample and a thin layer coating the model tongue was formed (Figure 4C). Increasing the interfacial area has been found to enhance the release of VOCs under non-equilibrium conditions.[24]

The initial tongue position and the movement direction toward the sample had a major contribution on the intensity release of the VOCs (Figures 2 and 4). When the tongue moved downward toward the sample, the maximum intensity was reached when the tongue was initially located above the sample surface (+3.5 mm). Once the tongue position was in the sample (−5 mm), a clear reduction in the release was observed, despite following the same mastication movement. Figure 3 shows the reduction in the release as a linear regression, with a high correlation coefficient ($r^2 > 0.95$), with the distance above the bottom of the model mouth. The change in the release was highly related to the change in the surface area (eq 1). The deeper the tongue was in the sample, the smaller the surface area was between the sample and the headspace. Interestingly, in the case of the upward mastication movement (Figure 2B and shown schematically in images D and E of Figure 4), the VOC release was initially reduced (shown as a negative peak for ethyl butanoate) and continued with a sharp increase until reaching the baseline. This trend was only noticed for the more

dx.doi.org/10.1021/jf3028232 | J. Agric. Food Chem. 2012, 60, 9918−9927

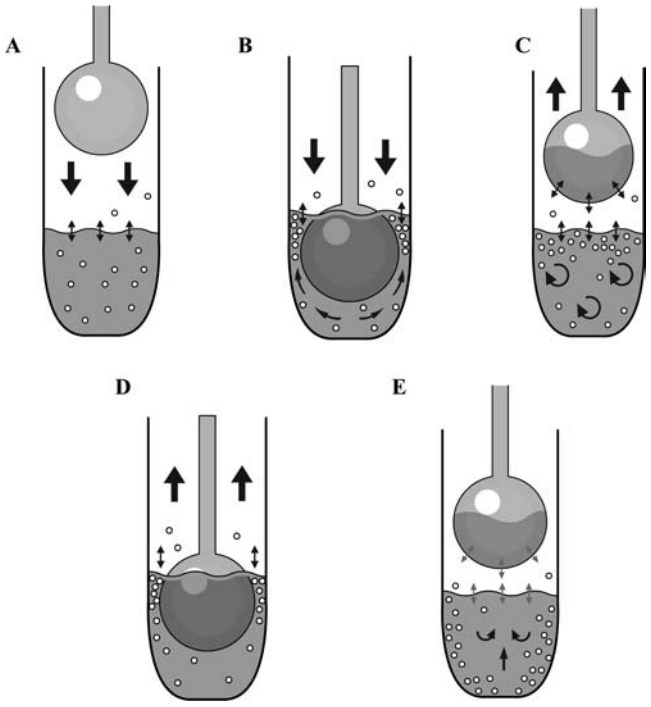

Figure 4. Schematic illustrations of the artificial tongue masticating the sample in (A–C) forward and (D and E) backward movement directions. The VOCs are represented by small white droplets. The large black arrows represent the movement direction of the tongue. The small black arrows demonstrate the movement of the liquid solution. The small gray double-headed arrows represent the VOC partitioning between the aqueous and gas phases.

volatile compounds with high vapor pressure and high log *P*; as for the other VOCs, there was barely any change. By positioning the tongue inside the sample and pulling it upward, a new surface area was created. This might explain the observed reduction until the VOCs adsorbed to the newly created interfacial area and were available for release (images D and E of Figure 4). The behavior was again less prevalent when the tongue was located closer toward the surface (−5.5 mm). Despite the differences between model mouth mastication and what actually takes place in the human mouth, it can be assumed that the mass transfer of VOCs is affected by the way that the tongue manipulates the liquid bolus by pressure, duration, and movement direction.[25]

Saliva Type. To understand the effect of saliva composition variables on VOC release, the flow of fresh human saliva was compared to no saliva flow, water, and artificial saliva with and without mucin protein. The total VOC release (as measured by the AUC) was measured for a period of 4 min of mastication, which included an initial 2 min of saliva flow (Table 2). The effect of dilution in the sample VOC concentration was clearly seen for all VOCs when water or artificial saliva without mucin was added to the sample. A reduction of more than 30% in AUC was measured at a total dilution ratio of 3:4 saliva/sample. The dilution effect was the main reason given for the continuous reduction of the headspace concentration of aldehydes with an increasing amount of human saliva in a previous study.[26] The AUC values for artificial saliva plus mucin and human saliva were comparable for all VOCs. The findings are in agreement with the results presented by the aforementioned study,[26] as long as the samples did not contain compounds that could be degraded by salivary enzymes. In comparison to artificial saliva without mucin, the saliva solutions containing mucin resulted in a greater release, while no significant difference ($p > 0.05$) was observed for most VOCs when compared to no saliva flow. This finding is in contrast to studies that have examined the effect of mucin on VOC headspace concentrations under static conditions,[11,12] where reductions were due to the ability of mucin protein to bind aroma compounds via hydrophobic interactions and, in some cases, bind covalently with aldehyde compounds. This indicates that static equilibrium experiments may not be representative of what occurs in short-time processing in the mouth.[27] A plausible explanation for the difference in VOC release may be related to the viscosity increase of the sample after mixing with saliva. The measured viscosities at 37 °C and 100 s^{-1} shear rate were 2.7 mPa s for artificial saliva with 1 wt % mucin and 2.6 mPa s for human saliva compared to 0.69 mPa s for water. The similar viscosity between the saliva solutions indicates the relatively high content of mucin in both. Human unstimulated saliva is known to be much richer in mucin than stimulated saliva.[28] The viscous saliva sample mixture was observed to form a longer lasting coating on the artificial tongue and sides of the chamber that extended the surface area from which VOCs could be continuously released.

To provide more information about the impact of saliva on VOC release, a different approach was used and the relative change (%) in the release during the mastication period was measured (Table 3). A large negative change between the first and last mastication cycles indicates a strong depletion of VOCs from the sample to the headspace, whereas values closer to 0 indicate VOC retention in the sample. In the absence of saliva, the change in the release was caused by air flow depletion. The depletion was most apparent for the hydrophobic VOCs, which were released quickly from the aqueous phase. Mixing the sample with artificial saliva without mucin caused a significant reduction ($p < 0.05$) in the extent of depletion for the highly volatile compounds compared to water. The presence of salts in saliva raised the ionic strength of the sample to about 0.013 M from 0.005 M. This could promote some VOC release because of the salting out effect.[29] The

Table 2. Total Release (×10^6, AUC) of Volatile Compounds from Aqueous Solution Mixed with Different Types of Saliva[a]

	1-butanol	2-butanone	ethyl butanoate	*trans*-4-heptenal	benzaldehyde	2-octanone	ethyl hexanoate
no saliva	5.7 ± 0.7 b	14.5 ± 1.4 b	8.7 ± 0.4 b	11.2 ± 0.4 c	6.6 ± 0.8 b	3.4 ± 0.2 b	1.0 ± 0.0 b
water	3.3 ± 0.3 a	7.9 ± 0.7 a	5.8 ± 0.4 a	7.2 ± 0.4 a	3.6 ± 0.3 a	2.2 ± 0.2 a	0.7 ± 0.1 a
artificial saliva without mucin	3.4 ± 0.7 a	8.3 ± 0.3 a	4.9 ± 0.4 a	7.0 ± 0.3 a	3.8 ± 0.1 a	2.0 ± 0.1 a	0.5 ± 0.0 a
artificial saliva with mucin	4.5 ± 0.1 ab	10.1 ± 0.5 a	7.8 ± 0.1 b	9.8 ± 0.3 bc	4.9 ± 0.2 a	3.1 ± 0.0 b	1.1 ± 0.0 b
human saliva	3.8 ± 0.5 a	10.0 ± 1.2 a	8.9 ± 0.7 b	9.3 ± 1.0 b	4.5 ± 0.6 a	3.0 ± 0.3 b	1.1 ± 0.1 b

[a]The results are shown as the mean with standard errors ($n = 3$). Values with different letters within a column differ significantly ($p < 0.05$). AUC = area under the curve.

Table 3. Release Change (%) between the First Peak ($I_{max,1}$) and the Last Peak ($I_{max,7}$) of Volatile Compounds from an Aqueous Solution Mixed with Different Types of Saliva[a]

	1-butanol	2-butanone	ethyl butanoate	*trans*-4-heptenal	benzaldehyde	2-octanone	ethyl hexanoate
no saliva	0.5 ± 6.4 a	−10.3 ± 3.3 a	−49.9 ± 7.6 b	−25.5 ± 5.6 a	1.9 ± 5.5 a	−42.8 ± 7.0 ab	−64.7 ± 6.1 b
water	−40.0 ± 7.9 b	−45.1 ± 4.5 b	−68.9 ± 6.0 c	−59.2 ± 8.7 b	−31.7 ± 5.6 b	−63.8 ± 6.6 c	−74.0 ± 5.0 b
artificial saliva without mucin	−24.4 ± 3.0 ab	−33.3 ± 2.7 b	−48.1 ± 4.0 b	−31.7 ± 4.0 a	−24.7 ± 1.5 b	−45.1 ± 2.0 b	−60.4 ± 1.9 b
artificial saliva with mucin	−5.0 ± 15.5 a	−18.9 ± 11.4 a	−42.4 ± 1.6 ab	−17.5 ± 5.0 a	−2.2 ± 13.7 a	−38.6 ± 1.9 ab	−62.8 ± 2.2 b
human saliva	−12.4 ± 10.6 ab	−18.0 ± 1.7 a	−27.9 ± 3.2 a	−21.5 ± 2.3 a	−13.7 ± 0.7 ab	−24.1 ± 5.8 a	−34.5 ± 7.4 a

[a]The results are shown as the mean with standard errors (n = 3). Values with different letters within a column differ significantly (p < 0.05).

comparable rates of depletion (%) for human saliva and artificial saliva with mucin compared to no saliva flow emphasize the contribution of viscosity to the increased rate of release. The hydrophobic VOCs showed a slight retention trend when the sample was mixed with human saliva. The only significant change in release was found for ethyl hexanoate, the most lipophilic VOC (log P = 2.8). The VOC was most likely hindered by hydrophobic interactions with the proteins in the human saliva, more so than the artificial saliva containing only mucin as protein. Overall, the artificial saliva was found to be a suitable alternative to human saliva for modeling *in vitro* volatile release, with the effect of increasing the dilution, viscosity, and ionic strength.

Model Systems. The total VOC release (as measured by AUC) was significantly different between the model systems (aqueous solution, O/W emulsion, and oil) for almost all VOCs (Figure 5A). The lipid phase, as expected, had the strongest impact on the partitioning of VOCs between the sample and the gas phases. With only 5% oil in the O/W emulsion, there was a reduction of more than 80% in AUC for the hydrophobic VOCs (log P > 2) compared to the aqueous solution. With a system containing only oil, almost all of the VOCs, except 2-butanone, had a 90% lower AUC compared to the VOCs in water. The VOCs in general are known to be more lipophilic, with strong affinity to lipid molecules through hydrophobic and van der Waals interactions.[30] The relationship between VOC hydrophobicity (log P) and the release was calculated by the Pearson correlation coefficient (data not shown). The oil and emulsion systems both demonstrated a significant linear correlation of r = 0.7 between the VOC hydrophobicity and the release. The more hydrophobic the VOC, the lower the VOC concentration measured in the headspace. However, no significant relationship between these two parameters (p > 0.05) was observed for the aqueous solution. The results strengthen the claim that the affinity of VOCs to the lipid phase is due to the hydrophobicity. In an aqueous solution, the release was probably affected by multiple factors, such as VOC solubility, vapor pressure, and hydrophobicity. The release behavior of VOCs from different food systems has been studied by both static and dynamic headspace analysis.[19,31−33] The current study introduces a highly dynamic approach to monitor the release from food systems under simulated oral conditions using the model mouth and PTR−MS, where the release parameters can be easily measured. As an example, the release duration for ethyl butanoate and 1-butanol in aqueous solution ranged from 3.6 to 9.8 s (Table 1). In comparison to water, the peaks from oil were much sharper and had a much shorter duration of about 2 s for all VOCs. In the emulsion system, the duration of VOC release was the opposite order than observed for water, where 1-butanol had the shortest duration of 6.5 s, whereas the hydrophobic VOCs had longer durations of 9.5 s on average (data not shown). The duration length was proportional to the affinity of the VOC to the medium composition (e.g., presence of oil) and the diffusion rate through the aqueous and oil phases. The release rates from different systems have been reported for various VOCs.[34] The slowest release rate in oil was found for hydrophobic compounds because of their strong retention to the lipid phase. These authors found that the diffusion in water was 17 times faster than in oil. This could explain the shallow short release peaks after mastication of the oil sample. In the case of the emulsion system, the release rate of hydrophobic VOCs, such as 2-nonanone, was reported to drop drastically compared to the release in water because of a rate-limiting diffusion step in the lipid phase before reaching the water−gas interface.[35]

The addition of artificial saliva with mucin to the sample had a major impact on the release from the aqueous solution and oil

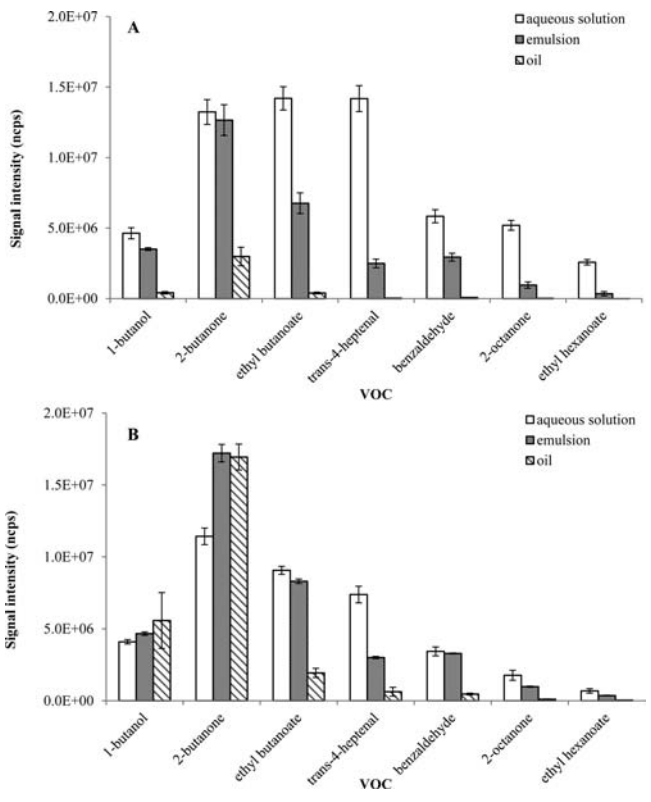

Figure 5. Total release of different VOCs from three types of food matrix: aqueous solution, 5 wt % O/W emulsion, and oil, (A) without artificial saliva addition and (B) with artificial saliva. Error bars represent standard deviations, and LSD values were determined for each VOC.

dx.doi.org/10.1021/jf3028232 | J. Agric. Food Chem. 2012, 60, 9918−9927

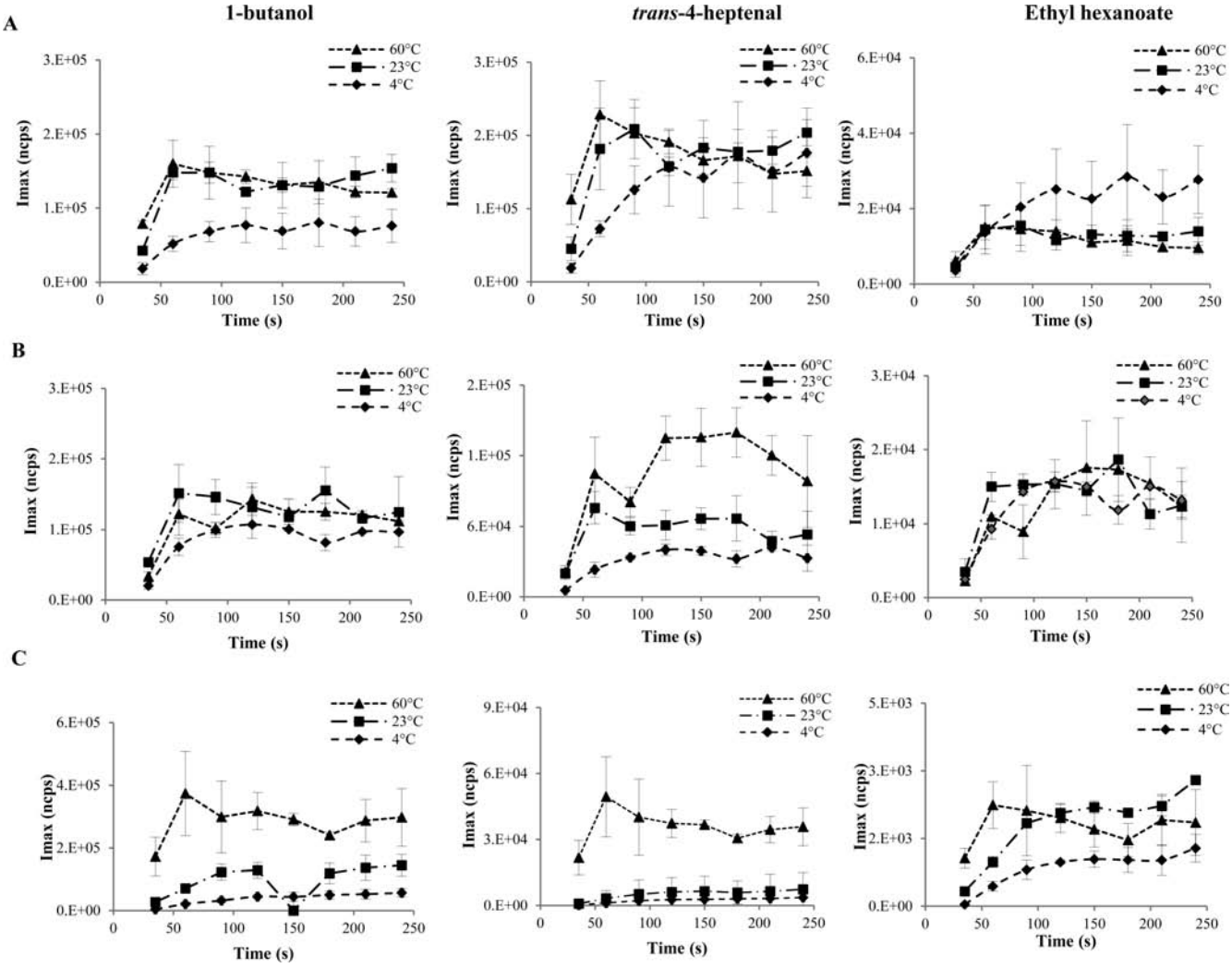

Figure 6. Influence of the sample temperature (4, 23, and 60 °C) on the maximum signal intensity (I_{max}) after mastication over time from different liquid systems: (A) aqueous solution, (B) oil, and (C) 5 wt % O/W emulsion. The profiles of three VOCs (1-butanol, *trans*-4-heptenal, and ethyl hexanoate) are presented. Error bars represent standard deviations.

(Figure 5B). The dilution effect was the main reason for the reduction in the release observed in the aqueous solution, as explained before in the saliva-type results part. The prominent increase in the AUC results for the VOCs in oil was mainly associated with the combination of highly volatile and hydrophobic compounds. The compounds 1-butanol and 2-butanone had similar release intensities between the oil and emulsion systems in the presence of saliva, despite the difference in the oil content. The additional water phase from the saliva to the emulsion and oil systems improved the mass-transfer rates of the VOCs to the interface by lowering the overall sample viscosity and changing the medium polarity. The initial VOC flux of benzaldehyde from the VOC-rich aqueous phase to the lipid phase was found to be ~20 times higher than from the lipid phase to the aqueous phase, highlighting the importance of VOC affinity to oil on the release.[36] Increasing the water/oil ratio in the emulsion system by adding saliva significantly enhanced the release of the hydrophilic VOCs and VOCs of intermediate hydrophobicity. The most nonpolar VOCs (2-octanone and ethyl hexenaote) were retained in the emulsion to the same extent, with or without saliva, indicating the strong affinity to the lipid phase despite the dilution. Saliva containing mucin also increased the viscosity for both the aqueous solution and the emulsion systems, which could result in an extended surface coating over the tongue after masticating, as previously described. This behavior appeared to be less for oil because of the incompatibility of the glass tongue and the chamber to the oil phase.

Sample Temperature. The effect of the temperature (4, 23, and 60 °C) on VOC release from three model systems was analyzed using the model mouth and artificial saliva containing 1 wt % mucin at 37 °C. Three VOCs [1-butanol (m/z 57), *trans*-4-heptenal (m/z 95), and ethyl hexanoate (m/z 145)] are reported in Figure 6, representing different degrees of hydrophobicity, vapor pressure, and chemical class. I_{start} and I_{max} signals of the VOCs were typically lower at 4 °C, with 23 and 60 °C being either similar or above these values. The difference between 4 and 23 °C for the release was less pronounced, probably because of a general small change in vapor pressure for VOCs compared to 60 °C.[37] The relationship between the temperature (T) and partition equilibrium coefficient (K) of VOCs can be described by the van't Hoff's law

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^0}{RT^2} \quad (2)$$

dx.doi.org/10.1021/jf3028232 | J. Agric. Food Chem. 2012, 60, 9918−9927

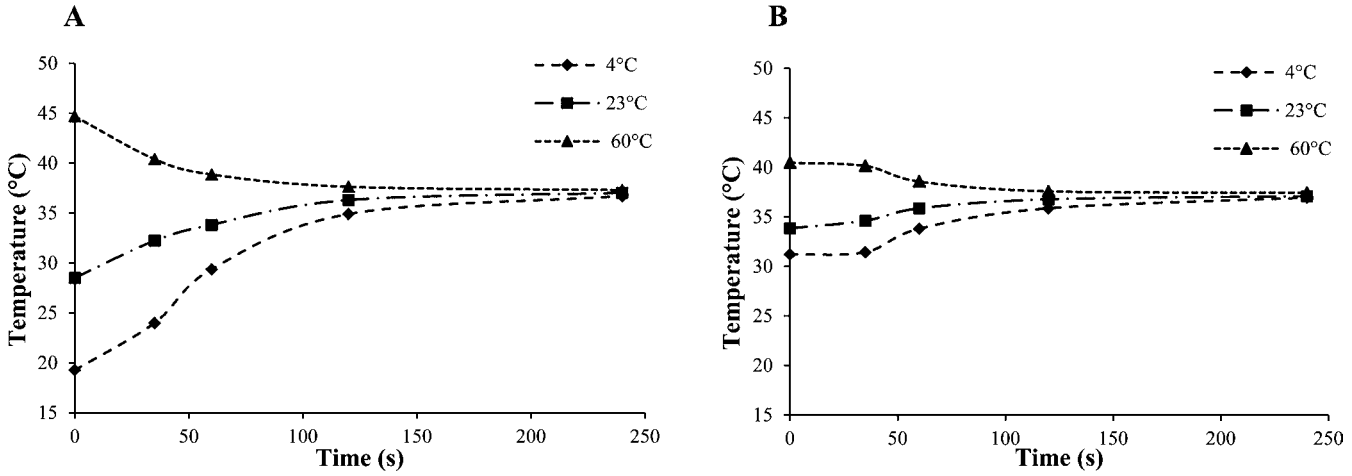

Figure 7. Temperature curves in the model mouth containing (A) aqueous solution and (B) oil samples versus the mastication period. The sample temperatures were 4, 23, and 60 °C.

where ΔH^0 (kJ mol^{-1}) is the enthalpy of vaporization of the VOC and R is the universal gas constant. The higher the temperature becomes, the more VOCs partitioning to the gas phase (high K) because of lower ΔH^0. From the literature, ΔH^0 of pure VOCs at 25 °C follows the order: *trans*-4-heptenal (39 kJ mol^{-1}) < 1-butanol (51 kJ mol^{-1}) ~ ethyl hexanoate (52 kJ mol^{-1}), which mainly depends upon the volatility of the compounds.[38] When the compounds are dissolved in a medium, ΔH^0 usually increases because of interactions between the compound and the medium. The compounds 1-butanol and ethyl hexanoate have similar values for ΔH^0 in an aqueous solution (~56 kJ mol^{-1}), despite their different chemical structures. The strong affinity of alcohol to water with a relatively high vapor pressure may be the reason for equal ΔH^0 values for the hydrophobic ester, which requires additional energy to overcome the hydration forces around it before evaporation can take place.[39] The release from the aqueous solution was most pronounced for *trans*-4-heptenal, with the lowest ΔH^0 in the group showing an increase for I_{start} of more than 84%, from 1.8×10^4 ncps at 4 °C to 1.13×10^5 ncps at 60 °C. The release for ethyl hexanoate and other hydrophobic VOCs (data not shown) from the aqueous solution showed the opposite trend, where the highest release appeared at 4 °C but only after mastication had started. The lower solubility of large nonpolar VOCs is further reduced at low temperatures compared to the hydrophilic VOCs that can interact with water through hydrogen bonds.[40] The less soluble compound at 4 °C was likely to be present at a higher concentration at the interface after mastication than at a higher temperature where the VOC solubility increased. The change in the sample temperature to 60 °C had a great impact on the release in the oil system, mainly for *trans*-4-heptenal. The oil viscosity is affected by the temperature, from around 100 mPa s at 4 °C to less than 20 mPa s at 60 °C.[41] The mass transfer by eddy diffusion and the molecular diffusion of VOCs from the interface are increased by the low viscosity.

The temperature change in the model mouth was measured after introducing the sample at different temperatures (Figure 7). The temperature of the sample changed immediately according to the temperature of the model mouth containing 1 mL of saliva. The change was more pronounced in the oil system where the sample temperature quickly approached the model mouth temperature of 37 °C. The heat capacity of soybean oil is 1.88 J g^{-1} K^{-1} compared to 4.18 J g^{-1} K^{-1} for water.[42] The time to reach the highest I_{max} for the oil (~100 s) was shorter than for other systems and seems to be correlated with the fast temperature exchange between the oil and fluid in the model mouth. The influence of the sample temperature on flavor perception *in vivo* has been reported in several studies.[43,44] These studies showed that subjects perceived higher odor intensities from the food sample when the sample temperature was higher. These authors attributed their observations to higher volatility of VOCs and reduction in the sample viscosity, facilitating VOC release, similar to the model mouth results for this current study.

This study showed the capability of the model mouth to generate important data regarding VOC release from liquid samples under mouth conditions. The release behavior was highly dependent upon the VOC physiochemical properties and their affinity to the system medium. The changes in the sample surface area after tongue mastication had a significant role on the VOC release rate. The incorporation of oral parameters of saliva and temperature, as well as simulated tongue pressure patterns, in the model mouth provided useful knowledge on possible dynamic release situations in the mouth that could affect the way flavor is perceived.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +64-3-479-7545. Fax: +64-3-479-7567. E-mail: ofir.benjamin@otago.ac.nz.

Funding

This research was supported by the Riddet Institute, New Zealand, and the DAAD German Academic Exchange Service Scholarship.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for use of the facilities at Fraunhofer IVV (Freising, Germany), where the PTR−MS analyses were conducted. The authors also thank Luca Cappellin for the assistance in the data processing using R software.

REFERENCES

(1) Salles, C.; Chagnon, M. C.; Feron, G.; Guichard, E.; Laboure, H.; Morzel, M.; Semon, E.; Tarrega, A.; Yven, C. In-mouth mechanisms leading to flavor release and perception. *Crit. Rev. Food Sci. Nutr.* **2011**, *51*, 67−90.

(2) Land, D. G. Perspectives on the effects of interactions on flavor perception: An overview. In *Flavor−Food Interactions*; McGorrin, R. J., Leland, J. V., Eds.; American Chemical Society (ACS): Washington, D.C., **1996**; ACS Symposium Series, Vol. *633*, pp 2−11.

(3) Buettner, A.; Beer, A.; Hannig, C.; Settles, M.; Schieberle, P. Physiological and analytical studies on flavor perception dynamics as induced by the eating and swallowing process. *Food Qual. Pref.* **2002**, *13*, 497−504.

(4) Hodgson, M.; Linforth, R. S. T.; Taylor, A. J. Simultaneous real-time measurements of mastication, swallowing, nasal airflow, and aroma release. *J. Agric. Food Chem.* **2003**, *51*, 5052−5057.

(5) Mestres, M.; Kieffer, R.; Buettner, A. Release and perception of ethyl butanoate during and after consumption of whey protein gels: Relation between textural and physiological parameters. *J. Agric. Food Chem.* **2006**, *54*, 1814−1821.

(6) Kieser, J.; Bolter, C.; Raniga, N.; Waddell, J. N.; Swain, M.; Farland, G. Tongue−palate interactions during swallowing. *J. Texture Stud.* **2011**, *42*, 95−102.

(7) Kennedy, D.; Kieser, J.; Bolter, C.; Swain, M.; Singh, B.; Waddell, J. N. Tongue pressure patterns during water swallowing. *Dysphagia* **2010**, *25*, 11−19.

(8) de Wijk, R. A.; Janssen, A. M.; Prinz, J. F. Oral movements and the perception of semi-solid foods. *Physiol. Behav.* **2011**, *104*, 423−428.

(9) Prinz, J.; de Wijk, R. A.; Weenen, H. The role of oral processing on perception of semi solids. *Abstr. Pap., Am. Chem. Soc.* **2003**, *226*, 71.

(10) Humphrey, S. P.; Williamson, R. T. A review of saliva: Normal composition, flow, and function. *J. Prosthet. Dent.* **2001**, *85*, 162−169.

(11) Friel, E. N.; Taylor, A. J. Effect of salivary components on volatile partitioning from solutions. *J. Agric. Food Chem.* **2001**, *49*, 3898−3905.

(12) van Ruth, S. M.; Grossmann, I.; Geary, M.; Delahunty, C. M. Interactions between artificial saliva and 20 aroma compounds in water and oil model systems. *J. Agric. Food Chem.* **2001**, *49*, 2409−2413.

(13) Benjamin, O.; Silcock, P.; Kieser, J. A.; Waddell, J. N.; Swain, M. V.; Everett, D. W. Development of a model mouth containing an artificial tongue to measure the release of volatile compounds. *Innovative Food Sci. Emerging Technol.* **2012**, *15*, 96−103.

(14) Gal, J. Y.; Fovet, Y.; Adib-Yadzi, M. About a synthetic saliva for in vitro studies. *Talanta* **2001**, *53*, 1103−1115.

(15) Lawrence, G.; Septier, C.; Achilleos, C.; Courcoux, P.; Salles, C. In vivo sodium release and saltiness perception in solid lipoprotein matrices. 2. Impact of oral parameters. *J. Agric. Food Chem.* **2012**, *60*, 5299−5306.

(16) Singer, W.; Beauchamp, J.; Herbig, J.; Dunkl, J.; Kohl, I.; Hansel, A. I. Dynamic gas dilution system for accurate calibration of analytical instruments such as PTR−MS. In *3rd International Conference on Proton Transfer Reaction Mass Spectrometry and Its Applications*; Hansel, A., Märk, T. D., Eds.; Innsbruck University Press: Obergurgl, Austria, 2007; pp 232−237.

(17) van Ruth, S. M.; Roozen, J. P. Delivery of flavours from food matrices. In *Food Flavour Technology*, 2nd ed.; Andrew, T., Ed.; CRC Press: Boca Raton, FL, 2010; pp 190−207.

(18) van Ruth, S. M.; Villeneuve, E. Influence of β-lactoglobulin, pH and presence of other aroma compounds on the air/liquid partition coefficients of 20 aroma compounds varying in functional group and chain length. *Food Chem.* **2002**, *79*, 157−164.

(19) Benjamin, O.; Leus, M.; Everett, D. W. Static headspace analysis of volatile compounds released from β-lactoglobulin-stabilized emulsions determined by the phase ratio variation method. *Food Res. Int.* **2011**, *44*, 417−424.

(20) Harrison, M.; Hills, B. P. Mathematical model of flavor release from liquids containing aroma-binding macromolecules. *J. Agric. Food Chem.* **1997**, *45*, 1883−1890.

(21) Linforth, R. Modelling flavor release. In *Food Flavor Technology*; Taylor, A. J., Ed.; Academic Press: Sheffield, U.K., 2002; pp 185−209.

(22) Farland, G. Generic and individual intra-oral pressure profiles in liquid swallows. Ph.D. Thesis, University of Otago, Dunedin, New Zealand, 2011.

(23) van Ruth, S. M.; Buhr, K. Influence of mastication rate on dynamic flavour release analysed by combined model mouth/proton transfer reaction−mass spectrometry. *Int. J. Mass Spectrom.* **2004**, *239*, 187−192.

(24) Rabe, S.; Krings, U.; Berger, R. G. In vitro study of the influence of physiological parameters on dynamic in-mouth flavour release from liquids. *Chem. Senses* **2004**, *29*, 153−162.

(25) de Wijk, R. A.; Engelen, L.; Prinz, J. F. The role of intra-oral manipulation in the perception of sensory attributes. *Appetite* **2003**, *40*, 1−7.

(26) van Ruth, S. M.; Roozen, J. P. Influence of mastication and saliva on aroma release in a model mouth system. *Food Chem.* **2000**, *71*, 339−345.

(27) Linforth, R.; Martin, F.; Carey, M.; Davidson, J.; Taylor, A. J. Retronasal transport of aroma compounds. *J. Agric. Food Chem.* **2002**, *50*, 1111−1117.

(28) Navazesh, M.; Mulligan, R. A.; Kipnis, V.; Denny, P. A.; Denny, P. C. Comparison of whole saliva flow-rates and mucin concentrations in healthy caucasian young and aged adults. *J. Dent. Res.* **1992**, *71*, 1275−1278.

(29) Rabe, S.; Krings, U.; Berger, R. G. Initial dynamic flavour release from sodium chloride solutions. *Eur. Food Res. Technol.* **2003**, *218*, 32−39.

(30) Plug, H.; Haring, P. The role of ingredient−flavor interactions in the development of fat-free foods. *Trends Food Sci. Technol.* **1993**, *4*, 150−152.

(31) Philippe, E.; Seuvre, A. M.; Colas, B.; Langendorff, V.; Schippa, C.; Voilley, A. Behavior of flavor compounds in model food systems: A thermodynamic study. *J. Agric. Food Chem.* **2003**, *51*, 1393−1398.

(32) Frank, D.; Appelqvist, I.; Piyasiri, U.; Delahunty, C. In vitro measurement of volatile release in model lipid emulsions using proton transfer reaction mass spectrometry. *J. Agric. Food Chem.* **2012**, *60*, 2264−2273.

(33) Shiota, M.; Isogai, T.; Iwasawa, A.; Kotera, M. Model studies on volatile release from different semisolid fat blends correlated with changes in sensory perception. *J. Agric. Food Chem.* **2011**, *59*, 4904−4912.

(34) Seuvre, A. M.; Philippe, E.; Rochard, S.; Voilley, A. Kinetic study of the release of aroma compounds in different model food systems. *Food Res. Int.* **2007**, *40*, 480−492.

(35) Seuvre, A. M.; Diaz, M.; Cayot, P.; Voilley, A. Influence of the composition and the structure of different media on the release of aroma compounds. *Lait* **2004**, *84*, 305−316.

(36) Seuvre, A. M.; Diaz, M. A. E.; Voilley, A. Transfer of aroma compounds through the lipidic−aqueous interface in a complex system. *J. Agric. Food Chem.* **2002**, *50*, 1106−1110.

(37) Zhao, H.; Unhannanant, P.; Hanshaw, W.; Chickos, J. S. Enthalpies of vaporization and vapor pressures of some deuterated hydrocarbons. Liquid−vapor pressure isotope effects. *J. Chem. Eng. Data* **2008**, *53*, 1545−1556.

(38) National Institute of Standards and Technology (NIST). *Chemistry WebBook*; http://webbook.nist.gov/chemistry/ (accessed April 25, 2012).

(39) Tromelin, A.; Merabtine, Y.; Andriot, I.; Lubbers, S.; Guichard, E. Retention−release equilibrium of aroma compounds in polysaccharide gels: Study by quantitative structure−activity/property relationships approach. *Flavour Fragrance J.* **2010**, *25*, 431−442.

(40) Covarrubias-Cervantes, M.; Bongard, S.; Champion, D.; Voilley, A. Temperature effect on solubility of aroma compounds in various aqueous solutions. *LWT—Food Sci. Technol* **2005**, *38*, 371−378.

(41) Wang, T.; Briggs, J. L. Rheological and thermal properties of soybean oils with modified FA compositions. *J. Am. Oil Chem. Soc.* **2002**, *79*, 831−836.

(42) Tochitani, Y.; Fujimoto, M. measurement of specific heat capacity of vegetable oils. *Jpn. J. Therm. Prop.* **2001**, *15*, 230−236.
(43) Ventanas, S.; Mustonen, S.; Puolanne, E.; Tuorila, H. Odour and flavour perception in flavoured model systems: Influence of sodium chloride, umami compounds and serving temperature. *Food Qual. Pref.* **2010**, *21*, 453−462.
(44) Engelen, L.; de Wijk, R. A.; Prinz, J. F.; Janssen, A. M.; Weenen, H.; Bosman, F. The effect of oral and product temperature on the perception of flavor and texture attributes of semi-solids. *Appetite* **2003**, *41*, 273−281.
(45) Syracuse Research Corporation (SRC). *Physical Properties Database*; http//syrres.com/interkow/physdemo.htm (accessed June, 21 2012).