

Influence of the texture of gelatin gels and pectin gels on strawberry flavour release and perception

Aine B. Boland^a, Conor M. Delahunty^b, Saskia M. van Ruth^{a,*}

^a Department of Food and Nutritional Sciences, University College Cork, Western Road, Cork, Ireland

^b Sensory Science Research Centre, The University of Otago, P.O. Box 56, Dunedin, New Zealand

Received 5 November 2004; received in revised form 18 February 2005; accepted 21 February 2005

Abstract

The release of strawberry flavour compounds from pectin gels and gelatin gels was evaluated by instrumental and sensory analysis. Three gel textures were established based on Young's modulus of elasticity (E) for each gel. The E of the low, medium and high rigidity gelatin and pectin gels was 181, 300 and 493 N m⁻², respectively. Air/gel partition coefficients were determined by static headspace analysis. In-nose/proton transfer reaction-mass spectrometry analysis produced temporal release profiles. Sensory analysis was conducted to assess perceived odour, thickness, strawberry flavour and sweetness using magnitude estimation. The type of hydrocolloid affected static and in-nose compound concentrations significantly. The pectin gels showed lower air/gel partition coefficients than the gelatin gels, but increased flavour release. Increased gel rigidity resulted in lower air/gel partition coefficients; higher maximum concentrations of volatiles and lower release rates during in-nose analysis; decreased perception of odour, strawberry flavour and sweetness; and higher intensity ratings for thickness in sensory analysis. Consequently, both type of hydrocolloid and rigidity of the sample greatly affected flavour release and perception.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Flavour; Gel; PTR-MS; Sensory; Strawberry

1. Introduction

Flavour is defined as a “complex combination of the olfactory, gustatory and trigeminal sensations perceived during tasting”. The flavour of foods may be influenced by tactile, thermal, painful and/or kinaesthetic effects (ISO 5492, 1992). In order to further elucidate this process it is necessary to combine instrumental analysis of the release of volatile compounds from the food matrix with sensory evaluation of the food product.

As food is eaten, the release of the volatiles from the food is influenced by a number of factors including mastication, mixing with saliva and changes in temperature and pH. Therefore, to gain an insight into the kinetics of

volatile release in vivo techniques have been developed which are capable of monitoring real-time volatile release. Atmospheric-pressure-chemical-ionisation mass-spectrometry (APCI-MS) and Proton-transfer-reaction mass-spectrometry (PTR-MS) are most commonly used for this purpose. With these systems part of the participant's breath is continuously sampled, allowing for sensitive and fast monitoring of volatile release (Taylor, Linforth, Harvey, & Blake, 2000; Taylor, Besnard, Puaud, & Linforth, 2001).

Hydrocolloids are widely used ingredients in many food products. Increasing the amount of hydrocolloid in a food has been shown to cause an increase in the thickness of a product, as well as a reduction in the perceived flavour intensities (Mällki, Heiniö, & Autio, 1993; Overbosch, Afterof, & Haring, 1991; Pangborn, Misaghi-Gibbs, & Tassan, 1978). In-nose measurements of volatile compounds released from hydrocolloid gel

* Corresponding author. Tel.: +353 21 4902496; fax: +353 21 4270244.

E-mail address: s.vanruth@ucc.ie (S.M. van Ruth).

systems have been the focus of many studies. Using APCI-MS release curves, Baek, Linfoth, Blake, and Taylor (1999) observed that softer gelatin gels released larger concentrations of a volatile compound than harder gelatin gels. Flavour release from mixed phase gels demonstrated that both the properties of the volatile compound and the particular matrix influenced volatile release in vivo (Taylor et al., 2001). Hollowood, Linfoth, and Taylor (2002) examined the release of volatiles from a strawberry flavour mix in a hydroxypropyl methylcellulose system, while Weel et al. (2002) analysed the release of diacetyl and ethyl butyrate from whey protein gels. Both studies concluded that gel texture did not influence in-nose flavour concentration, but that it had an impact on flavour perception. Lethuaut, Brossard, Rousseau, Bousseau, and Genot (2003) observed that the perceived firmness of model dairy desserts increased with increased sucrose concentration and increasing the firmness of the dessert reduced sweetness perception. These authors also discovered that variations in sweetness perception could only partly be explained by changes in mechanical profiles and that gel strength was not the only factor leading to sweetness intensity modification. However, the questions remain: to what extent do interactions between the texture and flavour of a food influence its texture and flavour perception, and how do these interactions occur?

The aim of the present study was to investigate how changes in gelatin and pectin gel texture influenced the static headspace concentrations of strawberry volatiles, release of these volatiles in vivo, and sensory perception.

2. Materials and methods

2.1. Sample materials

Gelatin and pectin gels with low, medium and high rigidity textures were prepared for instrumental and sensory analysis. The composition of the gels is shown in Table 1. Distilled water was added to provide a final weight of 100 g. The gelatin (Type A, Bloom strength 150) was supplied by Croda Colloids Ltd. (Widnes, Cheshire, UK). The pectin (high-methyl pectin (HM), medium-rapid set) was supplied by Crestchem Ltd. (Amersham, Buckinghamshire, UK). Cargill (Bergen op Zoom, The Netherlands) supplied the glucose syrup (Dextrose Equivalent 40.8%), while food grade sucrose was purchased locally. The citric acid (citric acid-monohydrate) and sodium citrate (tri-sodium citrate) were obtained from BDH Ltd. (Poole, UK) and Riedel-de Haën (Seele, Germany), respectively.

The strawberry flavour mix was supplied by Givaudan (Duebendorf, Switzerland). It consisted of β -ionone (1 mg/g), styrallyl acetate (1 mg/g), methyl anthranilate

Table 1
Composition of the gels per 100 g, Young's modulus of elasticity (E) and the pH of each gel ($n = 3$)

	Gelatin gel			Pectin gel		
	1.30	1.50	1.80	–	–	–
Gelatin (g)	1.30	1.50	1.80	–	–	–
Pectin (g)	–	–	–	0.75	0.95	1.00
Sucrose (g)	37.00	37.00	37.00	37.00	37.00	37.00
Glucose syrup (g)	24.00	24.00	24.00	24.00	24.00	24.00
Citric acid (g)	1.00	1.00	1.00	1.00	1.00	1.00
Sodium citrate (g)	–	–	–	0.40	0.40	0.40
Water (g)	36.65	36.45	36.15	36.80	36.60	36.55
Flavour mix (g)	0.05	0.05	0.05	0.05	0.05	0.05
E [N/m ²]	181 ^c	300 ^b	493 ^a	181 ^c	300 ^b	493 ^a
pH	2.38	2.44	2.44	2.81	2.81	2.78
CV ^d [%]	9.0	6.5	4.6	9.3	10.8	5.8

^{a-c} Values with different superscripts within a row are significantly different, ANOVA and LSD tests, $P < 0.05$.

^d CV = coefficient of variance for E .

(1 mg/g), hexanal (1 mg/g), benzyl acetate (2 mg/g), vanillin (5 mg/g), methyl dihydrojasmonate (5 mg/g), furool (5 mg/g), *cis*-3-hexenyl acetate (5 mg/g), ethyl iso-pentanoate (10 mg/g), *cis*-3-hexenol (15 mg/g), γ -decalactone (20 mg/g), ethyl hexanoate, (20 mg/g), methyl cinnamate (24 mg/g), and ethyl butyrate (90 mg/g) in triacetin, as measured by the manufacturer. About 0.5 g kg⁻¹ of the strawberry flavour mix was added to all the gels.

2.2. Gel preparation

Gelatin gels were prepared by mixing the gelatin with cold water and then, dissolving it at 60 °C in a water bath. This was combined with the sucrose/glucose syrup, which had previously been heated in a water bath until all the sucrose was dissolved. The mixture was maintained at 60 °C for 2 min and constant stirring occurred throughout to ensure complete dissolution of solutes. Distilled water was added to compensate for water loss through vapourisation. At this stage citric acid was added and heating continued at 60 °C for a further 2 min. Finally, the mixture was allowed to cool to 50 °C and the flavour mixture was introduced. The jar was immediately sealed and stirring continued for 1 min to ensure equal distribution of the volatile compounds.

Pectin gels were prepared in a similar manner, except that 5 g of the sucrose was mixed with the pectin and sodium citrate before being dissolved in water. Also, a temperature of 85 °C was achieved while preparing the pectin gels and this temperature was maintained until the final stage, when the solution was cooled to 50 °C before the flavour mixture was added.

The gel samples were refrigerated at 4 °C for 24 h prior to analysis. Samples without the strawberry compound mix were analysed in all aspects of the study. The pH of the gels is shown in Table 1.

2.3. Gel characterisation

The gel systems were characterised by measuring how the samples behaved when compressed to a large degree of deformation. Immediately after the heat treatment and cooling down, 100 g gel samples were transferred into 71.3 mm diameter glass jars, sealed and refrigerated for 24 h. The samples were equilibrated to room temperature before the analysis began. Compression measurements were determined using a TA.TX2 Texture Analyzer (Stable Micro Systems Ltd., Surrey, UK), fitted with a 35 mm diameter cylinder aluminium probe at a constant speed of 1 mm s^{-1} , until compression was 75% of the initial height of the samples. Three replicates of each gel were analysed. Young's modulus of elasticity was calculated for each sample.

From the force deformation data, the true stress–strain curve was derived and the slope of the true stress–strain curve provides the value of Young's modulus of elasticity (E) (Dobraszczyk & Vincent, 1999). True stress and true strain were calculated according to the method described by Konstance (1993).

2.4. Static headspace analysis

For the analysis, 2 g of the gel was transferred into a 10 mL headspace vial and sealed immediately. The samples were incubated at 37°C and agitated at 750 rpm for 6 min in the automated headspace unit (Combipal-CTC Analytix system; JVA Analytical Ltd., Dublin, Ireland) of the gas chromatograph (Varian CP-3800; JVA Analytical Ltd.). After equilibration, 2 mL of headspace was automatically injected. The GC was equipped with an injector at 225°C , a BPX5 capillary column (60 m length, 0.32 mm i.d., and $1.0 \mu\text{m}$ film thickness; SGE; helium carrier gas 1.9 mL min^{-1}) and a flame ionisation detector at 300°C . An initial oven temperature of 30°C was used for 1 min, followed by a rate of $100^\circ\text{C min}^{-1}$ to 40°C . The oven temperature was maintained at 40°C for 4 min, and was subsequently programmed at 2°C min^{-1} to 90°C , further at 4°C min^{-1} to 130°C , and finally at 8°C min^{-1} to 270°C . Three replicates of each gel were analysed. Ten out of the 16 compounds in the strawberry flavour mix were detected at levels which sufficiently exceeded baseline. Five concentrations of each of the compounds were analysed in triplicate for calibration, allowing for quantification of the compounds in the air phase. For determination of air/gel partition coefficients of each of the compounds, air phase concentrations (w/w) were divided by the calculated concentrations in the gel phase (w/w).

2.5. In-nose PTR-MS analysis

A panel of 12 assessors participated in this study, consisting of 9 women and 3 men, aged 22–36. The

assessors had a U-shaped glass nosepiece inserted into their nostrils. During breathing, the air was drawn at 100 mL min^{-1} , 15 mL min^{-1} of which was lead into the PTR-MS through a heated transfer line (Ionicon Analytik, Austria). After breathing normally for 30 s, 5 g of gel was placed on a spoon and taken into the mouth. No instruction was given to the assessor regarding how to consume the sample. After the final swallow, the assessor continued breathing and the breath was monitored for a further 30 s. Samples were analysed according to the method described by Lindinger, Hansel, and Jordan (1998), while employing a constant drift voltage of 600 V. Transmission of the ions through the quadrupole was considered according to the specification of the instrument. Four compounds, (hexanal, ethyl butyrate, ethyl iso-pentanoate and ethyl hexanoate) out of the 16 compounds in the strawberry flavour mix, showed a response that sufficiently exceeded baseline and which parent ions or major fragment ions did not interfere with those of other compounds. Therefore, these are the only compounds whose release patterns are discussed. The odour descriptors for these compounds are hexanal: green, grassy; ethyl iso-pentanoate: fruity, ethyl hexanoate: fruity, ethyl butyrate: fruity, sweet (Sigma–Aldrich, 2004). After considering the fragmentation patterns of the individual compounds and ensuring that no interference from other fragments occurred, the concentrations of the volatile compounds were calculated (Buhr, van Ruth, & Delahunty, 2002; Lindinger et al., 1998). The mass fragments for these compounds are as follows: m/z 83 (hexanal), m/z 117 (ethyl butyrate), m/z 131 (ethyl iso-pentanoate), and m/z 145 (ethyl hexanoate) (Buhr et al., 2002). In addition, the ions m/z 21, m/z 32 and m/z 37 were observed to monitor the performance of the instrument, and m/z 59, which is a measure of breath acetone, was observed. The dwell time for each volatile compound was 0.4 s. Four replicates of each gel were analysed per assessor. From the PTR-MS data, the maximum concentrations reached (I_{max}), the time taken to reach the maximum concentrations (T_{max}), the slope of the release curves (release rate) and the area under the curve (AUC) were determined for each of the four compounds. The release rates were calculated using the following equation:

$$\text{Release rate} = I_{\text{max}} - I_{\text{start increase}} / T_{\text{max}} - T_{\text{start increase}}$$

The rates were measured from the time point that I sufficiently exceeded baseline to the maximum intensity measured. The cut off point for exceeding baseline ($I_{\text{start increase}}$) was defined as 10% of I_{max} . Accordingly, the time to reach this intensity was defined as $T_{\text{start increase}}$. The area under the curve (AUC) was calculated by trapezoidal integration (Hartel, Howell, & Hyslop, 1997).

2.6. Sensory analysis

The same panel of 12 assessors who carried out the in-nose PTR-MS analysis, were trained in the use of magnitude estimation against a fixed modulus (Moskowitz, 1998). A preliminary training session was held during which the panel developed common vocabulary to evaluate the sensory characteristics of the gels and agreed upon assessing four attributes odour (evaluated by smelling), thickness, strawberry flavour and sweetness (all evaluated during consumption) and the definitions for each attribute. Ten grams of each gel was placed in a clear-glass tumbler and covered with a clock-glass. Two test sessions were held, one for the pectin gels and the other for the gelatine gels. Samples were presented in groups of four, containing one reference sample and three test samples. The medium rigidity gel ($E = 300 \text{ N m}^{-2}$) was used as a reference and was assigned an arbitrary score of 100 for all attributes. Three replicates of each test gel were analysed. The test samples were randomly coded with three-digit numbers and presented in a balanced order using a complete block design. Assessors were instructed to assign a score to each sample, one attribute at a time, relative to the reference. No instruction was given to the assessor regarding how they consumed the sample. All evaluations were conducted in individual booths. Dry crackers and water were supplied between the samples and there was a break of 15 min between testing.

2.7. Statistical analysis

Data of texture measurements for triplicate gels were subjected to univariate analysis of variance (ANOVA) and least significant difference tests (LSD) to determine the significant differences between the samples. Data of

volatile compound measurements and sensory analysis for triplicate gels were subjected to multivariate analysis of variance (MANOVA) and least significant difference tests (LSD) to determine the significant differences between the samples. Student's *t* tests were used to analyse differences in volatile compound measurements and sensory data between gelatin gels and pectin gels (O'Mahony, 1986). SPSS 10.0 for Windows software was used for statistical evaluations. A significance level of $P < 0.05$ was maintained throughout the study.

3. Results

Three gelatin gels and three pectin gels were developed, such that gel rigidity, as assessed by Young's modulus of elasticity, was matched at a low, medium and high gel strength for each gel (i.e., $E = 181 \text{ N m}^{-2}$, $E = 300 \text{ N m}^{-2}$, $E = 493 \text{ N m}^{-2}$). Young's modulus of elasticity (E) is a measure for the rigidity of the gels (Bourne, 1982). The gels had significantly different values for Young's modulus of elasticity [$F(2,18) = 28.510$, $P < 0.05$] (Table 1).

The air/gel partition coefficients of 10 volatile compounds in the gelatin gel and pectin gel systems were determined by static headspace analysis (Table 2). The compounds had significantly different partition coefficients [$F(9,180) = 651.222$, $P < 0.05$]. Overall, gel texture and hydrocolloid type had significant effects on the partition coefficients (MANOVA and LSD, $P < 0.05$) (Table 2).

Dynamic headspace analysis was carried out by in-nose/PTR-MS analysis. Release curves were determined for each assessor for each of the compounds from the gelatin gels and pectin gels. The release of the ethyl butyrate and the level of breath acetone that was observed

Table 2
Air/gel partition coefficients ($k \times 1000$) in gelatin gels and pectin gels of low, medium and high rigidity for 10 volatile compounds ($n = 3$)

Volatile compound	Gelatin gels			Pectin gels		
	Low	Medium	High	Low	Medium	High
Ethyl butyrate	68.2 ^a	50.1 ^{ab}	40.3 ^b	51.4 ^a	29.9 ^{b*}	24.8 ^{b*}
Ethyl hexanoate	46.6 ^a	35.1 ^{ab}	31.3 ^b	27.0 ^{a*}	20.6 ^{b*}	17.8 ^{b*}
<i>cis</i> -3-Hexenol	4.7 ^a	4.6 ^a	4.6 ^a	4.5 ^{a*}	4.3 ^{ab*}	4.2 ^{b*}
Ethyl iso-pentanoate	176.2 ^a	129.8 ^b	105.6 ^b	122.6 ^{a*}	98.1 ^{b*}	60.6 ^{c*}
<i>cis</i> -3-Hexenyl acetate	28.8 ^a	26.7 ^a	25.4 ^a	21.7 ^{a*}	17.2 ^{b*}	18.2 ^{b*}
Benzyl acetate	14.1 ^a	14.6 ^a	14.3 ^a	14.4 ^a	13.6 ^{b*}	12.9 ^{b*}
Hexanal	37.7 ^a	34.2 ^b	31.5 ^c	29.3 ^{a*}	25.9 ^{b*}	13.8 ^{c*}
Methyl anthranilate	30.5 ^a	15.8 ^b	4.8 ^c	18.3 ^{a*}	11.3 ^b	1.7 ^c
Styrallyl acetate	1.3 ^a	0.9 ^b	0.3 ^c	5.6 ^a	3.2 ^b	0.3 ^c
β -Ionone	13.8 ^a	9.3 ^b	6.9 ^c	24.2 ^a	18.4 ^b	5.6 ^c
CV ^d [%]	12.5	7.2	15.0	9.6	8.7	13.4

^{a-c} Values with different superscripts within a row are significantly different, MANOVA and LSD tests, $P < 0.05$.

^d CV = coefficient of variance averaged over 10 compounds.

* These values are significantly different in pectin gels compared to gelatin gels of identical rigidity, Student's *t* tests, $P < 0.05$.

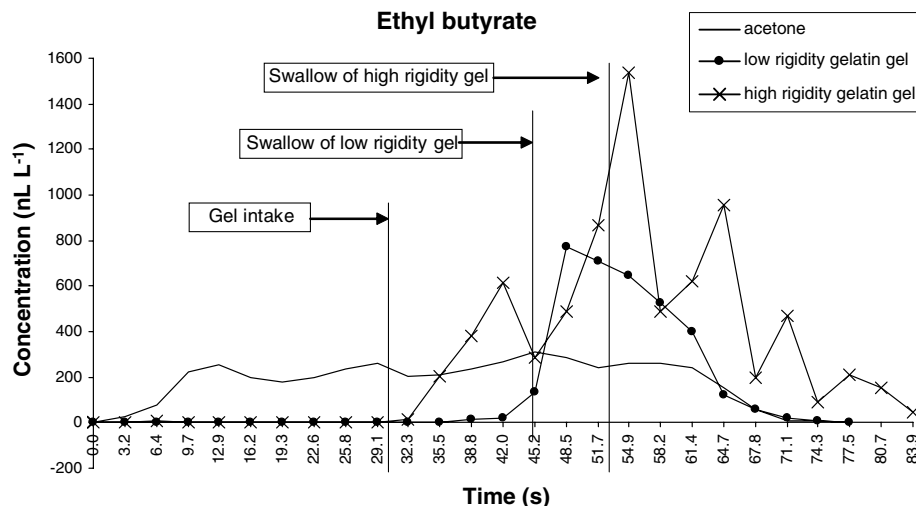


Fig. 1. Release curves for ethyl butyrate from a low rigidity gelatin gel and from a high rigidity gelatin gel, when consumed by a participant using in-nose/PTR-MS analysis.

while one of the participants consumed low and high rigidity gelatin gels are shown as an example in Fig. 1. The calculated results are displayed in Table 3. The four compounds monitored by PTR-MS had significantly different values for T_{\max} [$F(3,1152) = 22.262$, $P < 0.05$], I_{\max} [$F(3,1152) = 351.917$, $P < 0.05$], the release rates

[$F(3,1152) = 221.600$, $P < 0.05$] and the AUC [$F(3,1152) = 417.293$, $P < 0.05$]. Gel texture had an overall significant effect on T_{\max} , I_{\max} , the release rates and on the AUC (MANOVA and LSD, $P < 0.05$). Hydrocolloid type had no overall significant effect on T_{\max} , however, it did have a significant effect on I_{\max} , the re-

Table 3

Effect of gel texture on the release of volatiles from gelatin gels and pectin gels determined by in-nose PTR-MS analysis (12 assessors, 4 replicates)

Volatile compound		Gelatin gels			Pectin gels		
		Low	Medium	High	Low	Medium	High
T_{\max} (s)	Hexanal	16	18	18	15	17	17
	Ethyl butyrate	13	14	15	12 ^b	14 ^{ab}	15 ^a
	Ethyl iso-pentanoate	13	14	14	12 ^b	13 ^{ab}	15 ^a
	Ethyl hexanoate	15	16	16	13 ^b	15 ^{ab}	16 ^a
	CV ^d [%]	9	9	10	11	9	8
I_{\max} (nL L ⁻¹)	Hexanal	16	18	20	18 ^{b*}	27 ^{a*}	31 ^{a*}
	Ethyl butyrate	863	864	1016	1126 [*]	1371 [*]	1489 [*]
	Ethyl iso-pentanoate	58	56	73	71 ^{b*}	143 ^{a*}	145 ^{a*}
	Ethyl hexanoate	43	45	61	46 ^{b*}	133 ^{a*}	135 ^{a*}
	CV ^d [%]	21	25	23	32	22	19
Release rate (nL L ⁻¹ s ⁻¹)	Hexanal	2	2	1	2	2	1
	Ethyl butyrate	105	77	86	132 [*]	121 [*]	98
	Ethyl iso-pentanoate	8	5	6	14 ^{a*}	12 ^{a*}	6 ^b
	Ethyl hexanoate	6	4	4	13 ^{a*}	11 ^{b*}	4 ^b
	CV ^d [%]	20	28	37	31	21	25
AUC (nL L ⁻¹ s)	Hexanal	175	164	220	194 ^b	313 ^{ab*}	421 ^{a*}
	Ethyl butyrate	7881	7831	9450	9325 ^{b*}	12524 ^{ab*}	17191 ^{a*}
	Ethyl iso-pentanoate	603	592	759	686 ^{b*}	1398 ^{a*}	1837 ^{a*}
	Ethyl hexanoate	694	709	1022	727 ^{b*}	2063 ^{a*}	2598 ^{a*}
	CV ^d [%]	22	23	22	31	21	22

^{a-c} Values with different superscripts within a row are significantly different, MANOVA and LSD tests, $P < 0.05$.

^d CV = coefficient of variance averaged over four compounds.

* These values are significantly different in pectin gels compared to gelatin gels of identical rigidity, Student's t tests, $P < 0.05$.

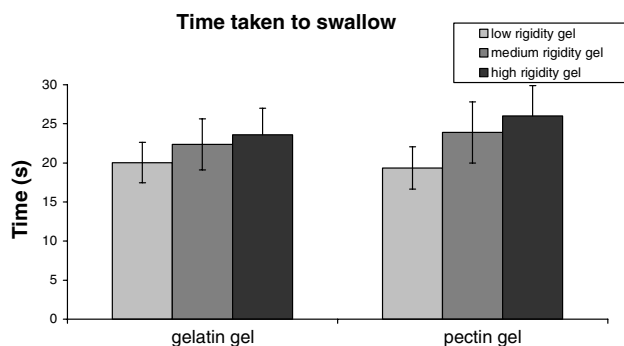


Fig. 2. The effect of gel texture on the time taken to swallow for gelatin gels and pectin gels as monitored during in-nose/PTR-MS analysis.

lease rates and on the AUC (MANOVA and LSD, $P < 0.05$) (Table 3). There was also an overall significant effect of assessor on T_{max} , I_{max} , the release rates and on the AUC (MANOVA and LSD, $P < 0.05$).

The amount of time spent by the participants chewing each gel before swallowing increased significantly as gel rigidity increased for both gelatin gels and pectin gels [$F(2,288) = 12.268$, $P < 0.05$] (Fig. 2). The individual assessors had significant different amounts of time before swallowing [$F(11,288) = 7.281$, $P < 0.05$]. There was no overall significant effect of hydrocolloid type on amount of time before swallowing [$F(1,288) = 1.382$, $P < 0.05$].

Sensory analysis required the participants to rate the intensities of four attributes: odour, thickness, strawberry flavour and sweetness. These results are displayed in Table 4. There was no overall significant effect of assessor on any of the sensory scores [$F(11,864) = 0.845$, $P > 0.05$]. Hydrocolloid type had an overall significant effect on the sensory scores [$F(1,864) = 6.437$, $P < 0.05$]. Gel texture had a significant effect on the sensory scores in gelatin gels [$F(2,432) = 3.923$, $P < 0.05$] and in pectin gels [$F(2,432) = 7.866$, $P < 0.05$].

Table 4

The effect of gel texture on the perceived intensity for gelatin gels and pectin gels by sensory analysis (12 assessors, 3 replicates)

Attribute	Gelatin gels			Pectin gels		
	Low	Medium	High	Low	Medium	High
Odour	157 ^a	116 ^b	107 ^b	145 ^a	111 ^{ab}	96 ^b
Thickness	82 ^c	134 ^b	236 ^a	76 ^c	126 ^b	383 ^a
Sweetness	169 ^a	140 ^{ab}	113 ^b	156 ^a	120 ^b	107 ^b
Strawberry flavour	180 ^a	130 ^b	115 ^b	132 ^a	121 ^a	109 ^b
CV ^d [%]	27	27	29	29	25	29

^{a-c} Values with different superscripts within a row are significantly different, MANOVA and LSD tests, $P < 0.05$.

No values are significantly different in pectin gels compared to gelatin gels of identical rigidity, Student's t tests, $P < 0.05$.

^d CV = coefficient of variance averaged over the four attributes.

4. Discussion

4.1. Flavour compounds

In both gel systems and for all gel textures, as the chain length of esters increased (ethyl iso-pentanoate C-7, ethyl hexanoate C-8, *cis*-3-hexenyl acetate C-8, methyl anthranilate C-8, benzyl acetate C-9, styrallyl acetate C-10), there was a decrease in the air/gel partition coefficients. These data show the higher affinity of larger, more hydrophobic flavour compounds for the gel matrices. This can be due to binding/trapping of the flavour compounds. As the changes are not compound specific, it is more likely that the matrices have non-polar characteristics. Similar patterns have previously been reported in a previous study of the authors (Boland, Buhr, Giannouli, & van Ruth, 2004), and by Hansson, Leufvén, & van Ruth (2003) and Braudo et al. (2000). When ranking compounds according to their partition coefficients the four compounds with the highest partition coefficients are ethyl iso-pentanoate, ethyl butyrate, ethyl hexanoate and hexanal. These are also the four compounds that were analysed by PTR-MS analysis.

4.2. Effect of hydrocolloid type (gelatin or pectin)

Although the texture of the gels were matched (Table 1), differences in the partition coefficients and results from PTR-MS analysis between gelatin gels and pectin gels were observed. As Table 2 shows, in the majority of cases where hydrocolloid type had a significant effect on the partition coefficients of volatile compounds, the values from the pectin gels were significantly lower than the results from the gelatin gels (Student's t test, $P < 0.05$). These results reveal the higher affinity of the compounds for the pectin matrix. The differences in partition coefficients for the two gel systems tend to increase with chain length and, therefore, with hydrophobicity of the compounds. In contrary to the static headspace analysis, in PTR-MS analysis (Table 3), the majority of values were significantly higher in the pectin gels compared to the gelatin gels (Student's t test, $P < 0.05$). The amount of time spent chewing the gels before swallowing was not significantly different between the gelatin gels and the pectin gels [$F(1,288) = 1.3832$, $P > 0.05$]. A possible explanation for the differences between the gel systems may be differences in the rates of mass transfer of volatile compounds out of the gel systems. An indication for this is the higher rate values for the pectin gels (Table 3). This could be due to the fact that pectin gels have generally lower melting temperatures than gelatin gel systems (Clark, Evans, & Farrer, 1994). The static headspace analyses were carried out at 37 °C, whereas in PTR-MS analysis the samples were served at room temperature. The temperature increased after

the sample was placed in the mouth, but its actual temperature profile during consumption is unknown. The different temperatures could have affected the air/gel partitioning of the flavour compounds, besides the aspect of mass transfer.

Despite the differences observed in static headspace and PTR-MS analysis no significant differences in sensory characteristics between the two gel systems were observed (Table 4).

4.3. Effect of gel texture

Seven out of the 10 compounds had significantly lower partition coefficients in the most rigid gelatin gels compared to the least rigid gels. In the case of pectin gels, all 10 compounds had significantly lower partition coefficients in the most rigid gel compared to the least rigid gel (Table 2). As thermodynamic and not mass transfer factors determine headspace concentrations under static conditions, the differences between the gels with different textures are likely to originate from volatile–matrix interactions. The increase of hydrocolloid concentration changed the properties of the matrix resulting in a more non-polar matrix. This is indicated by larger retention of the more hydrophobic compounds (e.g., methyl anthranilate) than the less hydrophobic compounds (e.g., hexanal) in the more rigid gels. The air/gel partition coefficient results are in agreement with a previous study of the authors (Boland et al., 2004) and also with studies of Landy, Druaux, & Voilley (1995), Hansson, Anderson, & Leufven (2001) and Lubbers & Guichard (2003).

In-nose PTR-MS analysis revealed a general trend that for all compounds for both gelatin gels and pectin gels, the most rigid gels had higher values for T_{\max} , I_{\max} and the AUC than the less rigid gels (Table 3). However, the release rate values were higher for the low rigidity gels. Thus, there was more extensive release of volatiles from the more rigid gels, but the increase from background to maximum intensity was much steeper for the softer gels. In all cases, analysis began by the participant breathing for 30 s and then the gel sample was taken into the mouth (Fig. 1). After the final swallow, the assessor continued breathing and the breath was monitored for a further 30 s. When the least rigid gel was taken into the mouth, there was no change in the nose-space concentration until the time of swallowing. Then, there was a large increase in nose-space concentration. After this peak the concentration decreased steadily. This explains why the release rate values were higher for the softer gels. In the case of the high rigidity gel, as soon as the gel was taken into the mouth the nose-space concentration increased gradually. The concentration peaked at the time of swallowing, and after swallowing the concentration declined but this decline was not as steady as the decline observed for the less rigid gel.

These results are in agreement with Hansson, Gianouli, & van Ruth (2003) and Buettner, Beer, Haning, & Settles (2001), who observed that the release of volatile compounds from a viscous solution into the nose did not occur until the sample was swallowed. In the case of a stronger gel/semi-solid food, the authors found that volatile compounds were reaching the nose prior to swallowing. These findings, along with the results in the current study, indicate that when a viscous solution is being consumed the oral cavity can be considered to be more or less a closed system, i.e., the junction of the oral cavity and pharynx is closed by the soft palate. During this closure no volatile compounds can transfer via the retro-nasal route into the nasal cavity and olfactory epithelium. Then, when swallowing occurs the soft palate is displaced and this allows the consumed sample to pass into the oesophagus and also opens the nasal cavity for the passage of volatile compounds into the nose (Buettner & Schieberle, 2000; Buettner et al., 2001). During mastication of the firmer sample, intermittent opening of the connection between the nasal cavity and oral cavity was observed using videofluoroscopy (Buettner et al., 2001). This could explain the increased concentration of volatiles in the nose prior to swallowing. These authors also observed that after the swallow of the firmer sample, a viscous salivary coating on the back of the tongue was formed. They proposed that this coating may contain volatiles and could induce a prolonged perception of volatiles. In the current study, this coating could have contributed to the less steady decline in the concentration of volatiles (i.e., small peaks occurred) which was observed for the more rigid gels but not for the less rigid gels.

The pattern of in-nose results found in the current study for I_{\max} , release rate and AUC contradict those observed by some others. Baek et al. (1999) found a significant decrease in I_{\max} values as the rigidity of gelatin gels increased. Carr et al. (1996) and Guinard & Marty (1995) demonstrated similar findings. Conversely, more recent studies have observed no changes to the nose-space concentrations with increasing texture of hydroxyl propyl methylcellulose and whey protein gels (Hollowood et al., 2002; Weel et al., 2002). However, the protocol for analysis implemented by Hollowood et al. (2002) did not allow for mixing or swirling of the sample in the mouth, thereby reducing the ability to examine the effects of sample rigidity on volatile release. In the case of the study by Weel et al. (2002), these authors instructed their participants to “chew regularly (independent of gel hardness) for 30 s without swallowing, then to swallow the entire bolus”. Delahunty et al. (2004) found that when using liquid guar gum samples which were held in the mouth for 1 min and continuously swirled, the concentration of the volatile compound de-

creased as viscosity increased beyond C^* . In comparison, the current study placed no restriction on how and the length of time the gel was chewed. As demonstrated in Fig. 2, the more rigid gels were chewed for longer than the less rigid gels, therefore allowing more time for the volatiles to be released from the gel systems and to pass into the nasal cavity. Baek et al. (1999), Linforth, Baek, & Taylor (1999) and Carr et al. (1996) demonstrated that harder gels had higher T_{\max} values than softer gels. van Ruth, de Witte, & Rey Uriarte (2004) also observed that firmer gel samples were chewed more extensively than softer samples and that this resulted in increased nasal concentrations for the firmer gel samples. Therefore the more extensive chewing could account for the more rigid gels taking longer to consume, resulting in more time available for the release of volatiles and thus higher I_{\max} , T_{\max} and AUC values. Also, mastication has been shown to cause a breakdown of the food structure, an increase in the surface area available for the diffusion of volatiles and therefore an increase in the release of volatile compounds (Harrison & Hills, 1997; van Ruth, Roozen, & Cozijnsen, 1994). Mastication, therefore, leads to a gradual increase in release of volatile compounds.

As can be observed from Table 4, the perceived odour, strawberry flavour and sweetness decreased for both gels as gel rigidity increased, while perceived thickness increased (MANOVA and LSD tests, $P < 0.05$). The findings for the perceived sensory results were also reported by other authors. Pangborn et al. (1978) demonstrated that increasing the hydrocolloid concentrations of beverages significantly decreased the perceived taste and aroma intensities. Baek et al. (1999) observed a clear trend of decreasing perceived flavour intensity with increasing gelatin gel concentration. Similar results have been reported by Delahunty et al. (2004) and by Guinard & Marty (1995). The increase in perceived thickness intensity is in agreement with Young's modulus of elasticity values of the samples (Table 1). The decrease in odour intensity of the samples with increased rigidity correlates well with the air/gel partition coefficient data, which showed a decrease in headspace concentration of volatile compounds for the more rigid gels (Table 2). The sweetness perception of the samples is likely to be mostly related to the release of sucrose into the oral cavity as shown before by van Ruth et al. (submitted). The interaction of texture and chewing movements determine eventually the release of sucrose into saliva. Sucrose release is expected to be lower for the more rigid samples. Increasing the hydrocolloid content of a system can cause a reduction in the transport of small molecules, e.g., taste and aroma molecules, out of the gel system and to their respective olfactory receptors (Baines & Morris, 1987). Lethuaut et al. (2003) demonstrated that the perceived sweetness of model dairy desserts decreased with increased sample firmness although

a direct relation between sample strength and sweetness perception was not found. The decrease of strawberry flavour intensity perception for the more rigid gels is not in agreement with the I_{\max} values determined by in-nose analysis. It is, however, in agreement with the release rates which were lower for the more rigid gels. The higher release rates for the softer samples, despite the lower I_{\max} values, resulted in a higher overall flavour impression. A more gradual increase could be perceived as a less intense overall flavour. Studies of Baek et al. (1999) showed a similar correlation. Prolonged exposure to volatile flavour compounds may have resulted in adaptation. An additional explanation for the decreased strawberry flavour intensities in the more rigid gels may be the occurrence of cross-modality interactions, such as taste–aroma interactions. In this particular case, sweetness–strawberry flavour interactions may have occurred. Therefore, reduced sucrose release rates from the more rigid gels may have led to a reduction in sweetness perception. Strawberry flavour and sweetness are congruent attributes, which could result in additive effects (Noble, 1996). A reduction in sweetness perception could potentially account for the decline in strawberry perception. An indication for this hypothesis is that the sweetness intensity and the strawberry flavour intensity very similarly changed with the rigidity of the gels. Similar results were observed by Hollowood et al. (2002) and Delahunty et al. (2004).

A third explanation for the findings is the possibility of texture, taste and aroma interactions. Hollowood et al. (2002) proposed that gustatory (i.e., taste and aroma) and texture inputs converge and thus perception of thickness affects the perception of flavour. This could explain that as the assessors perceived an increased in gel rigidity, this could have caused them to neglect the other sensations of sweetness and strawberry flavour. Evidence of these types of interactions was also reported by Hollowood et al. (2002), Weel et al. (2002) and Delahunty et al. (2004).

5. Conclusions

In conclusion, both rigidity of the gels and the type of hydrocolloid had a considerable effect on the gels' flavour release and/or perception. Gelatin gels showed higher static headspace concentrations of strawberry flavour, but decreased flavour release compared to the pectin gels. Both type of gels showed similar effects on flavour release and perception when their texture was changed. When the rigidity of the gels increased, the air/gel partition coefficients decreased, the maximum in nose concentrations increased, the release rates decreased, the perceived thickness intensity increased, and the odour, sweetness and strawberry flavour intensities decreased.

References

- Baek, I., Linforth, R. S. T., Blake, A., & Taylor, A. J. (1999). Sensory perception is related to the rate of change of volatile concentration in-nose during eating of model gels. *Chemical Senses*, 24, 155–160.
- Baines, Z. V., & Morris, E. R. (1987). Flavour/taste perception in thickened systems: the effect of guar gum above and below c^* . *Food Hydrocolloids*, 1(3), 197–205.
- Boland, A. B., Buhr, K., Giannouli, P., & van Ruth, S. M. (2004). Influence of gelatin, starch, pectin and artificial saliva on the release of 11 flavour compounds from model gel systems. *Food Chemistry*, 86(3), 401–411.
- Bourne, M. (1982). Principles of objective texture measurements. In M. Bourne (Ed.), *Food texture and viscosity: Concept and measurement* (pp. 44–117). London, UK: Academic Press.
- Braudo, E. E., Plashchina, I. G., Kobak, V. V., Golovnya, R. V., Zhuravleva, I. L., & Krikunova, N. I. (2000). Interactions of flavour compounds with pectic substances. *Nahrung*, 44(3), 173–177.
- Buhr, K., van Ruth, S., & Delahunty, C. (2002). Analysis of volatile flavour compounds by proton transfer reaction-mass spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds. *International Journal of Mass Spectrometry*, 221, 1–7.
- Buettner, A., & Schieberle, P. (2000). Exhaled odourant measurements (EXOM) – a new approach to quantify the degree of in-mouth release of food aroma compounds. *Lebensmittel Wissenschaft & Technologie*, 33, 553–559.
- Buettner, A., Beer, A., Hanning, C., & Settles, M. (2001). Observation of the swallowing process by application of videofluoroscopy and real-time magnetic resonance imaging – consequences for retronasal aroma stimulation. *Chemical Senses*, 26, 1211–1219.
- Carr, J., Baloga, D., Guinard, J. X., Lawter, L., Marty, C., & Cordelia, S. (1996). The effect of gelling agent type and concentration on flavour release in model systems. In R. J. McGorin & J. V. Leland (Eds.), *Flavour–food interactions. Symposium series* (Vol. 6334, pp. 98–108). Washington, DC: American Chemical Society.
- Clark, A. H., Evans, K. T., & Farrer, D. B. (1994). Shear modulus-temperature meltdown profiles of gelatine and pectin gels. A cascade theory description. *International Journal of Biological Macromolecules*, 16(3), 125–130.
- Delahunty, C. M., O'Meara, S., Barry, F., Morris, E. R., Giannouli, P., & Buhr, K. (2004). The influence of random coil overlap on perception of solutions thickened using guar gum. In K. D. Deibler & J. Delwiche (Eds.), *Handbook of flavour characterisation: Sensory analysis, chemical and physiology* (pp. 177–188). New York, USA: Marcel Dekker.
- Dobraszczyk, B. J., & Vincent, J. F. V. (1999). Measurements of mechanical properties of food materials in relation to texture: The materials approach. In A. J. Rosenthal (Ed.), *Food texture, measurement and perception* (pp. 99–184). Gaithersburg, MD: Aspen Publishers.
- Guinard, J. X., & Marty, C. (1995). Time–intensity measurement of flavour release from a model gel system: effect of gelling agent type and concentration. *Journal of Food Science*, 60(4), 727–730.
- Hansson, A., Anderson, J., & Leufven, A. (2001). The effect of sugars and pectin on flavour release from a soft drink-related model system. *Food Chemistry*, 72, 363–368.
- Hansson, A., Giannouli, P., & van Ruth, S. (2003). The influence of gel strength on aroma release from pectin gels in a model mouth and in vivo, monitored with proton-transfer-reaction mass spectrometry. *Journal of Agricultural and Food Chemistry*, 51(6), 4732–4740.
- Hansson, A., Leufven, A., & van Ruth, S. (2003). Partition and release of 21 aroma compounds during storage of a pectin gel system. *Journal of Agricultural and Food Chemistry*, 51(7), 2000–2005.
- Harrison, M., & Hills, B. P. (1997). Mathematical model of flavour release from liquids containing aroma-binding molecules. *Journal of Agricultural and Food Chemistry*, 45, 1883–1890.
- Hartel, R. W., Howell, T. A., & Hyslop, D. B. (1997). Calculus. In *Math concepts for food engineering* (pp. 80–81). Pennsylvania, USA: Technomic Publishing Company.
- Hollowood, T. A., Linforth, R. S. T., & Taylor, A. J. (2002). The effect of viscosity on the perception of flavour. *Chemical Senses*, 27, 583–591.
- ISO 5492 (1992). Standard 5492: Terms relating to sensory analysis. International Organisation for Standardization.
- Konstance, R. P. (1993). Axial compression properties of calcium caseinate gels. *Journal of Dairy Science*, 76, 3317–3326.
- Landy, P., Druaux, C., & Voilley, A. (1995). Retention of aroma compounds by proteins in aqueous solution. *Food Chemistry*, 54(4), 387–392.
- Lethuaut, L., Brossard, C., Rousseau, F., Bousseau, B., & Genot, G. (2003). Sweetness–texture interactions in model dairy desserts: effect of sucrose concentration and the carrageenan type. *International Dairy Journal*, 13, 631–641.
- Lindinger, W., Hansel, A., & Jordan, A. (1998). On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry: medical applications, food control and environmental research. *International Journal of Mass Spectrometry*, 173, 191–241.
- Linforth, R. S. T., Baek, I., & Taylor, A. (1999). Simultaneous instrumental and sensory analysis of volatile release from gelatine and pectin/gelatine gels. *Food Chemistry*, 65, 77–83.
- Lubbers, S., & Guichard, E. (2003). The effects of sugars and pectin on flavour release from a fruit pastille model system. *Food Chemistry*, 81(2), 269–273.
- Mällki, Y., Heiniö, R.-L., & Autio, K. (1993). Influence of oat gum, guar gum and carboxymethyl cellulose on the perception of sweetness and flavour. *Food Hydrocolloids*, 6, 525–532.
- Moskowitz, H. (1998). Magnitude estimation: Scientific background and use in sensory analysis. *Applied sensory analysis of foods* (Vol. 1, pp. 193–223). Florida, USA: CRC Press.
- Noble, A. C. (1996). Taste–aroma interactions. *Trends in Food Science and Technology*, 7(12), 439–444.
- O'Mahony, M. (1986). *Sensory evaluation of food*. New York, USA: Marcel Dekker.
- Overbosch, P., Afterof, W. G. M., & Haring, P. G. M. (1991). Flavour release in the mouth. *Food Reviews International*, 7(2), 137–184.
- Pangborn, R. M., Misaghi-Gibbs, Z., & Tassan, C. (1978). Effect of hydrocolloids on apparent viscosity and sensory properties of selected beverages. *Journal of Texture Studies*, 9, 415–436.
- Sigma–Aldrich (2004). Search Centre Available from <http://www.sigma-aldrich.com>.
- Taylor, A. J., Linforth, R. S. T., Harvey, B. A., & Blake, A. (2000). Atmospheric pressure chemical ionization mass spectrometry for in vivo analysis of flavour release. *Food Chemistry*, 71, 327–338.
- Taylor, A. J., Besnard, S., Puaud, M., & Linforth, R. S. T. (2001). In vivo measurement of flavour release from mixed phase gels. *Biomolecular Engineering*, 72, 143–150.
- van Ruth, S. M., de Witte, L., & Rey Uriarte, A. (2004). Volatile flavour analysis and sensory evaluation of custard desserts varying in type and concentration of carboxymethyl cellulose. *Journal of Agriculture and Food Chemistry*, 52, 8105–8110.
- van Ruth, S. M., Roozen, J. P., & Cozijnsen, J. L. (1994). Comparison of dynamic headspace model mouth systems for flavour release from rehydrated bell pepper cuttings. In H. Maarse & D. G. van der Heij (Eds.), *Trends in flavour research* (pp. 59–64). Amsterdam: Elsevier.
- Weel, K. G. C., Boelrijk, A. E. M., Alting, A. C., van Mil, P. J. J. M., Burger, J. J., Gruppen, H., et al. (2002). Flavour release and perception of flavoured whey protein gels: Perception is determined by texture rather than by release. *Journal of Agricultural and Food Chemistry*, 50, 5149–5155.