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Influence of gelatin, starch, pectin and artificial saliva on the release of 11 flavour compounds from model gel systems

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Abstract

The release of 11 flavour compounds from gelatin, starch and pectin gels was investigated. The gels were characterised by Young's modulus of elasticity (E). Static headspace analysis was used to determine the partition coefficients of compounds. Model mouth/proton transfer reaction-mass spectrometry analysis produced flavour release profiles. The most rigid gel, gelatin gel, had the lowest partition coefficients for six compounds and the lowest maximum concentrations released for all compounds. While the rigidity of the starch and pectin gels were not significantly different from each other, there was greater release of hydrophilic compounds from pectin gels than starch gels, while the opposite was observed for hydrophobic compounds. These results indicated matrix–volatile interactions occurring in the starch and pectin gels. The gelatin gel showed large increases in flavour release in the presence of saliva, while the starch and pectin gels showed a reduction in flavour release.

Keywords: Flavour release; Gel; Gelatin; Pectin; PTR-MS; Starch

1. Introduction

Hydrocolloids are widely used in the food industry as thickeners, stabilisers and gelling agents in products such as ice cream, beverages, jellies and sauces. In recent years, due to increased health consciousness amongst consumers, hydrocolloids are increasingly being extended into the area of reduced fat products. Therefore, the formulation of new food products containing hydrocolloids has led to an increased demand for knowledge of their mechanical and physical properties, including the flavour release properties of hydrocolloids.

Only compounds released in sufficiently high concentrations will be perceived as a flavour and even slight variations in the compositions of the gel system can change the perceived flavour. Therefore, the food industry would benefit greatly from an improved understanding of the mechanisms involved in the breakdown of the food matrix and more importantly the release of flavour compounds.

Many studies have shown that hydrocolloids influence the rate and intensity of flavour release in foods (Baines & Morris, 1987; Pangborn, Misaghi-Gibbs, & Tassan, 1978; Pangborn & Szczesniak, 1974). Most studies in this area are concerned with the effect of the hydrocolloids on flavour perception. However, in order to understand these phenomena, physico-chemical studies are required. The influence on perception may be related to changes in concentrations of flavour volatiles released from the gel system or to the perception of a thickener solution. Also, evidence indicates that the thickener system, the firmness of the gel and the particular flavour compound used must be considered as they all influence the rate and degree of flavour release (Carr et al., 1996; Guinard & Marty, 1995).

Flavour release is influenced by both thermodynamic and kinetic mechanisms. Thermodynamic factors determine the partitioning of volatiles between the food and air phases under equilibrium conditions. The kinetic factors influence the rate at which equilibrium is

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achieved (de Roos, 1994). The rate is affected by resistance to mass transport, which determines the rate of diffusion of volatiles out of the food and into the air phase.

Static headspace analysis is carried out to determine the air/product partition coefficients of compounds. At equilibrium, the air/product partition coefficient is defined as the ratio of the concentration of the volatile in the gas phase to its concentration in the liquid phase (Buttery, Bomben, Guadagni, & Ling, 1971). Dynamic headspace analysis provides information about the temporal release of compounds. Temporal release is determined by both the thermodynamics and kinetics of release.

Three commonly used hydrocolloids in the food products are gelatin, starch and pectin. Gelatin is commercially derived from collagen extracted from the bone, skin or tendons of animals. It contains glycine, proline and hydroxyproline, and is used as a thickening agent in dessert jellies, confectionery jellies and gums (Johnston-Banks, 1990). Starch is mainly used as a gelling system in puddings and desserts. Its sources include maize, wheat and potato, which can contain between 14% and 27% amylose (a linear chain of glucose linked by α-1,4-glucosidic bonds) and 73–86% amylopectin (a branched chain of glucose linked by α-1,4-glucosidic bonds with α-1,6-glucosidic bonds at the points of branching) (Chinachoti, 1995). Pectin is obtained from citrus fruits and consists of a linear chain of α-(1-4)-linked D-galacturonic acid units, in which varying proportions of the acid groups are present as methyl esters (Voragen & Pilnik, 1995). It is used in jellies, jams, marmalades and confectionery products (Barfod & Pedersen, 1990). High-methoxy pectins (HMP) are used to form gels in acidic media of high sugar content.

In the present study three gels varying in hydrocolloid (gelatin, starch and pectin) were examined for their flavour release properties. Flavour release was analysed in terms of both the thermodynamic and kinetic factors affecting flavour release.

2. Materials and methods

2.1. Sample materials

The composition of the gels is shown in Table 1. Distilled water was added to provide a final weight of 100 g. The gelatin (G-2625, derived from porcine skin, Type A, bloom strength 175), starch (S-2004, potato starch, containing 23% amylose and 77% amylopectin) and pectin (P-9135, high-methyl pectin (degree of esterification 79.5%)) were all supplied by the Sigma–Aldrich company (Poole, Dorset, UK). Glucose syrup (dextrose equivalent 40.8%) was supplied by Cargill (Bergen op Zoom, The Netherlands). 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 Han (Seele, Germany), respectively.

The flavour compound stock solution contained 11 aroma compounds: diacetyl, 2-butanone, ethyl acetate, 1-butanol, 3-methyl-1-butanol, ethyl butyrate, hexanal, 2-heptanone, heptanal, 2-octanone and 2-decanone (suppliers: Table 2). These were dissolved in distilled water (0.050% v/v per compound for the static headspace analysis, 0.025% v/v per compound for the model mouth analysis), and were refrigerated overnight to ensure equal distribution prior to addition to the gel systems.

The artificial saliva consisted of $NaHCO_3$ (5.208 g), $K_2HPO_4 \cdot 3H_2O$ (1.369 g), NaCl (0.877 g), KCl (0.447 g), $CaCl_2 \cdot 2H_2O$ (0.441 g), mucin (2.160 g), and 200,000 U of α-amylase (hog pancreas α-amylase; Fluka Chemie) in 1 L of distilled water, and was adjusted to pH 7 (van Ruth, Roozen, & Cozijnsen, 1994). Differing from the method described by van Ruth et al. (1994), NaN_3

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

Ingredients	Gelatin gel	Starch gel	Pectin gel
Gelatin (g)	2	0	0
Starch (g)	0	2	0
Pectin (g)	0	0	2
Sucrose (g)	37	0	36
Glucose syrup (g)	45	0	24
Citric acid (g)	1	0	1
Sodium citrate (g)	0	0	0.4
Water (g)	15	98	36.6
Flavour concentration of each compound in the gels for			
Static headspace analysis (μL kg^{-1})	10	10	10
PTR-MS analysis (μL kg^{-1})	0.5	0.5	0.5
E (N m^{-2})	400.25[a]	53.15[b]	48.61[b]

[a,b] Values with different superscripts within a row are significantly different, ANOVA and LSD tests, $P < 0.05$.

Table 2
Eleven aroma compounds, their octanol/water partition coefficients (log *P*), densities, major product ions, fragmentation correction factors and suppliers

Flavour compound	log *P*[a]	Density (g mL^{-1})	Major product ions[b]	Fragmentation correction factors[b] (%)	Supplier
Diacetyl	0.8	0.98	87	89.29	Aldrich[c]
2-Butanone	0.29	0.80	73	95.24	Aldrich
Ethyl acetate	0.73	0.90	61	49.50	Aldrich
1-Butanol	0.84	0.81	57	90.09	Lancaster[d]
3-Methyl-1-butanol	1.28	0.81	71	37.10	Lancaster
Ethyl butyrate	1.9	0.88	117	55.25	Merck[e]
Hexanal	1.78	0.82	83	62.50	Aldrich
2-Heptanone	1.98	0.81	115	91.74	Aldrich
Heptanal	–	0.82	97	61.35	Aldrich
2-Octanone	2.37	0.82	129	100.00	Merck
2-Decanone	3.77	0.82	157	90.09	Fluka Chemie[f]

[a] Lide, 1997.
[b] Buhr, van Ruth, and Delahunty (2002), e.g., ion 87 accounts for 89.29% of parent and product ions.
[c] Aldrich, Steinheim, Germany.
[d] Lancaster, Walkerburn, UK.
[e] Merck, Hohenbrunn, Munich, Germany.
[f] Fluka Chemie, Buchs, Switzerland.

was omitted in order to avoid interference with dynamic analysis due to release of HN_3 at low pH values.

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 vaporization. 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 compound mixture was introduced. For static headspace analysis, the 0.05% v/v stock solution was added to the gels to produce a final concentration of each flavour compound of 10 μL kg^{-1} of gel. For the model mouth analysis, the 0.025% v/v stock solution was added to the gels to produce a final concentration of each flavour compound of 0.5 μL kg^{-1} of gel (Table 1). The jar was immediately sealed and stirring continued for 1 min to ensure equal distribution of volatiles.

Pectin gels were prepared in a similar manner, except that 10 g of the sucrose was mixed with the pectin and sodium citrate before being dissolved in water and a temperature of 85 °C was maintained throughout.

For preparation of the starch gels, starch and water were mixed for 2 min with a hand blender. Then, the flavour compound mixture was added and the jar was sealed immediately. The starch gels were placed in an 80 °C water bath for 15 min, followed by 12 min in a 20 °C water bath. Constant stirring was maintained throughout to ensure complete dissolution of solutes and equal distribution of volatiles.

The gel samples were refrigerated for 24 h prior to analysis. All gel samples were prepared in triplicate. Samples without flavour compounds were analysed in all aspects of the study. The pH of the gels was 2.34 ± 0.05 for gelatin gels, 4.30 ± 0.05 for starch gels and 3.29 ± 0.05 for pectin gels.

2.3. Gel characterization

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 Analyser (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 deformation was 75% of the initial height of the samples. Young's modulus of elasticity was calculated for each sample, as described in the calculations section.

2.4. Static headspace analysis

For the analysis, 2 g of the gel was transferred into a 10-mL headspace vial. For the analysis with saliva, 0.8 mL of artificial saliva and 1.2 g of gel were transferred into a 10-mL headspace vial. The samples were incubated at 37 °C and agitated at 750 rpm for 6 min in the automated headspace unit (Combipal-CTC Analytics 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 μm film thickness; SGE; helium carrier gas 1.9 mL min^{-1}) and a flame ionization detector at 300 °C. An initial oven temperature of −30 °C was used for 1 min, followed by a rate of 100 °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. Five concentrations of each of the compounds were analysed in triplicate for calibration, allowing for quantification of the compounds in the air phase.

2.5. Proton transfer reaction-mass spectrometry analysis

Aroma compounds were isolated in a model mouth system, the latest version of which has been reported by van Ruth and Roozen (2000). Ten grams of the gel sample, or 6 g gel and 4 mL artificial saliva, were transferred into the flask (70 mL, 37 °C) of the model mouth system. Mastication was simulated by the plunger, which made up-and-down and circular movements (52 cycles min^{-1}). The headspace was drawn from the model mouth flask at 100 mL and 15 mL min^{-1} of which was lead into the proton transfer reaction-mass spectrometry (PTR-MS) (Ionicon Analytik, Austria). The dwell time for each flavour compound was 0.2 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. The concentrations of the flavour compounds were calculated by considering the fragmentation patterns of the individual compounds (Buhr et al., 2002) (Table 2). The release of the compounds from the gels was monitored over a 5-min period. The 11 flavour compounds and their major product ions are displayed on Table 2.

2.6. Calculations

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 strain is calculated by the relative change in height and true stress is the force exerted divided by the cross-sectional area over which the force is acting. True stress and true strain were calculated using the following equations:

$$\text{True stress} = \ln(h_0/h_0 - \Delta h)$$

and

$$\text{True strain} = Ft/A_o \ * h_0 - \Delta h/h_0,$$

where h_0 is the original height of the sample, Δh is the change in height during compression, Ft is the compression force at time t and A_0 is the original cross-sectional area of the sample (Konstance, 1993; Tang, McCarthy, & Munro, 1995).

For determination of air/gel partition coefficients of each of the compounds, air phase concentrations (w/w) were divided by the concentrations in the gel phase (w/w).

The flavour release profiles were calculated as described by Hansel et al. (1995). Maximum concentrations released (I_{max}) and the cumulative release in the initial 5 min for each flavour compound were calculated

Table 3
Air/gel partition coefficients ($k \times 1000$) of 11 flavour compounds ($n = 3$)

Flavour compound	Air/gel partition coefficients					
	−saliva			+saliva		
	Gelatin gel	Starch gel	Pectin gel	Gelatin gel	Starch gel	Pectin gel
Diacetyl	2.9[a]	1.6[b]	2.8[a]	2.9	**1.8**	2.6
2-Butanone	8.2[a]	3.3[c]	7.4[b]	6.1*	3.4	4.9*
Ethyl acetate	12.9[b]	8.1[c]	17.3[a]	14.6	7.9	11.4*
1-Butanol	1.8[a]	0.7[c]	1.3[b]	1.3*	**1.0**	1.2
3-Methyl-1-butanol	1.8[b]	0.9[c]	3.0[a]	1.7	**1.1**	2.5*
Ethyl butyrate	7.2[c]	10.1[b]	18.0[a]	**16.5**	3.3*	14.7*
Hexanal	3.1[c]	7.7[b]	10.4[a]	**9.2**	5.3*	10.6
2-Heptanone	3.3[c]	4.0[b]	6.3[a]	**6.8**	4.3	5.4*
Heptanal	1.6[b]	5.6[a]	5.7[a]	**6.3**	4.0*	**6.7**
2-Octanone	1.6[c]	3.1[b]	3.9[a]	**4.8**	3.5	4.1
2-Decanone	0.6[c]	1.5[a]	1.1[b]	**2.8**	**2.9**	1.3
CV[A] (%)	6.2	5.8	5.9	5.1	5.6	7.0

Values in bold are significantly increased by saliva, Student's t-tests, $P < 0.05$.
[a–c] Values with different superscripts within a row are significantly different, MANOVA and LSD tests, $P < 0.05$.
* These values are significantly decreased by saliva, Student's t-tests, $P < 0.05$.
[A] Average coefficients of variance.

from data of triplicate gels. Average curves were created, and from these the time taken to reach maximum concentrations (T_{max}) and the slope of the initial release curves (I_{max}/T_{max}) were determined.

2.7. Statistical analysis

Data of texture measurements for triplicate gels was subjected to univariate analysis of variance (ANOVA) and least significant difference tests (LSD) to determine the significant differences between the samples. Data of aroma measurements 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 individual differences between samples containing saliva to those without saliva (O'Mahony, 1986). SPSS 10.0 for Windows software was used for statistical evaluations. The significance level was $P < 0.05$ throughout the study.

3. Results and discussion

To study the impact of the texture of the gel on the release of flavour compounds, Young's modulus of elasticity was determined for each gel. Young's modulus of elasticity (E) is a measure for the rigidity or stiffness of the gels (Bourne, 1982). For the gelatin gel, the value of E was significantly higher than that for pectin and starch gels, which were not significantly different from each other (ANOVA and LSD, $P < 0.05$) (Table 1). Therefore, the gelatin gel system used in this study was significantly more rigid than the other two gel systems.

The log P values of the 11 compounds, which is a measure for hydrophobicity, is shown in Table 2. These values varied from 0.8 for the hydrophilic compounds (diacetly) to 3.77 for the most hydrophobic compound (2-decanone). The air/gel partition coefficients of 11 flavour compounds in the three gel systems (gelatin, starch and pectin) were determined by static headspace analysis

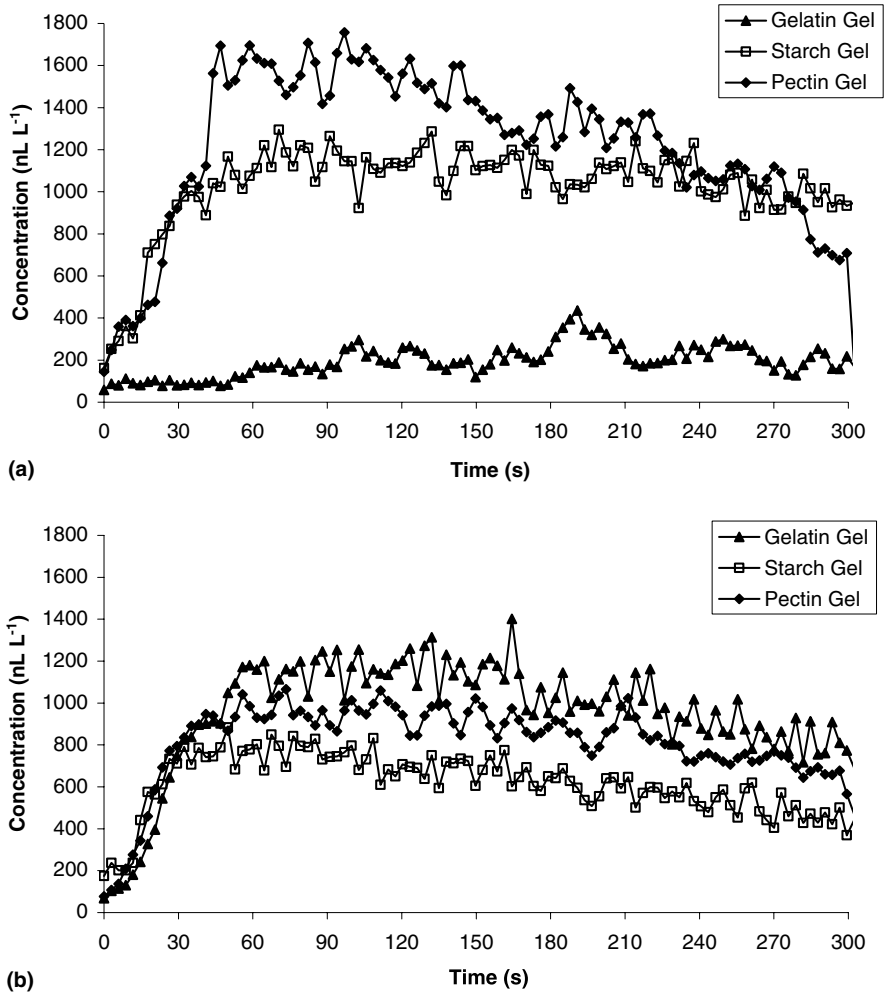

Fig. 1. The temporal release of ethyl acetate from the gel systems, without saliva (a) and in the presence of artificial saliva (b), as determined by model mouth/proton transfer reaction-mass spectrometry analysis.

(Table 3). The flavour compounds had significantly different partition coefficients [$F(10,99) = 685.850$, $P < 0.05$]. Overall, the flavour compounds had significantly higher partition coefficients in the pectin gel, while the gelatin and starch gels were not significantly different from each other (MANOVA and LSD, $P < 0.05$) (Table 5).

Dynamic headspace analysis was carried out by model mouth/PTR-MS analysis. Flavour release profiles of each flavour compound from the gelatin gel, the starch gel and the pectin gel were determined for the first 5 min of release. The release of ethyl acetate from the three gels is shown as an example in Fig. 1a. The calculated results are displayed in Table 4. The 11 flavour compounds analysed by PTR-MS had significantly different I_{max} values [$F(10,99) = 51.983$, $P < 0.05$] and values for cumulative release from the gels [$F(10, 99) = 130.878$, $P < 0.05$]. Overall, both the I_{max} values and cumulative release values of the 11 flavour compounds as a group were significantly lower for the gelatin gel than from the other two gels, which were not significantly different from each other (MANOVA and LSD, $P < 0.05$) (Table 5).

3.1. Flavour compounds

Generally, in all gel systems the homologous series of ketones (2-butanone C-4, 2-heptanone C-7, 2-octanone C-8, 2-decanone C-10) exhibited a decrease in partition coefficients with increasing chain length (Fig. 2). Similarly, the same homologous series of ketones displayed decreased concentrations released with increasing chain length (Fig. 3) by PTR-MS analysis. Similar results have previously been reported for ketones in pectin and starch systems (Boutboul, Giampaoli, Feigenbaum, & Duvruet, 2000; Braudo et al., 2000; Golovnya, Terenina, Krikunova, Yuryev, & Misharina, 2001).

3.2. Comparisons between the three gel systems

The partition coefficients were significantly influenced by the type of hydrocolloid [$F(2,99) = 419.108$, $P < 0.05$] (Table 3). In the PTR-MS analysis, the I_{max} values and values for the cumulative release under dynamic conditions were also significantly influenced by the type of hydrocolloid [$F(2,99) = 133.782$, $P < 0.05$] and [$F(2,99) = 417.001$, $P < 0.05$] (Table 4).

3.2.1. Influence of the rigidity of the gels

Six of the flavour compounds had the lowest partition coefficients in the gelatin gel (MANOVA and LSD tests, $P < 0.05$) (Table 3). As Table 5 shows, overall the hydrophilic compounds had the significantly highest partition coefficients in the gelatin gel, while the hydrophobic compounds had the significantly lowest partition coefficients in the gelatin gel. These results indicate an effect of the rigidity of the gelatin gel on the ther-

Table 4
The maximum intensity of flavour released (I_{max}), the time taken to reach maximum intensity (T_{max}), the slope of the initial release curve (I_{max}/T_{max}) and the cumulative release from each gel in the first 5 min ($n = 3$)

Flavour compound	I_{max} (nL L^{-1})			T_{max} (s)			I_{max}/T_{max} (nL L^{-1} s^{-1})			Cumulative release (nL L^{-1})		
	Gelatin gel	Starch gel	Pectin gel	Gelatin gel	Starch gel	Pectin gel	Gelatin gel	Starch gel	Pectin gel	Gelatin gel	Starch gel	Pectin gel
Diacetyl	61^{c}	212^{b}	300^{a}	194	238	144	0.3	0.9	2.1	3927^{c}	16801^{b}	21869^{a}
2-Butanone	363^{c}	822^{b}	1322^{a}	191	214	191	1.9	3.8	6.9	19112^{c}	64748^{b}	99056^{a}
Ethyl acetate	435^{c}	1295^{b}	1758^{a}	191	70	97	2.3	18.4	18.2	20269^{b}	106478^{a}	126209^{a}
1-Butanol	89^{b}	166^{a}	234^{a}	191	214	191	0.4	0.8	1.2	5436^{c}	11646^{b}	17273^{a}
3-Methyl-1-butanol	60^{b}	218^{a}	290^{a}	264	197	211	0.2	1.1	1.4	3865^{c}	16085^{b}	20197^{a}
Ethyl butyrate	155^{b}	1051^{a}	1036^{a}	191	65	47	0.8	16.3	22.1	6635^{b}	79494^{a}	65558^{a}
Hexanal	95^{c}	1043^{a}	802^{b}	191	132	85	0.5	7.9	9.4	4453^{c}	79781^{a}	56977^{b}
2-Heptanone	100^{b}	727^{a}	705^{a}	191	214	97	0.5	3.4	7.3	5109^{b}	55566^{a}	50618^{a}
Heptanal	171^{b}	732^{a}	603^{a}	79	132	123	2.2	5.5	4.9	11132^{b}	54816^{a}	41908^{a}
2-Octanone	45^{c}	487^{a}	349^{b}	191	132	144	0.2	3.7	2.4	2233^{c}	36695^{a}	25512^{b}
2-Decanone	5^{b}	62^{a}	25^{b}	159	261	217	0.0	0.2	0.1	138^{c}	3738^{a}	1295^{b}
CV^{A} (%)	40.3	10.8	13.4	–	–	–	–	–	–	27.5	9.8	14.9

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

Table 5
Young's modulus of elasticity (E), air/gel partition coefficients (K), maximum concentrations (I_{max}) released and cumulative release after the initial 5 min, ranked in accordance to the levels that occurred in the three gel systems[a]

	Gelatin gel	Starch gel	Pectin gel
All 11 flavour compounds			
E	2	1	1
K	1	1	2
I_{max}	1	2	2
Cumulative	1	2	2
Four hydrophilic flavour compounds[b]			
E	2	1	1
K	3	1	2
I_{max}	1	2	3
Cumulative	1	2	3
Seven hydrophobic flavour compounds[c]			
E	2	1	1
K	1	2	3
I_{max}	1	2	2
Cumulative	1	3	2

[a] 1 = significantly lowest value, 2 = significantly greater value than 1, etc. (MANOVA and LSD tests, $P < 0.05$).
[b] $\log P < 1$.
[c] $\log P > 1$.

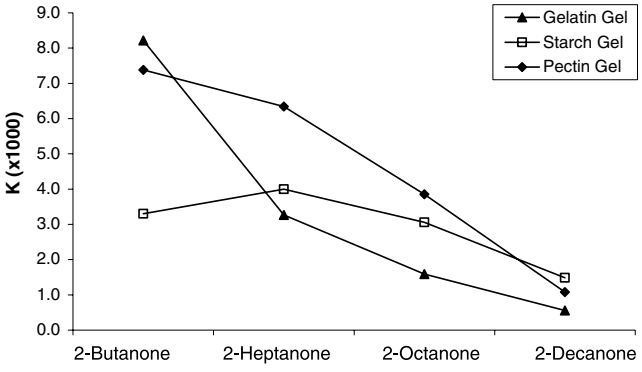

Fig. 2. Influence of chain length on the partition coefficients (K) of ketones in the gelatin gel, starch gel and pectin gel.

modynamic component of flavour release (i.e., the ability of the flavour compounds to partition between the air/gel phases under equilibrium conditions). Gelatin gel displays a marked difference in the dynamic release of flavour compounds compared to starch gel and pectin gel (Fig. 1a). In general, the gelatin gel had the lowest I_{max} values, the slope of the release curve values, and cumulative release values for all the flavour compounds. Also, five of the flavour compounds had the highest T_{max} values in gelatin (Table 4).

These findings are in agreement with other studies. Carr et al. (1996) found that increasing gel hardness reduced the amount of flavour compound in the headspace. Guinard and Marty (1995) showed that firm gels made with carrageenan and gelatin released flavour with lower maximum intensity than soft or medium carrageenan and gelatin gels. Baek, Linforth, Blake, and Taylor (1999) observed that softer gels had higher I_{max} values and lower T_{max} values than harder gels.

The effects of hydrocolloids on flavour release may be due to two mechanisms. One is the physical entrapment of flavour molecules within the food matrix. Baines and Morris (1987) observed that the presence of an entangled polymer network in thickened systems inhibits the transport of small molecules, such as flavour volatiles from within the gel system to the surface. The second mechanism involves interactions between the flavour molecules and the gel components, e.g., gelatin (Mällki, Heiniö, & Autio, 1993). In the current study, no evidence of the binding ability of volatiles to gelatin was determined. The information available from other studies is also limited. Bakker et al. (1996) found that binding occurred between diacetyl and gelatin, while Baek et al. (1999) concluded that gelatin did not bind furfuryl acetate.

Mastication has been shown to result in a breakdown of the food matrix, increase in surface area available for the diffusion of volatiles and therefore, an increase in the release of flavour volatiles (Harrison & Hills, 1997; van

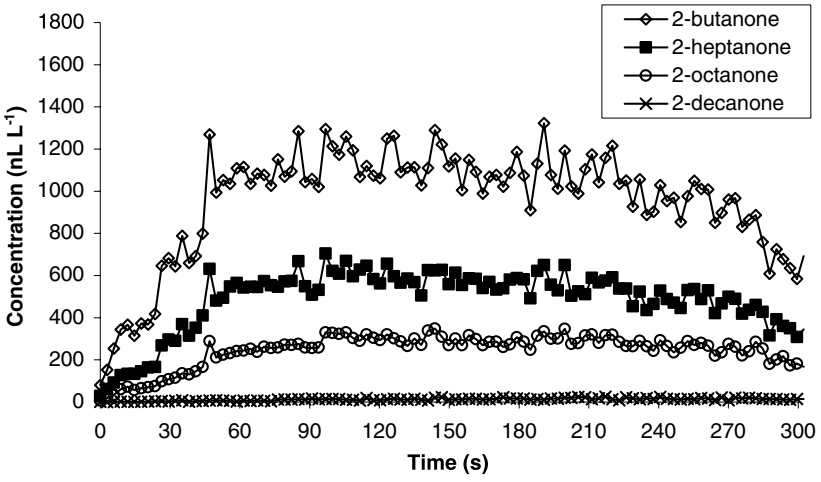

Fig. 3. The temporal release of ketones from the pectin gel by model mouth/PTR-MS analysis.

Ruth et al., 1994). Wilson and Brown (1997) observed that when subjected to mastication, harder gelatin gels had higher break strengths and lower perceived flavour intensities. In the current study, since the gelatin gel used was significantly more rigid than the starch and pectin gels, gel breakdown during mastication would not have been as great for the gelatin gel. This was likely to contribute to the lower release of volatiles from the gelatin gel compared to the starch and pectin gels.

Therefore, the release of flavour volatiles from the gelatin gel system was partially reduced by the physical entrapment of volatiles within the gel matrix, because of the lower static headspace concentrations. Hence, the determining step for the release of flavour compounds from the gelatin gel is likely to be the rate of mass transfer of flavour compounds from the gel to the air phase.

3.2.2. Interactions between components of the gel systems and the flavour volatiles

Although the texture of the gels was not significantly different between the starch and pectin gels (Table 1), differences occurred between the partition coefficients and the I_{max} and cumulative release concentrations of the flavour compounds. Ten flavour compounds had higher partition coefficients in the pectin gel than the starch gel (Table 3). Only one flavour compound, 2-decanone, had a lower partition coefficient in the pectin gel than the starch gel. This compound is the hydrophobic compound 2-decanone. The rest of the compounds had higher partition coefficients in the pectin gel than the starch gel. From the model mouth analysis (Table 4), compounds that had higher I_{max} values and cumulative release values from pectin gel were hydrophilic compounds. While 2-octanone and 2-decanone, which are hydrophobic compounds, had higher I_{max} values and cumulative release values in the starch gel. As Table 5 shows, in general there was greater release of hydrophilic flavour compounds from pectin gels, and greater release of hydrophobic flavour compounds from the starch gels. These results could be attributed to the combined effect of a number of matrix–volatile interactions, involving matrix components such as starch, pectin, sucrose and glucose.

Starch–volatile interactions have been classified into two types. The first involves the flavour compound becoming surrounded by the amylose helix through hydrophobic bonding, known as an inclusion complex. The second involves hydrogen bonding between the hydroxyl groups of starch and the flavour compounds (Arvisenet, Le Bail, Voilley, & Cayot, 2002; Boutboul, Giampaoli, Feigenbaum, & Duvruet, 2002), and it is this interaction, which appears to constitute the most probable mechanism for flavour volatile retention in starch gels. Similar results were observed by Arvisenet et al. (2002) for starch pastes. As the pectin molecules begin to form a gel, they stretch out and align with other pectin molecules to form pectin micelles. These micelles make the pectin solution more hydrophobic as intermolecular hydrogen bonds replaced bound water (Chinachoti, 1995). Hydrophobic compounds can be captured in the hydrophobic parts of the pectin solution (Hansson, Anderson, & Leufven, 2001b). Similar results were reported by Hansson et al. (2001b) and Lubbers and Guichard (2003) for pectin gels. Sucrose can affect volatile release by a "salting-out" effect (Friel, Linforth, & Taylor, 2000; Hansson et al., 2001b). This occurs when the sucrose binds to the free water and therefore, increases the hydrophobic character of the solution (De Roos & Wolswinkel, 1994), and usually occurs at relatively high sucrose levels (60% w/w; Roberts, Elmore, Langley, & Bakker, 1996). Glucose syrup behaves similarly to sucrose in that it further increases the hydrophobic nature of the system (Hansson et al., 2001b). The pectin gel contains 36% w/w sucrose and 24% w/w glucose syrup, while the starch gel contains neither. Effects of sucrose and glucose syrup have been observed by Friel et al. (2000) and Hansson et al. (2001b).

Therefore, hydrogen bonding between starch and the hydrophilic compounds, interactions between hydrophobic compounds and the pectin molecules, and the "salting-out" effect of sucrose and glucose syrup in the pectin gel were the likely contributors to the retention of hydrophilic compounds in the starch gel and the retention of hydrophobic compounds in the pectin gel (Table 5).

3.2.3. Influence of the pH of the gel systems

Varying the pH of systems can affect the dissociation of acids and the release of volatile flavour compounds (Guyot et al., 1996; van Ruth, Roozen, Nahon, Posthumus, & Jansen, 1999). The gelatin and pectin gels contained citric acid and had different pH values (gelatin gels = 2.34 and pectin gels = 3.29). Hansson, Anderson, Leufven, and Pehrson (2001a) investigated the effect changes in pH on the release of flavour compounds from a soft drink model system and they found that high concentrations of citric acid caused a decreased release of esters. However, when the pH was regulated with sodium hydroxide no effect on flavour release was observed. In the current study, the two esters (ethyl acetate and ethyl butyrate) had lower partition coefficients in the gelatin gel than the pectin gel (Table 3); therefore there was greater retention of the esters in the gelatin gel. While both gels contained the same amount of citric acid, the pectin gel also contained sodium citrate (Table 1). Therefore, similar to the findings of Hansson et al. (2001a), the citric acid was unlikely to affect the release of esters from the pectin gel. Citric acid in its dissociated form has a greater tendency to interact with flavour volatiles than the un-dissociated form and in a lower pH system the citric acid tends to exist in the un-dissociated form (Hansson et al., 2001a). Since the pH of the gelatin

Table 6
The percentage (%) effect of saliva on the partition coefficients (K) and I_{max} values of flavour compounds in gelatin, starch and pectin gels

Flavour compound	Gelatin gel			Starch gel			Pectin gel		
	K	I_{max}	$I_{max} - K$	K	I_{max}	$I_{max} - K$	K	I_{max}	$I_{max} - K$
Diacetyl	−1	**275**	277	**9**	−39	−48	−8	**−39**	−31
2-Butanone	−25	**155**	180	2	**−34**	−36	**−34**	**−45**	−11
Ethyl acetate	14	**222**	208	−2	−32	−30	**−34**	**−39**	−5
1-Butanol	**−26**	63	89	**30**	**−38**	−68	−10	**−49**	−39
3-Methyl-1-butanol	−9	**203**	212	**19**	**−35**	−54	**−16**	**−32**	−17
Ethyl butyrate	**128**	**490**	362	**−67**	−24	42	**−18**	−17	1
Hexanal	**198**	**551**	353	**−31**	−20	11	2	−15	−17
2-Heptanone	**108**	**496**	389	8	**−31**	−39	**−15**	**−26**	−11
Heptanal	**280**	**210**	−70	−28	−14	14	**18**	−19	−37
2-Octanone	**203**	**695**	491	16	−17	−33	7	−8	−15
2-Decanone	**405**	**432**	27	**97**	2	−95	25	20	−5

Values in bold are significantly affected by saliva, Student's t-test, $P < 0.05$.

gel was low, a large amount of the citric acid would exist in the un-dissociated form. However, some of the remaining dissociated form of the citric acid may have interacted with the esters and contributed to their retention in the gelatin gel.

3.3. Effect of saliva

The release of ethyl acetate from the systems with and without the addition of artificial saliva is shown as an example in Fig. 1. The percentage effect of saliva on the partition coefficient (K) of a flavour compound represents the influence of saliva on the thermodynamic factors of aroma release, including the dilution effect of saliva (Table 6). Since dynamic headspace analysis provides information about the temporal release of compounds and temporal release is determined by both the thermodynamic and kinetic aspects of release, the percentage effect of saliva on the kinetic factors that affect aroma release (i.e., rate of diffusion of flavour compounds) was calculated as the effect on the partition coefficient subtracted from the effect on the I_{max} values for each flavour compound (Table 6).

In general, for both gelatin and pectin gels, the addition of saliva reduced the partition coefficients of the hydrophilic compounds (e.g., diacetyl and 2-butanone) and increased the partition coefficients of hydrophobic compounds (e.g., 2-octanone and 2-decanone) (Tables 3 and 6). This was likely due to the increased hydrophilic nature of the system in the presence of saliva.

Six compounds had large increases in their partition coefficients in the gelatin gel in the presence of saliva (Table 3). In the previous section, the ability of these six compounds to partition between the air and gelatin gel phases was identified as being affected by the rigidity of the gelatin gel. From the dynamic analysis, large increases in the kinetic factors (i.e., rate of diffusion of flavour compounds) affecting aroma release from gelatin gel were observed in the presence of saliva (Fig. 1 and Table 6). Therefore, before the gelatin gel was combined with saliva, the kinetic component of flavour release was obviously the rate-limiting step for the release of all the flavour volatiles from the gelatin gel. This can be attributed to saliva's ability to enhance the water content of the system, thereby increasing the surface area available for the diffusion of flavour compounds. This effect was only seen for the gelatin gel because it was the most rigid gel and the addition of saliva seems to level out the influence of gel rigidity, which was seen in the previous section.

The effect of saliva on the partition coefficients of flavour compounds in starch gels was related to the functional group of the compounds. The esters and alcohols displayed decreases in partition coefficients while the ketones and alcohols had increased partition coefficients in the presence of saliva. Saliva components, mucin and α-amylase, have been shown to influence flavour release (van Ruth, Roozen, & Cozijnsen, 1995). Mucin was identified by van Ruth et al. (1995) to the key component in saliva to affect flavour release, by binding to and reducing the release of hydrophobic compounds. Sucrose and the flavour volatiles compete for binding to mucin. However, mucin has a finite number of binding sites, which are preferentially occupied by sucrose (Friel & Taylor, 2001). Therefore, it was not likely to observe a decrease in partition coefficient in the sugar containing gels, such as the gelatin and pectin gels. While the starch gel did not contain sucrose, significant decreases in the partition coefficients of the aldehydes were determined for the starch gel. In previous studies (van Ruth, Grossmann, Geary, & Delahunty, 2001; van Ruth, Roozen, Nahon, Cozijnsen, & Posthumus, 1996), the release of flavour compounds, especially aldehydes, has been has been affected by mucin.

4. Conclusions

Flavour release was significantly affected by the texture of the gels: the most rigid gel, gelatin gel, showed

the lowest flavour release. The two gels that had similar textures, starch gel and pectin gel, also showed differences in flavour release. These could be attributed to matrix–flavour interactions.

Saliva has been shown to influence both the thermodynamic and kinetic components of flavour release from all three gel systems. The largest effect was seen with the most rigid gel, the gelatin gel, where saliva caused large increases in flavour release, due to an increased surface area for diffusion of flavour compounds. A combination of factors, such as salivary proteins and the increased hydrophilic nature of the system, contributed to reduce the release of flavour compounds from the starch and pectin gels.

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