

## Multivariate Analysis of the Influence of Pectin, White Syrup, and Citric Acid on Aroma Concentration in the Headspace above Pectin Gels

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Pectin gels consist of polysaccharide networks surrounded by water. The gel networks can prevent release of aroma molecules from the gel to the gas phase above. In this study static headspace measurements were performed to correlate aroma concentration in the gas phase above pectin gels to different amounts of the gel ingredients. As a consequence, aroma concentration in the headspace in relation to gel texture, as characterized by rheology measurements, was also studied. Aroma concentration in the headspace above strong gels was low, due to entrapment of aroma molecules within the gel structure. Viscous solutions generally gave a high aroma concentration in the headspace, but owing to a complex matrix, this was lowered when large amounts of the gel ingredients were added. However, a high correlation between interaction terms and square terms of design variables and rheology parameters with aroma compounds indicated nonlinear and complex relationships.

**KEYWORDS:** Aroma compounds; gel; multivariate analysis; pectin; retention; viscosity

### INTRODUCTION

Polysaccharides are often used as thickeners in food to achieve a certain texture, “mouthfeel”, and body. They increase the viscosity of a system when dissolved in water, and many polysaccharides are also able to form gels, as a result of intermolecular associations that give rise to three-dimensional networks. Pectin is one of the most important gelling polysaccharides in food (1). It is found in the primary cell wall of, for example, citrus fruit (mainly limes and lemons) and apples (2). Pectin gels are built up by polymers of D-galacturonic acid, which form a tangled, interconnected network surrounded by water (3). The cross-linkages in the network usually consist of 18–250 galacturonic acid units called junction zones stabilized by hydrophobic interactions and hydrogen bonding (4).

To obtain the appropriate gel strength of pectin gels, knowledge about setting time and setting temperature (the gelation time/temperature) is important. During cooling (from 95 to 20 °C) molecules are formed in junction zones to create an initial network and the system’s behavior changes from mainly viscous to mainly elastic behavior as the gelation proceeds (5). The setting time is a secondary property and depends on the temperature conditions. Several factors influence the setting behavior, such as the degree of methylation, pH, cooling rate, and amount of soluble solids. Increased pH results in decreased setting temperature and decreased setting time (6). Sugar, which is the most commonly used cosolute in pectin

gels, reduces water activity and thereby interactions between pectin and water. It also influences hydrophobic bonding by disrupting the cage of water molecules surrounding the ester groups. However, when the sugar content increases the setting temperature, both the gel strength and the pH optimum for gel building increase (5). In this study, high-esterified pectin with a degree of methyl esterification of >50% was used as gelling agent. To achieve a gelation with this pectin, a pH <3.7 and a low water activity (obtained by white syrup >60%) were required (2).

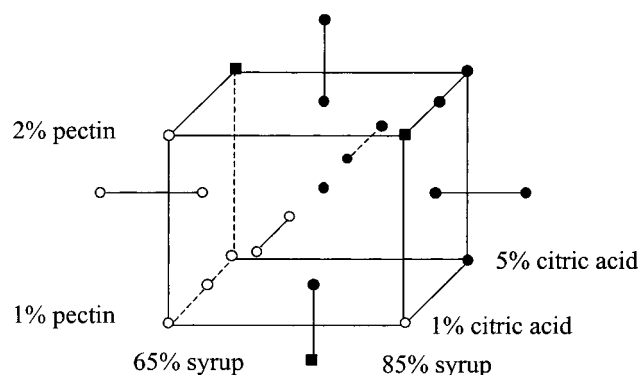
Pectin gels are viscoelastic materials; they possess characteristics of both viscous fluids and elastic solids. The most commonly used method to study viscoelastic properties involves oscillatory measurements in which a small oscillatory stress is applied to the sample and the phase angle of the responding strain is measured or vice versa. For a viscoelastic system the strain response to an applied oscillatory stress will be out of phase; this phenomenon is termed “phase angle” ( $\delta$ ). The value of the phase angle is a common indicator of gel strength, and if it falls below 45°, the system is defined as a system with an established gel network (7). The ratio between the applied stress and the responding strain is defined as the “complex modulus” ( $G^*$ ), which includes an elastic part,  $G'$ , and a viscous part,  $G''$  (8). When a gel begins to form,  $G'$ ,  $G''$ , and  $\delta$  will be registered against time, and at a given time there will be a crossover where  $G'$  exceeds  $G''$ , which could be defined as the gelation time (i.e., when  $\delta$  becomes <45°) (7).

Polysaccharides with the ability to form gels may influence the rate and intensity of aroma release. This may be due to physical entrapment of aroma molecules within the food matrix

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**Figure 1.** Schematic representation of the central composite design used in this study. Pectin concentration was varied between 1 and 2%, the concentration of white syrup was varied between 65 and 85%, and citric acid concentrations varied between 1 and 5%. Black circles indicate strong gels, white circles indicate viscous solutions, and black squares indicate weak gels.

or binding of aroma molecules to thickening or gelling agents (9). Connections between pectin and aroma release have been shown in previous studies, with mostly sensorial investigations. Lundgren et al. (10) showed that in a series of pectin gels, with a fixed concentration of an aroma component, the perceived aroma intensity depends on the rigidity of the gel; the firmer the gel, the weaker the aroma intensity. Guichard et al. (11) reported on the effect of pectin on aroma release from strawberry jam. They determined the composition of the headspace, consistency, taste, and flavor characteristics in jams made with different pectins. High-methoxylated pectin (HMP) resulted in a modification of the typical jam aroma and intensity of aroma and taste, but low-methoxylated pectin (LMP) did not have any significant effects on flavor release (11). Interactions of aroma compounds with HMP and LMP have been studied by Braudo et al. (12). Their results indicate that 2-ketones bind to low-esterified pectin via van der Waal's interactions and that these interactions increase with an increase in alkyl chain length. The authors further showed that interactions in acid media occur via hydrogen bonding and that metal ions inhibit these interactions.

In the present study the focus was on how different concentrations of the main pectin gel ingredients [citric acid 0.1–5% (v/w), white syrup 60–90% (w/w), and pectin 0.75–2.25% (w/w)] affect the equilibrium of aroma compounds to the gas phase above the gel during static conditions. Various amounts of these ingredients were seen to give rise to gels with various gel properties and strengths. The effects of the different gel structures on aroma equilibrium were also studied.

## MATERIALS AND METHODS

**Experimental Design.** A multivariate experimental design can be used to simultaneously test several variables at different levels at the same time and to study interaction effects and nonlinearities between the variables (13). In this study white syrup, citric acid, and pectin were each used at three different concentrations (citric acid at 1, 3, and 5%; white syrup at 65, 75, and 85%; and pectin at 1, 1.5, and 2%) according to a central composite design (CC design) (Figure 1). A CC design includes not only the cube and center samples but also the star samples with the middle level of all variables except the last, an extreme level of which is used (14). In our study the CC design was also supplemented with some samples inside the cube. The number of samples was 42 including 7 center samples, which were used to calculate the experimental error. Thirteen different variables were tested, namely, headspace concentration of eight aroma compounds and

rheology measurements of five different parameters [ $G^*$ ,  $G'$ ,  $G''$ ,  $\delta$ , and force values ( $F$ ) from texture analyzer measurements].

**Gel Manufacturing.** The pectin gel system basically consisted of water, HMP, white syrup (Danisco Cultor, Arlöv, Sweden) citric acid, and a noncommercial flavor mixture (donated by Danisco Cultor, Aarhus, Denmark). The pectin used was Grindsted Pectin CF 120 (Danisco Cultor), an extra slow-setting, high-ester pectin standardized with sugars. The aroma mixture contained eight compounds (ethyl hexanoate, isopentyl acetate, *cis*-3-hexenyl acetate, hexane, menthone, *cis*-3-hexenol, linalool, and limonene), all dissolved in propylene glycol. As the first step in gel preparation white syrup was mixed with water and heated. Pectin was mixed with sodium citrate and added to the syrup solution, which was then heated until boiling. After boiling for 2 min, water was added to the mixture to compensate for water loss through vaporization. Thereafter, the aroma mixture was added at a concentration of 0.1% (v/w), and citric acid was added to the mixture as the last preparation step.

### Static Headspace and Gas Chromatography–Flame Ionization

**Detection.** An amount of 12 g of the gel mixture was placed in a gastight vial (21 mL). The sample was placed in a gas chromatograph (GC) oven, and the temperature was decreased by 4 °C/min from 80 to 40 °C to imitate the temperatures used for the rheological measurements. After equilibration for 1 h at 40 °C, the aroma compounds in the gas phase were injected by an autosampler HS2000 on a GC combined with a flame ionization detector (GC-FID) and mass spectrometry (GC-MS). An equilibration time of 1 h was arrived at after multiple injections at 30 min and 1 h. The analytical instrumentation consisted of a Thermo Quest gas chromatograph Trace GC 2000 (Thermoquest, San Jose, CA) equipped with a fused silica capillary column with a 1.0  $\mu$ m thick film of DB-1, 30 m  $\times$  0.32 mm i.d. (J&W Scientific Inc., Folsom, CA), a Thermo Quest Automass solo MS, and an FID. The temperature was increased by 4 °C/min from 25 to 130 °C and by 50 °C/min from 130 to 225 °C. Aroma headspace concentrations were calculated from peak areas in relation to an external standard and are expressed as nanograms per milliliter.

**Rheological Measurements.** Gel strength was determined by oscillation measurements, performed using a Bohlin VOR rheometer (Bohlin Reologi AB, Lund, Sweden). The measuring system used consisted of a serrated cup and bob (25 mm  $\varnothing$ ) with the temperature being reduced from 80 to 40 °C during 13 min and kept at 40 °C for 1 h. According to our measurements the gel structure was stable after 1 h, as determined by constant  $G'$ ,  $G''$ , and  $\delta$  values. The frequency was 1 Hz and the strain amplitude 4%. During the measurements the complex modulus ( $G^*$ ), storage modulus ( $G'$ ), loss modulus ( $G''$ ), and phase angle ( $\delta$ ) were registered. The final values of each of those parameters were used for the statistical evaluation.

As a complement to the other rheological measurements, the gel strength was measured in 10 of the samples (three replicates of each sample) by a texture analyzer (model TA-XT2, Stable Micro Systems, Godalming, U.K.). The sample was poured into a headspace vial, which was placed in a GC oven, and the temperature was decreased from 80 to 40 °C by 4 °C/min followed by equilibration for 1 h at 40 °C. At equilibrium the sample was placed in the texture analyzer and penetrated by a probe until the surface was broken. The force (kilograms) required to break the surface was registered. The probe used was 3 mm  $\varnothing$ , the test speed was 2 mm/s, and the penetration depth was 5 mm.

**Multivariate Data Analysis.** Principal component analysis (PCA) was performed to gain an overview of how the samples were correlated to each other with regard to aroma concentration in the headspace at equilibrium. Partial least squares (PLS) regression was used to evaluate the correlation between aroma concentration in the headspace and gel strength and to investigate other possible relationships between the different parameters (14, 15). Validation of the regression was established using cross-validation (16) and significant testing by jack-knife estimation (17). All calculations were performed using the Unscrambler Extended version 7.5 (Camo ASA, Oslo, Norway) software.

## RESULTS AND DISCUSSION

**Design Variables and Aroma Headspace Concentrations.** The total variation ( $V_{\text{total}}$ ) between the samples for each of

**Table 1.** Total Variance ( $V_{\text{total}}$ ) of the Aroma Compounds Divided by the Variance of the Replicates ( $V_{\text{rep}}$ )<sup>a</sup>

	flavor compound							
	isopentyl acetate	ethyl hexanoate	cis-3-hexenyl acetate	menthone	hexanal	linalool	limonene	cis-3-hexenol
$V_{\text{total}}/V_{\text{rep}}$	91.7	31.0	34.2	18.3	27.6	7.17	1.84	0.73

<sup>a</sup> cis-3-Hexenol, linalool, and limonene did not exceed the variation between the replicates ( $V_{\text{rep}}$ ) ( $V_{\text{total}}/V_{\text{rep}} > 10$ ) and, consequently, were deleted from the matrix.

**Table 2.** Results from a PLS Regression of Design Variables for Aroma Compounds for All Samples<sup>a</sup>

	white syrup	citric acid	pectin	white syrup ×	
				pectin	pectin <sup>2</sup>
isopentyl acetate	—***	—**	—**	+***	+***
ethyl hexanoate	—***	—**	—**	+***	+***
cis-3-hexenyl acetate	—***	—**	—**	+***	+***
menthone	—**	—**	—**	+***	+***
hexanal	—***	—**	—**	+***	+***

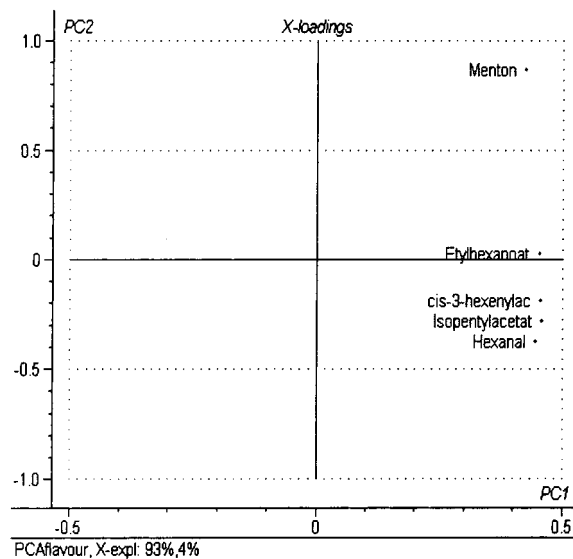
<sup>a</sup> Variables that showed a significant influence on a certain parameter are marked by \*\*\* (0.01 significance level), \*\* (0.05 significance level), or \* (0.1 significance level). Positive correlation is indicated by a + and negative correlation by a —. Only variables that significantly influenced any parameter are shown. Correlation of the PLS regression according to cross-validation was 0.63.

following aroma compounds, cis-3-hexenol, linalool, and limonene, did not exceed the variation between the replicates ( $V_{\text{rep}}$ ) ( $V_{\text{total}}/V_{\text{rep}} > 10$ ), and consequently they were deleted from the matrix (Table 1). These variables either had an experimental error that was larger than the systematic variation or were not affected by the changes of the matrix. However, isopentyl acetate showed the largest variation between the samples, indicating that it is the most sensitive compound to this type of variation.

The results of a PLS regression showed that white syrup, citric acid, and pectin correlate negatively to the aroma concentration in headspace (Table 2). However, square terms of pectin were positively correlated to aroma concentration in the headspace, indicating that the relations were nonlinear. In addition, interaction effects between the design parameters white syrup and pectin hinted at more complex relationships than the ones caused separately by each ingredient.

To further study these interactions, response surfaces for the design variables and aroma compounds were plotted (Figure 2). In a PCA plot the aroma compounds showed strong correlation to each other (Figure 3), which made it possible to use only one of the aroma compounds for plotting response surfaces. The aroma compound chosen was isopentyl acetate because it showed the largest variation between the samples ( $V_{\text{total}}/V_{\text{rep}} = 91.7$ ). From the response surface plots it was seen that the relationship was nonlinear, and pectin was seen to have an optimal concentration that should not be exceeded if a low aroma headspace concentration is wanted. The lowest possible aroma concentration in the headspace was found when the amount of white syrup was >75%, pectin concentration was <1.2%, and the concentration of citric acid exceeded 3.5%. It was seen that to attain the highest possible amount of the aroma compounds in the headspace above these pectin gels, concentrations of the ingredients should be low. Thus, the white syrup concentration should be <65%, the pectin concentration <0.75%, and the citric acid concentration <3.5%. The response surface plots had, however, large curvatures, showing that the relationships between the different ingredients and aroma concentrations in the headspace at equilibrium were more complex than presented here.

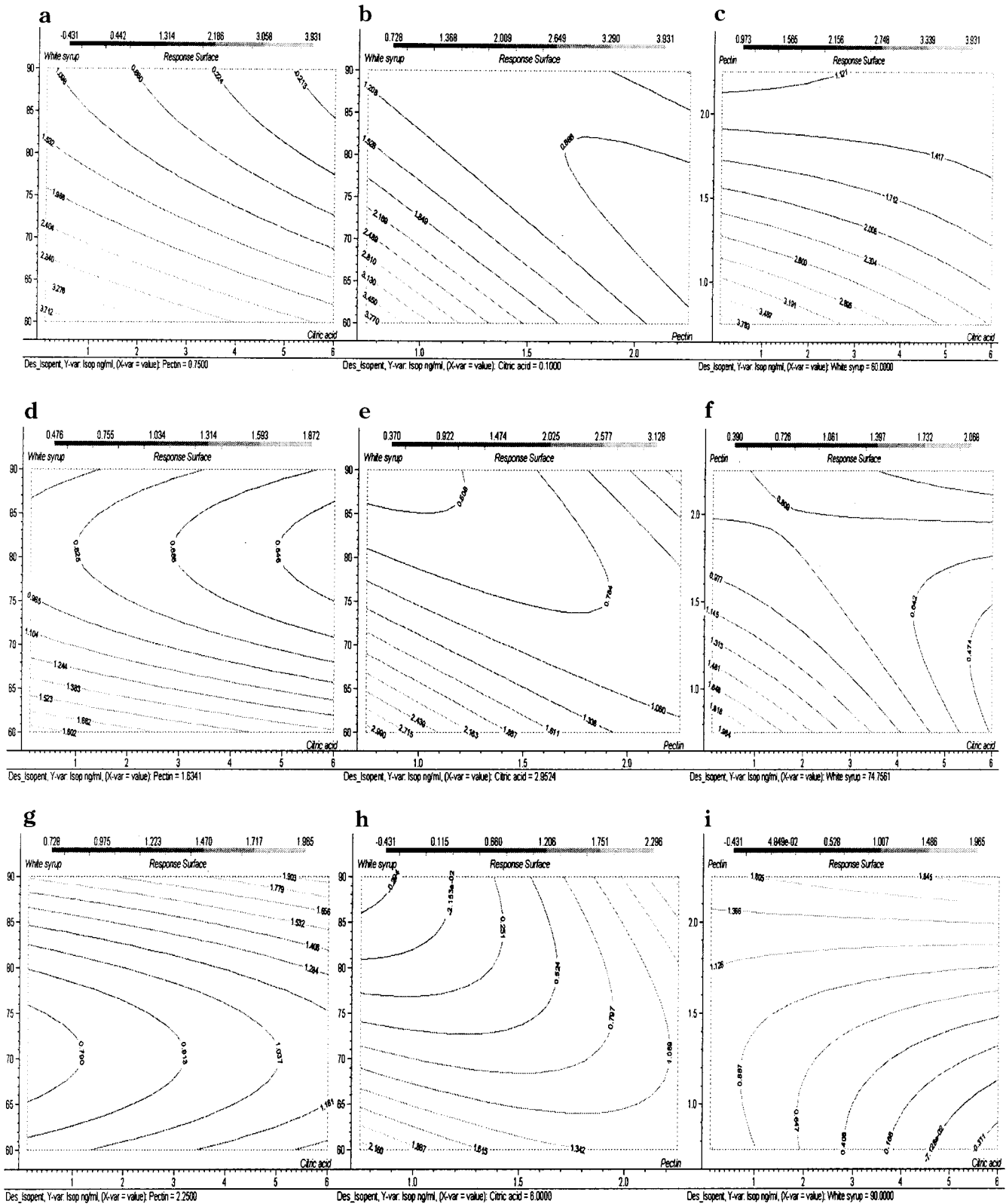
**Design Variables and Rheology.** Varying the different ingredients affected not only aroma headspace concentrations

**Figure 2.** PCA plot of all aroma compounds, showing strong correlations. The degree of explanation was 93% for PC1.**Table 3.** Results from a PLS Regression of Design Variables to Rheology Parameters for All Samples<sup>a</sup>

	white syrup	citric acid	pectin	white syrup ×		white syrup <sup>2</sup>	citric acid <sup>2</sup>
				pectin	pectin <sup>2</sup>		
$\delta$	—***	—***	—***	ns	+**	+**	
$G^*$	+***	ns	+***	—*	—**	ns	
$G'$	+***	ns	+***	—*	—**	ns	
$G''$	+*	ns	+*	—*	ns	ns	
$F$	ns	ns	+*	ns	ns	ns	

<sup>a</sup> Variables that showed a significant influence on a certain parameter are marked by \*\*\* (0.01 significance level), \*\* (0.05 significance level), or \* (0.1 significance level); others are termed ns (not significant). Positive correlation is indicated by a + and negative correlation by a —. Only variables that significantly influenced any parameter are shown. Correlation of the PLS regression according to cross-validation was 0.79.

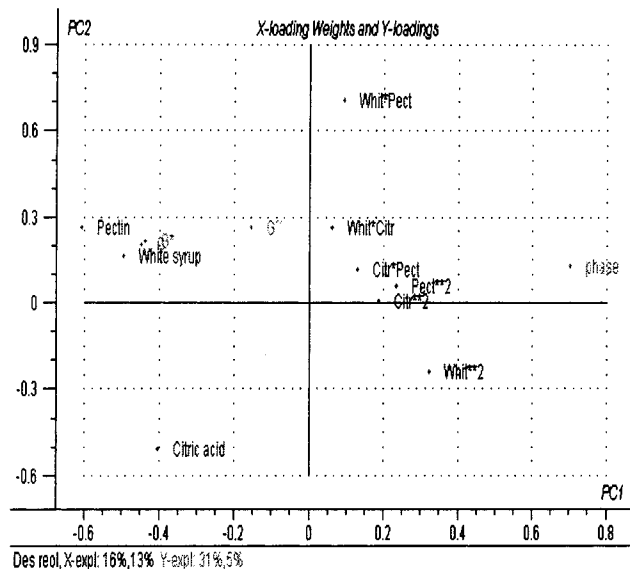
but also the structure and strength of the gels. Results of a PLS regression showed that the phase angle was negatively correlated to white syrup, citric acid, and pectin (Table 3). This means that if large amounts of each one of these ingredients are used for gel making, the phase angle reaches a value of <5°, indicating the formation of a strong gel. The complex modulus and  $G'$  were highly correlated to each other (Figure 4) as well as to white syrup and pectin content (Table 3), indicating that when large amounts of these ingredients are used for gel formation, the gel will contain a large elastic part. Force values from texture analyzer measurements ( $F$ ) were correlated to pectin, which showed that if more pectin is used for gel formation, a stronger force was needed to penetrate the surface. These force values were strongly correlated to  $G^*$  and  $G'$  and, therefore, gave no further information about gel strength, unlike the other rheological measurements taken by Bohlin rheometer. White syrup and pectin separately had the largest influence on gel making because they showed the highest correlation to all



**Figure 3.** Response surface plots of design variables correlated to aroma headspace concentrations exemplified by isopentyl acetate: (a) white syrup related to citric acid, pectin concentration held constant at 0.75%; (b) white syrup related to pectin, citric acid held constant at 0.1%; (c) pectin related to citric acid, white syrup concentration held constant at 60%; (d) white syrup related to citric acid, pectin concentration held constant at 1.63%; (e) white syrup related to pectin, and citric acid held constant at 2.95%; (f) pectin related to citric acid, and white syrup concentration held constant at 75%; (g) white syrup related to citric acid, and pectin concentration held constant at 2.25%; (h) white syrup related to pectin, and citric acid held constant at 6.0%; (i) pectin related to citric acid, and white syrup concentration held constant at 90%. Aroma concentration is expressed as ng/mL. Aroma concentration values of <0 are only a product of statistical modeling and are not valid.

measured parameters, except  $F$ . However, interaction terms between these ingredients correlated negatively to  $G^*$ ,  $G'$ , and

$G''$ , suggesting a more complex relationship than the one shown between each ingredient and gel strength. In addition, the



**Figure 4.** PLS loading plot of design variables correlated to rheology parameters, where  $G^*$  and  $G'$  were seen to be highly correlated to each other.

**Table 4.** Results from a PLS Regression of Rheology Parameters to Aroma Compounds<sup>a</sup>

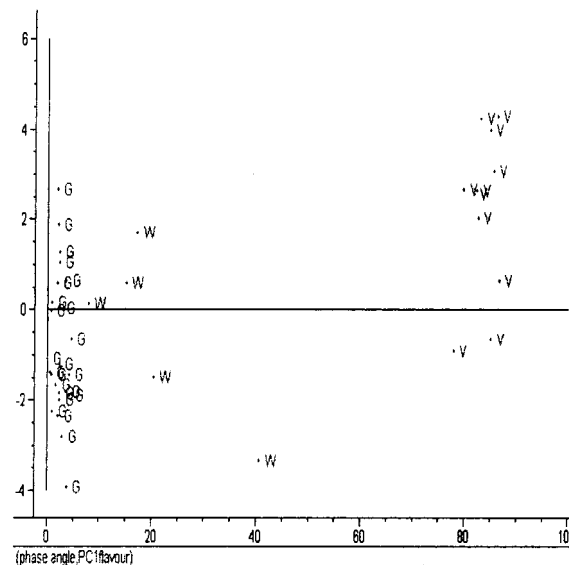
	$\delta$	$G^*$	$G'$	$\delta \times G^*$	$\delta \times G'$	$\delta \times F$	$G^* \times F$	$\delta^2$
isopentyl acetate	+	-	-	-	-	-	+	+
ethyl hexanoate	+	-	-	-	-	-	+	+
cis-3-hexenyl acetate	+	-	-	-	-	-	+	+
menthone	+	-	-	-	-	-	+	+
hexanal	+	-	-	-	-	-	+	+

<sup>a</sup> Parameters that showed a significant influence on a certain aroma compound are marked by \*\*\* (0.01 significance level), \*\* (0.05 significance level), or \* (0.1 significance level). Positive correlation is indicated by a + and negative correlation by a -. Only parameters that significantly influenced any aroma compound are shown. Correlation of the PLS regression according to cross-validation was 0.64.

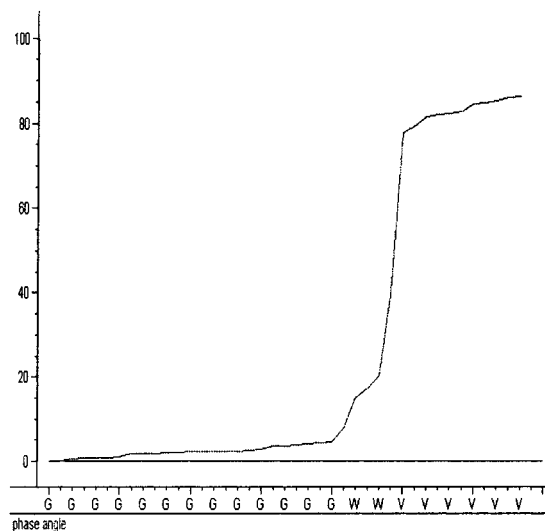
correlation of rheological parameters to square effects of pectin and citric acid showed that correlations between design variables and rheology parameters were nonlinear.

**Rheology and Aroma Headspace Concentrations.** Correlation of rheology parameters to the headspace concentrations of the aroma compounds showed that the phase angle was positively correlated to the aroma compounds in the headspace at equilibrium (Table 4). The complex modulus,  $G^*$ , and  $G'$  were negatively correlated to the headspace concentrations of aroma compounds (Table 4). There was, however, high correlation of interaction terms between the phase angle  $G^*$ ,  $G'$ , and  $F$  to aroma concentrations in the headspace and also to square terms of the phase angle, which indicates a nonlinear relationship between rheology parameters and aroma concentrations in the headspace.

The correlation between gel strength and aroma headspace concentrations at equilibrium is further shown in a two-dimensional scatter plot in which the phase angle is plotted against PC1 for all aroma compounds (Figure 5). The results show that two different groups of samples could be distinguished on the basis of phase angle values: one with high and one with low values. Five samples fell between the two groups with phase angle values of between 5° and 45°. Samples of the group with phase angle values of >45° were designated viscous solutions, meaning that a gel network was probably not formed. Samples of the group with values of <5° were designated gels with strong



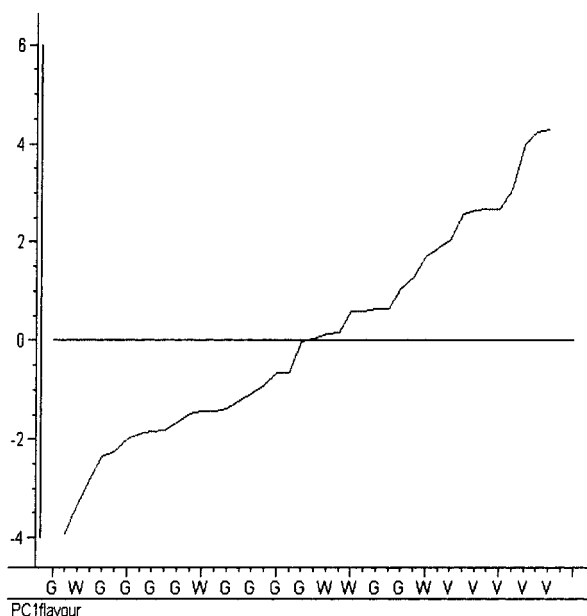
**Figure 5.** Two-dimensional scatter plot of PC1 aroma compounds related to the PC1 phase angle. Two different groups of samples could be distinguished on the basis of phase angle values, one with high and one with low values. Five samples fell between the two groups with phase angle values of between 5° and 45°. Abbreviations: G, gels; V, viscous solutions; W, weak gels.



**Figure 6.** Two-dimensional scatter plot of gel samples ordered by their values on the phase angle. Samples with a low value of the phase angle were named gels (G). Samples with a phase angle value of between 5° and 45° were named viscous solutions (V). Samples with high phase angle values were named weak gels (W).

networks. Samples between these two groups were classified as gels with weak networks. The samples in the three groups gave different aroma concentrations in the headspace. Gel samples showed lower aroma headspace concentrations than did the viscous solutions, which was probably owing to the entangled pectin network, which inhibited transport of aroma molecules from the inner part of the solution to the surface (18). The headspace concentrations of aroma molecules above the weak gels were about as low as that from the strong gels (Figures 6 and 7).

A distribution in aroma concentrations in the headspace was seen between the samples within the different groups. For the viscous samples it could be seen that all aroma compounds except menthone correlated negatively to  $G''$  when plotted



**Figure 7.** Two-dimensional scatter plot of gel samples ordered by their values on aroma concentration in headspace. Gel samples showed lower aroma headspace concentrations than did the viscous solutions, and the headspace concentration of aroma molecules above the weak gels was about as low as that from the strong gels. Abbreviations: G, gels; V, viscous solutions; W, weak gels.

**Table 5.** Results from a Two-Dimensional Scatter Plot of Rheology Parameters for Aroma Compounds<sup>a</sup>

variable 1	variable 2	samples	correlation
$\delta$	isopentyl acetate	all	0.69
$\delta$	ethyl hexanoate	all	0.71
$\delta$	hexanal	all	0.71
$G'$	isopentyl acetate	viscous solution	-0.77
$G''$	ethyl hexanoate	viscous solution	-0.80
$G'$	<i>cis</i> -3-hexenyl acetate	viscous solution	-0.70
$G''$	hexanal	viscous solution	-0.84

<sup>a</sup> Positive correlation between phase angle and headspace concentration for three aroma compounds. Negative correlation between  $G''$  and headspace concentration for four aroma compounds.

against each other (Table 5). Even though there was no gel network in these samples, according to the above-mentioned definition of a gel (7), a more viscous solution made it more difficult for the aroma molecules to diffuse through the solution, and the release to the gas phase could therefore be lower. However, according to an earlier investigation using the same pectin (19), an increase in pectin concentration of up to 2% does not have any effect on aroma headspace concentrations. The reduced release may therefore be caused not only by an increase in viscosity but also by the combination of the ingredients leading to a more complex matrix that is difficult for the molecules to pass through.

With the strong gels there was no correlation between any of the rheological parameters and aroma headspace concentrations. This could be explained by the fact that in all gels the networks were comparatively strong, with approximately the same phase angle value and high values of  $G'$  and  $G''$ . Changes in  $G$  and  $G''$  were therefore too small to influence the diffusion of aroma molecules.

None of the other rheology parameters correlated to aroma concentrations in the headspace for any subgroup of samples.

**Table 6.** Results from a PLS Regression of Design Variables and Rheology Parameters to the Aroma Compounds for the Viscous Solutions<sup>a</sup>

	white syrup	pectin	white syrup $\times$ pectin	pectin <sup>2</sup>
isopentyl acetate	—***	—**	+ns	ns
ethyl hexanoate	—***	—**	+*	—*
<i>cis</i> -3-hexenyl acetate	—*	—*	ns	ns
menthone	ns	ns	ns	ns
hexanal	—***	—**	ns	ns

<sup>a</sup> Variables that showed a significant influence on a certain aroma compound are marked by \*\*\* (0.01 significance level), \*\* (0.05 significance level), or \* (0.1 significance level); others are termed ns (not significant). Positive correlation is indicated by a + and negative correlation by a -. Only parameters and variables that significantly influenced any aroma compound are shown. Correlation of the PLS regression according to cross-validation was 0.89.

### Design Variables and Aroma Headspace Concentrations in the Subgroups.

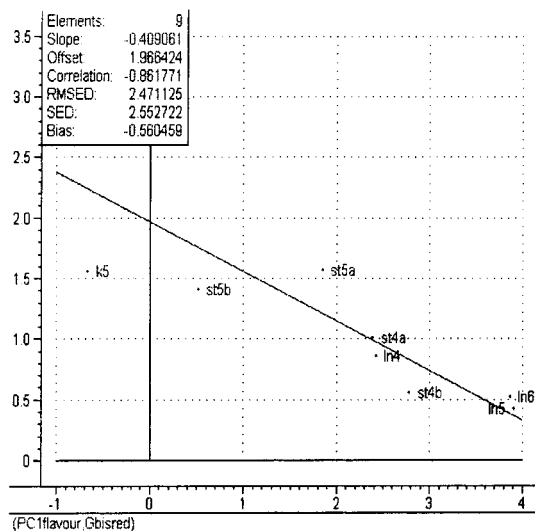
To find additional explanations for the spread in aroma concentrations in the headspace between the samples in the different subgroups, the design variables were related to aroma concentrations in the headspace at equilibrium separately for each subgroup. For the viscous solutions it was shown that pectin and white syrup concentrations were negatively correlated to aroma concentrations in the headspace (Table 6). This could be due to the effect of the viscosity; the more of these ingredients that were used for gel formation, the higher the viscosity and the lower the concentrations of the aroma compounds in the headspace. Correlation between square terms of pectin and aroma headspace concentrations indicated nonlinear relationships. Interaction terms of pectin and white syrup were also correlated to aroma headspace concentrations, showing a potentially more complex relationship than that between each ingredient and aroma headspace concentrations. There was, however, no further correlation between aroma headspace concentrations and the design parameters for the subgroup containing viscous samples.

The strong gel samples did not show any correlation between the aroma headspace concentrations and the design parameters. The distribution could possibly be related to rupture strength, which could be obtained by performing large deformations and could therefore give another description of the gel structure (20).

The gels with weak networks also showed variations in concentrations, but none of the rheology parameters or design variables alone could explain this variance. Unfortunately, it was difficult to form samples with a weak gel network with the pectin used because this was designed mainly for jellied sweets. Consequently, strong gels were formed when the ingredients were added in amounts recommended by the pectin manufacturer, and otherwise mostly viscous solutions were formed. The pectin was chosen on the grounds that it should be suitable for soft drinks, marmalades, and jellied sweets and that it has been used in different studies (19, 21).

### Gel-Building Process and Aroma Headspace Concentrations.

The effect of the entire gel-building process on aroma headspace concentrations was also investigated for all subgroups combined. The rheology parameter values for the various samples can be represented by curves, which were integrated and reduced to one value per sample and parameter. These values were then related to the concentrations of the aroma compounds in the headspace by performing a PLS regression. The result indicated correlation between  $G''$  during the entire gel-building process in the viscous samples and the aroma headspace concentrations (Figure 8). There was, however, no



**Figure 8.** Two-dimensional scatter plot of PC1 aroma compounds against  $G''$  shows correlation between  $G''$  during the entire gel-building process in the viscous samples and the aroma headspace concentrations.

correlation between any of the other rheology parameters during the gel building and aroma headspace concentrations for any of the samples. This shows that the amount of aroma compounds in the headspace at equilibrium was dependent only on the gel structure actually formed at the time of headspace measurement. Aroma headspace concentrations were not affected by the gel formation during the decrease in temperature from 80 to 40 °C. There was, however, a small effect of the viscosity during the whole gelling process on aroma headspace concentrations for the subgroup of viscous solutions, although this relationship was also seen when the final registration values of viscosity were correlated to aroma headspace concentrations.

Because this study was based on an experimental design, it was possible to study the interaction effects between the different variables and to use multivariate data analysis to find correlations that were nonlinear. So far, the reason for the observed nonlinear relationships has not been determined, and this may be further investigated using more elaborate data analysis. Still, the reported results give an overview of the relationship between aroma headspace concentrations at equilibrium and gel strength in this pectin gel system.

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