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Effect of Emulsion Characteristics on the Release of Aroma As Detected by Sensory Evaluation, Static Headspace Gas Chromatography, and Electronic Nose

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The effects of emulsion structure and composition of the matrix on the release of linalool (nonpolar) and diacetyl (polar) were studied using sensory evaluation, static headspace gas chromatography, and an electronic nose. The matrices used were water, rapeseed oil, and eight oil-in-water emulsions differing in oil volume fraction (0.05/0.5), emulsifier type (sucrose stearate/modified potato starch), and homogenization pressure (100/300 bar). Fat content strongly affected the release of linalool, but it was not as critical a factor in the release of the more polar compound, diacetyl. A slight effect of the emulsifier type on the release of aromas was observed with sensory and gas chromatographic methods. The reduced droplet size, resulting from higher homogenization pressure, enhanced the release of linalool but had no effect on diacetyl. Sensory and gas chromatographic methods detected aroma changes quite similarly. The electronic nose was capable of detecting only the effect of fat on linalool.

KEYWORDS: Aroma release; emulsion; static headspace gas chromatography; electronic nose; sensory evaluation

INTRODUCTION

Aroma release from emulsions depends on the affinity of the aroma components for the liquid phases (water and oil) and the proportions of these liquid phases. It also depends on the structure of the emulsion. The structure of the emulsion is characterized by the nature of the dispersed phase (water or oil), the surface area of the lipid−water interface, and the nature and amount of the surface-active agent adsorbed at the interface (*1*).

Nonpolar aroma compounds are more soluble in the emulsion fat phase than in the aqueous phase; thus, their volatility should be reduced when the oil content increases (*2*, *3*). On the other hand, polar aroma compounds tend to be more odorous when the oil content is high (*4*). However, Wendin et al. (*5*−*7*) have recently reported some conflicting results of the effects of fat on aroma release. They found that the odor of citral (a semipolar compound) and pyroligneous acid (a polar compound) remained unaffected when the fat content of mayonnaise varied (70 or 82% fat). An increased fat content tended to increase the odor and flavor of citral and to decrease the odor and flavor of pyroligneous acid in reduced-fat mayonnaises (15 or 30% fat). The odor and flavor of maltol (polar) increased in sour milk with higher fat content (0.1 or 4.2% fat), whereas those of ethyl 2-methylbutyrate (nonpolar) were unaffected.

Druaux and Voilley (*8*) concluded that there is no general rule for understanding the effects of oil−water interfaces on the partition coefficients of aroma volatiles between air and a product. The results obtained on the effect of oil-in-water emulsion droplet size (amount of surface area) on the aroma release are conflicting. For example, Druaux et al. (*9*) and Le Thanh (*10*) failed to find an effect, but Charles et al. (*1*) found effects that depended on the polarity of the aroma compound. Different emulsifiers have different interfacial properties, and they can chemically or physically interact with aroma compounds. Guyot et al. (*4*) found that the presence of an emulsifier may or may not affect the release of aroma compounds, depending on the particular compound. Landy et al. (*11*) found that the effect of the type of emulsifier on the aroma release was dependent on the compound.

Both sensory and gas chromatographic methods are expensive, and sensory methods in particular are also time-consuming. Thus, there is a growing interest in rapid and inexpensive methods, such as gas detectors (e.g., electronic noses) to study aroma intensity. Electronic noses have so far been mainly used in quality control for detecting possible off-odors. However, they could also be used for rapid and inexpensive screening in product development, if they were sensitive enough to detect

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Table 1. Sample Matrices (Matrix Codes Refer to Codes Used in PCA Biplots)

		emulsifier		homogenization pressure	
matrix code	% oil[a]	E1[b]	E2[c]	100 bar	300 bar
M1	5	x		x	
M2	5	x			x
M3	5		x	x	
M4	5		x		x
M5	50	x		x	
M6	50	x			x
M7	50		x	x	
M8	50		x		x
M9	0				
M10	100				

[a] Karlshamns AB; contains citric acid as antioxidant. [b] Modified potato starch, Trecomex Twelve, Lyckeby Stärkelsen Food & Fibre Ltd. [c] Sucrose stearate, SP70, Sisterna C.V.

changes in the aroma profile, for instance, when a recipe is changed. The electronic nose mimics the human olfactory system because it assesses the mixture of volatiles released from a sample, whereas other instrumental methods usually separate the aroma into its individual components. The electronic nose MGD-1 (Environics Ltd. Mikkeli, Finland), used in this study, has been successfully used for on-line measurement of ethanol in beer and in yeast fermentation (*12*) and for detecting pesticides in liquid matrices (*13*). In a recent study the MGD-1 was capable of detecting aroma differences of ice creams of various fat contents (*14*).

The aim of the study was to investigate the effects of oil-in-water emulsion structure (droplet size) and composition of the matrix (oil volume fraction and the type of the emulsifier) on the release of two chemically different aroma compounds (polar vs nonpolar). A secondary aim was to compare sensory evaluation and two instrumental methods (electronic nose, MGD-1, and static headspace gas chromatography) for their capability to detect aroma changes.

MATERIALS AND METHODS

Materials. Ten different matrices were used in the study: rapeseed oil, deionized distilled water, and eight different oil-in-water emulsions (**Table 1**). The oil content of emulsions was 5 or 50%. Modified potato starch (starch sodium octenylsuccinate, E1450) and sucrose stearate (E 473) were chosen as emulsifiers (1% w/w) because of their ability to form stable emulsions over a wide range of oil volume fraction (in this study $\phi = 0.05$ or 0.5) and because they were odorless according to the manufacturers. The emulsions were prepared following the manufacturers' instructions and homogenized with a Rannie homogenizer (model LAB, Rannie Ltd., Copenhagen, Denmark) at 100 or 300 bar pressure until the entire matrix was forced through the homogenization needle four times. The laser diffractometer (Malvern 2600c droplet and particle sizer, Malvern Instruments Ltd., Malvern, U.K.) was used for particle size analysis of emulsions. Particles were measured in a stirred cell system using deionized−distilled water as a medium. The results are mean values of two replicates (**Table 2**). Span values (width of the distribution of the diameters of the droplets) indicate that the pressure of 300 bar gave a wider distribution in particle sizes than did 100 bar. The droplet sizes in emulsions were near the lower measurement limit of the laser diffractometer. At this level of droplet size, the relative error can be >10% (*15*), so the values should be considered as trend-setting.

The matrices were flavored with either diacetyl [2,3-butanedione; Sigma Aldrich, Steinheim, Germany; purity > 95%; log(*P*) value = −2.0] or linalool [*dl*-3,7-dimethyl-3-hydroxy-1,6-octadiene; Sigma Aldrich; purity > 97%; log(*P*) value = 4.0]. To provide a range of low to high aroma intensities, a concentration series of 0.05, 0.25, 1.25, 6.25, and 31.25 mg/kg of both aroma compounds was chosen on the basis of sensory pretests. For instrumental measurements, an additional concentration (156.25 mg/kg) was used. The samples were refrigerated in tightly capped and sealed glass bottles.

Table 2. Droplet Sizes of Emulsions

	$D_{3,2}$[a] (μm)		span[b]	
emulsion[c]	100 bar	300 bar	100 bar	300 bar
5/95 E1	2.0	0.7	0.3	1.3
5/95 E2	0.8	0.7	1.4	1.2
50/50 E1	6.3	1.5	0.6	2.6
50/50 E2	1.7	0.7	0.1	1.3

[a] $D_{3,2}$ = surface area mean diameter. [b] Span = width of the distribution of the diameters of the droplets. [c] 5/95 = emulsion containing 5% fat; 50/50 = emulsion containing 50% fat; E1 = modified potato starch emulsifier; E2 = sucrose stearate emulsifier.

Methods. *Sensory Evaluation.* Ten subjects (one male, nine females, mean age = 31 years, staff of the university) who all had previous experience in sensory evaluation participated in the study. All of the panelists had a regular sense of smell based on SOIT (Scandinavian Odor Identification Test, *16*) (12−16 of 16 correct identifications, mean = 13.9). In a training session, panelists were familiarized with the aromas (labeled as "buttery" for diacetyl and "bergamot" for linalool), the sniffing technique, and the intensity rating procedure.

Samples (8 ± 0.5 g) in 50 mL noseless beakers, covered with watch glasses, were allowed to equilibrate at room temperature for ~2 h prior to being evaluated. Evaluations were conducted in individual booths under white illumination. At the beginning of each session assessors smelled both aromas at moderate concentrations (1.25 mg/kg linalool in water and 1.25 mg/kg diacetyl in rapeseed oil) and the blank matrices of both emulsifiers (in order to concentrate only on the aroma compounds in the samples). Assessors had a total of 20 evaluation sessions, 2 sessions per day each separated by a 10 min break outside the evaluation booths. At each session, 10 samples (a concentration series of one aroma in two different matrices) were presented. The presentation order for matrices was randomized for each assessor, and the order of samples within a concentration series was also randomized. In half of the evaluations, linalool samples were evaluated in the first session and in the other half diacetyl samples were evaluated first. All samples were replicated once.

Assessors were required to bring the sample close to the nose, raise the watch glass of the sample to be assessed, and sniff carefully. They were instructed to close the watch glass immediately after sniffing and score the sample for the intensity of either buttery (diacetyl) or bergamot (linalool) aroma on an unstructured 10-cm line scale (anchors were no aroma and very strong aroma) using computerized data collection (CSA Computerized Sensory Analysis System, Compusense Inc., Guelph, Canada, version 3.8). The assessors were instructed to take a short break between the samples.

Static Headspace Gas Chromatography. The relative amounts of volatile compounds in the headspace of the samples were measured by static headspace chromatography (Perkin-Elmer Autosystem YL gas chromatograph with a Perkin-Elmer headspace sampler HS40XL) using an NB54 (5% phenyl 1% vinyl methylpolysiloxane phase, Nordion Ltd.) column (25 m × 32 μm) at 80 °C. Helium was used as carrier gas (45 mL/min). The compounds were detected with a flame ionization detector at 250 °C.

For the gas chromatographic (GC) headspace analysis 2 mL of the sample was placed in a 22 mL headspace vial at least 1 h prior to measurements. Samples were equilibrated at 60 °C for 20 min, and sampling time was 0.2 min. All of the experimental conditions were chosen on the basis of pretests. Each sample was replicated three times. The peak area was measured as a result.

Electronic Nose, MGD-1. The electronic nose was the MGD-1 (Environics Ltd. Mikkeli, Finland). The MGD-1 has six sensors, in which the detection is based on the ionization of gas molecules in a patented IMCELL measurement cell. In the IMCELL, a ^{241}Am (160 μCi) source is used for ionizing. The clusters formed through ion−

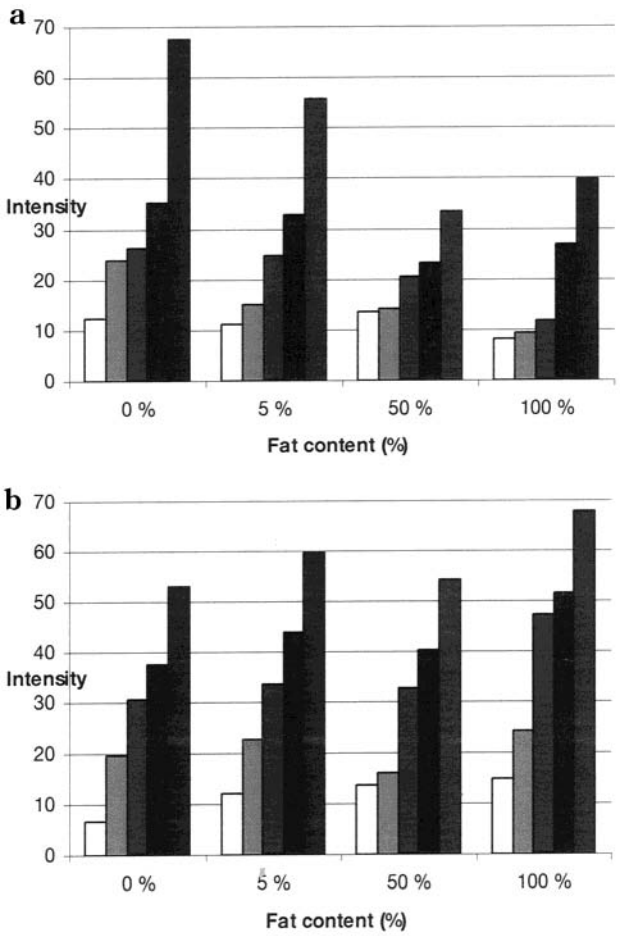

Figure 1. Effect of fat content on the intensity of (a) linalool and (b) diacetyl aroma (means for replications, assessors, different homogenization pressures and different emulsifiers). Bars represent, from left to right in each grouping, 0.05, 0.25, 1.25, 6.25, and 31.25 mg/kg.

molecule reactions are brought into different electrical fields perpendicular to the sample flow. The clusters hit different electrodes depending on their size and charge and are detected as the resulting current on the electrodes. In addition, the MGD-1 has one semiconductor metal oxide sensor, which is mainly used when the response of electrodes needs to be further confirmed. The operation principle of MGD-1 has been described in detail elsewhere (*12*, *13*).

Triplicated samples (100 mL) were placed in 500 mL glass bottles and stored (at least 1 h prior to measuring) horizontally in order to get a large surface area for the samples. During the measurements the sample air was led to MGD-1 via an Erlenmeyer containing phosphorus(V) oxide (P_2O_5) in order to control the humidity of the sample air. The humidity was kept between 30−40% by this method. The air flow of the MGD-1 was adjusted to ∼2.0 L/min, and the cell temperature was set at 35 °C. Before measurements, the device was zeroed on the ambient air. A portable PC (Toshiba Satellite 100 CS/528 model no. PAI217E YV, Toshiba Europe GmbH) equipped with a specific MGD1-UIP interface program (Environics Ltd.) was used to control the operation of the MGD-1 and to collect the data.

The maximum response of the sum of the channels was treated as a measurement result. This was based on results of a previous study, where different parameters of the MGD-1 responses were calculated and their capabilities of describing the samples compared (*14*).

Statistical Analysis. For the sensory data, three-way analysis of variance (GLM procedure) was done to assess the effects of fat level (0, 5, 50, or 100%), assessors ($N = 10$), and aroma concentration (five levels) on the perceived intensity of aromas. In the case of GC results, effects studied were fat level and aroma concentration (six levels). Separate analyses of variance were performed to assess the effects of emulsifier (modified potato starch or sucrose stearate) and homogenization pressure (100 or 300 bar) at different concentration levels (five in sensory and six in GC results) and fat level (5 or 50%). A one-way ANOVA, followed by Tukey's test at $p < 0.05$, was used to test the differences of intensity values/GC peak areas obtained for different matrices. To compare different methods, principal component analysis (PCA) was performed for the results obtained for linalool samples. The PCA was computed and the biplots created using Survo (*17*). All analyses were done separately for both aromas.

RESULTS

Sensory Evaluation. The composition of the matrix affected the release of both aromas. The effect of fat on the release of aromas was pronounced in the case of the nonpolar compound, linalool: the release was greatest from water and then from emulsions containing 5% fat, whereas the release levels from pure oil and 50% fat emulsions were quite similar [main effect of fat, $F(3;199) = 26.1$, $p < 0.001$] (**Figure 1a**; **Table 3**). The more polar compound, diacetyl, was more easily released from pure oil than from water matrix [main effect of fat, $F(3;199) = 10.0$, $p < 0.001$] (**Figure 1b**; **Table 3**). However, in the case of emulsion matrices, there was a trend of greater release from the emulsions containing less fat.

The effect of droplet size was observed in the case of linalool; the release was enchanced from small droplets resulting from higher homogenization pressure (P2 in **Figure 2**) [main effect, $F(1;94) = 7.3$, $p < 0.007$]. The effect of the type of emulsifier on the aroma release was detected in the case of diacetyl [main effect, $F(1;94) = 10.6$, $p < 0.001$]: more aroma was released when the sucrose stearate emulsifier (E2 in **Figure 3**) was used than when modified potato starch (E1) was used. The emulsifier type did not affect the release of linalool. Different concentrations were easily detected [main effect of concentration for

Table 3. Mean Values of the Aroma Intensities (on a scale 0–100)[a]

mg/kg	water	E1P1 5%	E1P2 5%	E2P1 5%	E2P2 5%	E1P1 50%	E1P2 50%	E2P1 50%	E2P2 50%	oil
					Linalool					
0.05	12 (2.7)	13 (3.1)	11 (2.0)	10 (2.0)	12 (2.6)	13 (3.0)	15 (3.7)	14 (2.4)	13 (2.7)	8 (2.1)
0.25	24 (4.4)	20 (3.8)	14 (3.4)	11 (2.3)	15 (3.5)	9 (1.9)	14 (2.6)	22 (4.8)	12 (2.3)	9 (2.6)
1.25	26 (4.1)ab	21 (3.9)ab	34 (5.7)b	19 (3.8)ab	26 (5.4)ab	19 (3.9)ab	19 (3.4)ab	30 (5.3)ab	15 (3.4)ab	12 (3.1)a
6.25	35 (4.6)ab	28 (4.2)ab	44 (4.9)b	28 (5.3)ab	33 (5.8)ab	23 (4.6)ab	24 (4.3)ab	21 (5.0)a	26 (5.2)ab	27 (3.7)ab
31.25	68 (5.6)d	53 (5.3)bcd	56 (5.1)cd	52 (4.6)bcd	63 (3.9)d	26 (4.8)a	40 (6.0)abc	31 (5.9)ab	36 (5.3)abc	40 (4.1)abc
					Diacetyl					
0.05	7 (1.9)	11 (2.9)	12 (2.0)	14 (3.1)	12 (3.3)	15 (3.4)	13 (4.0)	13 (3.5)	15 (2.8)	15 (2.3)
0.25	20 (4.5)	23 (3.9)	16 (3.1)	29 (4.0)	23 (4.3)	17 (4.3)	18 (4.1)	14 (3.4)	17 (3.0)	24 (3.5)
1.25	31 (4.0)	31 (4.3)	30 (4.9)	33 (5.4)	41 (5.4)	30 (4.4)	28 (5.0)	37 (4.9)	37 (3.7)	47 (5.5)
6.25	38 (5.0)	39 (4.9)	45 (4.9)	42 (5.1)	50 (4.7)	35 (4.6)	44 (5.1)	38 (5.3)	44 (4.9)	52 (3.8)
31.25	53 (6.7)	56 (5.9)	53 (5.9)	68 (3.7)	63 (4.0)	51 (5.9)	53 (4.8)	56 (5.8)	56 (4.2)	68 (3.3)

[a] Means within a row with the same letter are not significantly different ($p = 0.05$). SEM values are given in parentheses.

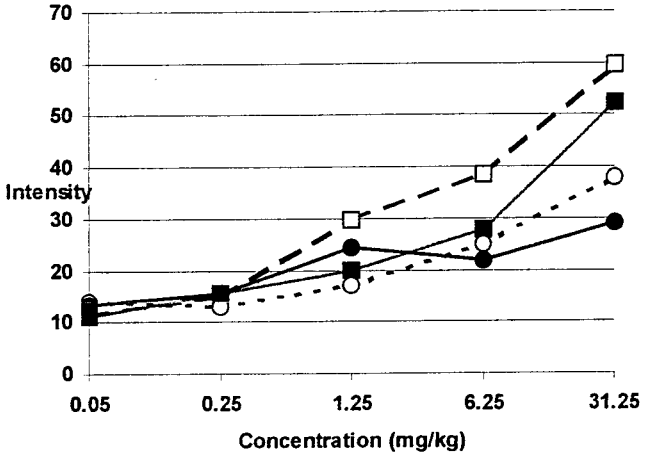

Figure 2. Effect of homogenization pressure on the intensity of aroma of linalool: (□) 5% P2; (■) 5% P1; (○) 50% P2; (●) 50% P1 (means for assessors, replications, and different emulsifiers; P1, homogenization pressure = 100 bar; P2, homogenization pressure = 300 bar; 5%, emulsion with 5% fat; 50%, emulsion with 50% fat).

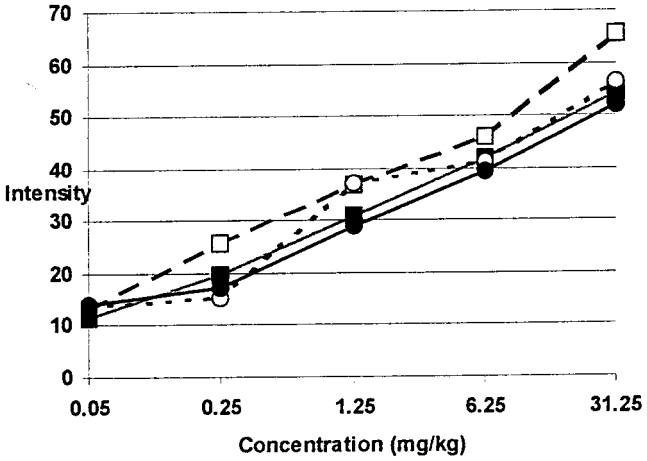

Figure 3. Effect of emulsifier type on the intensity of aroma of diacetyl: (□) 5% E2; (■) 5% E1; (○) 50% E2; (●) 50% E1 (means for assessors, replications, and different homogenization pressures; E1, modified potato starch emulsifier; E2, sucrose stearate emulsifier; 5%, emulsion with 5% fat; 50%, emulsion with 50% fat).

linalool, $F(4;199) = 114.4$, $p < 0.001$, and for diacetyl $F(4;199) = 144.1$, $p < 0.001$]. The interaction of fat level and concentration for linalool [$F(12;199) = 7.2$, $p < 0.001$] suggested possibly that the effect of fat was better perceived in the higher concentrations of linalool.

An interaction fat level and homogenization pressure was found for linalool [$F(1;94) = 4.7$, $p < 0.03$]. However, the average results (**Figure 2**) indicate that this interaction is possibly due to a somewhat unexpectedly high intensity value obtained for one sample (1.25 mg/kg linalool in emulsion containing 50% fat and homogenized at 100 bar of pressure). In addition, effects of the assessors (main effects and some interactions) were observed, but these were not considered to be critical. Standard deviations were quite large in sensory measurements, which was expected, but resulted in only a few significant differences between matrices in one-way ANOVA (**Table 3**).

Static Headspace Gas Chromatography. The static headspace GC results were well in line with the sensory results when the effect of fat on the release of linalool [main effect of fat, $F(3;23) = 12683.4$, $p < 0.001$] and diacetyl [main effect of fat, $F(3;23) = 11.2$, $p < 0.001$] was measured. The amount of linalool was greatest in the headspace of the water matrix and smallest in the headspace of the pure oil matrix (**Table 4**). The headspace results indicate that the release of the more polar compound diacetyl was not so dependent on the fat content of the matrix compared with the release of the very nonpolar compound, linalool. The amounts of diacetyl in the headspaces of water and oil matrices were similar. Different concentrations were well detected [main effect of concentration for linalool, $F(5;23) = 13899.8$, $p < 0.001$, and for diacetyl, $F(5;23) = 1043.5$, $p < 0.001$]. Fat level−concentration interactions [$F(15;23) = 7967.6$, $p < 0.001$, for linalool and $F(15;23) = 6.2$, $p < 0.001$, for diacetyl] were found probably due to the fact that lower concentrations were below the detection limit, especially in the case of linalool.

No significant effect of the droplet size on the headspace concentration of diacetyl or linalool was observed. The type of emulsifier affected the headspace concentrations of aromas [$F(1;26) = 23.9$, $p < 0.001$, for linalool and $F(1;26) = 33.5$, $p < 0.001$, for diacetyl]. The release of diacetyl was greater from emulsions containing modified potato starch (E1) as the emulsifier than from those containing sucrose stearate. This result was not in accordance with the sensory results. The same trend was also found in the release of linalool, but only in the 5% fat emulsion [$F(1;26) = 25.8$, $p < 0.001$, for the interaction of fat and emulsifier]. In 50% fat-containing emulsions, the release of linalool seemed to be slightly greater when sucrose

Table 4. Gas Chromatographic Results, Mean Peak Area Values (Three Replications)[a]

mg/kg	water	E1P1 5%	E1P2 5%	E2P1 5%	E2P2 5%	E1P1 50%	E1P2 50%	E2P1 50%	E2P2 50%	oil	range for SD%
					Linalool						
0.05	400b	0a	0a	0a	0a	0a	0a	0a	0a	0a	26
0.25	1700b	0a	0a	0a	0a	0a	0a	0a	0a	0a	29
1.25	5900c	0a	0a	550b	490b	0a	0a	0a	0a	0a	5–23
6.25	28400c	2300b	3000b	2500b	2600b	0a	0a	200a	300a	0a	1–93
31.25	145200c	15000b	14300b	11900b	11300b	1500a	1400a	1500a	1600a	550a	1–20
156.25	813000d	82900c	81200c	62700b	63700b	7900a	6900a	8400a	7800a	2900a	1–8
					Diacetyl						
0.05	80	0	0	0	0	0	0	70	0	0	20–28
0.25	250d	130b	150bc	0a	240d	160bc	0a	250d	130b	200cd	4–34
1.25	1180ef	1970g	1200f	1270f	1100def	760bc	630ab	970cde	470a	900cd	0–19
6.25	5400cd	6800ef	7130f	6320e	5680d	400d	4500ab	4860bc	4800b	4250a	1–8
31.25	26100cd	28500de	33900f	30300e	25800cd	21800ab	20500a	23700bc	24400bc	24200bc	2–5
156.25	139700def	153000f	148500ef	117700bcd	142000ef	117400bc	137000cdef	97700ab	90000a	130700cde	1–14

[a] Means within a row with the same letter are not significantly different ($p = 0.05$).

Table 5. MGD-1 Results, Mean Values (Three Replications) of the Maximum of the Sum of the Channels (SD% in Parentheses)

mg/kg	water	E1P1 5%	E1P2 5%	E2P1 5%	E2P2 5%	E1P1 50%	E1P2 50%	E2P1 50%	E2P2 50%	oil
					Linalool					
0.05	15700 (3)	1500 (23)	1700 (19)	1100 (11)	1000 (25)	1200 (27)	1200 (22)	900 (28)	1100 (28)	400 (13)
0.25	13000 (9)	2300 (31)	960 (17)	800 (47)	1400 (18)	1500 (20)	16000 (2)	900 (63)	1100 (17)	400 (13)
1.25	1300 (29)	1700 (29)	1300 (27)	800 (20)	1000 (68)	900 (31)	01400 (17)	700 (51)	900 (32)	900 (38)
6.25	1900 (21)	1000 (15)	1000 (37)	13000 (7)	900 (16)	1500 (14)	13000 (8)	1300 (33)	800 (30)	8000 (1)
31.25	3200 (11)	1600 (23)	2200 (10)	1900 (38)	1900 (38)	1800 (4)	0 1700 (22)	1300 (12)	14000 (4)	600 (36)
156.25	58000 (5)	3000 (30)	40000 (7)	3700 (29)	3500 (30)	2200 (7)	2200 (16)	2400 (15)	2500 (20)	9000 (2)
					Diacetyl					
0.05	120 (35)	130 (28)	100 (11)	70 (20)	70 (10)	90 (27)	80 (74)	80 (70)	90 (35)	55 (10)
0.25	170 (23)	160 (46)	130 (15)	50 (70)	70 (37)	60 (8)	60 (82)	80 (25)	100 (46)	60 (31)
1.25	130 (33)	140 (15)	60 (49)	80 (34)	80 (34)	60 (60)	80 (32)	60 (36)	120 (29)	60 (54)
6.25	150 (24)	130 (8)	60 (5)	70 (56)	70 (56)	70 (28)	60 (93)	100 (47)	100 (66)	40 (30)
31.25	130 (19)	150 (4)	70 (9)	60 (90)	60 (90)	80 (50)	130 (10)	50 (60)	90 (38)	70 (16)
156.25	130 (53)	120 (12)	90 (17)	60 (47)	60 (47)	100 (54)	80 (36)	100 (50)	80 (24)	80 (25)

stearate was used as the emulsifier. The standard deviations were satisfactory in static headspace measurements (**Table 4**).

Electronic Nose, MGD-1. The effect of fat as a solvent of nonpolar aroma compounds was also seen with the other instrumental method used, the electronic nose. The release of linalool was greatest from water matrix and from emulsions containing 5% fat (**Table 5**). The release was also greater from 50% fat emulsions than from pure oil. The MGD-1 was able to detect the increasing concentrations of linalool, although only in the cases of the highest concentrations. No connection was observed between results (maximum response of the sum channels) and the amount of diacetyl in the sample (increasing concentration), and the standard deviations were very large. Thus, the release of diacetyl could not be detected with the MGD-1, although the profile of response of diacetyl was different from that of linalool. The response seemed to be more related to the matrix than to its diacetyl content. However, it was not simply related to the fat content of the matrix. Although the responses of the water samples were higher than the responses of the oil samples, the emulsion samples did not obey this trend. No clear evidence was found using the MGD-1 that the droplet size would affect aroma release. Neither was any effect of the emulsifier type on aroma release found.

Overall Performance of Different Methods. PCA was performed for the results obtained with different methods for linalool samples (PCA biplots in **Figure 4**) in order to get an overview of the capability of different methods to detect the aroma differences among samples. The linalool samples were chosen to describe the capabilities of different methods because the results obtained for linalool were clearer to interpret than those for diacetyl. The first two principal components explained most of the variance among the samples (82.0% in sensory measurements, 99.6% in GC measurements, and 83.7% in MGD-1 measurements).

The greatest determining factor in the release of linalool was the fat content of the matrix. There was a trend of decreasing fat content along the PC1, and this trend was seen with all of the methods used. In the GC results, the amount of linalool in the headspace of water matrix was so great that this matrix was left out of the PCA in order to find subtle differences among the remaining samples.

A slight indication was found in the sensory biplot that the emulsion samples were distinguished by the homogenization pressure (in the case of emulsions containing 5% fat M1 and M3 vs M2 and M4 and in the case of emulsions containing 50% fat M5 and M7 vs M6 and M8). In the biplot of GC results, the effect of emulsifier type (M1 and M2 vs M3 and M4) was seen in the case of emulsions containing 5% fat. The effect of fat was probably, despite the removal of the water matrix, so strong that this effect was not seen in the 50% fat-containing emulsions. A slight indication of sample distribution based on the emulsifier type was also found in the biplot of MGD-1 results. However, this was not supported by the average results (**Table 5**).

DISCUSSION

Influence of Fat Content on the Aroma Release. The effect of fat as a solvent of nonpolar aroma compounds was seen as with increasing fat content the release of linalool was decreased. The opposite was observed in the sensory results for the release of diacetyl, a more polar compound; it was slightly more retained in the aqueous than in the oil matrix. However, the release of diacetyl seemed to be slightly greater from emulsions containing 5% fat than that of those containing 50% fat. Gas chromatographically, the release of diacetyl seemed to be slightly greater from aqueous samples (water and 5% fat-containing emulsions) than from oil and 50% fat-containing emulsions. Fat may not be as critical in the release of diacetyl as it is in the case of linalool. This is in accordance with earlier studies. Only very polar compounds behave opposite to nonpolar compounds (*18*). Guyot et al. (*4*) observed that the intensity of diacetyl was lowest in an emulsion containing 49% fat; in both higher fat-containing matrices (83 and 99% fat) and lower fat-containing matrices (0 and 15% fat) the odor was more intense. These findings agree with the results of this study.

Influence of Droplet Size on Aroma Release. A reduced droplet size results in an increased total surface area of the droplets, which may increase binding/entrapment of the volatiles at the interface assuming that the amount of emulsifier is sufficient to cover the formed smaller droplets (*19*). On the other hand, the increased surface area available for volatilizing may enhance the release of hydrophobic compounds (*1*). The effect of droplet size is likely to be very specific, depending on the nature of the aroma compound and the type and amount of the surface-active agent used. In the present study it was not investigated if the amount of emulsifier was sufficient for complete coverage of the droplets. However, no signs indicating poor coverage were observed: both 5 and 50% fat-containing emulsions were very stable during the storage time of 3 weeks.

The smaller the droplet size, the more intense was the perceived aroma of linalool, indicating that the increased surface area enhanced the volatilization of this compound. This is in good accordance with results by Charles et al. (*1*). The droplet size had no significant effect on the release of diacetyl. Earlier studies have reported conflicting results. Charles et al. (*1*) found

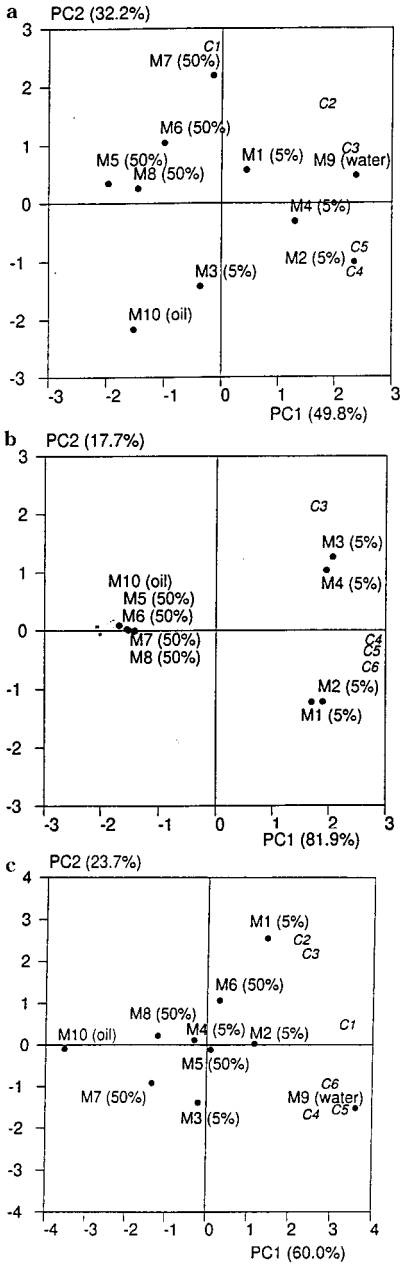

Figure 4. PCA biplots for linalool samples measured with (a) sensory method, (b) static headspace gas chromatography, and (c) electronic nose, MGD-1 (symbols M1–M10 are matrix codes explained in **Table 1**; percentage in parentheses refers to the fat content of that sample; c1–c6 refer to mean intensity in sensory evaluation/mean response in instrumental methods for different concentration levels).

that bigger droplets led to a greater release of polar compounds. Dubois (*21*) found, using a model cheese with 11−22% calcium caseinate, that the headspace concentrations of diacetyl and allyl sulfide decreased when the surface area of oil droplets increased. However, in a model emulsion prepared with 1% calcium caseinate, the surface area had no effect on volatility, probably due to the poor coverage with proteins on the surfaces of fat globules. Considering the structure of an oil-in-water emulsion in which the polar compounds are likely to dissolve in the aqueous continuous phase, it seems logical that the size of the oil droplets would not have a major effect on the release of polar compounds.

Influence of Emulsifier Type on Aroma Release. A significant effect of the emulsifier type on the aroma release was observed only in the case of diacetyl in the sensory evaluations. The perceived intensity of diacetyl was greater from emulsions containing sucrose stearate based emulsifier than from emulsions containing modified potato starch emulsifier. This effect was more pronounced in the emulsions containing 5% fat than in those containing 50% fat. These results could indicate that potato starch based emulsifier binds diacetyl. However, this is not likely in the light of GC results, as the headspaces of the emulsions prepared with potato starch contained more diacetyl than those prepared with sucrose stearate. The effect was, however, pronounced in the samples containing the highest amount of aroma, that is, in samples that were not even included in sensory measurements. A possible explanation for sensory results could be that the slight odor of sucrose stearate itself enchanced the perceived aroma of diacetyl. Although a criterion for the choice of emulsifiers was that they were odorless, both possessed a slight odor. However, neither of the blank matrices was considered to have an odor resembling that of diacetyl or linalool. No detectable volatile compounds were observed in the GC analysis of blank emulsion containing sucrose stearate, whereas in the case of potato starch, there was an unidentified peak of matrix with a retention time (1.60 min) near diacetyl's (1.97 min). However, the peaks were well separated, and there is no indication that this compound could interfere with the sensory properties of diacetyl. Yet this unidentified peak may have imparted a slight odor to the matrix and thereby possibly enhanced the aroma intensity of diacetyl.

Droplet size was also influenced by the type of emulsifier, which complicates the interpretation. The emulsions prepared with sucrose stearate had smaller droplet sizes than those with potato starch. Thus, the possible effect of the type of emulsifier could originate from the differences in droplet sizes. However, this does not seem to be likely as the headspace concentrations of aromas were greater in emulsions containing modified potato starch, which also had greater droplet size, than in those with sucrose stearate. However, when the effect of droplet size (within an emulsifier type) was studied, no effect on aroma release was observed. As the reduction in droplet size is almost equal whether the homogenization pressure was raised from 100 to 300 bar in the case of potato starch emulsion or the emulsifier was substituted with sucrose stearate, the effect must stem from the type of emulsifier per se. In the case of sensory evaluation, the release of diacetyl was greater from emulsions prepared with sucrose stearate. As there was no indication that the droplet size affected the release of diacetyl, the effect should have arisen from the emulsifier type.

Compared with the effect of fat on the release of aromas, the effects of droplet size or emulsifier type were very slight. Similarly, Wendin et al. (*5*) found that variation in fat content had a greater effect than homogenization on the sensory attributes of mayonnaise. Landy et al. (*11*) suggested that the affinity of the volatile substances for the fat phase was too strong to allow the detection of difference in volatility due to the nature of the surface-active agent present or to the surface area of the oil-in-water interface.

Overall Performance of Different Methods. The effect of fat content of the matrix was observed with all of the methods used, as shown in the PCA biplots for linalool. As neither of the instrumental methods found the effect of droplet size on the aroma release whereas the sensory method did, the latter might be considered the most sensitive in this respect. The MGD-1 results did not show any effect of emulsifier, and thus it can be considered to be less sensitive in this respect than the two other methods used. However, no final conclusions of the

MGD-1 can be made on the basis of this study as the maximum response of the sum of the channels was treated as a result. Although there was no sign that more selectivity could have been found in a more careful study of the responses of individual channels, it might be worthwhile to further study the data treatment of the MGD-1.

The rising concentrations of both aromas in all matrices were easily detected by the sensory evaluations. The intensities increased approximately as a logarithmic function of concentration predicted by Fechner's law (*23*) (plots not shown here, R^2 values varied from 0.81 to 0.99, except for one curve $R^2 = 0.57$). The sensitivity of the sensory method seemed to be better (lower concentrations detected) than in either of the instrumental methods used, although no definitive conclusions can be made since the blank matrices were not included in the sample series. The fact that the lowest concentrations of either aroma did not clearly obey trends observed for the effect of fat supports the possibility that the lower concentrations were around the odor thresholds, at least for some assessors. On the basis of the literature (for diacetyl, refs *8*, *24*, *25*, and *27*; and for linalool, ref *27*) the concentrations used were at suprathreshold level. However, individual variations in perception are great. For example, the group average of odor recognition threshold for diacetyl in aqueous solution reported by Lawless et al. (*26*) was 0.005 mg/kg, but the mean individual thresholds varied by a factor of 256.

With the GC method, two to six concentrations of linalool could be detected, the extreme cases being pure oil, where only two highest concentrations were detected, and water, in which all concentrations could be measured. Increasing diacetyl concentrations from 1.25 to 156.25 mg/kg could be detected in all matrices, and the concentration steps (coefficient of five) were easily detected. The two lowest concentrations of diacetyl (0.05 and 0.25 mg /kg) were detected only in some matrices.

Comparisons between GC and sensory methods are complicated by the fact that the temperatures used in the analyses were not the same. Due to the sensitivity problems in the GC method the equilibration temperature was 60 °C, whereas the sensory evaluations were done at room temperature. For example, Guyot et al. (*4*) used a 10 times greater concentration of diacetyl and higher temperatures in instrumental measurements than in sensory measurements in order to get a significant response. The volatiles released at 60 °C versus those released at room temperature are likely to be different quantitatively and perhaps also qualitatively. In the present study, it remains unclear whether the difference in temperatures made some contribution to the conflicting results obtained for the effect of emulsifier type. However, as the sensory measurements were done at room temperature, this method could be considered to be more sensitive and more relevant to real life situations than the GC method. On the other hand, in sensory measurements there was slight evidence of synergistic effects of matrix volatiles and aromas. In this sense an instrument that divides sample into individual components (like GC) can better determine the effect of conditions on certain aromas (molecules). However, if we are interested in the quality of end products, the most relevant are the perceived aroma changes. Due to the large standard deviations in the sensory data, not many of the matrices showed significant differences in aroma intensities. In this sense the GC results were more reliable.

The MGD-1 was less sensitive in detecting the differences in the aromas of different matrices. In the case of linalool, it was able to detect only the highest concentrations in the right order. In the case of diacetyl, the device was less successful, as it was unable to distinguish between different concentrations. This variability in the sensitivity for different volatile compounds is a limiting factor for possible aroma applications of the MGD-1. However, the inexpensiveness, speed, and possibile applications for on-line detection make it an attractive screening tool for aroma measurements for those applications where it is sufficiently sensitive and selective.

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