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Headspace GC and Sensory Analysis Characterization of the Influence of Different Milk Additives on the Flavor Release of Coffee Beverages

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Previous investigations of coffee flavor have been confined to the analysis of the aroma substances. These investigations showed that about 30 volatile compounds were substantially responsible for the coffee flavor. The aim of this study was to investigate the influence of different milk additives and one coffee whitener on the release of flavor impact compounds from coffee beverages. For the investigation of these effects an external static headspace technique was developed. With this technique the most potent odorants of the coffee beverage were determined. Analyses were performed by gas chromatography/olfactometry, flame ionization detection, and mass spectrometric detection. In addition, sensory studies of the odor profiles were performed. Milk and vegetable products as additives for coffee beverages affected the release of aroma substances in the brew through their lipid, protein, and carbohydrate components. All beverages with an additive showed reduced, but typical, odor profiles for each additive.

KEYWORDS: Coffee beverage; flavor release; headspace; sensory analysis

INTRODUCTION

Analyses of the aroma substances contributing to coffee flavor have shown that about 30 volatile compounds are substantially responsible for its flavor (*1*−*3*). Most of these investigations were confined to roasted coffee powder, some used the coffee brew, and, although the addition of creamer or milk is the most common practice by consumers, only one investigation has been done on such additives (*4*). The latter study used only instant coffees and very few milk additives. The purposes of adding these products to the coffee beverage are to develop a desirable color change, to impart a body to the coffee beverage, to reduce bitter and sour tastes, and to reduce the astringency of the coffee. Components of these additives such as lipids, proteins, and carbohydrates affect the retention of volatiles (*5*). Consequently, these aroma interactions affect the quality and quantity of the coffee headspace aroma.

The major objective of this work was to investigate the influence of different milk additives and one coffee whitener on the release of flavor impact compounds from different coffee beverages. Therefore, this study could provide the industry with information about the release of aroma components dependent on the additive. This could lead to practical applications such as the development of new, consumer-oriented products.

Direct injection of a headspace sample onto a GC capillary column gives a representative sample of coffee aroma prior to consumption. However, working with static headspace using a gastight syringe is not suitable, because only low amounts of aroma compounds can be collected. Therefore, a new device had to be developed which could collect a larger volume of headspace above the coffee beverage. In the present study the external static headspace analysis was carried out by GC/FID/olfactometry and GC/mass spectrometry/olfactometry. In addition, sensory studies with a trained panel were performed.

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MATERIALS AND METHODS

Coffee. Arabica coffee (Columbia) and Robusta coffee (Indonesia) beans, both with an average roasting degree, were supplied by Kraft Jacobs Suchard (Bremen, Germany).

Additives. Eight products, purchased from a local market or from Kraft Jacobs Suchard (Munich, Germany) or J. M. Gabler Saliter (Obergünzburg, Germany), were selected as typical coffee additives. The ingredients of the additives are listed in **Table 1**.

Chemicals. Compounds 1, 2, 8, 9, 11, 12, 14, and 18 (**Table 2**) were obtained from Aldrich (Steinheim, Germany), compounds 3−7 and 16 were purchased from Merck (Darmstadt, Germany), compounds 13 and 19 were from Lancaster (Mühlheim, Germany), compound 17 was obtained from ACROS (Gelnhausen, Germany), and compounds 20 and 21 were purchased from ABCR (Karlsruhe, Germany). Compounds 10 and 15 were gifts from Kraft Jacobs Suchard (Bremen, Germany)

Isolation of the Volatile Compounds. The beans were stored at −17 °C and ground directly prior to use in a coffee grinder of the style that is normally used in coffee shops. The brew was prepared in a household coffeemaker with 12 g of coffee powder and 225 g of tap water.

For the external static headspace device 220 g of freshly brewed coffee beverage with a temperature of 85 °C and 45 g of additive were

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Table 1. Content of Lipids, Carbohydrates, and Proteins of the Pure Milk Additives (in %)

additives	lipids	carbohydrates	proteins
ultrahigh-temperature milk (UHT 0.3)	0.3	4.8	3.5
ultrahigh-temperature milk (UHT 3.5)	3.5	4.8	3.3
condensed milk (CM 0.1)	0.1	10.6	7.8
condensed milk (CM 10)	10.0	12.5	8.8
coffee creamer (CC 10)	10.0	3.1	4.0
whipping cream (WC)	30.0	3.2	2.5
skim milk powder (SMP)	1.0	65.5	24.0
coffee whitener (vegetable fat) (CW)	34.0	55.0	6.0

used. These liquids were added to the lower of the two glass vessels (**Figure 1**). To achieve the most accurate reproducibility preliminary experiments were carried out with different equilibrium times and temperatures. These studies showed that only 15 min at room temperature was necessary. During this period of time the temperature of the coffee beverage decreased from 65 to 45 °C. After this equilibrium time the lower vessel was replaced by an empty one. Nitrogen was flushed at 100 mL/min for 30 min, and the volatiles were collected on a Tenax TA tube (6 mm × 16 cm with 100 mg Tenax TA 60/80).

High-Resolution Gas Chromatography (HRGC)/Mass Spectrometry (MS) and GC/Olfactometry (GC/O). Volatiles were desorbed from the Tenax TA tubes by use of a thermal desorber system TDS 2 (Gerstel, Mühlheim a. d. R., Germany) and injected into a CIS 3 cold injection system (Gerstel) with nitrogen cooling (−150 °C). To start the GC run, the trap was heated very rapidly to 300 °C. HRGC/MS was performed with a Hewlett-Packard model Series II gas chromatograph coupled with an HP 5971A mass spectrometer run in the electron impact mode at 70 eV. A BGB-1701 column (BGB-Analytik, Adliswil, Switzerland; 14% cyanopropylphenylpolysiloxane, 60 m × 0.25 mm i.d., 0.5 μm film thickness) was used with the following temperature program: 40 °C held for 3 min, raised at 5 °C/min to 220 °C, then raised at 20 °C/min to 280 °C, and held for 15 min.

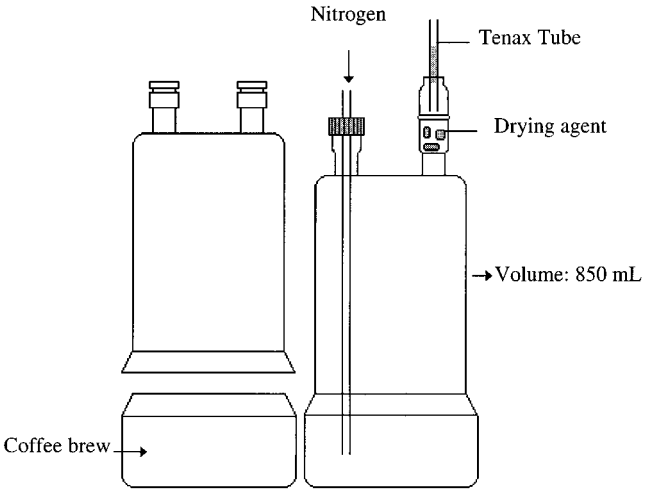

Figure 1. External static headspace device.

For GC/O the capillary columns were connected to a splitter (Graphpack-3D/2, Gerstel), and the effluent was split 3:1 into two uncoated deactivated restriction capillaries (50 cm × 0.1 mm i.d. and 40 cm × 0.1 mm i.d., respectively) leading to the MS detector (280 °C) and to the sniff detector (250 °C, humified, makeup gas nitrogen).

Identification of the compounds was achieved by comparison of retention data on DB-5 and OV-1701 columns and mass spectrometric data, as well as comparison of sensory properties with those of authentic reference substances. Coefficients of variance of 8 GC−MS replications ranged from 2 to 20% for most of the peak areas of volatile compounds.

For generation of the odor profiles a second system was used. Volatiles were desorbed from the Tenax TA tubes by use of the purge and trap system CP 4010 PTI/TCT, (Chrompack, Frankfurt, Germany) which was connected to a Hewlett-Packard model 5890 Series II gas chromatograph with a flame ionization detector (FID) and a sniff detector (SGE, Weiterstadt, Germany). The trap was cooled with liquid nitrogen (−120 °C) to start the GC run, and the trap was then flash-heated to 250 °C. A RTX-5 column (95% dimethyl−5% diphenyl polysiloxane, 30 m × 0.53 mm i.d., 1.5 μm film thickness; Restek, Bad Soden, Germany) and the following temperature program were used: −5 °C for 1 min, 4 °C/min to 50 °C, at 6 °C/min to 120 °C, at 8 °C/min to 250 °C, and held for 2 min. The end of the capillary was split 1:1 into two uncoated deactivated restriction capillaries (50 cm ×

Table 2. Examples of Identified Potent Odorants (GC/MS)

		retention index on			
	compound	DB-5	OV-1701	aroma quality	previous identification[a]
1	methanethiol	<600	<600	putrid	*2*, *10*
2	dimethyl sulfide	<600	<600	putrid	*8*
3	2-methylpropanal	<600	616	cocoa	*2*, *8*, *10*
4	2,3-butanedione	610	665	buttery	*2*, *8*, *10*
5	3-methylbutanal	653	720	malty	*2*, *8*, *10*
6	2-methylbutanal	665	726	fruity/malty	*2*, *8*, *10*
7	2,3-pentanedione	696	755	buttery	*2*, *8*, *10*
8	hexanal	797	876	leaf-like	-
9	2- & 3-methylbutanoic acid	869	980	sweaty	-
10	3-methyl-2-buten-1-thiol	881	728	foxy	*2*, *10*
11	methional	903	1027	potato-like	*2*, *10*
12	2-furfurylthiol	906	1010	roasty/coffee-like	*2*, *10*
13	1-octen-3-one	972	1057	mushroom	*10*
14	2, 3, 5-trimethylpyrazine	1002	1072	roasty	*8*
15	3-mercapto-3-methylbutylformate	1027	1218	foxy	*10*
16	phenylacetaldehyde	1055	1171	sweet/honey-like	-
17	2-ethyl-3,5-dimethylpyrazine	1062	1151	earthy/roasty	*10*
18	guaiacol	1096	1219	phenolic/burnt	*10*
19	2-isopropyl-3-methoxypyrazine	1144	1144	earthy/roasty	-
20	*(E)*-2-nonenal	1154	1266	cucumber-like	-
21	2-isobutyl-3-methoxypyrazine	1186	1237	sweet pepper – burnt	*10*

[a] Previously identified in the headspace of a coffee beverage: literature citation.

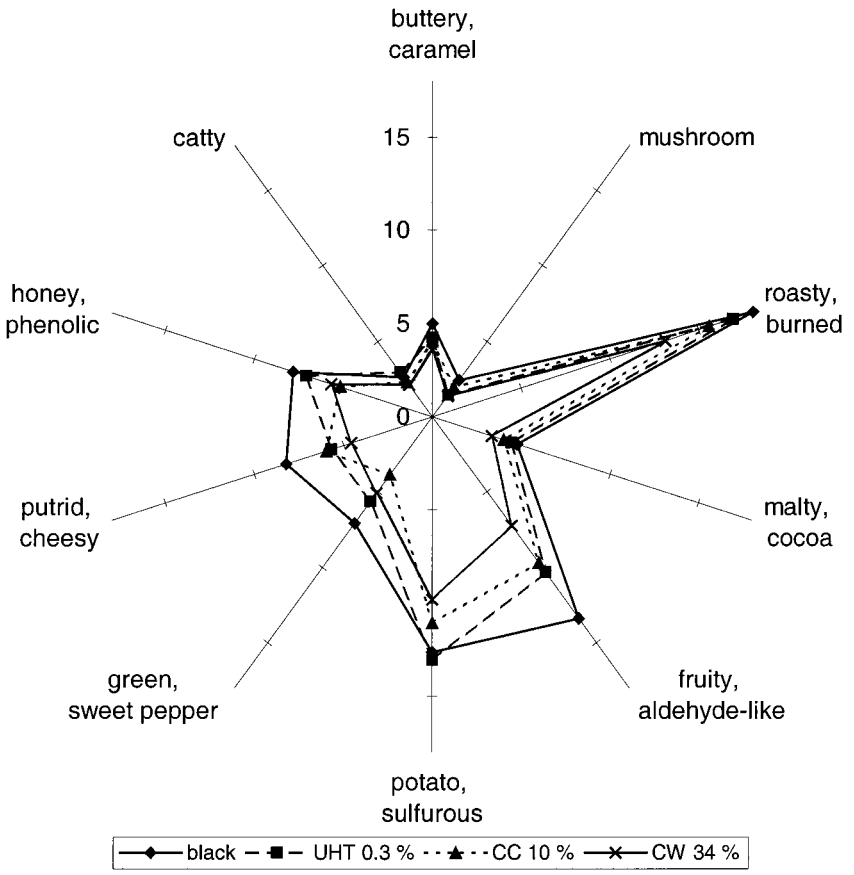

Figure 2. Influence of UHT-milk (UHT, 0.3% fat), coffee creamer (CC, 10% fat) and coffee whitener (CW, 34% fat) on the intensity of GC/O descriptors used for coffee volatiles (Robusta coffee).

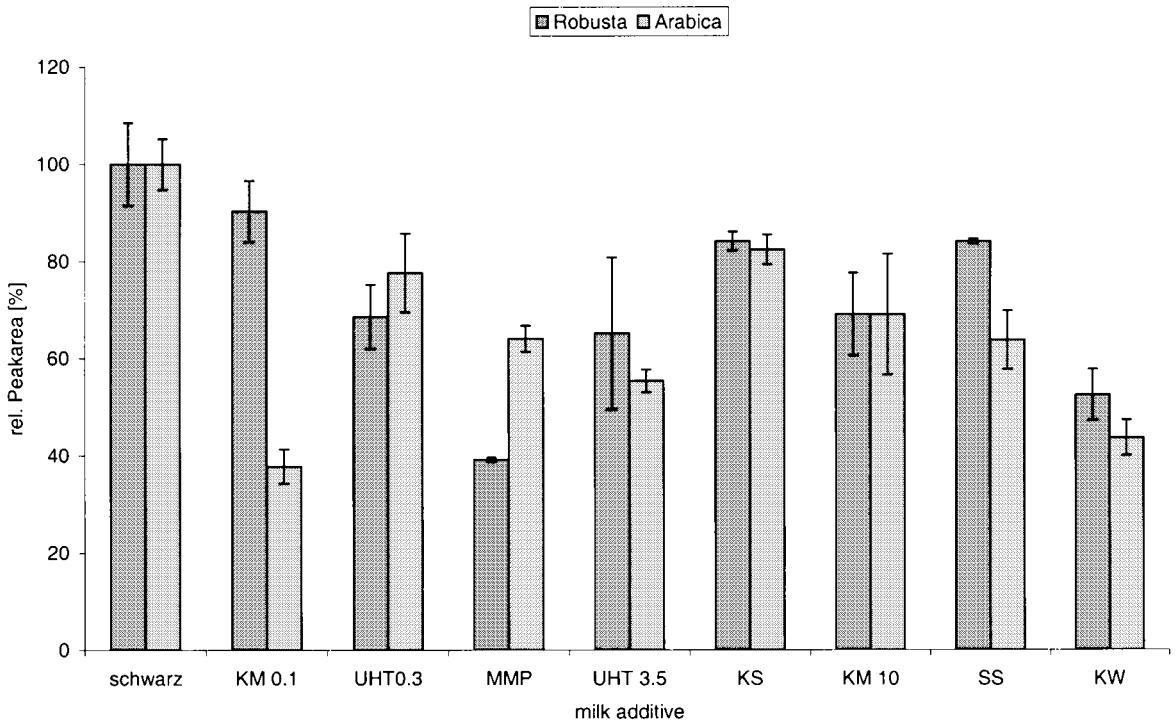

Figure 3. 2-Furfurylthiol: Comparison of the different additives (percentage specifies the fat content of the additive). Results are expressed relative to peak area (target ion GC/MS, *m/z*: 81) of black Robusta and Arabica coffee (for explanation of abbreviations see **Table 1**).

0.53 mm i.d. and 50 cm × 0.53 mm i.d., respectively) leading to the FID (300 °C) and to the sniff detector. The identification of the compounds was achieved by comparison of retention data on an RTX-5 column, as well as comparison of sensory properties with those of authentic reference substances.

The assessors recorded the aroma substances in parallel with the sniff runs recording instrument (W+W Electronic Inc., Basel, Switzerland). When the compound exceeded its threshold, the sniffer recorded the event (chartspeed: 10 cm/min); when the concentration dropped below the threshold again, the sniffer also recorded the event.

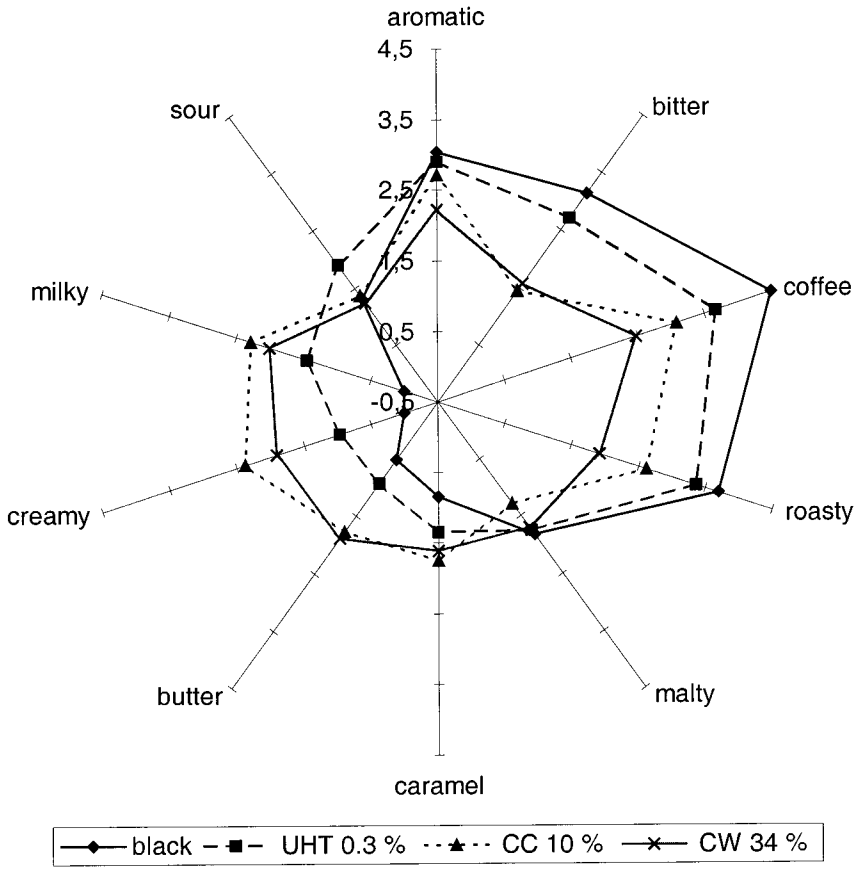

Figure 4. Intensity test: odor profiles of black coffee, and coffee with UHT-milk, coffee creamer, or coffee whitener.

Flavor descriptions for over 50 odors were generated during preliminary GC/sniffing experiments with different coffee beverages, with and without additive, and clustered into 10 useful descriptors after group sessions of the panel, which consisted of five trained assessors. The lengths of the recorded signals for each descriptor were added, and the values were presented in spider-web diagrams.

Sensory Studies. For the beverage samples, a coffee blend supplied by Tchibo (Hamburg, Germany) was used. Samples (50 g) were brewed with 1200 g of tap water in a household coffeemaker. Coffee (75 mL) was mixed with 15 mL of additive (**Table 1**) and served in coffee cups after 5 min at a temperature of 55 °C. Sweetened beverages contained 3.35 g of sucrose. A panel of 20 trained assessors (consisting of students or co-workers of the Institute of Food Chemistry, University of Hamburg, Germany), performed a triangular test (*6*) with samples of coffee beverages. The assessors had to find the sample that was different by sniffing. After a correct answer the assessors performed an intensity test (*7*) for smell and taste of the coffee beverage. The attributes were determined in preliminary group sessions of the panel, and the intensities of these attributes were scored using a six-point scale from 0 (no smell/taste) through 5 (very strong smell/taste)

RESULTS AND DISCUSSION

GC/O and GC/MS. In contrast to conventional static headspace sampling using a gastight syringe, higher amounts of volatiles were collected with this modified system. Therefore, it was possible to identify more major impact compounds, and also some less volatile aroma compounds (**Table 2**), than described in the literature (*2, 8*−*10*). Over 50 potent odorants, resulting in a list of 10 descriptors, were recognized at the sniffing port (GC/O). The identification of these volatiles verified most of the contributors of the coffee aroma. From this fact the external static headspace technique was comparable to conventional simultaneous distillation/extraction or vacuum distillation. The results of GC/O of the black coffee beverages showed that their odor profile was characterized by the descriptors roasty and burned, fruity and aldehyde-like, potato and sulfurous, and honey and phenolic.

All milk or vegetable additives reduced the perception of the major impact compounds.

This retardation effect was caused by components of the milk and vegetable additives, and thus the different coffee beverages had typical odor profiles (**Figure 2**). Descriptors such as roasty, burned and malty, cocoa and fruity, and aldehyde-like showed a significant decrease.

The concentration of volatiles in the headspace of the coffee brew was in particular influenced by products with a high fat content, such as whipping cream and coffee whitener.

However, additives with a high protein content such as skim milk powder may also affect the retardation of volatiles. There was no obvious correlation between carbohydrate content and flavor release, except, because of high contents, for the skim milk powder.

These results were confirmed by GC/MS analysis of the beverages. **Figure 3** illustrates the effect of the additives on 2-furfurylthiol, a potent odorant with a roasty/coffee-like aroma quality. Overall, all beverages with an additive had a lower volatile concentration in their headspace than the black coffee beverage. The changes in the concentration of coffee volatiles with an additive can be caused by several effects (*11*): lipids readily adsorb most volatiles, whereas proteins and carbohydrates can interact by adsorption, entrapment, and encapsulation. Because of these different effects, a simple correlation between flavor release and fat content cannot be established. However, the tendency toward a high fat content having a more important influence than a low-fat content is apparent. One exception was the condensed milk (0.1% fat) in the case of arabica coffee

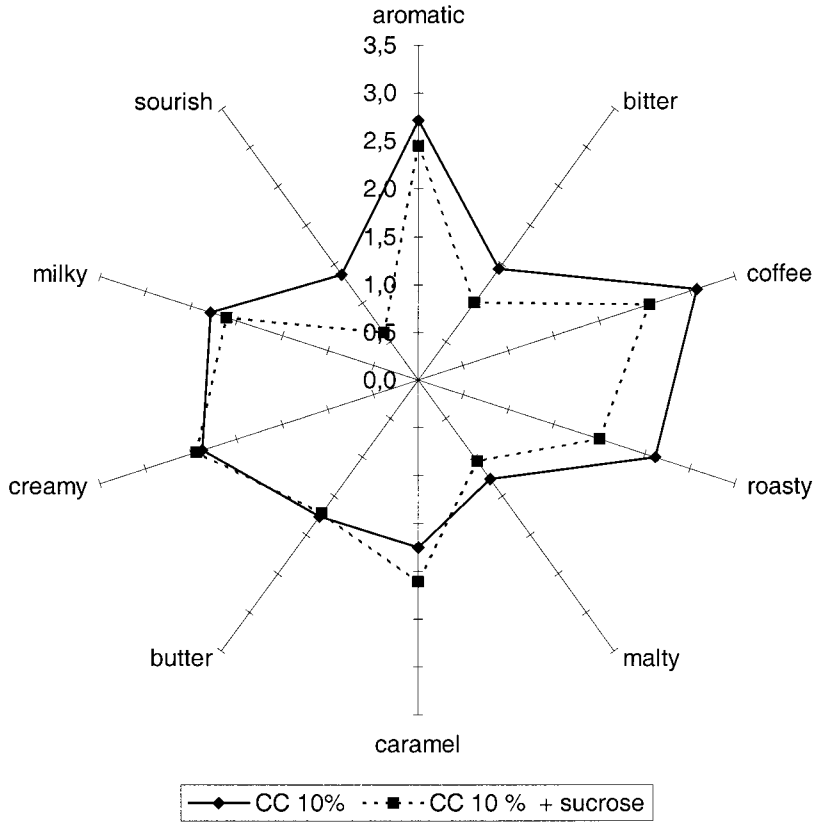

Figure 5. Intensity test: odor profiles for coffee with coffee creamer and coffee with coffee creamer and sucrose.

samples where the coagulation of the ingredients of the condensed milk (0.1% fat) during the experiments led to a nonreproducible flavor release.

Sensory Studies. The results of the triangular tests showed that each assessor identified the odd samples. This meant that all 20 assessors performed the intensity test for all samples. The attributes of smell, resembling the high specific descriptors of the GC/O, were partially replaced by descriptors related to the human perception during coffee consumption. The shift of odor profiles after addition of the milk or vegetable products was obvious (**Figure 4**). The intensity of coffee-like attributes was reduced: for example, there was an intensity change for the attribute "roasty" after adding coffee creamer (from 4.5 to 3). On the other hand, the intensity of milk-like attributes ("milky, creamy, butter") increased. In agreement with the results of GC/O the odor profiles of coffee beverages with low-fat or high-fat additives differed strongly. Coffee attributes were reduced more strongly by coffee creamer (10% fat) than by ultrahigh-temperature-milk (UHT-milk; 0.3% fat). In contrast to this, milk-like attributes were increased more strongly by coffee creamer than by UHT-milk.

Sucrose. The triangular test showed that the panel could not differentiate a black coffee beverage and a black coffee beverage with sucrose by sniffing. These results were in agreement with previous investigations (*12*−*14*) which did not observe interactions of sucrose with flavor compounds, when sucrose was used in such low concentrations. In contrast to these results, the panel differed with high significance between coffee beverages with coffee creamer (10% fat) and coffee beverages with the same amount of additive and sucrose. Therefore, the intensity test showed different odor profiles for these beverages (**Figure 5**). Except for the attribute "caramel", which increased after the addition of sucrose, all attributes showed a lower intensity in the beverage with sucrose. The decrease was most obvious for the attributes "bitter" and "sourish" (approximately 30% and 55%, respectively). In particular with regard to these attributes the assessors were able to distinguish between the samples.

GC/O and GC/MS investigations could not confirm these sensory evaluations. It is obvious that the long period of external static headspace sampling (30 min) had a leveling influence on the effects of sucrose. Therefore, this kind of interaction, not described in the literature, can be supposed to be reversible. For this reason more investigations to clarify this phenomenon are necessary.

With the static headspace method the most potent odorants of coffee beverages were determined. The addition of different milk or vegetable products reduced the amount of volatiles in the headspace of the coffee beverage. This retardation effect, caused by components of the additives, was typical for each additive. Sensory studies confirmed these results. Furthermore they showed that sucrose had an influence on the flavor release of coffee with coffee creamer. Further studies will concentrate on structural characteristics that lead to the retention of coffee aroma substances.

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