Headspace Gas Chromatography Profiles of Fruit-Flavored Malt Beverages Using Solid-Phase MicroExtraction

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ABSTRACT

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A solid-phase microextraction (SPME) headspace sampling technique has been applied to the gas chromatographic (GC) analysis of fruit-flavored malt beverages. The procedure provides an alternative to direct headspace, solvent extraction, and purge and trap methods for the monitoring of volatile components. The sampling technique is readily adapted to most capillary gas chromatographic systems with flame ionization detectors (FID). Over 40 components were identified by mass spectroscopy (MS) and monitored by GC-FID to evaluate 14 products containing raspberry, cherry, apple, and apricot flavors. Control of sample temperature and volume as well as SPME fiber position were important factors in obtaining consistent responses required for quantitation. Further application of this technique to monitor volatiles in unflavored beers and malt beverages is apparent.

Keywords: Ale, Beer, Fruit flavor, Gas chromatography Malt beverage, Solid-phase microextraction (SPME)

RESUMEN

Una técnica de muestreo por microextracción en fase sólida (SPME) en cámara gaseosa ha sido aplicado al análisis por cromatografía de gases (GC) de bebidas de malta con sabores de frutas. El procedimiento representa una alternativa adicional a los métodos de extracción con solvente y de purga y trampa para el monitoreo de componentes volátiles. La técnica de muestreo es fácilmente adaptable a la mayoría de los sistemas de cromatografía de gases capilar con detectores de ionización de flama (FID). Más de 40 componentes fueron identificados por espectroscopía de masas (MS) y monitoreados por GC-FID para evaluar 143 productos conteniendo sabores de frambuesa, cereza, manzana y albaricoque. El control de la temperatura y volumen de la muestra, así como la posición de la fibra SPME fueron factores importantes para obtener respuestas consistentes requeridas para la cuantificación. La posible aplicación de esta técnica para la determinación de volátiles en cervezas y bebidas de malta resulta obvio.

The increased variety of fruit-flavored beers available from foreign and domestic breweries has brought a new challenge to the brewing analyst. These flavorings, either natural or artificial, contribute components to the base products which may require new or improved methods for analysis. Due to the variety of products on the market, the authors perceived a need for a simple sampling procedure to provide at least a qualitative profiling approach to characterize the volatile components in these products. No literature references were found which directly addressed this application.

Initial investigation into flavoring methods was prompted by in-house experimentation with flavor additions to beer, along with curiosity of competitive products. The authors' preliminary evaluation of several commercial fruit-flavor mixtures by direct capillary gas chromatography (GC), along with literature profiles, indicated the presence of many higher boiling components. Some established methods for beer analysis such as the ASBC Beer-29 (1) and those reported by Baker (3) addressed only the lower boiling volatiles. Elaborate methods have been utilized to obtain more extensive profiles of beer and similar products. Recent examples of these include solvent extraction using methylene chloride by Stenroos et al (9), purge and trap (P&T) techniques published by Chen (4), Dercksen et al (5), and Murakami et al (8) and combined solvent extraction and P&T as published by Chen (4) and Harayama et al (7). Although the more elaborate approaches are suitable for higher-boiling components, minimal use of solvents was preferred, and P&T required expensive equipment and more analyst time and expertise than desired. Commercial introduction of the manual solid-phase microextraction (SPME) syringe in 1993 provided an alternative to previous sampling techniques. An earlier article by Arthur et al (2) indicated SPME eliminated the need for solvents and provided good sensitivity using cryofocusing and GC with flame ionization detector (FID). Later work by Yang and Peppard (11) demonstrated analysis of fruit juice beverages by SPME and indicated that, with some sacrifice of resolution for early peaks, cryofocusing could be eliminated by using a 1-mm i.d. injection liner. Ulrich et al (10) used headspace SPME sampling to quantify aroma volatiles of fresh strawberries.

This article describes the application of a manual SPME sampling procedure to profile or measure volatiles in a variety of fruit-flavored malt beverages (including lagers and ales). The procedure is relatively simple and provides a clean sample for gas chromatographic profiles without the use of solvents. It is especially attractive because it utilizes common analytical instrumentation, capillary-GC with FID, and is therefore amenable to sporadic or routine monitoring. Many of the identified components are found in unflavored malt beverages, and this approach could be extended to monitoring fermentation and hop-derived volatiles in these products.

EXPERIMENTAL

Reagents

The chemicals used for verification were obtained from Aldrich Chemical Co. (Milwaukee, WI) with the exceptions being terpinolene, *i*-methyl-α-ionone and *n*-methyl-α-ionone obtained from TCI America (Portland, OR). The ethyl heptanoate internal standard (IS) solution was prepared by diluting 100 µl (86 mg) to 50 ml with ethanol to obtain a concentration of 1,720 mg/L.

Instrumentation and Equipment

The gas chromatograph was a HP5880 (Hewlett Packard, Wilmington, DE) equipped with a splitless injector (200°C) and flame ionization detector (280°C). A J&W DB1301 column, 0.32 mm i.d., 30 m, 1 µm, was used. Conditions for GC operation were: helium flow 1.5 ml/min, make-up 20 ml/min; and oven program: 45°C hold 5 min, 4°C/min to 105°C hold 1 min, 2°C/min to 155°C, 5°C/min to 210°C hold 4 min. Component identification was accomplished on a Varian Saturn II GC/MS system (Varian Associates, Inc., Palo Alto, CA) using a similar column. A direct-injection liner was used on the HP5880 injection port, the GC/MS was fitted with a 1-mm narrow-bore liner. The SPME syringe assembly (Supelco, Inc. Bellefonte, PA) included a holder and a

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fiber coated with a 100-μm polydimethylsiloxane (pdms) film. The 20-ml sample vials were obtained from Fisher Scientific (Pittsburgh, PA) and Teflon-faced black butyl rubber septa and crimp caps from Hewlett Packard. A block heater (Scientific Products, McGaw Park, IL) equipped for 20-ml vials was used to obtain SPME headspace samples above ambient temperature.

Sample Preparation for Routine GC Profiles

The general procedure is best described as a static headspace sampling method. Routine sample preparation involved the transfer of 10 ml of cold carbonated product directly to a vial using a pipet with a wide-bore tip. The vial was purged with nitrogen, sealed with a septum and cap, and refrigerated at 5°C until used. Before analysis, 5 μl of the IS solution was added by syringe (resulting in 860 μg/L IS), and the sample was hand-swirled to mix. The SPME fiber was preconditioned in a GC inlet at 200°C for at least 15 min before sample exposure. Vials were placed in the preheated block (45°C for routine sampling), the SPME needle inserted through the septum, the fiber exposed, and lowered to ≈5 mm above the sample surface and maintained in this condition for 45–60 min. For injection into the GC, the fiber was withdrawn into the needle, the needle removed from the vial and inserted into the injector, the fiber was exposed for 2.5 min and then removed from the injector.

RESULTS AND DISCUSSION

Methodology

The focus of this work was to design a simple manual sampling technique for malt beverages which would provide analysts with useful flavor profiling. A number of SPME fiber coatings were available from Supelco, but the pdms film was chosen as a suitable phase for routine profiling. The 20-ml sample vial used for this study was a somewhat arbitrary size, but common in many laboratories and convenient for 5–15 ml sample volumes. All septa tested exhibited blank peaks and should be carefully selected. Anomalous peaks were also noted when the SPME needle was touched with bare hands. More than 100 peaks were observed in some product GC profiles, many yet to be identified, and some peak coelutions were encountered. The GC conditions used were a

TABLE I
Chromatographic Peak Information and Product Comparison

Component	Retention (min)	Peak[a]	Identification (formula weights)	Area Ratios[b] (low–high)	Product[c] (ranking)
Amyl alcohols	9.25	1,R1	(88) MS +known	0.085–0.241	M,N,H,B
i-Butyl acetate	9.82	2	(116) MS	nd–0.010	G,M,H
Ethyl *n*-butanoate	10.92	3	(116) MS +known	0.004–0.610	H>>>L
n-Butyl acetate	11.70	4	(130) MS	nd–0.005	C>>D
Propylene glycol	11.90	5	(76) MS	nd–0.021	E,H,N>F
i-Propyl butanoate	12.82	6	(130) MS	nd–0.004	D
Ethyl 2-methyl butanoate	13.15	7	(130) MS	nd–0.176	H>>>J>>I
Ethyl *i*-valerate	13.40	8	(130) MS +known	nd–0.219	H>>>C>J
i-Amyl acetate	14.55	9,R2	(130) MS +known	0.020–0.495	M>L,H,E,G
Ethyl *n*-pentanoate (valerate)	16.50	10	(130) MS +known	nd–0.004	I>J
Benzaldehyde	19.55	11	(106) MS	nd–0.331	L>>>>I
Ethyl hexanoate (caproate)	20.05	12,R3	(144) MS +known	0.031–0.142	M,C,H,N,G
3-Hexenyl acetate	20.55	13	(142) MS	nd–0.100	H>>>I>N
Limonene; coelution with 15	20.80	14	(136) MS +known	0.004–0.056	H>I>>D,G
Hexyl acetate	20.84	15	(144) MS +known	0.004–0.056	H>I>>D,G
2-Hexenyl acetate	20.95	16	(142) MS	nd–0.016	I,H,D
γ-Terpinene	22.35	17	(136) MS +known	nd–0.004	E,I
Terpinolene	23.82	18	(136) MS +known	<0.001–0.004	I>K
Ethyl heptanoate	25.08	19,R4	(158) IS	. . .	. . .
Pentyl *i*-valerate, or isomer	25.63	20	(172) MS	<0.001–0.025	C>>>J,D
Heptyl acetate	25.95	21	(158) MS	nd–0.044	C>>>G,H
Linalool	26.10	22	(154) MS +known	0.002–0.091	N>D>>E
Phenylethyl alcohol	28.60	23	(122) MS +known	0.017–0.063	H,M,B,N,G
Phenylmethyl acetate	30.00	24	(150) MS +known	nd–0.268	H>>>E
3-Hexenyl butanoate	30.20	25	(170) MS	nd–0.293	H>>>J
Hexyl butanoate	30.42	26	(172) MS	nd–0.070	H>>>I
Ethyl octanoate (caprylate)	30.75	27,R5	(172) MS	0.233–1.283	N>F,B,J
Octyl acetate	31.70	28	(172) MS	nd–0.006	L,E,G,H
Octanoic acid	33.52	29	(144) MS	0.019–0.101	M,N,E,H,C
Nerol	34.20	30	(154) MS	0.001–0.007	D,N
Phenylethyl acetate	35.70	31	(164) MS +known	0.009–0.121	M>G,H,L
Neryl acetate	41.30	32	(196) MS +known	<0.001–0.008	N>E,D
Geranyl acetate	42.45	33	(196) MS +known	0.002–0.009	D,E,B,G
Ethyl decanoate (caprate)	42.90	34,R6	(200) MS	0.021–0.877	N>K,J,B,H
Methyl eugenol	44.80	35	(178) MS	nd–0.037	E>F>>D
Decanoic acid	45.28	36	(172) MS	0.013–0.178	N>K,J,C,H
α-Ionone	47.00	37	(192) MS +known	nd–0.378	H,I>>>D>G
i-methyl-α-Ionone	49.30	38	(206) MS +known	nd–0.071	C>E>F
β-Ionone, + system peak	49.90	39	(192) MS	0.01–0.51	H>>I>D,E
n-methyl-α-Ionone	51.10	40	(206) MS +known	nd–0.029	C>E>>F
α-Irone	51.25	41	(206) MS	nd–0.021	D,H,E>I,F
β-Irone, +unknown	52.22	42	(206) MS	0.002–0.029	D,E,H,F,B
Ethyl dodecanoate	52.75	43,R7	(228) MS	0.003–0.121	N,C,H,F
Benzyl benzoate	59.60	44	(212) MS	nd–0.178	E,F

[a] R1–R7 = reference components.
[b] Area ratio: A/IS = (peak area component)/(peak area IS); IS = internal standard; nd = not detected.
[c] Products (A–N) with highest levels, descending: > to >>>> designate decreases of more than 25, 50, 75, and 90%, respectively.

compromise to provide relatively fast analyses but better resolution would be necessary to identify or quantify some components in selected products. The authors have obtained similar chromatographic success, with some peak shifting, using the more common DB5 (J&W) column. Samples were tested for endogenous ethyl heptanoate by sampling without IS addition. The largest peak area measured was equivalent to 2.3 µg/L or <0.3% of the IS addition level of 860 µg/L. The mass spectra or retention times of known components were obtained by SPME sampling of spiked 5% (v/v) ethanolic solutions or a few seconds exposure to the headspace of the reagent bottles, followed by the normal SPME injection procedure.

SPME sampling involves multiple equilibria, and this results in some unique characteristics which have been examined by other authors (2,10,11). Sensitivity and reproducibility were very dependent on sampling conditions (11). Two experiments used to evaluate various parameters are presented to illustrate this point. The first experiment involved running single analyses of a flavored product using the routine procedure but at sampling temperatures of 23, 35, and 45°C. The resulting peak areas for six common beer components and the internal standard (see peak listing in Table I [R1-7]), which spanned the chromatographic profile, were used to monitor temperature dependence. A comparison of component responses is shown in Figure 1, in which peak area responses are related to the values obtained at room temperature (23°C). In general, the sensitivity or area response increased with increasing temperature, but with obvious differences for individual components. Sensitivity for the amyl alcohols (R1) doubled at 45°C when compared to 23°C. Sensitivity for the esters (R2-7) increased with temperature and molecular weight, resulting in 1.3- and 3.1-fold increases for *i*-amyl acetate (R2) and ethyl dodecanoate (R7), respectively.

Preliminary work by the authors indicated that the sample volume, positioning of the SPME fiber and the specific pdms fiber might significantly alter the responses for various analytes. A second experiment was conducted and included: 1) maintaining a sampling temperature of 45°C; 2) varying the sample volume to 5, 10, and 15 ml; 3) tests run by two analysts using comparable SPME samplers three days apart; and 4) one analyst positioned the fiber at 5 mm above the liquid, while the second always positioned the fiber at the top of the vial. In general, there were increases in response for most analytes as the sample volume increased (headspace decreased) but with obvious discrimination among components not noted by Yang and Peppard (11). Experimental results depicted in Figure 2 with responses for components (R1-7) indicated: 1) the positioning of the fiber in the headspace was a significant factor in the responses; 2) for the 15-ml sample, the sample volume resulted in the two analysts positioning the fibers in similar positions and obtaining the closest agreement; 3) with the 15-ml sample, both tests indicated the greatest enhancement for the midboiling components (R3-5); 4) with the fiber always at the top of the vial (dashed lines), response for R1 did not change significantly; and 5) with the fiber above the liquid (solid lines), the least change was noted for R7 with the 10- and 15-ml samples. The observation believed unique to SPME sampling was that the headspace position of the fiber was a critical factor in analyte response. This may be due in part to the static (not stirred) sampling technique. Results also indicated that the specific fiber, analyst, or sampling date were not major causes of different responses. It should be noted, however, that further experiments with similar fibers of different length did show a sensitivity difference believed due to fiber capacity.

Analyses obtained using 5- or 10-ml samples have shown good repeatability when fiber position and other conditions are fixed. Table II contains the results for 16 components determined in a bottle of raspberry-flavored product and using five replicates and 10-ml samples. The peak area ratios (A/IS = peak area component/peak area IS) ranged from 0.004 to 0.810 and coefficient of variation (CV) values ranged from 2.0 to 10.9% with a mean of 5%. Actual peak area of the IS averaged 313,100 with a CV = 5.8%. The authors have used this technique to quantify several components using A/IS response. For example, a four-level calibration by standard addition of 20–200 µg/L of linalool, a component found in fruit flavors and hops, gave a linear correlation with a R^2 = 0.998. Sensitivity or response factors (RF) versus ethyl heptanoate for calibrated components indicated selectivity with

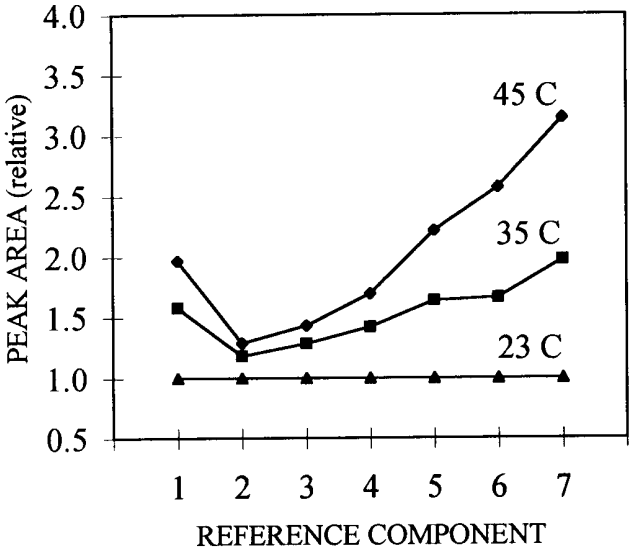

Fig. 1. Influence of sampling temperatures (23, 35, and 45°C) on response for reference components (R1–R7, Table I). A general, but different increase in response with temperature is noted for all components including the internal standard (R4). Relative peak areas are normalized to values obtained at room temperature (23°C).

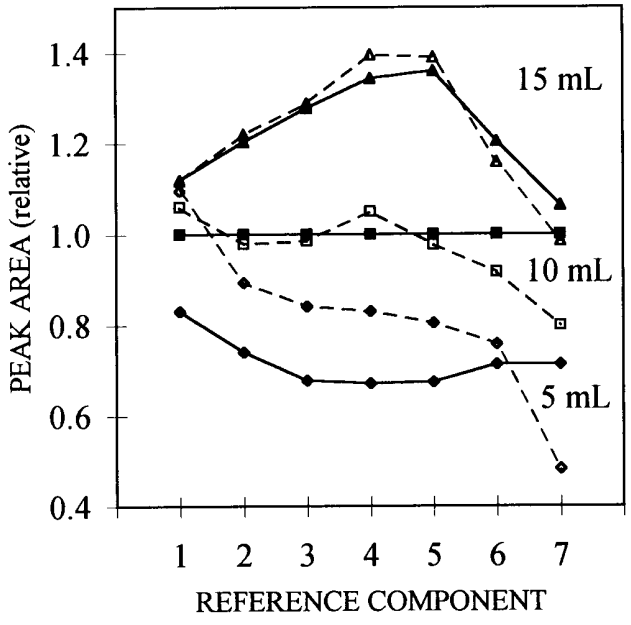

Fig. 2. Influence of sample volume (5, 10, and 15 ml) and headspace position of solid-phase microextraction (SPME) fiber (5 mm above sample, solid lines and at top of vial, dashed lines) for reference components. Peak areas normalized relative to values obtained using 10-ml sample and SPME at 5 mm above sample. Results emphasize the importance of consistency with static headspace sampling.

SPME sampling of spiked products. As examples, linalool, neral, and geranial had RF values of 0.078, 0.074, and 0.082, respectively, while *d*-limonene, γ-terpinene, neryl acetate, and geranyl acetate exhibited better sensitivity with RF values of 1.02, 1.15, 1.01, and 1.02, respectively. Comparing actual peak intensities of SPME-GC profiles was therefore more valid for specific components between products than between components. The selectivity was easily observed by comparing GC profiles obtained by direct injection of flavor solutions to profiles obtained by SPME sampling of a beer spiked with the flavoring.

Product GC Profiles and Evaluations

A variety of flavored beverages were commercially available, but raspberry-flavored products appeared to be the most common. Descriptions from product labels indicated 10 products (A–J) had raspberries, raspberry juice, or flavor; K and L had cherry juice or flavor; M contained apple juice; and N had apricot flavor. The conditions described above were used for the survey of 14 products and to generate the GC profiles. Visual comparison of the GC profiles provides a means to appreciate the qualitative differences in the volatile compositions. Comparing component peak intensities between products is reasonably valid because CV = 10.3% for IS peak areas of 14 products. Profiles are scaled to 4 mV except for H (5 mV). Table I contains a component listing of the labeled peaks along with retention times, formula weights (FW), and means of identification by mass spectral libraries and use of known compounds (+known). The table also includes a range of component intensities (A/IS) and a ranking of some products according to A/IS levels. Both β-ionone and β-irone had interference peaks, but GC-MS analysis indicated they were major peak components for the high ranking products listed in Table I. Because many of the compounds in Table I are found in unflavored beers (4,5,7–9), Fenaroli's *Handbook of Flavor Ingredients* (6) was used as a reference to justify assignment of enhanced component levels to fruit flavoring.

TABLE II
Repeatability for some Components in a Raspberry-Flavored Beer

Component	Peak[a]	Area Ratio[b]	CV (%)[c]
Amyl alcohols	1,R1	0.147	5.6
i-Amyl acetate	9,R2	0.142	2.6
Ethyl hexanoate	12,R3	0.066	2.0
Linalool	22	0.006	2.5
Phenylethyl alcohol	23	0.033	5.0
Ethyl octanoate	27,R5	0.810	3.5
Octanoic acid	29	0.056	3.4
Phenylethyl acetate	31	0.028	3.0
Geranyl acetate	33	0.004	7.1
Ethyl decanoate	34,R6	0.314	4.2
i-methyl-α-Ionone	38	0.019	4.5
β-Ionone	39	0.075	7.0
n-methyl-α-Ionone	40	0.006	6.1
α-Irone	41	0.007	10.9
Ethyl dodecanoate	43,R7	0.092	4.9
Benzyl benzoate	44	0.126	9.4

[a] R1–R7 = reference components.
[b] Area ratio: A/IS = (peak area component)/(peak area IS); IS = internal standard.
[c] Coefficient of variation (n = 5).

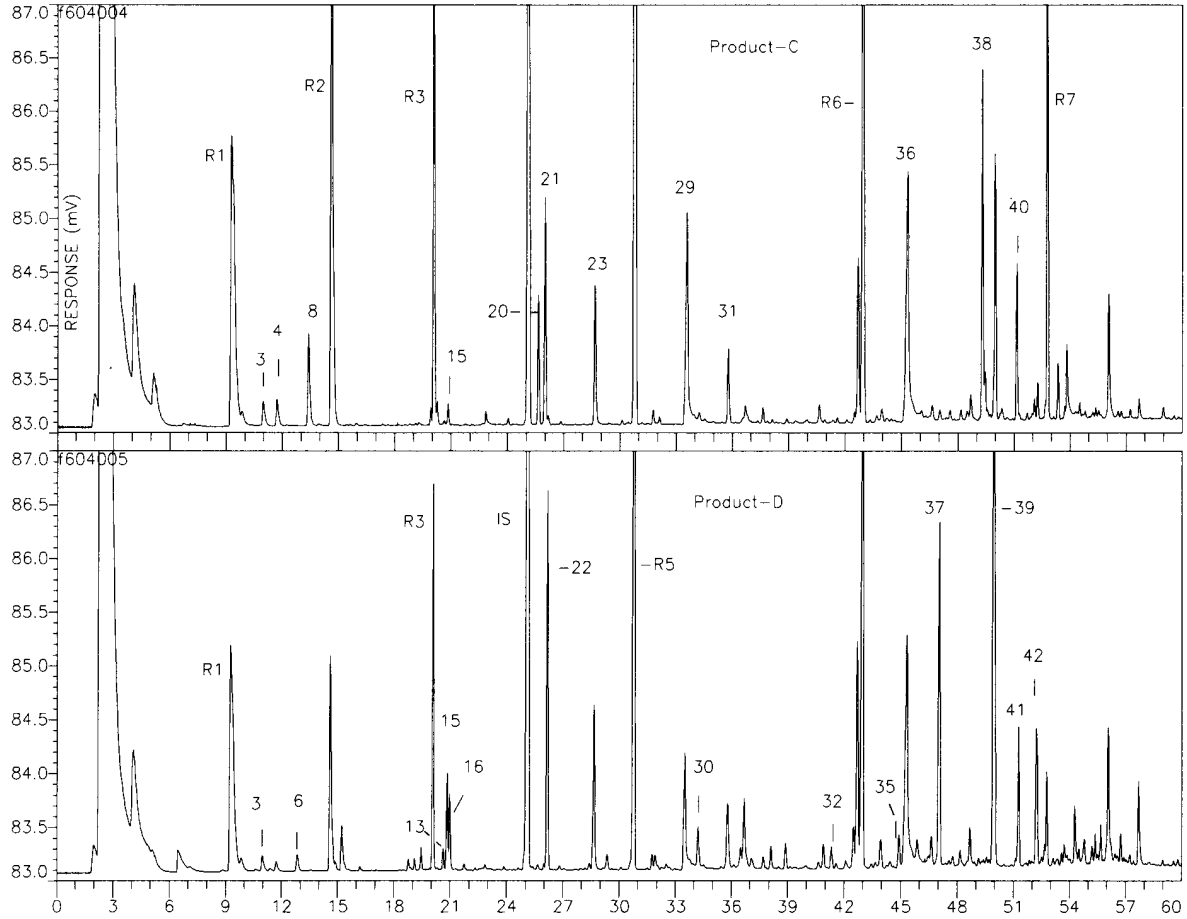

Fig. 3. A comparison of gas chromatography profiles of Product C (top) an ale "brewed with raspberry and natural flavor" and Product D (bottom) a beer "fermented with raspberry juice". Methyl ionones (peaks 38 and 40) in C indicate flavor addition. Ionones (peaks 37 and 39) and irones (peaks 41 and 42) in D are common in raspberries and flavorings. IS = internal standard, R1–R7 = reference components. See Table I for peak identification.

In general, all the products evaluated had distinguishable GC profiles (see examples Fig. 3–6).

Some of the prominent product characteristics are highlighted here. Relatively uncomplicated GC profiles were observed for A, a wheat ale "brewed with red raspberries" and B, an ale "fermented with red and black raspberries". Raspberry flavors typically include mixtures of ionones, irones and many esters. Products A and B had the lowest and third lowest combined content of ionones and irones (37–42). A also had the lowest levels of ethyl hexanoate and octanoate, phenylethyl alcohol, and octanoic acid. Products C (Fig. 3), E (Fig. 4), and F, a wheat beer "blended with the essence of raspberries", had the highest levels of *i*-methyl-α-ionone (38, A/IS = 0.071, 0.037, and 0.023) and *n*-methyl-α-ionone (40, A/IS = 0.029, 0.016, and 0.006). These compounds are not found in nature (6) and agreed with label indications of flavor addition. Products G and H were wheat-based with flavorings that apparently lacked the methyl ionones. Product G had moderate α- and β-ionone (37 and 39) levels (A/IS = 0.032 and 0.024). H (Fig. 4) contained the highest levels of several esters (3, 7, 8, 13, 15, 24–26), α- and β-ionones, and phenylethyl alcohol (23). Flavor additions were indicated in E, F, and H by the presence of propylene glycol (5), a flavor carrier, and in E and F by benzyl benzoate (44), a flavor stabilizer and enhancer. E and F had similar patterns for peaks 5, 38–42, and 44, indicating a similar flavoring was used by two breweries. I (Fig. 5) had high levels of ionones and moderate irones (41 and 42), A/IS = 0.375, 0.167, 0.009, and 0.012, respectively, all confirmed present by GC-MS and benzaldehyde (11, A/IS = 0.009). J, an imported ale "flavored with real raspberries", had an unidentified peak at 12.6 min, also seen in I, and the next to lowest combined ionone and irone content.

Product L (Fig. 5), with cherry flavoring, had an intense benzaldehyde peak (11) that distinguished it from all other products, including K, which contained cherry and cranberry juices. Products K and L had obvious differences in levels of ethyl butanoate (3,A/IS = 0.003 vs. 0.068), phenylethyl acetate (31, A/IS = 0.01 vs. 0.06), ethyl decanoate (R6, A/IS = 0.59 vs. 0.03), and β-ionone (39, A/IS = 0.011 vs. 0.045). Compounds 3, 11, and 39 are components of cherry flavor (6). M (Fig. 6), with apple juice, had the highest responses for amyl alcohols (R1), amyl acetate (R2), ethyl hexanoate (R3), octanoic acid (29), and phenylethyl acetate (31), and lowest for ethyl decanoate (R6). Apricot-flavored N (Fig. 6), contained propylene glycol (5) and had the highest responses for linalool (22), ethyl esters (R5, R6, and R7), and neryl acetate (32).

Some components in Table I, such as terpinene and neryl acetate, seemed of small consequence in the product evaluations. However, the 14 products evaluated were only a sampling of those commercially available. Subsequent analysis of a citrus-flavored beer had much higher A/IS responses for several components including; limonene (0.218), γ-terpinene (0.358), terpinolene (0.060), neryl acetate (0.489), and geranyl acetate (0.151). Additional investigations with SPME sampling of unflavored beer and ale resulted in the identification of several hop-derived components, including; myrcene, linalool, β-caryophyllene, methyl geranate, α-humulene, and citronellyl acetate.

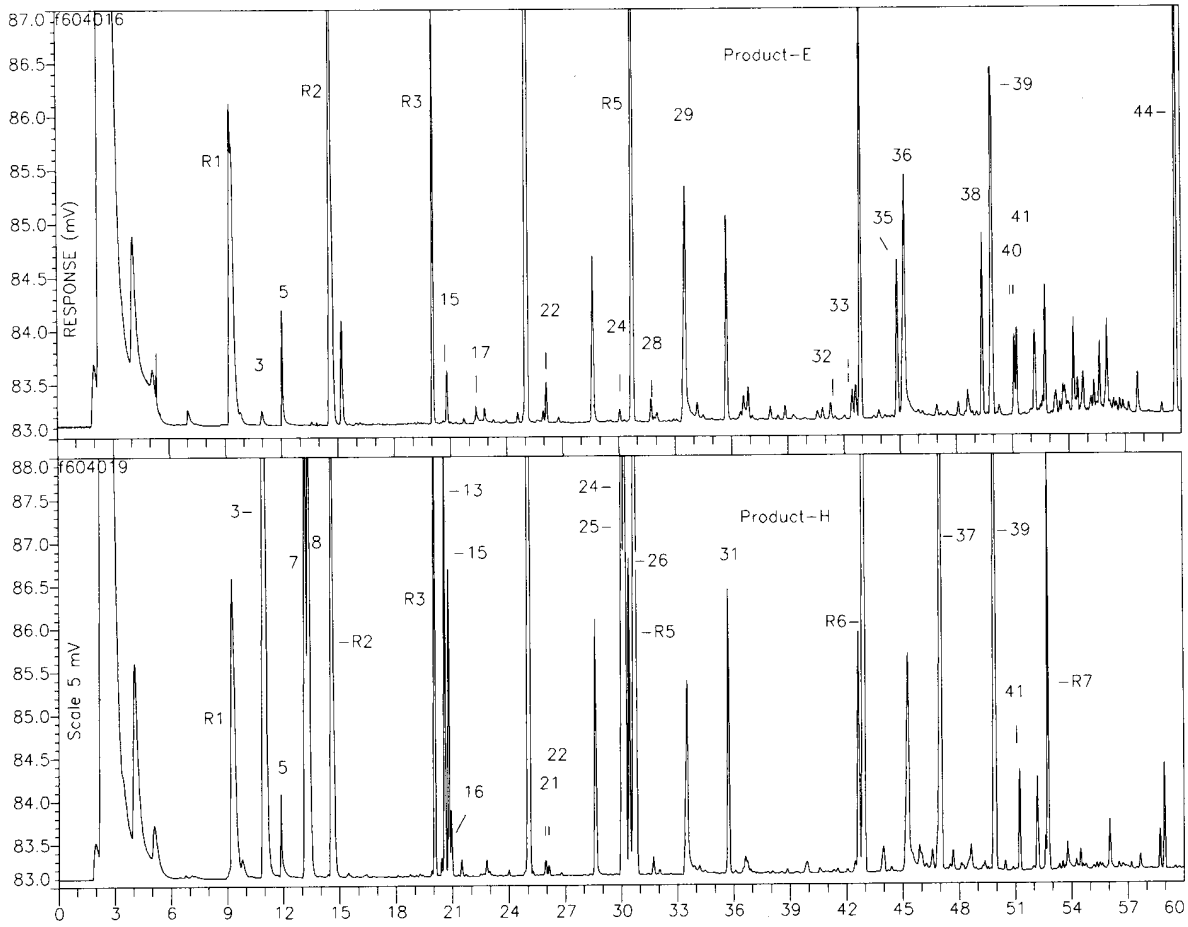

Fig. 4. A comparison of Product E (top) a malt beverage with "natural raspberry flavor added" and Product H (bottom) a wheat ale "with natural flavors" (raspberry). Propylene glycol (peak 5) and benzyl benzoate (peak 44) in E indicated probable flavor addition. H contained propylene glycol and highest levels of many components. IS = internal standard, R1–R7 = reference components. See Table I for peak identification.

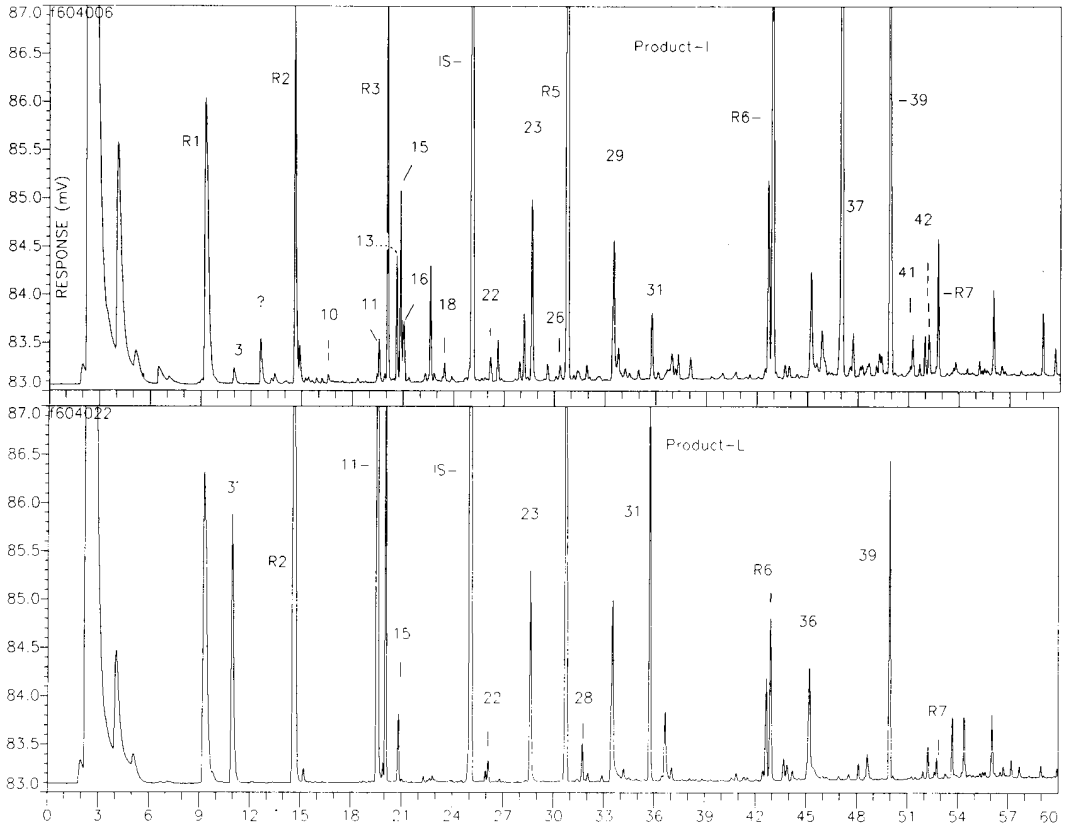

Fig. 5. Profiles of Product I (top) an imported ale "flavored with fresh raspberries and raspberry juice" and Product L (bottom), a malt beverage with "natural cherry flavor added". I had the second highest benzaldehyde (peak 11) and Ionone (peaks 37 and 39) levels. L had the largest benzaldehyde peak along with other cherry flavor components (peaks 3 and 39). See Table I for peak identification.

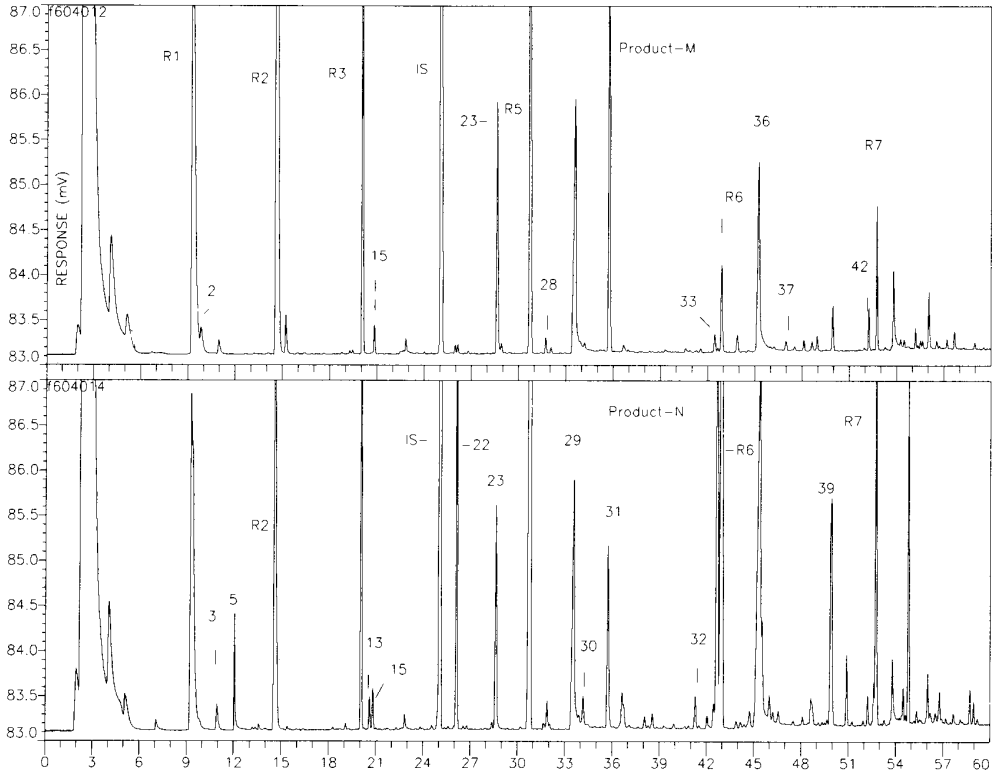

Fig. 6. Chromatograms of Product M (top) an ale "brewed with apple juice" and Product N (bottom) an "apricot flavored" ale. M had several highest component levels (R1, R2, and R3) and a lowest level (R6). N had highest levels of linalool (peak 22) and other components (R5, 32, R6, peak 36, and R7) and contained propylene glycol (peak 5). IS = internal standard, R1–R7 = reference components. See Table I for peak identification.

CONCLUSIONS

Solid-phase microextraction is a valuable technique for profiling fruit flavors and natural components of malt beverages. Many mid- to high-boiling components were detected and identified without the use of solvents or expensive P&T equipment. The evaluation of 14 fruit-flavored products indicated that SPME sampling for GC analyses is an alternative or complementary to other techniques. Introduction of only volatile components (clean samples) is especially advantageous when using MS detectors. The technique is relatively easy but requires a consistency in sampling conditions to obtain reproducible results. Increasing the sampling temperature provided a means to enhance higher boiling components, which would be difficult without using more elaborate techniques. Evaluation of alternative SPME fibers and matrix modifiers, along with analysis of other flavorings, would serve to enhance the value of this technique. Application of SPME to monitor fermentation and hop-derived components would provide the brewing chemist with a technique to address quality and research investigations for a variety of products.

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