Application of Solid Phase Microextraction and Gas Chromatography/Time-of-Flight Mass Spectrometry for Rapid Analysis of Flavor Volatiles in Tomato and Strawberry Fruits

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Solid phase microextraction (SPME), a relatively new sampling technique, was examined as a means to investigate volatile compounds produced by tomato (*Lycopersicon esculentum* Mill.) and strawberry (*Fragaria* × *ananassa* Duch.) fruit. SPME had sufficient sorptive capacity to permit detection of aroma compounds having a variety of functional groups. The advantages of using SPME were its simplicity, absence of solvent, and speed. Fiber cleaning, sample collection, and desorption required ~6 min. The total analysis time was ~10 min per sample when SPME was combined with rapid gas chromatographic (GC) separation and time-of-flight mass spectrometry (TOFMS). The major volatile compounds detected from tomato and strawberry and their relative abundance were comparable with published results from purge-and-trap/GC/FID analyses. One of the primary flavor impact compounds in strawberry, 2,5-dimethyl-4-methoxy-3(2*H*)-furanone was detected by using SPME/GC/TOFMS. SPME appears to be suitable for rapid and quantitative analysis of volatile aroma compounds in tomato and strawberry fruit.

Keywords: *Lycopersicon esculentum; Fragaria* × *ananassa; headspace; aroma; chromatography; time-of-flight mass spectrometry*

INTRODUCTION

The aroma of tomato and strawberry fruit has received an increasing amount of attention from both producers and consumers due to perceived deficiencies in the sensory quality of commercially produced cultivars. Among the >300 volatile compounds produced by whole and pureed tomato fruit (Petro-Turza, 1987) and the ~200 volatile compounds produced by whole and macerated strawberry fruit (Tressl et al., 1969), only a small number are important for characteristic odors and, of these, several are odor-active at extremely low concentrations. Buttery et al. (1989) used purge-and trap extraction, with GC/FID separation and detection and olfactory threshold analysis, to determine that (*Z*)-3-hexenal, (*E*)-2-hexenal, hexanal, 1-penten-3-one, 2-isobutylthiazole, and 6-methyl-5-hepten-2-one are important volatiles for fresh ripe tomato flavor. For strawberries, similar analyses were used to determine that methyl butanoate, ethyl butanoate, methyl hexanoate, hexyl acetate, and ethyl hexanoate play an important role in aroma (Dirinck et al., 1977; Pyysalo et al., 1979; Miszczak et al., 1995). In addition to these compounds, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone and its methyl ether [2,5-dimethyl-4-methoxy-3(2*H*)-furanone], which can be present at low levels relative to the other volatile materials, are considered to be among the most important aroma constituents of strawberry (Hirvi, 1983).

The development of analytical methodologies for aromas of horticultural produce has been important for the identification of volatiles and understanding their role in aroma quality (Werkhoff and Bretschneider, 1987; Buttery et al., 1988; Dirinck et al., 1989; Pérez et al., 1992). For instance, only solvent extraction, followed by GC/MS (Pickenhagen et al., 1981), GC/selected ion monitoring MS (Hirvi and Honkanen, 1982; Hirvi, 1983), or high-performance liquid chromatography (HPLC)/UV detection (Sanz et al., 1995), has been employed successfully to detect the furanones in strawberry. Sanz et al. (1995) suggested chemical instability of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone and its derivatives [2,5-dimethyl-4-methoxy-3(2*H*)-furanone and Furaneol glucoside] prevented detection by purge-and-trap/GC/FID (Dirinck et al., 1977) or purge-and-trap/GC/MS (Pyysalo et al., 1979; Miszczak et al., 1995).

Purge-and-trap and/or simultaneous steam distillation are expensive and time-consuming processes that can be prone to methodological difficulties. The development of alternative analytical techniques that are rapid and simple has become increasingly important to reduce per sample time investment and to conduct real-time analyses. SPME is a rapid sampling technique that is well-adapted to GC analysis of volatile compounds. SPME has been applied to the analysis of volatile and nonvolatile compounds in gaseous and liquid samples (Arthur and Pawliszyn, 1990) and has been used to analyze volatiles of apple fruit, fruit beverages, and vegetable oils (Yang and Peppard, 1994; Matich et al., 1996; Song et al., 1997b). The principle of SPME technology is the partitioning process of the analyte between the fiber coating and the sample. At equilibrium, this relationship can be expressed as the partition coefficient (*K*) between the fiber and sample (Zhang and Pawliszyn, 1993). The higher the partition coefficient, the higher the fiber's affinity for the compounds. SPME provides a linear response to concentra-

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tions covering 4 orders of magnitude (Arthur et al., 1992; Louch et al., 1992).

SPME is complimentary to time-compressed gas chromatography (TCGC) and TOFMS, which permits analysis of dozens of compounds in 1−3 min (Gardner et al., 1995; Song et al., 1997b) due to the extremely rapid spectral acquisition capacity (up to 500 spectra/s) of the mass spectrometer. The use of TOFMS for detection allows compression of chromatography time by permitting significant overlap of eluting compounds without loss of analytical capacity as long as the mass spectra of overlapping compounds differ by a single *m*/*z* ratio. In addition, compression of chromatography time results in an increase in sensitivity in that the spectrometer response is concentrated over a shorter time interval than by conventional chromatography. Thus, sampling, chromatographic separation, detection, and analysis potentially can be completed in minutes per sample with enhanced sensitivity.

One objective of our investigation was to determine the partition coefficient of commercially available fiber coatings for the tomato aroma volatiles hexanal, (*E*)-2-hexenal, and 6-methyl-5-hepten-2-one, the strawberry volatiles butyl acetate, hexyl acetate, and 2,5-dimethyl-4-methoxy-3(2*H*)-furanone, and the ester precursors 1-butanol and 1-hexanol. A second objective was to compare rapidly obtained SPME/TCGC/TOFMS volatile profiles to published results from slower, more traditional purge-and-trap/GC/MS analyses of tomato and strawberry volatiles.

MATERIALS AND METHODS

Volatile Standards. Authenticated, high-purity (>95%) standards of hexanal, (*E*)-2-hexenal, 6-methyl-5-hepten-2-one, butyl acetate, hexyl acetate, butanol, hexanol, and 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (Aldrich Chemical Co., Milwaukee, WI) were combined in equal volume aliquots to create an eight-component mixture. One-half microliter of the mixture was placed in a glass volumetric flask (4.4 L) fitted with a specially made ground glass stopper containing a gastight Mininert valve (Alltech Associates, Inc., Deerfield, IL). The flask was held at 22 °C until the liquid standards were fully volatilized.

Partition Coefficient of Impact Fruit Volatiles on Different SPME Fiber Coatings. The partition coefficients of the fiber coatings for the volatile standards were determined using the method of Zhang and Pawliszyn (1993)

$$K = (A_F V_G)/(A_G V_F)$$

where A_F and A_G were MS response (total ion count peak area) for SPME and direct gas injection, respectively; V_F was the volume of the SPME coating; and V_G was the volume of the gas injected (100 μL). The sorptive coating materials for the SPME were poly(dimethylsiloxane) (PDMS, 1 cm long, 100 μm thickness, 0.612 μL volume), poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB, 1 cm long, 65 μm thickness, 0.357 μL volume), and Carbowax/divinylbenzene (Carbowax/DVB, 1 cm long, 65 μm thickness, 0.357 μL volume). The direct gas injection was by a glass 100-μL gastight syringe (Hamilton, Reno, NV). Some of the volatile materials adsorbed to the needle of the gastight syringe, resulting in an elevated MS response. Care had to be taken in optimizing the sampling procedure. Data were corrected for this effect by correction with blank injection (Song et al., 1997b). The reported data are the result of five measurements.

Before use, the SPME fiber was conditioned at 250 °C for 0.5−1 h. Sampling was accomplished by placing the SPME fiber through the Mininert valve and into the 4.4-L flask. Sampling temperature was 23 °C, and sampling duration was 12 min., which is sufficient to permit the establishment of near equilibrium for the compounds tested (Song et al., 1997b).

Absorbed volatiles were desorbed from the fiber coating by inserting the SPME fiber through a predrilled septum (Thermogreen LB-2, Supelco Co., Bellefonte, PA) and into a glass-lined, splitless injector port (200 °C) of a gas chromatograph (HP-6890, Hewlett-Packard Co., Wilmington, DE). The desorption time was 90 s. The first 20 cm of the column was cooled to <−100 °C with liquid nitrogen during the heat desorption process to cryofocus the volatile material. Volatiles were separated on a 30 m × 0.25 mm i.d. capillary column (HP-5, Hewlett-Packard) having a film thickness of 0.25 μm. Ultrapurified helium (99.999%) was used as carrier gas at a flow rate 1.5 mL/min. Linear velocity was 44 cm/s. The initial temperature of the column was 40 °C and was increased upon removal of the cryofocusing coolant at 60 °C/min to a final temperature of 250 °C, which was maintained for 1 min.

Volatile detection was by TOFMS with an electron ionization source (FCD-650, LECO Corp, St. Joseph, MI). Mass spectra were collected at a rate of 40/s over the mass range (*m*/*z*) 40−300. The electron ionization energy was 70 eV. The temperature of the ion source was 180 °C. The GC/MS transfer line temperature was 180 °C.

Fruit Aroma Collection. Ripe tomato fruit (Pik Rite) were obtained from the Horticultural Teaching and Research Center, Michigan State University. Tissue homogenates for tomatoes were prepared according to the method of Buttery et al. (1988), with a reduction in homogenization time to 15 s and incubation duration to 3 min prior to the addition of calcium chloride (Song, 1994). Ripe strawberry fruit of an unknown cultivar were obtained from a local market.

Two hundred grams of whole strawberry fruit or 350 g of tomato puree was placed in a 1.9-L jar, which was ventilated with air at rate of 30 mL/min at 23 °C. The tomato puree was agitated with a stir bar. A glass "tee" on the outlet line was fitted with a Teflon-lined half-hole septum (Alltech Associates) to create a sampling port. All of the connecting gas lines were composed of Teflon-PFE (Cole-Parmer Instrument Co., Vernon Hill, IL). After the container had been flushed for 60 min, the SPME fibers (previously cleaned by heating to 200 °C for 3 min) were exposed to the effluent gas stream for 4 min and immediately transferred to the GC injection port and desorbed for 1.5 min. GC and MS protocols were identical to those described previously. All measurements were made three times.

Identification of volatile components was confirmed by comparison of collected mass spectra with those of authenticated chemical standards and to reference spectra in a mass spectral library (National Institute for Standard Technology, Search Version 1.5, Gaithersburg, MD). In cases when the MS response was low, background noise (*m*/*z* 40−300) obtained just prior to or just after the compound of interest was subtracted from the mass spectra of the compound of interest. Data for tomato were compared to results obtained by Maul et al. (1997) using direct headspace GC/MS, and data for strawberry fruit were compared to results obtained by Pérez et al. (1992) using purge-and-trap/GC/MS.

RESULTS

Partition Coefficients of SPME Fiber Coatings. The partition coefficients of the PDMS, PDMS/DVB, and Carbowax/DVB coatings for the impact compounds differed markedly (Table 1). Among tested coatings, PDMS had the highest partition coefficient for 6-methyl-5-hepten-2-one and the lowest for the more highly polar butanol, hexanol, hexanal, and (*E*)-2-hexenal. PDMS/DVB and Carbowax/DVB had, respectively, partition coefficients that were 18- and 8-fold higher than that of PDMS for the most polar molecule, butanol. Similarly, the partition coefficient of PDMS/DVB and Carbowax/DVB was also markedly higher for hexanol,

Table 1. Partition Coefficient (*K*), Estimated Limit of Quantitation (LOQ)[a] Level for the Various SPME Fibers Using Produce Relevant Reference Standards, and Relative Standard Deviation (RSD)

	PDMS			PDMS/DVB			Carbowax/DVB		
compound	*K*	LOQ (ppb)	RSD%	*K*	LOQ (ppb)	RSD%	*K*	LOQ (ppb)	RSD%
1-butanol	4.81×10^3	71	1.5	8.14×10^4	8.6	12.2	1.63×10^4	37	11.0
1-hexanal	8.64×10^3	70	2.3	9.90×10^4	36	6.7	2.66×10^4	33	8.8
(*E*)-2-hexenal	2.07×10^4	60	2.5	1.84×10^5	20	4.3	7.48×10^4	84	5.6
butyl acetate	2.69×10^4	8.8	8.6	8.07×10^4	9.2	8.3	2.48×10^4	75	3.7
1-hexanol	2.83×10^4	10	6.7	1.55×10^5	2.0	3.4	6.83×10^4	23	6.5
hexyl acetate	4.23×10^4	2.9	13.2	8.71×10^4	1.9	1.7	6.16×10^4	3.4	3.5
4-methoxy-2,5-dimethyl-3(2*H*)-furanone	1.11×10^5	4.2	6.6	1.44×10^5	3.2	3.2	1.07×10^5	3.0	3.0
6-methyl-5-hepten-2-one	5.65×10^5	1.1	5.6	2.76×10^5	1.4	1.4	2.41×10^5	1.2	1.2

[a] The limit of quantitation was estimated to be the concentration of the analytes that produces a signal 10 times that of noise.

hexanal, and (*E*)-2-hexenal relative to PDMS. Thus, PDMS/DVB and Carbowax/DVB generated a higher system sensitivity for smaller, more polar molecules such as alcohols and aldehydes, whereas PDMS more efficiently absorbed larger, less polar molecules. All three coatings had similar partition coefficients for 2,5-dimethyl-4-methoxy-3(2*H*)-furanone. All of the fiber coating materials had the greatest affinity for 6-methyl-5-hepten-2-one relative to the other volatiles tested.

The range in partition coefficients of the fiber coatings for the volatiles tested varied widely. The partition coefficient of PDMS for 6-methyl-5-hepten-2-one was ~120-fold greater than for the compound for which the coating had the least affinity, butanol. The partition coefficient of PDMS/DVB for 6-methyl-5-hepten-2-one was ~3.4-fold greater than for the compound for which the coating had the least affinity, butyl acetate. The partition coefficient of Carbowax/DVB for 6-methyl-5-hepten-2-one was ~15-fold greater than for the compound for which the coating had the least affinity, butanol. In addition, the lowest partition coefficient PDMS/DVB had for any of the volatiles was markedly greater than the lowest partition coefficient measured for the other two coating materials. The partition coefficient of PDMS/DVB for butyl acetate was approximately 5 and 17 times greater, respectively, than the partition coefficients of Carbowax/DVB and PDMS for 1-butanol.

Volatile Compounds from Homogenized Tomato Fruit. Approximately 30 volatiles were collected and concentrated sufficiently by PDMS/DVB SPME from fresh tomato fruit to be identified by TCGC/TOFMS (Figure 1; Table 2). The identity and chromatographic order of identified compounds and the relative amounts of several of the compounds based on instrument response were roughly similar to those previously reported by Maul et al. (1997). Hexanal, (*E*)-2-hexenal, and 2-methylbutanol were relatively more abundant than other compounds in both studies. 6-Methyl-5-hepten-2-one, linalool, 1-penten-3-one, methyl salicylate, heptanal, and the nitrogen-containing compounds dimethyldiazene and 1-nitropentane were also detected using SPME/GC/TOFMS.

Volatile Compounds from Ripe Strawberry Fruit. A total of 34 aroma compounds were collected and concentrated sufficiently by PDMS/DVB SPME from whole strawberry fruit to enable detection and identification by TCGC/TOFMS (Figure 2; Table 3). Among these compounds, methyl butanoate, methyl 2-methylbutanoate, ethyl butanoate, methyl hexanoate, and hexyl acetate were the most abundant volatiles. In addition, dimethyl disulfide and 2,5-dimethyl-4-methoxy-3(2*H*)-furanone, one of the primary character impact

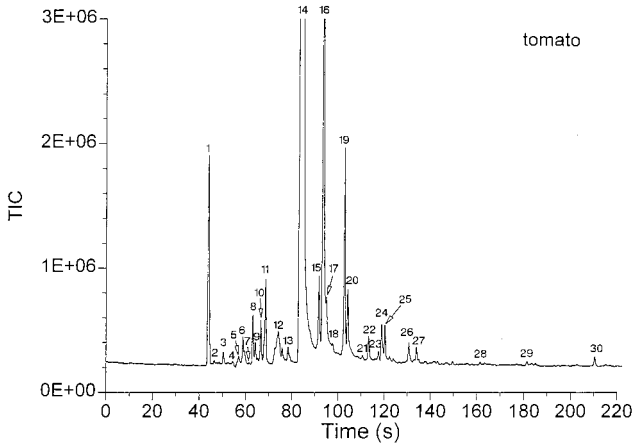

Figure 1. TIC chromatogram of headspace aroma volatile compounds from the headspace of tomato fruit puree in a ventilated jar sampled by SPME (PDMS/DVB, 65 μm thickness) and separated and detected by TCGC/TOFMS. Numbered peaks relate to numbered compounds listed in Table 1.

compounds, were also detected in the sample. The total ion count (TIC) of 2,5-dimethyl-4-methoxy-3(2*H*)-furanone represented ~4.5% of the total aroma TIC response.

DISCUSSION

SPME has been tested and has compared favorably to the commonly used purge-and-trap sample collection and concentration devices (MacGillivary and Pawliszyn, 1994; Song et al., 1997b). The variation of sorption properties of the SPME coating materials permits optimization for different analytes or analyte mixtures in a manner similar to stationary phase choices for purge-and-trap systems. In our work, the data suggest the polarity of the fiber coatings was Carbowax/DVB ≥ PDMS/DVB > PDMS. PDMS/DVB was the preferable coating material for tomato and strawberry volatile flavor analysis, as has been suggested for apples (Song et al., 1997a). Compared to the other two coatings, PDMS/DVB had the highest partition coefficient for the more polar molecules butanol, hexanol, hexanal, and (*E*)-2-hexenal. Ketones and short- and long-chain esters were efficiently extracted by all three coating materials. As a result, PDMS/DVB had a similar response to all volatiles tested and exhibited only a 3.5-fold variation in the partition coefficients for the volatile materials tested. It is also interesting to note that PDMS/DVB was able to extract the nitrogen-containing compounds such as 1-nitropentane and 2-isobutylthiazole.

The chromatographic order of the 30 compounds detected from tomato samples using PDMS/DVB fiber

Table 2. Retention Time and Relative Amount of Volatile Compounds from the Headspace of Tomato Fruit Puree As Extracted by SPME (PDMS/DVB, 65 μm Film Thickness)/TCGC/TOFMS and Direct Headspace Injection/GC/FID[a]

peak	volatile compound	SPME/TCGC/TOFMS retention time (s)	SPME/TCGC/TOFMS rel amt (%)	direct headspace/GC/FID rel amt[b] (%)
1	CO_2	43.2		
2	acetaldehyde	45.0	0.3	3.4
3	dimethyldiazene	50.1	0.3	
4	2-methylpropanal	54.2	0.9	
5	2-methylfuran	56.5	0.5	
6	2-methylpropanol	58.2	0.9	
7	3-methylbutanal	58.8	1.6	
8	2-methylbutanal	61.8	2.4	
9	1-pentene-3-one	62.4	0.5	0.1
10	2-ethylfuran	67.4	0.5	
11	2-methylbutanol	69.5	2.9	4.9
12	2-methyl-butenal	71.8	0.6	
13	pentanol	78.0	0.5	
14	hexanal	85.0	42.7	29.0
15	(*Z*)-3-hexenal	91.8	3.3	0.6
16	(*E*)-2-hexenal	92.1	22.2	5.6
17	butanol	95.1	2.8	
18	heptanal	96.0	0.2	0.31
19	1-nitropentane	103.2	8.5	
20	(*E*,*E*)-2,4-hexadienal	104.2	2.9	
21	(*E*)-2-heptenal	110.2	0.9	0.3
22	6-methyl-5-hepten-2-one	114.5	0.9	7.1
23	methyl salicylate	118.2	0.3	0.1
24	2-isobutylthiazol	119.1	1.8	0.4
25	(*E*)-2-octenal	120.2	0.8	0.8
26	linalool	130.5	0.1	0.2
27	(*E*,*E*)-2,4-decadienal	135.6	0.8	0.8
28	(*E*)-5,9-undecadien-2-one, 6,10-dimethyl	161.8	0.2	
29	2,6-dimethyl-4,7-octadien-6-ol	182.0	0.1	
30	geranylacetone	210.2	0.5	2.8

[a] Data for relative amounts are based only on instrument response, rather than quantitation using authenticated standards for each component. [b] Relative amount reported by Maul et al. (1997).

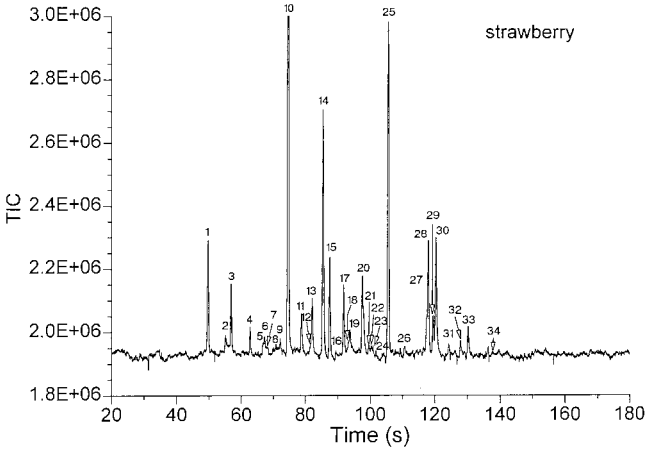

Figure 2. TIC chromatogram of headspace aroma volatile compounds from the headspace of strawberry fruit in a ventilated jar sampled by SPME (PDMS/DVB, 65 μm thickness) and separated and detected by TCGC/TOFMS. Numbered peaks relate to numbered compounds listed in Table 2.

was identical with and the relative amounts were consistent with the earlier findings of Buttery et al. (1988, 1989), Baldwin et al. (1991), and Maul et al. (1997). In the cited investigations, the headspace of tomato puree was concentrated by flushing the puree with nitrogen and capturing the released volatiles on a trapping material (Buttery et al., 1988, 1989) or by concentrating the headspace volatiles at the head of the column using a combination of pressure and low temperature (Baldwin et al., 1991; Maul et al., 1997). The similarity of results suggests that SPME is a satisfactory alternative to these two sampling techniques. Of the compounds detected by Baldwin et al. (1991) and Maul et al. (1997), only β-ionone and β-damascenone were not found in our samples, which may be a result of differences in the cultivars evaluated or the lower temperature of the homogenate in our study.

The esters methyl butanoate, ethyl butanoate, and ethyl hexanoate (Pérez et al., 1992) and 2,5-dimethyl-4-methoxy-3(2*H*)-furanone (Hirvi, 1983) found in our study play an important role in flavor acceptability of strawberry fruit. 2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone and its methyl ether 2,5-dimethyl-4-methoxy-3(2*H*)-furanone have been identified in overripe strawberries by using HPLC/UV detection (Sanz et al., 1995). Whereas these compounds were not detected with purge-and-trap sampling and GC/FID or GC/MS, despite the relatively high sensitivity of FID (Dirinck et al., 1977; Pyysalo et al., 1979; Pérez et al., 1992), they were detected in our system, suggesting SPME can collect and concentrate sufficient volatile material to assay compounds present in the atmosphere at extremely low levels. The failure to detect 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone in our study may be caused either by its low abundance in the headspace and/or by chemical instability (Hirvi and Honkanen, 1982). However, we were able to identify 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone in the vapor phase over the powder of an authenticated standard using SPME/TCGC/TOFMS (data not shown), which does not support the latter possibility. The differences in volatile production may also be a result of differences in cultivars and the developmental stage of the fruits, both important factors in aroma analysis (Douillard and Guichard, 1990).

Although the data for the relative amount based on detector response shown in Tables 2 and 3 cannot be used for quantitative purposes, the data give general

Table 3. Retention Time and Relative Amount of Volatile Compounds from the Headspace of Whole, Ripe Strawberry Fruit As Extracted by SPME (PDMS/DVB, 65 μm Film Thickness)/TCGC/TOFMS and Purge-and-Trap/GC/FID by Pérez et al. (1992)[a]

peak	volatile compound	SPME/TCGC/TOFMS retention time (s)	SPME/TCGC/TOFMS rel amt (%)	P&T/GC/FID rel amt[b] (%)
1	CO_2	49.7		
2	acetone	55.1	0.5	
3	methyl acetate	56.8	0.8	
4	ethyl acetate	62.7	2.3	
5	methyl propionate	64.3	0.9	
6	1-methylethyl acetate	67.3	0.3	
7	butanol	71.1	0.3	
8	ethyl propionate	73.1	0.4	2.2
9	propyl acetate	76.4	0.5	
10	methyl butanoate	74.6	28.2	18.2
11	dimethyl disulfide	78.8	1.3	0.6
12	2-methylpropyl acetate	82.1	0.1	
13	methyl 3-methylbutanoate	82.3	3.2	
14	methyl 2-methylbutanoate	85.5	13.2	0.7
15	ethyl butanoate	87.5	1.7	22.9
16	butyl acetate	89.4	0.2	1.9
17	methylethyl butanoate	91.7	2.4	0.4
18	ethyl 3-methylbutanoate	93.8	0.3	3.5
19	3-methylpentanol	96.6	0.4	
20	3-methylbutyl acetate	97.9	1.6	1.1
21	ethyl 3-methylpentanoate	99.5	0.4	
22	*s*-methylbutanethioic acid	100.6	0.1	
23	propyl butanoate	100.9	0.2	4.5
24	hexyl acetate	104.2	0.2	
25	methyl hexanoate	105.5	24.5	8.5
26	2-methylpropyl butanoate	110.7	0.6	0.6
27	methylpropyl butanoate	117.5	0.9	
28	ethyl hexanoate	118.0	3.4	28.5
29	3-hexenyl acetate	119.5	1.2	0.3
30	hexyl acetate	120.3	9.6	4.5
31	3-methylpentyl acetate	123.8	0.4	
32	3-methylbutyl 2-methylpropionate	127.9	0.4	
33	2,5-dimethyl-4-methoxy-3(2*H*)-furanone	130.2	4.5	
34	methyl octanoate	137.7	0.5	

[a] Data for relative amounts are based only on instrument response, rather than quantification using authenticated standards for each component. [b] Data were calculated directly from relative amount reported by Pérez et al. (1992).

information about performance of the SPME system and are comparable to those from purge-and-trap sampling. In the strawberry profile of our study, there appear to be marked differences between the content of the methyl and ethyl butanoate and hexanoate esters as measured by SPME versus the purge-and-trap results of Pérez et al. (1992). However, the fact that the methyl butanoate and methyl hexanoate are, respectively, enhanced in our study relative to ethyl butanoate and ethyl hexanoate suggests that methyl alcohol was esterified to a greater extent than ethyl alcohol by alcohol acetyl transferase (EC 2.3.1.84) in the fruit in our study. The opposite appears to be true for the study by Pérez et al. (1992), in which the ethyl esters appear to predominate. This contention is further supported by the relative amounts of methyl and ethyl propionate in our study, in which the methyl ester is more abundant. Also consistent is the relatively greater proportion of ethyl propinoate in the Pérez et al. (1992) study relative to the present study. Thus, the differences between the two studies probably reflects a divergence in the physiology of aroma formation, which is widely noted as affecting the quantitative and qualitative volatile constituents of fruit (Baldwin et al., 1991; Miszczak et al., 1995), rather than differences in performance of the volatile collection and detection systems. Similarly, the differences in the relative quantities of tomato volatiles between our study and that of Maul et al. (1997) may, to a significant extent, reflect differences in the makeup of substrates of aroma-generating reactions.

The data for strawberry and tomato are supportive of earlier findings that SPME appears to be a convenient and appropriate sampling technology for rapid qualitative and quantitative volatile sampling in horticultural produce (Matich et al., 1996; Steffen and Pawliszyn, 1996; Song et al., 1997b). The limit of quantitation (Table 1) based on a signal-to-noise ratio of ~10 suggests SPME is suitable for GC/MS analysis in which the original volatile components are present in the low to middle parts per billion range in the headspace surrounding fresh fruit and vegetables and their products. The combination of SPME with a high-speed analysis system such as TCGC/TOFMS should be useful for real-time physiological evaluations, plant breeding screening programs, and quality control processes in which rapid analysis is required.

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LITERATURE CITED

Arthur, C. L.; Pawliszyn, J. Solid-phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem*. **1990**, *62*, 2145−2148.

Arthur, C. L.; Killam, L. M.; Buchholz, K. D.; Pawliszyn, J.; Berg, R. Automation and optimization of solid-phase microextraction. *Anal. Chem*. **1992**, *64*, 1960−1966.

Baldwin, E. A.; Nispero-Carriedo, M. O.; Moshonas, M. G. Quantitative analysis of flavor and other volatiles and for certain constituents of two tomato cultivars during ripening. *J. Am. Soc. Hortic. Sci.* **1991**, *116*, 265−269.

Buttery, R. G.; Teranishi, R.; Ling, L. C.; Flath, R. A.; Stern, D. J. Quantitative studies on origins of fresh tomato aroma volatiles. *J. Agric. Food Chem.* **1988**, *36*, 1247−1250.

Buttery, R. G.; Teranishi, R.; Flath, R. A.; Ling, L. C. Fresh tomato volatiles: composition and sensory studies. In *Flavor Chemistry: Trends and Development*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; ACS Symposium Series 388; American Chemical Society: Washington, DC, 1989; pp 213−222.

Dirinck, P.; Schreyen, L.; Schamp, N. Aroma quality evaluation of tomatoes, apples, and strawberries. *J. Agric. Food Chem.* **1977**, *25*, 759−762.

Dirinck, P.; De Pooter, H.; Schamp, N. Aroma development in ripening fruits. In *Flavor Chemistry: Trends and Developments*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; ACS Symposium Series 388; American Chemical Society: Washington, DC, 1989; pp 23−34.

Douillard, C.; Guichard, E. The aroma of strawberry (*Fragaria ananassa*): characterisation of some cultivars and influence of freezing. *J. Sci. Food Agric.* **1990**, *50*, 517−531.

Gardner, B. D.; Johnson, J. A.; Artaev, V. B.; Sparkman, O. D.; Holland, J. F. Rapid sampling for rapid analysis: a new method for VOCs in drinking water. *Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics*, Atlanta, GA, May 21−26, 1995; ASMS: Sante Fe, NM, 1995.

Hirvi, T. Mass fragmentographic and sensory analyses in the evaluation of the aroma of some strawberry varieties. *Lebensm.-Wiss. Technol.* **1983**, *16*, 157−161.

Hirvi, T.; Honkanen, E. The volatiles of two new strawberry cultivars, Annelie and Alaska Pioneer, obtained by backcrossing of cultivated strawberries with wild strawberries, *Fragaria vesca*, Rügen and *Fragaria virginiana*. *Z. Lebensm. Unters. Forsch.* **1982**, *175*, 113−116.

Louch, D.; Motlagh, S.; Pawliszyn, J. Liquid-coated fused silica fibers. *Anal. Chem.* **1992**, *64*, 1187−1199.

MacGillivary, B.; Pawliszyn, J. Headspace solid-phase microextraction versus purge and trap for the determination of substituted benzene compounds in water. *J. Chromatogr. Sci.* **1994**, *32*, 317.

Matich, A. J.; Rowan, D. D.; Banks, N. Solid-phase microextraction for qualitative headspace sampling of apple volatiles. *Anal. Chem.* **1996**, *68*, 4114−4118.

Maul, F.; Sargent, S. A.; Huber, D. J.; Balaban, M. O.; Luzuriaga, D. S.; Baldwin, E. A. Non-destructive quality screening of tomato fruit using Electronic Nose technology. *1997 Proceedings of the Florida State Horticultural Society*; 1998; in press.

Miszczak, A.; Forney, C. F.; Prange, R. K. Development of aroma volatiles and color during postharvest ripening of Kent strawberries. *J. Am. Soc. Hortic. Sci.* **1995**, *120*, 650−655.

Pérez, A. G.; Rios, J. J.; Sanz, C.; Olias, J. M.. Aroma components and free amino acids in strawberry variety Chandler during ripening. *J. Agric. Food Chem.* **1992**, *40*, 2232−2235.

Petro-Turza. Flavor of tomato and tomato products. *Food Rev.* **1987**, *2*, 309−351.

Pickenhagen, W.; Velluz, A.; Passerat, J.; Ohloff, G. Estimation of 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Furaneol) in cultivated and wild strawberries, pineapples and mangoes. *J. Sci. Food Agric.* **1981**, *32*, 132−1134.

Pyysalo, T.; Honkanen, E.; Hirvi, T. Volatiles of wild strawberries, *Fragaria vesca* L., compared to those of cultivated berries, *Fragaria x ananassa* cv. Senga Sengana. *J. Agric. Food Chem.* **1979**, *27*, 19−22.

Sanz, C.; Richardson, D. R.; Pérez, A. G. 2,5-dimethyl-4-hydroxy-3(2H)-furanone and derivatives in strawberries during ripening. In *Fruit Flavors: Biogenesis, Characterization and Authentication*; Rouseff, R., Leahy, M. M., Eds.; ACS Symposium Series 596; American Chemical Society; Washington, DC, 1995; pp 268−275.

Song, J. Einfluss verschiedener Erntzeitpunkte auf die Fruchtreif unter besonderer Berüksichtigung der Aromabilding bei Äpfeln, Tomaten und Erdbeeren. Ph.D. Thesis, Universität Hohenheim, Stuttgart, Germany, 1994.

Song, J.; Gardner, B.; Holland, J.; Beaudry, R. Solid-phase micro-extraction time-of-flight mass spectrometry for rapid and quantitative analysis of aroma. *Proceedings of the 45th ASMS Conference on Mass Spectrometer and Allied Topics*, Palm Springs, CA, June 1−5, 1997; ASMS: Santa Fe, NM, 1997a.

Song, J.; Gardner, B.; Holland, J.; Beaudry, R. Rapid analysis of volatile flavor compounds in horticultural produce using SPME and GC/time-of-flight mass spectrometry. *J. Agric. Food Chem.* **1997b**, *45*, 1801−1807.

Steffen, A.; Pawliszyn, J. Analysis of flavor volatiles using headspace solid-phase microextraction. *J. Agric. Food Chem.* **1996**, *44*, 2187−2193.

Tressl, R.; Drawert F.; Heimann, W. Gas chromatographic and mass spectrometry inventory of aromatic constituents of strawberries. *Z. Naturforsch.* **1969**, *B24*, 1201.

Werkhoff, P.; Bretschneider, W. Dynamic headspace gas chromatography: concentration of volatile components after thermal desorption by intermediate cryofocusing in a cold trap. *J. Chromatogr.* **1987**, *405*, 87−98.

Yang, X.; Peppard, T. Solid-phase microextraction for flavor analysis. *J. Agric. Food Chem.* **1994**, *42*, 1925−1930.

Zhang, Z. Y.; Pawliszyn, J. Headspace solid-phase microextraction. *Anal. Chem.* **1993**, *65*, 1843−1852.

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