Rapid Analysis of Volatile Flavor Compounds in Apple Fruit Using SPME and GC/Time-of-Flight Mass Spectrometry

Jun Song,[†] Ben D. Gardner,[‡] John F. Holland,[§] and Randolph M. Beaudry*[,†]

Department of Horticulture, Department of Chemistry, and Department of Biochemistry, Michigan State University, East Lansing, Michigan 48824

Solid-phase microextraction (SPME), time-compressed chromatography (TCC), and time-of-flight mass spectrometry (TOFMS) were examined for their suitability and compatibility for rapid sampling, separation, and detection of apple flavor volatiles. Flavor-contributing volatile compounds were found to have relatively high partition coefficients on a 100 μm thick coating of polydimethylsiloxane (PDMS) on a SPME fiber. The time required to saturate the PDMS coating was highly volatile-dependent, varying from less than 2 min to greater than 30 min. However, the response of this system was linear in the ppb to ppm range when the adsorption duration was standardized. The speed of the TOF mass spectrometer permitted identification and quantification of compounds having chromatographic peak widths of only a fraction of a second. The unskewed nature of fragmentation patterns obtained allowed individual component spectral characterization of unknown compounds even when not fully chromatographically separated. Thus, the time required for chromatography could be reduced by an order of magnitude without loss in analytical performance. Typical analysis times for complex mixtures were 2−5 min as compared with 20−60 min required for standard purge-and-trap analyses.

Keywords: *SPME (solid-phase microextraction); time-compressed chromatography; time-of-flight mass spectrometry; headspace sampling; partition coefficient; purge-and-trap; volatiles; flavor; apples*

INTRODUCTION

Aroma is one of the most important quality criteria of fruit and vegetable products, and a considerable amount of research has been devoted to developing analytical techniques for characterizing aroma-producing compounds. Both qualitative and quantitative information is desired in order to monitor produce flavor quality and ripeness and to provide quality control for fresh and processed products. Progress in aroma research is impeded, however, by slow sampling, separation, and detection methodologies. Fruit aroma research is subject to a number of constraints that make more rapid analysis desirable. The seasonal nature of fruit harvest and production requires that new protocols be worked out quickly and efficiently in order to meet research 'time windows' established by the commodity. Typical horticultural and biochemical research requires multiple experimental treatments as part of a statistically relevant design, so sample numbers for most experiments are relatively large (tens to hundreds), and often an entire study must be completed in a limited time. In fruit aroma biosynthesis studies, especially those evaluating the response to metabolic precursor feeding, aroma production is dynamic with short (minute) and long-term (hour) temporal components. As a result, sampling must be repetitive and span a wide range of time intervals. Furthermore, an analytical system should be sufficiently flexible to work with both flow-through and static systems having a broad range of components. Volatile aroma compounds are typically analyzed using either direct headspace (Neubeller and Buchloh, 1978) or dynamic headspace purge-and-trap methods (Streif, 1981; Werkhoff and Bretschneider, 1987). While direct headspace analysis is largely confined to higher concentration samples, purge-and-trap sampling can enhance sensitivity by enriching volatile components on a polymer bed. The dynamic headspace purge-and-trap method has been thoroughly standardized by Buttery *et al.* (1989), Mattheis *et al.* (1991), and Song and Bangerth (1993) for routine analysis of tomato and apple fruit volatiles. However, this technique is expensive, time-consuming, and prone to methodological difficulties. During analysis, the sample preparation step for purge-and-trap analyses is frequently the most time-consuming and labor intensive step. It is also the primary point of analyte loss from the matrix.

An alternate sampling methodology, solid-phase microextraction (SPME), has the potential to reduce the time investment in sampling and should work well in combination with rapid separation and detection systems. SPME has been applied to the analysis of volatile and nonvolatile compounds (Arthur and Pawliszyn, 1990) in gaseous and liquid samples and to analyze flavor in fruit juice beverages, in vegetable oils (Yang and Peppard, 1994), and in orange juice (Steffen and Pawliszyn, 1996). SPME has been shown to be a simple and effective sampling method providing a linear response to concentrations covering four orders of magnitude (Arthur *et al.*, 1992; Louch *et al.*, 1992). It is also rapid, providing complete extraction and transfer of volatile organic compounds in under five min (Gardner *et al.*, 1995).

The recent development of a gas chromatographic detector utilizing TOFMS with time array detection (TAD) has the analysis speed needed to take advantage of the rapidity of SPME sampling technology. This instrument system additionally enables the use of time-compressed chromatography (TCC) whereby temporally unresolved components can be characterized by their

* Author to whom correspondence should be addressed.
[†] Department of Horticulture.
[‡] Department of Chemistry.
[§] Department of Biochemistry.

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unique mass spectra. TCC permits a significant reduction in the time invested in separation. To date, SPME in conjunction with TCC and TOFMS for analysis of flavor volatiles in horticultural produce has not been evaluated. In this paper, we report on SPME sampling characteristics (speed, variability, linearity, saturation kinetics, and matrix effects) in combination with rapid GC techniques (short, narrow bore columns, high linear flow rates, and high temperature ramp rate) and a TOF mass spectrometer for detection as a system for rapid and quantitative analysis of aroma volatiles in apples.

EXPERIMENTAL PROCEDURES

Volatile Aroma Standards Preparation. Volatile aroma compounds were purchased from Sigma Co. and Fluka Chemical Corp. Standard mixtures were prepared with 0.3−1.0 μL of butyl acetate, ethyl 2-methyl butanoate, hexyl acetate, 1-butanol, 1-hexanol, and 6-methyl-5-hepten-2-one in specially-built gas-tight 4.4-L glass volumetric flasks fitted with a tapered ground glass stopper containing a gas-tight Mininert valve (Alltech Assoc., Inc., Deerfield, IL). The mixed standards sample was applied to a small paper filter disk in the neck of the flask and dropped to the flask bottom. The flask was sealed, and the liquid material was allowed to vaporize to provide known headspace concentrations ranging from 5 to 10 μL L^{-1}.

Sampling. *SPME Procedure.* A SPME (Supelco Co., Bellefonte, PA) fiber coated with polydimethylsiloxane (PDMS, 1 cm long, 100 μm thickness) was used to collect and concentrate volatiles by virtue of its sorption characteristics (Arthur and Pawliszyn, 1990). The SPME device consisted of a retractable fiber enclosed in a sheath. During sampling, after entering the sample container, the fiber was extended, exposing the sorption surface. The fiber was then retracted prior to removal from the sample container. The fiber was preconditioned at 250 °C for 1−2 h. Various sample exposure times were used for adsorption, and the volatiles were desorbed from the fiber for 90 s at 250 °C into the glass-lined, splitless injector port of a GC (HP-6890, Hewlett Packard Co.). All SPME samplings were carried out at 23 °C in triplicate unless otherwise noted.

SPME Saturation Kinetics. SPME fibers were exposed to the headspace of 4.4-L flasks containing a mixture of butyl acetate and hexyl acetate at a concentration of approximately 5 μL L^{-1}. Fibers were held in the atmosphere of the flask for specific lengths of time ranging from 5 to 480 s. Analyses were carried out using a GC with a flame ionization detector (FID).

To determine saturation kinetics in complex mixtures of volatiles, apple fruit (*Malus domestica* Borkh. cv. Golden Delicious) stored for 2−3 months at 0 °C were warmed to room temperature (23 °C). Intact apple fruit (300−450 g) were placed in a 3-L flask with purified air passing through at a flow rate of 25−30 mL min^{-1}. Sampling of volatile compounds was accomplished by placing the SPME fiber into a glass tee, fitted with a Teflon-lined halfhole septum (Alltech Assoc. Inc., Deerfield, IL) located at the outlet of the flask. All the connecting gas lines were composed of Teflon.

Apple fruit volatiles reached steady-state concentration in the flask within 4−6 h, after which time SPME fibers were exposed to the volatiles emanating from the flask for varying lengths of time up to 24 min. Response determinations were made three times for each exposure period. While numerous volatiles were tracked, data are reported for butyl acetate, butanol, hexyl acetate, hexyl 2-methyl butanoate and α-farnesene, as these compounds appeared to exhibit the full range of responses detected.

SPME Response Linearity. A gas mixture containing butyl acetate, ethyl 2-methyl butanoate, and hexyl acetate was prepared for the standards described above. A stream of volatiles-free nitrogen gas (1−2 mL L^{-1}) was passed through the flask to dilute the volatiles and to generate a wide range of volatile concentrations. The flask was periodically sealed, and the concentration of the volatiles in the flask was determined by comparison to the gas standards described previously. A 100-μL gas sample was removed by using a gas-tight syringe (Hamilton No. 1810 with stainless steel needle) and directly injected to a gas chromatograph (Carle AGC Series 400) equipped with a FID, which was used to measure volatile vapor concentrations. The GC was equipped with a packed column (10% DEGS-PS, 80/100 mesh Supelcoport, 3.3 m long, 3 mm id.) and was maintained at 140 °C. Helium was used as the carrier gas at a flow rate of 20 mL min^{-1}. Some volatiles, such as hexyl acetate and 6-methyl-5-hepten-2-one, were found to adsorb to the steel needle (data not shown), and care had to be taken in optimizing the sampling procedure. Pumping the syringe plunger 15−20 times (which apparently saturated the adsorption sites inside the needle) gave a consistent GC response, such that the standard's response had a coefficient of variation of only 2−5%. By this means, any effect of needle adsorption was removed from GC response.

After establishing the gas concentrations in the dilution flask, the TOFMS response was determined using the SPME fiber with a 6-min sampling time (see below). TOFMS response was correlated with volatile concentration.

SPME Partition Coefficient. The partition coefficient (K) of the SPME fiber coating was determined for standard mixtures (5−10 μL L^{-1}) of butyl acetate, ethyl 2-methyl butanoate, hexyl acetate, butanol, hexanol, and 6-methyl-5-hepten-2-one. The SPME fiber was exposed to the volatiles for sufficient time (6−8 min) to allow the coating to reach equilibrium with the flask headspace. K was determined using the following equation (Zhang and Pawliszyn, 1993):

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

where A_F and A_G are, respectively, the peak areas from the GC response to the fiber coating and direct gas injection, V_F is the volume of the coating (calculated to be 8×10^{-4} cm^3), and V_G is the volume of the gas injected (100 μL). Five measurements of K were made per volatile.

Purge-and-Trap Procedure. Purge-and-trap analysis was performed for comparison to the SPME technique. Tenax TA (100 mg, 60/80 mesh, Alltech) was placed in glass tubes (5 cm long, 4 mm id.) with glass wool plugs at both ends of the Tenax. Apple aroma volatiles were collected by inserting a Tenax glass tube into the gas outlet of the above-mentioned sample jars containing apple fruit. Volatiles were adsorbed onto the Tenax for 10 min at a flow rate of 100 mL min^{-1}. The tubes were desorbed using a specially-built desorption unit heated to 250 °C for 10 min while being purged with ultra purified helium (99.999%) at a flow rate of 35 mL min^{-1}. A short 0.2 m long × 0.53 mm id. deactivated fused silica precolumn was attached to the injection port of a Varian 3400 (Varian Analytical). A specially-built cryofocusing unit was used to cool the precolumn to less than −100 °C during the heat desorption process. After cryofocusing, the aroma compounds were then volatilized by heating the cryofocusing unit to 150 °C in a few seconds.

Separation and Detection. *SPME/GC/TOFMS of Apple Volatiles*. Adsorbed volatiles were desorbed from the fiber into the HP-6890 GC as described previously. Volatiles were separated using a capillary column (HP-5, 5 m × 0.1 mm id., 0.34 μm coating thickness). The carrier gas was ultra purified helium (99.999%) at a flow rate of 0.5 mL min^{-1}. The temperature program was isothermal for 1.5 min at 40 °C and then raised at the rate of 50 °C min^{-1} to 250 °C, and held for 2 min. The GC/MS transfer line temperature was 220 °C. Volatile detection was performed by TOFMS using electron impact ionization (FCD-650, LECO Corp., St. Joseph, MI). Mass spectra were collected at a rate of 40 spectra/s over a range of m/z 40−300. The ionization energy was 70 eV.

Data were analyzed using LECO deconvolution software. Identification of volatile components was confirmed by comparison of collected mass spectra with those of authenticated standards and spectra in the National Institute for Standards and Technology (NIST) mass spectral library, Search Version 1.1.

Purge-and-Trap/GC of Apple Volatiles. Volatiles were desorbed from the Tenax as described above and separated using a capillary column (HP-5, 45 m long × 0.25 mm id., 0.25 μm thick coating). The temperature program was isothermal

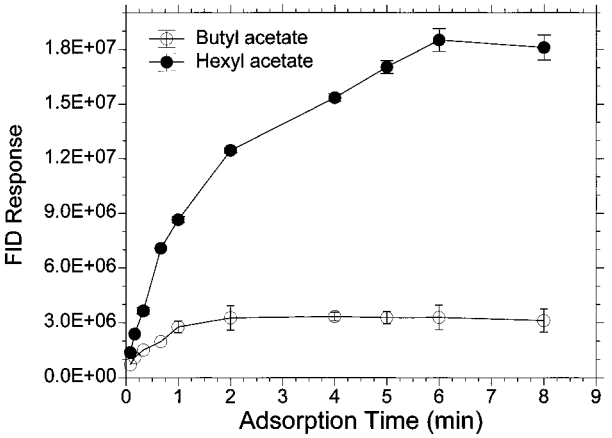

Figure 1. GC/FID response for a mixture of butyl acetate and hexyl acetate as affected by adsorption time on a SPME fiber.

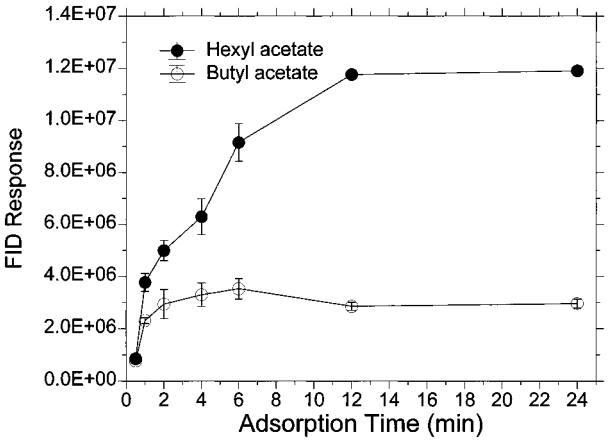

Figure 2. GC/FID response for butyl acetate and hexyl acetate in a complex mixture of apple volatiles as affected by adsorption time on a SPME fiber.

for 5 min at 40 °C and then raised 8 °C min^{-1} to 250 °C and held for 15 min. Detection was by FID at 300 °C.

RESULTS

Sampling. *SPME Saturation Kinetics.* The equilibration times for butyl acetate and hexyl acetate standards using the PDMS coating were approximately 2 and 6 min, respectively (Figure 1). The times required for butyl and hexyl acetate to reach equilibrium when in a complex mixture from ripe apple fruit were approximately 4 and 12 min, respectively (Figure 2). Other compounds in the mixture having rapid adsorption kinetics included 2-methylbutyl acetate and 1-butanol (Figure 3). However, hexyl 2-methyl butanoate and α-farnesene did not reach equilibrium in 24 min (Figure 4). The GC response as shown in Figure 3 for 2-methylbutyl acetate in the complex mixture declined as the adsorption time increased beyond 12 min. The nearly linearly increasing response for most compounds appeared to be in the first 1−4 min.

SPME Response Linearity. The response of SPME fiber to volatile concentration was linear for the three compounds tested after 6-min adsorption (Figure 5). For TOFMS detection at 10× background noise, the concentrations of butyl acetate, ethyl 2-methyl butanoate, and hexyl acetate extrapolated to 0.008, 0.0012, and 0.004 μL L^{-1}, respectively.

SPME Partition Coefficients. The PDMS coating/air partition coefficients of SPME fibers for tested aroma impact apple volatiles ranged 33-fold from 1-butanol

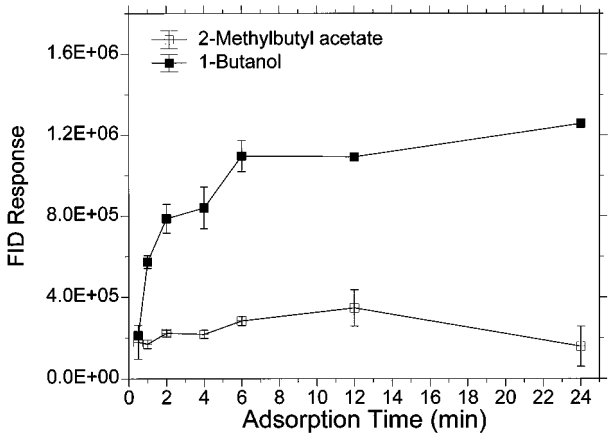

Figure 3. GC/FID response of 2-methylbutyl acetate and butanol in a complex mixture of apple volatiles as affected by adsorption time on a SPME fiber.

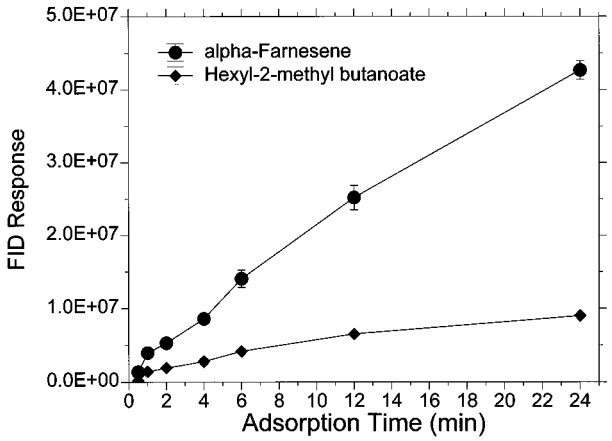

Figure 4. GC/FID response of α-farnesene and hexyl 2-methylbutanoate in a complex mixture of apple volatiles as affected by adsorption time on a SPME fiber.

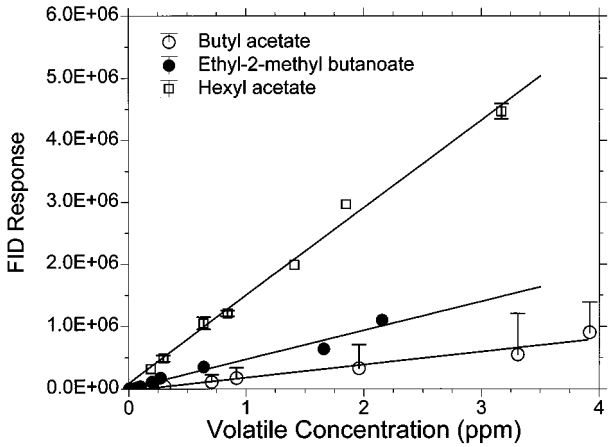

Figure 5. Effect of volatile headspace concentration on the linearity of GC/FID response for butyl acetate, ethyl 2-methylbutanoate, and hexyl acetate adsorbed onto a SPME fiber for 6 min at 23 °C.

with 1.7 × 10^4 to 6-methyl-5-hepeten-2-one with 5.6 × 10^5 (Table 1). The dominant influence appears to be the number of carbons in these linear molecules.

SPME Response Variability. With the exception of butyl acetate, the calculated standard errors in these tests resulted in coefficients of variation ranging from 2 to 10%. Butyl acetate varied beyond this range in the linearity tests at concentrations above 3 μL L^{-1}.

Separation. *SPME/GC of Apple Volatiles.* Using rapid chromatography techniques, apple volatiles con-

Table 1. Experimental Partition Coefficient (log *K*) Values between Coating and Gas Phase of Some Volatiles in Apples

compound	partition coeff	log *K*
butyl acetate	2.7×10^4	4.44
ethyl 2-methylbutanoate	3.35×10^5	5.51
hexyl acetate	2.3×10^5	5.36
1-butanol	1.7×10^4	4.21
1-hexanol	2.1×10^5	5.32
6-methyl-5-hepten-2-one	5.65×10^5	5.75

Table 2. Volatile Compounds in Golden Delicious Apple Fruit, Sampled with SPME (PDMS, 100 μm) and Identified by TOFMS

		retention time (min)	
peak	volatile compd	SPME	purge-and-trap
1	pentane	1.082	
2	acetone	1.132	
3	1-butanol	1.322	
4	propyl acetate	1.494	
5	propyl propanoate	1.524	
6	butyl acetate	1.619	13.45
7	ethyl 2-methylbutanoate	1.639	13.80
8	2-methylbutyl acetate	1.753	15.80
9	propyl butanoate	1.802	
10	butyl propyrate	1.932	
11	pentyl acetate	2.005	
12	butyl 2-methylbutanoate	2.105	
13	butyl butanoate	2.164	
14	hexyl acetate	2.396	21.34
15	butyl-2-methylbutanoate	2.437	
16	pentyl butanoate	2.460	
17	hexyl propyrate	2.492	
18	propyl 2-methyl-2-butenoate	2.650	
19	hexyl 2-methylpropyrate	2.855	
20	not identified	2.893	
21	hexyl butanoate	3.183	
22	butyl hexanoate	3.202	
23	4-methoxyallylbenzene	3.223	
24	hexyl 2-methylbutanoate	3.264	32.76
25	2-methylbutyl hexanoate	3.395	
26	hexyl pentanoate	3.633	
27	2-methylpropyl 2-methyl-butanoate	3.754	
28	hexyl hexanoate	4.002	38.82
29	α-farnesene	4.453	41.75

taining 1−15 carbons could be eluted in about 2 min (Table 2, Figure 6a). In all, 29 compounds other than CO_2 were detected and identified in Golden Delicious apple fruit. Using the SPME, dominant volatiles by response were in decreasing order as follows: α-farnesene, hexyl 2-methylbutanoate, hexyl hexanoate, hexyl butanoate, butyl hexanoate, hexyl acetate, and 2-methylbutyl acetate. There was a tendency for the response to increase with larger, more lipophilic and nonpolar compounds. Propyl acetate, butyl acetate, hexyl acetate, ethyl 2-methylbutanoate, 2-methylbutyl acetate, hexyl butanoate, butyl hexanoate, and hexyl hexanoate are dominant volatile compounds in apples (Paillard, 1991). α-Farnesene and 4-methoxyallylbenzene were also identified.

Purge-and-Trap/GC of Apple Volatiles. The chromatography of the purge-and-trap sampled volatiles took in excess of 40 min, which was roughly 10 times longer than for the rapid chromatography techniques used with the SPME device. Five of the compounds separated were identified by comparison of retention times to those of authenticated compounds (Figure 6b).

Detection. *SPME/GC/TOFMS of Apple Volatiles.* Detection and quantification of apple volatiles from a complex matrix via TOFMS using TCC did not require baseline resolution. The rapid spectral acquisition rate of 40 spectra/s of the TOFMS permitted 40−80 spectra to be collected over the typical 1−2-s peak widths (Figure 7). Co-eluting compounds such as butyl hexanoate and hexyl butanoate differing by at least one *m/z* could be identified and quantified. For instance, butyl hexanoate and hexyl butanoate were successfully deconvoluted using *m/z* 117 and *m/z* 89, respectively, although elution times differed by only 0.2 s. Since TOFMS generates unskewed spectra consisting of true fragmentation relationships, complete spectral characterization is readily accomplished for each analyte. These compounds were quantified using the unique ions found in the full spectra, which were identified either in the NIST library or generated from authenticated standards. The total time invested per analysis for SPME/TCC/TOFMS was approximately 10 min.

Purge-and-Trap/GC/FID of Apple Volatiles. Detection and quantification of apple volatiles from a complex matrix using an FID required baseline resolution. This was obtained using a longer column and slower chromatographic techniques (Figure 6b). The total time invested per analysis for purge-and-trap/traditional GC/FID was between 100 and 120 min.

DISCUSSION

Investigations of aroma synthesis in biological systems often require an analytical system that is capable of both high throughput and adaptability to static and flow-through measurements of various volumes. To date, much of the time investment in flavor analyses has been for sample collection and preparation. Sampling methods for extracting flavor compounds from horticultural products include direct headspace (Neubeller and Bochloh, 1982), liquid−liquid extraction (Weurman, 1969), supercritical extraction (Bundschuh *et al.*, 1986), and dynamic headspace with adsorbents such as charcoal (Streif, 1981) or Tenax (Dirinck *et al.*, 1989). However, the disadvantages of these methods are the lengthy analysis time, which has significantly limited sample throughput and added to experimental complexity.

Ideally, analytical methods for flavor research on horticultural produce should be fast, inexpensive, solventless, relatively independent of the instrument design, and amenable to automation. They should also be applicable to gaseous and liquid samples and have a large linear dynamic range while retaining excellent detection limits. Furthermore, they should be able to function as a screening technique or be used in the quantitative analysis of selected volatile compounds or classes of compounds for monitoring physiological processes that can be directly related to biochemical changes. SPME meets these criteria (Louch *et al.*, 1992; Zhang and Pawliszyn, 1993; Buchholz and Pawliszyn, 1994).

The primary factors affecting the linear range and sensitivity of detection using SPME are the fiber's stationary phase and the properties of the GC detector. In our research, SPME exhibited good linearity of response for volatiles ranging in concentration from ppb to ppm with negligible effects from matrix variations (i.e., water vapor). Volatile concentrations in horticultural produce vary from 0.01 to 10 ppm (Paillard, 1990). Dominant volatiles like butyl acetate and hexyl acetate can reach the 0.5−1 ppm level during fruit ripening (Paillard, 1990), and hexanal in tomatoes can be as high as 3.1 ppm (Buttery *et al.*, 1989). This suggests that SPME sampling should be sensitive enough to be used for dynamic investigations of impact volatiles. For

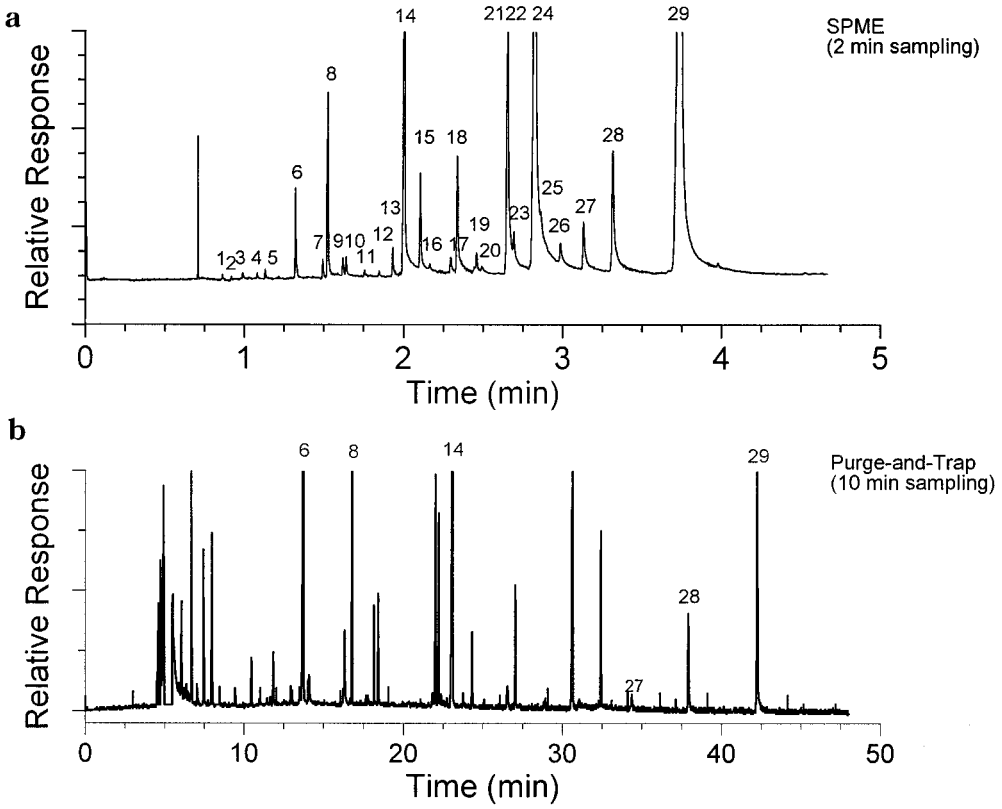

Figure 6. Qualitative comparison of chromatograms for SPME/GC/TOFMS and traditional purge-and-trap volatile headspace analysis with GC/FID.

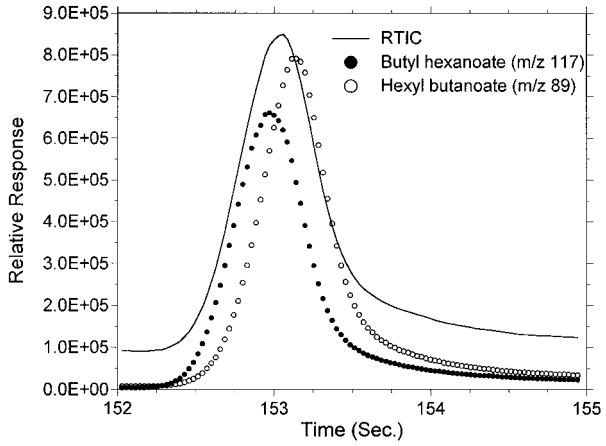

Figure 7. Demonstration of high speed spectral generation (40 spectra/s) enabling the detection and quantification of coeluting compounds by using GC/TOFMS. The solid line represents the reconstructed total ion current (RTIC). Retention times differ by approximately 0.2 s.

SPME, the capacity of the fiber is a function of the stationary-phase volume and adsorption coefficient for the various volatiles. The PDMS coating used in this study favored adsorption of larger, more lipophilic compounds. However, adsorption can be tailored to fit the needs of a particular research thrust. For instance, it is most efficient to use thick films for compounds with low partition coefficients (Zhang and Pawliszyn, 1993); in our case, thin films are adequate for analytes with high partition coefficients such as 6-methyl-5-hepten-2-one and α-farnesene. To date, however, there are not adequate data regarding partition coefficients of SPME coatings for fruit volatiles.

The equilibration time of the SPME fiber plays an important role in quantitative sampling and is affected by the *K* value of the SPME coating for individual volatiles and their respective diffusion coefficients. Zhang and Pawliszyn (1993) reported that BTEX (benzene, toluene, ethyl benzene, and xylene isomers) require just 2−5 min to reach equilibration. In our experiments using the mixed standards and apple samples, 6−8 min were required for most volatiles. Some compounds like hexyl 2-methylbutanoate and α-farnesene take more than 24 min to reach equilibrium. These observations suggest that the kinetic behavior of the adsorption process, which differs with the nature of each analyte, is a factor that must be accommodated in any experimental protocol. Some compounds, such as butyl acetate and 2-methylbutyl acetate, exhibited matrix effects and are negatively influenced by other materials, which continue to increase in concentration (e.g., α-farnesene and hexyl 2-methylbutanoate). This strongly suggests that a competition for a limited adsorption capacity exists making it advisable to avoid approaching a saturation condition of the fiber coating material. Since the response variation in sampling is relatively low, the SPME can be used quantitatively if adsorption time is precisely maintained and the adsorption has not approached saturation.

Two minutes were required for sampling via SPME, generating a volatile profile that is qualitatively comparable with data using purge-and-trap techniques from this and earlier reports (Dirinck *et al.*, 1977; Kakiuchi, 1986; Song and Bangerth, 1993). However, it should be pointed out that there may be marked quantitative differences in the same compounds between SPME and purge-and-trap sampling. For example, the higher proportion of α-farnesene relative to other volatiles for SPME as compared to purge-and-trap reported here (Table 2) and elsewhere (Kakiuchi *et al.*, 1986; Song and Bangerth, 1993) is most likely due to discrimination on the basis of partition coefficients and also adsorption

kinetics. Calibration of the SPME fiber will be required for accurate quantification.

The rapid sampling of apple volatiles by SPME is complemented by the features of the TCC/TOFMS employed, which enabled analysis times to be reduced from hours to minutes. While a narrow bore column (0.1 mm i.d.) has been used to improve GC resolution and speed (Sacks and Akard, 1994), co-elution was unavoidable. However, the high spectral acquisition rate of the TOF mass spectrometer and the data quality is sufficient to permit quantitation of co-eluting compounds with elution times differing by as little as 0.2 s.

SPME sampling is solventless and much faster than purge-and-trap sampling. With the combination of fast GC and the time-of-flight mass spectrometer, the quantitative and qualitative analysis time can be shortened at least 10-fold. The system should be appropriate for real-time analysis of time-course studies on volatile biosynthesis by horticultural produce. It is independent of sample size, which opens the new possibilities for biochemical investigations using small (1−2 mL) vials of plant material.

CONCLUSIONS

The SPME system was found to be a convenient and appropriate sampling technology for rapid qualitative and quantitative analysis of volatile from horticultural produce. Sampling time can be reduced approximately 60-fold relative to conventional purge-and-trap. The primary limitation of the SPME system is that samples cannot be conveniently stored.

Time-compressed chromatography was successfully accomplished using a narrow bore (0.1 mm i.d.), short (5-m) column, and rapid temperature ramp rate (50 °C/min). Chromatographic time was reduced 10-fold relative to conventional methods with good resolution.

Use of TOFMS was found to be of sufficient sensitivity and speed to permit rapid and efficient detection of apple aroma volatiles. The speed of the detector, based on time array detection, makes it well-suited for application to rapid GC separations with the resultant time compression of peaks. Importantly, the rapid spectral generation rates and unskewed nature of spectra obtained enabled analytical resolution of chromatographically unseparated compounds. Because of the independence from chromatographically induced fragmentation pattern skewing, the resulting spectra were 'classic' in nature and easily library searchable. Additional speed is possible, since the mass spectrometer was operating at approximately 10% of its maximum rate, raising the possibility of having detection times of as little as 12 s for complex mixtures.

The analysis system described here appears to be highly appropriate for aroma analyses. The speed of the system overcomes the primary limitation of SPME fiber (i.e., sample storage) and permits collection of pertinent biological data in real time. Typical daily sampling throughput was in the range of 10−20 samples and could be increased to over 100. The factor now limiting total analytical speed is the data handling (i.e., identification, quantification, and reporting of detected compounds).

ABBREVIATIONS USED

FID, flame ionization detector; *m/z*, mass to charge ratio; PDMS, polydimethylsiloxane; RTIC, reconstructed total ion current; SPME, solid-phase microextraction; TCC, time compressed chromatography; TOFMS, time-of-flight mass spectrometry.

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