Solid Phase Microextraction: Solventless Sample Preparation for Monitoring Flavor Compounds by Capillary Gas Chromatography

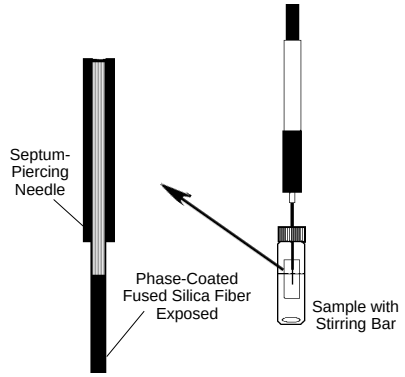
Solid phase microextraction is a fast, solventless alternative to conventional sample extraction techniques. In SPME, analytes establish equilibria among the sample matrix, the headspace above the sample, and a stationary phase coated on a fused silica fiber, then are thermally desorbed from the fiber to a capillary GC column. Because no solvent is injected, and the analytes are rapidly desorbed onto the column, minimum detection limits are improved and resolution is maintained. SPME is useful in many diverse analyses, including characterization of flavor components in foods and beverages and fragrance compounds in a wide range of products.

Key Words:
• flavors • fragrances • solid phase microextraction • SPME

In analyses of flavor and fragrance compounds, sample preparation usually involves concentrating the analytes of interest, using headspace, purge and trap, liquid-liquid extraction, solid phase extraction, or simultaneous distillation/extraction techniques. These methods have various drawbacks, including excessive preparation time and extravagant use of organic solvents. Solid phase microextraction (SPME),* an adsorption/desorption technique developed by investigators at the University of Waterloo (Ontario, Canada), eliminates most of the drawbacks to sample preparation (1-4). SPME requires no solvents or complicated apparatus, can be used to concentrate volatile and nonvolatile compounds in liquid samples or headspace, provides linear results over wide concentrations of analytes (often down to parts per trillion), and can be used with any gas chromatograph or gas chromatograph-mass spectrometer system.

The SPME device consists of a 1cm length of fused silica fiber, coated on the outer surface with a stationary phase and bonded to a stainless steel plunger, and a holder that looks like a modified microliter syringe (Figure A). The fused silica fiber can be drawn into a hollow needle by using the plunger on the fiber holder. To use the unit, simply draw the fiber into the needle, pass the needle through the septum that seals the sample vial, and depress the plunger, lowering the fiber into the sample (1-4) or the headspace above the sample (5). Organic analytes adsorb to the phase coating the fiber. Adsorption equilibrium is attained in 2 to 30 minutes. After sample adsorption, draw the fused silica fiber into the needle, and withdraw the needle from the sample vial and introduce it into the gas chromatograph injector, where the adsorbed analytes are thermally desorbed and delivered to a capillary GC column.

Figure A. Solid Phase Microextraction Apparatus



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You can alter selectivity by changing the phase type or thickness on the fiber according to the characteristics of the analytes. For example, the small distribution constants and low polarity of chlorinated and aromatic volatile organic compounds dictate the use of a thick, nonpolar phase for efficient adsorption. SPME can be used with split-splitless or on-column injectors. Results compare very favorably to those for other sample preparation methodology.

In SPME, equilibria are established among the concentrations of an analyte in the liquid or solid sample, in the headspace above the sample, and in the phase on the fused silica fiber. The amount of analyte adsorbed by the fiber depends on the thickness of the stationary phase coating and the distribution constant for the analyte. Extraction time is determined by the time required to obtain precise extractions for the analyte with the highest distribution constant. The distribution constant generally increases with increasing molecular weight and boiling point of the analyte. Volatile compounds require a thick phase coat; a thin coat is most effective for adsorbing/desorbing semivolatile analytes. You also can improve analyte recovery, or alter selectivity in favor of more volatile or less volatile compounds, by agitating or adding salt to the sample, changing the pH or temperature, or sampling the headspace rather than the sample (or vice versa).

Full equilibration is not necessary for high accuracy and precision from SPME, but consistent sampling time and other sampling parameters are essential. It also is important to keep consistent the vial size, the sample volume and, when using liquid samples, the depth the fiber is immersed in the sample (an adjustable gauge on the SPME unit minimizes variation in the depth of fiber immersion).

Because liquid and headspace sampling methods differ in kinetics, the two approaches can be considered complementary (6). Equilibrium is attained more rapidly in headspace SPME than in immersion SPME, because there is no liquid to hinder diffusion of the analyte onto the stationary phase. For a given sampling time, immersion SPME is more sensitive than headspace SPME for analytes predominantly present in the liquid (6). The reverse is true for analytes that are primarily in the headspace. These generalizations can be used to advantage to selectively adsorb more volatile or less volatile flavor compounds, as a situation warrants.

Several additional factors can affect SPME, and can influence the choice between immersion and headspace sampling. Addition of an electrolyte (e.g., a salt) to a solution generally increases the adsorption of analytes by both immersion SPME and headspace SPME. Increasing the sample volume from 200µL to 3mL, while keeping the ratio of liquid to headspace constant (1:1), increased analyte adsorption by both immersion and headspace SPME (6). For higher sensitivity from headspace SPME, the sample headspace should be as small as is practical. A detailed theoretical discussion of headspace SPME is presented in reference 5.

Desorption of an analyte from the SPME fiber depends on the boiling point of the analyte, the thickness of the coating on the fiber, and the temperature of the injection port. Some analytes can take up to 30 seconds to desorb, and cryogenic cooling might be required to focus these compounds at the inlet of the capillary column. Use of an inlet liner with a narrow internal diameter (e.g., 1mm) generally provides sharp peaks and can eliminate the need for cooling. As with any other extraction/concentration technique, it is best to use multiple internal standards in SPME methods, and to treat the standards and the analytes in an identical manner.

Flavor Analyses

Because it is simple, fast, inexpensive, and requires no solvents, SPME is potentially a very useful technique for analyses of flavor compounds in solid or liquid samples. The chromatograms in this bulletin show typical applications.

Fruit Juice Beverage

Yang and Peppard used headspace sampling SPME and immersion SPME to monitor 25 common flavor components in spiked water and in ground coffee, fruit juice beverage, and butter-flavored vegetable oil (6). The sensitivity of immersion SPME was comparable to or higher than that of conventional solvent extraction (dichloromethane) for most esters (e.g., ethyl isovalerate, cis-methyl cinnamate, trans-methyl cinnamate), terpenoids (e.g., linalool, α-terpineol, β-terpineol) and γ-decalactone in fruit juice beverage (Figure B). Weak affinity of the 100µm polydimethylsiloxane phase for fatty acids in the beverage was considered an advantage, because it reduced the potential for interference with the flavor compounds.

Whole Fruits

Investigators in the Department of Horticulture at Michigan State University, J. Song, L. Fan, and R.M. Beaudry, have used solid phase microextraction to monitor flavor volatiles in several fruits, including strawberry, tomato, and apple. According to these researchers, Z-3-hexenal, E-2-hexenal, hexanal, 1-pentene-3-one, 2-isobutylthiazole, and 6-methyl-5-heptene-2-one are important volatiles for fresh, ripe tomato flavor; for strawberries methyl butanoate, ethyl butanoate, methyl hexanoate, hexyl acetate, and ethyl hexanoate play important roles in aroma. Two compounds present at low levels relative to the other volatiles, 2,5-dimethyl-4-hydroxy-3(2H)furanone and its methyl ether, 2,5-dimethyl-4-methoxy-3(2H)furanone, are among the most important aroma constituents of strawberry.

These volatile flavor constituents have been collected primarily by purge-and-trap and/or simultaneous steam distillation techniques, which are expensive, time-consuming, and prone to difficulties. The authors ascertained that SPME had the potential to reduce sampling time, and is complementary to rapid separa-

Figure B. Flavor Compounds in Fruit Juice Beverage

SPME:	100µm polydimethylsiloxane phase fiber
Cat. No.:	**57300-U** (manual version)
	10 min immersion sampling with stirring
	(3mL sample, 0.6g NaCl added) 3 min desorption
GC Column:	**Carbowax® 20M-type phase, 30m x 0.25mm ID, 1µm film**
Supelco Equivalent:	**SUPELCOWAX 10,** available on request
Oven:	50°C (2 min) to 220°C at 4°C/min
Carrier:	helium, 20cm/sec
Det.:	MS (m/z = 35–400)
Inj.:	200°C, splitless (closed 2 min)
	(1mm ID injector liner)

1. Dichloromethane
2. Ethyl butyrate
3. Ethyl isovalerate
4. Limonene
5. Ethyl hexanoate
6. Isoamyl butyrate
7. Hexanyl acetate
8. cis-3-Hexenyl acetate
9. Hexanol
10. cis-3-Hexenol
11. cis-3-Hexenyl butyrate
12. Furfural
13. Benzaldehyde
14. Linalool
15. β-Terpineol
16. Butyric acid
17. 2-Methylbutyric acid
18. α-Terpineol
19. Hexanoic acid
20. cis-Methyl cinnamate
21. 1-(2-Furyl)-2-hydroxyethanone
22. Furaneol
23. trans-Methyl cinnamate
24. γ-Decalactone
25. Dodecanoic acid
26. (Hydroxymethyl)furfural

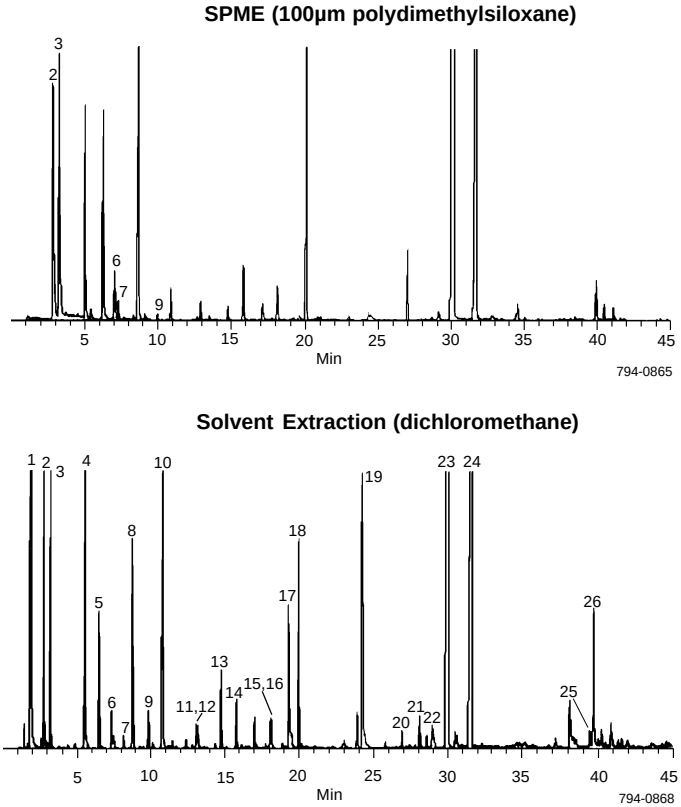

Figure courtesy of Xiaogen Yang and Terry Peppard, Givaudan-Roure Corporation, Clifton, NJ, USA.

tion/detection techniques such as time-compressed gas chromatography (TCGC) and time-of-flight mass spectrometry (TOFMS), to permit analysis of dozens of compounds in 1-3 minutes. The investigators exposed 100µm polydimethylsiloxane (PDMS), 65µm PDMS/divinylbenzene (DVB), and 65µm Carbowax®/DVB SPME fibers to effluent gas streams from ripe tomatoes and ripe strawberries for 4 minutes, then immediately transferred the collected volatiles to the chromatograph for analysis. Approximately 30 tomato volatiles were collected and sufficiently concentrated by the PDMS/DVB fiber for identification by TCGC/TOFMS. Hexanal, Z-3-hexenal, E-2-hexenal, 3-methyl butanal, 6-methyl-5-hepten-2-one, and 2-iso-butylthiazole were present at high levels. Linalool, 1-penten-3-one, methyl salicylate, and two nitrogen-containing compounds, dimethyldiazene and 1-nitro-pentane, also were detected.

A total of 34 aroma compounds of strawberry were collected and sufficiently concentrated by the PDMS/DVB fiber for identification by TCGC/TOFMS. Among these, methyl butanoate, methyl 2-methylbutanoate, ethyl butanoate, methyl hexanoate, and hexyl acetate were prominent; dimethyl disulfide and 2,5-dimethyl-4-methoxy-3(2H)furanone also were detected.

The investigators concluded that SPME compared favorably to purge-and-trap approaches, and the variety of SPME coating materials permitted optimization of adsorption for different analytes or analyte mixtures.

In a separate investigation of flavor volatiles from "Mutsu" apples, Song exposed the same three SPME fibers (100µm PDMS, 65µm PDMS/ DVB, 65µm Carbowax/DVB) to volatiles emanating from fruit stored for 3-4 months at 0°C. The PDMS/DVB fiber was the best choice, providing a full scan of aroma profiles (Figure C), but the Carbowax/DVB and PDMS fibers also extracted volatiles well. In addition, all three fibers provided little variation from one extraction to another (Table 1).

Flavor Oils

Menthol, the primary component in peppermint oil, is very efficiently adsorbed by a 100µm coating of polydimethylsiloxane on an SPME fiber. By using headspace SPME to quantify menthol, the percentage of peppermint oil in mint-flavored chocolate can be easily determined. A short extraction time, 1 to 3 minutes, is sufficient to quantify menthol while minimizing interference by other components in the chocolate (Figure D).

Headspace SPME coupled with analysis on a capillary GC column is an ideal approach for characterizing quality and composition of flavor oils. For example, selective losses of flavor components sometimes occur during processing. These losses can be detected by comparing chromatograms for the final product to chromatograms for the flavor ingredients. In Figure E, headspace SPME/capillary GC analyses of pure spearmint oil and a spearmint gum yielded very similar chromatograms. Figures F and G show the distinct SPME/GC profiles for ginger and lemon oils. A chiral capillary GC column was used for the analyses in Figures E and F, to resolve various enantiomer pairs present in the oils.

Figure C. Aroma Volatiles from Stored Apples, Extracted with a 65µm PDMS/DVB SPME Fiber

Sample: 300-450g intact fruit in a 3 liter flask at ambient temp., exposed to an air flow of 25-30mL/min.

SPME: 65µm polydimethylsiloxane/divinylbenzene fiber
Cat. No.: **57310-U** (manual version)
headspace extraction (as described for Sample), 4 min; analytes desorbed to a cool (<-100°C) precolumn, then volatilized by heating to 150°C in 15 sec.

GC Column: poly(5% diphenyl/95% dimethylsiloxane) type, 25m x 0.25mm ID, 0.34µm film
Supelco Equivalent: **SPB-5**, available on request
Oven: 40°C (1.5 min) to 250°C at 50°C/min, hold 1 min
Carrier: helium, 1.5mL/min (44cm/min)
Det.: mass spectrometer, m/z = 40-300 (40 spectra/sec)

1. 2-Methyl butanol
2. Butyl acetate
3. Hexanol
4. 2-Methyl butyl acetate
5. Methylpropylbutanoate
6. Hexyl acetate
7. Butyl-2-methylbutanoate
8. Pentyl butanoate
9. Butyl hexanoate/Hexyl butanoate
10. p-Methyoxyalylbenzene
11. Hexyl-2-methylbutanoate
12. 3-Methylbutylhexanoate
13. Pentyl hexanoate
14. 2-Pentenylhexanoate
15. 2-Methylpropyl-2-methylbutenoate
16. Hexyl hexanoate
17. α-Farnesene

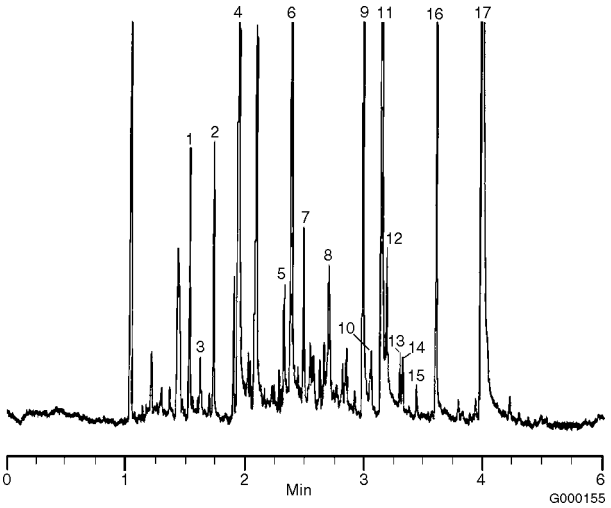

Figure provided by Jun Song, Department of Horticulture, Michigan State University, East Lansing, MI 48824 USA.

Table 1. Minimal Sampling Variation for SPME Fibers: Volatile Aroma Compounds in Apples

Analyte	PDMS/DVB Fiber Counts	PDMS/DVB Fiber %RSD	Carbowax/DVB Fiber Counts	Carbowax/DVB Fiber %RSD	PDMS Fiber Counts	PDMS Fiber %RSD
2-Methylbutanol	14835380	12.2	4460643	11.0	510007	1.5
Butyl acetate	12435118	8.3	4683817	3.7	1331047	8.6
2-Methyl butyl acetate	5575805	2.5	31459777	5.2	85910250	11.1
Hexyl acetate	10634831	1.7	26126266	3.5	50616659	13.2
Hexyl-2-methylbutanoate	46182861	5.5	38970820	3.3	66654419	10.5
2-Methylbutylhexanoate	4763813	5.5	3852886	4.6	13460625	10.5
Hexyl hexanoate	24446829	9.0	22214768	3.9	27178556	7.7
α-Farnesene	1.94E08	3.9	1.83E08	3.2	2.01E08	1.4

4 min extractions, N = 3 extractions by each fiber.
Data provided by Jun Song, Department of Horticulture, Michigan State University, East Lansing, MI 48824 USA.

Figure D. Peppermint Oil in Chocolate Cookie Bar

Sample: 4g peppermint cookie bar

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
1 min headspace sampling, 45°C
5 min desorption, 250°C

GC Column: **PTE-5 (poly[5% diphenyl/95% dimethylsiloxane] phase), 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24135-U**
Oven: 60°C (1 min) to 230°C at 10°C/min
Carrier: helium, 35cm/sec
Det.: FID, 250°C
Inj.: splitless (splitter closed 3 min), 250°C

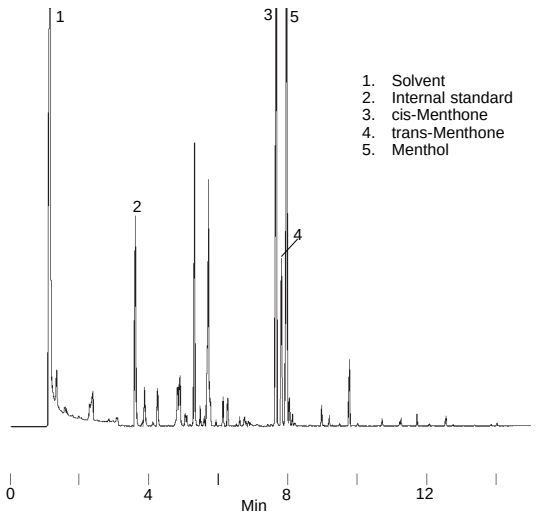

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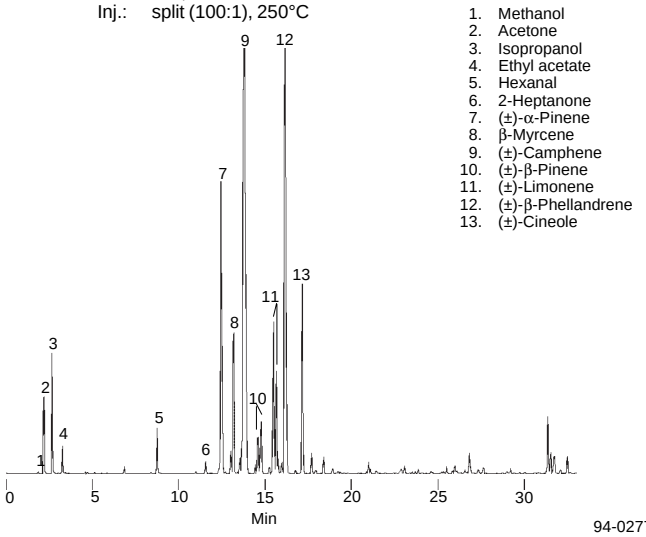
Figure F. Ginger Oil

Sample: 0.5g ginger oil

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
1 min headspace sampling, 30°C
5 sec desorption, 250°C

GC Column: **β-DEX 120 (modified β-cyclodextrin phase), 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24304**
Oven: 40°C to 220°C at 4°C/min
Carrier: helium, 35cm/sec
Det.: FID, 250°C
Inj.: split (100:1), 250°C



94-0277

Figure E. Spearmint Flavor Components

Sample: 0.5g spearmint oil or spearmint gum

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
1 min headspace sampling, 30°C
5 sec desorption, 250°C

GC Column: **β-DEX 120 (modified β-cyclodextrin phase), 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24304**
Oven: 40°C to 220°C at 4°C/min
Carrier: helium, 35cm/sec
Det.: FID, 250°C
Inj.: split (100:1), 250°C

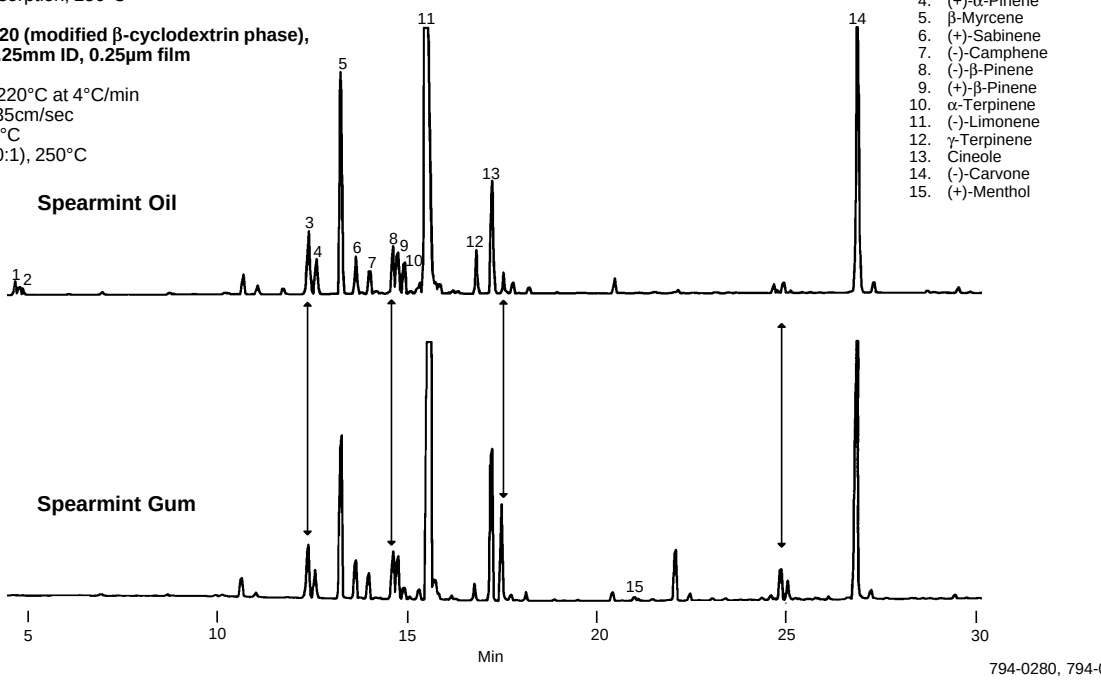


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Figure G. Lemon Oil

Sample: 0.5g lemon oil

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
1 min headspace sampling, 30°C
5 sec desorption, 250°C

GC Column: **SPB-1 (poly[dimethylsiloxane] phase), 100m x 0.25mm ID, 1.0µm film**
Cat. No.: **24220-U**
Oven: 40°C to 220°C at 4°C/min
Carrier: hydrogen, 40cm/sec
Det.: FID, 300°C
Inj.: split (100:1), 250°C

1. α-Thujene
2. α-Pinene
3. Camphene
4. Sabinene
5. β-Myrcene
   β-Pinene
6. Octanol
7. α-Phellandrene
8. α-Terpinene
9. p-Cymene
10. D-Limonene
11. γ-Terpinene
12. trans-Ocimene
13. Nonanal
14. Linalool
15. Terpinolene
16. Camphor
17. α-Terpinol
18. Nerol
19. Neral
20. Geraniol
21. Geranial
22. Citronellyl acetate
23. Neryl acetate
24. Geranyl acetate
25. trans-
    α-Bergamotene
26. Caryophyllene
27. β-Bisabolene

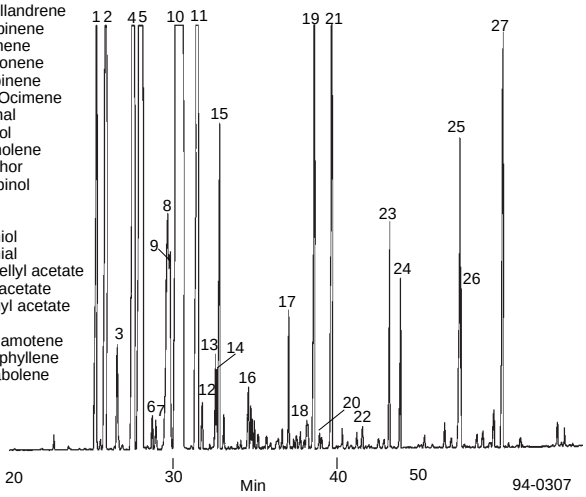


Figure H. Headspace SPME Eliminates Glycerin Interference with Punch Flavor Analysis

Sample: punch flavor (10 drops) equilibrated 5min at 40°C

SPME Fiber: **polydimethylsiloxane, 100µm film**
Cat. No.: **57300-U** (manual version)
Extraction: 10min, headspace, 40°C
Desorption: 1min, 235°C

Column: **polydimethylsiloxane, 30m x 0.25mm ID, 1µm film**
Supelco Equivalent: **SPB-1, Cat. No. 24029**
Oven: 60°C (1min) to 230°C at 4°C/min
Carrier: hydrogen, 40cm/sec (set at 150°C)
Det.: FID, 300°C
Inj.: split/splitless, 235°C

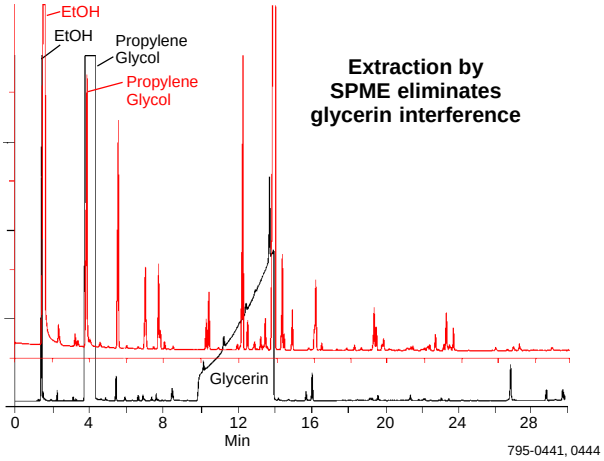


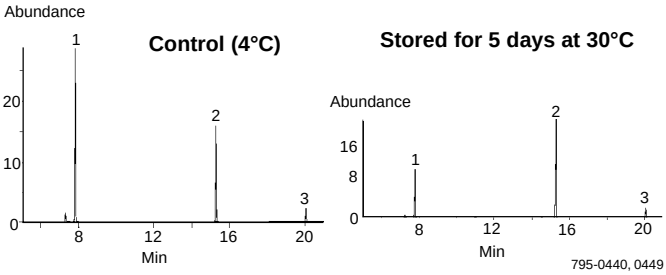
Figure used with permission of Alan Harmon, McCormick & Co., Inc., Hunt Valley, MD 21031 USA.

Figure I. Volatile Flavor Components in Seafood Cocktail Sauce

Sample: 4mL of cocktail sauce spiked with phenyl, 5 day exposure at 85°C
SPME Fiber: **polydimethylsiloxane, 100µm film**
Cat. No.: **57300-U** (manual version)
Extraction: 20 min, headspace, 40°C
Desorption: 1 min, 235°C

Column: **polydimethylsiloxane, 30m x 0.25mm ID, 1µm film**
Supelco Equivalent: **SPB-1, Cat. No. 24029**
Oven: 60°C (1min) to 230°C at 4°C/min
Carrier: helium, 30cm/sec (set at 150°C)
Det.: MS (m/z = 38-200, 2.3 scans/min)
Inj.: split/splitless, 235°C

1. Allyl isothiocyanate
2. Phenyl isothiocyanate (int. std.)
3. Phenylethyl isothiocyanate



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Other Flavor Compounds

Ethanol, an "analytically well-behaved" solvent, is the solvent of choice for most flavors applications, but flavor compounds also are prepared in propylene glycol, glycerin, triacetin, benzyl alcohol, triethyl citrate, fruit juices, sugar syrups, and other less well-behaved compounds that potentially can interfere with monitoring the flavor compounds. Alan Harmon of McCormick & Co. used a 100µm PDMS fiber to solve a particularly difficult analytical problem – analyzing punch flavor in the presence of glycerin. Headspace SPME eliminated the glycerin peak and revealed 13 additional flavor components that were obscured by the solvent peak in direct split injection (Figure H). According to Harmon, a Likens-Nickerson extraction of the flavor also was unsatisfactory – the sugars underwent thermal decomposition during the steam distillation and formed numerous artifacts (7).

Harmon also used headspace SPME to determine changes in concentrations of horseradish volatiles allyl isothiocyanate and phenylethyl isothiocyanate in seafood cocktail sauce (7). Practical methods are needed to monitor these compounds, which provide the characteristic pungency and flavor of horseradish, to determine how much flavor is being lost through evaporation, chemical conversion, absorption by packaging, and other effects of aging. Figure I clearly shows that storing a sample for 5 days at 30°C reduces the concentration of allyl isothiocyanate (by approximately 71%). The concentration of the less volatile and less reactive phenylethyl isothiocyanate decreased by approximately 29%. Harmon felt the kinetics of the concentration changes could be studied by using SPME.

Rancid Corn Oil

Polyunsaturated oils are susceptible to oxidation over time, and at accelerated rates on exposure to sunlight, elevated temperatures, or metals. Increased levels of volatile compounds formed from oxidation of linoleic acid (particularly pentane, hexanal, and 2-heptenal), linolenic acid (2,4-heptadienal), and oleic acid (octanal and nonanal) are indicators of rancidity in vegetable oils, and headspace analysis is an effective means of detecting these compounds (8-10). The needle on the SPME device will penetrate the foil or plastic seal on a bottle of oil and enable the analyst to sample the headspace in the bottle without changing its composition. Headspace SPME/capillary GC easily enables the analyst to monitor the volatiles of interest (Figure J). Note that butylated hydroxytoluene (BHT) also can be detected through the SPME/GC analysis.

Similarly, headspace SPME allows an analyst to quickly detect rancidity in potato chips (Figure K). For Figure K, the extraction was performed at 65°C, but results are nearly identical at 40°C.

Figure J. Rancid Corn Oil

Sample: 3.0g corn oil

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
45 min headspace sampling, 40°C
1.5 min desorption, 250°C

GC Column: **SPB-5, 30m x 0.53mm ID, 5.0µm film**
Cat. No.: **25347**
Oven: 40°C (5 min) to 220°C at 4°C/min
Carrier: helium, 5mL/min
Det.: FID, 300°C
Inj.: splitless (1 min), 250°C

1. Propane
2. Pentane*
3. Pentanol
4. Hexanal*
5. 2-Hexenal
6. 2-Heptanone
7. 2-Heptenal*
8. 1-Octen-3-ol
9. 2-Pentylfuran
10. 3-Octen-2-one
11. 2-Octenal
12. 2-Nonenal
13. 2-Decenal
14. trans,cis-2,4-Decadienal
15. trans,trans-2,4-Decadienal
16. 2-Undecenal
17. BHT

*Indicators of rancidity.

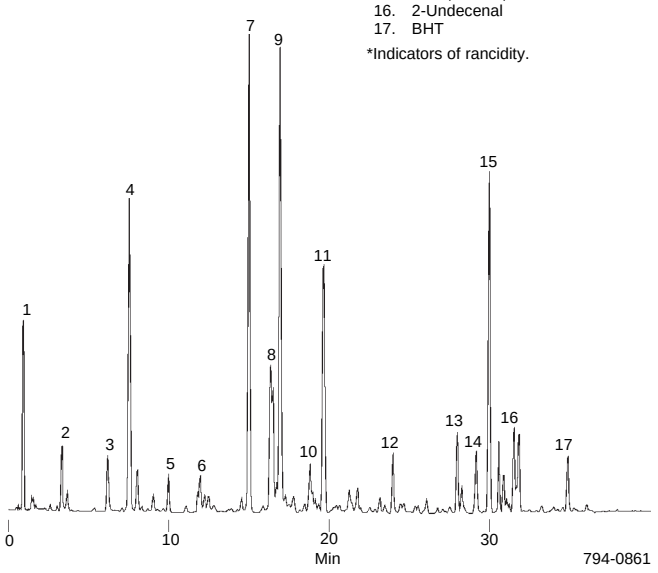


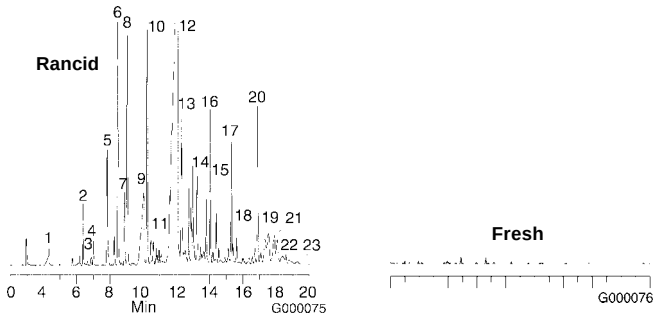
Figure K. Rancid and Fresh Potato Chips

Sample: 3g crushed potato chips in 15mL vial

SPME: 100µm polydimethylsiloxane fiber
Cat. No.: **57300-U** (manual version)
heated headspace, 65°C, 20 min, with stirring
3 min desorption, 250°C

GC Column: **SPB™-1 SULFUR, 30m x 0.32mm ID, 4.0µm film**
Cat. No.: **24158**
Oven: 45°C (1.5 min) to 250°C at 12°C/min, hold 10 min
Carrier: helium, 40cm/sec
Det.: quadrupole mass spectrometer, m/z = 35-290 at 0.6 sec/scan
Inj.: splitless/split (closed 2 min), 250°C

1. Acetic acid
2. Pentanal
3. Butanoic acid
4. Propyl acetate
5. Methyl butyrate
6. Hexanal
7. Octane
8. Methyl hexanal
9. Hexanoic acid
10. Heptanone
11. Heptanal
12. Heptanoic acid
13. Octanal
14. Octanoic acid
15. Nonanone
16. Nonanal
17. Butyl hexanoate
18. Decanal
19. Undecanone
20. Pentyl hexanoate
21. Dodecanone
22. Methyl heptanol
23. Dodecanal



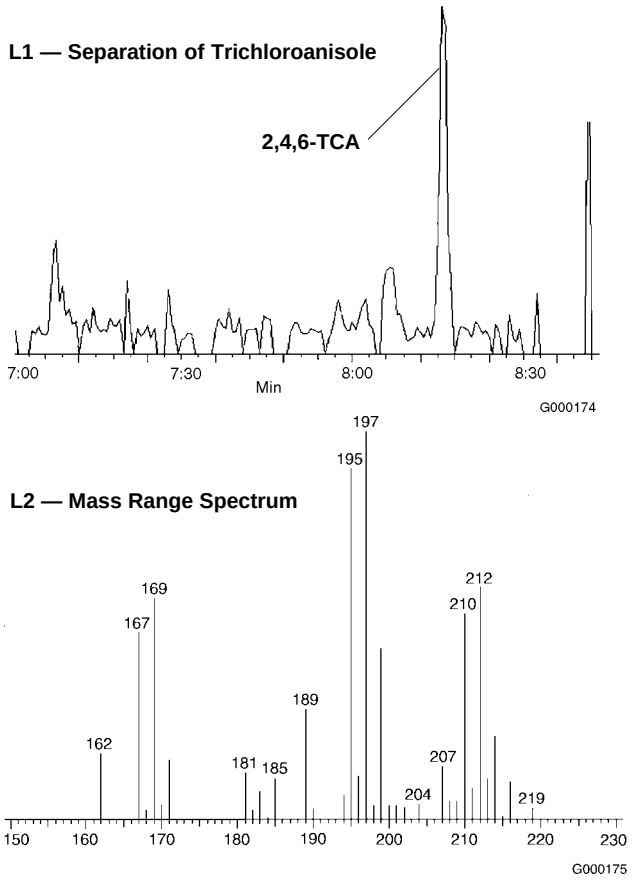
Odor in Wines: Trichloroanisole

2,4,6-Trichloroanisole (TCA) is the main compound in wine responsible for the characteristic unpleasant aroma/odor often described as woody, dank, and acrid. Human sensory thresholds for TCA are very low, estimated to be approximately 5 parts per trillion. Figure L1 was obtained using an ion trap GC/MS. To reduce background interference from the wine, we limited the mass scan range to incorporate only the key ions in TCA (160 to 220). A trace of 3 specific ions is evident: 195, 197, and 210. With a quadrupole MS (Figure L2), the selected ion mode uses ions 195, 197, 210, 212, 169, and 167. The presence of these ions in their proper ratios helps confirm identification.

Prior to the development of SPME-based techniques, the analysis for TCA included extracting each wine sample with 1 liter of methylene chloride, then concentrating the extract to 200µL, in a process that required 3 days to complete. SPME makes the analysis both much faster and much less expensive. In situations using autosamplers, while one sample is undergoing chromatographic analysis, the next can be undergoing extraction.

Figure L. TCA in White Wine

Sample:	10ppt of 2,4,6-TCA spiked in 12mL of white wine and 2.5g of NaCl
SPME Fiber:	**100µm polydimethylsiloxane**
Cat. No.:	**57300-U**
Extraction:	heated headspace, 50°C, 30 min, with rapid stirring
Desorption:	5 min, 250°C
Column:	**Meridian MDN-5, 30m x 0.25mm ID, 0.25µm film**
Cat. No.:	**24096**
Oven:	60°C (1 min) to 250°C at 15°C/min
Carrier:	helium, 30cm/sec, 60°C
Det.:	MS, m/z = 160-220 at 0.6sec/scan
Inj.:	splitless/split, closed 2 min, 250°C



Conclusions

The diverse results summarized here make several common points. SPME is fast and easy, and eliminates the costs and hazards associated with using organic solvents. SPME can be used for screening samples prior to a detailed analysis. Good precision under consistent sampling conditions also makes the technique viable in quantitative analyses. If you are interested in reducing the time and expense of sample concentration in your analyses, SPME might be the ideal answer to your needs.

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References not available from Supelco.

Trademarks

For many additional references on SPME in foods applications, request publication 494044.

Ordering Information:

SPME Fiber Assemblies

SPME fiber assemblies can be reused for up to 100 analyses, or more, depending on the particular application and the care that they are given. For reuse, simply condition with solvent or heat before and after every analysis.

Stationary Phase	Recommended Use	For Manual Holder (57330-U) Cat. No.	For Automated or HPLC Holder (57331) Cat. No.
Polydimethylsiloxane (PDMS)			
100µm / non-bonded	volatiles	**57300-U**	**57301**
30µm / non-bonded	nonpolar semivolatiles	**57308**	**57309**
7µm / bonded	nonpolar to moderately polar semivolatiles	**57302**	**57303**
Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)			
65µm / partially crosslinked	polar volatiles	**57310-U**	**57311**
60µm/ partially crosslinked	general purpose (for HPLC only)	—	**57317**
Polydimethylsiloxane/Carboxen (PDMS/Carboxen)			
75µm / partially crosslinked	trace-level volatiles	**57318**	**57319**
Carbowax/Divinylbenzene (CW/DVB)			
65µm / partially crosslinked	polar analytes	**57312**	**57313**
Carbowax/Templated Resin (CW/TPR)			
50µm / partially crosslinked	surfactants (for HPLC only)	—	**57315**
Polyacrylate			
85µm / partially crosslinked	polar semivolatiles	**57304**	**57305**
Fiber Assortment Kits			
Fiber Kit 1 (one fiber of each), 85µm polyacrylate, 100µm PDMS, 7µm PDMS		**57306**	**57307**
Fiber Kit 2 (one fiber of each), 65µm CW/DVB, 65µm PDMS/DVB, 75µm PDMS/Carboxen		**57320-U**	**57321-U**
Fiber Kit 3 (one fiber of each), 50µm CW/TPR, 60µm PDMS/DVB, 100µm PDMS		—	**57323-U**

Non-bonded phases are stable with some water-miscible organic solvents, but slight swelling may occur. NEVER use or rinse with nonpolar organic solvents.
Bonded phases are stable with all organic solvents. Slight swelling may occur when used with some nonpolar solvents.
Partially crosslinked phases are stable in most water-miscible organic solvents. They may be stable in some nonpolar solvents, but slight swelling may occur.

SPME Fiber Holders

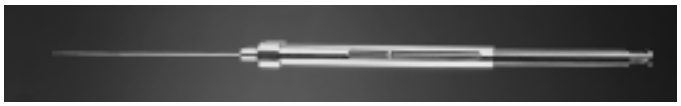
The holder is reusable indefinitely and accepts any of the replaceable fiber assemblies. First time users must order both a holder and a fiber assembly.

The holder for automated sampling or HPLC analysis can be used with a Varian 8100/8200 AutoSampler, or with our SPME/HPLC interface. (An SPME upgrade kit is necessary for operation with the Varian AutoSampler — contact Varian Instrument Division for information concerning system requirements). The holder for manual sampling features an adjustable depth guide to manually position the fiber for sampling and for correct placement in the GC injection port.

Description	Cat. No.
SPME Fiber Holder for Automated Sampling or HPLC Analysis	**57331**
SPME Fiber Holder for Manual Sampling	**57330-U**

For SPME accessories (including our SPME/HPLC interface), refer to the current Supelco catalog.

Automated or HPLC Holder



9950125

Manual Holder

9950125

Description	Cat. No.
Capillary GC Columns	
PTE-5, 30m x 0.25mm ID, 0.25µm film	**24135-U**
β-DEX 120, 30m x 0.25mm ID, 0.25µm film	**24304**
SPB-1, 30m x 0.25mm ID, 1.0µm film	**24029**
SPB-1, 100m x 0.25mm ID, 1.0µm film	**24220-U**
SPB-1 SULFUR, 30m x 0.32mm ID, 4.0µm film	**24158**
SPB-5, 30m x 0.53mm ID, 5.0µm film	**25347**
Meridian MDN-5S, 30m x 0.25mm ID, 1.0µm film	**24385-U**

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