Optimization of Extraction Conditions for Low-Molecular-Weight Analytes Using Solid-Phase Microextraction

Robert E. Shirey
Supelco Inc., Supelco Park, PA 16823

Abstract

A group of volatile analytes under a molecular weight of 90 and representing 11 organic classes are extracted using identical conditions with 6 different solid-phase microextraction fiber coatings. The amount of each of the analytes extracted by the various fibers is shown. The effects of sample modifiers, such as pH and ionic strength, on the recovery of the analytes are presented. A comparison of headspace and immersion extraction techniques is shown.

Introduction

In 1993, solid-phase microextraction (SPME) became commercially available with the introduction of the 100-µm polydimethylsiloxane (PDMS) coated fiber. Since this time, many different fiber coatings have been introduced. This number of fiber coatings can make selection of the proper SPME fiber difficult for specific applications. The choice between an adsorbent- versus an absorbent-type fiber is greatly dependent upon the concentration of the analytes and the application required (1).

There have been numerous studies that have compared fibers for the extraction of specific analytes or classes of analytes. SPME has been extensively studied for the analysis of volatile organic compounds (VOCs) in environmental matrices (2,3,4). Aldehydes have been extracted from milk (5) and oils (6), and short-chained acids have been extracted by SPME from cheese (7). Gaines et al. (8) used SPME for the extraction of ethers and hydrocarbons from sea water. Furton et al. (9) demonsrated that trace amounts of gasoline volatiles in arson samples could be evaluated by SPME. Methanol (10) and ethanol (11,12) have been quantitated from human blood by headspace SPME, and ethanol, acetone, and isoprene have been monitored in human breath (13). These are just a small sampling of examples of how SPME has been used as a quantitative extraction technique for a variety of low-molecular-weight analytes.

This study is the first to focus specifically on optimizing the extraction of small analytes from a variety of organic classes. The parameters for optimization involve fiber selection; the effects of sample modifiers, pH, and ionic strength; and a comparison of SPME extraction techniques.

Experimental

Chemicals

The chemicals used as analytes and organic solvents (American Chemical Society certified grade) used to prepare the mixtures were purchased from Aldrich Chemicals (Milwaukee, WI). Potassium phosphate salts and sodium chloride were obtained from Sigma Chemicals (St. Louis, MO). Deionized (DI) water was used to prepare samples.

Instrumentation

A Varian (Walnut Creek, CA) 3400 gas chromatograph (GC) was equipped with a flame ionization detector (FID) and fitted with a Varian 8200 autosampler adapted for SPME use. The injection port contained a 0.75-mm-i.d. low-volume liner, and a Merlin Microseal was used instead of septum to seal the inlet. A thick-film capillary column (30 m × 0.32-mm i.d., 4-µm SPB-1) with a bonded PDMS phase (Supelco, Bellefonte, PA) was used to resolve the components. An HP Chemstation (Agilent Technologies, Wilmington, DE) was used to collect the data.

Materials

The SPME fibers, 100-µm PDMS, 85-µm polyacrylate (PAcrylate), PDMS–divinylbenzene (DVB), StableFlex (SF), Carbowax (CW)–DVB SF, Carboxen™–PDMS SF, and DVB–Carboxen–PDMS SF were obtained from Supelco. All of the fibers used in the study were 23-gauge versions instead of the normal 24-

gauge fibers. All fibers were conditioned according to the manufacturer's specifications prior to the extraction of samples.

Preparation of standard stock mixes

The 11 components were divided into 3 mixes at a concentration of 2 mg/mL in methanol (Figure 1). Isopropanol, acetone, and methylacetate were in Mix 1. Mix 2 contained propanal, methylene chloride, acetic acid, and 1,4-dioxane. The analytes in Mix 3 were isopropylamine, propionitrile, and nitropropane. All of the mixes contained an internal standard (pentane) at a concentration of 2 mg/mL. The vials were stored at –4°C when not in use.

Preparation of buffers and final solutions

One liter of each buffer solution at pH levels of 2, 7, and 11 were prepared at a concentration of 0.05M with various combinations of tribasic, dibasic, and monobasic potassium phosphate salts. To reach a pH of 2, less than 0.5 mL of HCl was required (in addition to monopotasium phosphate). The Henderson–Hasselbach equation was used to assure that the ionic strength was consistent in all of the solutions. In addition to the buffer, 25 ± 0.05% NaCl was added to the solutions used as solvents to extract the analytes.

Extraction conditions by immersion

The samples were prepared by placing 1.2 mL of buffer solution or DI water in a 2-mL vial and spiking it with 1.2 µL of the appropriate stock mix. Each of the 6 SPME fibers extracted the analytes of each mix in the three pH levels and DI water in triplicate. Blanks were run in between each triplicate set. Table I shows the order of the samples extracted with each SPME fiber. Vial positions not indicated on the chart are blanks (water without analytes).

Each fiber was run through the aforementioned set of vials. The autosampler was set to extract the sample in the immersion mode for 15 min with the agitator turned on throughout the extraction process. The "prep ahead" mode on the autosampler was set so that the extraction process could be ongoing during the analysis of the previous sample. The total cycle time for one analysis was 20 min.

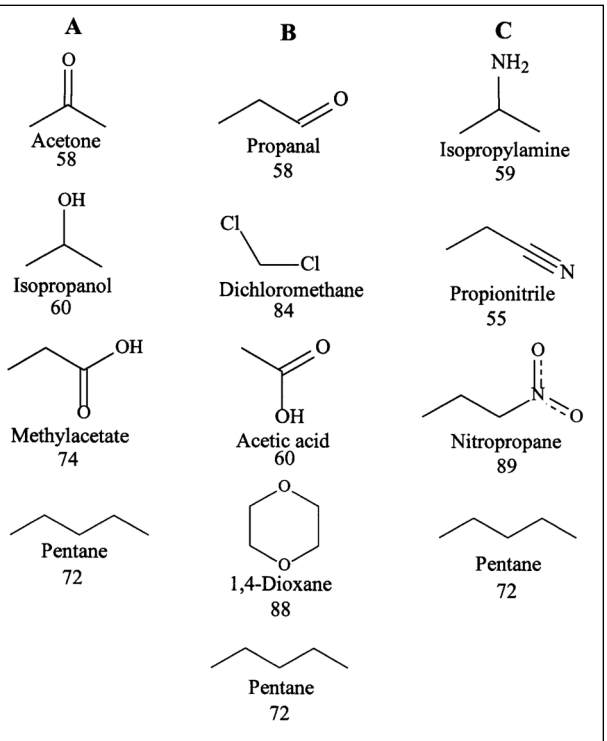

Figure 1. The analyte structures, molecular weights, and names used in this study: the analytes in stock mixture 1 (A), stock mixture 2 (B), and mixture 3 (C).

Extraction conditions by headspace

For ambient headspace extractions, the vials were filled with 1 mL of buffer plus 1 µL of standard, and the autosampler was adjusted to the headspace mode. Samples were extracted using the same setup and conditions used for the extraction of samples by fiber immersion. Only two fibers were evaluated in the headspace mode: 100-µm PDMS and Carboxen–PDMS SF fibers.

For heated headspace, the 2-mL vials were filled with 1 mL of water and 1 µL of standard mix. The vials were place in a metal tray on a stirrer hotplate set at 50°C. The fiber was placed in the headspace for 15 min. The samples were stirred with a 10-mm bar. The headspace samples were extracted with the Carboxen–PDMS fiber and the 100-µm PDMS fiber.

Desorption and analysis of samples

The samples were desorbed into a splitless/split injection port. The desorption temperature varied depending upon the fiber type, as shown in Table II. The fibers were desorbed for 2 min in the injection port, and the analytes were delivered into the analytical column. The oven of the GC was programmed to start at 40°C, hold for 2 min, then ramp to 140°C at 8°C/min, and hold for 0.5 min. The column was attached to an FID set

Table I. Vial Position of Samples in the Autosampler Tray*

	pH 2	pH 7	pH 11	DI water
Mix 1	2, 3, 4	6, 7, 8	10, 11, 12	14, 15, 16
Mix 2	18, 19, 20	22, 23, 24	26, 27, 28	30, 31, 32
Mix 3	34, 35, 36	38, 39, 40	42, 43, 44	45, 46, 47

*Position of vials placed in a 48-sample autosampler tray for extraction by immersion and ambient headspace. Vial positions not listed contain distilled water only.

Table II. Desorption Temperatures Used with SPME Fibers

Fiber coating	Temperature
100-µm PDMS	250°C
85-µm PAcrylate	280°C
PDMS–DVB SF	250°C
CW–DVB SF	250°C
Carboxen–PDMS SF	310°C
DVB–Carboxen–PDMS SF	260°C

at 280°C. Helium, as a carrier gas, was maintained at a constant pressure of 13 psi throughout the oven program. This was equivalent to a linear velocity of 35 cm/s at 40°C or 2.4 mL/min. Normal integration parameters were used.

Determination of response factors

Response factors were determined by making five direct injections (1 µL) of each mix into the GC using the conditions listed previously but with one exception. Instead of a splitless injection, the sample was split at a ratio of 50:1. Under these conditions, about 40 ng of each analyte was delivered to the column. Based upon the area counts of each analyte from the direct injections of the standard mixes, FID response factors were determined. The response for pentane was assumed to be a 100% response for the FID. The area response of each analyte was averaged from the multiple direct injections. The average response of each analyte was divided into the average response for pentane in each mix. The resulting quotient was the calculated response factor for each analyte, as shown in Table III. All area counts obtained for analytes extracted by the fibers were multiplied by the response factors.

Results and Discussion

Selection of mixtures and stability

The selection of components was based primarily on size and structure, encompassing a variety of organic classes. It was desirous to have as low of a molecular weight as possible but not a gas at ambient temperature. It was important to keep the molecular weights about the same to minimize the effect that size would have on the fibers. For many analytes, this was simple, such as with isopropanol, acetone, and isopropylamine: all of the structures are the same except for the functional group on the central carbon. To obtain an aldehyde and nitrile, the functional had to be on an outside carbon, but the chain length remained the same. It became more difficult to select analytes to represent other organic classes, because the molecular weight needed to increase.

Table III. FID Response Factors* for Analytes

Analyte	Response factor
Acetone	1.78
Isopropanol	1.79
Methylacetate	3.11
Propenal	2.11
Methylene Cl	7.13
Acetic acid	6.41
1,4-Dioxin	2.60
Isopropylamine	1.93
Propionitrile	1.73
Nitropropane	2.15

* FID response factors based upon the response of pentane. The area responses of the respective analytes were multipled by the response factor.

Esters and acids must be larger because of the need for two oxygen molecules. Methyl acetate was selected as the smallest ester, and acetic acid was selected instead of formic acid due to the poor response and reactivity of formic acid. In addition, there was no history on the capability of the fibers to extract it.

It became more difficult to select an analyte to represent ethers. The best fit was methyl ether, but it is a gas at room temperature. Diethyl ether was investigated, but it coeluted with pentane. Pentane was the smallest nongaseous hydrocarbon that could be used as an internal standard. Therefore, 1,4-dioxane was selected as a representative of the ether class.

Nitropropane was the smallest nongaseous alkyl nitrate. Methylene chloride was the smallest chlorinated organic that was not a gas at ambient temperature. The final molecular weight range was 58–89.

Initially, it was hoped that the analytes could be resolved in one mixture, but this was not the case. The analytes were injected individually on the thick-film bonded PDMS column and a Supel-Q (DVB PLOT) column. Several analytes were absorbed on the DVB PLOT column, and some were not resolved. The thick-film PDMS column, as listed in the Experimental section, was selected because of its better inertness and the fact that methanol eluted much earlier than the analytes of interest. There were three analytes that coeluted (acetone, propanal, and isopropylamine), which resulted in a need for 3 mixes. Also, methylene chloride, methylacetate, and propi-

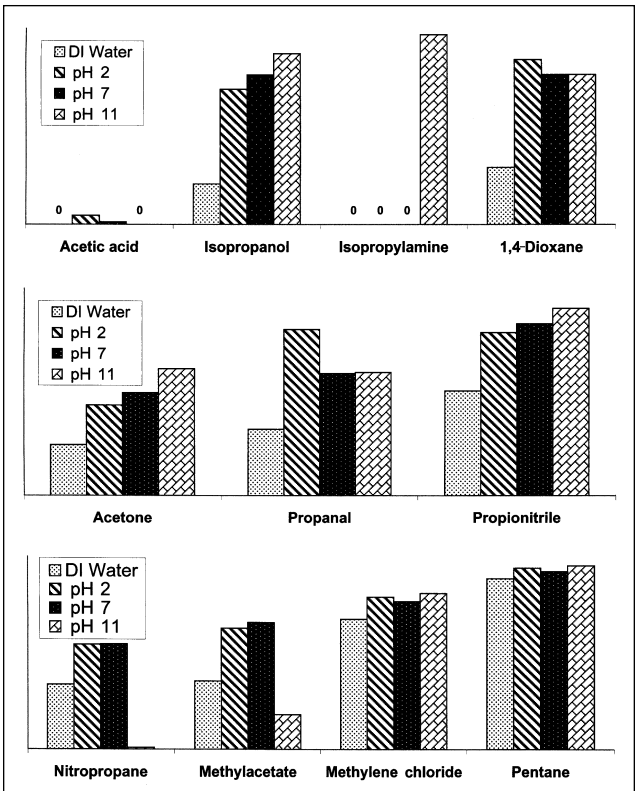

Figure 2. The effects of pH and ionic strength on the extraction of analytes. The graphs show average normalized area responses from all of the SPME fibers at each pH level for each analyte. Analytes were extracted by immersion as described in the Experimental section.

onitrile eluted closely. Each of these analytes was placed into separated mixes.

In addition to resolution, stability was also considered when developing the mixes. There was a conscious effort to attempt not to combine analytes that might react with each other, such as acetic acid and isopropylamine. To assure that the mixes were stable throughout the study, a direct injection of each mix was made prior to preparing the samples for extraction with a given fiber. The area counts of the peaks needed to be within 5% of the area counts from the average of the injections used to obtain the response factors. This was always the case. There appeared to be no interactions or change in concentrations throughout the study. The mixes were stored at –4°C when not in use.

The effects of pH and ionic strength

When comparing the fibers, it is best to give results using optimized conditions. It is important to determine the best pH and the effect of ionic strength on the extraction of analytes. In this study, three pH levels were used to determine the effects on extraction efficiency. The three pH levels of 2, 7, and 11 were selected to represent a strong base and acid and be within the stability range of the fibers. Careful precautions were taken to ensure that all of the solutions were the same ionic strength. The sodium chloride level was 25 ± 0.05%, and the concentration of the buffers was constant at 0.05M. The buffered solutions were compared to DI water to show the effects of the addition of salt. The intention of this study was not to evaluate varying concentrations of salt, only to observe the difference between the presence and absence of NaCl.

The responses for each analyte at the three pH levels and in DI water were averaged from all of the fibers. The effects of pH and ionic strength were not fiber dependent. The ratio of responses between pH levels were the same for all of the fibers. Figure 2 shows the comparison of responses for each analyte at the three pH levels and in DI water. The charts show that pH affects the extraction efficiency of many of the analytes.

When comparing DI water to the solutions with water, all of the analytes were better extracted with salt than without salt; however, the less polar the analytes, the less effect salt had on extraction efficiency. It is not important to add salt to water for the extraction of nonpolar analytes, such as pentane and methylene chloride, but it was not detrimental to add salt. The addition of salt greatly enhanced the extraction recovery of the more-polar analytes, such as isopropylamine and isopropanol. For low-molecular-weight analytes, the addition of salt is usually advantageous and recommended. This may not always be the case for higher-molecular-weight analytes, such as chlorinated pesticides (14). In some cases, the salt may cause the analytes to adhere to the glass vials.

The effects of pH were somewhat similar to ionic strength. Polar analytes were affected more greatly by pH than nonpolar analytes. As expected, acetic acid is best extracted from a water solution that is acidic, and isopropylamine and propionitrile are best extracted from water that is basic. It was not expected that pH would affect the extraction of alcohols, ketones, or ethers; however, the results indicate that isopropanol and acetone were best extracted from basic water solutions. A trend indicates that as the pH increases, the recovery increases.

For less-polar analytes, the trends were not as obvious. Both propanal and 1,4-dioxane were best extracted at pH 2, but there was no trend as the pH increased. The amount of analyte extracted was nearly identical at the pH levels of 7 and 11. Pentane and methylene chloride were extracted nearly the same at all three pH levels.

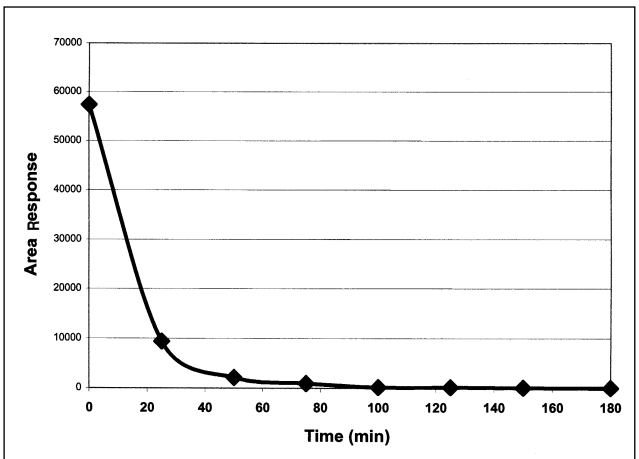

Figure 3. Area response of nitropropane versus time in basic solution (pH 11) prior to extraction. Extraction was with the Carboxen–PDMS fiber by immersion as described in the Experimental section.

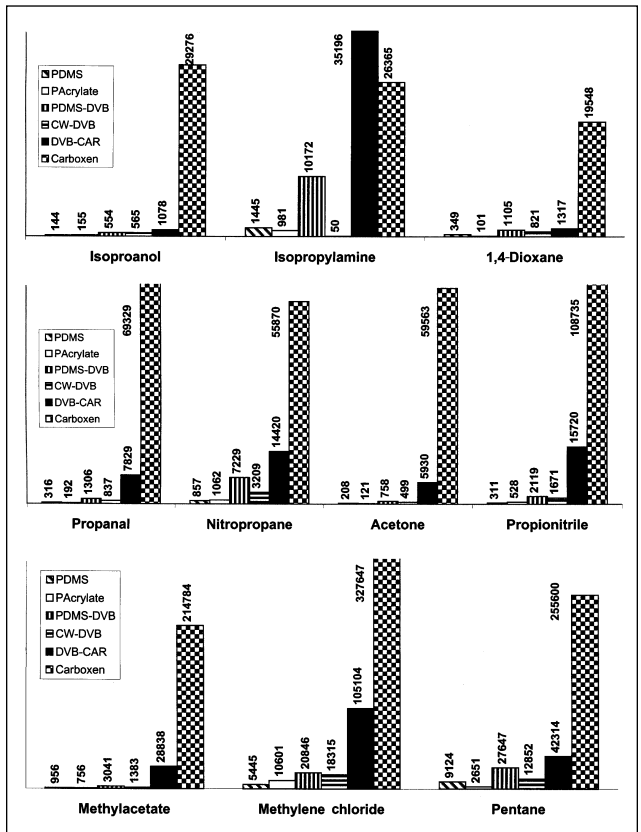

Figure 4. Area responses for each analyte extracted by the six SPME fibers. These are absolute responses that have been adjusted for FID discrimination. Analytes were extracted by immersion as described in the Experimental section.

Nitropropane and methylacetate were extracted nearly the same at pH 2 and 7 but showed a marked decrease at pH 11. The cause of the low response is due to the poor stability of the analytes in bases. Both nitropropane (15) and methylacetate (16) can hydrolyze in basic solutions. To demonstrate this point, a plot of the recovery of nitropropane versus time in solution was monitored, as shown in Figure 3. After setting in solution for only 20 min, the recovery of nitropropane was markedly decreased. After 2 h, virtually no nitropropane was detected. This shows the importance of determining analyte stability when adjusting the pH for the extraction or storage of samples.

Area responses of analytes

The area responses for each analyte extracted with the 6 types of SPME fibers are shown graphically in Figure 4. Area responses were adjusted for FID discrimination with response factors to provide a better representation of the amount of analyte extracted by the fibers.

The results show in the three charts that the response for the analytes extracted with the Carboxen–PDMS fiber were much greater than the responses with the other fibers, except in the case of isopropylamine. In many cases, the responses for the analytes extracted with the Carboxen–PDMS fiber were over 200 times greater. Popp (17) showed similar results when he compared Carboxen–PDMS fibers to other fibers for the extraction of VOCs. Carboxen 1006 (the Carboxen used in the fiber) acts as an adsorbent, in comparison with a liquid phase, which works more by partitioning or as an absorbent. Smaller analytes are not well retained by fibers coated with only liquid phases, but the pores in Carboxen are designed to retain smaller analytes. Studies have shown that the Carboxen–PDMS fiber can retain analytes for several days on the fiber, even when not sealed (18).

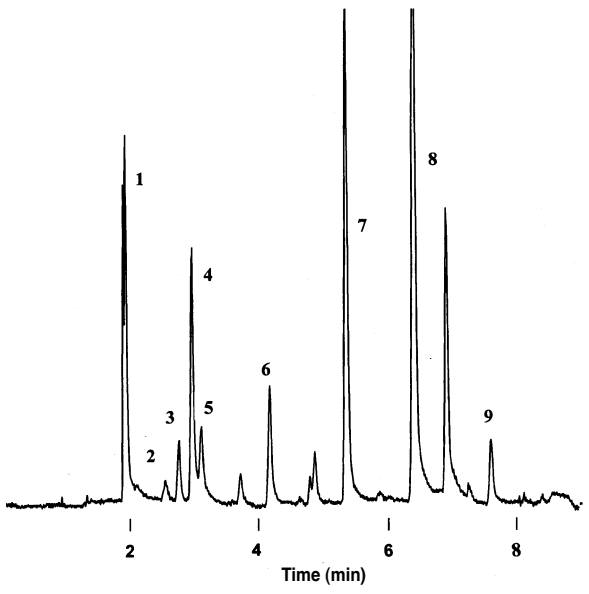

Figure 5. Chromatogram of solvents at 20 ppb each in water containing 25% NaCl extracted with the Carboxen–PDMS fiber. Extraction was by immersion using the conditions listed in the Experimental section. Components: 1, methanol; (used as a solvent for standard) 2, ethanol; 3, acetonitrile; 4, acetone; 5, isopropanol; 6, *n*-propanol; 7, ethyl acetate; 8, 3-methyl-2-butanone; 9, 1,4-dioxane.

Because of the better efficiency of the Carboxen–PDMS fiber to extract small analytes, it is suitable for trace-level analysis. Previous studies have shown that many of the more-polar analytes, and even smaller analytes such as ethanol and acetonitrile, could be detected at 20 ppb in water with the Carboxen–PDMS fiber (Figure 5). However, adsorbent-type fibers can become more easily overloaded, because they retain more analyte than absorbent-type fibers (19). Absorbent-type (liquid coating) fibers have been shown to have good linear range over 3 orders of magnitude and are ideal for high level (upper parts-per-billion to percent levels) screening of small analytes as demonstrated by T. Schumacher at Lancaster Laboratories. This work is summarized in the chapter by Shirey (20).

The fiber coatings containing DVB (also adsorbent-type fibers) extracted better than the fiber coatings with only liquid phase; however, the amount of analyte extracted in comparsion with Carboxen was much less. This difference was due primarily to the pore size. Carboxen is primarily a mixture of micro-, meso-, and macropores, whereas DVB is primarily mesoporous (Table IV). Mesopores do not tightly retain lower-molecular-weight analytes (21).

The one exception in the analytes monitored in this study was isopropylamine. The PDMS–DVB fiber has a high affinity for small amines (22,23). It was not surprising that the fiber containing PDMS–DVB layered over Carboxen–PDMS was the best fiber for extracting isopropylamine. The combination of the attraction of amines to the PDMS–DVB surface and the strong retention of Carboxen make this fiber ideal for small amines. The PDMS–DVB fiber also extracted this analyte much better than the fibers with only liquid phase coatings.

Unlike the PDMS–DVB fiber, the CW–DVB poorly extracted isopropylamine. Even though the CW–DVB fiber is more polar, the affinity it has for small amines is poor. Interestingly, this fiber extracts aniline and other nitrogen-based aromatics efficiently (24,25). The PDMS–DVB fiber also has a high affinity for aromatic amines (26).

The response for acetic acid on the various fibers is not shown. The combination of the wrong column and too low of a concentration level were major factors. Only the Carboxen fiber and the CW–DVB fibers were capable of extracting acetic acid. The responses were so low that the results are not graphed. The amount extracted relative to other analytes can be seen in Figure 2. Propionic acid, which is extracted more

Table IV. Physical Properties of Divinylbenzene and Carboxen

Material	Surface area (m^2/g)	Porosity (mL/g)			
		Macro*	Meso	Micro	Total
Divinylbenzene	750	0.58	0.85	0.11	1.54
Carboxen 1006	720	0.23	0.26	0.29	0.78

* Macropore, > 500 Å.
† Mesopore, 20–500 Å.
‡ Micropore, 2–20 Å.

efficiently than acetic acid, should have been used, or the concentration of acetic acid should have been doubled.

In general, the strong adsorbent (Carboxen) extracted these analytes better than the weaker adsorbent (DVB), which extracted better than the absorbent or liquid phase coated fibers (PDMS and PAcrylate).

Effects of fiber polarity

In general, it is expected that more-polar fibers will extract more-polar analytes. This has been demonstrated in several studies comparing fibers for the extraction of polar analytes such as phenols (27,28), triazine herbicides (29), and barbituates(30). However, for the extraction of low-molecular-weight analytes, such as those used in this study, the effects of polarity were minimal.

To verify this result, the responses for the analytes extracted by two pairs of fibers are plotted against analyte polarity in Figure 6. Figure 6A plots two absorbent type fibers (100-µm PDMS and the 85-µm PAcrylate fiber). Both fibers have a similar film thickness, although the 100-µm PDMS is nonpolar and the 85-µm PAcrylate fiber is polar. The second pair of fibers shown in Figure 6B are adsorbent-type fibers. The polar CW–DVB fiber and the less-polar PDMS–DVB fiber both have a coating thickness of 65-µm.

With polarity decreasing from left to right, the results indicate that polar fibers do not increase the amount of polar analytes in comparison with the similar nonpolar fiber. However, there was a marked decrease in the amount of pentane extracted by the polar fibers with respect to the nonpolar fibers. This was the case for both sets of fibers. It does indicate that there is some selectivity with the polar fibers by extracting less of the nonpolar analytes. This would be advantageous if polar analytes were present in a sample that contains a higher concentration of nonpolar analytes.

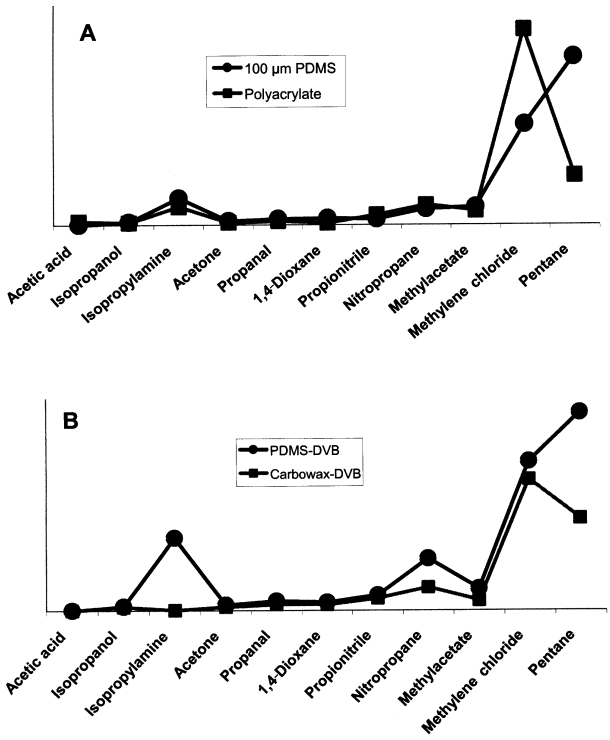

Figure 6. Analyte response using various SPME fibers versus analyte polarity: plots of the nonpolar 100-µm PDMS fiber and the polar 85-µm polyacrylate fiber (both are absorbent type fibers) (A) and plots of nonpolar PDMS-DVB fiber and the polar CW-DVB fiber (both are adsorbent type fibers) (B). All of the analytes were extracted by immersion as described in the Experimental section.

It appears that the extraction of small analytes is more dependent upon fiber coating thickness than the polarity of the coating. For a small analyte to be retained in fibers at trace levels, they must be trapped (such as in pores), retained by a thick coating (31), or react with the coating (such as one containing a derivative) (32,33). Both of the liquid coatings are similar in thickness and retain similar amounts of these analytes. The DVB is the same in both of the CW and PDMS–DVB fibers. The polar fibers may attract more-polar analytes but cannot retain them because of the fast movement of the small analytes out of the absorbent and adsorbents with mostly meso- or macropores. Polar coatings that contain adsorbents such as Carboxen 1006 have not been successfully made.

Comparison of headspace extraction to extraction by immersion

It is also important to determine the best SPME extraction technique for each analyte. There are three options for extraction from a liquid sample: immersion of the fiber in the water, ambient headspace, and heated headspace. It was not necessary to evaluate every fiber for this evaluation. In this section, an absorbent-type fiber (100-µm PDMS fiber) and the adsorbent-type fiber (Carboxen–PDMS) were selected.

When comparing the types of extractions using the Carboxen–PDMS fiber, there was not much difference observed between the techniques. Figure 7A contains the more-polar analytes. With the exception of isopropylamine, the responses for the other analytes among the types of techniques were similar. In some cases, the responses from ambient headspace measurement was less than the other two techniques. Response from heated headspace and immersion were similar. For isopropylamine, heated headspace provided the best response. It appears that once the analyte is out of solution, it is more easily extracted.

Figure 7B shows the less-polar analytes extracted with the Carboxen fiber. There appears to be a reduction in the analyte response for heated headspace. Because these analytes are less polar, they are easily released from water without heat. The heat used may be warming the fiber, which could cause some of these analytes to be desorbed off the fiber, especially pentane with a boiling point under 40°C. However, this phenomenon is not commonly observed with a strong adsorbent-type fiber (34).

In the evaluation of the 100-µm PDMS fiber for the three extraction techniques, the results are more intriguing. As shown in Figure 8A, the more-polar analytes are extracted better using heated headspace. Immersion was shown to be slightly better than ambient headspace; however, there was not much difference between the extraction techniques. The use of heat drove the polar, more water-soluble analytes into the headspace. As the fiber extracted the analytes, more of the

analytes were released from the solution, which allowed more analyte to migrate into the fiber coating. Why would this be more evident with this fiber in comparison with the Carboxen? The 100-µm PDMS poorly extracts polar analytes out of water by immersion, whereas the adsorbent nature of the Carboxen fiber enables it to extract analytes from solution more efficiently.

In Figure 8B, one can see the same effect that was observed with the Carboxen fiber, particularly for the extraction of pentane. In this case, it appears that the heat was driving the analyte off of the fiber, because the ambient headspace response is better than heated headspace but not as good as immersion. As stated previously, pentane has a low boiling point that could cause it to be easily released out of a liquid phase. It has been shown, especially for small analytes, that the rate of diffusion out of the fiber is slower in water than in the headspace; therefore, when the fiber is immersed, more analyte is retained in the coating (35). For the other less-polar analytes, the difference between extraction techniques is minimal. The ambient headspace extraction technique appears to be the best choice for the extraction of nonpolar analytes.

Conclusions

For the extraction of small, low-molecular-weight molecules, the effects of porosity far exceed the effects from polarity and film thickness. The micropores of the Carboxen–PDMS fiber make it ideal for extracting these analytes. The fiber is nonselective and extracted all of the analytes at magnitudes better than the other SPME fibers. The only exception to this conclusion was for isopropylamine. The ability of the PDMS–DVB coating to extract small amines enabled the dual-layered DVB–Carboxen–PDMS to be the better fiber.

The effect of fiber polarity on small amines was minimal. The polar fibers did not extract more of the polar analytes than the nonpolar analytes. However, the polar fibers extracted much less of the nonpolar analytes than the nonpolar fibers. The reduction in the extraction of nonpolar analytes by the polar fibers does provide some selectivity for polar analytes.

The results from the study of the effects of pH and ionic strength were, for the most part, as expected. Basic compounds are best extracted from a solution at high pH levels, and acidic compounds are best extracted from solutions at low pH levels. It was somewhat of a surprise to determine that some analytes that are relatively neutral are extracted best in acidic or basic solutions. It was also shown that nitropropane and methylacetate were not stable in solutions at pH 11, which shows the importance of determining the effect of pH on the stability of analytes. Increasing ionic strength with 25% NaCl compared with deionized water improved the recovery of all of the analytes, with polar analytes being more greatly affected than nonpolar analytes.

In selecting the type of extraction, it appears that heated

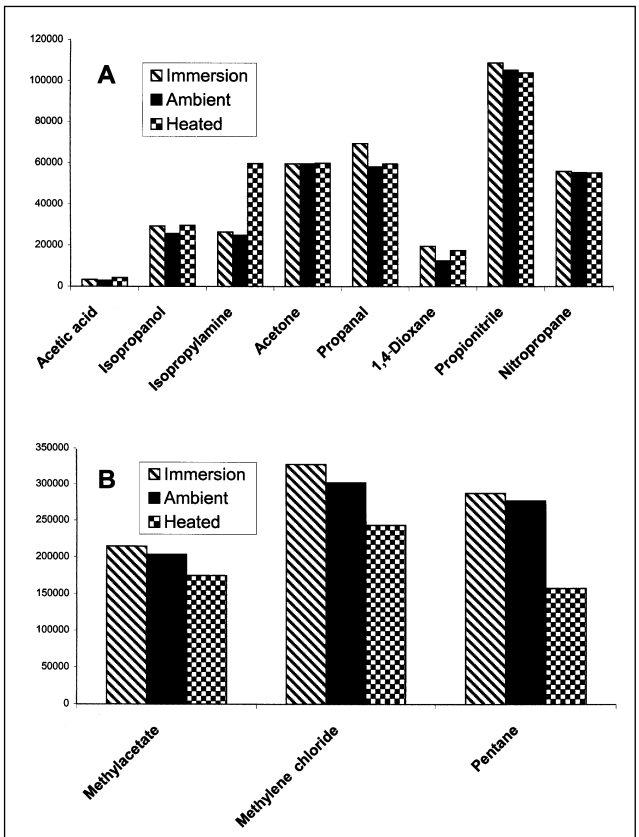

Figure 7. The comparison of SPME extraction techniques using the Carboxen-PDMS fiber: polar analytes (A) and less-polar analytes (B).

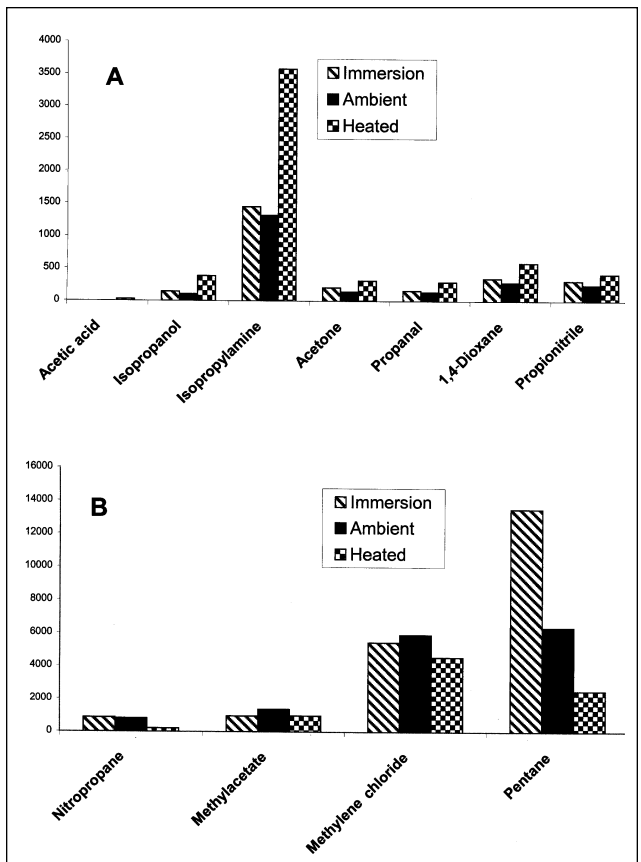

Figure 8. The comparison of SPME extraction techniques using the 100-µm PDMS fiber: polar analytes (A) and less-polar analytes (B).

headspace and immersion techniques are best for extracting polar analytes, and ambient headspace and immersion are the best techniques for extracting nonpolar analytes. For an adsorbent-type fiber such as Carboxen, the type of extraction used does not greatly affect the amount of analyte extracted. For an absorbent-type fiber, the type of extraction used was more critical. Heated headspace was best for extracting polar analytes, and either direct immersion or ambient headspace are suitable for extracting nonpolar analytes. There will be exceptions to these conclusions, but they serve as a general guideline.

References

1. R. E. Shirey. *Solid Phase Microextraction A Practical Guide,* S.S. Wercinski, Ed. Marcel Dekker, New York, NY, 1999, pp 83–94.
2. T. Nilsson, R. Ferrari, and S. Facchetti. Inter-laboratory studies for the validation of solid-phase microextraction for the quantitative analysis of volatile organic compounds in aqueous samples. *Anal. Chim. Acta* **356:** 113–23 (1997).
3. F. Santos, M. Galceran, and D. Fraisse. Application of solid-phase microextraction to the analysis of volatile organic compounds in water. *J. Chromatogr. A* **742:** 181–89 (1996).
4. R. Shirey. Rapid analysis of environmental samples using SPME and narrow bore capillary columns. *J. High Resol. Chomatogr.* **18:** 495–99 (1995).
5. R. Marsilli. Comparison of dynamic headspace methods for the GC–MS analysis of light induced lipid oxidation products in milk. *J. Chromatogr. Sci.* **37:** 17–23 (1999).
6. T. Peppard and X. Yang. Solid-phase microextraction for flavor analysis. *J. Agric. Food Chem.* **42:** 1925–30 (1994).
7. H. Chin, R. Bernard, and M. Rosenberg. SPME for cheese volatile compound analysis. *J. Food Sci.* **61:** 1118–29 (1996).
8. R.B. Gaines, E.B. Ledford, Jr., and J.D. Stuart. Analysis of water samples for trace levels of oxygenate and aromatic compounds using headspace solid-phase microextraction and comprehensive two-dimensional gas chromatography. *J. Microcolumn Sep.* **10:** 597–604 (1998).
9. K.G. Furton, J. Bruna, and J.R. Almirall. A simple, inexpensive, rapid sensitive solventless technique for the analysis of accelerants in fire debris based on SPME. *J. High Resol. Chromatogr.* **18:** 625–29 (1995).
10. X. Lee, T. Kumazawa, T. Jurosawa, K. Aklya, Y. Aklya, S. Fruta, and K. Sato. Simple extraction of methanol in human whole blood by headspace SPME. *Jpn. J. Forens. Toxicol.* **16:** 64–68 (1998).
11. Z. Penton. Blood alcohol determination with automated solid phase microextraction (SPME): a comparison with static headspace sampling. *Can. Soc. Forens. Sci.* **30:** 7–12 (1997).
12. X. Lee, T. Kumazawa, T. Sato, H. Sano, A. Ishi, and O. Suzuki. Improved extraction of ethanol from human body fluids by headspace SPME with Carboxen/PDMS fiber. *Chromatographia* **47:** 593–95 (1998).
13. C. Grote and J. Pawliszyn. Solid phase microextraction for the analysis of human breath. *Anal. Chem.* **69:** 587–96 (1997).
14. A.A. Boyd-Boland, S. Magdic, and J.B. Pawliszyn. Simultaneous determination of 60 pesticides in water using solid-phase microextraction and gas chromatography–mass spectrometry. *Analyst* **121:** 929–38 (1996).
15. J. March. Advanced Organic Chemistry: Reaction, Mechanisms and Structures. McGraw-Hill, New York, NY, 1968, p 778.
16. J. March. Advanced Organic Chemistry: Reaction, Mechanisms and Structures. McGraw-Hill, New York, NY, 1968, p 310.
17. P. Popp and A. Paschke. Solid phase microextraction of volatile compounds using Carboxen–polydimethylsiloxane fibers. *Chromatographia* **46:** 419–24 (1997).
18. R. Shirey, V. Mani, and R. Mindrup. On-site sampling for volatiles and pesticides using SPME. *Am. Environ. Lab* **10:** 21–22 (1998).
19. R.E. Shirey, V. Mani, and W.R. Betz. *SPME: Using Porous Materials as Fiber Coatings.* Presentation to Canadian Chemical Society, Supelco Publication T497110, 1997, pp 1–17.
20. R.E. Shirey. *Solid Phase Microextraction A Practical Guide.* S.S. Wercinski, Ed. Marcel Dekker, New York, NY, 1999, pp 74–76.
21. K.S.W. Sing, D.H. Evertt, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Ronquerol, and T. Siemieniewska. Reporting physiosorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure and Appl. Chem.* **57:** 603–19 (1985).
22. H. Lasko and W. Ng. Determination of chemical warfare agents in natural water samples by SPME. *Anal. Chem.* **69:** 1866–72 (1997).
23. L. Muller, E. Fattore, and E. Benfenati. Determination of aromatic amines by SPME GC–MS in water samples. *J. Chromatogr. A* **791:** 221–30 (1998).
24. R.E. Shirey. *Solid Phase Microextraction A Practical Guide.* S.S. Wercinski, Ed. Marcel Dekker, New York, NY, 1999, pp 65–68.
25. S. Barshick and W. Griest. Trace analysis of explosives in seawater using SPME and GC ion trap mass spectrometry. *Anal. Chem.* **70:** 3015–20 (1998).
26. M. Durrach, A. Chujitan, and G. Plett. Trace explosives signitures from World War II unexploded undersea ordinance. *Environ. Sci. Technol.* **32:** 1354–58 (1998).
27. K. Buchholz and J. Pawliszyn. Determination of phenols by SPME and GC analysis. *J. Environ. Sci. Technol.* **27:** 2844–48 (1993).
28. P. Bartak and L. Cap. Determination of phenols by solid-phase microextraction. *J. Chromatogr. A* **767:** 171–5 (1997).
29. R. Ferrari, T. Nilsson, R. Arena, P. Arlati, and G. Bartolucci. Inter-laboratory validation of solid-phase microextraction for the determination of triazine herbicides and their degradation products at ng/L level in water samples. *J. Chromatogr. A* **795:** 371–76 (1998).
30. B. Hall and J. Brodbelt. Determination of barbituates by SPME and ion trap GC–MS. *J. Chromatogr. A* **777:** 275–82 (1997).
31. Z. Zhang and J. Pawliszyn. Headspace solid phase microextraction. *Anal. Chem.* **65:** 1843–52 (1993).
32. P. Martos and J. Pawliszyn. Sampling and determination of formaldehyde using SPME with on-fiber derivatization. *Anal. Chem.* **70:** 2311–20 (1998).
33. L. Pan and J. Pawliszyn. Derivatizaion/SPME: new approaches to polar analytes. *Anal.Chem.* **69:** 190–95 (1997).
34. R.E. Shirey and V. Mani. New carbon-coated solid phase microextraction (SPME) fibers for improved analyte recovery. Pittsburgh Conference Presentation, Supelco Publication T497015, 1997, pp 1–17.
35. K. Pratt, R. Shirey, and V. Mani. Solid-phase microextraction of VOCs in water. *Volatile Organic Compounds in the Environment,* ASTM STP 1261, W. Wang, J. Schnoor, and J. Doi, Eds. American Society for Testing and Materials, Philadelphia, PA, 1996, pp 142–43.

Manuscript accepted January 19, 2000.