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Selective stationary phase for solid-phase microextraction analysis of sarin (GB)

S.D. Harvey*, D.A. Nelson, B.W. Wright, J.W. Grate

Pacific Northwest National Laboratory, P.O. Box 999/MSIN P7-07, Richland, WA 99352, USA

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Abstract

A number of critical field applications require monitoring air samples for trace levels of chemical warfare agents. Solid-phase microextraction (SPME) is a convenient format to conduct these analyses. Measurements could be significantly improved if a SPME phase selective for nerve agents were substituted for non-selective polymers typically used (e.g., polydimethylsiloxane). This paper evaluates a novel stationary phase, previously developed for methylphosphonate sensor applications, for use with SPME sampling. The phenol-based polymer, BSP3, was found to offer far higher selectivity toward sarin (GB) than polydimethylsiloxane due to a pronounced affinity toward the target analyte and a lower affinity toward hydrocarbons. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solid-phase microextraction (SPME) was first described by Arthur and Pawliszyn in 1990 as a versatile concentration/sampling procedure [1]. Since its inception, this technique has found widespread acceptance for headspace sampling above solids and liquids, and for direct sampling of liquids and gases. SPME sampling typically exposes a fiber coated with a thin polymer film to a gas or liquid sample for a defined period of time, during which analytes partition into the polymer. If the fiber is exposed for a sufficient period, equilibrium will be reached where further fiber exposure does not result in additional collection of analyte [2]. After sampling, the fiber is retracted into a protective syringe-type needle in preparation for analysis. Typically the retracted fiber is inserted into a heated gas chromatographic injection port, the fiber exposed, and the analytes thermally desorbed [2]; although solvent stripping of the fiber in combination with analysis by high-performance liquid chromatography also can be employed [3]. Advantages of the SPME approach over traditional sampling include complete elimination of solvent, simplification of sampling procedure, reduction in analysis time and cost, near real-time analysis, and regeneration of the fiber for immediate reuse [4]. As further detailed below, the goal of this study is to investigate SPME using a fiber polymer coating that exhibits selectivity toward the chemical warfare agent sarin.

A variety of applications highlight the versatility of SPME for trace analysis of atmospheric constituents. For static equilibrium sampling, the fiber is

*Corresponding author. Tel.: +1-509-372-1144; fax: +1-509-376-5021.

E-mail address: scott.harvey@pnl.gov (S.D. Harvey).

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exposed for sampling periods ranging from seconds to hours depending on target analyte volatility [4]. The resulting concentration of analyte in the fiber polymer will be proportional to the atmospheric concentration. On the other hand, very fast sampling (typically on the order of minutes for most analytes) can be achieved in the nonequilibrium mode where sampling times fall short of those required to achieve equilibrium [5]. Yet another mode of SPME sampling is time-weighted average sampling using a retracted fiber configuration. In all the cases above, detection limits are typically in the low part-per-billion (ppb) or high part-per-trillion concentration ranges [6]. An additional possibility is sampling with a fiber that is preloaded with derivatization reagent. This on-fiber derivatization approach has been used to advantage for enhancing detection selectivity and sensitivity for formaldehyde by forming an electrophoric derivative [7,8]. In general SPME provides faster analysis with lower detection limits compared to conventional air sampling methods.

SPME sampling in the nonequilibrium mode has been used in combination with fast gas chromatography (GC) for rapid field analysis of a number of atmospheric constituents [9]. These studies used a field-portable gas chromatograph (SRI Model 8610C) fitted with a capacitive discharge-heated injection port. Rapid fiber heating and desorption produces a very narrow sample plug that is ideal for introduction into small diameter capillary columns used for fast GC. Rapid sample turnaround of approximately 15 min has been demonstrated with this combination, and it is likely these times could be significantly reduced. Automation of the SPME–fast GC instrumentation is possible and would allow continuous near real-time analysis of target analytes.

A clear need exists for rapid and reliable air testing for nerve agents during military actions as well as monitoring weapon storage bunkers and decommissioning facilities for agent leakage. Reports that address field air sampling using SPME fibers for nerve agents or pesticides are absent from the literature. Other studies describing general air sampling using SPME typically use fibers that contain thick films of non-selective polymers, usually either polydimethylsiloxane (PDMS) or PDMS–divinylbenzene (DVB). Analytical measurements could be significantly improved if selective stationary phases were used rather than non-selective polymers.

Recently, a polymer having selectivity toward nerve agent simulants was designed at Pacific Northwest National Laboratory for incorporation into sensor arrays [10–13]. This polymer, BSP3, consists of hydrogen-bond acidic hexafluorobisphenol groups, alternating with oligo(dimethylsiloxane) segments. Evaluation of BSP3 in a sensor format verified selectivity toward a methylphosphonate nerve agent surrogate, dimethyl methylphosphonate (DMMP), as well as other basic analytes. The detection limit toward DMMP using a surface acoustic wave (SAW) sensor was extrapolated to be approximately 1 ppb. Previous studies have shown that SAW sensors coated with hydrogen bond acidic polymers such as fluoropolyol provide high sensitivity toward nerve agent simulants and actual nerve agents [14]. Simulant studies have shown that BSP3 provides higher sensitivity and faster response times than fluoropolyol [11]. BSP3 applications have also been extended to a dye composite film sensor that operates on changes in the dye fluorescence spectrum induced by analyte competition for available BSP3 hydrogen bonding sites [15].

The goal of this study is to evaluate the BSP3 phenol-based stationary phase for its selectivity toward methylphosphonate nerve agents. Although the selectivity of this polymer toward methylphosphonate agent surrogates has been demonstrated, studies described here will verify polymer selectivity toward an actual nerve agent (sarin) by determining the chromatographic partition coefficient (k') compared to PDMS. Furthermore, SPME fibers containing this polymer will be prepared and evaluated for their ability to selectively sample sarin. The SPME–GC application should be more selective and sensitive than the sensor-based approach, and these studies set the necessary background for incorporating the selective polymer into field-portable SPME–fast GC instrumentation.

2. Experimental

2.1. Standards and solutions

Sarin (*o*-isopropyl methylphosphonofluoridate) was

obtained by special arrangement from the US Army Soldier and Biological Chemical Command (SBCCOM). Sarin purity, as determined by GC analysis, was in excess of 95%. *n*-Tridecane and *n*-tetradecane were obtained from Alltech (Deerfield, IL, USA) and hexane from Burdick and Jackson (Muskegon, MI, USA). For SPME studies, a stock solution was prepared by diluting 2.0 ml GB standard and 20 μl *n*-tetradecane to 10.0 ml with hexane. Analyte concentrations in this solution were 2.92 ppm (parts per million) and 1.53 ppt (parts per thousand) for sarin and *n*-tetradecane, respectively. For packed GC studies, a 14.6-ppm sarin standard was used along with a standard that contained 20 ppm each of *n*-tridecane and *n*-tetradecane dissolved in hexane.

2.2. Polymer preparation

Synthesis of the selective BSP3 polymer was based on hydrosilylation reaction chemistry, which has been described [10]. BSP3(b) was prepared using a truncated procedure. Initial reaction conditions and the reactant mol ratio of 1,1,3,3,5,5-hexamethyltrisiloxane to 2,2-bis(3-allyl-4-hydroxyphenyl)hexafluoropropane were the same as used for BSP3, however, the reaction was terminated and polymer isolated after the siloxane starting material had been consumed. Capacity factors were determined on both phases individually, whereas SPME studies were carried out exclusively with the BSP3 phase.

2.3. Polymer characterization

Size-exclusion chromatography was conducted at 40 °C using a 25 cm×10 mm I.D. Jordi Associates DVB column (Bellingham, MA, USA) that contained 5-μm particles (10^4 Å pores). This column was capable of separating analytes within the molecular mass range of approximately 10^2–2×10^7. Tetrahydrofuran (99.9+%, HPLC grade, Aldrich) mobile phase was delivered to the column at a flow-rate of 1.0 ml/min by an Alltech Model 526 pump. Polymer samples, prepared at 6% (w/v) in tetrahydrofuran, were introduced (100 μl) to the column by use of a Rheodyne Model 7000 injector. Two serially connected detectors were used for molecular mass determinations: a MiniDAWN multiple-angle light scattering detector followed by a Wyatt Technology Optilab DSP interferometric refractometer operated at 690 nm (both detectors from Wyatt Technology, Santa Barbara, CA, USA). The refractive index detector was used for determining the specific refractive index increment. Weight-average (M_w) and number-average (M_n) molecular mass values along with polydispersity (M_w/M_n) calculations were provided by Wyatt Technology's ASTRA software [16].

2.4. Packed column studies

2.4.1. Column preparation

Stationary phases for packed columns contained 10% (w/w) polymer loading. Phases were prepared by dissolving adequate polymer in methylene chloride (Aldrich, St Louis, MO, USA), mixing with the Chromosorb WHP 100/120 mesh support (Supelco, Bellefonte, PA, USA), and removing the solvent by rotary evaporation. The coated support was packed into 10 ft.×1/8 in. stainless steel column blanks and held in place with plugs of deactivated glass wool (1 ft.=30.48 cm; 1 in.=2.54 cm). Three columns that differed only in the identity of the stationary phase film were produced in this fashion. Columns contained BSP3, BSP3(b), and finally for comparison OV-1 (PDMS) polymer (Supelco) liquid phases. BSP3 and BSP3(b) columns were conditioned with helium flow at 150 °C for 5 h, whereas the OV-1 column was conditioned at 200 °C overnight before use. Retention times obtained from isothermal gas chromatographic runs at 130 °C were used for capacity factor determinations.

2.4.2. GC instrumentation

A Hewlett-Packard (Palo Alto, CA, USA) 5890 Series II gas chromatograph was used for these studies after suitable modifications for packed column use. Modifications included installation of injector and detector sleeves designed for use with 1/8 in. columns and substitution of a large diameter flame orifice jet [conversion supplies obtained from Agilent (Palo Alto, CA, USA)]. Packed columns were installed and helium pressure adjusted to give a flow-rate of 30 ml/min at room temperature.

2.4.3. Capacity factor determinations

Capacity factor calculations made use of column

void times determined by methane injections. Injection of the sarin and the hydrocarbon mixture (*n*-tridecane and *n*-tetradecane) standards followed. Each standard was analyzed three to five times on each column. The average and standard deviation was then calculated for the void time and analyte retention times. Capacity factors were calculated using retention averages by dividing the adjusted retention times (retention time minus the void time) by the void time. Error associated with the capacity factor values was determined by a propagation of error calculation using the retention standard deviation values.

2.5. SPME experiments

2.5.1. Fiber preparation

Fibers used for SPME were 200-μm O.D. fused-silica with a 9-μm coating of polyimide obtained from Polymicro Technologies (Phoenix, AZ, USA). Fibers were approximately 15 cm in length with the last 1.0 cm of polyimide removed to expose the fused-silica. In preparation for coating, the exposed fused-silica was immersed in a 10% solution of dichlorodimethylsilane in methylene chloride for 30 min followed by a 5-min methanol rinse. The deactivated fused-silica was then coated with BSP3 by repetitive dipping into a 0.2% solution of polymer dissolved in methylene chloride. The polymer was partially cured by placing it in a 110 °C oven for 20 min at which time the BSP3 coating was molded by withdrawing into a 356-μm I.D. SPME needle. The coating and molding process was repeated (usually about four times) until a reasonably uniform coating of polymer was obtained. The fiber was then completely cured by heating at 110 °C overnight. Fiber assemblies were then constructed by inserting the polyimide-coated fiber end through the needle and septum of a surplus Supelco SPME needle assembly. SPME fibers were conditioned at 150 °C for 30 min with helium flow in the injection port of a GC system before use. As discussed below, BSP3-coated fibers used in these experiments had a film thickness of 12–13 μm. For comparison, Supelco SPME fibers were evaluated that contained either a 100- or 30-μm coating of PDMS. The 30-μm PDMS film was coated on a 110-μm diameter cylindrical fiber core. These fibers were conditioned at 250 °C for 1 h in accordance with the manufacturer's suggested pretreatment.

2.5.2. Determination of film thickness

BSP3 fibers were imaged under a Leica Model DMRXP microscope used in the reflectance mode at 50 times magnification. Photographs were taken along the entire coated fused-silica length. Enlarged fiber reproductions were constructed from photocopies of the fiber photographs. Film thickness was determined by cut-and-weigh comparison between the coated and blank fiber reproductions. The blank fiber diameter of 200 μm, as measured by the manufacturer, was used as a reference for the determination of average film thickness.

2.5.3. SPME sampling

For SMPE sampling, a 1.0-ml aliquot of the sarin–*n*-tetradecane solution was placed in a 4-ml amber headspace vial. Sampling proceeded at room temperature above the stirred hexane solution. The solution was stirred by use of a small PTFE-coated stir bar revolving at approximately 180 rpm. Sampling periods were typically 20 min, although for kinetic studies, sampling times ranged from 10 to 120 min.

2.5.4. Capillary GC analysis

A Hewlett-Packard 5890 Series II gas chromatograph in its capillary GC configuration was used for these studies. Chromatography was conducted on a 15 m×250 μm I.D. column that contained a 0.5-μm film of Carbowax/BTR (Quadrex, New Haven, CT, USA). Helium flow was maintained through the column by a constant 8.0 p.s.i. column head pressure (1 p.s.i.=6894.76 Pa). The injector was fitted with a 0.75-mm I.D. SPME injection sleeve (Supelco) and the split flow was adjusted to 100 ml/min. Predrilled thermogreen LB-2 septa along with a SPME inlet guide (both from Supelco) were used to minimize injection liner contamination due to septum coring. Injections involved inserting the SPME needle into the 150 °C injection port for 4 min under splitless conditions at which time the split valve was opened for 1 min before the needle was removed and the oven temperature program initiated. The column was programmed from 35 to 170 °C at a rate of

4 °C/min and maintained at the final temperature for 10 min. Compound elution was monitored by flame ionization detection and recorded on a Hewlett-Packard Model 3395 integrating recorder.

3. Results and discussion

3.1. Polymer characterization

Size-exclusion chromatography (SEC) of BSP3 and BSP3(b) polymers indicated the presence of a low-molecular-mass component (M_w of 3000 and 4620 for BSP3 and BSP3(b), respectively), that was hypothesized to be a cyclic siloxane, in addition to the high-molecular-mass polymer. The polydispersity of the low-molecular-mass component was close to unity indicating a simple composition for this component. The relative amount of cyclic component was greater for the BSP3 polymer (46%) than for the BSP3(b) polymer (8%). The molecular mass of BSP3 was significantly higher (M_w=29 800, M_n= 12 700) than that of the BSP3(b) (M_w=20 670, M_n= 11 240) polymer. A decision to utilize BSP3 for SPME experiments was made before SEC results for this polymer were obtained. Compared to the extended synthesis, the truncated methodology typically results in an equivalent or higher-molecular mass polymer with a lower proportion of cyclic by-product. The lower molecular mass of the BSP3(b) polymer obtained here is somewhat atypical. Regardless, the two polymers clearly differ in their molecular mass and relative amount of the cyclic component and therefore manifestation of different chromatographic characteristics would be expected.

3.2. Capacity factors at 130 °C

Table 1 displays the capacity factor values obtained during the packed column study. These values dramatically confirm the high affinity of the BSP3 and BSP3(b) phases for sarin relative to OV-1. Capacity factors were over 20 times higher on the fluorinated phenol phases than on OV-1. Both BSP3 and BSP3(b) have a much lower affinity (by at least a factor of two) toward *n*-alkanes compared to OV-1. The selectivity of phenol-based phases, whether incorporated in SAW or SPME formats, is therefore due to a far greater affinity toward methylphosphonates and a low affinity toward hydrocarbons. Although DMMP was studied in previous sensor studies, this chromatographic experiment quantitatively verifies the high affinity toward sarin, an actual methylphosphonate nerve agent, at elevated temperatures.

Table 1
Capacity factors for hydrocarbons and sarin on PDMS, BSP3, and BSP3(b) stationary phases

Phase	Analyte		
	n-Tridecane	*n*-Tetradecane	Sarin
PDMS (OV-1)	13.5±0.1	23.2±0.1	1.6±0.1
BSP3	6.8±0.1	12.0±0.1	36.2±0.3
BSP3(b)	3.6±0.1	6.1±0.1	34.2±0.7

More subtle differences were also observed between the two different fluorinated phenol-based phases. Although both polymers displayed similar high affinity toward sarin and low affinity toward hydrocarbons, the BSP3 phase retained hydrocarbons roughly twice as strongly as BSP3(b). Consistent with the differing physical properties of these phases is the fact that BSP3 displayed an approximate fivefold higher column bleed at 130 °C than did BSP3(b). The higher column bleed likely reflects the greater proportion of cyclic siloxane by-product contained in BSP3. The lower thermal stability of BSP3 made capacity factor determinations difficult to perform due to the high background signal.

The molecular basis for the high affinity of BSP3 and BSP3(b) phases toward methylphosphonates stems from a structure designed to facilitate strong hydrogen bond interactions between basic analytes and the phenol groups in the polymer. Electron withdrawing properties of the polymer trifluoromethyl groups intensify the acidic character of the phenols. Selective molecular interactions for organophosphorus compounds are derived from hydrogen bonding that occurs between the double bonded oxygen in the organophosphate and the strongly acidic phenol groups in the polymer. BSP3 will also preferentially interact with other compounds that can act as Lewis bases including compounds that contain carbonyl oxygens. Functional groups incorporated in the polymer are not expected to yield exceptional

temperature stability, which is a limitation for the present application.

3.3. SPME analysis

Initial SPME studies exposed BSP3 coated fibers to thermal conditioning at temperatures up to 200 °C. Microscopic examination of fibers exposed to 200 °C for extended periods indicated that the polymer had been vaporized from the silica surface. Based on these observations, as well as the packed GC work described above, it was decided to limit the thermal exposure of BSP3 fibers to no more than 150 °C. BSP3 coated fibers used for this work were conditioned (for 30 min) and desorbed (for 5 min) during analysis at 150 °C.

Since the use of neat chemical agents was not possible, our studies were limited to examining the headspace above dilute solutions of agents dissolved in hexane. Taking a SPME headspace sample above a hexane solution poses some unique challenges. Thick-film PDMS fibers were destroyed by this sampling treatment. The PDMS polymer swells in the saturated hexane environment and is partially stripped from the fiber with retraction into the SPME needle. Further damage was inflicted after GC injection where flash vaporization of phase-sequestered solvent caused further disruption of film integrity. For these reasons, fibers coated with the 30-μm PDMS were evaluated. These thinner film fibers tolerated the hexane headspace environment far better than the 100-μm counterparts, although visible damage was still evident after a few sampling episodes. On the other hand, fibers coated with the BSP3 phase were resilient toward the hexane headspace environment and did not display damage or phase stripping even after numerous sampling periods. For studies presented here, a fresh 30-μm PDMS SPME fiber was used for each sample, whereas the BSP3 fibers were reused for numerous analyses.

Initial SPME experiments verified that thermal desorption conditions were adequate to completely remove analyte from the SPME fibers. For these experiments, fibers used for sampling the sarin–*n*-tetradecane solution were immediately reanalyzed to check for sample carryover. Sarin was found to be completely removed from both PDMS and BSP3 fibers during the initial thermal desorption. Carryover of *n*-tetradecane was determined to be less than 5% on the BSP3 fiber and about 1% on the 30-μm PDMS fiber. Both compounds were therefore essentially quantitatively desorbed from the polymers by the 5-min 150 °C desorption conditions.

Comparisons between PDMS and BSP3 fibers were conducted at two different times using two different BSP3 fibers. These different experimental comparisons are referred to as experiments 1 and 2 below. Film thickness for the BSP3 fibers, as determined by examination of two fibers in the same preparation batch as those used for the SPME experiments, was determined to be 12 and 13 μm. The polymer volume present on the 30-μm PDMS fibers was therefore about 1.6 times that contained on the BSP3 fibers. Representative chromatograms of the headspace above a sarin–*n*-tetradecane hexane solution are presented in Figs. 1 and 2. Fig. 1 shows a chromatogram that resulted from a 20-min sampling on PDMS. This chromatogram is characterized by a relatively small sarin (retention time of 10.48 min) peak, the *n*-tetradecane internal standard (retention time of 14.91 min), and a sampling artifact that appears at 22.75 min. Fig. 2 shows a chromato-

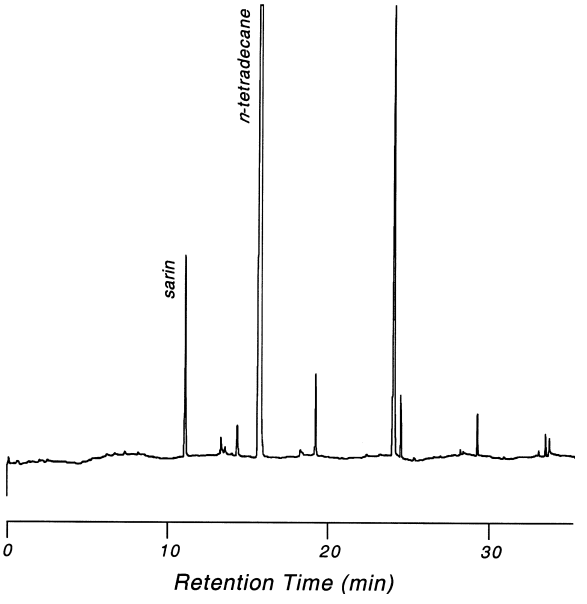

Fig. 1. Chromatogram of the headspace above a sarin- and *n*-tetradecane-containing hexane solution sampled with a PDMS-based SPME fiber.

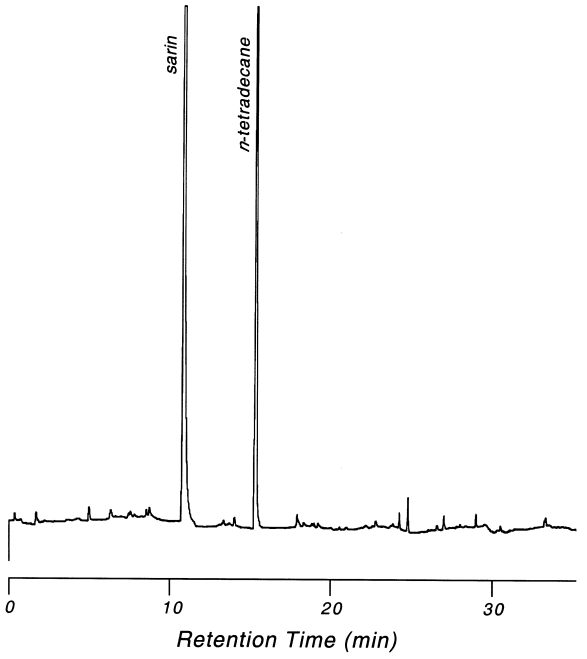

Fig. 2. Chromatogram of the headspace above a sarin- and *n*-tetradecane-containing hexane solution sampled with a BSP3-based SPME fiber.

gram that results when an identical solution is sampled using a BSP3 fiber. GB is present with a much higher peak area and the analysis is clean without the presence of artifact peaks. In comparing Figs. 1 and 2, it is somewhat less obvious that the *n*-tetradecane peak area that results from PDMS sampling is approximately four times that found for the BSP3 analysis.

Quantitative differences between SMPE sampling with PDMS and BSP3 are highlighted in Table 2. This table gives the peak area average of three analyses along with the standard deviations and the relative standard errors for average ratios. Both of the two different fibers tested exhibited a pronounced affinity toward sarin that was consistent with the capacity factor experiments. Peak areas for sarin were 8.2 and 14 times larger for experiments 1 and 2, respectively, when sampling with BSP3 fibers compared to PDMS (Table 2). If normalized for equal phase volumes, the results for fibers 1 and 2 display a 13- and 22-fold higher affinity toward sarin, respectively, than PDMS. The average of these values (18) compares favorably to the 22-fold increase expected based on the capacity factor results. Using a similar line of reasoning based on the capacity factor data, about half the *n*-tetradecane quantity per volume of BSP3 would be expected compared to PDMS. Peak areas in Table 2 indicate that the BSP3 fibers contained 0.47 and 0.32 the quantity of *n*-tetradecane compared to PDMS. Phase volume adjusted values of 0.75 and 0.51 relative to PDMS are again in reasonable agreement with the amount of hydrocarbon expected based on the capacity factor data. Table 2 also lists average peak area ratios for sarin–*n*-tetradecane values as an indication of fiber selectivity. The fairly large relative percent errors are a consequence of difficulties inherent in sampling from a hexane headspace matrix.

To investigate BSP3 uptake kinetics, headspace samples were taken for 10, 20, 45, and 120 min. The peak areas of sarin and *n*-tetradecane as a function of sampling time are presented in Fig. 3. The amount of

Table 2
Quantitative comparison between BSP3 and PDMS SPME fibers

	Average sarin peak area±SD	Average *n*-tetradecane peak area±SD	Sarin–*n*-tetradecane area ratio±rel.% error
Experiment 1			
BSP3 Fiber #1 ($n=6$)	$(1.82\pm0.24)\times10^6$	$(5.18\pm3.06)\times10^6$	0.429±38%
PDMS ($n=3$)	$(0.22\pm0.01)\times10^6$	$(11.0\pm2.77)\times10^6$	0.021±25%
Experiment 2			
BSP3 Fiber #2 ($n=3$)	$(2.55\pm0.01)\times10^6$	$(3.83\pm1.01)\times10^6$	0.703±31%
PDMS ($n=3$)	$(0.18\pm0.01)\times10^6$	$(12.0\pm4.62)\times10^6$	0.016±25%

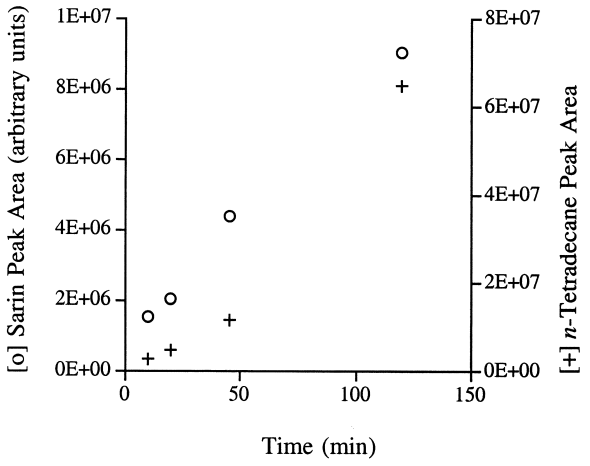

Fig. 3. Kinetics of sarin and *n*-tetradecane uptake on a SPME fiber coated with BSP3 polymer.

sarin is increasing even at the 120-min sampling period, a result that suggests equilibrium has not been reached. A corresponding plot for *n*-tetradecane indicates a similar result except uptake accelerates somewhat with time (concave upward). The sluggish uptake kinetics observed suggest that the more rigorous curing used for BSP3 SPME fiber preparation resulted in a glassy polymer composition rather than the elastomeric material used during previous sensor studies. The peak area ratio of sarin to *n*-tetradecane versus sampling time yields a linearly decreasing plot that starts at a ratio of 0.55 for a 5-min sample and ends at a ratio of 0.13 for a 120-min sample. This plot would be expected to achieve a constant ratio value at equilibrium. A possible consequence of the observed kinetic uptake is that shorter sampling times, typical of times used for nonequilibrium SPME sampling, would result in a higher relative discrimination against interfering hydrocarbons than would be predicted from capacity factors. This phenomenon could be used to advantage during SPME sampling to obtain even higher selectivity.

SPME analysis with sampling on selective polymers, such as BSP3, combined with separation by high-resolution capillary GC should offer exquisite selectivity, especially when used in combination with selective and sensitive chromatographic detectors. The thermal stability of BSP3 is the limiting factor for the SPME application described in this work. While the 150 °C temperature ceiling is adequate for analysis of sarin (and probably for several methylphosphonate precursor compounds), this temperature may be insufficient for analysis of less volatile G-series agents such as soman (GD) and tabun (GA). Several means to increase the temperature stability of the BSP3 phase through alterations in synthetic methodology, polymer purification, and immobilization on the SPME fiber are under consideration to allow extension to less volatile agents.

4. Conclusions

Chromatographic experiments with two different batches of phenol-based polymer, BSP3 and BSP3(b), demonstrated a remarkable affinity toward sarin and lower affinity toward hydrocarbons compared to PDMS. Our initial studies determined capacity factors for sarin and two hydrocarbons, *n*-tridecane and *n*-tetradecane, on packed GC columns that contained BSP3, BSP3(b), or PDMS (OV-1) stationary phases. Results indicate that BSP3 and BSP3(b) phases had a greater than 20-fold higher affinity toward sarin than PDMS. BSP3 and BSP3(b) also exhibited at least a twofold lower affinity toward *n*-tridecane and *n*-tetradecane. SPME experiments followed, using fibers prepared from the BSP3 polymer. Fibers were evaluated by sampling the headspace above a hexane solution that contained both sarin and *n*-tetradecane. Relative to PDMS, the BSP3 fiber exhibited a pronounced selectivity toward sarin characterized by a high affinity toward the nerve agent and a lower affinity toward hydrocarbons. Quantities of sarin and *n*-tetradecane found in the fiber after sampling were in reasonable agreement with amounts expected based on capacity factor studies.

Studies described herein verify the high affinity of BSP3 and BSP3(b) polymers toward an actual nerve agent. This significantly extends previous studies that demonstrate selectivity toward a chemical warfare surrogate, DMMP, using BSP3 as a coating on a SAW sensor device. Since SPME exploits both the selectivity of the polymer toward basic analytes and the high separation efficiency available from capillary gas chromatography, the overall selectivity can be expected to be superior to sensor-based ap-

proaches. SPME with a BSP3-coated fiber is expected to provide an order of magnitude or more higher sensitivity and lower detection limits for sarin than SPME with PMDS, based on the demonstrated higher affinity of BSP3 in both chromatographic and SPME experiments. The principal limitation of the SPME approach using BSP3 is the limited temperature stability of the selective polymer. This thermal lability limits application to highly volatile agents and precursors. Studies reported here lay the groundwork for field evaluation of BSP3-based SPME fibers. Especially attractive is the incorporation of these selective fibers in automated fast GC instrumentation for near real-time determination of sarin in several high-impact field scenarios.

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