Screening for Sarin in Air and Water by Solid-Phase Microextraction–Gas Chromatography–Mass Spectrometry

John F. Schneider[1,*], Amrit S. Boparai[2], and **Larry L. Reed[1]**

[1]Argonne National Laboratory, Energy Systems Division and [2]Argonne National Laboratory, Analytical Chemistry Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439

Abstract

A method of screening air and water samples for the chemical-warfare agent Sarin is developed using solid-phase microextraction (SPME)–gas chromatography (GC)–mass spectrometry (MS). The SPME field kit sampler is ideal for collecting air and water samples in the field and transporting samples safely to the laboratory. The sampler also allows the sample to be introduced into the GC–MS system without further sample preparation. Results of the tests with Sarin using the SPME technique indicate that a sample collection time of 5 min is sufficient to detect 100 ng/L of Sarin in air. For water samples, Sarin is detected at a concentration of 12 µg/mL or higher. This method is ideal for screening samples for quick response situations.

Introduction

A terrorist incident may involve chemical-warfare agents such as Sarin (GB). The ability to rapidly detect and confirm that chemical-warfare agents have been released is critical in handling emergency response and cleanup in a safe and cost-effective manner. Several onsite monitors are available that provide real-time screening for chemical agents, but these monitors are prone to false positives and typically do not provide a high degree of sensitivity. Sampling, analysis, and subsequent positive identification of a suspected chemical-warfare agent are necessary to advise the responding government agency in regards to actions necessary to protect human health and the environment.

Solid-phase microextraction (SPME) is a relatively new technique that combines the extraction, concentration, and sample introduction of organic compounds in a single step (1–5). Air and water samples can be collected directly on SPME fibers. SPME can also be used to sample the headspace of solids and nonaqueous liquids. The use of SPME offers a rapid analytical method for chemical agent screening (6–7). An SPME–gas chromatography (GC)–mass spectrometry (MS) method for sampling and analysis for the rapid detection of the chemical nerve agent Sarin has been developed.

Preparing samples for analysis is often the most time-consuming step in an analysis, but for SPME it is quick and involves no solvents. SPME uses a silica fiber coated with a sorbent to extract samples. The coated fiber concentrates organic contaminants on its surface. When the fiber is transferred to the heated injection port of a GC, the analytes are desorbed and analyzed. SPME minimizes the need for emergency response personnel to handle chemical agent samples in the field. SPME samples can be collected in the field and only the fiber containing minute amounts of chemical agent is returned to the laboratory for analysis. SPME can also be used in determining when an area has been successfully decontaminated.

In this study, laboratory tests were performed with Sarin to evaluate the performance of the SPME technique. Air sampling was simulated by exposing the SPME fiber to Sarin-containing vapor in the headspace of a vial with a septum cap. Water sampling was simulated by dipping the SPME fiber into distilled water spiked with dilute Sarin solutions.

Experimental

Chemicals

Certified standard solutions of Sarin isopropylmethylphosphonofluoridate ($C_4H_{10}PO_2F$) (CAS No. 107-44-88) were obtained from the U.S. Army Chemical Agent Standard Reference Material (CASARM) Group for use in Argonne National Laboratory's Dilute Chemical Agent Facility. All reagents were analytical-reagent grade.

* Author to whom correspondence should be addressed.

SPME

A commercially available SPME field sampler was used (SPME field sampler with 65-µm PDMS-DVB coating, Supelco, Inc., Bellefonte, PA, Catalog Number 57359-U). The SPME field sampler consisted of a holder from which a needle containing a fiber coated with a sorbent phase can be extended. All SPME fibers were conditioned before use by desorbing them in a GC injection port at 260°C for at least 30 min.

Sample preparations

The SPME sampler fiber was exposed to the headspace above 10 mL of a solution of Sarin (240 µg/mL methanol) in a 40-mL vial with a septum cap for 5 min, during which airborne contaminants sorbed onto the fiber. The fiber was then withdrawn into the needle, which was withdrawn back into the holder. In order to determine absolute detection limits, 2 µL of the Sarin solution in methanol was injected into a 40-mL vial with a septum cap and

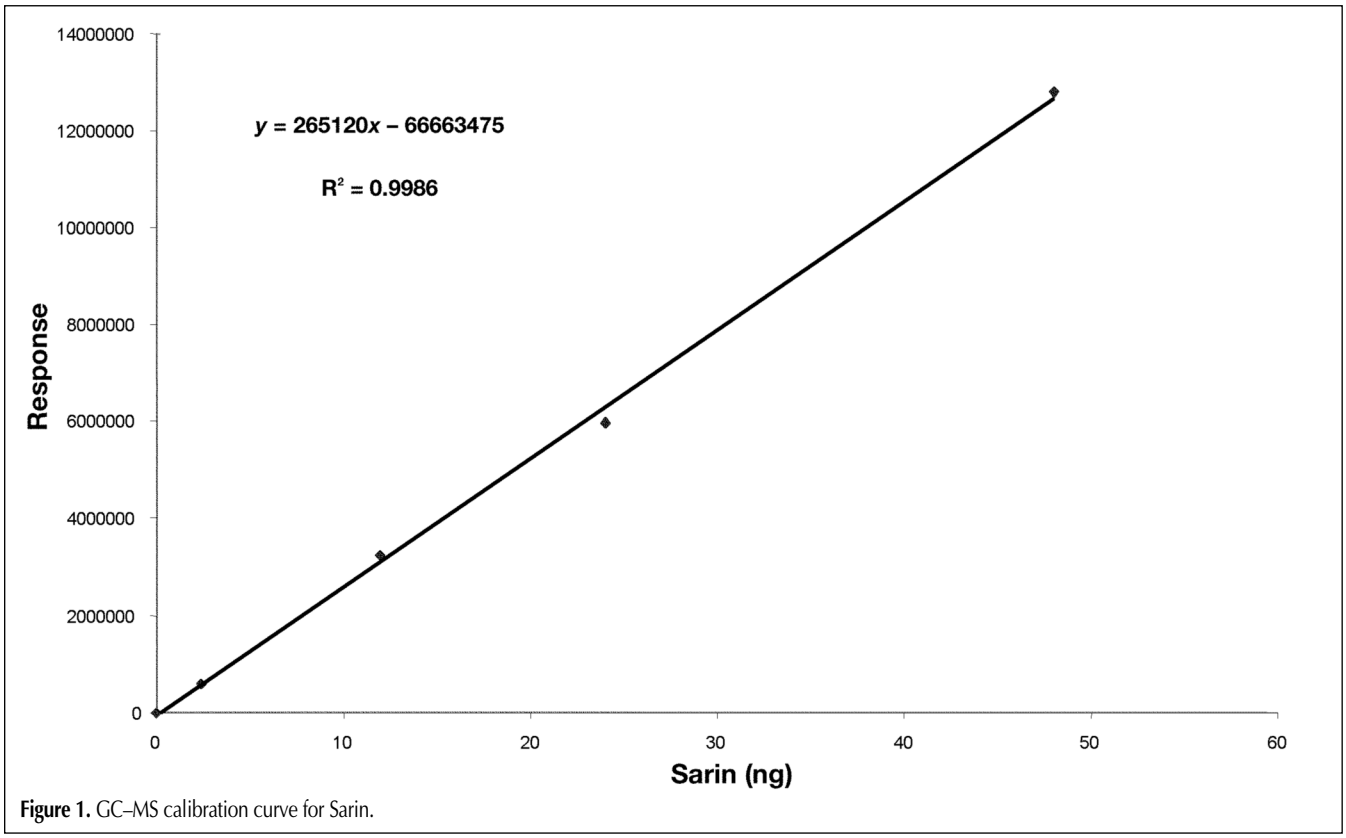

Figure 1. GC–MS calibration curve for Sarin.

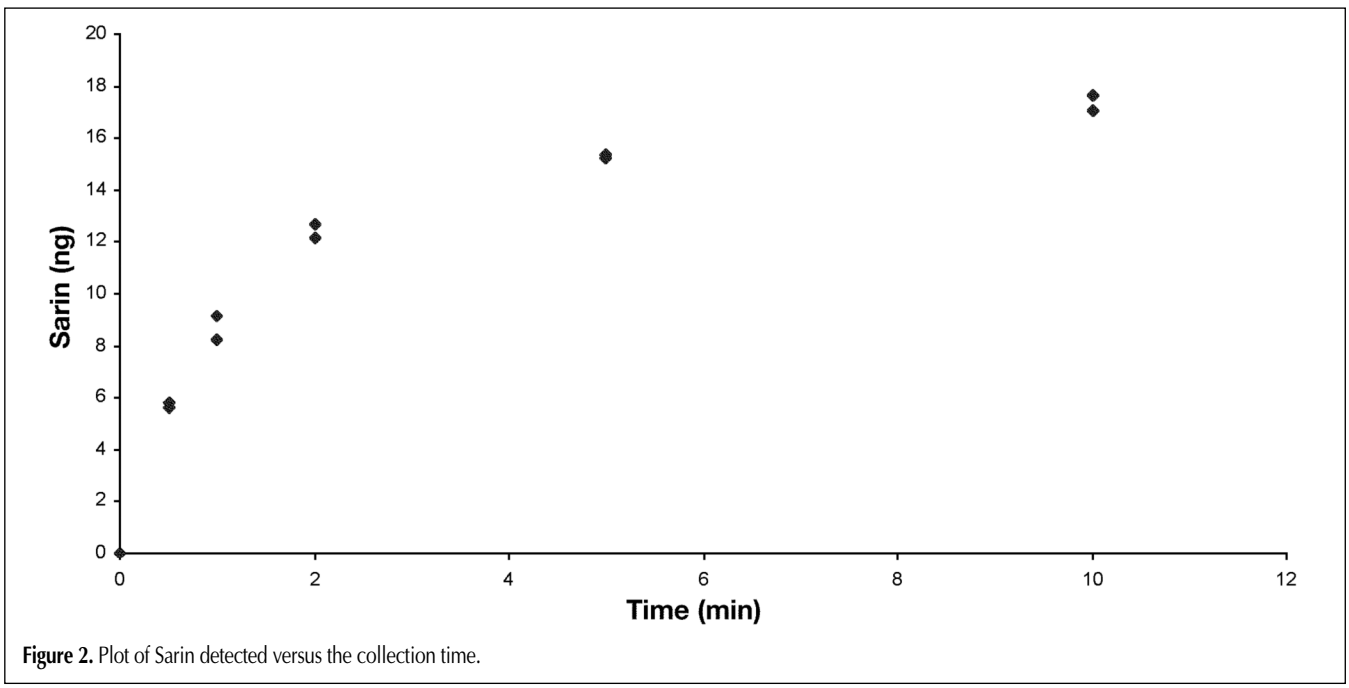

Figure 2. Plot of Sarin detected versus the collection time.

allowed to volatilize.

For this study, dilute solutions of Sarin in glass vials with septum caps were used for sampling. The SPME sampler fiber was placed directly into 20 mL of a dilute solution of Sarin for 5 min. These dilute solutions were prepared by adding a solution of Sarin in methanol (240 µg/mL) to distilled water. The resulting solutions were 12.0 µg/mL and 60.0 µg/mL Sarin.

Instrument and operating conditions

The SPME samples were analyzed with an Agilent 6890 GC coupled to a 5973 MS detector. The GC–MS was equipped with a glass liner suitable for SPME analysis (obtained from Supelco, but other equivalent glass liners can be used). The following GC parameters were used in this work: a GC column (30-m × 0.25-mm i.d., 0.25-µm film thickness) was used with HP-5MS 5% phenyl methyl siloxane, and the carrier gas was UHP helium. The GC was run in the splitless mode with a valve open time of 10 min and a flow rate of 1.0 mL/min for the helium carrier gas. The injector temperature was 250°C. The initial oven temperature was 45°C for 2 min, followed by a 10°C/min ramp to 110°C, held at 110°C for 1 min, ramped at 20.0°C/min to 280°C, and then held at 280°C for 2 min. The ion source temperature was 230°C, and the transfer line temperature was 280°C. The MS system was tuned with perfluorotributylamine by running the Autotune program. The MS was run in the scan mode from 50 to 350 amu with a threshold of 150 and a scan rate of 4.72 s^{-1}. The GC–MS was calibrated by the liquid injection of standard Sarin solutions. Quantitation was done on the extracted ion 99. Shown in Figure 1 is the calibration curve used for quantitation.

Table I. Results of Sarin Air Sampling

SPME fiber exposure time (min)	Sarin detected (ng)
0.5	5.84
0.5	5.62
1.0	8.24
1.0	9.17
2.0	12.67
2.0	12.17
5.0	15.37
5.0	15.21
10.0	17.06
10.0	17.64

Results and Discussion

Air is the most likely initial sample to be taken after a suspected terrorist incident, but suspect liquids should also be sampled. Emergency responders need to know if dangerous levels of Sarin are present. In order to simulate these types of samples in the laboratory, headspace techniques were used. Ten milliliters of Sarin methanol solutions of known concentration were placed into 40-mL glass vials with septum caps. Sampling the headspace gas above the liquid in the capped vial simulated air sampling. The Sarin in the solution and in the vapor above the solution were in equilibrium. Spectral libraries of standard chemical agents were previously produced and stored for library searching. Extracted ions were used for quantitation (99 amu) with two qualifying ions for agent confirmation (125 and 81 amu). Table I contains the results obtained with a solution of Sarin in methanol (0.240 mg/mL). Figure 2 is a plot of the amount of Sarin detected versus the collection time. The curve in Figure 2 appeared to be approaching a plateau region after 10 min of collection time. This plateau region represents the region in which equilibrium was reached between the Sarin in the vapor and the Sarin in the SPME fiber. It appears that after 2 min of col-

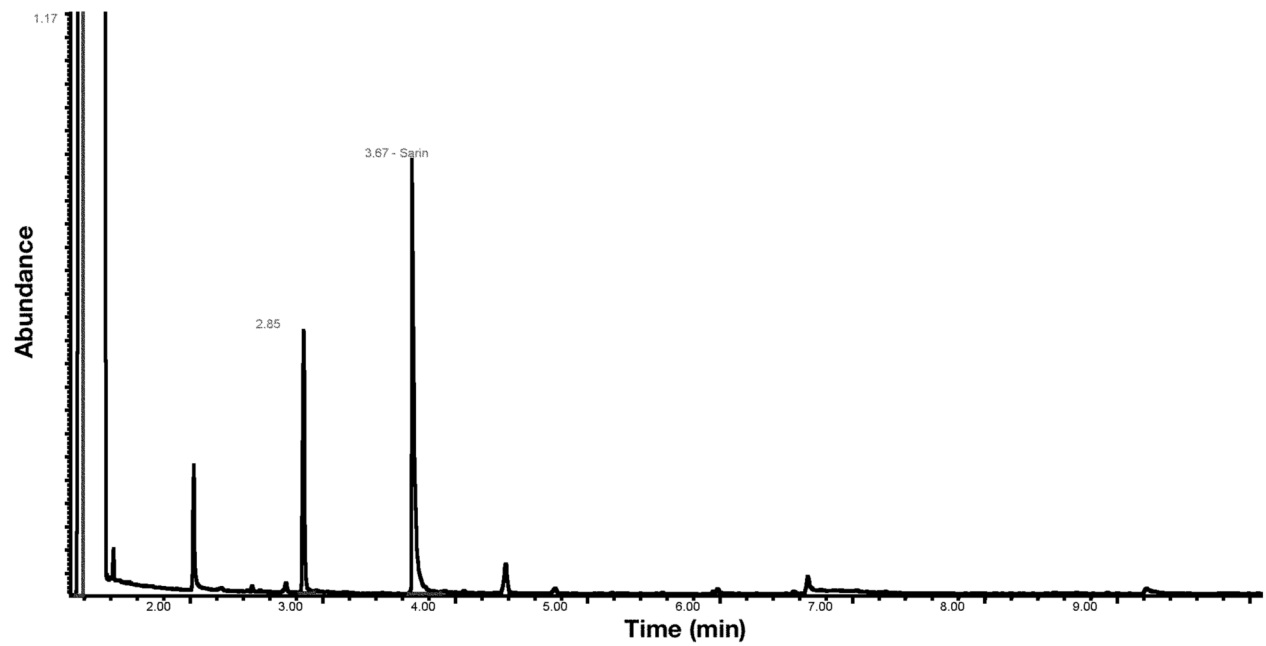

Figure 3. Total ion chromatogram for Sarin collected using SPME from air.

lection, 60% of the equilibrium amount was detected. The standard collection time of 5 min appears to be acceptable for collecting Sarin from air. Figure 3 is the total ion chromatogram of a SPME run of Sarin. Figure 4 is the extracted ion chromatogram showing the ions used to confirm the presence of Sarin. Figure 5 is the mass spectrum of the Sarin.

An estimated detection limit of 100 ng of Sarin per liter of air was determined for a collection time of 5 min at ambient temperature by injecting 2 µL of dilute solutions of Sarin in methanol into a 40-mL vial with a septum cap. The air in this vial was then sampled with an SPME sampler for 5 min. At the 100 ng/L concentration, 2.3 ng of Sarin was detected on the SPME fiber. This result was with a high level of confidence in the positive identification of Sarin, which is vital. Figure 6 is the extracted ion chromatogram for this analysis. This estimate was conservative; most likely not all the Sarin that was injected into the vial was volatilized into the headspace.

The SPME fiber was placed in water that was immediately spiked with Sarin at room temperature (19°C) for 5 min. The results are shown in Table II. Sarin proved to be unstable in water, degrading with time. The degradation of Sarin in water was expected (8). As shown in Table II, 12 µg/mL could not be detected in water samples after 113 min. For the 60-µg/mL solution, Sarin was not detected after 157 min with a 5-min collection time. An SPME sample of the 60-µg/mL solution that was collected for 10 min had 0.62 ng of Sarin on the fiber after 190 min.

The SPME method used for collecting Sarin was effective for

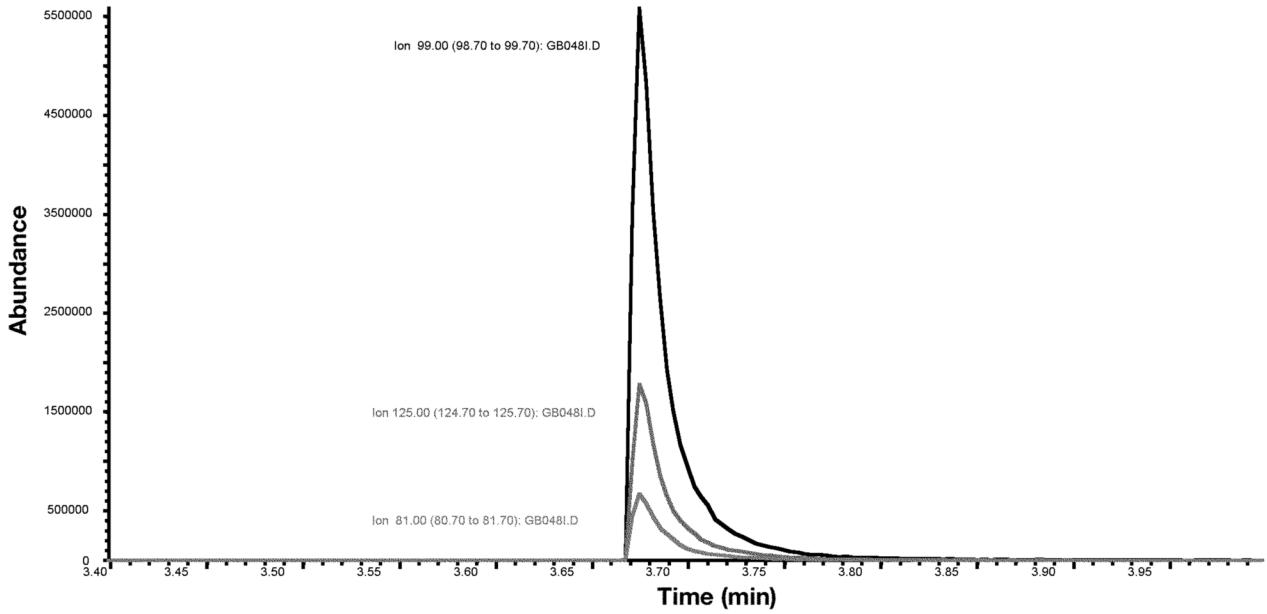

Figure 4. Extracted ion chromatogram for Sarin collected using SPME.

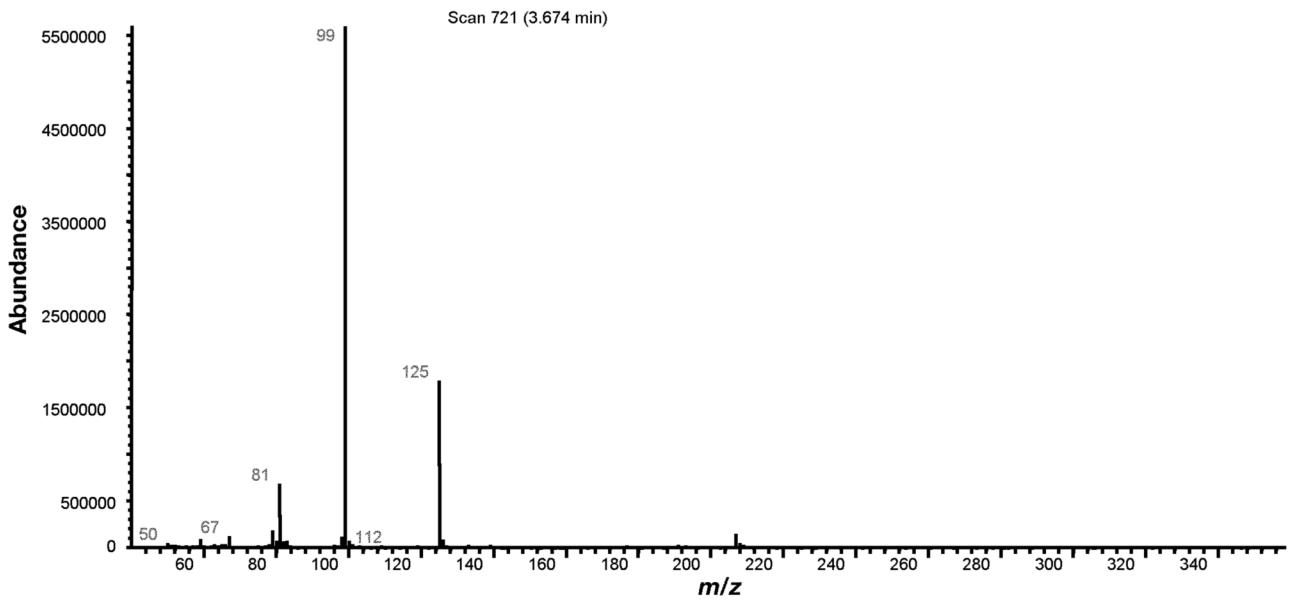

Figure 5. Mass spectrum obtained for Sarin collected using SPME from air.

air and water samples. In water, Sarin degrades rapidly in a matter of minutes or, at best, hours. The method presented works well with 5-min collection times. It is best suited as a semiquantitative screening method in response with potential emergencies in which a quick positive identification is required.

Acknowledgments

The authors would like to acknowledge support from the U.S. EPA Region 5 Emergency Response Branch for supporting this study and Ms. L. Nachowicz and Dr. H.J. O'Neill for reviewing this manuscript.

Table II. Results of Sarin Water Sampling

Sarin detected (ng)	SPME collection time (min)	preparation of solution (min)	Time after Sarin concentration (ppm)
4.68	5	0	60
2.61	5	34	60
1.48	5	73	60
nd*	5	157	60
0.62	10	190	60
0.72	5	0	12
0.32	5	53	12
nd	5	113	12

* nd, none detected.

References

1. Z. Zhang, M. Yang, and J. Pawliszyn. Solid-phase microextraction. *Anal. Chem.* **66:** 844A–53A (1994).
2. J. Pawliszyn. Solid phase microextraction: theory and practice. Wiley-VCH, New York, NY, 1997.
3. H.A. Lakso and W.F. Ng. Determination of chemical warfare agents in natural water samples by solid-phase microextraction. *Anal. Chem.* **69:** 1866–72 (1997).
4. J. Pawliszyn. Theory of solid-phase microextraction. *J. Chromatogr. Sci.* **38:** 270–78 (2000).
5. R. Shirey. Optimization of extraction conditions and fiber selection for semivolatile analytes using solid-phase microextraction. *J. Chromatogr. Sci.* **38:** 279–88 (2000).
6. A. Alcarez. *Analytical Chemistry Associated with the Destruction of Chemical Weapons, NATO ASI Series 65-76*. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.
7. K.G. Furton, J. Wang, Y. Hsu, J. Walton, and J.R. Almirall. The use of solid-phase microextraction–gas chromatography in forensic analysis. *J. Chromatogr. Sci.* **38:** 297–306 (2000).
8. D.N. Clark. *Review of Reactions of Chemical Agents in Water*. U.S. Army Medical Research and Development Command, U.S. Government Printing Office, Washington, D.C., 1989.

Manuscript accepted July 17, 2001.

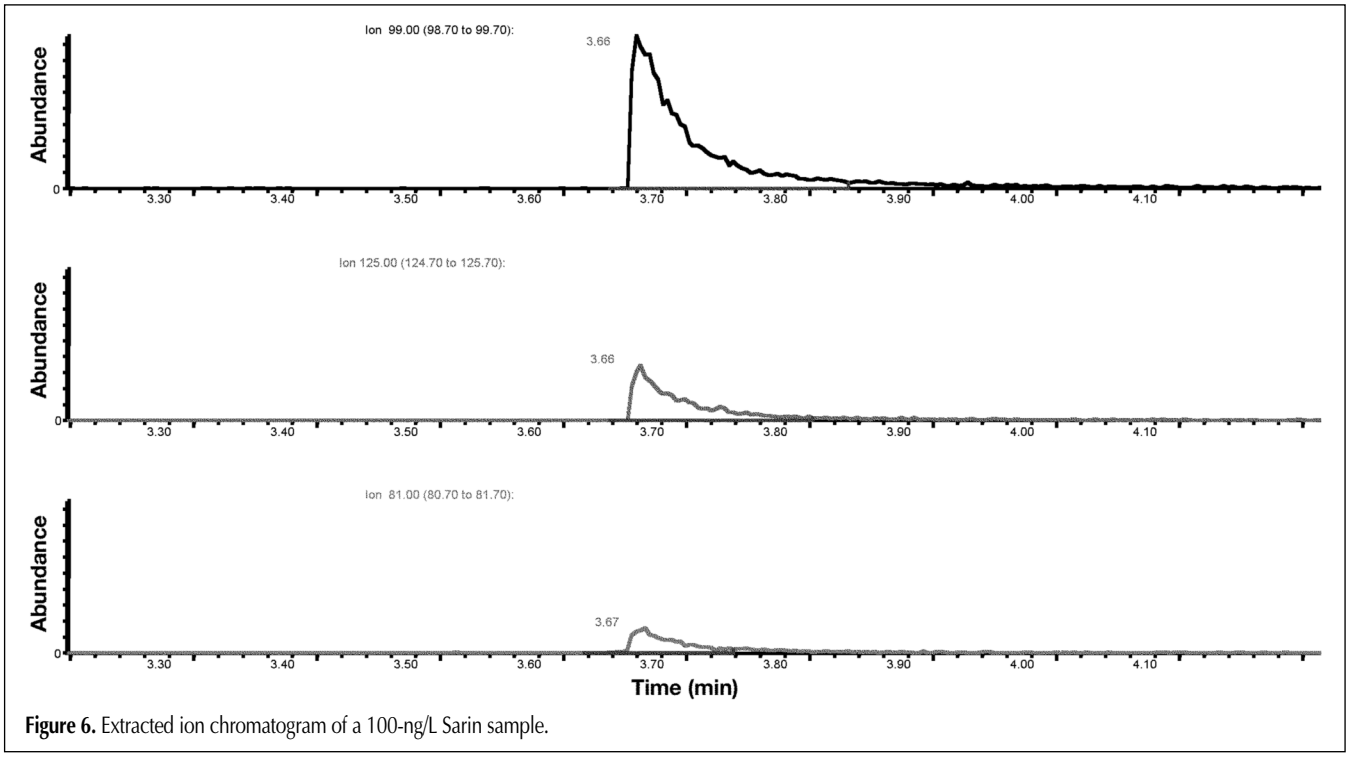

Figure 6. Extracted ion chromatogram of a 100-ng/L Sarin sample.