# Detection of Chemical Warfare Agents by Transportable GC/MS

## Application Note

Gas Chromatography/Mass Spectrometry


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## Abstract

The ability to quickly and accurately identify extremely dangerous chemicals is important for protection of the general public, first responder personnel, and deployed military forces. In this work, rapid gas chromatography-mass spectrometry (GC-MS) is described for chemical warfare agent compounds having a wide volatility range. Use of a Low Thermal Mass (LTM) resistively-heated GC column module in place of the typical air bath oven provides for a compact, transportable analytical system capable of rapidly separating a mixture containing O-isopropyl methylphosphonofluoridate (GB, or sarin), O-pinacolyl methylphosphonofluoridate (GD, or soman), bis(2-chloroethyl) sulfide (HD, or sulfur mustard), cyclohexyl methylphosphonofluoridate (GF), and O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX). Separations were completed in less than three minutes with rapid GC column temperature programming and high $H_2$ carrier gas linear velocity. Sample introduction means for the chemical warfare agents included direct injection and SPME sampling of headspaces. Data are also provided for chemical warfare agent simulants using standard thermal desorption approaches.


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## Introduction

Transportable GC/MS can rapidly collect analytical data in the vicinity of an incident or site where near real time detection is needed. This provides rapid response with appropriate environmental sampling based on early findings. Transportable GC/MS can provide responders with the fast and accurate identification of highly toxic chemicals based on NIST standard mass spectral libraries with instruments of the same quality as those in laboratory settings. This is essential for the protection of the public, first responder personnel, and deployed military forces.

Those responding to an incident suspected to involve toxic chemicals will choose analytical sampling means that fit the situation. This may involve the direct analysis of a liquid or extract, or the sampling of vapors known or suspected in the air. Direct sampling, solid phase microextraction (SPME), or thermal desorption of vapors sampled onto sorbent tubes can quickly introduce samples to the GC/MS instrumentation. Instrumentation should be sufficiently versatile so that responders have the necessary options for making a rapid determination of the hazard. If a full-capability GC/MS system must be used in the field, first responders should also have the means to move samples a short distance to the instrumentation so that the GC/MS can service a reasonable area and be positioned without becoming contaminated.

The standard split/splitless (SSL) inlet of a GC can accept a variety of samples. Both liquids and SPME samples can be introduced by direct injection through the septum. Thermal desorption must typically be preconfigured with a GC/MS instrument, but this can be implemented by a needle adaptor to an SSL inlet. While the GC does provide retention time information, it also provides a degree of separation needed by the mass spectrometer to match mass spectra to reference library data by the software. Low thermal mass (LTM) GC used with the mass spectrometer provides the features of small size, low power consumption, and rapid heating/cooling of the GC column to enhance transportability and speed of response. The use of a standard high performance quadrupole mass spectrometer provides the same mass spectral performance in a transportable instrument with data that is fully compatible with standard reference library data over a wide range of concentrations. This is especially critical for the analysis of unknown chemicals that will be introduced to the GC/MS in unknown concentrations.

## Experimental

Figure 1 shows a picture of the Agilent 5975T GC/MSD. The 5975T houses the Agilent 5975 MSD on the left, and retains the standard features and operation of the laboratory MSD using electron ionization. Housed on the right is a small isothermal oven that provides a convenient interface to the MSD for the SSL inlet, guard column, and the LTM module. The LTM module attaches from the front to the lower side of the oven. MSD ChemStation software provides all of the standard temperature programming and electronic pressure control (EPC) expected of the GC and its heated zones. The system additionally supports the standard Agilent automated liquid sampler (ALS) tower. For field operation the unit is conveniently controlled with the data system software installed on a laptop connected with a LAN cable.

*Figure 1. Photo of the Agilent 5975T LTM GC/MSD*

SPME samples of chemical warfare agents were taken by 10 s exposure of a 100 µm PDMS SPME fiber to the headspace of a piece of contaminated carpet. The carpet was contaminated with a dilute solution of O-isopropyl methylphosphonofluoridate (GB, or sarin), O-pinacolyl methylphosphonofluoridate (GD, or soman), bis(2-chloroethyl) sulfide (HD, or sulfur mustard), cyclohexyl methylphosphonofluoridate (GF), and O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX) in methylene chloride, followed by evaporation of the solvent. The carpet was placed in a small jar having a septum-equipped SPME sampling port and allowed to equilibrate for 30 min at room temperature prior to sampling. It was then stored at 110 °C for subsequent sampling at an elevated temperature. The temperatures of the SSL, transfer line oven, and the GC were held at 250 °C. The LTM column module contained a 30 m × 0.25 mm, 0.25 µm DB-5ms column. Hydrogen

carrier gas was used with an initial linear velocity (constant pressure mode) of 100 cm/s. The LTM temperature program started at 40 °C for 30 s, followed by heating at 120 °C/min. The MSD was operated in Scan mode with an *m/z* range of 50-300. A 0.75 mm id SPME inlet liner was used for the SPME injections. For direct injection of the chemical warfare agents, a 1 µL manual injection of the dilute agent solution in methylene chloride was made by syringe using a 4.0 mm id liner in the inlet. Splitless injection was done for both SPME and direct injection of the chemical warfare agents.

Thermal desorption measurements of chemical warfare simulants were demonstrated with the Agilent 5975T LTM GC/MSD using both the Markes Unity2 and the CDS ACEM 9300 thermal desorbers. Both thermal desorbers were operated with constant pressure helium carrier gas with the heated transfer lines butt-connected to a 1 m × 0.32 mm fused silica guard column in the oven to provide to the MS a flow rate of 1.5 mL/min at 50 °C. Both transfer lines were introduced to the oven through a small 0.25-in diameter hole in the top of the oven. Alternatively, the ACEM 9300 was connected through the septum of the SSL using a needle adapter with the EPC carrier directed from the SSL to the ACEM 9300 by a diverter valve. This provided a rapid connect/disconnect of the desorber to the Agilent 5975T LTM GC/MSD. A 0.75-mm id inlet liner was used with the needle adapter connection. The oven temperature was 250 °C. Standard Tenax thermal desorption tubes and focusing traps were used with both systems. The Unity2 control parameters were as follows: 1.0 min prepurge; sample desorption: 3 min at 250 °C; desorb flow: 15 mL/min; focusing trap: –10 °C; focusing trap heating: 3.0 min at 300 °C; heated valve and transfer line: 120 °C. The ACEM 9300 control parameters were as follows: dry tube purge: 1.0 min at 40 °C; tube heat: 3.0 min at 250 °C; tube cool: 0.5 min; focusing trap heat: 3.0 min at 250 °C; heated valve and transfer line: 150 °C; actual focusing trap temperature: 46 °C. Both thermal desorbers were controlled by their control software, which was resident on the laptop running concurrently with MSD ChemStation. The LTM column module was a 30 m × 0.32 mm, 1.0 µm DB-5ms column and the following temperature program was used: 2.0 min at 40 °C; 20 °C/min to 250 °C. (The larger volume and phase thickness was used in some testing to facilitate on-column focusing for larger volume transfers, but the more general use of the 0.25 mm x 0.25 um DB-5ms columns for reduced bleed is preferred.) An equimolar dilute solution of the methyl- through butyl- series of trialkyl phosphates was made in hexane. A small quantity of this solution was injected into a 5-L Tedlar gas sampling bag filled with helium to give a calculated concentration of 0.18 ppmv of each component. After 60 min of equilibration in the bag, vapor samples onto Tenax thermal desorption tubes were collected for 20 s using a flow rate of approximately 1.8 L/min.

## Results

The 10-s SPME sample of contaminated carpet completed at room temperature showed evidence for the presence of four G and H agents with some volatility at room temperature. The resulting chromatogram is shown in Figure 2. When the sampling temperature for the contaminated carpet was increased to 110 °C, VX was made sufficiently volatile to be sampled, and the same four G and H agents were observed along with VX (small peak at 2.748 min) as shown in Figure 3. The liquid injection (about 10 ng for each CWA) analysis results in Figure 4 show a chromatogram without matrix peaks related to the carpet material and SPME fiber coating.

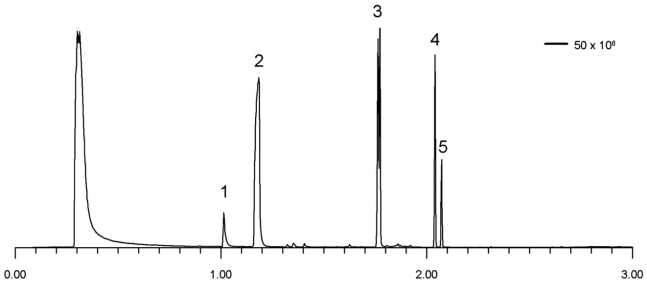


*Figure 2. Recovery of CW agents by SPME headspace sampling at room temperature from contaminated carpet.*
*1 Methylethylphosphonofluoridate*
*2 O-isopropyl methylphosphonofluoridate (GB, or sarin)*
*3 O-pinacolyl methylphosphonofluoridate (GD, or soman)*
*4 bis(2-chloroethyl) sulfide (HD, or sulfur mustard)*
*5 cyclohexylmethylphosphonofluoridate (GF)*

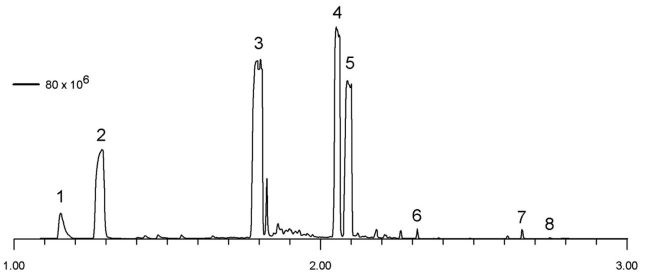


*Figure 3. Recovery of CW agents by SPME headspace sampling at 110 °C from contaminated carpet.*
*1 Methylethylphosphonofluoridate*
*2 O-isopropyl methylphosphonofluoridate (GB, or sarin)*
*3 O-pinacolyl methylphosphonofluoridate (GD, or soman)*
*4 bis(2-chloroethyl) sulfide (HD, or sulfur mustard)*
*5 cyclohexylmethylphosphonofluoridate (GF)*
*6 triethylphosphate*
*7 tributylphosphate*
*8 O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)*

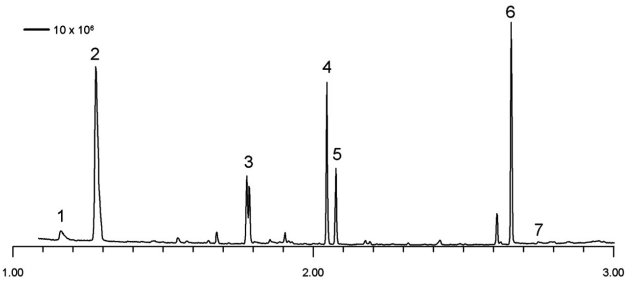


*Figure 4. Liquid injection of chemical agent solution.*
*1 Methylethylphosphonofluoridate*
*2 O-isopropyl methylphosphonofluoridate (GB, or sarin)*
*3 O-pinacolyl methylphosphonofluoridate (GD, or soman)*
*4 bis(2-chloroethyl) sulfide (HD, or sulfur mustard)*
*5 cyclohexylmethylphosphonofluoridate (GF)*
*6 tributylphosphate*
*7 O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)*

The Agilent 5975T LTM GC/MSD can easily be interfaced with thermal desorbers such as the Markes Unity2 or the CDS ACEM 9300. Figure 5 shows the recovery of 100-ng quantities of trialkyl phosphate simulants sampled by the Markes Unity2, as an example. As expected, both thermal desorbers reliably provided similar results that were repeatable and easily controlled from the laptop computer along with MSD ChemStation. When operating with a direct butt-connection of the transfer line to the column, the only difference noted in the analysis of the chemical warfare simulants was that the earliest simulant peak was broader with the ACEM 9300 when using a standard 6-mm od focusing trap. This difference with the trimethyl phosphate peak was attributed to the warmer starting temperature, and the larger diameter and heating time of the focusing trap in the ACEM 9300. Using a 1/8-in od focusing trap with a smaller heater in the ACEM 9300 provided faster heating and reduced this difference.

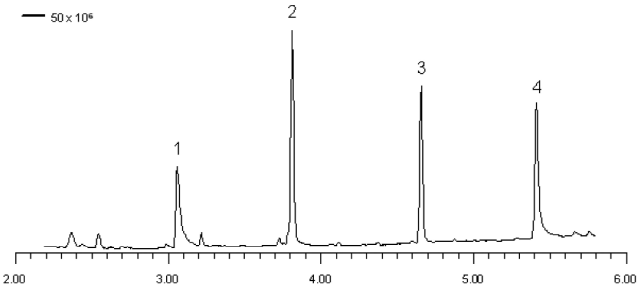


*Figure 5. Recovery of trialkylphosphates from air using a Markes Unity2 thermal desorber with the Agilent 5975T LTM GC/MSD.*
*1 trimethylphosphate*
*2 triethylphosphate*
*3 tripropylphosphate*
*4 tributylphosphate*

The ACEM 9300 has options allowing quick attaching and detaching of the heated transfer line to the SSL injector using a needle adapter through the septum of the inlet. This could be useful in the field for keeping the SSL inlet intact in the 5975T and having the thermal desorber unconnected for simplified transport. A simple diverter valve in the carrier line to the SSL can redirect gas to the thermal desorber when connected, although EPC performance will be most stable when operating the SSL in split mode. Using a 5:1 split ratio with a 1/8-in focusing trap and narrow liner results in significant narrowing of the early peak widths for hexanes. These results are similar to the Unity2 with direct (splitless) coupling to the GC column. The SIM/Scan example that follows was collected with the ACEM 9300 interfaced in this manner.

The dual SIM/Scan mode can be very useful to monitor for the presence of specific compounds of concern at trace levels using SIM while maintaining the ability to broadly detect other compounds of potential interest. Otherwise, the use of SIM alone for target compounds can leave the analyst blind to the presence of other compounds that are perhaps unanticipated. Demonstration of the use of dual SIM/Scan mode on a SPME sample of the series of alkyl phosphate vapors was made using ions 110 and 99 with a scan range of 50-350 amu. Dwell times were set at 100 ms for the two ions, and this resulted in a scan rate of 4.53 scans/s, a rate sufficient to provide four scans over the narrowest peak of interest. A 5-min air sample taken at a flow rate of 2 L/min was taken from a laboratory solvent cabinet following a 20 s sampling of 180 ppbv trialkyl phosphate mix in a Tedlar bag. This was desorbed from the ACEM 9300 to the SSL with a 5:1 split using the septum-needle adaptor and the 0.75 mm liner. The EPC was additionally pressure programmed with a 0.75 psi/min ramp during the temperature programming ramp to approximate constant flow. This analysis was immediately followed by a manual syringe injection of 1 µL of a 38 mM mix of the trialkyl phosphates in hexane with a 100:1 split ratio by exchanging the septum-needle adaptor for a standard septum nut. The results are shown in Figure 6. Ions at *m/z* values of 110 and 99 are principle ions for the methyl- and ethyl- to butyl- alkylphosphates, respectively, and these compounds are readily observed in the SIM chromatogram. For reference, the total ion chromatogram for the standard solution manually injected to the SSL inlet is shown in Figure 7. The SIM/Scan

mode allows simultaneous monitoring of specific ions of concern at low levels while maintaining a general awareness of other analytes present. In addition, this example shows the ability to rapidly change between standard SSL operation of the Agilent 5975T LTM GC/MSD and thermal desorption for introduction of analytes to the Agilent 5975T LTM GC/MSD via the SSL (Figures 6 and 7).

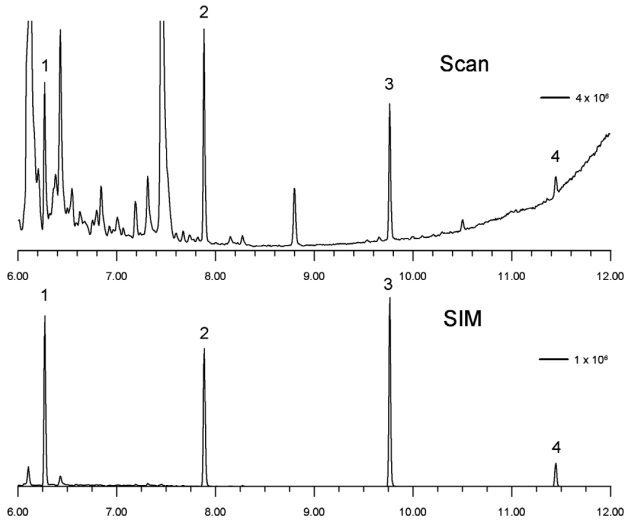


*Figure 6. Simultaneous SIM/Scan analysis of trialkylphosphates in air with solvent cabinet background using a CDS ACEM 9300 thermal desorber with the Agilent 5975T LTM GC/MSD using a needle adaptor to the S/SL inlet.*
*1 trimethylphosphate*
*2 triethylphosphate*
*3 tripropylphosphate*
*4 tributylphosphate*

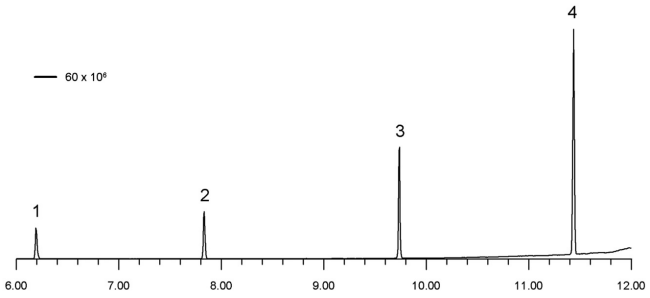


*Figure 7. Syringe injection of a reference mix to the S/SL inlet after retracting the ACEM 9300 needle adapter from the septum.*
*1 trimethylphosphate*
*2 triethylphosphate*
*3 tripropylphosphate*
*4 tributylphosphate*

## Acknowledgements

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