

## Rapid Field Detection of Chemical Warfare Agents (CWAs), Simulants, By-Products and Precursors

**Rapid on-site sample preparation and analysis of chemical warfare agents (CWAs), CWA simulants, by-products and precursors was achieved with a sample-to-sample cycle time of less than 4 minutes using the CUSTODION™ solid phase microextraction (SPME) syringe with a TRIDION™-9 portable capillary gas chromatograph toroidal ion trap mass spectrometer (GC-TMS). The samples were analyzed quickly and reliably with compound identification confirmed using a deconvolution algorithm together with an on-board target compound library.**

### Introduction

Rapid and accurate detection of chemical warfare agents (CWAs), CWA precursors, and CWA by-products is imperative for human protection in warfare and security domains<sup>1</sup>. Gas chromatography-mass spectrometry (GC-MS) is a selective and sensitive technique routinely used in laboratory settings. Now, GC-MS has been applied for near-real time detection of CWAs over a broad concentration range in situations (i.e. hot zones) requiring mobile, on-site analysis using a person-portable TRIDION-9 GC-TMS instrument in the field. Rapid sample preparation for air, headspace, liquids, and dissolved solid samples is accomplished by solid phase microextraction (SPME)<sup>2-3</sup>. In this application, low concentrations of CWAs, and low to high (neat, 100%) concentrations of CWA precursors, simulants, and by-products were sampled and identified in less than 3 min.

### Sample Preparation and Analysis

Six CWAs including VX, HD, HN3, GA, GB, and GD were prepared at 100 µg/ml in isopropyl alcohol (IPA). A CUSTODION SPME syringe with a 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was used for extraction by immersing the fiber directly into the sample for 5 sec. The CWA simulants, by-products, and precursors including diisopropylmethylphosphonate (DIMP),

methyl salicylate (MES) tributylphosphate (TBP), pinacolyl alcohol (PA), diethylmalonate (DEM), and dimethylmethylphosphonate (DMMP) were sampled in separate analytical runs at concentrations ranging from trace concentrations to neat (100%). For each sample, only the headspace above the IPA/analyte solution was sampled by exposing the 1 cm SPME fiber to the region above the liquid, taking care not to make contact with the liquid. The SPME fiber was then retracted into the CUSTODION syringe and transferred to the TRIDION-9 GC-TMS for analysis.

Following each sample preparation, the SPME syringe was inserted into the TRIDION-9 GC-TMS heated injection port where the target analyte(s) were desorbed into a low thermal mass injector (275°C) coupled with a metal-clad capillary GC column (MXT-5, 5 m x 0.1 mm, 0.4 µm d<sub>f</sub>). After an initial 10 s hold at 50 °C, the GC temperature was increased at 2 °C/s to 280 °C. The capillary GC is coupled to a TMS detector having a mass range of 45-500 *m/z*. A custom user defined compound library identified the target analytes with using an on-board deconvolution algorithm.

### Experimental Conditions

Sampling:	Solid phase microextraction (SPME)
SPME Phase:	Divinylbenzene/Polydimethylsiloxane (DVB/PDMS, 65 µm)
GC Inj. Temp:	275°C
GC Column:	MXT-5, 5 m x 0.1 mm, 0.4 µm d <sub>f</sub>
GC Carrier Gas:	Helium, 0.2ml/min, constant pressure
GC Column Temp:	50-280°C at 2°C/s
Transfer Line:	250°C
Injector Split Ratio:	20:1
Mass Analyzer:	Toroidal ion trap (TMS)
TMS Mass Range:	45-500 Da
Ionization Mode:	In-trap electron impact (EI)
Detector:	Electron multiplier
Vacuum:	Roughing and turbo molecular pumps
Mass Resolution:	Less than unit mass to 230 amu, nominal unit mass to 500 amu

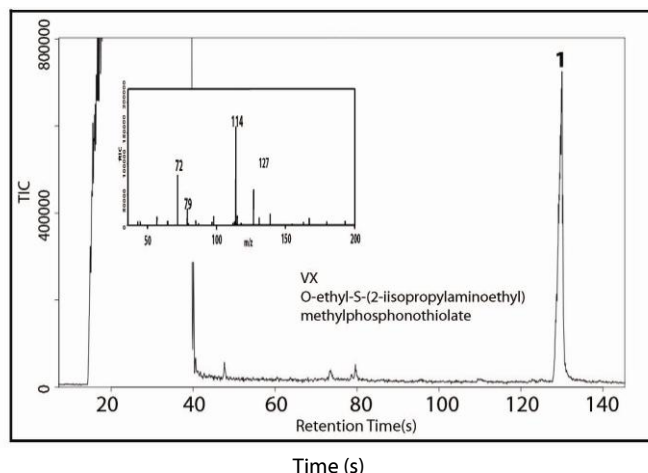


Figure 1. Chromatogram and spectra of VX sampling using a CUSTODION PDMS/DVB SPME fiber and analyzed on the TRIDION-9 GC-TMS.

## Results and Discussion

Figure 1 shows the GC-TMS chromatogram and mass spectrum for VX prepared in isopropyl alcohol after preparation at below regulated surety level. VX was positively identified by the TRIDION-9 in 130 s. Similar results were obtained for each of the compound classes analyzed. In all cases, the same GC temperature program was utilized, thus maintaining the sample-to-sample cycle time of approximately 4 min.

Prior to sample analysis, a target compound library containing each of the analytes of interest was created. Library entries were created using each analyte's GC retention time and major ion fragments created by the electron impact (EI) ion source in the toroidal ion trap mass spectrometer. Following sample introduction and analysis, each sample was subjected to the TRIDION-9's post-run deconvolution algorithm for comparison with the target library compounds. When a positive identification occurred, results of the confirmation were displayed on the TRIDION-9 LCD screen for review and the user can then make an informed decision on the next action regarding the potential threat. The user can also download the data to CHROMION™-1 software on a laptop to view the chromatogram and/or mass spectrum for secondary confirmation.

The CUSTODION SPME syringe and TRIDION-9 GC-TMS are uniquely suited for field or laboratory screening of CWAs and other organic compounds to support rapid decision making. The ability to analyze a wide variety of sample types at concentrations from trace to neat allows the CUSTODION SPME syringe and TRIDION-9 GC-TMS to provide near real-time field analysis results. The short cycle time between injections allows the user to quickly analyze multiple samples on-site in a short timeframe, with high sensitivity and specificity.

## References

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3. G.L. Hook, G. Kimm, G. Betsinger, P.B. Savage, A. Swifts, T. Logan, P.a. Smith, "Solid phase microextraction sampling and gas chromatography/mass spectrometry for field detection of the chemical warfare agent O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothiolate (VX)", *J. Sep. Sci.*, 26 (12-13), **2003**, 1091-1096.

## Acknowledgements

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