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Journal of Chromatography A, 1067 (2005) 285–294
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Towards smaller and faster gas chromatography–mass spectrometry systems for field chemical detection

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Available online 30 November 2004

Abstract

Gas chromatography–mass spectrometry (GC–MS) is already an important laboratory method, but new sampling techniques and column heating approaches will expand and improve its usefulness for detection and identification of unknown chemicals in field settings. In order to demonstrate commercially-available technical advances for both sampling and column heating, we used solid phase microextraction (SPME) sampling of both water and air systems, followed by immediate analysis with a resistively heated analytical column and mass spectrometric detection. High-concern compounds ranging from 140 to 466 amu were analyzed to show the applicability of these techniques to emergency situations impacting public health. A field portable (about 35 kg) GC–MS system was used for analysis of water samples with a resistively heated analytical column externally mounted as a retrofit using the air bath oven of the original instrument design to heat transfer lines. The system used to analyze air samples included a laboratory mass spectrometer with a dedicated resistive column heating arrangement (no legacy air bath column oven). The combined sampling and analysis time was less than 10 min for both air and water sample types. By combining dedicated resistive column heating with smaller mass spectrometry systems designed specifically for use in the field, substantially smaller high performance field-portable instrumentation will be possible.
Published by Elsevier B.V.

Keywords: Field analysis; Gas chromatography; Mass spectrometry; Solid phase microextraction; Resistive heating

1. Introduction

Many fieldable rapid detection and identification methods for chemicals of high concern to military forces rely on color changes to a chemical-impregnated paper for liquid samples, or to so-called “detector tubes” for air samples. Rapid detection in water samples is also available through military test kits based upon chemical reactions that produce visible color changes. These colorimetric methods, while relatively easy to use in the field, offer only tentative chemical identification and poor sensitivity.

Widely fielded instrumental techniques for detecting this type of chemical include systems based on ion mobility spectrometry and a man-portable system that combines a gas sampler with a gas chromatography–mass spectrometry (GC–MS) instrument. Ion mobility spectrometry-based methods are not compound-specific and offer poor quantification dynamic range. The widely available man-portable GC–MS instrument (with an inseparable sampler) can provide compound-specific data. The combined GC–MS/sampler system provides a sampling device of 16 kg, and offers sampling/analysis times of around 15–20 min with

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0021-9673/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.chroma.2004.11.008

chromatography performance (e.g. peak shapes and widths) generally inferior to laboratory instrumentation. Both of these instrument systems are limited to gas phase analytes unless additional hardware is used.

Laboratory-based mass spectrometry is a mature analysis method that has become an indispensable tool for researchers worldwide. Large mass spectral libraries are available when 70 eV electron impact ionization mass spectrometry (EIMS) is used. This allows detection and identification of trace levels of many mixture components when a separation method is used prior to examining the clean spectra produced from the separated compounds. Even sub-optimal separation can allow deconvolution software to assist in identifying unknown chemicals present when EIMS detection is used. For EIMS analysis, the separation method of choice is typically GC. In addition to the usefulness of existing mass spectral libraries, proven laboratory-based MS instrumentation and highly developed and robust open tubular GC columns are available at reasonable cost.

Besides the use of GC, other inlet methods are available to support the use of mass spectrometry in field settings. These inlet methods range from simple to complex: with a pinhole inlet, atmosphere gases give a high background and shorten the mass spectrometer filament life when EIMS is used; membrane inlet methods provide some analyte discrimination and help reduce the presence of atmosphere gases [1], but are problematic for detection and identification of trace level components in complex mixtures. An ion trap MS system can perform MS/MS analyses, effectively retaining target analyte ions in the trap with confirmatory daughter spectra provided [2]. However, MS/MS used without a prior separation step is typically selective for expected analytes, and ions resulting from unanticipated compounds would be retained in the trap only by chance.

The ability to separate complex mixture components in time prior to mass spectrometric detection offers the unambiguous ability to complete spectrum matching of clean EIMS spectra. Eckenrode [3] describes environmental and forensic applications of field-portable GC–MS and makes the point that field GC–MS is useful for situations where rapid analyte identification, and where a high degree of certainty are required. In 1994, McDonald et al. [4] reviewed and discussed the state-of-the-art GC–MS instrumentation then available and useful for completing analysis in field settings. Ten years later, essentially all field-portable GC–MS instruments commercially available and capable of analyzing the full range of compounds traditionally expected from a GC–MS instrument still rely on the traditional column heating method used in most laboratory instruments: air bath heating.

The costs associated with adding a GC separation step to mass spectrometry in field settings include the added weight, complexity, and power consumption of the resulting sampling and detection hardware. In order to make gas chromatography more compatible with EIMS in field settings, sampling and column heating methods are needed that significantly improve upon those typically used. This should allow rapid detection of extremely hazardous chemicals from the standard environmental matrices (air, water, and soil), with relatively little sample handling and preparation. An ideal fieldable GC–MS chemical detection/identification system must have the capability to rapidly sample, detect, and identify a wide range of high concern chemicals from a variety of sample matrices. The footprint of such a system must be small, power consumption and weight must be low, and it should be easy to use.

In this work, we used solid phase microextraction (SPME) to sample five dangerous chemical compounds and a high molecular weight fungal toxin as water contaminants, and four dangerous chemical compounds with appreciable volatility as air contaminants. The presence of any of these chemicals in water supplies or as air contaminants would be of public health concern. For both air and water samples, a low thermal mass (LTM) GC column with resistive heating was used to separate the sampled compounds prior to mass spectrometric detection. Two instruments were used: for water samples, a field-portable GC–MS system was used. This system weighs about 35 kg, and the LTM column assembly was retrofitted to the exterior of the instrument's isothermally-heated air bath oven. As an example of a GC–MS system where the entire air bath GC oven was omitted and LTM column heating was engineered by design, SPME samples from contaminated air were analyzed using a typical commercial production mass spectrometer. For this instrument, rather than retrofitting the LTM GC column assembly to an existing air bath oven, the LTM GC column was interfaced directly to the mass spectrometer through a small heated box that contained the GC injector and the transfer line into the mass spectrometer.

The use of LTM GC column heating technology and a sampling method such as SPME that allows rapid sampling of air, water, and soil matrices point towards improvements in both equipment systems and sampling/analysis methods that will allow reductions in the size and weight of a GC–MS instrument with excellent performance. High sample throughput and the ability to detect and identify compounds with widely different physical properties can be demonstrated with the sampling methods and instrumentation systems described in this work.

2. Materials and methods

2.1. SPME sampling

The SPME fibers and holder used are commercially available from Supelco (Bellefonte, PA). The fiber coating used for water samples was the polyacrylate type (PA, 85 μm coating thickness), as it is capable of withstanding injector temperatures up to 315 °C. A high injector temperature is necessary to desorb the large T2 mycotoxin compound present in water samples [5]. For air samples, the SPME fiber coating was polydimethylsiloxane/divinylbenzene (PDMS/DVB,

65 μm coating thickness). Prior to use, SPME fibers were conditioned following the manufacturer's recommendations. Blank runs were completed at least once daily before the use of any fibers for sampling to ensure no carryover of analytes from previous extractions.

2.2. Chemicals and sample preparation

The individual components of the chemical agent mixture sampled from water included *O*-isopropyl methylphosphonofluoridate (sarin, or GB), *O*-pinacolyl methylphosphonofluoridate (soman, or GD), *O*-ethyl *N*,*N*-dimethyl phosphoramidocyanidate (tabun, or GA), bis(2-chloroethyl) sulfide (sulfur mustard, or HD), and *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate (VX). These were synthesized in house by DSO National Laboratories (Singapore) and were used under controlled conditions. A 10^3 mg/L stock solution containing a mixture of GB, GD, GA, HD, and VX was prepared by dissolving the neat compounds volumetrically in dichloromethane. A 10^3 mg/L stock solution of T2 fungal toxin (98% purity, Sigma, St. Louis, MO) was prepared by dissolving 5.0 mg of the solid toxin into 5.0 mL of methanol. ^{1}H NMR and ^{31}P [^{1}H] NMR verified the purity of the compounds synthesized in house.

Water sample preparation was completed by placing a stir bar into a 4 mL silanized glass vial having a screw thread closure and an open top for piercing by the SPME sampler, fitted with a PTFE-lined septum. To the vial 1.5 g Na_2SO_4, 3.0 and 15.0 μL aliquots of the T2 and chemical agent stock solutions respectively were then added, followed by 3.0 mL of deionized water. The sample was stirred for 5 min before the PA fiber was inserted through the vial septum and immersed in the aqueous sample. Sampling was carried out with stirring for 5.0 min at ambient temperature.

The individual components of the chemical agent mixture sampled from air included sarin, soman, sulfur mustard, and cyclohexylmethylphosphonofluoridate (GF). Except for sulfur mustard, these compounds were synthesized by Defence R&D Canada-Suffield (Medicine Hat, AB, Canada). Sulfur mustard used at that facility for research purposes has been retained from Canada's past holdings of chemical weapons. All chemicals were used under controlled conditions. A stock solution of each compound was prepared from neat material freshly distilled at the Canadian National Single Small Scale Facility using a Kugelrohr apparatus. Purities were verified by ^{1}H NMR and GC–MS to be >99% for each of the G-series compounds and >97% for sulfur mustard. Dilution of individual neat compounds with methylene chloride and aliquot combination provided a single stock solution with a concentration of 620 ng/μL for each compound.

A vapor sample with 0.65 mg/m^3 concentration for each agent was prepared by filling a pliable air-tight bag made of PTFE material (SKC Inc., Eighty Four, PA) with 5.0 L of air using a Hamilton Gastight macro-volume syringe and injecting 5.2 μL of the 620 ng/μL solution into the bag through the septum of the bag's valve assembly. The PTFE bag, containing chemical agent contaminated air, was then immersed in a temperature controlled water bath held at 21 °C during SPME sampling. Sampling was completed by piercing the septum found on the air-tight bag with the SPME fiber, and sample duration was 5.0 min.

2.3. GC–MS instrumentation and conditions

The field-portable Viking 573 GC–MS system used to analyze water samples (Bruker Daltonics, Billerica, MA) has a mass spectrometer portion derived from an Agilent Technologies 5973 ion source, monolithic quadrupole mass filter and mass spectrometer printed circuit board. Split and splitless injections are possible using the available heated injection port. The instrument closely mirrors typical GC hardware; heated transfer lines and a temperature programmable air bath oven (as typically used) allow for separation of organic compounds with a range of physical properties. The air bath GC oven requires considerable time to heat and cool, limiting the sample throughput rate to about three samples/h. The mass spectrometer vacuum components consist of a traditional internal turbodrag-molecular pump combined with an external roughing pump. As H_2 carrier gas was used in this work, an oil-lubricated rotary vane roughing pump was used. An externally mounted LTM analytical column assembly (described in more detail below) was used for analytical separation, and the legacy air bath oven of the instrument was used as an isothermal heated zone for transfer lines from the injector to the externally mounted LTM column assembly and from the LTM column to the mass spectrometer.

For the instrument described above, the injector head pressure was maintained at 5 psi g, providing an initial carrier gas linear velocity of 100 cm/s. A deactivated injection port liner designed for thermal desorption of analytes from the SPME fiber was used (0.75 mm i.d., Supelco). Analyses were performed with the injector operating in splitless mode (2.0 min, followed by 10 mL/min injector purge). In the standard configuration of the Viking instrument as it is sold, a heated transfer line connects the injector to the air bath oven. The injection port and this internal instrument transfer line from the injector were maintained at 315 °C, and the isothermal temperature of the instrument's GC oven was 300 °C. The legacy air bath oven was used only to heat deactivated fused silica transfer lines; one of these connecting the line from the injector into the resistively heated LTM column; the other ran from the LTM column back through the air bath oven and then connected into the MS transfer line. The externally mounted LTM GC column temperature parameters were as follows: 40 °C initial temperature for 5 s, then to 100 °C at 80 °C/min, 20 °C/min to 115 °C, followed by ramping at 200 °C/min to 300 °C, which was maintained until the run was completed. The mass spectrometer transfer line was kept at 300 °C. Mass spectra were collected over the range 90–500 *m*/*z* to avoid a persistent dichloromethane background (84 *m*/*z*) resulting as a sample preparation artifact. The ion source (70 eV) and quadrupole temperatures

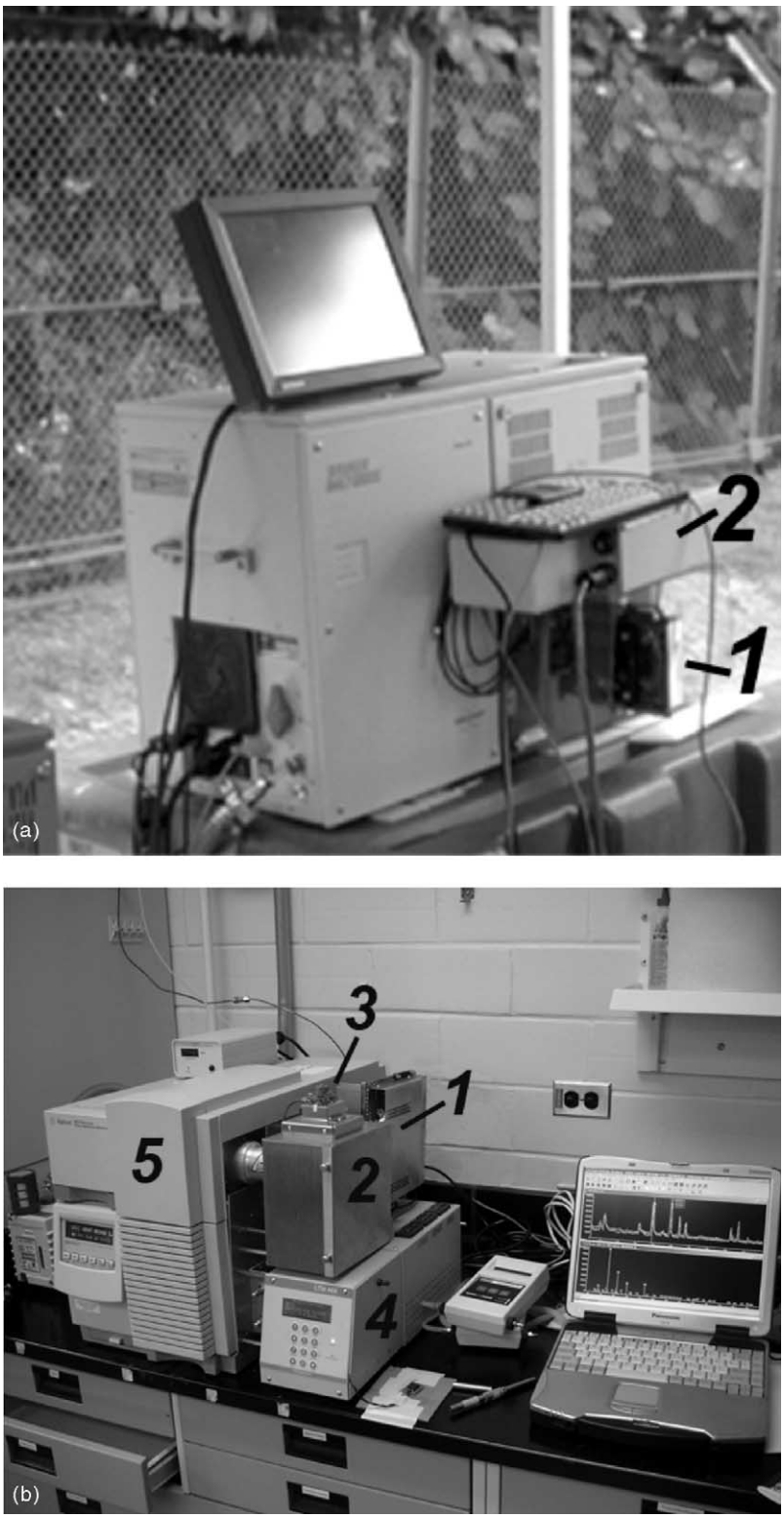

Fig. 1. (a) Field portable GC–MS system operating in a field setting; showing (1) retrofit externally-mounted resistively heated GC column module; (2) control unit for the resistively heated analytical column module. (b) Laboratory mass spectrometer; showing (1) resistively heated GC column module; (2) isothermally heated injector housing (transfer line to mass spectrometer passes from the LTM column assembly to the mass spectrometer through this box also); (3) GC injector; (4) control unit and power supply for the resistively heated analytical column module; (5) mass spectrometer.

were kept at 250 and 106 °C, respectively. A scan rate of 6.62 Hz was achieved using the mass range 90–500 *m/z* and suitable mass spectrometer duty cycle settings. This instrument is shown in Fig. 1a.

The instrument used to analyze air samples incorporates the same basic LTM GC column assembly as used above, but coupled directly to an Agilent 5973 mass spectrometer (Wilmington, DE) with no legacy air bath analytical GC column oven. Split and splitless injections with septum purge are accomplished with an injector designed for use in an Agilent 5890 gas chromatograph (Restek, Bellefonte, PA). Aside from internal components of the Agilent mass spectrometer that are actively heated, this GC–MS system has three heated zones regulated by three separate digital heater controllers (Watlow, St. Louis, MO). The injector is actively heated, and is housed within an actively heated mini-oven that holds transfer lines from the injector to the LTM column assembly and from the LTM column to the standard Agilent mass spectrometer transfer line. This mass spectrometer transfer line is also actively heated under control of one of the digital heater controls. Temperatures for the ion source and the quadrupole assembly are controlled through the Agilent software that runs the mass spectrometer and were 230 and 150 °C, respectively.

The injector head pressure for H_2 carrier gas was maintained at 13 psi g in this instrument, giving a corresponding initial linear velocity of 104 cm/s. A deactivated SPME injection port liner (0.75 mm i.d., Restek) was used with the injector operating in the splitless mode for 0.5 min. The injector temperature was 200 °C, while the mini-oven and MS transfer line were maintained at 230 °C. The GC column temperature parameters were: 40 °C initial temperature, hold for 0.5 min, ramp at 75 °C/min to 210 °C, and hold for 0.5 min producing a total run time of 3.27 min. MS data were collected over a mass range of 45–300 *m/z*, and quadrupole duty cycle settings provided a scan rate of 5.56 Hz. The LTM resistively heated GC column and associated components are shown in Fig. 1b for the GC–MS system based on the Agilent mass spectrometer where the entire air bath GC oven was omitted.

The analytical column used in the LTM assembly retrofitted to the outside of the Viking instrument's air bath oven was a 15 m length of commercially-available DB-1MS open tubular fused silica with 0.25 μm film thickness and 0.25 mm i.d. (J&W Scientific, Folsom CA). The analytical column used in the LTM assembly joined directly to the Agilent mass spectrometer (no air bath oven) was a 30 m length of RTX-5 type (Restek) having 0.25 μm film thickness and 0.25 mm i.d. The LTM GC column module used for both instruments is commercially available (RVM Scientific, Santa Barbara CA) and can incorporate off-the-shelf open tubular GC columns of varying lengths. It is typically sold as a retrofit kit where an air bath oven is already present on the GC instrument used.

Sloan et al. [6] have described the basic column configuration, heating, and temperature control of the type of LTM column assembly used in both instruments. This design incorporates resistive heating and temperature sensing wires intertwined with an open tubular GC column. The resistive heating wire is insulated to prevent hot spots. The column intertwined with these heating and temperature sensing wires is then wound in a circular form and wrapped with aluminum foil. Heating of the analytical column is controlled through a small stand-alone module with keypad for temperature programming. A small separate power supply (110–230 V AC input) provides electrical power for heating the LTM column assembly.

For comparison of water samples analyzed with the field-portable instrument to a laboratory-based GC–MS system, SPME samples were collected under identical conditions and were analyzed using an ion trap instrument system (GCQ, Thermo Finnigan, San Jose, CA) with the following conditions: injector temperature was 300 °C, and injections were performed in the splitless mode (held for 8 min). A 30 m DB-5 analytical column was used (J&W Scientific) having 0.25 mm i.d. and 0.25 μm film thickness. Constant velocity flow mode was used, with He carrier gas linear velocity of 35 cm/s. The GC column temperature (standard air bath type oven) began at 40 °C, was held at this temperature for 2 min, ramped at 20 °C/min to 270 °C, and then was held at this final temperature for 15 min providing a total analysis time of 28.5 min. The mass spectrometer transfer line temperature was kept at 275 °C throughout the analysis, and the source temperature was maintained at 200 °C. The scan range was 40–500 *m/z*.

3. Results and discussion

3.1. Results

A GC–MS total ion current chromatogram produced by SPME water sampling and analysis using the field portable Viking instrument retrofitted with the LTM column is shown in Fig. 2a. Clean spectra were available from each compound to complete a mass spectrum search and library match. The analysis time of 4 min was sufficient to elute all of the analytes, and after including a 5 min sampling time, gave a combined sampling/analysis time of <10 min.

A GC–MS total ion current chromatogram produced from a SPME air sample is shown in Fig. 2b. This sample was analyzed using the GC–MS instrument with the LTM column joined directly to the Agilent mass spectrometer (no legacy air bath oven). Clean spectra were available from each compound to complete a mass spectrum search and library match. The analysis time of 2.5 min was sufficient to elute all of the analytes, and after including a 5 min sampling time, also gave a combined sampling/analysis time of <10 min.

In both water and air samples the soman diastereomer pair is poorly resolved, partly due to the relatively high analyte loading on the GC column, and partly due to the rapid temperature programs used.

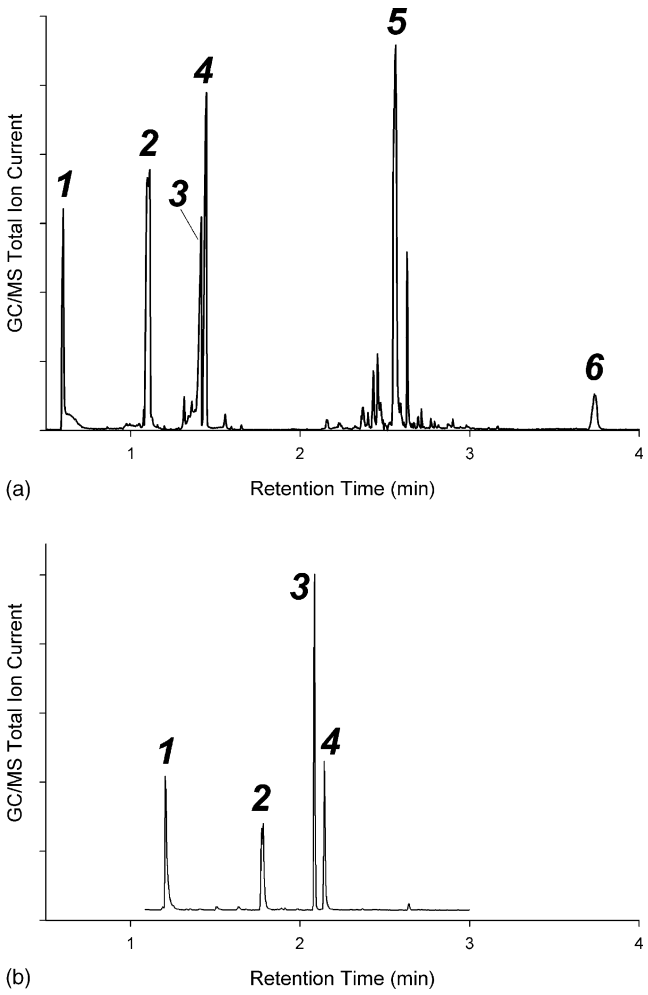

Fig. 2. (a) SPME water sampling/Viking/LTM resistive column heating analysis of six-agent mixture; 5.0 min SPME sample; (1) sarin (140 amu); (2) soman (182 amu); (3) tabun (162 amu); (4) sulfur mustard (158 amu); (5) VX (267 amu); (6) T2 toxin (466 amu). (b) SPME air sampling/Agilent MS/LTM resistive column heating analysis of four-agent mixture; 5.0 min SPME sample: (1) sarin (140 amu); (2) soman (182 amu); (3) sulfur mustard (158 amu); (4) cyclohexylmethylphosphonofluoridate (180 amu).

The elution time for the fungal toxin using He carrier and the laboratory-based GC–MS system with air bath column heating and the 30 m column was >25 min. A chromatogram showing typical results for an analysis using this instrument system with SPME sample introduction is provided as Fig. 3. The peak width for T2 toxin with the LTM column analysis is smaller in Fig. 2 (LTM column analysis, high velocity H_2 carrier gas) than in Fig. 3 (analysis with laboratory-based GC–MS system, He carrier gas). Abscissa scaling differences for each chromatogram do not give this impression, but the actual width of this peak in the Fig. 2a chromatogram was 4 s, while the corresponding peak in Fig. 3 was measured to be 10 s wide.

Fig. 4a shows a 70 EV EI mass spectrum for T2 mycotoxin as observed in the National Institute of Standards and Technology mass spectrum database [7]. Fig. 4b shows the same mass spectrum ignoring ions having $m/z < 90$, and with the

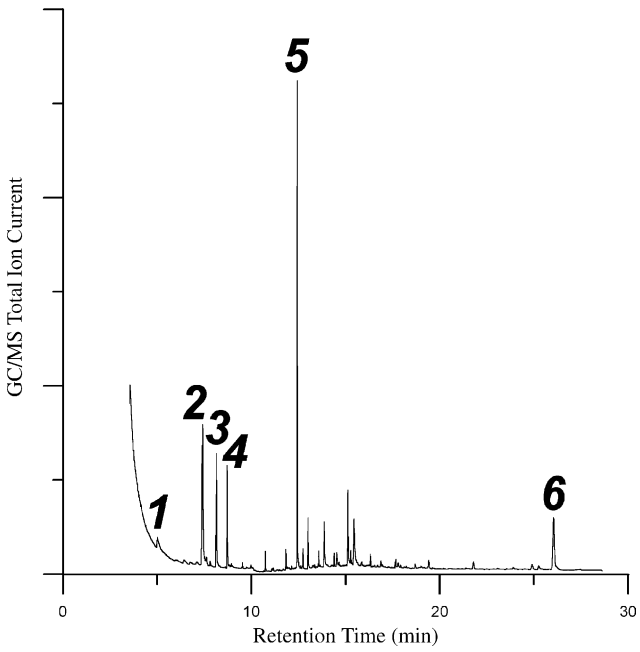

Fig. 3. SPME water sampling/laboratory-based GC–MS analysis of the six-agent mixture; 5.0 min SPME sample: (1) sarin (140 amu); (2) soman (182 amu); (3) tabun (162 amu); (4) sulfur mustard (158 amu); (5) VX (267 amu); (6) T2 toxin (466 amu).

121 m/z peak scaled to highest intensity. As our scan range during data collection was 90–500 m/z, Fig. 4b can be compared to our spectrum obtained for T2 mycotoxin, which is shown in Fig. 4c. Our mass spectrum shown in Fig. 4c compares favorably to that shown by Onji et al. [8], who completed GC–MS analysis of eight underivatized *Fusarium* mycotoxins, including T2 toxin. The mass spectrum collected by Onji et al. for T2 mycotoxin shows a small peak at 382 m/z (as also seen in our spectrum), which is not observed in the main library NIST mass spectrum. A replicate library mass spectrum for T2 mycotoxin in the NIST database shows a peak at 382 m/z, but the intensities of many ions in the mass spectrum from the replicate library do not match well with that from the main library, nor with that provided by Onji et al.

3.2. Sampling considerations

The passive SPME method has been recognized as offering potential for rapid sampling in field settings. Little or no preparation or handling is needed following sample collection, and no additional analytical instrumentation is needed when using a gas chromatograph with a standard septum-equipped injector [9]. Using non-orthogonal detectors, Koziel et al. [10] used on-fiber derivatization SPME for field sampling with laboratory GC analysis to detect formaldehyde in indoor air; Koziel et al. [11] and Jia et al. [12] used SPME to sample and analyze organic analytes in the field. Smith et al. [13] used SPME with GC–MS analysis completed in the field to detect thermal degradation products

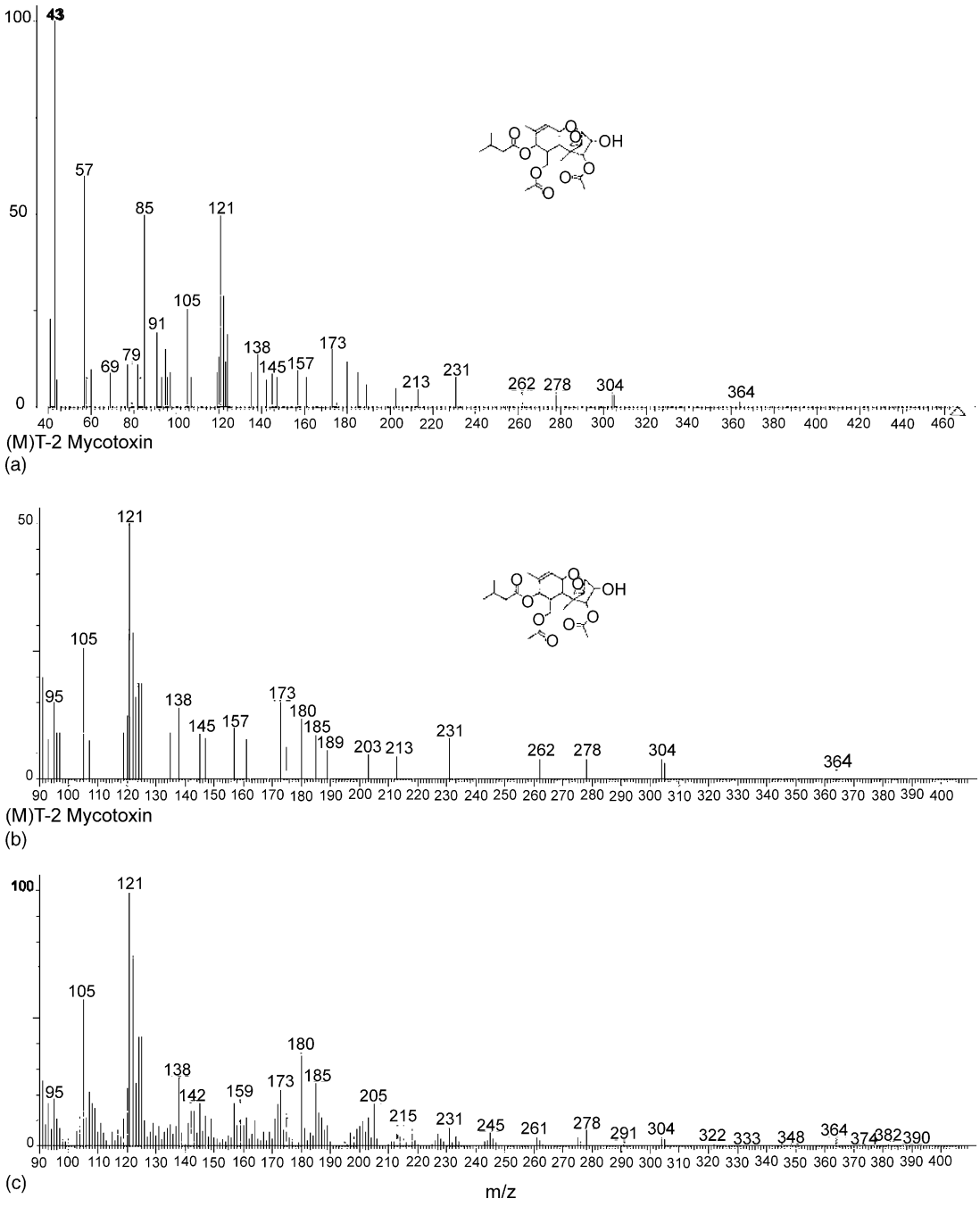

Fig. 4. (a) 70 eV EI mass spectrum for T2 mycotoxin taken from the NIST Mass Spectral Database main library. (b) The same mass spectrum as in (a) above; *m*/*z* ratios >90 are shown to allow comparison to our mass spectrum for T2 mycotoxin that was collected while scanning 90–500 *m*/*z*. (c) The mass spectrum for T2 mycotoxin produced during the current work; 90–500 *m*/*z* scan range was selected to avoid persistent background at 84 *m*/*z* resulting from $MeCl_2$ solvent artifact from sample preparation.

from high temperature dispersion of CS riot-control agent. Hook et al. used SPME sampling with GC–MS analysis in several field scenarios, including during emergency response operations shortly following a large fire involving aviation fuel [14]. The SPME method has been shown to be useful in sampling highly dangerous chemical compounds from water [15–17], air [18], soil [19], and clothing material [20].

No attempt was made to optimize sensitivity of the combined SPME/GC–MS method for the compounds analyzed. For our water samples, the chemical concentrations detected are higher than relevant short-term military exposure guideline (MEG) standards promulgated by the US Army for their presence in drinking water [21]. The water concentrations we worked with were 40 times higher than the relevant short-term standards found in this reference for tabun, sulfur mustard, and T2 mycotoxin, and were several hundred times higher than the standards for soman, sarin, and VX. This same reference lists the MEGs for airborne exposure, and the air con-

centrations sampled are close to two times higher than the highest MEG values given for sarin, soman, and cyclohexylmethylphosphonofluoridate, and one-sixth that of the highest MEG value given for sulfur mustard.

The chromatograms shown in Fig. 2a and b show that for most of the analytes, the chromatographic peaks are well above the baseline and lower concentrations likely could have been detected using similar sampling parameters. It also should be recognized that longer sampling time would generally provide increased sensitivity as the concentration of analyte in the SPME fiber coating would approach equilibrium with the medium sampled. From previous work reported in the literature for SPME sampling of some of these compounds from water [15], SPME/GC–MS (selected ion monitoring) provided detection limits for sarin, soman, and tabun of about 0.05 μg/mL. The detection limit for VX was reported to be about 0.5 μg/mL. With the exception of the detection limit value reported for VX, these values are below or slightly above the respective short-term exposure limits for their presence in drinking water promulgated by the US Army. In the case of T2 mycotoxin, Lee et al. [5] report an optimized limit of detection of 0.010 μg/mL (SPME/GC–FID), below the US Army short-term exposure limit for its presence in drinking water.

Traditional thermal desorption methods have been used in the investigation of chemical warfare agents present in environmental samples. Black et al. [22] detected sulfur mustard from soil using active headspace sampling and full scan GC–MS. Their samples and analyses were completed fairly rapidly (about 30 min) for contaminated soil, by pumping soil headspace air through a tube loaded with Tenax^{TM} for thermal desorption and GC–MS analysis. The thermal desorption apparatus is an additional piece of equipment beyond a standard GC–MS system and adds complexity to the analysis compared to the use of SPME where no additional equipment is needed. Solid phase extraction (SPE) is another sampling method that could be useful for aqueous samples. Sample preparation with SPE requires movement of water through the SPE sampling medium, and although solvent usage is greatly reduced with SPE sampling and subsequent analysis, some solvent use is still required. Extraction of soil, water, or air sampling media using a liquid solvent with subsequent GC–MS analysis is a more traditional laboratory method. In terms of simplicity and speed, neither SPE, solvent extraction, nor traditional thermal desorption methods useful in the laboratory compare favorably with SPME for sampling/analysis completed in a field setting.

3.3. GC performance considerations

A number of methods have been recognized to speed GC analysis. Some of these include the use of narrow bore capillary GC columns, the use of short capillary GC columns, the use of rapid GC column heating, and the use of high carrier gas velocities [23]. A resistive heating arrangement can be combined with some or all of these strategies by choosing the column diameter and length needed to suit the analytical conditions desired, and the use of H_2 carrier gas allows a relatively high carrier gas velocity near optimum Van Deemter curve performance conditions. The ability to generate this carrier gas in a pure form by electrolysis makes this an attractive choice for field analyses, as no hazardous materials or high pressure gas need be shipped or brought to the field. Further developments in miniaturization of H_2 generation by electrolysis or other means are desirable in order to make this carrier gas available for low power/low mass GC–MS systems specifically designed for field use.

The possibility of resistive heating for GC analysis with fast column heating was first recognized by Lee et al. [24]. Subsequent developments with electrically resistive materials for GC column heating have used an aluminum clad open tubular column [25], a resistive metallic paint to coat the analytical column [26], heating and temperature-sensing wires [6,27] placed in close proximity to the column, and a small tubular metal sheath surrounding the column [27]. The possibility of improved GC performance has driven these developments in resistive column heating, and results have included faster heating and cooling, lower power consumption, and smaller GC instrument mass and size compared to the use of a traditional air bath GC oven.

3.4. MS system considerations

The Agilent quadrupole MS system used in the field portable GC–MS system for analysis of SPME water samples is designed for laboratory-based analysis, and is not optimized (miniaturization, ruggedization, and power consumption) for field use. The second instrument used (the Agilent mass spectrometer that was used to analyze SPME air samples with LTM column mounted directly to the mass spectrometer) is designed for use in the laboratory. Badman and Cooks [28] review advances in miniaturization of MS detectors designed for use in non-laboratory environments and predict increasing use of mass spectrometers outside of the laboratory as the associated hardware, vacuum, and electronics components are further refined for these types of applications.

3.5. Future directions for field GC–MS instrumentation

Future trends for field GC–MS will capitalize on advances in both GC and MS systems designed specifically for field applications. The data obtained here using SPME combined with LTM column heating demonstrate the ability to rapidly complete analyses of compounds with a wide mass range (in this case ranging from 140 to 466 amu) using the retrofit LTM GC system fitted to a legacy air bath GC oven. Although the masses of air analytes analyzed using the LTM GC hardware joined directly to the Agilent mass spectrometer (no air bath oven) did not extend to that of T2 mycotoxin, similar performance is expected from that system. It is noteworthy

that heating performance in some ways superior to current laboratory-based instrument designs is possible with a system where the LTM heating method is used.

An instrumentation design incorporating LTM column heating from the start eliminates legacy components of a typical GC–MS system. A future system based on a miniaturized mass spectrometer should incorporate the important features that allowed the demonstrated performance while optimizing the resulting system for field portability and use. The air bath oven present on the field-portable Viking GC–MS instrument used only served to heat transfer lines and takes up about 1/4 of the instrument's size (by volume). The LTM column heating arrangement used with the Agilent mass spectrometer (no legacy air bath oven) replaced a large Agilent Air bath oven that weighs 49 kg. The weight of the LTM GC system mounted directly to that mass spectrometer (including injector, injector heating box, controller and all other ancillary components) is 7 kg.

It is logical that the LTM column heating design should be coupled to a mass spectrometer designed for field use, with the interface to the analytical column engineered specifically to reduce size, weight, and power consumption. While the "next generation" system, combined with a suitable rapid sampling method will allow deployment of GC–MS detection systems better suited to use in the field, our use of the basic enabling technologies, even with the presence of unnecessary legacy hardware in one instance, and with a laboratory mass spectrometer in another (although without the legacy air bath oven) shows that such a system is possible.

4. Conclusion

Gas chromatography–mass spectrometry was used with SPME sampling to detect five high concern chemical agents and a high molecular weight fungal toxin from spiked water (masses ranging from 140 to 466 amu), and four of the more volatile compounds from spiked air samples. The field-portable GC–MS system used to analyze water samples was retrofitted with a 15 m resistively heated analytical column, and high velocity H_2 was used as the carrier gas. The analysis time was <4 min, comparing favorably to >25 min with the use of traditional air bath oven column heating, a standard 30 m column, and using He carrier gas at standard flow rates. The system used for analysis of SPME air samples was based on a laboratory mass spectrometer where the LTM GC column assembly was joined directly to the mass spectrometer with no legacy air bath GC column oven, and analysis times of <3 min were achieved for the relatively volatile compounds analyzed using this system. A future system having a dedicated resistive column heating design and a MS detector engineered for field performance (size, ruggedness and power consumption) will provide for reductions in the mass and size of an instrument with excellent performance characteristics, capable of analyzing compounds with a wide mass range.

Acknowledgments

Grateful appreciation is acknowledged to the International Division, Edgewood Chemical Biological Center, and to the US Marine Corps Systems Command and the Assistant Secretary of the Army for Defense Exports and Cooperation for supporting the participation of US personnel in this research. Support for participation of DSO National Laboratories personnel by the Directorate of Research and Development, Singapore Defence Science and Technology Agency is gratefully acknowledged. Support for participation of Dr. Jackson Lepage by Defence R&D Canada is gratefully acknowledged. Finally, the Federal Bureau of Investigation, Laboratory Division is acknowledged for supporting the participation of Dr. Eckenrode.

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