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# **Rapid Analysis of Chemical Warfare Agents and their Hydrolysis Products by Desorption Electrospray Ionization Mass Spectrometry (DESI-MS)**

*Paul A. D'Agostino and Claude L. Chenier*

**Defence R&D Canada**

Technical Memorandum

DRDC Suffield TM 2009-027

October 2009

**Canada**



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Paul A. D'Agostino and Claude L. Chenier  
DRDC Suffield

**Defence R&D Canada** □ **Suffield**

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Chair/DRP

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## Abstract

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A "dip and shoot" analytical method was developed for the rapid sampling and desorption electrospray ionization mass spectrometric (DESI-MS) analysis of chemical warfare agents and their hydrolysis products in liquid samples. Sampling was performed by simply dipping fused silica, stainless steel or SPME tips into the organic or aqueous samples. Replicate analyses were completed within several minutes under ambient conditions with no sample pre-treatment, resulting in a significant increase in sample throughput over conventional solid phase microextraction (SPME) sampling and DESI-MS analysis or liquid chromatographic electrospray ionization mass spectrometric (LC-ESI-MS) analysis. The developed sample handling and analysis method was applied to the determination of chemical warfare agent content in samples containing unknown chemical and/or biological warfare agents. Ottawa sand was spiked with mustard, extracted with water and autoclaved to ensure sterility. Mustard was completely hydrolysed during the extraction/autoclave step and thiodiglycol was identified by DESI-MS, with analyses generally being completed within one minute using the "dip and shoot" method developed for the rapid analysis of liquid samples.

## Résumé

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Une méthode analytique "dip and shoot" a été mise au point pour le prélèvement rapide et l'analyse DESI-MS, électro-nébulisation ionique par désorption en spectrométrie de masse, des agents de guerre chimiques et leurs produits d'hydrolyse contenus dans les prélèvements de liquides. Les prélèvements ont été effectués simplement en trempant de la silice fondue, de l'acier inoxydable ou SPME tips dans les prélèvements organiques ou aqueux. Des analyses parallèles ont été complétées en plusieurs minutes, dans des conditions ambiantes, sans aucun traitement préalable du prélèvement et qui ont résulté en une augmentation importante de la vitesse de traitement du prélèvement comparé au prélèvement de micro-extraction en phase solide (SPME) classique et aux analyses DESI-MS ou analyses de chromatographie en phase liquide et électro-nébulisation ionique en spectrométrie de masse (LC-ESI-MS). La manipulation du prélèvement et de la méthode d'analyse ainsi mises au point ont été appliquées à déterminer le contenu d'un agent de guerre chimique en présence d'agents chimiques et / ou d'agents de guerre biologiques inconnus. Le sable d'Ottawa a étéensemencé avec de la moutarde, extraite de l'eau et passé à l'autoclave pour assurer la stérilité. La moutarde a été complètement hydrolysée durant les étapes de l'extraction et de l'autoclave et on a identifié du thiodiglycol par DESI-MS, avec des analyses généralement complétées en une minute qui utilisaient la méthode "dip and shoot" mise au point pour l'analyse rapide de prélèvements liquides.

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## Executive summary

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### **Rapid Analysis of Chemical Warfare Agents and their Hydrolysis Products by Desorption Electrospray Ionization Mass Spectrometry (DESI-MS)**

**Paul A. D'Agostino and Claude L. Chenier, DRDC Suffield TM 2009-027,  
Defence R&D Canada □ Suffield, October 2009.**

**Introduction:** Liquid samples are regularly taken during scenario-based training and presumably will be during real terrorist situations. DRDC Suffield, the lead Canadian laboratory for chemical warfare agent identification, identified a need for rapid analysis of liquid samples thought to contain chemical warfare agents. The present study focused on the development and application of a rapid sample handling and analysis method for organic and aqueous samples.

**Results:** A "dip and shoot" analytical method was developed for the rapid sampling and desorption electrospray ionization mass spectrometric (DESI-MS) analysis of chemical warfare agents and their hydrolysis products in liquid samples. Sampling was performed by simply dipping fused silica, stainless steel or SPME tips into the organic or aqueous samples. Replicate analyses were completed within several minutes under ambient conditions with no sample pre-treatment, resulting in a significant increase in sample throughput over conventional solid phase microextraction (SPME) sampling and DESI-MS analysis or liquid chromatographic electrospray ionization mass spectrometric (LC-ESI-MS) analysis. The developed sample handling and analysis method was applied to the determination of chemical warfare agent content in the presence of unknown chemical and/or biological warfare agents. Ottawa sand was spiked with mustard, extracted with water and autoclaved to ensure sterility. Mustard was completely hydrolysed during the extraction/autoclave step and thiodiglycol was identified by DESI-MS, with analyses generally being completed within one minute using the "dip and shoot" method developed for the rapid analysis of liquid samples.

**Significance:** Application of the developed sample handling and analysis methodology is anticipated in the field and laboratory during forensic investigations where evidence of chemical warfare agent use is required for criminal prosecution or to assess remediation/restoration efforts following an incident.

**Future plans:** The reported method will be a valuable addition to the present methods for the identification of chemical warfare agents and their hydrolysis products in samples collected in support of counter-terrorism. Continued development and application of tandem mass spectrometry to samples containing chemical warfare agent contamination is anticipated with the 2009 arrival of a new high resolution tandem mass spectrometer at DRDC Suffield.

# Sommaire

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## Rapid Analysis of Chemical Warfare Agents and their Hydrolysis Products by Desorption Electrospray Ionization Mass Spectrometry (DESI-MS)

D'Agostino Paul A.; Chenier Claude L., R & D pour la défense Canada  
Suffield; Octobre 2009.

**Introduction :** Des prélèvements de liquides sont normalement effectués durant l'instruction basée sur scénarios et seront probablement effectués durant des situations de terrorisme réelles. RDDC Suffield, le laboratoire canadien principal d'identification d'agents de guerre chimiques, a identifié un besoin d'analyser rapidement les prélèvements liquides suspects de contenir des agents de guerre chimiques. L'étude actuelle est axée sur la mise au point et l'application d'une manipulation de prélèvements et d'une méthode d'analyse rapides de prélèvements organiques et aqueux.

**Résultats :** Une méthode analytique «dip and shoot» a été mise au point pour le prélèvement rapide et l'analyse DESI-MS, électro-nébulisation ionique par désorption en spectrométrie de masse, des agents de guerre chimiques et de leurs produits d'hydrolyse contenus dans les prélèvements de liquides. Les prélèvements ont simplement été effectués en trempant de la silice fondue, de l'acier inoxydable ou SPME tips dans les prélèvements organiques ou aqueux. Des analyses parallèles ont été complétées en plusieurs minutes, dans des conditions ambiantes, sans aucun traitement préalable du prélèvement et ont résulté en une augmentation importante de la vitesse de traitement du prélèvement comparé au prélèvement de micro-extraction en phase solide (SPME) classique et aux analyses DESI-MS ou analyses de chromatographie en phase liquide et électro-nébulisation ionique en spectrométrie de masse (LC-ESI-MS). La manipulation du prélèvement et la méthode d'analyse ainsi mises au point ont été appliquées à déterminer du contenu d'un agent de guerre chimique en présence d'agents chimiques et / ou d'agents de guerre biologiques inconnus. Le sable d'Ottawa a étéensemencé avec de la moutarde, extraite avec de l'eau et passé à l'autoclave pour assurer la stérilité. La moutarde a été complètement hydrolysée durant les étapes de l'extraction et de l'autoclave et on a identifié du thiodiglycol par DESI-MS, avec des analyses généralement complétées en une minute qui utilisaient la méthode «dip and shoot» mise au point pour l'analyse rapide de prélèvements liquides.

**Portée des résultats :** On prévoit d'appliquer la mise au point de la manipulation du prélèvement et de la méthodologie des analyses sur le terrain et en laboratoire durant les investigations légistes quand on requiert la preuve d'utilisation d'un agent de guerre chimique pour poursuite de matière criminelle ou pour évaluer les efforts en correction/restauration qui suivent un incident.

**Perspectives d'avenir :** La méthode documentée sera une addition précieuse aux méthodes actuelles d'identification d'agents de guerre chimiques et de leurs produits d'hydrolyse dans les échantillons collectés en soutien aux activités antiterroristes. On prévoit de continuer la mise au point et application de la spectrométrie de masse en tandem aux échantillons contenant un agent de guerre chimique de contamination avec l'apparition de nouvelle spectrométrie de masse en tandem de haute résolution à RDDC Suffield.

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# Introduction

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The ending of the Cold War and the widespread acceptance of the Chemical Weapons Convention has reduced the likelihood of battlefield chemical weapons use, but there remains serious concern world-wide that other parties may use chemical warfare agents against civilian or military targets. Sarin, a well known nerve agent, was used by the Aum Shinrikyo sect in Japan in 1995 during an attack on the Tokyo underground transit system, during which a dozen people were killed and thousands more were injured. Public concern about the use of chemical or biological warfare agents reached a new peak following the al-Qaeda terrorist attacks of September 2001 and the subsequent delivery of anthrax letters. These events heightened security concerns within many countries and considerable resources have been expended to improve both field and laboratory based detection and identification methods for chemical warfare agents.

Analytical methods for the detection and identification of chemical warfare agents, their degradation products and related compounds has been thoroughly reviewed with different emphases on several occasions [1-10]. Much of the analytical methods development was driven by the requirements of the military and their need to be able to detect and identify these compounds in typical battlefield samples. These methods focus largely on the mass spectrometric determination of chemical warfare agents or their degradation products in environmental matrices such as soil [10-20], water [17, 19-22], air [27, 28], recovered munitions and munition blocks [13, 14, 29-31], decontamination solutions [32-34] and military clothing/gear [11, 13, 14]. Newer methods based on solid phase microextraction (SPME) sampling followed by gas chromatography-mass spectrometry GC-MS analysis [35-43] and direct analysis by secondary ion mass spectrometry [44, 45] have been reported for environmental analyses, but most of the reported analytical methods are based on GC-MS analysis of an extract of the collected medium. Organic extracts of chemical warfare agents may be analysed directly by GC-MS, but the hydrolysis products of chemical warfare agents usually require derivatization prior to GC-MS analysis [8, 16-19, 23, 25, 42, 43].

More recently researchers have demonstrated the value of LC-MS as a complementary or replacement method for GC-MS, particularly for the confirmation of hydrolysis products of chemical warfare agents in aqueous extracts or samples [46-58], as the hydrolysis products may be analysed directly by LC-MS without the need for additional sample handling and derivatization. In addition, LC-MS has the added benefit that it may also be utilized for the determination of organophosphorus chemical warfare agents and related compounds in aqueous extracts of soil, water, snow and other samples [52-55, 58-60].

Recently a novel mass spectrometric method for sample ionization and analysis, developed by Cooks' group and referred to as desorption electrospray ionization (DESI), was described [61]. During the DESI experiment charged droplets in the solvent being electrosprayed impact the surface of interest, desorbing and ionizing the analyte. Ionized large biomolecules and small organic molecules may then be detected by mass spectrometry, often in the tandem mode. Cooks recently reviewed ambient mass spectrometry with an emphasis on the DESI method [62] and included discussion on direct analysis in real time (DART) [63], a related direct analysis approach.

DESI-MS has been used for a variety of direct analyses [64] including the analysis of pharmaceutical products [65-75], dyes on thin layer chromatography plates [76], explosives on a

variety of surfaces [72, 77-79], polymers [80], alkaloids on plant tissue [81], chemical warfare agents on solid phase microextraction (SPME) fibers [60, 82], hydrolysis products of chemical warfare agents on Teflon or glass surfaces [83], dimethyl methylphosphonate (DMMP) [34, 72, 74, 78, 79], pesticides [84] from a variety of surfaces and fentanyl hydrochloride in counterfeit tablets [85]. Both the DESI and DART techniques allow rapid, direct sample analysis and have attracted considerable interest in the chemical defence and public security communities due to the minimal sample handling requirements and potential for rapid sample throughput [60, 63, 82].

The chemical defence and public security communities have identified a number of chemicals that might pose a risk if involved in a terrorist event. These include common chemical warfare agents, pesticides such as malathion, diazaron and parathion, and pharmaceuticals such as codeine, fluothene and fentanyl(s).

DMMP, a chemical warfare agent stimulant, has been included in many MS method evaluations as it provides an indication of method applicability to chemical warfare agents. Cooks first reported DESI-MS data for DMMP from a nitrile glove surface [34]. A protonated adduct of DMMP at  $m/z$  124 (should be  $m/z$  125) was observed. This assignment was corrected during subsequent investigations involving the DESI and/or desorption atmospheric pressure chemical ionization (DAP CI) analysis of DMMP from a variety of surfaces including paper [74, 78, 79], computer plastic [79] and metal [79]. Similar results were also obtained during DESI-MS analysis of cloth spiked with DMMP [72].

Chemical warfare agents, including sarin, soman and mustard have been successfully analysed by DESI-MS from SPME fibers used to sample the headspace above chemical warfare agents and chemical warfare agents spiked onto Dacron sampling swabs and office media including office carpet, office fabrics and photocopy paper [60, 82]. During these DRDC Suffield studies mustard, a chemical warfare agent that does not produce ions during LC-ESI-MS, ionized during DESI-MS. It is possible that these compounds are being ionized during DESI-MS by an atmospheric chemical ionization mechanism where ionization results from gas phase proton transfer to a neutral analyte that has evaporated from the SPME surface [77]. If this were the case then it would be possible to protonate analytes, including mustard, based on the ability of the analyte to accept a proton from a donor of lesser proton affinity [77]. It was also noted after removal of a highly exposed SPME fiber that the signal for an analyte remained for some time. Vaporized chemical warfare agent could be ionizing by either an ESI like mechanism where the surface is now a gas or by the atmospheric pressure chemical ionization mechanism described above. The possibility of both mechanisms occurring during DESI-MS analyses of chemical warfare agents cannot be ruled out.

Common hydrolysis products of chemical warfare agents, including methyl phosphonic acid, isopropyl methylphosphonic acid, ethyl methylphosphonic acid, pinacolyl methylphosphonic acid and thiodiglycol have also been analysed by DESI-MS [83, 86]. Surfaces analysed included SPME fibers used to collect headspace samples above spiked glass surfaces and/or canola oil [86] and glass or Teflon [83]. A variant of DESI using boric acid, reactive DESI, was also employed to determine the presence of methyl phosphonic acid, isopropyl methylphosphonic acid and ethyl methylphosphonic acid at ng levels in urine applied to a glass surface [83].

Malathion, a toxic industrial chemical of concern, and several other low-volatility organophosphates spiked onto immobilized powders (fixed on double sided tape) or surfaces

(glass, PTFE, Kapton and paper) have been analysed by DESI-MS [84]. These compounds, considered chemical warfare agent simulants by the researchers, were also analysed by a complementary technique, ultraviolet laser desorption/ionization [84]. Two pharmaceuticals of concern, codeine [65, 67, 70, 73, 74] and a fentanyl [85] have been analysed by DESI-MS. DESI-MS identification of both compounds in pharmaceutical tablets [65, 67, 85] has been reported as well as the identification of codeine on glass [73] or Teflon [70] surfaces and human skin [74].

SPME sampling has been widely used for methods development [87], including the chemical warfare agent sampling and analysis strategy developed for counterterrorism purposes in Canada. Direct analysis of SPME fibers by DESI-MS complements existing thermal desorption GC-MS based identification methods for chemical warfare agents and provides several advantages. The hydrolysis products of chemical warfare agents may be analysed directly without the need for derivatization procedures associated with GC-MS analyses and DESI-MS may ultimately enable higher sample throughput with less sample handling. SPME sampling and analysis can take minutes and a more rapid method of sampling for DESI-MS analysis would be desirable to increase throughput. Many of the collected samples during scenario-based counter-terrorism training exercises are liquids and the "dip and shoot" method using fused silica or stainless steel tips should reduce sampling and analysis times to less than one minute. Unlike SPME fiber sampling, the method has application to both organic and aqueous samples and does not require fiber conditioning prior to sampling. Analysis times are much quicker as desorption is immediate, tips are disposable and useful for rapid sampling and identification of both chemical warfare agents and their hydrolysis products (without derivatization).

DESI-MS was evaluated for the detection and identification of common chemical warfare agents (GB, GD, GA, GF and VX) and their hydrolysis products using stainless steel and fused silica tips to sample organic and aqueous samples spiked with these compounds. Sampling and analysis was completed in less than a minute using the developed approach and application was demonstrated for five organophosphorous chemical warfare agents, their hydrolysis products and thiodiglycol, the hydrolysis product of mustard. The developed approach to rapid sampling and DESI-MS analysis was applied to the analysis of spiked sand samples for chemical warfare agents using accepted DRDC Suffield procedures for samples where chemical/biological warfare agent contamination is unknown.

## Experimental

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### Samples and sample handling

Standard stock solutions of chemical warfare agents and their hydrolysis products were prepared in water or dichloromethane in the 0.01 to 1 mg/mL range.

Ottawa sand samples (3.0 g) were spiked in triplicate at the 47 µg/g level with mustard to simulate a chemical sample where the chemical and biological content is unknown. Each sample (and blank) was ultrasonically extracted with water (10 mL) for 10 minutes in a 20 mL scintillation vial. The lid on the scintillation vial was tightened finger tight (still allows airflow) and then autoclaved for two hours at 121°C at 15 psi (liquid cycle) to ensure sterilization of any biological content. The sterilized aqueous extract was allowed to cool and an aliquot (1.5 mL) was removed, centrifuged for 10 min at 14,000 rpm and retained for DESI-MS and LC-ESI-MS analysis.

Sampling was performed by quickly dipping a stainless steel and/or fused silica tips (or Supelco carbowax/divinyl benzene SPME fiber for the Ottawa sand extracts) into the liquid samples. The dipped tip (sealed in an Supelco SPME manual injector) was introduced immediately through the septum port on the ESI housing during DESI-MS analyses.

### Instrumental

Mass spectrometric data were acquired in the laboratory using a Waters (Milford, MA, USA) Q-ToF Ultima tandem mass spectrometer equipped with a Z-spray electrospray interface. The electrospray capillary was operated in the 1.5 to 3 kV range. The collision energy was generally maintained at 5 V for MS operation and was varied from 3 to 12 V (depending on the precursor ion selected) for MS/MS operation. RF1 was varied between 20 and 60 V during MS/MS/MS experiments to ensure product ion formation in the ESI interface. Argon was continually flowing into the collision cell at 9 psi during all analyses. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow rate of 300 L/h and nitrogen cone gas was introduced at a flow rate of 50 L/h. MS data were typically acquired from 70 to 700 Da and MS/MS (product ion mass spectra) data were acquired for the protonated molecular ions of the spiked compounds (0.3 to 1 s). All data were acquired in the continuum mode with a resolution of 8000 (V-mode, 50% valley definition).

During DESI-MS and DESI-MS/MS analyses a laboratory stand was used to hold and position the SPME manual holder so that the fiber could be introduced into the ESI plume. The plexiglass sleeve on the Z-spray interface contained a septum port to facilitate the safe introduction of SPME fibers or tips contaminated with chemical warfare agents. The LC solvents, 50:50 acetonitrile/water (0.1% trifluoroacetic acid), were sprayed at 10 µL/min during DESI analyses.

LC-MS separations were performed with an Agilent 1100 capillary LC (Palo Alto, CA, USA) using a 5% to 75%B gradient over 5 minutes and a flow rate of 10  $\mu$ L/min or under isocratic conditions (2%B) at the same flow rate. The following solvent compositions were prepared for the mobile phase: Solvent A (0.1% trifluoroacetic acid in water) and Solvent B (acetonitrile). All LC separations were performed with Agilent 50 mm x 0.3 mm i.d. capillary column packed with Zorbax SB C18 (1.8  $\mu$ m particle size). An autosampler was used to introduce 1  $\mu$ L aqueous injections.

## Results and Discussion

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DRDC Suffield first reported the usefulness of DESI-MS for chemical warfare agent applications in 2005 at the ASMS [88] and has since reported successful use of this technique for the direct analysis of SPME fibers exposed to a variety of spiked office environment and consumer product media [60, 82, 86]. Hydrolysis products of chemical warfare agents were also identified by DESI-MS [86] as well as mustard and several other compounds related to mustard that do not ionize by ESI-MS [82, 86].

SPME forms a cornerstone in the analytical strategy developed at DRDC Suffield for the identification of chemical warfare agents under realistic field sampling and analysis conditions. Samples (i.e., swabs, liquids, soil, materials) taken in the field would typically be contained in a septum-sealed vial, the headspace above which may be sampled by SPME using a manual holder without exposing the analyst to potentially harmful chemicals [89]. Analyses would typically be performed by fast gas chromatography-mass spectrometry (GC-MS) with DESI-MS and/or LC-ESI-MS being used to confirm identification [82]. DESI-MS could be considered for primary analysis for large number of samples, as analysis times are typically minutes faster than fast GC-MS. DESI-MS would be preferred if identification of chemical warfare agent hydrolysis products was also required. DESI-MS does not require the derivatization step associated with GC-MS analyses, enabling identification of the actual compound with reduced sample handling and analysis time.

SPME headspace sampling can take a little as a few seconds for concentrated samples with higher volatility. For lower volatility samples, particularly at lower concentration levels, heating and sampling times of five or more minutes may be required. Direct sampling of liquid solutions with SPME fibers generally requires more time and mixing and is limited to aqueous liquids as swelling occurs following exposure to organic solutions. Many of the samples taken in the field are organic or aqueous liquids containing unknown toxic chemicals, including chemical warfare agents. Their concentration is often relatively high (mg/mL or higher), which might allow DESI-MS identification by a simple "dip and shoot" method. This would reduce sampling time, minimize the amount of analyte introduced into the MS instrument and ultimately increase throughput. Uncoated fused silica and fused silica and/or stainless steel tips associated with a SPME manual holder where the SPME coating was stripped away were investigated for sampling of organic and aqueous solutions of chemical warfare agents and their hydrolysis products at concentrations ranging from 0.01 to 1 mg/mL. The dipped tips were introduced directly into the mass spectrometer for DESI analysis.

### Chemical warfare agents

Sampling involved simply a dip of the tip into the liquid. DESI-MS analysis was rapid with individual analyses being completed in 1 minute or less. Samples can be screened for the presence of target compounds by DESI-MS and confirmed using this approach or by DESI-MS/MS when more specificity is required. Figures 1 to 4 illustrate DESI-MS/MS data obtained following sampling of 1 mg/mL solutions of GB, GD, GF and GA in dichloromethane using a manual SPME holder where the SPME coating was stripped away. Interestingly, best results were obtained for these compounds when both the fused silica and stainless steel portion (as opposed to

just the fused silica) of the needle was dipped, perhaps indicating an adsorption preference for stainless steel for these compounds. All four compounds exhibit some tailing which suggests initially DESI from the surface was observed followed by some evaporation and DESI in the gas phase, consistent with the diminishing signal observed after tip removal from the ESI plume. The lower volatility chemical warfare agent VX (and low volatility hydrolysis products) exhibited a much sharper profile (Figure 5) and no signal at all when the tip was removed from the ESI plume. MS/MS spectra for GB, GD, GF and GA were similar to ESI-MS data obtained during LC-ESI-MS, with the main product ion being due to the loss of the alkene associated with the alkoxy group. The principal product ion observed in the MS/MS spectrum acquired for VX was at  $m/z$  128, due to neutral loss of  $\text{CH}_2\text{CH}_2\text{N}(i\text{Pr})_2$ .

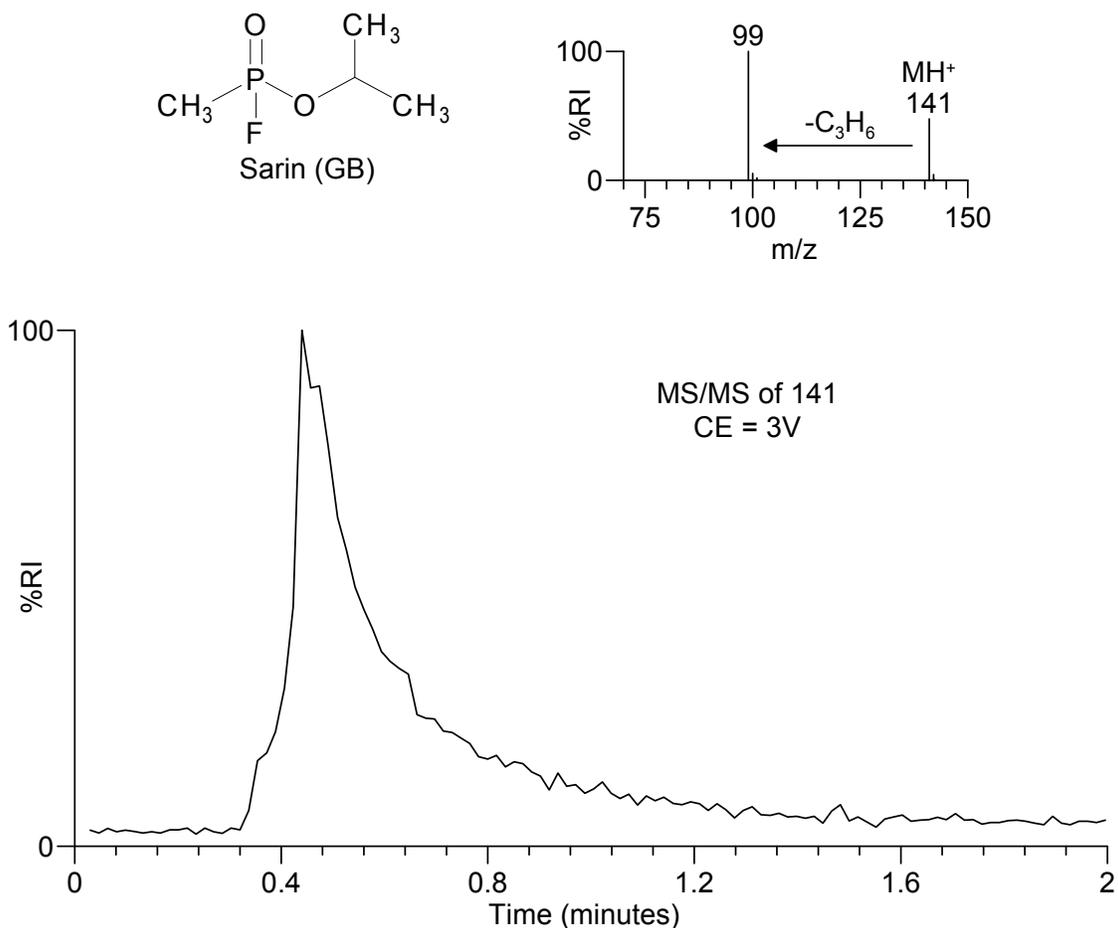


Figure 1: DESI-MS/MS chromatogram for  $m/z$  141 obtained during analysis of a stainless steel and fused silica tip (stripped of SPME coating) dipped into a 1 mg/mL sarin (GB) standard (in dichloromethane). Inset: Typical product ion mass spectrum for GB.

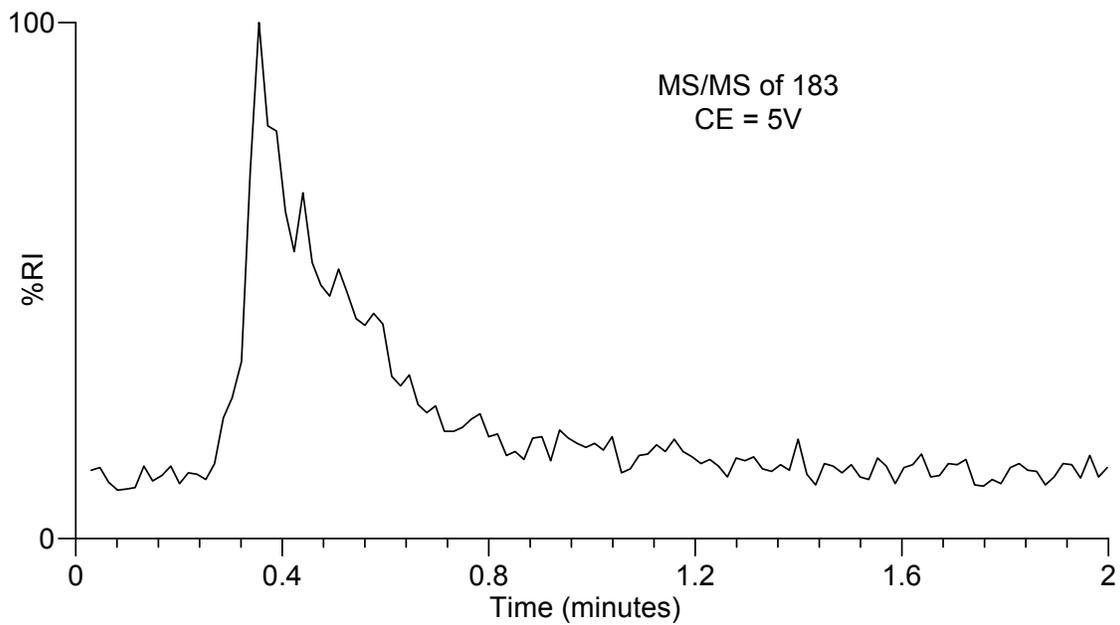
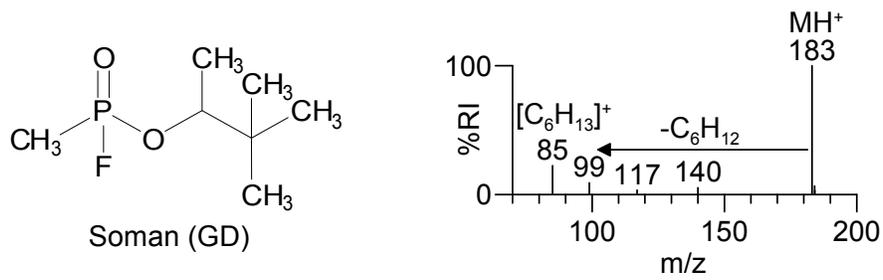


Figure 2: DESI-MS/MS chromatogram for m/z 183 obtained during analysis of a stainless steel and fused silica tip (stripped of SPME coating) dipped into a 1 mg/mL soman (GD) standard (in dichloromethane). Inset: Typical product ion mass spectrum for GD.

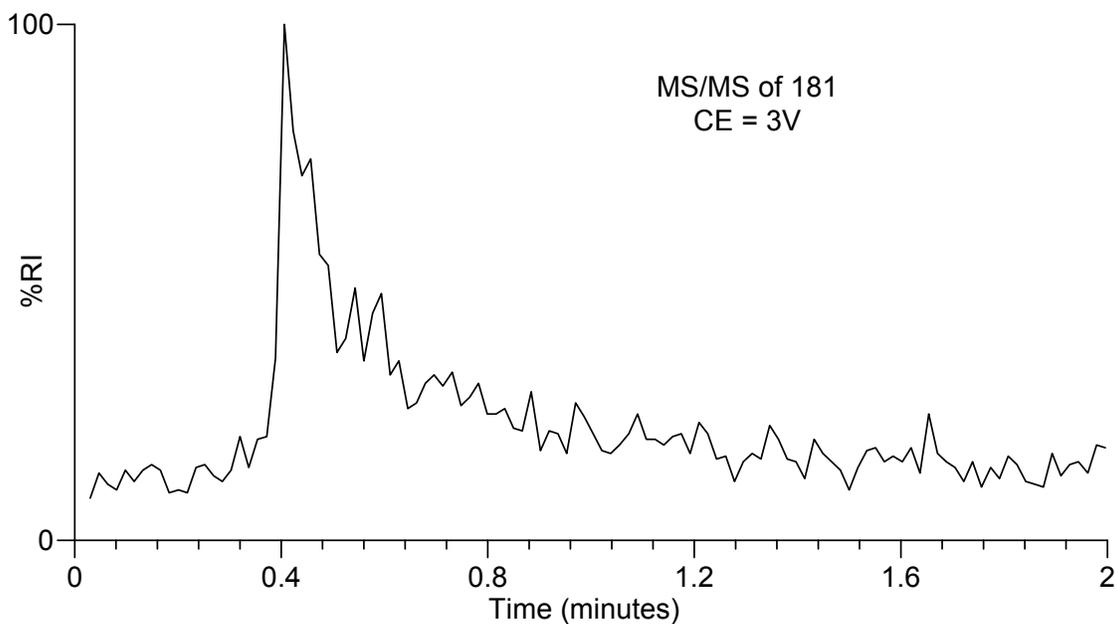
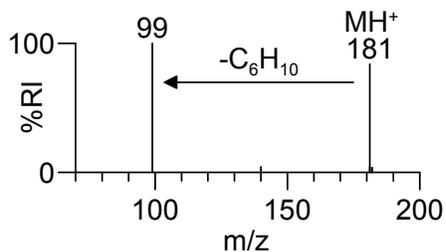
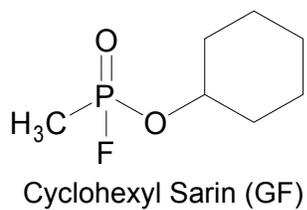


Figure 3: DESI-MS/MS chromatogram for m/z 181 obtained during analysis of a stainless steel and fused silica tip (stripped of SPME coating) dipped into a 1 mg/mL cyclohexyl sarin (GF) standard (in dichloromethane). Inset: Typical product ion mass spectrum for GF.

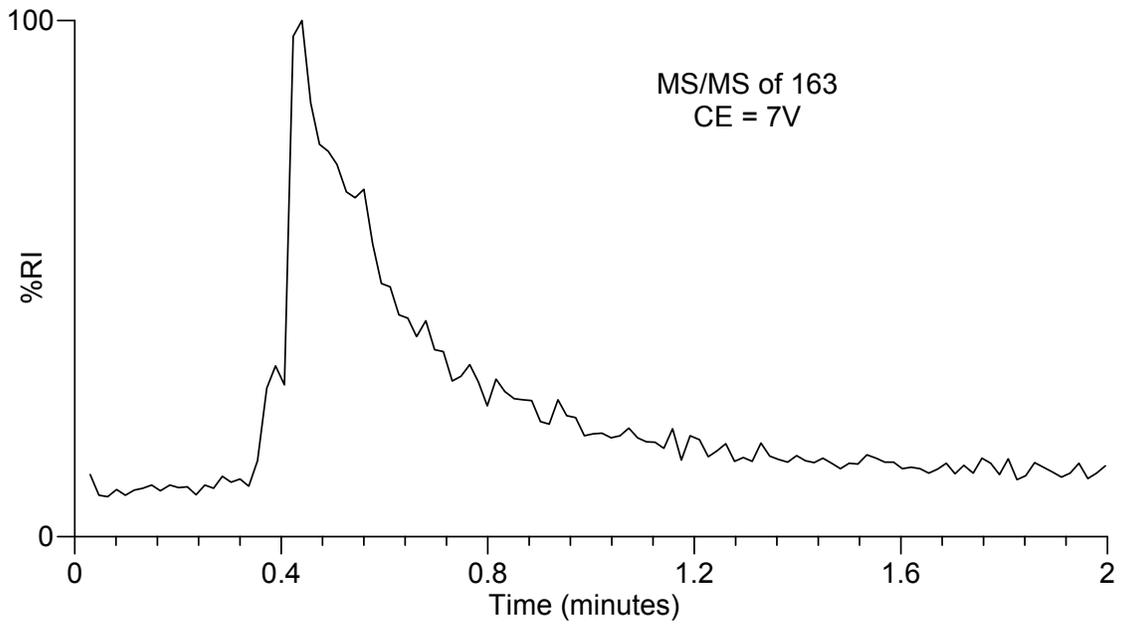
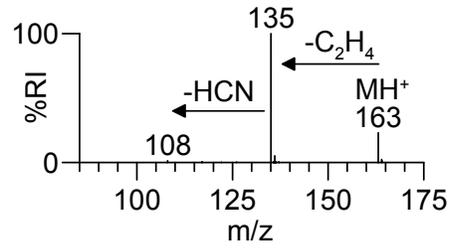
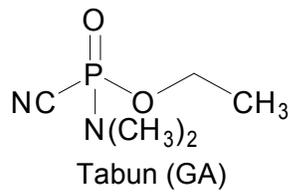


Figure 4: DESI-MS/MS chromatogram for  $m/z$  163 obtained during analysis of a stainless steel and fused silica tip (stripped of SPME coating) dipped into a 1 mg/mL tabun (GA) standard (in dichloromethane). Inset: Typical product ion mass spectrum for GA.

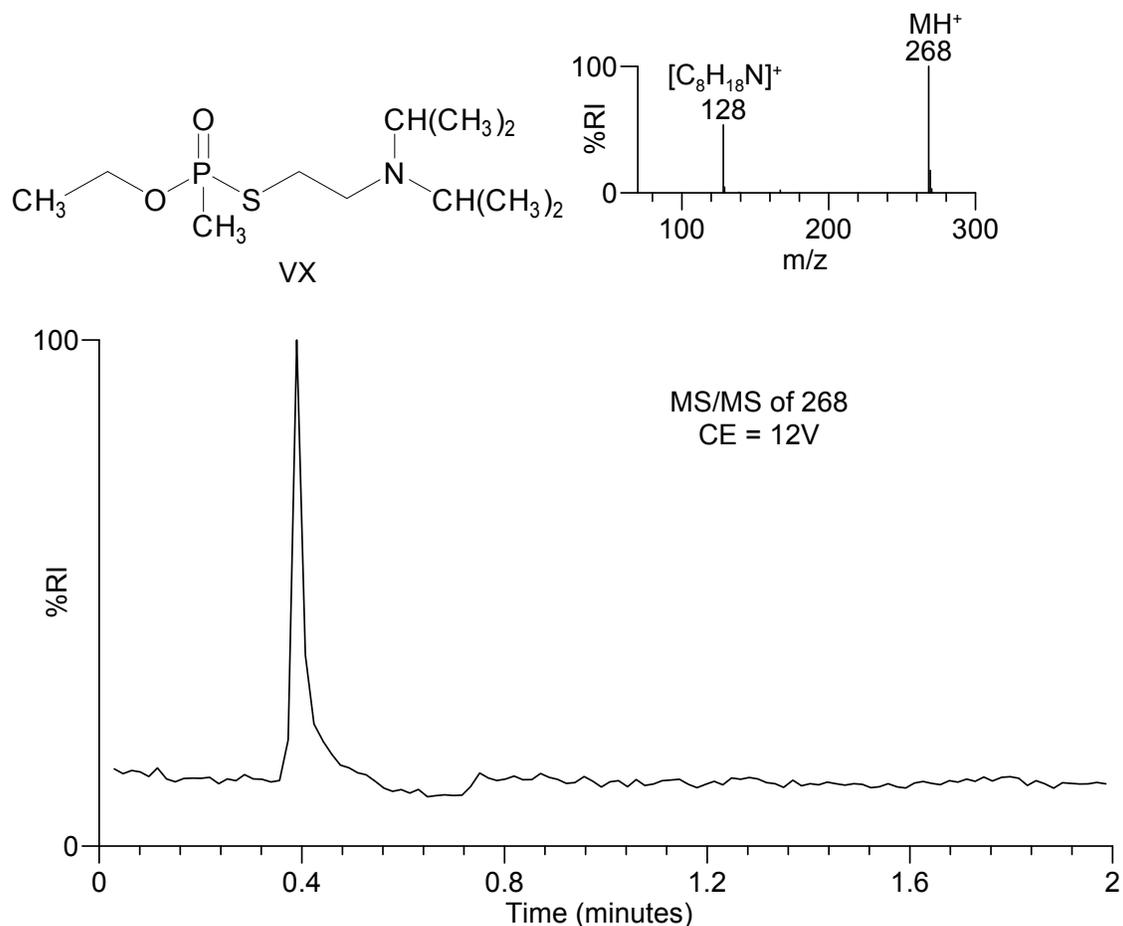


Figure 5: DESI-MS/MS chromatogram for  $m/z$  268 obtained during analysis of a stainless steel and fused silica tip (stripped of SPME coating) dipped into a 1 mg/mL VX standard (in dichloromethane). Inset: Typical product ion mass spectrum for VX.

The chemical warfare agents were also analysed by DESI-MS/MS repeatedly over several minutes to demonstrate the ability to analyse a number of samples over a short period of time. Figure 6 illustrates repeated analysis of a tabun sample (0.04 mg/mL in dichloromethane) using a stainless steel tip. Area measurements (arbitrary units) for repeated analysis of the tabun samples were  $59 \pm 20$  (34%), consistent with the semi-quantitative nature of the method. In total, nine dip and shoot analyses were completed in less than ten minutes with all the sample manipulation and analysis being done manually by the operator. The acquired DESI-MS/MS data for tabun contains a product ion at  $m/z$  135.

Additional structural information for tabun was obtained by promoting the formation of additional characteristic ions during DESI-MS/MS/MS analyses (Figure 7), a novel approach that makes use of higher RF1 settings. The voltage in the RF1 region of the source was increased to promote product ion formation prior to the quadrupole. This setting was increased to 60 V from

the usual setting of 20 V resulting in significant  $m/z$  135 product ion (from the  $MH^+$  ion for tabun at  $m/z$  163). The  $m/z$  135 ion was selected with the quadrupole mass analyser and subjected to increasing collision energies (7 to 12 V) in the collision cell located between the quadrupole and time-of-flight mass analysers. Increasing collision energies led to increasing relative intensities of the product ions at  $m/z$  117 and  $m/z$  108, due to loss of water and HCN, respectively, from the  $m/z$  135 ion. Acquisition of complementary MS/MS/MS data typically increases the number of ions associated with identification of a given compound. Acquisition of this additional data improves the certainty of identification and would be quite valuable for structural elucidation of unknowns.

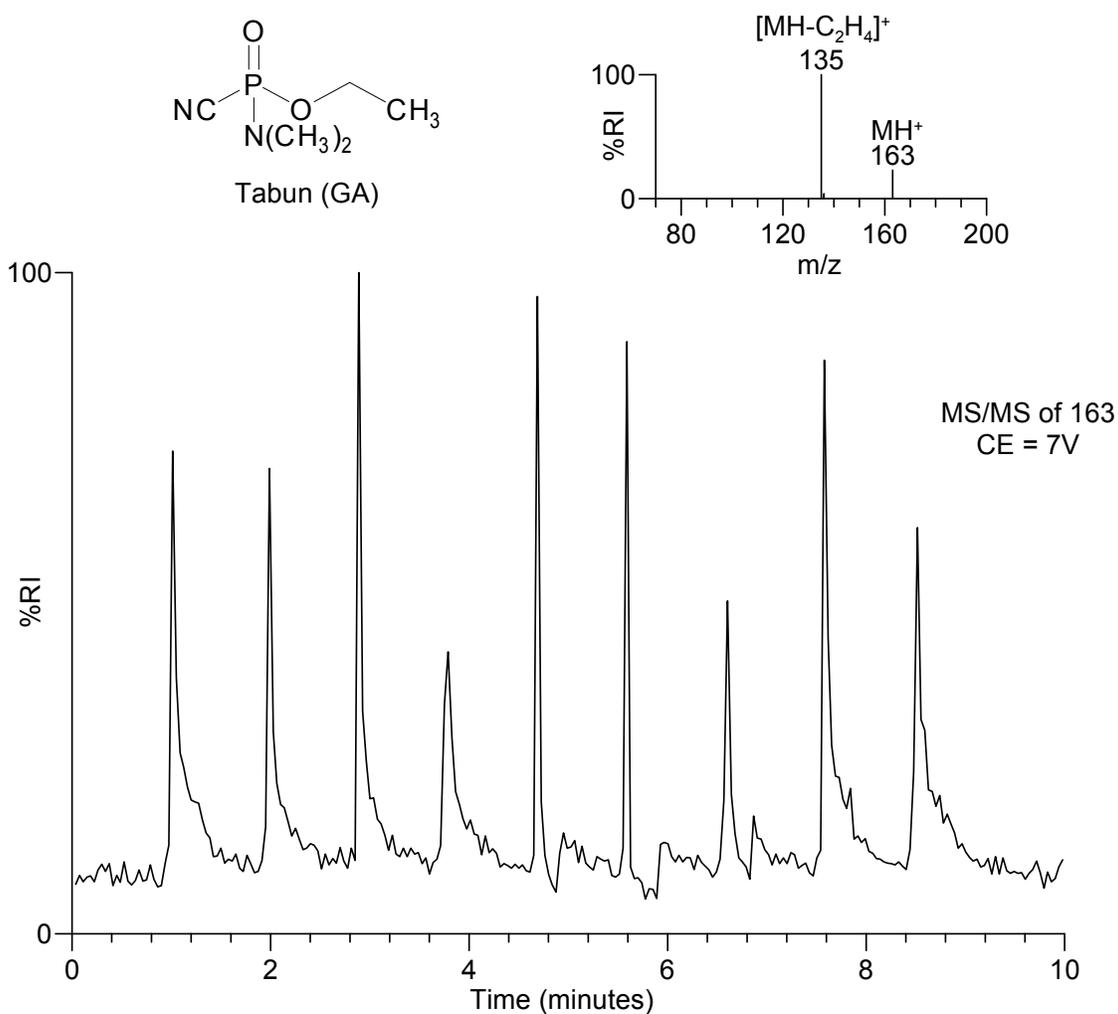


Figure 6: DESI-MS/MS chromatogram for  $m/z$  163 obtained during replicate analyses of a stainless steel tip dipped into a 0.04 mg/mL tabun (GA) standard (in dichloromethane). Inset: Typical product ion mass spectrum for GA.

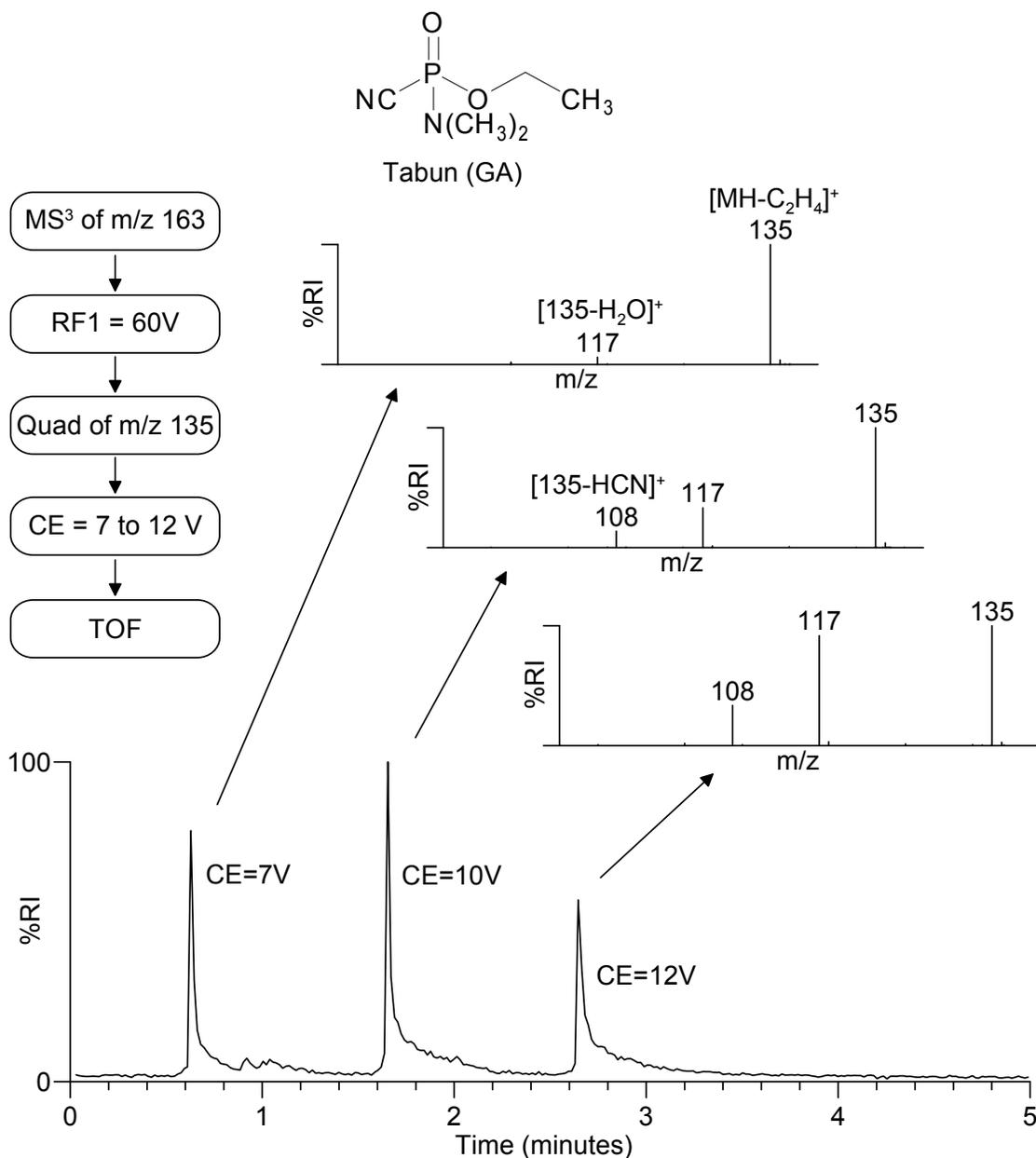


Figure 7: DESI-MS/MS/MS chromatogram obtained during replicate analyses of a stainless steel tip dipped into a 0.2 mg/mL tabun (GA) standard (in dichloromethane). The initial product ion at m/z 135 was generated by increasing the RF1 voltage to 60 V. The m/z 135 ion was selected with the quadrupole mass analyser and products of this ion were generated with increasing collision energies.

## Hydrolysis products

Chemical warfare agent hydrolysis products analysed by GC-MS require an additional (undesirable) derivatization step that is not required for DESI-MS (or LC-ESI-MS) analysis. The hydrolysis products would typically be associated with aqueous samples and the "dip and shoot" method was evaluated for the hydrolysis products of VX, sarin, soman and mustard at the 1 mg/mL level in water using a fused silica tip. Figures 8, 9 and 10 illustrate repeated analysis of ethyl methyl phosphonic acid (hydrolysis product of VX), isopropyl methylphosphonic acid (hydrolysis product of sarin) and pinacolyl methylphosphonic acid (hydrolysis product of soman), respectively. Samples were analysed quickly (approximately 1 minute or less per sample) with area measurement variability in the 35 to 40 % range, as was observed for tabun. DESI-MS/MS data contained the  $MH^+$  ion and the product ion due to the loss of the alkene associated with the alkoxy group.

Similar data were also obtained for the hydrolysis product of mustard, thiodiglycol. Figure 11 illustrates repeated analysis of a thiodiglycol sample using a fused silica tip. Eight analyses were completed within eight minutes. The acquired DESI-MS/MS contained the  $MH^+$  ion and a product ion at  $m/z$  105 due to loss of water. DESI-MS/MS data obtained for the hydrolysis products of mustard and the organophosphorus chemical warfare agents was identical to that obtained during LS-ESI-MS analyses of these compounds.

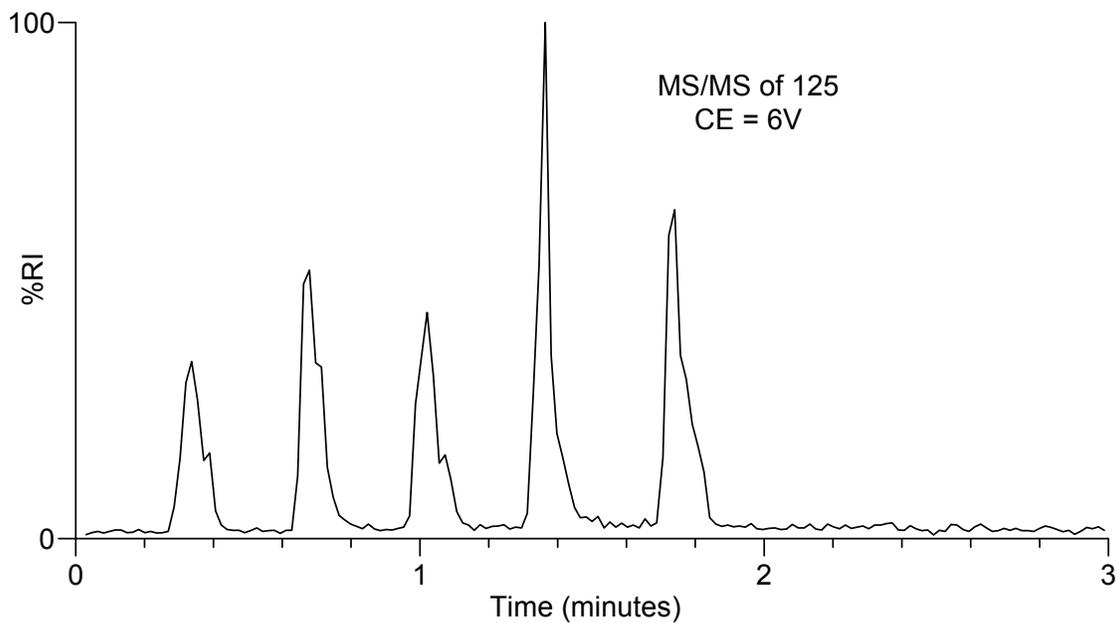
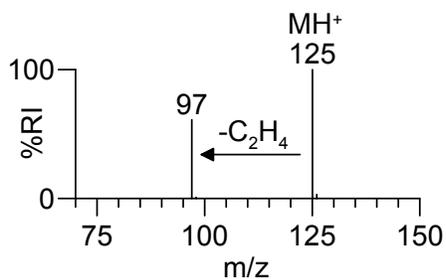
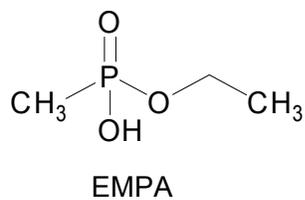


Figure 8: DESI-MS/MS chromatogram for  $m/z$  125 obtained during replicate analyses of a fused silica tip dipped into a 1 mg/mL ethyl methylphosphonic acid (EMPA) standard (in water). Inset: Typical product ion mass spectrum for EMPA.

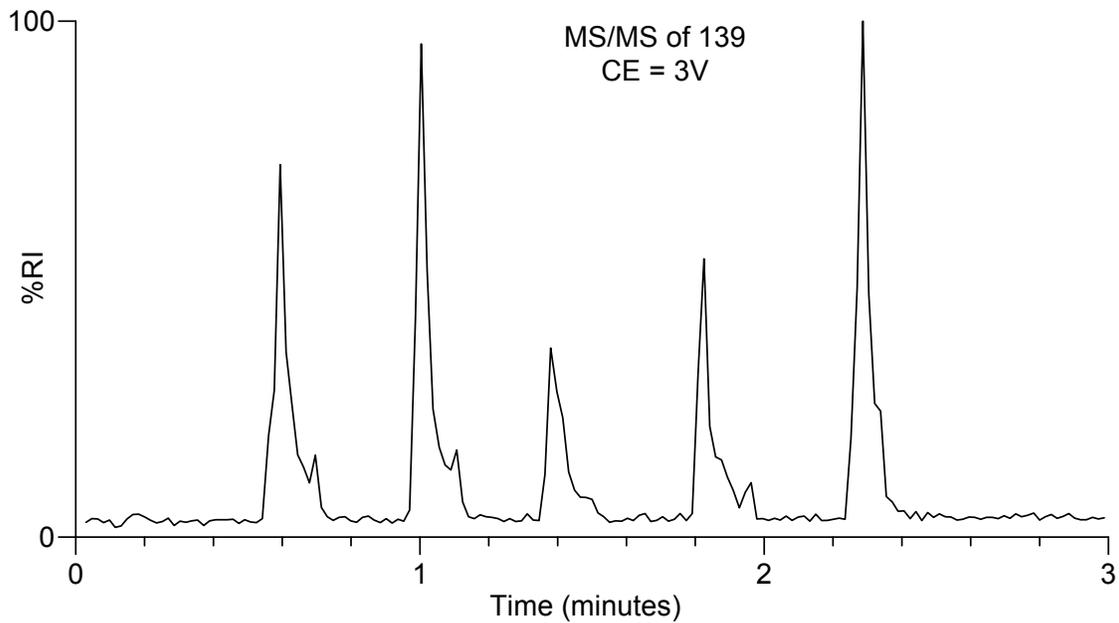
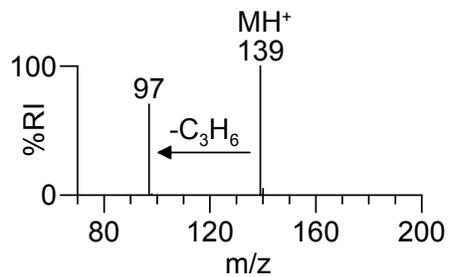
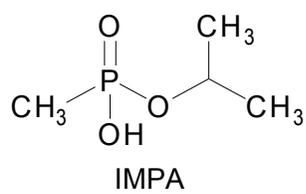


Figure 9: DESI-MS/MS chromatogram for m/z 139 obtained during replicate analyses of a fused silica tip dipped into a 1 mg/mL isopropyl methylphosphonic acid (IMPA) standard (in water).  
Inset: Typical product ion mass spectrum for IMPA.

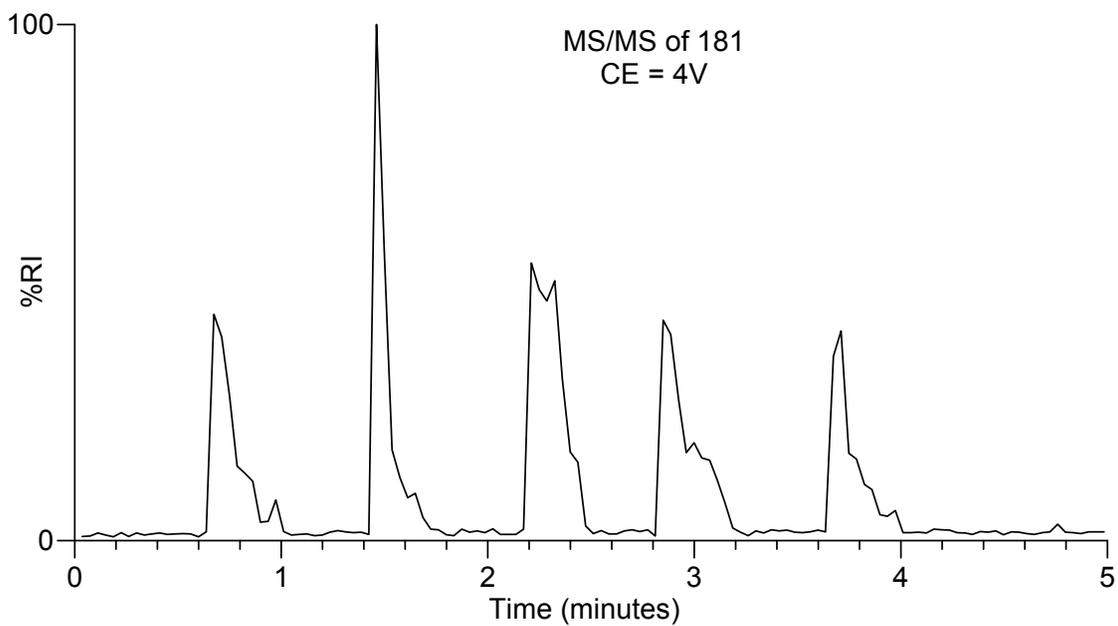
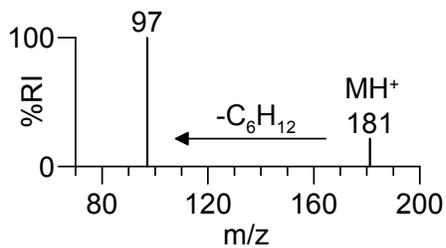
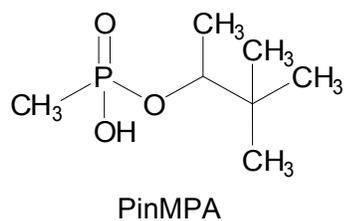


Figure 10: DESI-MS/MS chromatogram for m/z 181 obtained during replicate analyses of a fused silica tip dipped into a 1 mg/mL pinacolyl methylphosphonic acid (PinMPA) standard (in water). Inset: Typical product ion mass spectrum for PinMPA.

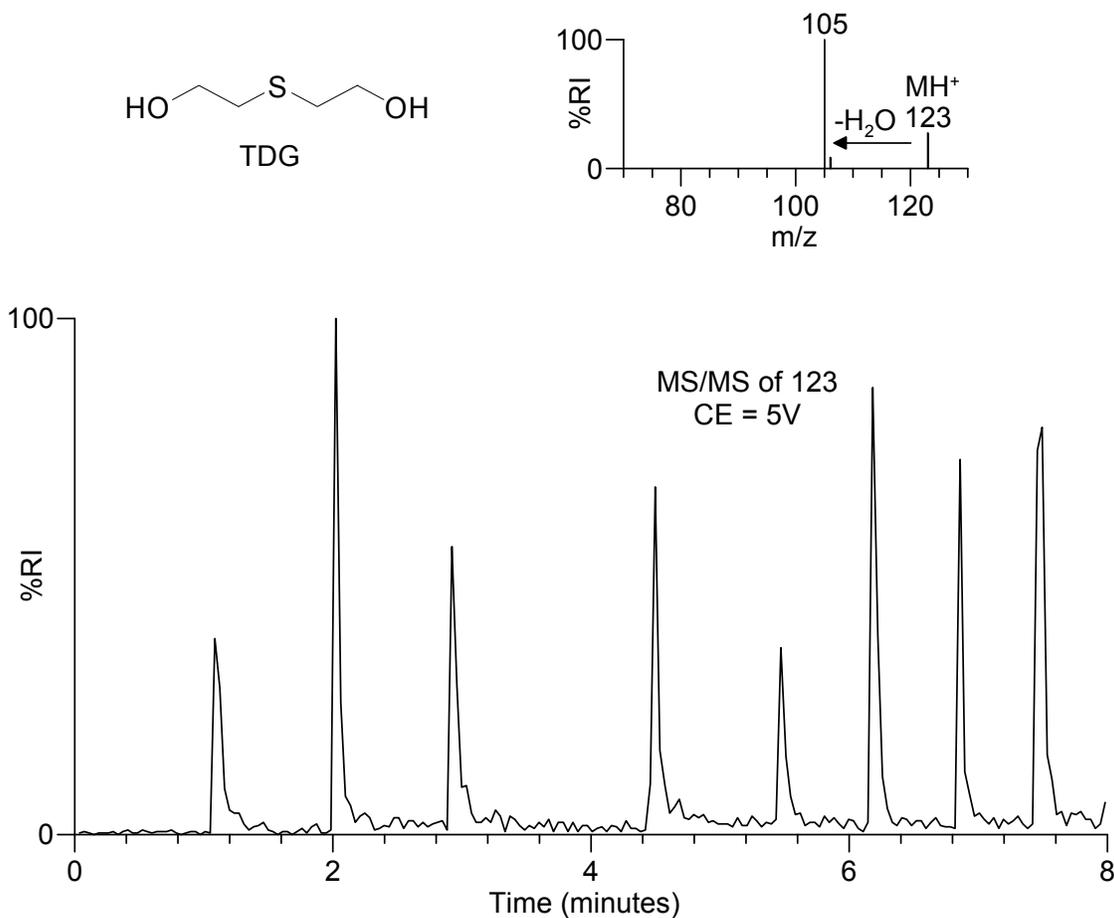


Figure 11: DESI-MS/MS chromatogram for m/z 123 obtained during replicate analyses of a fused silica tip dipped into a 1 mg/mL thiodiglycol (TDG) standard (in water). Inset: Typical product ion mass spectrum for TDG.

## Application to CB unknowns

Samples contaminated with unknown chemical and/or biological warfare agents pose a unique problem to chemical and biological specialists tasked with determining the presence of chemical or biological warfare agents. Such a sample would initially be received into biocontainment level 3 (BL-3) at DRDC Suffield where biological identification may be safely carried out. Under normal circumstances, a sample extract requiring removal from BL-3 for use in a BL-2 or chemical laboratory would be sterilized by 0.22  $\mu\text{m}$  filtration. A sterility check of the filtered extract would then be conducted in BL-3, a process that may take up to two weeks. During this time chemical detection within BL-3 would be limited to devices such as the Chemical Agent Monitor. A more rapid sample handling and analysis method that could determine the presence (or absence) of chemical warfare agent contamination would be valuable to the defence community or during crime scene investigations. Rapid determination of the absence of chemical warfare agent would also benefit those working in BL-3 as the level of precautions required could be reduced.

The most rapid and effective means of sterilizing a sample contaminated with biological warfare agents that allows removal of the sample from BL-3, without a sterility check, involves autoclaving the sample for 2 hours. Any sample undergoing this process is necessarily exposed to water vapour at a high temperature, making the likelihood of chemical warfare agent hydrolysis high. An analytical method for chemical warfare agent identification must therefore be able to identify the principal hydrolysis products of the common chemical warfare agents. LC-ESI-MS may be used for this purpose and has the added benefit of being able to also detect and identify intact organophosphorus chemical warfare agents and many related compounds in aqueous sample extracts.

A sample handling method was developed based on aqueous extraction of the soil (or other media) sample in BL-3, followed by sterilization of the aqueous extract in the autoclave between BL-3 and the chemistry laboratories. The sterilized container and aqueous contents may then be safely manipulated in the chemical analysis laboratory and analysed for the presence or absence of chemical warfare agents, their hydrolysis products or related compounds by LC-ESI-MS.

Three compounds were used for evaluation of the sample handling and analysis method. Triethyl phosphate, an organophosphorus compound that has been used as a nerve agent simulant, was selected to investigate the extent of hydrolysis during autoclaving, as this compound is much more resistant to hydrolysis than the common organophosphorus chemical warfare agents (nerve agents). Isopropyl methylphosphonic acid, the hydrolysis product of the nerve agent sarin, was selected as a typical nerve agent hydrolysis product and to investigate the likelihood of further hydrolysis to methylphosphonic acid during the process. Finally thiodiglycol was selected since this product would be expected following mustard hydrolysis. It should be noted that mustard cannot be detected by LC-ESI-MS, but hydrolyses readily in the presence of water to thiodiglycol, a compound that may be detected by LC-ESI-MS.

All three spiked compounds were readily extracted from Ottawa sand samples at the 80 µg/g level (recovery efficiencies not estimated). This spiking level was below typical battlefield contamination levels, estimated to be in the 100 to 1000 µg/g range, based on a contamination density of 1 to 10 g/m<sup>2</sup> (soil density about 1 g/cm<sup>3</sup> and a 1 cm sampling depth) and considered typical of soil contamination levels that might be expected hours to days after an attack. Soil samples were extracted with water using ultrasonic vibration and a portion of the aqueous extract was removed and autoclaved to eliminate biological activity. This aqueous extract was centrifuged and analysed by LC-ESI-MS to confirm compound identity. Triethyl phosphate underwent some hydrolysis (about 10-20%) to diethyl hydrogen phosphate, suggesting that hydrolysis of nerve agents to their initial acids would be significant following autoclaving. Hydrolysis of isopropyl methylphosphonic acid to methylphosphonic acid, the common hydrolysis product for many nerve agents, was not observed. The method was in place for the 2002 Kananaskis G8 meeting [56, 90]. No chemical warfare agents were evaluated with this procedure and all analyses were by LC-ESI-MS.

DESI-MS methods developed to rapidly identify chemical warfare agents and their hydrolysis products would increase throughput over conventional LC-ESI-MS analyses performed on samples suspected to contain chemical and/or biological warfare agents. In the present application the actual chemical warfare agent, mustard, was spiked onto Ottawa sand at the 47 µg/g level for method evaluation. Each sample (and blank) was ultrasonically extracted with water for 10

minutes in a scintillation vial. The lid on the scintillation vial was tightened finger tight (still allows airflow) and then autoclaved for two hours at 121°C at 15 psi (liquid cycle) to ensure sterilization of any biological content. The sterilized aqueous extract was allowed to cool and an aliquot (1.5 mL) was removed, centrifuged and retained for DESI-MS and LC-ESI-MS analysis.

A variety of Supelco SPME fibers were initially investigated for their ability to concentrate over time thiodiglycol (and any residual mustard) directly from the aqueous extract. None were effective as the thiodiglycol largely remained in the aqueous layer. However it was noted that the more polar carbowax/divinyl benzene SPME fiber did adsorb a small amount of thiodiglycol from the autoclaved aqueous extract of the spiked Ottawa sand samples. This was independent of the dip time so the "dip and shoot" approach was applied to the actual SPME fiber.

Figure 12 illustrates the reconstructed-ion-current chromatograms ( $m/z$  123) for the aqueous extract of the spiked Ottawa sand sample and blank. Thiodiglycol was not detected in the blank extract, but was readily identified in the spiked Ottawa sand sample extract (maximum concentration of thiodiglycol 14 ng/ $\mu$ L). The acquired mass spectrum, containing the  $MH^+$  ion and its product due to loss of water, is inset in Figure 12. Mustard was not detected by DESI-MS, consistent with the expectation of complete hydrolysis under the relatively harsh autoclave conditions [56, 90]. Figure 13 illustrates replicate analyses of the dipped carbowax fiber into the spiked Ottawa sand extract under MS/MS/MS conditions. A product ion at  $m/z$  87 due to loss of water was observed for the  $m/z$  105 ion generated in the ESI interface.

The same sand extract was also analysed by LC-ESI-MS (Figure 14) and compared to the DESI-MS data (Figure 12). The carbowax/divinyl benzene SPME fiber dip absorbs significantly less than 1  $\mu$ L of extract as the S/N was much higher for a 1  $\mu$ L LC-ESI-MS injection. The DESI-MS response, based on peak area, suggests an ionized sample load of about 140 pg, approximately 100 times less than the LC-ESI-MS injection. The acquired data were similar ( $m/z$  123 to  $m/z$  105 ratios) with the exception being the presence of a significant sodium adduct at  $m/z$  145 during LC-ESI-MS (Figure 15).

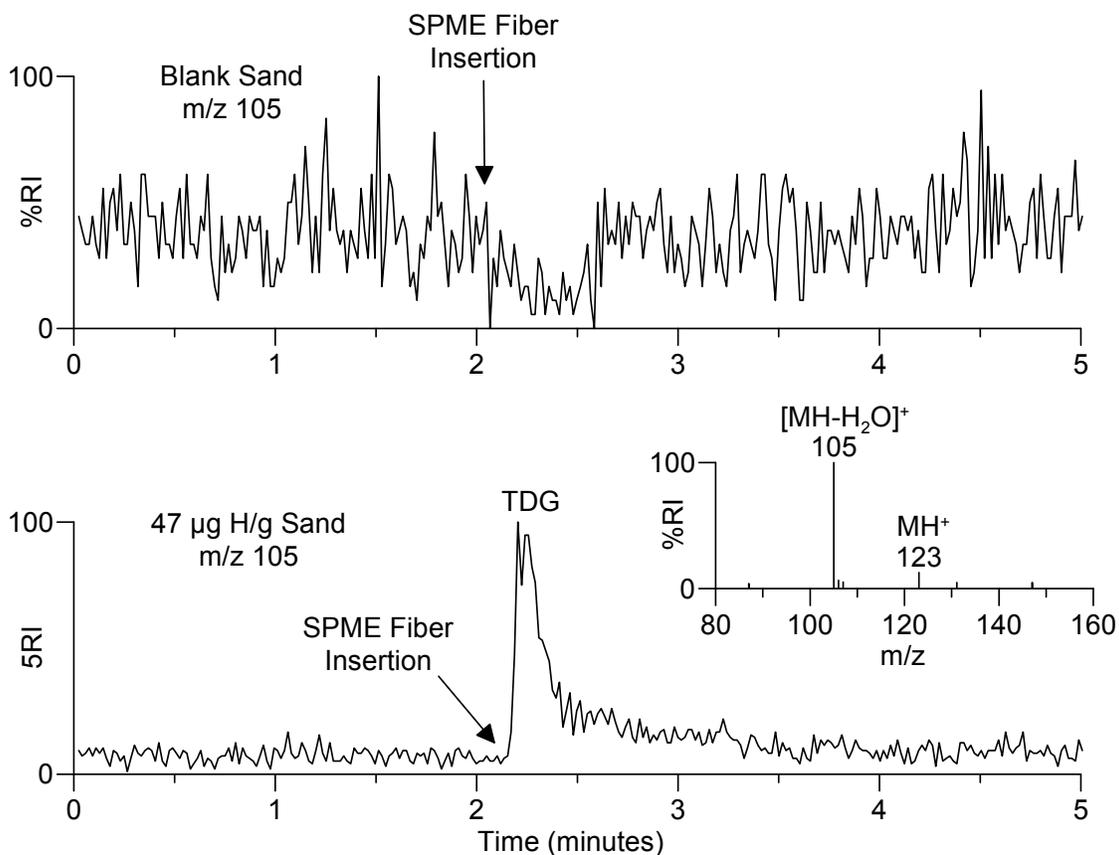


Figure 12: Reconstructed-ion-current chromatogram for  $m/z$  105 (base ion for thiodiglycol) obtained during DESI-MS analysis of an autoclaved aqueous extract of blank Ottawa sand (upper) and Ottawa sand spiked at the  $47 \mu\text{g/g}$  level with mustard (lower). Aqueous samples were sampled by simply dipping a carbowax SPME fiber into each extract. Inset: Typical mass spectrum for thiodiglycol. Mustard was not detected in either of the extracts.

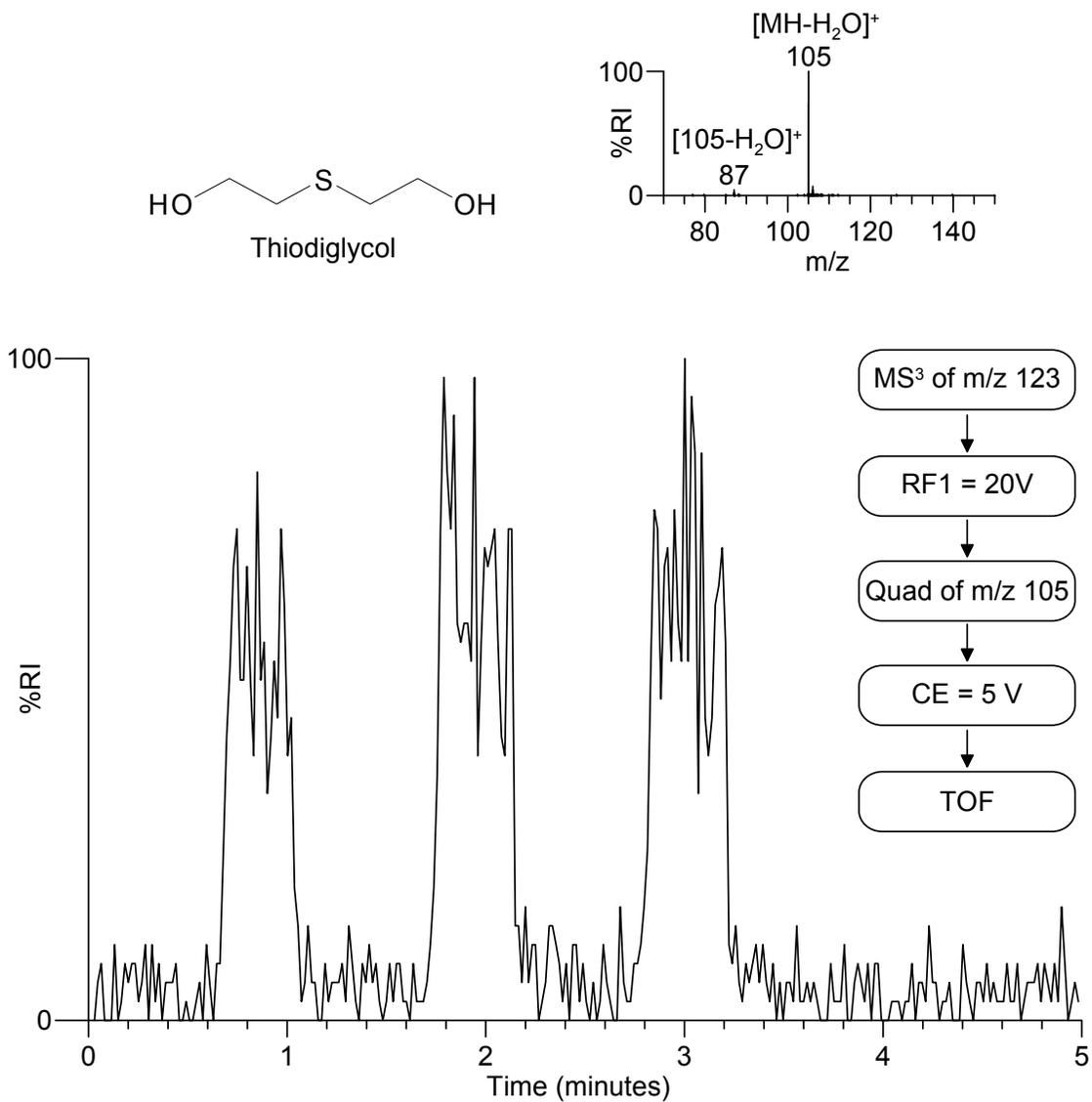
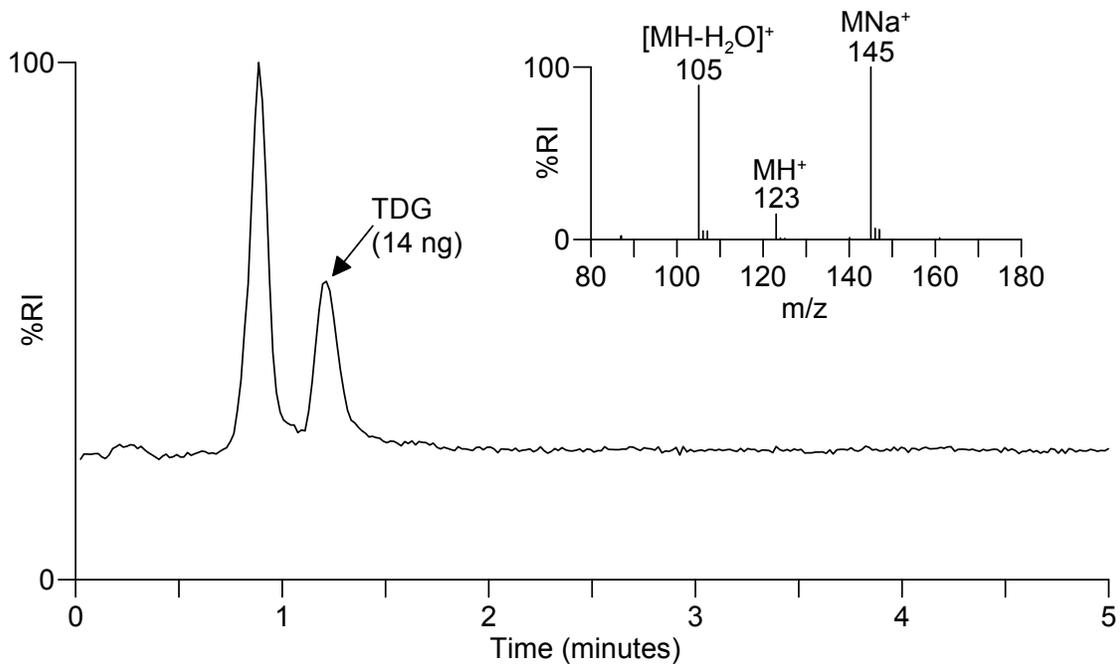


Figure 13: DESI-MS/MS/MS chromatogram obtained during replicate analyses of carbowax SPME fiber tip dipped into an autoclaved aqueous extract of Ottawa sand spiked at the 47  $\mu\text{g/g}$  level with mustard. The initial product ion at m/z 105 was generated with an RF1 voltage of 20 V. The m/z 105 ion was selected with the quadrupole mass analyser and the products of m/z 105 were generated with a collision energy of 5 V.



*Figure 14: Isocratic (2%B) LC-ESI-MS total-ion-current chromatogram obtained following injection of 1  $\mu$ L of an autoclaved aqueous extract of Ottawa sand spiked at the 47  $\mu$ g/g level with mustard. Thiodiglycol (mass spectrum inset) was detected with a significant sodiated adduct..*

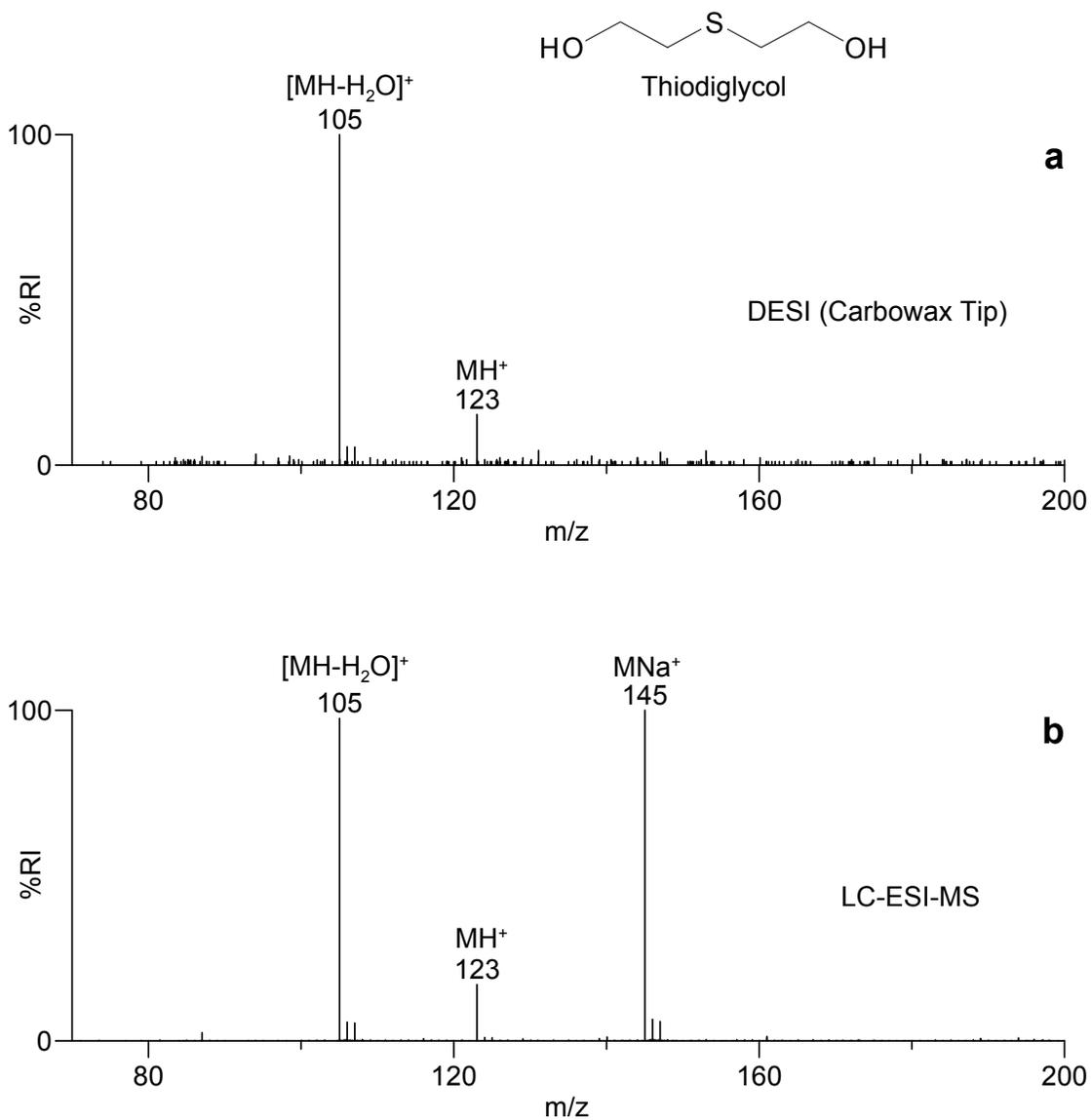


Figure 15: Comparison of thiodiglycol mass spectra obtained following a) DESI-MS and b) LC-ESI-MS analysis of an autoclaved aqueous extract of an Ottawa sand sample spiked at the 47  $\mu\text{g/g}$  level with mustard.

## Conclusions

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Chemical warfare agents and their hydrolysis products were readily detected by DESI-MS using the "dip and shoot" analytical approach developed as a rapid, complementary alternative to SPME headspace sampling of liquid samples containing these compounds. Sampling was performed by simply dipping fused silica or stainless steel tips into the organic or aqueous samples. Tips were inexpensive, can be disposable and do not require conditioning. Replicate analyses were completed within several minutes under ambient conditions with no sample pre-treatment, resulting in a significant increase in sample throughput over conventional SPME sampling and DESI-MS analysis or conventional LC-ESI-MS analysis. The approach has application to a large variety of chemicals besides chemical warfare agents, including explosives, pharmaceuticals and polymers and deserves investigation for other chemicals of concern to the Public Safety community.

The developed sample handling and analysis method was applied to the determination of chemical warfare agent in sand samples where the chemical and/or biological warfare agent content was unknown. Ottawa sand, a typical environmental medium, was spiked with mustard, extracted with water and autoclaved to ensure sterility. Mustard was completely hydrolysed during the extraction/autoclave step and thiodiglycol was identified by both DESI-MS and LC-ESI-MS. DESI-MS analyses were generally completed within one minute using the "dip and shoot" method developed for rapid analysis of liquid samples and the acquired mass spectra did not contain sodiated adducts associated with LC-ESI-MS analysis.

MS/MS/MS data were also collected for several for the compounds by selecting an appropriate RF1 setting in the ESI source. Product ions formed in this region were selected by the quadrupole and fragmented in the collision cell prior to the time-of-flight mass analyser. Acquisition of complementary MS/MS/MS data typically increases the number of ions associated with identification of a given compound. Acquisition of this additional data improves the certainty of identification and would be quite valuable for structural elucidation of unknowns.

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A dip and shoot analytical method was developed for the rapid sampling and desorption electrospray ionization mass spectrometric (DESI-MS) analysis of chemical warfare agents and their hydrolysis products in liquid samples. Sampling was performed by simply dipping fused silica, stainless steel or SPME tips into the organic or aqueous samples. Replicate analyses were completed within several minutes under ambient conditions with no sample pre-treatment, resulting in a significant increase in sample throughput over conventional solid phase microextraction (SPME) sampling and DESI-MS analysis or liquid chromatographic electrospray ionization mass spectrometric (LC-ESI-MS) analysis. The developed sample handling and analysis method was applied to the determination of chemical warfare agent content in presence of unknown chemical and/or biological warfare agents. Ottawa sand was spiked with mustard, extracted with water and autoclaved to ensure sterility. Mustard was completely hydrolysed during the extraction/autoclave step and thiodiglycol was identified by DESI-MS, with analyses generally being completed within one minute using the dip and shoot method developed for the rapid analysis of liquid samples.

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Desorption Electrospray Ionization; DESI; Mass Spectrometry; Chemical Warfare Agents; Hydrolysis Products



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