



## APPLICATION NOTE

### Gas Chromatography / Mass Spectrometry

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## On-site Screening of Explosive Materials by Portable SPME-GC/MS and CME-GC/MS

Frontline security teams tasked with detecting and identifying potential threats are increasingly reliant on improved detection technologies capable of responding to a wide range of scenarios.

Explosive materials are composed of energy-rich substances that release stored energy through a series of violent chemical processes upon ignition. The chemicals responsible for these explosive reactions are typically unstable without the presence of secondary compounds that act as stabilizers for the reactive materials.<sup>1</sup> The inclusion of stabilizers along with other chemical components used in the formulation like propellants, solvents, and tagging agents can be used to aid in the identification of explosive materials.

#### Introduction

Explosive threats are continually evolving as terrorist groups around the globe develop new methods for concealing and delivering homemade explosives (HME) and improvised explosive devices (IED).

In this study, we demonstrate the capability of Custodion Coiled Microextraction (CME) and Solid Phase Microextraction (SPME) field collection and injection devices to detect explosive related materials using the Torion T-9 Portable GC/MS for the separation, detection, and identification of explosive materials and secondary identifiers (e.g., stabilizers, propellants, solvents and tagging agents).

## Experimental

### Hardware/Software

All chromatographic separation and mass spectral detection were done with a PerkinElmer Torion® T-9 Portable GC/MS. Post analysis identification and data deconvolution were performed using Chromion® PC analytical software. Purchased reference standards were used to manually create a library for the compounds investigated in this study.

### Method Parameters

The GC and MS method parameters are shown in Table 1.

Table 1. GC/MS Method Parameters.

GC/MS Method Parameters	
Sampling Methods	Coiled Microextraction (CME) Solid Phase Microextraction (SPME)
SPME Phase	Divinylbenzene/Polydimethylsiloxane (DVB/PDMS, 65 $\mu\text{m}$ )
Injection Type	Splitless
GC Injector Temp.	175 $^{\circ}\text{C}$
GC Column	MXT-5, 5 m x 0.1 mm, 0.4 $\mu\text{m}$ $d_f$
GC Column Temp.	40-280 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{s}$ , hold for 60 s
GC Carrier Gas	Helium, 0.2 mL/min.
Transfer Line Temp.	175 $^{\circ}\text{C}$
Ionization Source	In-trap electron impact (EI)
Mass Analyzer	Toroidal Ion Trap
Mass Range	41-500 Da
Detector	Electron Multiplier
Resolution	<0.5 m/z at 300 amu, nominal unit mass to 500 amu

### Solvents and Standards

All Solvents, reagents, and standards used were purchased from Sigma-Aldrich® Inc.

### Sample Preparation

The sampling of all explosive related materials was performed by Custodion® Solid Phase Microextraction (SPME) and Custodion Coiled Microextraction (CME).

### Solid Phase Microextraction

Explosive standards were prepared to concentrations of 1000  $\mu\text{g}/\text{mL}$  and 100  $\mu\text{g}/\text{mL}$ . A small amount of each standard (liquid phase standards: 20  $\mu\text{L}$ ; solid phase standards:  $\sim 30$  mg) was placed in an 8 mL headspace vial and heated at 37  $^{\circ}\text{C}$  for a minimum of 10 minutes. Once equilibrium was achieved a Custodion SPME fiber (DVB/PDMS; 65  $\mu\text{m}$ ) was exposed to the headspace for 5 minutes before injection into the GC/MS. If no signal was detected another sample was prepared in an 8 mL headspace vial and heated to 70  $^{\circ}\text{C}$  for 1 minute with the SPME fiber exposed for 5 minutes before injection.

### Coiled Microextraction

For nonvolatile liquid standards, a Custodion CME wire (shown in the picture) was directly immersed into 100  $\mu\text{g}/\text{mL}$  standards for  $\sim 5$  seconds, left to dry for  $\sim 60$  s before injection into the Torion T-9. For solid phase explosives Tetryl, PETN and RDX, a small amount of solid ( $\sim 30$  mg), was dissolved in methanol before performing the same procedure for the liquid standard.

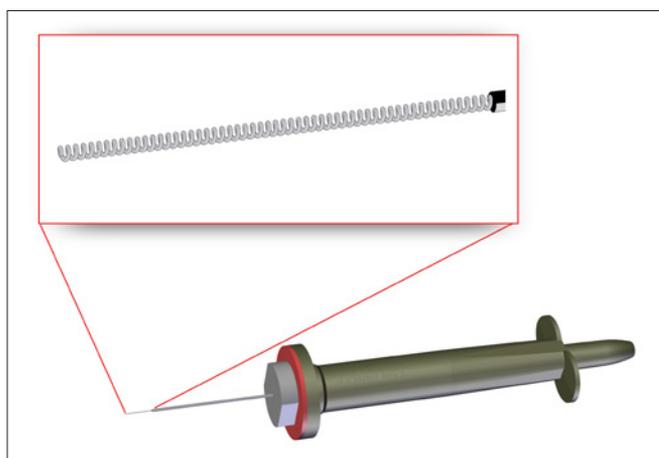


Figure 1. Custodion Coiled Micro-extraction (CME) Sampler.

## Results and Discussion

When screening for explosive materials, not every explosive compound or metabolite is sufficiently volatile enough for detection by SPME sampling; therefore volatile stabilizers, propellants, and tagging agents are useful indicators. Extending SPME sampling times can provide an adequate signal for detection with some compounds, but semi-volatile compounds with boiling points higher than 200  $^{\circ}\text{C}$  are best suited for liquid injection using CME to ensure proper detection with minimal sample preparation. All compounds of interest including explosives, explosive metabolites, stabilizers, propellants, and tagging agents investigated shown in Table 2 along with the sampling technique that provided successful identification. Findings in this application note were reproduced from Abacus Analytical Systems GMBH.<sup>2</sup>

Table 2. Summary sampling techniques used for investigated materials.

Explosives	Cas #	SPME	CME
TATP (Triacetone Triperoxide)	10788-37-8		
Nitroglycerin	55-63-0		
DEGDN (Diethylene Glycol Dinitrate)	693-21-0		
2,4-Dinitrotoluene	121-14-2		
Trinitrotoluene (TNT)	118-96-7		
1,3-Dinitrobenzene	99-65-0		
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	479-45-8		
RDX (Cyclonite, Hexogen)	121-82-4		
PETN (Nitropenta, Pentaerytrityl Tetranitrate)	78-11-5		
TEGDN (Triethylene Glycol Dinitrate)	111-22-8		
HMTD (Hexamethylene Triperoxide Diamine)	283-66-9		
HMX (Homocyclonite, Octogen)	2691-41-0		
<b>Metabolites</b>			
1,3,5-Trinitrobenzene	99-35-4		
2-Amino-4,6-Dinitrotoluene	19406-51-0		
4-Amino-2,6-Dinitrotoluene	35572-78-2		
2-Methyl-4-Nitroaniline	99-52-5		
<b>Stabilizers</b>			
Dimethyl Phthalate	131-11-3		
Diethyl Phthalate	84-66-2		
Diphenylamine	122-39-4		
Ethyl Centralite	85-98-3		
Methyl Centralite	611-92-7		
<b>Explosive Propellants</b>			
Nitrobenzene	98-95-3		
2,6-Dinitrotoluene	606-20-2		
1-Nitronaphthalene	86-57-7		
<b>Tagging Agents</b>			
EGDN (Ethylene Glycol dinitrate)	628-96-6		
2-Nitrotoluene	88-72-2		
DMNB (2,3-Dimethyl-2,3-Dinitrobutane)	3964-18-9		
3-Nitrotoluene	99-08-1		
4-Nitrotoluene	99-99-0		
<b>Solvents</b>			
Butyl Acetate	123-86-4		
Cyclohexanone	108-94-1		

Green (Detection Possible), Red (Detection Not Possible), Grey (Not needed, because detected with SPME)

## Explosives

As previously stated, not all explosive compounds are sufficiently volatile enough for detection by SPME. Investigated explosives were first screened using SPME, before further investigation with the CME sampler. Six of the 12 explosive compounds tested provided sufficient results by SPME. An example of this shown in

Figure 2 with the GC/MS data of an HS-SPME sample of Diethylene glycol dinitrate (DEGDN). As a comparison both SPME and CME sampling techniques were used to collect trinitrotoluene (TNT) shown in Figure 3. In the case of TNT, there was a 400-fold increase in signal intensity with CME liquid injection over HS-SPME due to TNT having a higher boiling point.

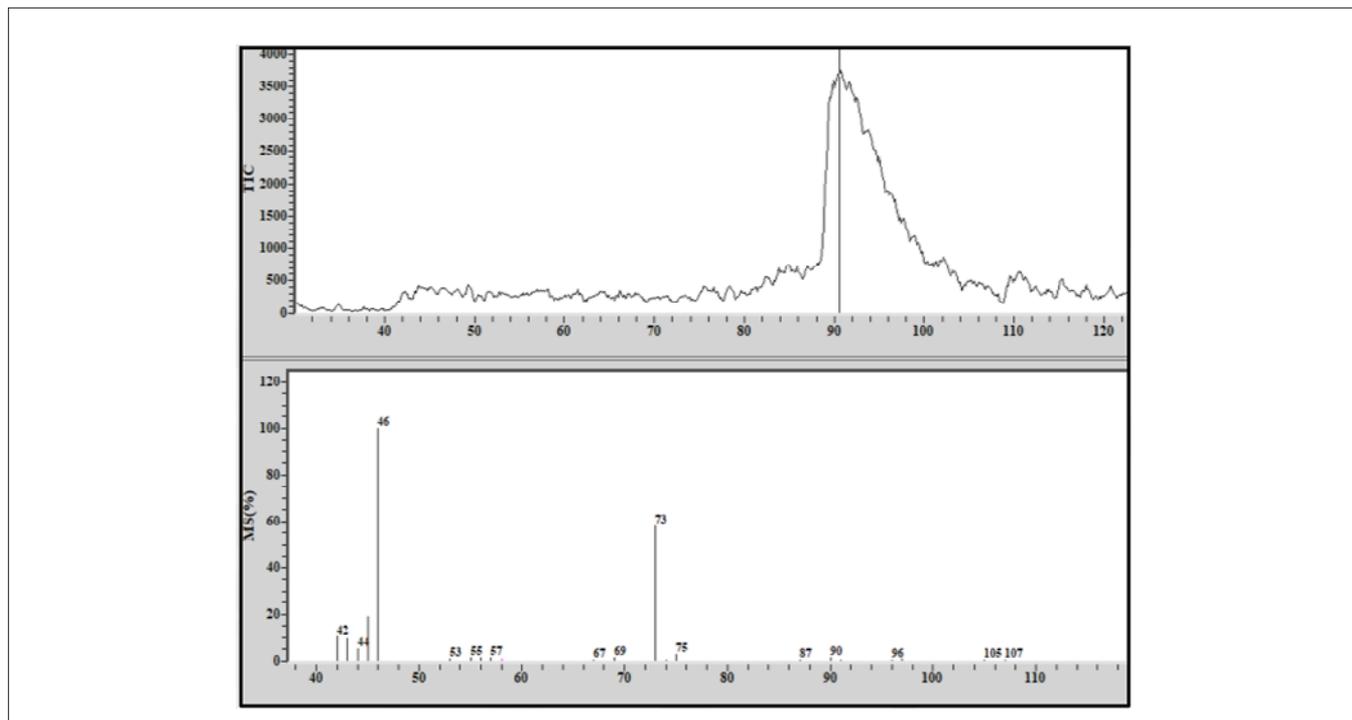


Figure 2. Total Ion Chromatograph (TIC) and Mass Spectra (MS) of Diethylene glycol dinitrate (DEGDN). Sampling: SPME, 5 min. 37 °C.

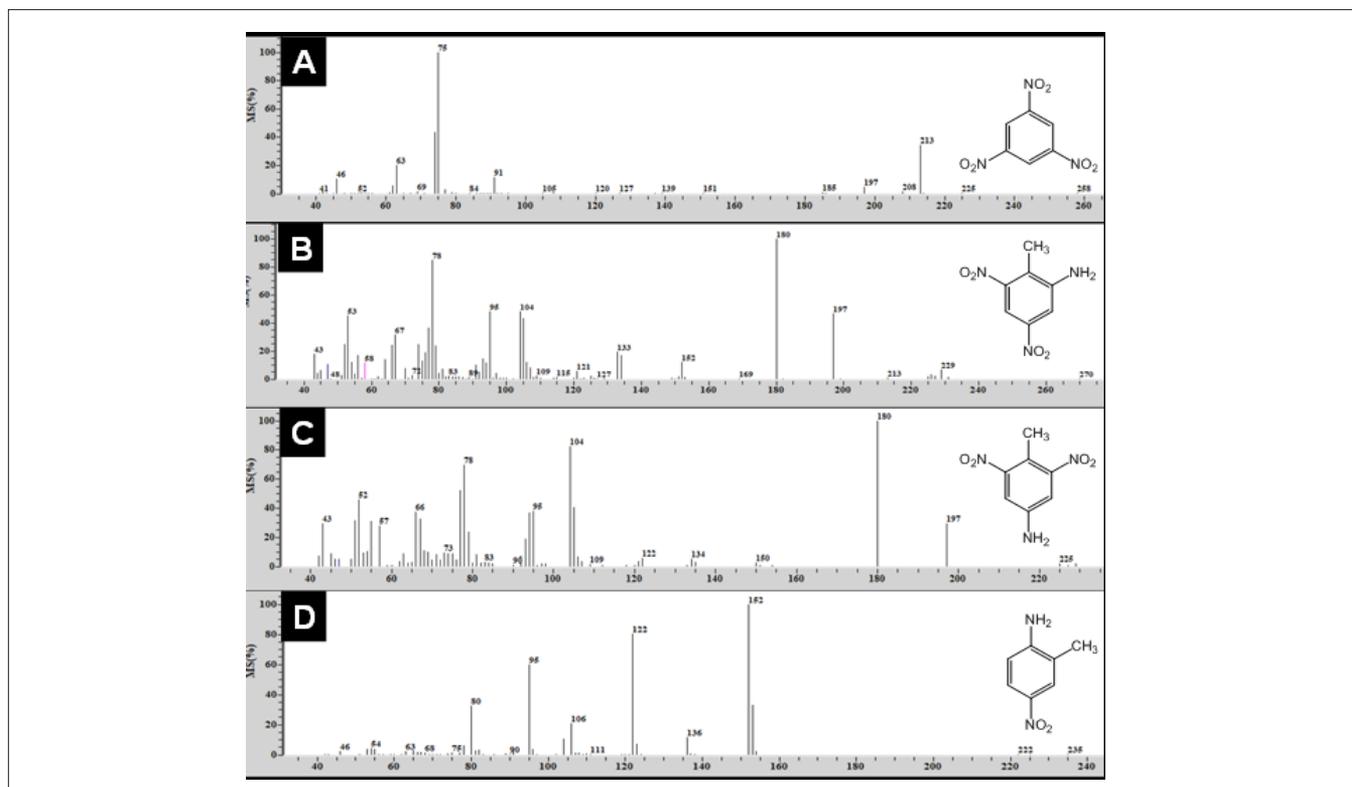


Figure 3. GC/MS Comparison between Custodian sampling techniques. (A) TIC and MS of TNT; Sampling: SPME, 37 °C, 5 min. (B) TIC and MS of TNT; Sampling: CME-liquid injection.

**CME sampling for Explosive Metabolites of Trinitrotoluene (TNT)**

Explosive compounds are relatively unstable and readily decompose when exposed to the environment. TNT is commonly used for commercial mining, construction processes and military applications since the World Wars.<sup>3</sup> Residual TNT readily decomposes into TNT metabolites when left in the soil. If tasked with assessing the environmental impact of these materials in soil, liquid-liquid extractions and sample preparation techniques with suitable solvents can be used in conjunction with CME sampling for semi-volatile compounds in liquid samples. An example of

this is shown in Figure 4, where TNT metabolites were identified with a Torion T-9 after directly immersing the CME sampler in a methanol extraction of TNT contaminated soil.

**Tagging Agents**

In the production process of plastic explosives, volatile odorous substances are added to aid in the detection of explosives by specialized canine units and suitable detection devices like SPME-GC/MS. HS-SPME sampling is the preferred technique for the identification of tagging agents with a relatively high vapor pressure, e.g., EDGN, DMNB, and derivatives of Nitrotoluene.

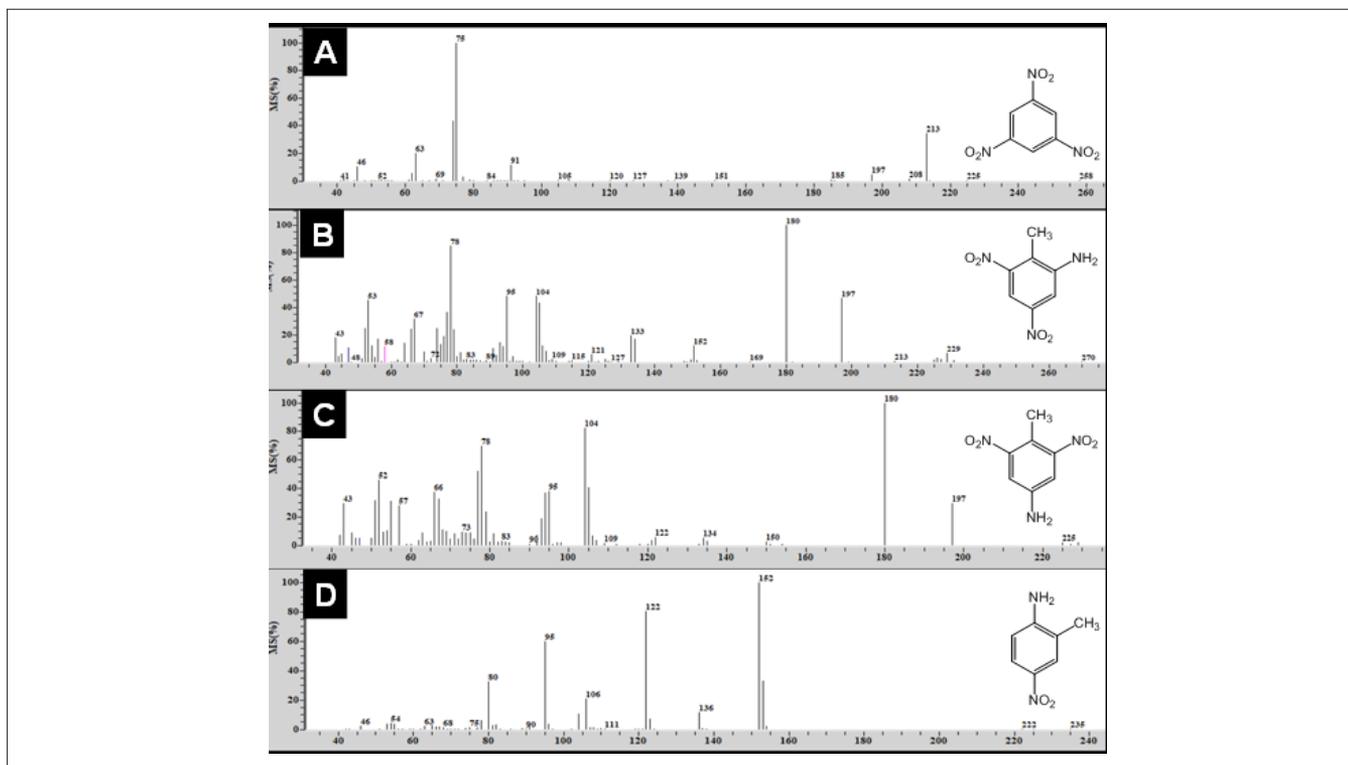


Figure 4. MS analysis of TNT metabolites collected by CME-direct immersion. (A) MS of 1,3,5-Trinitrotoluene. (B) MS of 2-Amino-4,6-nitroaniline. (C) MS of 4-Amino-2,6-nitroaniline. (D) MS of 2-Methyl-4-nitroaniline.

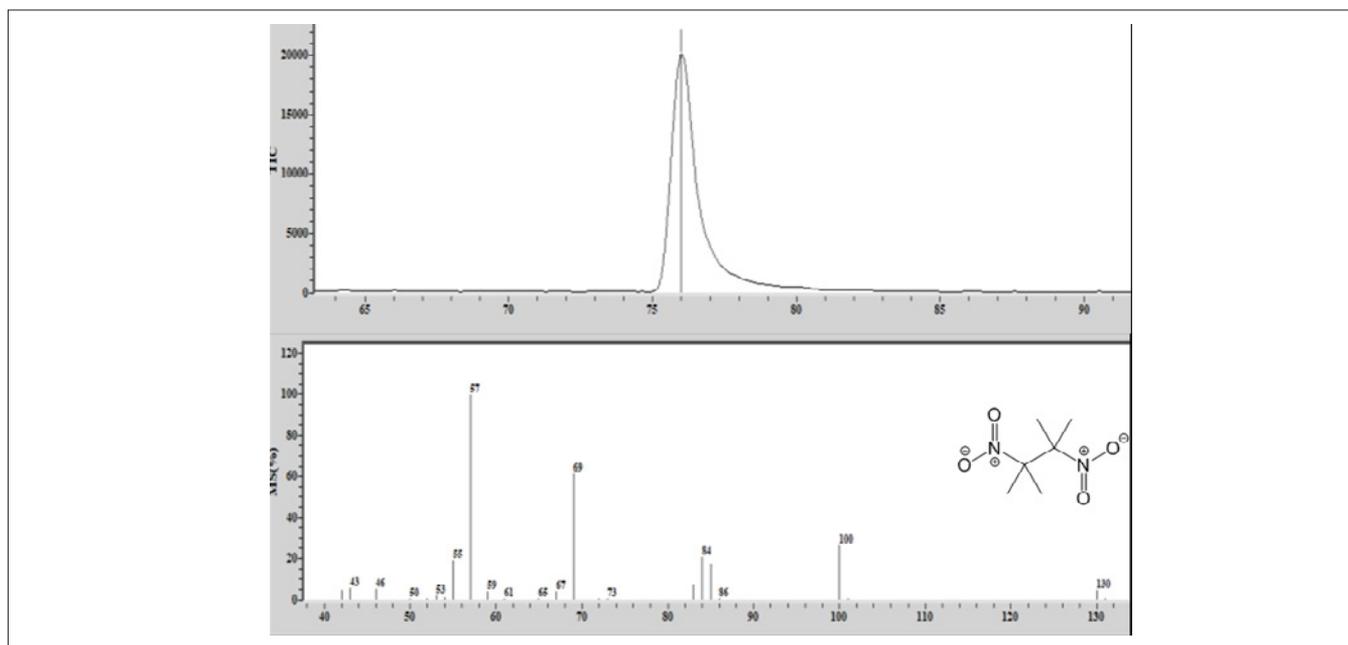


Figure 5. GC/MS analysis of explosive tagging agent 2,3-Dimethyl-2,3-dinitrobutane (DMNB); Sampling: SPME, 70 °C, 5 min.

### Stabilizers and Phthalates

The stabilizers and phthalates used in the formulation of explosive materials are typically more volatile than the explosive compounds and may indicate the presence of explosive materials. All the stabilizer compounds investigated were detected using HS-SPME as shown in Figure 6.

### Propellants and Solvents

Like stabilizers and phthalates, propellants and solvents are typically more volatile than explosive materials and are readily detected using SPME. All the propellants and solvents were identified using HS-SPME within 5 minutes. As an example, the propellant 1-Nitronaphthalene shown in Figure 7.

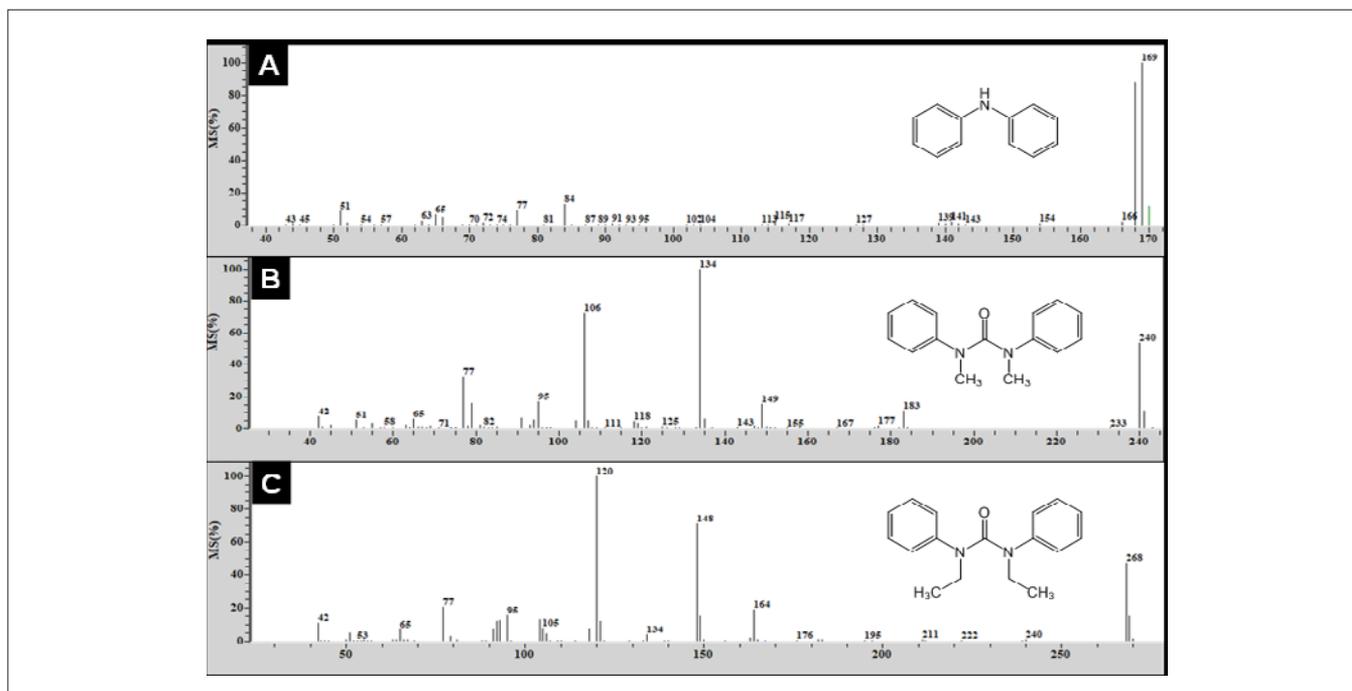


Figure 6. MS analysis of stabilizer compounds collected by HS-SPME. (A) MS of Diphenylamine; Sampling: SPME, 37 °C, 5 min. (B) MS of Methyl Centralite; Sampling: SPME, 70 °C, 5 min. (C) MS of Ethyl Centralite; Sampling: SPME, 70 °C, 5 min.

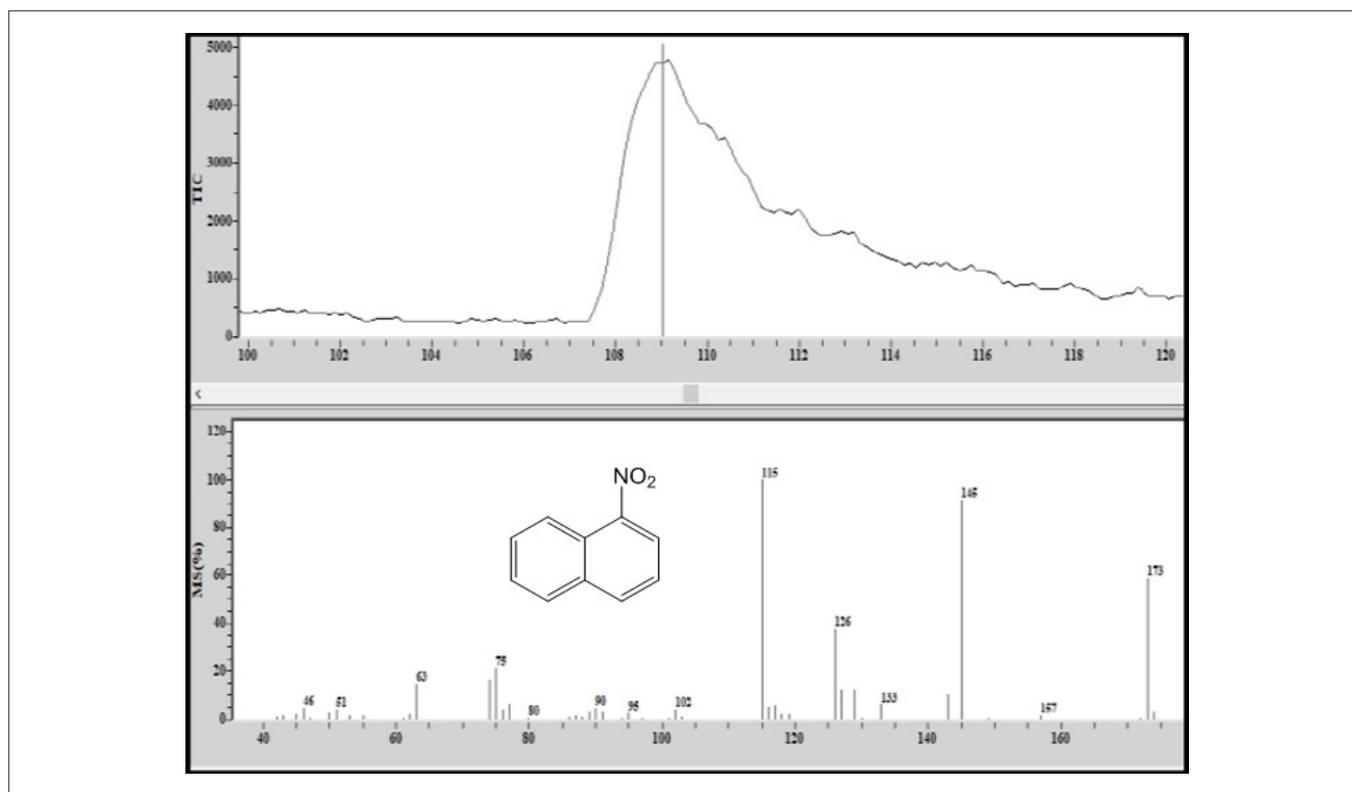


Figure 7. GC/MS analysis of propellant 1-Nitronaphthalene; Sampling: SPME, 37 °C, 5 min.

## Conclusions

The combination of both Custodion SPME and CME samplers allowed for the identification of explosives materials and secondary identifiers (i.e., tagging agents, stabilizers, propellants, and solvents) with the Torion T-9 Portable GC/MS. The capability of a field portable GC/MS for on-site screening of explosive materials and secondary identifiers is a valuable tool for security officials. While explosive compounds TEGDN, HMTD, and HMX were not directly identified, the detection of accompanying compounds found in explosive materials allows for rapid decisions to be made on-site to assess the risk of potential threats to the public and infrastructure.

## Summary

In this application, explosives and related materials (e.g., tagging agents, metabolites, stabilizers, explosive propellants and solvents) were collected using Custodion SPME and CME syringes and identified on a Torion T-9 Portable GC/MS.

## References

1. Vogelsanger, B. Chemical Stability, Compatibility and Shelf Life of Explosives. *Chimia (Aarau)*. 2004, 58 (6), 401–408.
2. Heinlein, T. Rapid Field Identification of Explosives, Tagging Agents and Metabolites by the Portable Torion T-9; 2017.
3. Heinlein, T. Determination of Explosive Compounds in Soil Samples Using the Torion T-9 GC/MS with SPME sampling. 2017.