

## Introduction

Analysis of explosives and explosive residues, has routinely utilized gas chromatography with mass selective detectors (MSD). The MSD provides sensitivity, selectivity, and permits structural identification of the specific compounds found in explosives and residue matrices. The purpose of this research is to demonstrate that several recent advances in gas chromatography, found in the Agilent Technologies 9000 Intuvo GC, can be successfully incorporated into current proven methods of explosive analysis. The advancements in GC design facilitates the Intuvo to be a viable remedy for a field mobile GCMS solution. This work seeks to illustrate this with minimal disruption to the established practices of data acquisition and analysis while demonstrating the improvements that can be derived from recent developments in GC technology. In addition, due to the common weight and space limitations for a mobile laboratory, H<sub>2</sub> was utilized as the carrier gas, thus eliminating the need for compressed gas cylinders since a reliable source of H<sub>2</sub> can easily be produced using a variety of hydrogen generators on the market. This study utilizes an existing conventional explosives GCMS method, that incorporates H<sub>2</sub> as its carrier gas and depicts good peak shape and sensitivity, without excessive peak tailing or negatively affecting peak resolution. However, using H<sub>2</sub> carrier can cause reactions during fragmentation (especially nitrogen and oxygen containing compounds) resulting in non-standard EI spectra and spectral differences when compared to He carrier gas applications. In an attempt to mediate spectral differences, an in-house library was produced under H<sub>2</sub> carrier gas conditions and used for comparative purposes.

## Experimental

### Sample Preparation

Test study reference standards were purchased from Restek and included (6) phthalate esters (31031) and (18) nitroaromatics, nitrate esters, and nitramine explosives (33204) and diluted with acetonitrile to produce (5 - 1000 ppm) calibration standards. Additionally, 3 controls and matrix spiked samples (sand, cotton swab, and metal shrapnel) were produced by spiking each matrix with 100 µL of a 1000 ppm solution of TNT, PETN, and RDX. Each matrix was extracted with ~1.0 mL of acetone, filtered, and the recovered eluent placed in a 2 mL auto-sampler vial.

### Instrumentation

The new Agilent Intuvo 9000 GC (Figure 1) interfaced to an Agilent 5977B mass spectrometer was used in this study. A 1.0 µL sample was injected into a multi-mode split/splitless inlet (MMI) at 35°C, and ramped at 900°C/min to 185°C. The MMI was operated under a pulsed split mode at 16.7 psi for 0.75 minutes with a 10:1 split ratio. An Agilent 5190-2293 ultra deactivated single taper liner, with glass wool was utilized in the inlet. Chromatographic separation was achieved on a DB-5MS UI 15 m x 180 µm x 0.18 µm column. The Intuvo 9000 GC was equipped with a Guard Chip programed to track the oven ramp and a capillary flow bus temperature of 200°C. The 5977A acquired EI data in full scan-mode with a mass range of 40 - 350 m/z. EI data was generated with an Extractor Source with a 9 mm draw out lens, heated at 230°C, and operating at a standard electron energy of 70 eV. Acquisition, Qualitative, and Quantitative data analysis were accomplished using MassHunter software, revisions B.07.05 SR1, B.07.0 SP2, and B.08.0, respectively.



Figure 1. 5977B/9000 GCMS on mobile platform

## Results and Discussion

inlet and manifest itself in the resulting raw data as multiple break-down peaks, poor chromatography, poor sensitivity, and or no sensitivity at all.<sup>1</sup> Figure 2 shows the peak shape based on optimization of the MMI temperature ramp, the guard chip temperature ramp, temperature of the flow path bus, and an optimized oven program, low ppm response was achieved with most of the target compounds analyzed in this study. However, PETN (breakdown peaks), HMTD, and Nitroglycerin in Smokeless Powder were detected under the current method conditions but at higher concentrations of 125, 125, and 75 ppm, respectively.

Additionally, The EI mechanism of explosives leading to fragment ions may be viewed as an absorption of energy followed by bond cleavage, cyclization, ion-molecule reaction, and rearrangement. Using a H<sub>2</sub> rich environment, i.e. a H<sub>2</sub> carrier gas, can result in proton transfer and substitution reactions occurring during the fragmentation processes that can occur in the MS source.<sup>2</sup> Several compounds under went reactions with hydrogen and produced altered spectra and therefore altered identification. Figure 3 depicts the EI spectra of Tetryl in a helium rich MS source environment and Figure 4 illustrates Tetryl spectra in a H<sub>2</sub> rich MS source environment.

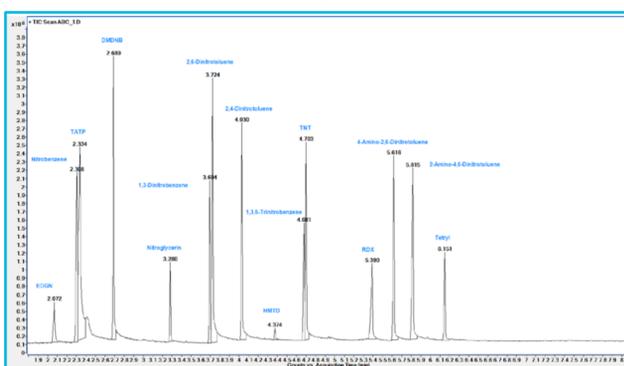


Figure 2. Total Ion Chromatogram of explosive standards

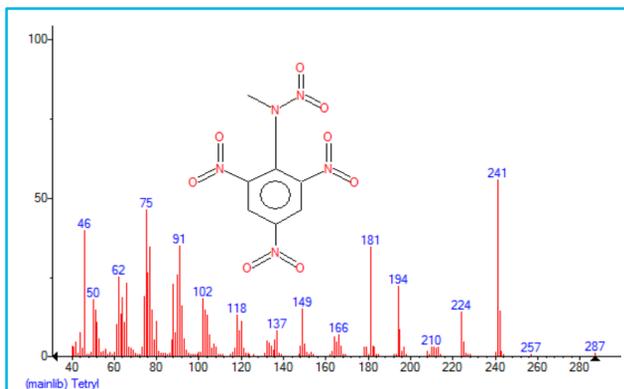


Figure 3. Tetryl EI spectra in a helium environment<sup>3</sup>

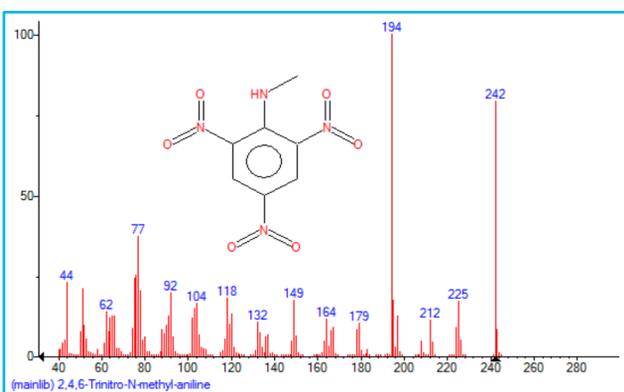


Figure 4. Tetryl EI spectra in a H<sub>2</sub> environment<sup>3</sup>

Due to the potential of spectral variations using H<sub>2</sub> as carrier gas, an in-house H<sub>2</sub> carrier gas spectral library was created to account for spectral differences and produce a higher quality spectral matches (Figure 5).

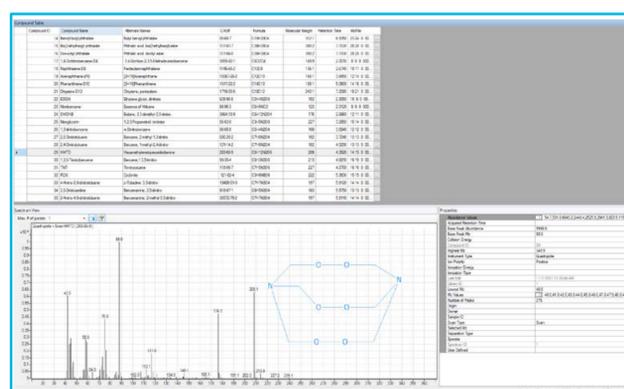


Figure 5. In-house EI spectral library based on H<sub>2</sub> carrier

## Results and Discussion

### Spiked Matrix Analysis

Quantitative standards were prepared for 9 individual explosive components producing linear R<sup>2</sup> responses ≥ 0.99 for all 9 compounds. Figure 6 illustrates the calibration curve for Cyclonite (RDX) based on a target ion of (46 m/z), and qualifier ions (75 and 120 m/z) producing an R<sup>2</sup> of 0.992 for a concentration range of 5 ppm to 150 ppm. Matrix samples were extracted and analyzed under the same calibration curves for RDX, TNT, and PETN. All 3 matrices were spiked with 100 µL of 1000 ppm for all 3 components. PETN was detected in all 3 matrices but at trace level responses, while RDX ranged from 64 ppm in soil, 120 in the swab, and 240 ppm on the shrapnel (Figure 7). TNT was detected from 69 ppm on the swab (Figure 8), 50 ppm in the soil, and not detected on the shrapnel (Figure 7).

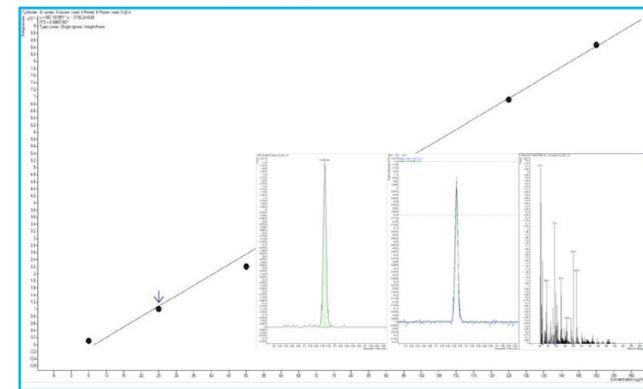


Figure 6. Calibration curve of RDX 5 - 150 ppm

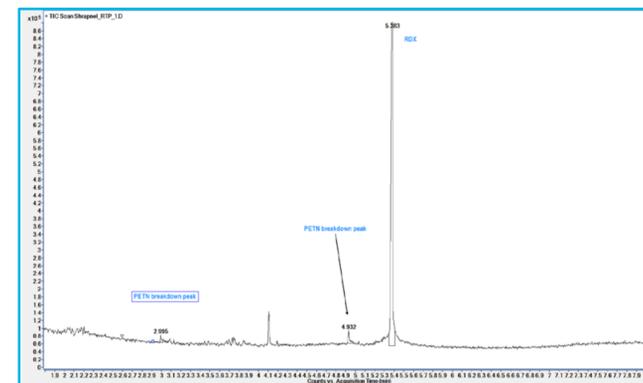


Figure 7. Shrapnel matrix spiked with RDX, TNT, PETN

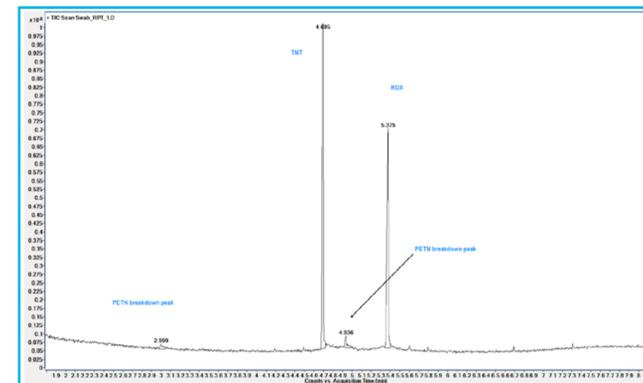


Figure 8. Swab matrix spiked with RDX, TNT, PETN

## Conclusions

- A conventional explosive method was applied to the Intuvo GC with H<sub>2</sub> carrier flow and achieved good peak shape and separation of the explosive compounds of interest.
- Peak shape and overall sensitivity improved with a 9 mm draw out plate when compared to a 3 mm draw out plate in the EI source of the 5977AMS
- An in-house library was created under H<sub>2</sub> acquisition parameters and helps account for spectral variations
- Linear responses were generated for all 9 individual explosive target compounds
- The 9000 Intuvo GC flow chips maintain an inert flow path, with H<sub>2</sub> as a carrier gas and thermally reactive and liable compounds
- The 5977A MSD and Intuvo 9000 GC make a practical mobile alternative for GCMS analysis in the field using H<sub>2</sub> or Helium as a carrier gas.

## References

1. Michal Kirchner, Eva Matisová\*, Svetlana Hrouzková, Renáta Hůšková, *Fast GC and GC-MS Analysis of Explosives*, Petroleum & Coal, 49 (2), 72-79, 2007.
2. Dietmar Kuck, *Mass spectrometry of alkylbenzenes and related compounds. Part II. Gas phase ion chemistry of protonated alkylbenzenes*, Mass Spectrometry Reviews, 9, 583-630, 1990.
3. U.S. Department of Commerce NIST MS Search Program, version 2.2, 2014.

## Results and Discussion

### Explosive Components and Extracted Matrices

A common problem when analyzing energetic compounds by GCMS is the thermal breakdown that can occur in the GC