An Assessment of Field-Portable Instrumentation for Pre-Blast Explosives Detection

Makenzie Kuehn, BS*; J. Tyler Davidson, PhD; Geraldine Monjardez, PhD

Department of Forensic Science, Sam Houston State University, Huntsville, TX 77340

MEMBER THE TEXAS STATE UNIVERSITY SYSTEM

ABSTRACT

The present study evaluates the detection capabilities of portable Raman and GC-MS for the detection and identification of trinitrotoluene (TNT), nitromethane (NM), ammonium nitrate fuel oil (ANFO), and smokeless powder; as well as to give context to those results by evaluating those same explosives with benchtop Raman and GC-MS. The sensitivity, reproducibility, and a survey of internal libraries using authentic homemade explosive (HME) samples were evaluated for each instrument. This evaluation of the detection capabilities of the portable instruments will provide a better understanding of their limitations, and in turn allow them to be better utilized in the field.

INTRODUCTION

In the past five years, there have been almost four thousand explosion incidents in the United States, and bomb threats have increased by 230% in the past year alone[1]. Field portable instruments allow investigators to detect explosives and their precursors on-site. Given the danger that HME precursors present to investigators, high-quality screening of evidence in the field can improve investigator safety by reliably identifying the compounds present.

Field-portable Raman spectrometers require no sample preparation, are nondestructive, and have extremely fast detection times. Portable GC-MS are much larger, but still field portable. They can analyze liquid or gas samples and while sample preparation is required, GC-MS instruments are typically much more sensitive than Raman spectrometers. While both are robust instruments commonly used in the field, there is very little literature exploring the detection capabilities of these instruments for the detection and analysis of the explosive compounds studied in this project.

The explosives analyzed in this study are based on compounds commonly encountered in current casework and include HME precursors such as ANFO nitromethane, TNT, and smokeless powder components including diphenylamine (DPA), methyl centralite (MC), and ethyl centralite (EC).

MATERIALS & METHODS

Portable Instruments – Three portable Raman spectrometers were used in this study: the ACE-ID from Smiths Detection operates with a 785nm laser (Figure 1a), the ResQ-CQL from Rigaku uses a 1064nm laser (Figure 1b), and the HandyRam from FieldForensics uses a 785nm laser (Figure 1c). The portable GC-MS used was the Griffin G510 from FLIR (Figure 1d).

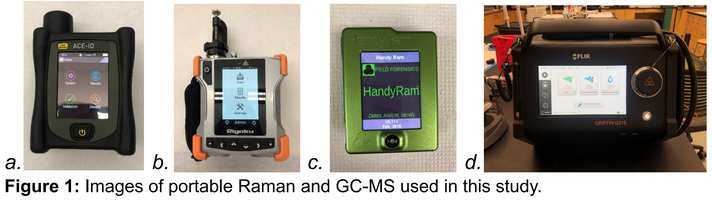

Figure 1: Images of portable Raman and GC-MS used in this study.

Benchtop Instruments – A Renishaw InSpect confocal Raman spectrometer was used to perform all benchtop Raman analyses, and an Agilent Technologies 7890A GC-5975C MS was used for method optimization and analysis of all GC-MS samples.

Sample Preparation – Solid and liquid samples were prepared for Raman analysis. Liquid samples were created at 1000mM, 750mM, 500mM, 250mM, 100mM, and 50mM. For GC-MS analysis, solutions were created at 100ppm, 50ppm, 25ppm, and 10ppm.

Measurement – Three replicates were collected on the portable Raman and one replicate was collected with the portable GC-MS. Authentic samples of TNT, nitromethane, ANFO, and smokeless powder were analyzed on all portable instruments.

Data Analysis – The sensitivity and reproducibility were evaluated, as well as the performance of the available internal libraries using authentic HME samples.

RESULTS & DISCUSSION

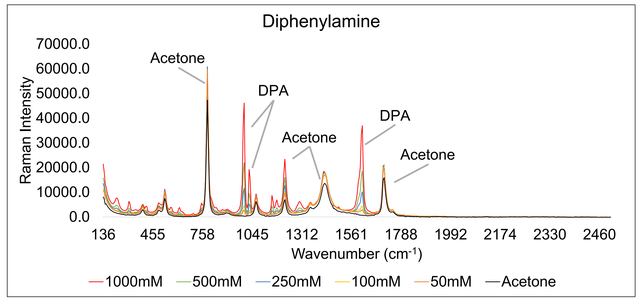

Figure 2: Stacked Raman spectra of DPA using ResQ-CQL portable Raman spectrometer (1064nm) at all studied concentrations.

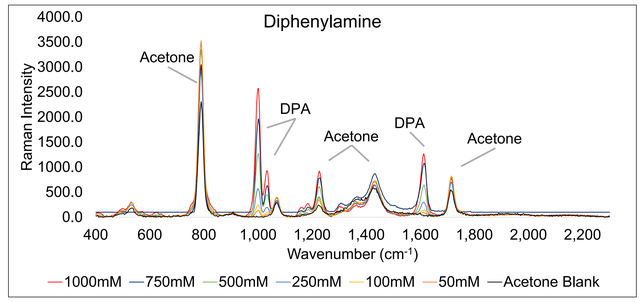

Figure 3: Stacked baseline corrected Raman spectra of DPA using HandyRam portable Raman spectrometer (785nm) at all studied concentrations.

	ResQ-CQL		ACE-ID	HandyRam
Explosive	***Library ID***	***LOD***	***Library ID***	***LOD***
TNT	500mM	49.0mM	750mM	183mM
NM	Pure Liquid	35.2mM	Pure	283.3mM
DPA	1000mM	29.9mM	None	107.1mM
MC	Solid	Solid powder	None	Solid powder
EC	Solid	122.3mM	1000mM	277.6mM
AN	100mM	29.1mM	750mM	41.6mM

Table 1: Comparison of the sensitivity of portable Raman spectrometers using the lowest concentration that the internal library correctly identified (Library ID) and the calculated limit of detection (LOD).

- As shown in **Figures 2 and 3**, the peak intensity is proportional to the concentration of the analyte of interest
- Peak position did not change for the ResQ-CQL spectrometer, but there were fewer data points to consider within the raw data
- Peak position experienced a slight shift using the HandyRam (average 2cm^{-1} shift)
- Spectra collected with the 1064nm laser showed better resolution and less fluorescence in the raw data than data collected with the 785nm spectrometer
- The most sensitive portable Raman was the ResQ-CQL from Rigaku (**Table 1**)
- Library identification using the ResQ-CQL was more accurate and able to correctly identify compounds at lower concentrations than the ACE-ID (**Table 1**)
- ACE-ID internal library was not as extensive or as sensitive as the ResQ-CQL (**Table 1**), however no internal library was available for the HandyRam spectrometer
- The calculated limit of detection for the 785nm spectrometer (HandyRam) was comparable, but lower than that of the 1064nm spectrometer (ResQ-CQL)
- All authentic samples were identified using the spectral library if the compound was present

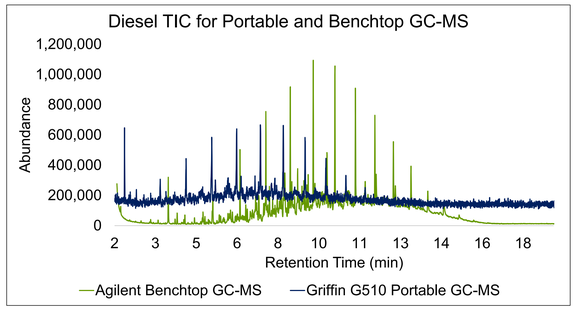

Figure 4: Diesel at 100ppm on Griffin G510 portable GC-MS and Agilent Benchtop GC-MS.

- The standard deviation of the peak position for the portable GC-MS was comparable to the benchtop GC-MS, the peak position didn't shift more than 0.02 minutes (**Table 2**)
- Noise was higher with portable GC-MS than on the benchtop GC-MS (**Figures 4 and 5**)
- Portable GC-MS can detect explosives down to 25ppm
- Based on the library matches for the portable GC-MS, only TNT and DPA could be identified, however the instrument has access to the NIST library so all compounds could be identified down to 50ppm using an external library if there is access to an internet connection

Compound	Portable RT	Benchtop RT
DPA	9.234 ± 0.013	11.316 ± >0.001
MC	10.912 ± 0.013	12.936 ± 0.003
EC	11.360 ± 0.010	13.335 ± >0.001
TNT	9.932 ± 0.0205	11.907 ± 0.005
NM	0.886 ± 0.013	1.731 ± 0.007
Diesel	7.322 ± 0.011	9.384 ± >0.001

Table 2: Average retention time (RT) and standard deviation for all explosive compounds for the portable and benchtop GC-MS.

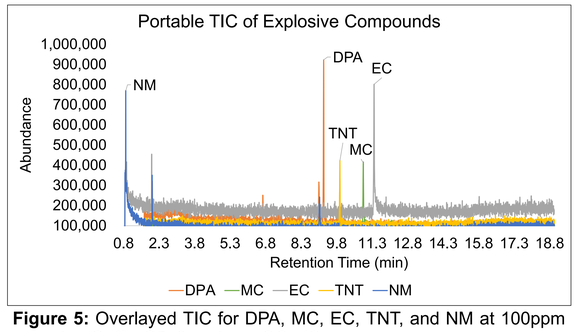

Figure 5: Overlayed TIC for DPA, MC, EC, TNT, and NM at 100ppm using the Griffin G510 portable GC-MS.

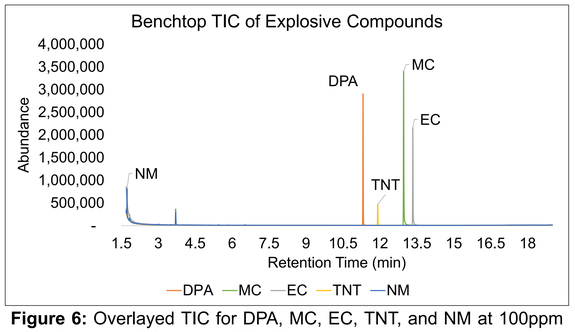

Figure 6: Overlayed TIC for DPA, MC, EC, TNT, and NM at 100ppm using the Agilent Benchtop GC-MS.

CONCLUSIONS

- A GC-MS method was created that was able to detect all explosive compounds on both the portable and benchtop instruments
- Detection of explosives depends on particle size for portable Raman
- Authentic samples were identified correctly using internal libraries when available using both techniques
- The complementarity of the two techniques allows for the identification of different explosive compounds commonly used in HME's

ACKNOWLEDGEMENTS

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REFERENCES

[1] United States Bomb Data Center, Explosives Incident Report, 2021.
[2] J. Akhavan, The Chemistry of Explosives, 3rd ed., Royal Society of Chemistry, United Kingdom, 2022.