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Field Testing of the COTS DESI/DART-MS/MS System Against High Explosives Residues

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August 12, 2013

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Field Testing of the COTS DESI/DART-MS/MS System Against High Explosives Residues (LLNL11-RS-136)

Summary Report of Evaluation Performed at LLNL's Remote Site-300

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Auspices Statement
This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

1. **Title**: Conduct field test at S300 to evaluate COTS DESI/DART-MS system (LLNL11-RS-136)
   Detail: LLNL will analyze several high-explosive compounds (e.g., TNT, HMX, RDX, PETN, and Comp B) on swipe samples without sample preparation at LLNL's remote S300 site. Thermo Scientific explosive detection tickets will be utilized for these tests and 100 nanogram per microliter of each explosive (Certified standards from Supelco and/or AccuStandard) diluted with analytical grade solvents will be deposited onto separate tickets for analysis. The testing will be conducted utilizing the DART (Direct Analysis in Real Time) sampling source, full scan mode and with a dopant (hexachloroethane) to enhance sensitivity and selectivity. Adding a specific dopant (i.e., hexachloroethane) to the DART gas initiates most high explosives to react with the dopant and therefore generating a unique chlorine adduct for analysis (improved sensitivity & selectivity for explosives). This is a standard procedure to enhance the detection of certain explosives and Ion Mobility Spectrometers (IMS) utilize it. The Direct ElectroSpray Ionization/Direct Analysis in Real Time-Mass Spectrometer (DESI/DART-MS) system alarming software will also be evaluated to determine if the alarming thresholds are set appropriately. Upon completion of the DESI/DART-MS system field test, LLNL will conduct minor modification if needed and provide a pdf overview to WebPMIS of the test at S300.

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SUMMARY REPORT

1. INTRODUCTION

This testing was performed to evaluate the performance of the FLIR systems® portable DESI/DART-MS/MS (Direct ElectroSpray Ionization)/Direct Analysis in Real Time-Mass Spectrometer/ Mass Spectrometer) system against high explosives residues under field conditions. The samples collected for analysis do not require sample preparation and are analyzed in less than 20 seconds. The unit is equipped with switchable DART and DESI sampling ion sources and it has positive/negative ion detection modes to facilitate or optimize the detection of various threat chemicals. For this field evaluation, the unit was operated with the DART sampling sources, MS full scan mode and negative ion detection. The field test was conducted at Lawrence Livermore National Laboratory's (LLNL) remote site 300 (Figure 1) to demonstrate that the DART-MS system could be transported to an out-of-the-way location, operated in open-air field conditions, and require only a 110v power source and nitrogen gas source (cylinder: 6 inch DIA X 24 inch LGTH). The DART-MS system was operated in the Level 1 software mode (First Responder operating method) to provide operator feedback in the events of explosives detection of questioned samples. The findings of this field demonstration will help identify possible issues that may occur and provide time to obtain solutions before the system is field-tested at Kirland Air force base in New Mexico.

Figure 1: Instructed Jim Fey (laboratory support staff) to analyze samples on DART-MS system at S300.

2. OBJECTIVE

The objective of this project was to demonstrate the capability of the FLIR systems® portable DART-MS to travel to a remote site and to correctly detect/identify each of five explosives (TNT, HMX, RDX, PETN, and CompB) from individual liquid reference standards and their corresponding bulk powder residues. The analytical grade liquid target compounds were deposited separately (known concentrations) and directly onto EGIS tickets™ for DART sampling with a 10µL syringe (Figure 2) and the powder residues were spiked onto the EGIS tickets by rubbing a Q-tip that had come in-contact with a known explosives onto an EGIS ticket (bulk explosive were synthesized at LLNL).

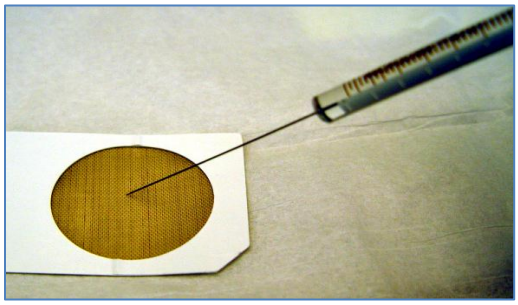


Figure 2. Depositing 1 µg of RDX standard onto an EGIS ticket™ for DART sampling and analysis

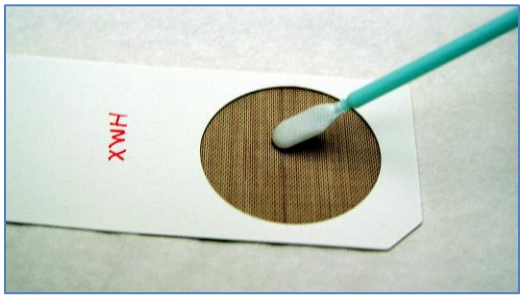
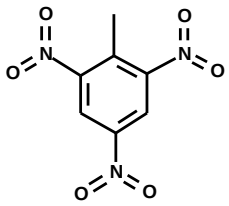
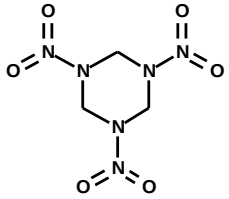
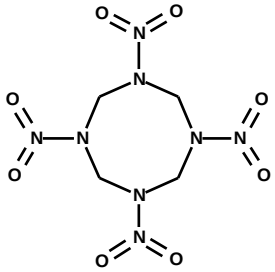
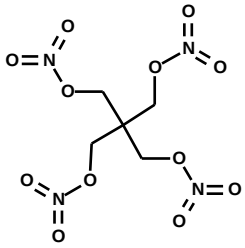


Figure 3. Depositing HMX bulk powder residue onto an EGIS ticket™ for DART sampling and analysis

Table 1. Explosives selected for the Site 300 field demonstration.

Common Name	IUPAC name/ CAS#	Molecule wt.	Structure
TNT	2-Methyl-1,3,5-trinitrobenzene/CAS# 118-96-7	227.13	
RDX	1,3,5-Trinitroperhydro-1,3,5-triazine/CAS# 121-82-4	222.12	
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine/CAS# 2691-41-0	296.15	
PETN	[3-Nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate/CAS# 78-11-5	316.14	
CompB	60/40 mixture of RDX/TNT with 1% wax added	N/A	See RDX and TNT

3. SCOPE

This evaluation was conducted to characterize the explosives residue detection capability of the DART-MS instrument during field operations. The explosives tested were limited to TNT, HMX, RDX, PETN, and CompB. They were chosen as representative explosives because they are believed to be the most likely threats for this concept-of-operations application. The DART-MS test procedures at Site-300 followed similar detection/analysis concept-of-operations applications. TheDART-MS test and evaluation Site-300 procedure was as follows:

a. Determine the reliability of detection for 1µg of each individual explosive using certified analytical liquid standards; i.e., the concentration ranges where repeatable detection readings are achieved for each selected explosive.

b. Investigate the effects of outdoor Site-300 (Livermore California) humidity and temperature on instrument performance during ambient summer conditions.

c. Observe any effects of potential interfering outdoor vapors and residues upon instrument performance in the laboratory.

4. EQUIPMENT AND TEST PROCEDURES

4.1 System Description.

FLIR systems® (West Lafayette, IN) portable DESI/DART-MS/MS instrument description and operating procedures originate from the manufacture's User's Guide. The testing was conducted utilizing the DART (Direct Analysis in Real Time) sampling source, full scan mode and with a dopant (hexachloroethane) to enhance sensitivity and selectivity. Adding a specific dopant (i.e., hexachloroethane) to the DART gas initiates most high explosives to react with the dopant and therefore generating unique chlorine adduct for analysis (improved sensitivity & selectivity for explosives). Additionally, a gas (typically nitrogen) is used with the DART source; it flows though the DART chamber (Figure 4) where an electrical discharge produces excited gas molecules (metastables) that transfer their energy to the analytes of interest.

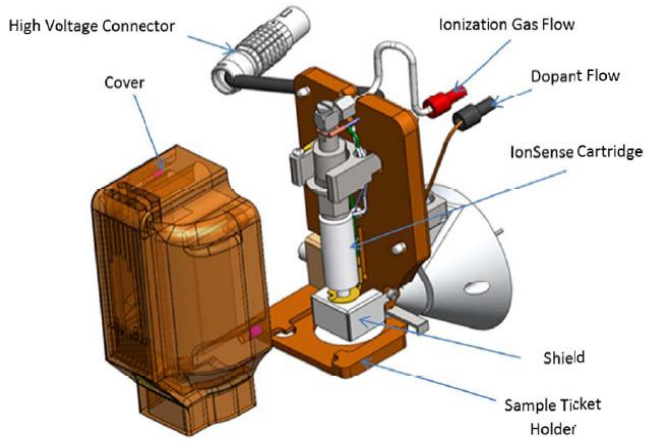


Figure 4: Exploded view of FLIR DART ion source.

To correctly identify the target explosive, the following negative ions were the major peaks measured in the DART-MS spectra of each explosive standard and were used to generate the selected RICs and subsequent data analysis.

RDX – m/z 257, 259, 284 [M + ^{35}Cl]-, [M + ^{37}Cl]-, [M + NO_3]-, respectively

PETN – m/z 61, 62, 351, 353, 378 $[NO_3]^-$, [M + ^{35}Cl]-, [M + ^{37}Cl]$^-$, [M + NO_3]-, respectively

TNT – m/z 197, 210-212, 226, 228 [M - NO]-, [M - N]-, [M - H]-, [M]-, respectively

HMX – m/z 331, 333, 342, 358 [M + ^{35}Cl]-, [M + ^{37}Cl]-, [M + NO_2]-, [M + NO_3]-, respectively

The DART-MS operates in two software modes, “Level 1 “and “Advanced Level”. For the site-300 field testing the system was operated using the Level 1 (i.e., First responder) mode. Level 1 mode has three software tabs to view the data collected and results; Detection, Monitor and Detailed views. The DART-MS has a 15 second response analyzing time using EGIS tickets™ and will display a Non-Detect (green light), Warning (yellow light) or Alarm (red light) system status when analyzing for explosives in the “Detection” tab (Figure 5). In some cases the operator may need to review the DART-MS results in a bar graph display to determine if other explosives were also detected during the analysis of a suspect sample (Figure 6, Monitor tab). For example, the explosive CompB is commonly a 60/40 mixture of RDX/TNT with 1% wax, and HMX is typically present as an impurity in RDX as well. The bar graph display (Figure 6) indicates that both RDX and TNT were detected, indicating the likely presence of CompB, and that trace amounts of HMX below the warning level were detected as well. The third tab, “Detailed” view, displays the negative-ion target intensities, ion retention time (min) and library search results, e.g., TNT (Figure 7).

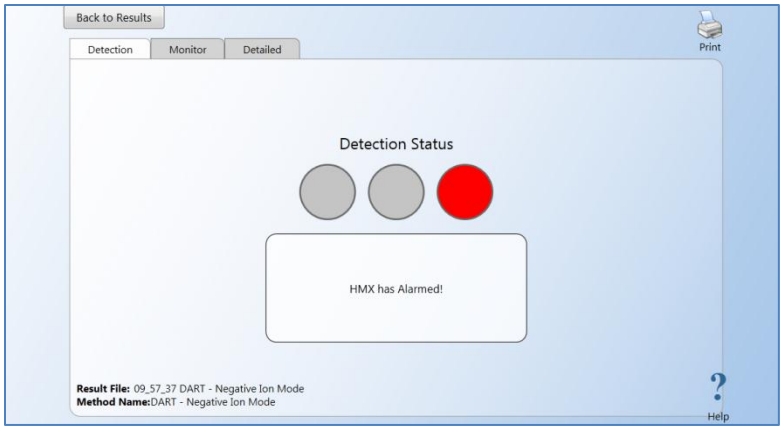


Figure 5: DART-MS operating in Level 1 software mode and alarming for HMX, Detection tab view.

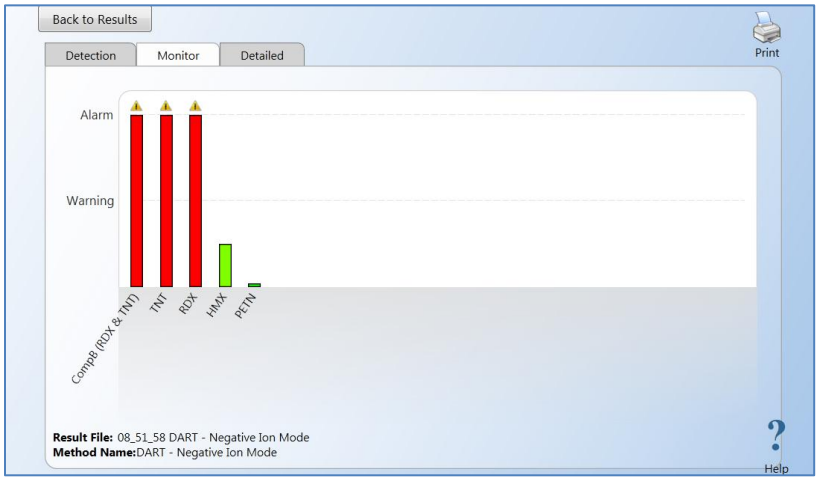


Figure 6: DART-MS operating in Level 1 software mode and alarming for CompB (TNT and RDX mixture), Monitor tab view.

Figure 7: DART-MS operating in Level 1 software mode and alarming for TNT, Detailed tab view.

The DART-MS will produce an alarm (visible) when the preset threshold levels for a specific explosive detection algorithm are matched. The alarm threshold signals are typically set at three concentration levels ("Low", "Medium", and "High") which correspond to Green, Yellow and Red status lights. “Green” alarms occur when the DART-MS ion signals are below the preset alarm threshold value. “Yellow” alarms occur when the DART-MS signals are 2-4 times higher than the alarm threshold signal and “Red” alarms occur when the DART-MS signals are 4 times higher than the alarm threshold.

For field operations, the DART-MS requires a 110V power supply, external nitrogen gas cylinder with a regulator set to 100 psi and flow of 1L/min, and a CI- dopant supply installed internally in the unit. After unpacking the system from the plastic pelican case, the nitrogen line and laptop computer are connected, and the unit is powered on and allowed to pump down (1X10^{-}5 torr). The DART-MS is relatively easy to operate and performs a self-diagnostic check before any analysis of samples is conducted (Figure 8). According to the User's Manual, the instrument can operate in temperatures from 0 to +40 °C at noncondensing relative humidity (RH) levels of 0 to 95%.

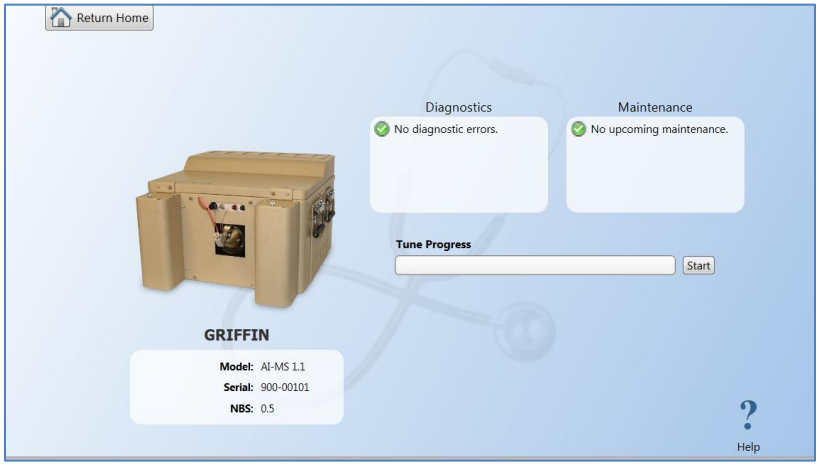


Figure 8: DART-MS self-diagnostics view.

4.2 Calibration.

No daily instrument calibration is required by the manufacturer to place the DART-MS into operation, but a quantitative exposure ("confidence check") is required. This confidence check was performed during the Site 300 field testing. To perform the confidence check, the DART-MS is operated in "Level 1", and 100 ng of RDX standard is deposited onto an EGIS ticket™ for sampling and analysis. The DART-MS software must "Alarm" (Red light) for at least 3 checks and "Non-Detect" (green light) for the blanks analyzed between the RDX-spiked standards. At the end of this measurement cycle, the unit will confirm weather it is functioning correctly. If the instrument is not alarming with the 100ng of RDX then DART capillary should be replaced and if needed, the instrument should be calibrated with a solution of 1 mg/mL (w/v) of salicylic acid, ascorbic acid and benzilic acid in methanol. This calibration process is outlined in the FLIR DART user's manual.

4.3 Site-300 Explosive Residue Challenge.

The explosives residue challenges were conducted using TNT, HMX, RDX, PETN, and CompB from both individual liquid commercial reference standards (Supleco and Cerilliant) and their corresponding bulk powder residues (synthesized at LLNL). The analytical grade liquid target compounds were deposited separately (1µg) directly onto EGIS ticket for DART sampling using a 10µL syringe and the powders residues were spiked onto the EGIS tickets by rubbing a Q-tip that had come in-contact with a known bulk explosive (non-quantitative) onto an EGIS ticket. Explosive residue challenges followed a successful instrument start up and the confidence check. The Site-300 field test was conducted on July 24, 2013 from 10:00 to 16:00, with a relative humidity of 20% and temperature range from 80-104^{o} F. The hot weather and low RH background air did not cause interferences with the instrument performance (Figure 9). However, the manufacture recommends not operating the system above 104^{o} F as the electronics/tuning may be unstable.

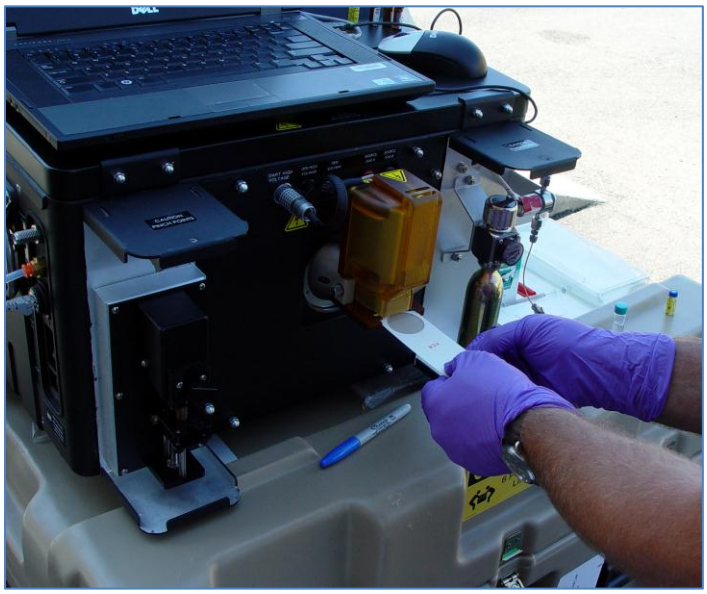


Figure 9: Analyzing an EGIS ticket with the DART-MS at Site-300.

4.4 Site-300 Interference Tests

The field interference tests were designed to assess the effect of potential interfering substances with the spiked explosives' residue during DART-MS analysis. Additionally, the Site 300 interference tests were likewise conducted to assess explosive detection capability in the presence of interferent residues. The DART-MS was tested against dust residue collected on a facility structure (Figure 10). As Site 300

conducts open-air testing, there is the potential for trace environmental contaminants to collect on the outside of building structures for sampling with a Q-tip. Dust residues were analyzed to determine whether false alarms were activated on the DART-MS in the Level 1 operating mode and preset alarm thresholds for the target explosives. The Site 300 dust residue did not alarm the DART-MS and adding the dust residue to an EGIS ticket after spiking it with COMPB (Figure 11).

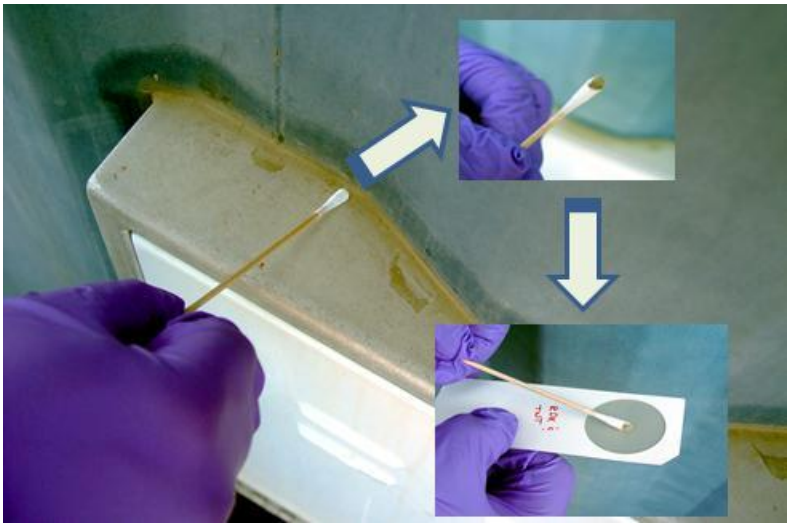


Figure 10: Collecting environmental dust from Site 300 and applying it to an EGIS ticket containing CompB residue.

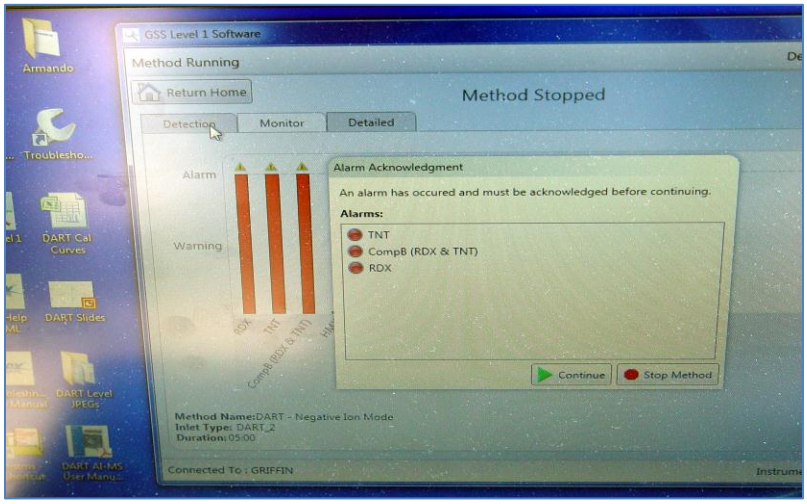


Figure 11: The DART-MS system correctly alarmed for CompB after an interferent (environmental dust from Site 300) was added to the EGIS ticket.

5. RESULTS AND DISCUSSION

The DART-MS system tested at Site 300 in July 2013 by the LLNL11-RS-136 project for explosives gave positive results for the evaluation. Performance of the system was stable throughout the evaluation and providing consistent responses with no detector malfunctions. No operational deficiencies or component failures were observed during this testing. However, the application of explosive onto the EGIS tickets with a Q-tip was not optimal. The fine powder did not adhere well to the polymeric EGIS ticket material and the static charge may also reduce inclusion of the particles onto the sampling tickets. Perhaps moistening the Q-tip with distilled water before collecting and transferring the explosive powders will improve the DART-MS response/detection to bulk powder explosives.

5.1 Site 300 Field Detection Results.

The detectable limit for the DART-MS instrument for this Site 300 demonstration was set at 1µg of each individual explosive. The explosive powder residues were not quantified.

Table 2. Explosives selected for the Site 300 field demonstration.

Explosive	Liquid 1µg deposited	Response to Target Explosive	Carry-over detected with subsequent blank	Comments
RDX	Alarmed	100%	ND	
RDX	Alarmed	100%	ND	
RDX	Alarmed	100%	ND	
RDX	Alarmed	100%	ND	
RDX	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
PETN	Warning	80%	ND	
PETN	Alarmed	100%	ND	
PETN	Green	40%	ND	
PETN	Warning	60%	ND	
PETN	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	

Table 3. Explosives selected for the Site 300 field demonstration.

Explosive	Powder Residue Deposited	Response to Target Explosive	Carry-over detected with subsequent blank	Comments
RDX	Alarmed	100%	ND	20% HMX
RDX	Alarmed	100%	10% RDX	25% HMX
RDX	Alarmed	100%	ND	20% HMX
RDX	Alarmed	100%	ND	15% HMX
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
TNT	Alarmed	100%	ND	
PETN	Warning	55%	15% PETN	
PETN	Green	40%	ND	
PETN	Warning	55%	ND	
PETN	Alarmed	100%	ND	
HMX	Alarmed	80%	ND	
HMX	Alarmed	100%	ND	10% RDX
HMX	Alarmed	100%	ND	
HMX	Alarmed	100%	ND	8% RDX
CompB	Alarmed	100%	ND	100%TNT, 100% RDX, 100% HMX
CompB	Alarmed	Warning*	ND	100%TNT, 80% RDX, 100% HMX
CompB	Alarmed	Warning*	ND	100%TNT, 50% RDX, 100% HMX
CompB	Alarmed	Warning*	ND	100%TNT, 80% RDX, 100% HMX

* Must alarm 100% on both TNT and RDX to alarm for CompB

Table 4. Explosives selected for the Site 300 field demonstration.

Explosive and Dust residue	Powder Residue Deposited	Response to Target Explosive	Carry-over detected with subsequent blank	Comments
CompB (Powder)	Alarmed	Warning	ND	100%TNT, 80% RDX, 100% HMX
PETN (powder)	Green	40%	ND	
CompB (liquid)	Alarmed	100%	ND	100%TNT, 100% RDX, 100% HMX

6. CONCLUSIONS

The portable DESI/DART-MS/MS instrument performed well for the detection of TNT, HMX, RDX, PETN, and CompB in the testing conducted at Site 300. The most observed operational weakness, such as inconsistent response, was during detection of powder explosive residues. This may be attributed to the application of the explosive residue by the Q-tip to the EGIS ticket. The detection capability may be improved by wetting the Q-tip with distilled water prior to sampling. This suggestion was discussed with the manufacture FLIR systems and they were in agreement. We plan to evaluate this approach before the field test at KAFB. The detection of PETN (liquid and powder) was also less responsive and it may have been due to operating the system near the temperature maximum (104^{o} F). There were no false alarms during the explosives testing and potential interferences did not generate non-detects (ND) or false positives. The blank EGIS tickets analyzed between each explosive spiked did not indicate explosive carry-over, including the powder residue tickets with a higher probability of higher explosive concentrations. That DART-MS appears ready for the next field demonstration at KAFB. However, a few laboratory sampling tests will be conducted to improve powder residue transfer performance onto the EGIS tickets.