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Detection of organic gunshot residue in smokeless powders using an on-site analytical approach

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Thesis

DETECTION OF ORGANIC GUNSHOT RESIDUE IN SMOKELESS POWDERS USING AN ON-SITE ANALYTICAL APPROACH

by

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ABSTRACT

Violence due to firearms has been an issue in the United States for numerous years. Due to the continuation of violence through the utilization of firearms, it is very important for law enforcement and forensic scientists to have various methods to detect and identify components of ammunition that have been discharged. These components, also known as gunshot residue, are usually left in trace amounts, meaning it cannot be seen to the unaided eye. These trace amounts are very important in identifying the shooter during an investigation, so it is crucial to have a sensitive and specific analytical method to detect the gunshot residue.

There are two types of Gunshot Residue: Inorganic Gunshot Residue (IGSR) and Organic Gunshot Residue (OGSR). Most firearm evidence that is examined focuses on IGSR and uses analytical techniques such as Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS) to detect it. Transferability of IGSR is not uncommon when detecting IGSR on a suspect, so it is very important to create an analytical approach that is rapid and reliable for detecting Organic Gunshot Residue. The persistence and collection of OGSR has many benefits in comparison to IGSR, so finding a way to both collect and analyze OGSR would be valuable to both law enforcement and laboratory analysts. In recent years, new methods have been developed to detect the organic

compounds discharged from firearms. One method that has been successful in the detection of OGSR compounds is the time-of-flight secondary ion mass spectrometer. The drawback to many methods of detecting GSR components is that it is very time consuming. One common and accepted technique for detecting OGSR has not been created.

During this research, a field portable, High Pressure Mass Spectrometer called the MX908 was used to create a library using the organic compounds Dibutyl Phthalate (DBP), Diphenylamine (DPA), Ethyl Centralite (EC), Nitroglycerin (NG), and Nitroguanidine (NQ) in the Explosives Hunter (EH) and Chemical Warfare Hunter (CWH) mission modes. After a library was created and validated on the device, assorted brands of smokeless powders, both burnt and unburnt, were tested to determine the accuracy of the library by analysis of the powders.

The MX908 demonstrated the ability to detect the OGSR components in the validation studies conducted and the smokeless powder testing. When conducting the validation studies, CWH mode, a predetermined, on-device method, was better at identifying the target compounds while producing the least number of false positives. NQ, EC, DBP, DPA, and NG were reliably detected in both CWH and EH mode. There were a significant number of false positives in EH mode for NQ and DBP. Contrary to the validation testing, when testing the smokeless powders, EH mode had greater accuracy and no false positives. EC, DBP, NG, and DPA were detected in EH mode for both unburnt and burnt samples. DPA, EC, and DBP were detected in CWH mode for the smokeless powder samples. The unburnt samples tested in both EH mode and CWH

mode had more red alarms than the burnt residue samples. This was expected because as smokeless powder burns, some of the components are consumed.

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LIST OF ABBREVIATIONS

APCI	Atmospheric Pressure Chemical Ionization
ASTM	American Society for Testing and Materials
CID	Collision-Induced Dissociation
CWH	Chemical Warfare Hunter
DBP	Dibutyl Phthalate
DPA	Diphenylamine
EC	Ethyl Centralite
EH	Explosives Hunter
EI	Electron Impact
g	grams
g/mol	grams per mole
GC	Gas Chromatography
IGSR	Inorganic Gunshot Residue
KS	Kansas
L	liter(s)
LC	Liquid Chromatography
µ	micro
MA	Massachusetts
MO	Missouri
MS	Mass Spectrometry

m/z	Mass to charge
NC	Nitrocellulose
NG	Nitroglycerin
NQ	Nitroguanidine
OGSR	Organic Gunshot Residue
OSAC	Organization of Scientific Area Committees
OH	Ohio
pGSR	Primer Gunshot Residue
SDS	Safety Data Sheet
SEM/EDS	Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy
SNR	Signal-to-Noise Ratio
TOF-SIMS	Time of Flight – Secondary Ion Mass Spectrometry

1. INTRODUCTION

Violence due to firearms has been a complication in the United States for numerous years. Despite the United States being one of the most developed nations in the world, it is relatively simple to gain possession of a firearm [1,2]. Consequently, the number of homicides and hospitalizations due to gun violence will continue to be an issue. According to the CDC, in 2021, there were 48,830 deaths due to firearms [3]. Therefore, it is important for law enforcement and forensic scientists to have various methods to detect and identify residue that have been discharged. This residue, also known as gunshot residue, is usually left in trace amounts, meaning it cannot be seen to the unaided eye. These trace amounts are very important during an investigation, so it is crucial to have a sensitive and specific analytical method to detect the gunshot residue. It would be valuable to have a technique that is on-site to decrease the time.

There are two types of firearms: handguns, which are fired from the hands of a person and utilizes small arms ammunition, and long guns, which are fired from the shoulder of a person. There are different subcategories of handguns including revolvers and pistols which can be automatic or semiautomatic. The subsets of long guns include rifles, shotguns, machine guns, and submachine guns [4]. Although there are various types of forensic examination related to firearms, trace evidence will be referenced in this study.

1.1 Ammunition and Smokeless Powders

There are two categories of small arms ammunition: cartridges, which have a metallic case, and shotshells, which are used in shotguns and contain many pellets.

Cartridges contain the following contents: the primer, the propellant, and the projectile, or bullet core, with a cross-section shown in Figure 1 [4,5].

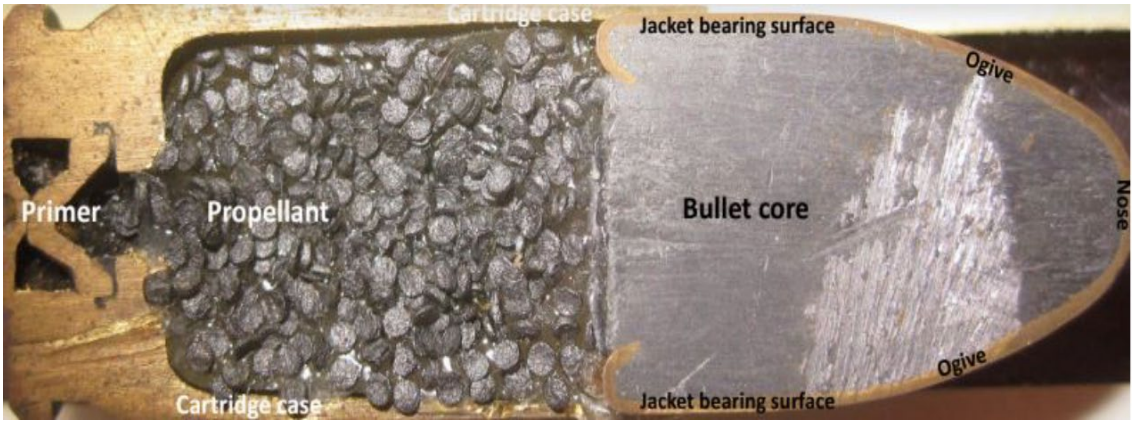

Figure 1. A cross section of a small-arms ammunition. (Photograph provided by Dr. Peter Diaczuk)

The primer, which is also referred to as the initiator, is a shock-sensitive explosive mixture, and is what allows the reaction of a firearm discharge to begin. The firing pin strikes the primer end of the cartridge, initiating the burning of primer, which in turn ignites the propellant. Most primers usually contain three different compounds: lead styphnate, barium nitrate, and antimony sulfide. The particles originating from the primer, which contain lead, barium, and antimony are discharged when a firearm is used.

The propellant, also known as smokeless powder, is a low explosive mixture that creates an explosive charge when initiated. This charge creates gas, causing pressure, and eventually causes the bullet to be ejected through the barrel of the gun at a high velocity. Smokeless powder has three different classes based on chemical composition: single, double, and triple-base. Single-base smokeless powders contain only nitrocellulose (NC), double-base powders contain nitrocellulose and nitroglycerin (NG), and triple-base

powders contain nitrocellulose, nitroglycerin, and nitroguanidine (NQ) [6]. Smokeless powders can come in many different shapes, depending on the brand. These shapes can include rod-shaped, tubes, balls, discs, and non-uniform flakes (Figure 2). There can also be various additional compounds in smokeless powder propellants including energetics, stabilizers, plasticizers, flash suppressants, deterrents, opacifiers, and dyes. When a firearm is discharged, the explosion results in both burnt and unburnt residue from the primer and propellant. These residues can be deposited on the shooter's hands, face, and articles of clothing [4,5].

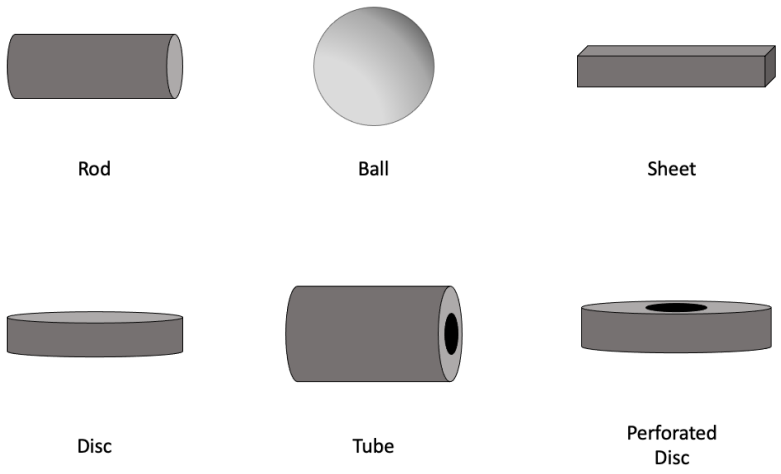

Figure 2. Several commonly manufactured smokeless powder morphologies.

1.2 Gunshot Residue

There are two types of gunshot residue that are relevant when examining firearms evidence: inorganic gunshot residue (IGSR) and organic gunshot residue (OGSR). GSR analysis is used in an attempt to identify a shooter. Most firearm evidence that is examined focuses on IGSR and uses analytical techniques such as Scanning Electron

Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS) to detect it [7]. When collecting IGSR, a suspect's hands are sampled due to the proximity to the weapon and clothing is sampled due to GSR particles becoming trapped within the fibers.

Organic Gunshot Residue (OGSR) is the second type of GSR that is encountered while examining forensic evidence. OGSR has some advantages over IGSR including low transferability and high persistence [8,9]. Persistence is the amount of time the compound stays on a surface, and it has been shown that OGSR has higher persistence than IGSR, meaning that the compounds have the potential to be identified for longer periods of time after discharge [8,9]. IGSR can be easily wiped off the hands and articles of clothing of the shooter and can be transferred to others, causing confusion in an investigation. Due to IGSR's high transferability, a positive IGSR test does not mean an individual shot a firearm. Inversely, due to IGSR's low persistence, a negative IGSR test does not mean that an individual did not shoot a firearm. Detecting OGSR rather than IGSR may allow analysts to have more confidence when reporting their results.

1.2.1 Chemistry of Inorganic Gunshot Residue and Current Method of Detection

As previously discussed, IGSR is commonly analyzed and detected when examining forensic evidence. The traditional method of detecting GSR is by looking for particles containing lead, barium, and antimony, known as IGSR/primer GSR (pGSR). Lead-free primers have been developed, but these are not commonly observed in casework [3,4]. The analysis of these compounds includes examining the morphology of the IGSR particles. Within the primer mixture, these elements exist separately, but when

a firearm is discharged, the elements morph together in a molten state, causing a spherical morphology, resulting in a single particle containing the three elements. This spherical morphology is important when analysts are identifying GSR. When analyzing IGSR, a positive identification of any combination of two of the elements, in addition to an observed spherical morphology, would be reported as "consistent" with GSR. If all three elements are observed with an observed spherical morphology, it would be reported as "characteristic" of GSR [7,10]. IGSR transfers easily, and there are many factors that contribute to how much GSR is deposited on an individual. One variable that could be attributed to this variation is the caliber of weapon the shooter used [11]. There have also been studies demonstrating that IGSR can be transferred from the shooter to another individual or another surface, also known as secondary transfer [12]. Inorganic Gunshot residue not only has low persistence and high transferability, but the metal compounds that analysts detect can be present naturally in certain environments. For example, lead, barium, and antimony have been detected in some brake pads and airbags [13–15]. Since it is a possibility for an individual to encounter these metals and not shoot a firearm, it is important for law enforcement to question the suspect about their occupation or whereabouts. However, it is not always possible to obtain this information due to the suspect being resistant to answering questions, lying to law enforcement, or if the suspect is deceased. Forensic scientists also need to take this into consideration, which increases the burden of the analysis.

The most common and accepted method for analyzing and identifying IGSR is SEM/EDS. This analysis uses the elemental and morphological composition of inorganic

particles to characterize GSR [16]. The American Society for Testing and Materials' (ASTM) E1588 standard provides widely-accepted and utilized guidance on IGSR collection and detection. When a firearm is discharged, GSR is expelled and lands on nearby surfaces including the hands and clothes of the individual that used the weapon [17]. To collect the trace evidence that is expelled, the current method used is an adhesive carbon stub. According to the ASTM E1588, this method of collection is required for SEM/EDS to be performed [16]. This stub is usually pressed on the areas of the hands where residues are most prominent after a firearm is discharged, picking up potential IGSR particles. The areas of the hands that are usually tested are the left and right palm and the back of each hand, but the stub can be used in other areas such as the face and clothes of the suspected shooter [17]. Although this method has been used in forensics for a very long time, it is a very time-consuming process. This process requires the unknown sample to be collected, transported to the laboratory, and analyzed.

1.2.2 Chemistry of Organic Gunshot Residue and Methods of Detection

The second type of gunshot residue that can be tested in forensic laboratories is OGSR. As previously discussed, smokeless powders have many organic compounds which vary among ammunitions [18]. Although smokeless powders can be single, double, and triple-based, double-base powders are the most common. Triple-base powders are relevant in the field, but they are less common due to their association with larger caliber weapons [6]. Many smokeless powders also have additives that help with degradation prevention, called stabilizers, and those that lower the viscosity, called plasticizers. The

three components associated with stabilizers and plasticizers that are relevant to the scope of this research are Dibutyl Phthalate (DBP), Diphenylamine (DPA), and Ethyl Centralite (EC) [19,20]. Since many organic compounds can be in smokeless powders, it is important to develop an analytical technique that encompasses a representative sample of these. The Organization of Scientific Area Committees (OSAC) divided OGSR components into two different categories, shown in Table 1. According to OSAC, Category 1 compounds are "used in the manufacture of smokeless powder or priming compound, and their related degradation products, which are uncommon in other commercial or environmental sources" [21]. Category 2 compounds are similar, except the compound is common in commercial or environmental sources. In this report, OSAC defined that a "characteristic" result of organic residues is a combination of the organic compounds that are not commonly found in anything other than smokeless powders. A "consistent with" OGSR result are organic residues that have a combination of the targets that can be found in smokeless powder residues, but also other sources. It is also said that if there is a compound from both categories, it would be "consistent with" OGSR [21].

Table 1. OSAC's classification of OGSR compounds.

Category	**Compounds**
1	Ethyl Centralite (EC) Methyl Centralite (MC) Nitroglycerin (NG) Nitroguanidine (NQ) 2 & 4-nitroDiphenylamine (2-, 4-NDPA) N-nitrosoDiphenylamine (N-NODPA)

2	Nitrocellulose (NC) Diphenylamine (DPA) and derivatives Other nitrotoluenes 2,4-dinitrotoluene (2,4-DNT) Akardite II (Ak II)

As previously stated, OGSR is more resistant to transfer than IGSR. This is due to the organic residue's lipophilic properties, allowing it to better adhere to the skin [8,9,19,21]. In one GSR persistence study, it was shown that IGSR has a maximum detection window of four hours, while some components of OGSR persisted on clothing for up to five days [9]. This is very important for analysts because the collection window of OGSR is longer, and the risk of transfer is highly reduced. However, some of the components of OGSR can also be found in the environment. DPA is found in many consumer products, and small amounts of DBP can be found in air and water [22,23].

Due to the advantages of detecting OGSR over IGSR, there has been a focus on developing methods for the detection of OGSR. One method that has been successful for the detection of OGSR compounds is the time-of-flight secondary ion mass spectrometer. Secondary ions are generated using an ion beam, which bombard the GSR. This technique has a very high resolution and creates a mass spectrum of OGSR compounds [24].

Another method that has been performed is Liquid Chromatography coupled with triple quadrupole Mass Spectrometry. This method screens and detects both inorganic and organic components of GSR. The study, performed by Suzanne Bell, was able to generate specific and confirmatory results to detect Ba, Pb, DPA, EC, other metals, and organic compounds. These results were detected based on isotopic results. The drawback

to this method is that it is very time-consuming [7]. Additional novel techniques are being developed, but one common and accepted method for detecting OGSR has not been created. According to OSAC, there are current topics of OGSR knowledge that need to be researched further. Some of those topics include, "additional OGSR targets, stability of OGSR on sampling media, and persistence and secondary transfer characteristics" [25].

1.3 MX908

The MX908 by 908 Devices (Boston, MA) is a High-Pressure Mass Spectrometer (HPMS) and uses a miniature 3D ion trap. The device is field portable and primarily used by law enforcement and other non-scientists, so the controls are intuitive. The MX908 was designed to be sensitive, specific, and still have good resolution in the field. Portability is not possible with traditional mass spectrometers due to the large pumps used to obtain low pressures as well as the necessary electrical requirements, making it very difficult to move the instrument. The high pressure of the device requires a smaller pump, allowing for the miniaturization of the mass spectrometer [26].

The ionization technique that this device uses is Atmospheric Pressure Chemical Ionization (APCI). In many ionization methods, a carrier gas is required, but since this is a portable device, ambient air is used. APCI is a soft ionization technique, meaning that there is less fragmentation in comparison to techniques like electron impact (EI) which bombards ions at a high energy, causing more fragmentation. APCI results in a molecular ion being produced. This in conjunction with a high pressure and collision-induced

dissociation (CID) application at the aperture between the ionization chamber and the ion trap ultimately helps the ionization efficiency and sensitivity of the device [27].

The MX908 mass spectrometer analyzes ions in the vapor phase as with typical mass spectrometers. To accomplish this for nonvolatile compounds such as powder traces of drugs, the device uses thermal desorption to vaporize the sample. After the sample is vaporized, it enters into the ionization chamber seen in Figure 3. This chamber utilizes a corona discharge for ionization and as previously stated, operates at atmospheric pressure. The energy from the needle strips electrons from the molecule, and the ions are dragged electrostatically into the ion trap through the aperture. As they pass through the aperture, additional voltage is applied, causing further fragmentation through collision-induced dissociation (CID). After fragmenting, the ions enter the 3D ion trap and oscillate in space as the radio frequency (RF) amplitude is increased, causing the ions to eject to the detector [26].

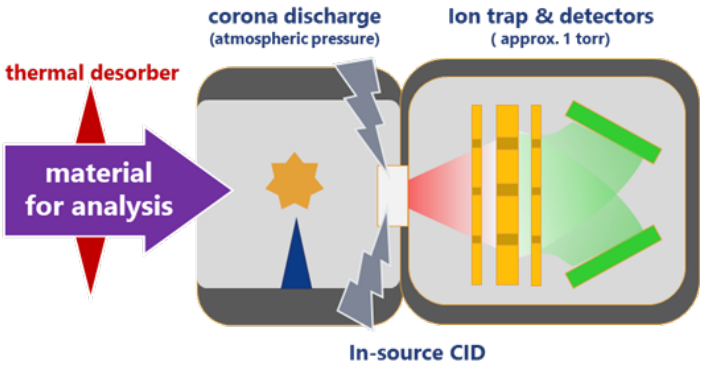

Figure 3. Ionization, fragmentation, and detection process of HPMS (Image provided by 908Devices)

The MX908 utilizes “mission modes,” which are pre-determined device parameters optimized for different classes of chemicals, such as drugs or explosives. The mission modes that the MX908 utilizes are differentiated by the ionization polarity and CID voltages. During the ionization process, the molecules form positive and negative ions, and the mission modes operate in either positive, negative, or both ionization modes. After the ionization process, CID voltages are applied at the aperture. The mission modes that the MX908 utilizes are differentiated in part by these voltages. The device applies low, mid, and high CID in which it can fragment ions, and within each CID level there is a certain mass range detected (Figure 4). As the aperture voltage increases, more fragmentation occurs, resulting in smaller fragments [26]. All these features allow the MX908 to be a portable mass spectrometer that can deliver an instantaneous and specific result to the user.

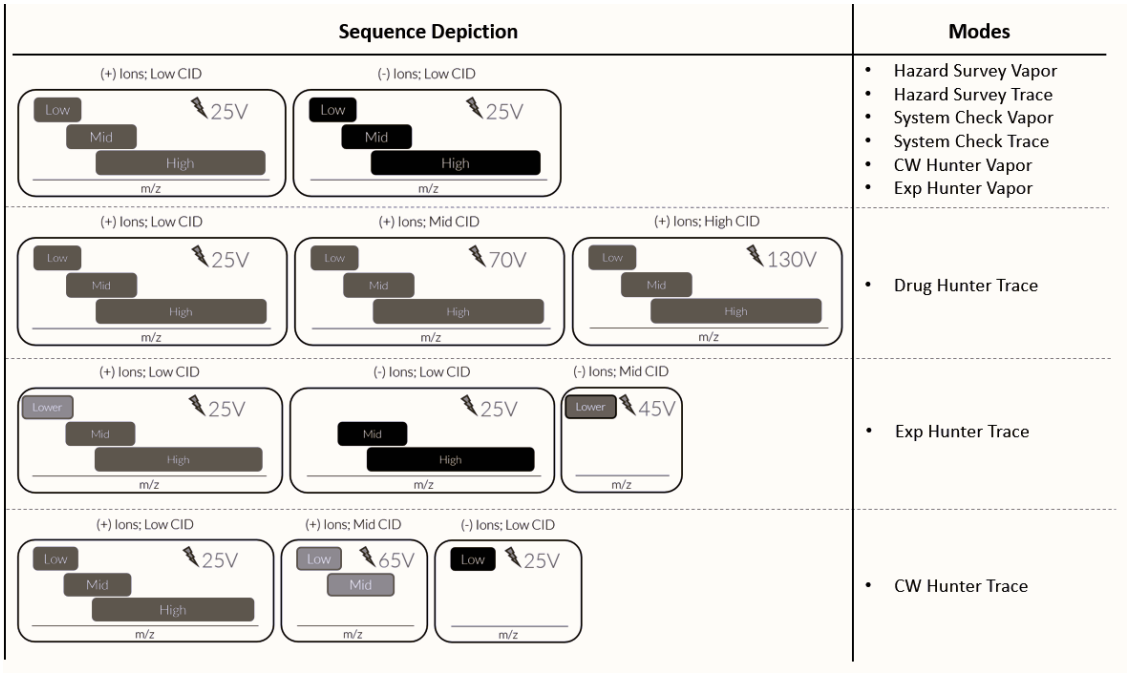

Figure 4. mission mode sequences depicting various voltages and mass ranges. (Image provided by 908Devices)

1.4 Objective of Thesis

Violence due to firearms has been increasing throughout previous years. This increase of violence calls for a sensitive and specific analytical method to detect GSR, especially on site. On site detection of GSR will decrease the time it takes to analyze this residue. This is important due to the high transferability of these particles. Although the current accepted methods of IGSR detection are implemented in many labs, the collection of OGSR has many advantages in comparison to IGSR, so finding a way to both collect and analyze OGSR is very important to both law enforcement and analysts.

The objective of this thesis was to create a library on the MX908 using the organic compounds DBP, DPA, EC, NG, and NQ in Explosives Hunter and Chemical Warfare Hunter mission modes. After a library was created and tested, the objective was to test smokeless powders, both burnt and unburnt, from different brands to determine if the MX908 could accurately detect and identify these components within the powders.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

The target organic compounds used included: Dibutyl Phthalate, Diphenylamine, Ethyl Centralite, and Nitroguanidine from Sigma (St. Louis, MO), and Nitroglycerin from Accustandard (St. Louis, MO). EC and DPA were diluted using 99.5% pure ethanol from Acros Organics, which is part of ThermoFisher Scientific (Waltham, MA). DBP was diluted using 99.5% pure acetone from ThermoFisher Scientific (Waltham, MA). All these compounds were weighed using a Mettler-Toledo ME204TE Analytical Scale (Columbus, OH). All the standards except NQ were measured to create a stock concentration of 1 mg/mL, and then the following dilutions were made for EC and DPA: 100 µg/mL, 10 µg/mL, 1 µg/mL, and 0.10 µg/mL. The DPB standard procedure was slightly different from EC and DPA due to DPB being a liquid standard. For the DPB standard, a 1:1000 dilution was made of the pure liquid standard, and that dilution was further diluted into six different dilutions. Those six dilutions included: 1:250, 1:400, 1:450, 1:500, 1:750, and 1:1000. Due to the insolubility of NQ in volatile organic solvents, NQ was tested as a powder. NQ was first collected using the bulk sampling swab, and then transferred to a trace sample swab, and tertiary and quaternary swabs were created and tested. These dilutions were created to test on the MX908 and ultimately generate JDX files for the library.

The following smokeless powders were used during this study: Hodgdon Hornady LEVEREVOLUTION Rifle Powder (Shawnee, KS), Hodgdon Lil' Gun Shotgun Powder (Shawnee, KS), IMR 7828 Smokeless Powder (Shawnee, KS), Red Dot Smokeless Target Shotshell Powder (Lewiston, ID), Reloader 19 Smokeless Heavy Rifle Powder (Lewiston,

ID), Winchester Ball Powder Smokeless Propellant (Shawnee, KS), and Winchester Western Ball Powder Smokeless Propellant (Shawnee, KS). These smokeless powders were chosen due to the various morphological compositions, sizes, and OGSR components. The powders were used to evaluate the effectiveness of the JDX files created.

2.2 Instrumentation

The devices used in this experiment were both MX908 Mass Spectrometers, SN#MX1799 and SN#MX0179. Two devices were used due to an internal malfunction, necessitating a repair to the device. Due to this malfunction, a loaner device was provided until the original device was repaired. In this device, the trace module was used to analyze solid and liquid samples and was where the thermal desorber was located. The core contained the ionization chamber and aperture that leads to the ion trap (Figure 5). These parts can become contaminated, so they occasionally need to be removed and cleaned, or sometimes replaced. The core is designed to be changed in the field and the device is operational within minutes after a core swap.

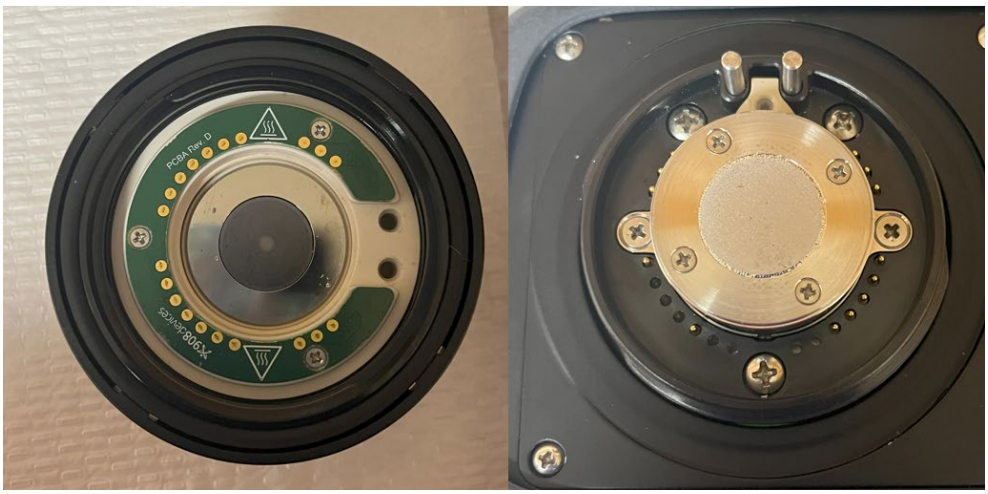

Figure 5. Photograph depicting the removeable trace module (left) and the removable core (right)

As outlined earlier, the device has many different modes that can be utilized. Each of these modes employ different voltages, polarity, and temperature parameters. Additionally, the modes each have designated libraries. These modes are as follows: Chemical Warfare Hunter (CWH), Drug Hunter, Explosives Hunter (EH), and Hazard Survey (Figure 6). The modes can be used in Trace, Vapor, or Aerosol mode. During this experiment, Chemical Warfare – Trace and Explosives Hunter – Trace were used due to their positive and negative ionization potential.

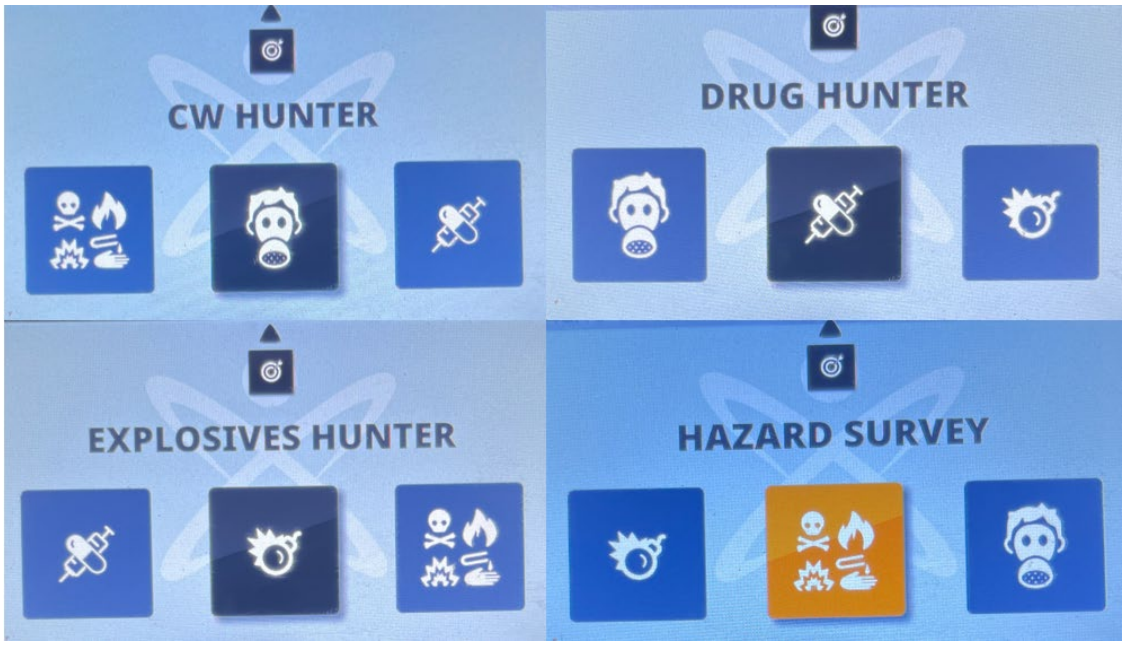

Figure 6. The various mission modes on the home screen of the MX908: Chemical warfare (top left), Drug hunter (top right), Explosives hunter (bottom left), and Hazard survey (bottom right).

2.3 Alarm Testing

Two different types of sampling swabs were provided and used with the MX908: the trace sampling swab (Figure 7) and the bulk sampling swab, also known as a foam-tipped applicator. The trace sampling swab must be used in Trace mode, which was the only sampling mode used during this study. This swab is used for sampling both powders and liquids. Two notches cut into the sides indicate to the user where the sample should be placed. This area of the swab is directly in line with both the thermal desorber and mesh that allows the sample to enter the ionization chamber. The trace sampling swabs can be rubbed directly against a surface that could potentially contain drugs, explosives, etc. The

sample can be “diluted” by rubbing a second swab against the primary swab, creating secondary and tertiary swabs. Although known concentrations were tested during this project, in the field unknown concentrations of unknown chemicals are encountered, and secondary swabs are preferred to keep the ion trap clean and free of contamination. The bulk sampling swabs were not used frequently but can be used to transfer compounds of interest from bulk samples onto the trace sampling swab. In this study, the liquid standards were deposited directly onto the trace sampling swabs, and smokeless powder was diluted in acetone and sampled by depositing the diluted solution directly onto the trace sampling swabs.

Figure 7. The trace sampling swabs provided by 908 Devices.

During this testing, both the Explosives Hunter and Chemical Warfare Hunter mission modes were used. This was done to observe the data generated in each mode and determine which produced the most specific and reproducible spectra. To do this, EC, DPA, and NG had 1 µL of the solutions of various concentrations deposited on the trace sampling swab using a FinnPipette F2 by ThermoFisher (Waltham, MA), and was tested on the MX908. A 1:1000 stock solution of DBP was created, 1 µL was added to a trace sampling swab, the swab-the-swab technique was performed, and the secondary swab was tested. Due to the insolubility of NQ in volatile organic solvents, NQ was tested as a powder. NQ was first collected using the bulk sampling swab, and then transferred to a trace sample swab, and tertiary and quaternary swabs were created and tested.

The analysis consisted of two steps. The first step was depositing the OGSR component onto the swab and allowing it to dry as described above. Next, the swab was inserted into the trace sampling module and run in the correct mode. The device provides real-time data on the signal-to-noise ratio (SNR) throughout the analysis. This helps the user have an idea of whether too much or too little sample was deposited on the swab. Each line on the graph represents ten SNR, and ideally, the maximum SNR should be above 25 SNR, similar to Figure 8 below.

Figure 8. Screen showing the SNR of a sample tested on the MX908.

After the device has concluded with its data collection, one of four different results would appear on the screen: “no signal,” “no target detected,” a red alarm, or a yellow alert. “No signal,” shown in Figure 9 indicates that the maximum SNR was below six and no material was detected. If this appears when testing a sample, a higher amount of sample needs to be added to a new swab and the analysis should be performed again. “No target detected” indicates that the material detected is not consistent with the expected analysis of any targets in the device’s library for that given mission mode. When conducting the initial testing in this experiment, “no target detected” was observed for most of the OGSR components, which was expected as they were not targets in the library. A red alarm, or target alarm indicates the signal from the sample tested is consistent with the reference spectrum of the compound which it alarmed for at a high probability. A yellow alert indicates that the sample tested shows similarities to the reference spectrum of that target at a lower probability, and the presence of that substance cannot be ruled out. When testing a sample, multiple red and/or yellow alerts can occur. Whenever a sample alarms, the

device will display the compound name, alarm level, classification, structure, and any other chemical information that could be useful to the user.

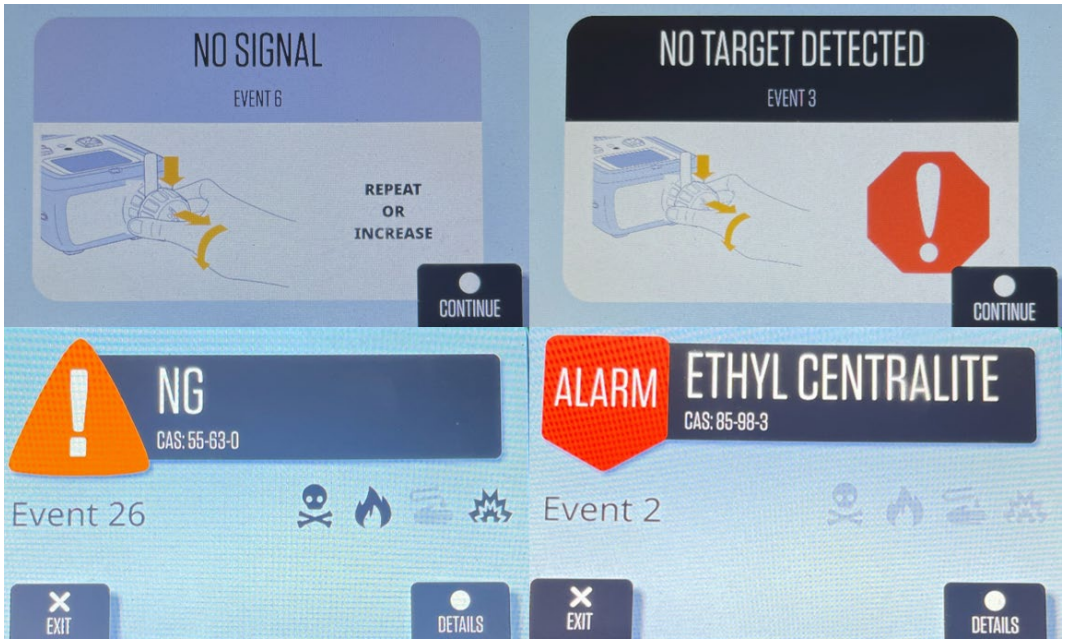

Figure 9. The various results the MX908 Device can display: No Signal (top left), No Target Detected (top right), Yellow alert (bottom left), and red alarm (bottom right).

2.4 Library Creation

A library of the five organic compounds was created next. It was decided that both the Explosives Hunter and Chemical Warfare Hunter mission modes would have libraries created because some components performed better in one mission mode, while some ionized better in the other. To prepare for the library creation, the individual organic components were diluted to have an adequate range of doses tested. When testing each component, an SNR above 25 was targeted. Each organic compound was tested at

three concentrations five times. If the maximum SNR was lower than 25, that dose was increased and retested. Once enough replicates were tested at various doses, the data was exported and transferred to a computer using a USB drive.

To create the library of OGSR targets, the 908 Devices TargetWikiManager software was used. This software allows analysts at 908 Devices to add new chemicals to existing mission mode libraries. When adding a new compound to the software, a ChemWiki must be created. The ChemWiki contains the chemical name, the name it will alarm as, the molecular weight, the Chemical Abstracts Service (CAS) number, and the Simplified Molecular Input Line Entry System (SMILES) code. Once that information was saved, a secondary software called JDX Builder was launched. A data file that is saved in the JCAMP-DX (Joint Committee on Atomic and Molecular Physics) format is a JDX file. These files include spectral x,y coordinate data that was obtained from a spectrometer; in this case, the JDX files are created based on data collected from a standard to form a reference spectrum which is used by the MX908 algorithm.

Once the JDX Builder software is open, data files can be imported. Once the files are imported, target construction can begin. As seen in Figure 10, there are three rows of graphs. The top row shows the signal intensity throughout the course of each event. The algorithm predicts if there is more than one chemical present, and the black or gray peaks seen in the row are indicative of each predicted component. The second row down displays the overall signal broken down by each detector, and when the user clicks at a certain time frame along the x-axis in the second row, the bottom row will display the mass spectrum at that time frame.

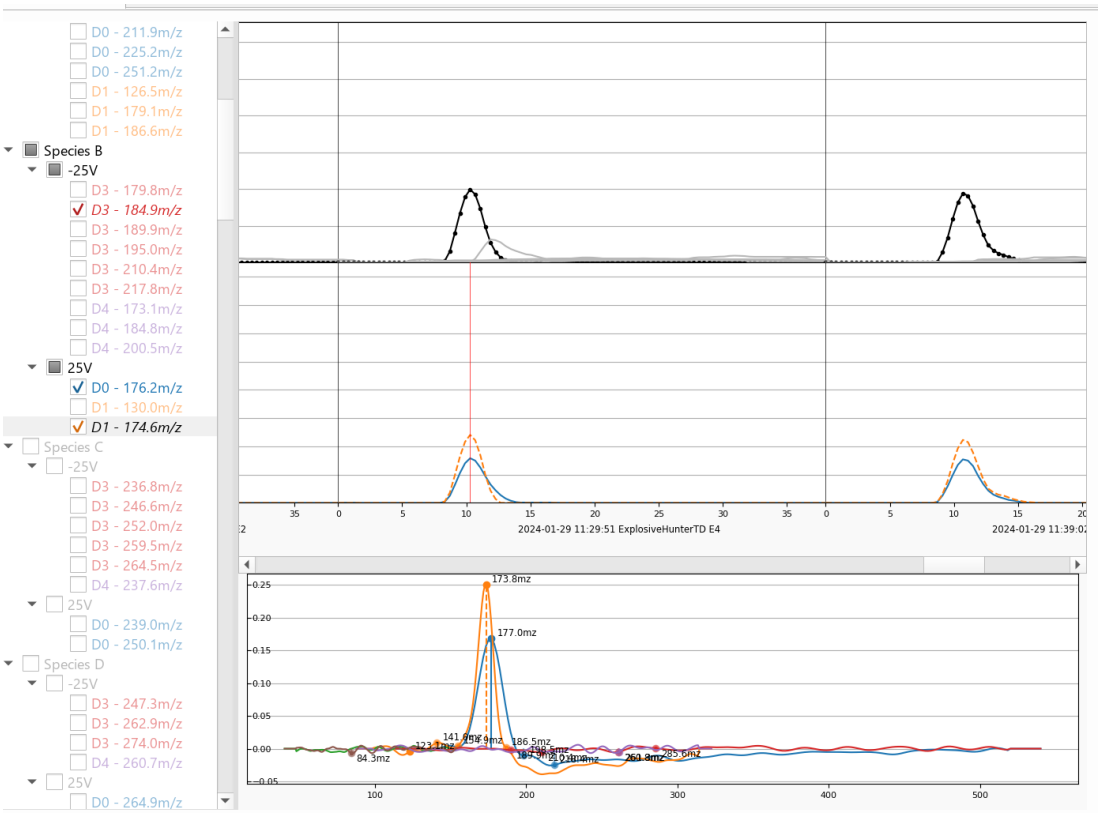

Figure 10. JDX builder software of DPA in Explosives Hunter. The overall signal of each event (top row), the overall signal broken down by the detector (middle row), and spectrum at a certain time frame (bottom row) is shown in this software.

The MX908 uses an algorithm relying on a reference spectrum of required and optional peaks which must be present in order to produce an alarm or alert for each target. Typically, the JDX Builder software will automatically select peaks and set them as required or optional. To create an effective JDX, tweaks usually need to be made to the peaks by manually adjusting which are required or optional. The selection of certain peaks can be tested by processing the uploaded data files, and each event will display a yellow, red, or no alarm. The peak selections can then be adjusted accordingly to obtain

the maximum number of red alarms from the data set. For this project, the goal was to have greater than 80% alarming before saving the JDX file. After saving the JDX file, it was shown in TargetWikiManager. In Explosives Hunter mode, this process was conducted for EC, DPA, DBP, and NQ. NG was already an existing target in EH mode on the MX908. For CWH, this process was utilized for all five compounds.

Once all JDX files were created and saved, the custom library was uploaded onto the device. Validation testing was then conducted to ensure that the JDXs built were able to detect the OGSR components. To prepare for the testing, three different concentrations of each compound were tested three times per mission mode. Again, if the SNR was below 25 then that concentration was increased and retested.

2.5 Smokeless Powder Testing

Finally, unburnt and burnt smokeless powder testing was conducted to determine if the device could detect the organic compounds in either type of sample using the library created. Seven different brands were tested to evaluate similarities and differences within brands of smokeless powder, since casework analysts come across many brands of smokeless powder. To prepare the unburnt powder, five individual grains of smokeless powder were added to a glass vial with 1 mL of acetone and left overnight to extract and dilute. For the testing of the powders, the concentration of each sample was calculated by dividing the weight of the powder by the total volume of acetone added. Three different concentrations per mission mode were tested, making sure the SNR was higher than 25 at the lowest concentration.

To prepare the burnt residue, five individual grains of smokeless powder were added to a small porcelain bowl and carefully burned under a hood using a Worthington Pro Grade propane torch. Caution was taken as the bowls became very hot. Once the bowls cooled off, 1 mL of acetone was added to each bowl, and the solutions were then transferred to glass vials. For the testing of the burnt residue, the concentration of each sample was calculated by dividing the weight of the burnt residue by the total volume of acetone added. Three different concentrations per mission mode were tested.

3. RESULTS & DISCUSSION

3.1 Validation Testing of JDX Files in Explosives Hunter Mode

As previously mentioned, four of the OGSR targets were analyzed in Explosives Hunter mode to create JDX files. When creating the JDX files for each of the OGSR targets, peaks were chosen as required or optional. Once these custom targets were imported into the on-device libraries, validation testing of the new targets was conducted. All targets were tested in their respective solutions, except NQ, where tertiary and quaternary swabs of the solid powder were prepared due to its insolubility in volatile organic solvents. Each target was tested in triplicate at three concentrations, ensuring that the SNR was above 25. The alarm rates were calculated (Table 2). To continue the experiment, a correct percentage of 80 or above was needed, meaning that the target tested needed to have a combined correct alarm percentage of at least 80%.

Table 2. Validation Testing of OGSR targets in Explosives Hunter Mode.

Chemical	**True Positive Red Alarm (Percent)**	**True Positive Yellow Alert (Percent)**	**False Positive Alarms (Percent)**
NQ	11.11%	88.89%	Red Alarm - Black Powder (88.89%)
EC	100%	N/A	N/A
DBP	11.11%	88.88%	Yellow Alert - EC (55.55%) Red Alarm - EC (33.33%)
DPA	88.89%	11.11%	N/A

The raw data generated from the device was analyzed using the 908 Devices DataViewer software. Mass spectral data and additional telemetry not shown on the device can be analyzed using this software. This software shows signal intensity by time or frame number, a heat map that displays the intensity of an ion over time, and mass spectral data during each frame. Within the spectra, specific colors differentiate the aperture voltage at which that ion was created. As previously mentioned, the aperture voltage ranges for Explosives Hunter Mode are 25V to 45V and collects in both positive and negative modes.

3.1.1 Nitroguanidine

During the validation test in Explosives Hunter Mode, NQ had many peaks to choose from due to its ability to fragment well (Table 3). Each event was analyzed, and the peaks which were the most prominent across all events were chosen to be required for an alarm. Peaks which were observed at lower levels and could be seen in most but not all events were chosen to be optional. The more peaks that are designated as required, the greater the specificity of the target.

Table 3. Peaks chosen at various voltages for Nitroguanidine JDX file creation in Explosives Hunter Mode.

CID Voltage	**Ionization Mode**	**Required Peaks**	**Optional Peaks**
45 V	Negative	95.5 m/z	N/A

25V	Negative	193.4 m/z	221.1 m/z
25V	Positive	97.5 m/z , 199.4 m/z	199.6 m/z

NQ was the only target that was not dissolved in solution. As a result, secondary, tertiary, and quaternary swabs were created to achieve varying signals. The validation samples from NQ often yielded a yellow alert for NQ and a red alarm for black powder (Table 3). Black powder is a mixture of charcoal, sulfur, and potassium nitrate. When working in high-threat situations, a false positive such as this is not desirable. NQ and black powder are not structurally similar, but their fragments have similar molecular weights of around 95 m/z. The similarities of their reference spectra can be seen in Figure 11. The JDX for black powder only has one required peak, making it less specific, so any compound with a peak in that voltage subscan may alarm for black powder. While many of the events false alarmed for black powder, NQ still successfully alarmed or alerted for itself in each event.

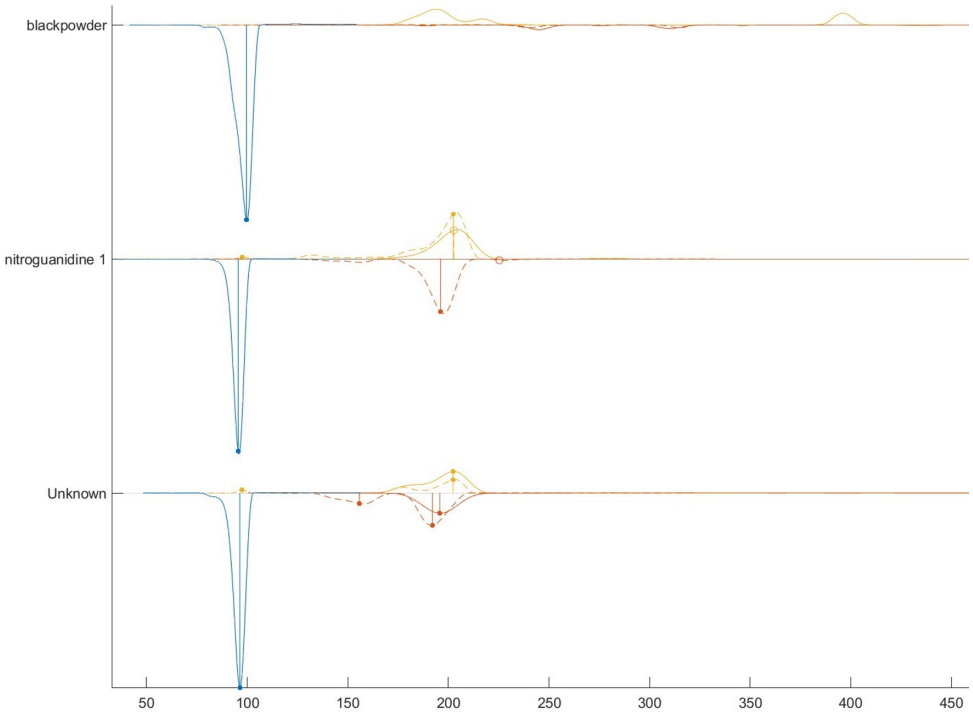

Figure 11. Mass spectra results from validation testing of NQ in Explosives Hunter showing reference spectra of the two compounds that alarmed: black powder (top), nitroguanidine (middle), and the pure powder sample of NQ (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.1.2 Ethyl Centralite

Unlike NQ, EC did not fragment well, meaning there was not enough voltage to cause significant fragmentation of the molecule, ultimately generating very few peaks (Table 4). EC did not fragment in the negative ion mode and only produced a few low-level fragmentation peaks in positive mode. The JDX file for EC therefore could not be made as specific as other OGSR targets.

Table 4. Peaks chosen at 25V for Ethyl Centralite JDX file creation in Explosives Hunter Mode.

Voltage	**Ionization Mode**	**Required Peaks**	**Optional Peaks**
25V	Positive	271.9 m/z	130.9 m/z, 185.5 m/z , 272.2 m/z

During the validation tests for EC, there were all true red alarm positives and no false positives (Table 1). The mass spectral data of EC exhibits the peak similarity between a sample that was tested in comparison to the JDX reference spectrum (Figure 12.)

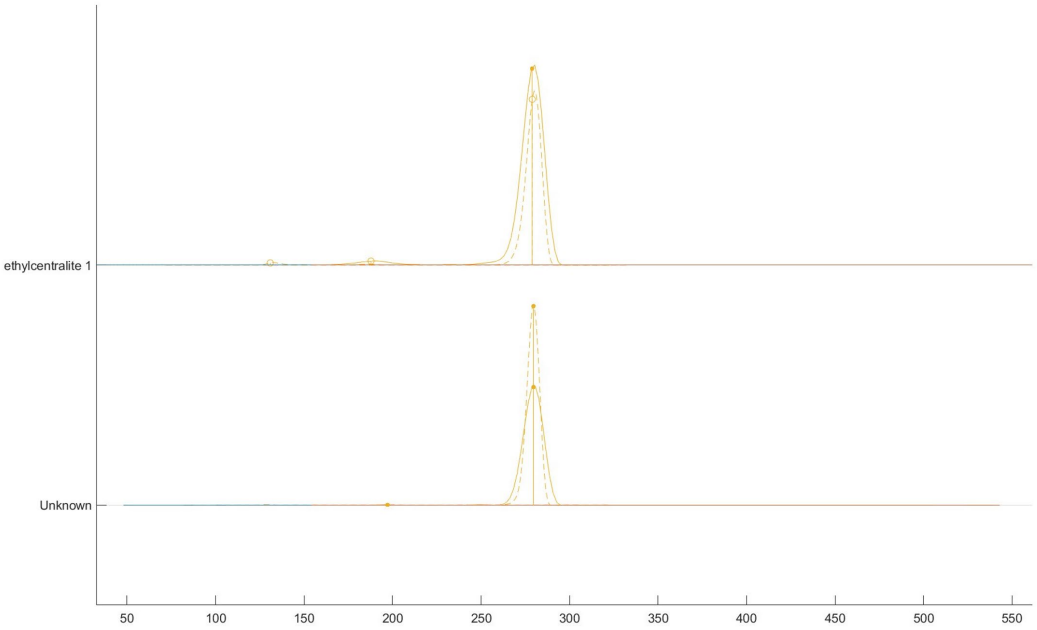

Figure 12. Mass spectra results from validation testing of EC in Explosives Hunter showing mass spectra of the compound that alarmed: ethyl centralite (top), and the diluted sample of EC (bottom). Peaks were ordered by voltage with m/z on the X axis and peak intensity on the Y axis.

Due to the lack of fragmentation of EC, there were limited options on the peaks that could be chosen for the JDX file. A reduced number of peaks within the reference spectrum resulted in reduced specificity, evidenced by some of the other OGSR targets false alarming for EC during the validation testing. Due to this, it was relevant to test the targets in both CWH and EH modes.

3.1.3 Dibutyl Phthalate

The CID voltage applied in EH mode was not sufficient for DBP to fragment effectively (Table 5). DBP did not have any significant peaks at 45V (negative ion mode) and had a few at 25V (positive and negative modes).

Table 5. Peaks chosen at various voltages for Dibutyl Phthalate JDX file creation in Explosives Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
25V	Negative	N/A	224.6 m/z, 227.5 m/z
25V	Positive	276.1 m/z	153.0 m/z

The data for DBP had many events that had a true positive yellow alert for DBP. There were also some false positive yellow or red alarms for EC (Table 2). These targets are not similar in chemical structure, but they are relatively close in molecular weight, with EC being 268.4 g/mol and DBP being 278.34 g/mol. Due to this, the required peaks

for both EC and DBP are in similar ranges, causing both EC and DBP to alarm, as shown in Figure 13.

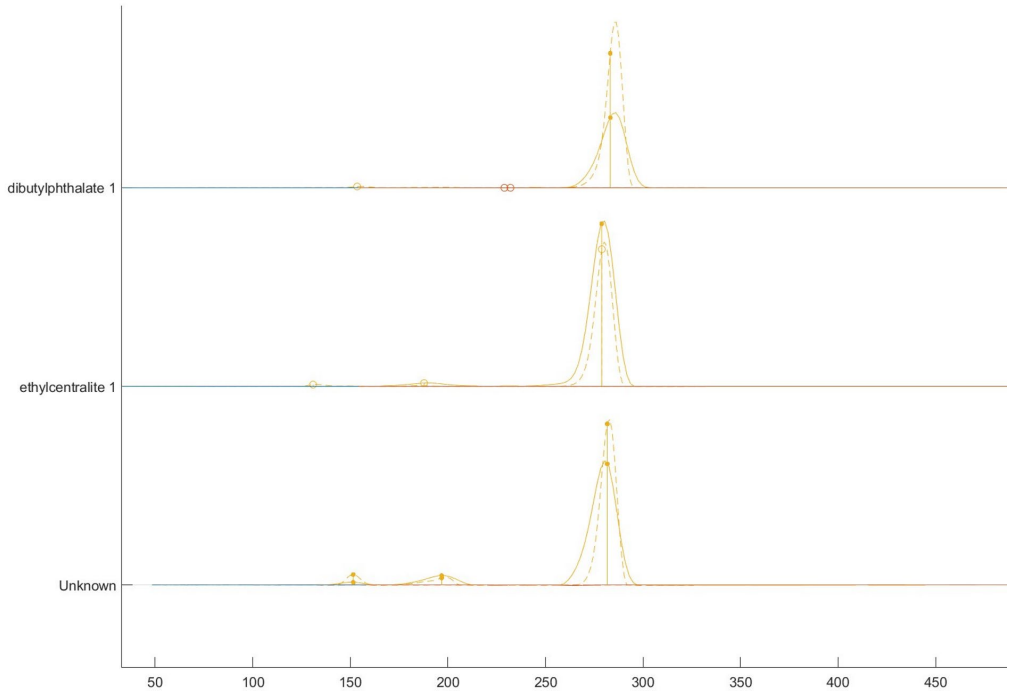

Figure 13. Mass spectra results from validation testing of DBP in Explosives Hunter showing reference spectra of the two compounds that alarmed: DBP (top), EC (middle), and the diluted sample of DBP (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.1.4 Diphenylamine

DPA fragmented well (Table 6). This resulted in a JDX with greater specificity, which alarmed correctly for 100% of DPA validation samples. No false positives were observed in this data set.

Table 6. Peaks chosen at various voltages for Diphenylamine JDX file creation in Explosives Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
45 V	Negative	N/A	83.2 m/z
25V	Negative	N/A	184.9 m/z, 235.7 m/z
25V	Positive	176.2 m/z	125.4 m/z, 174.6 m/z, 235.7 m/z

The mass spectral data of DPA seen in Figure 14 exhibits the peak similarity between a sample that was tested in comparison to the JDX reference spectrum.

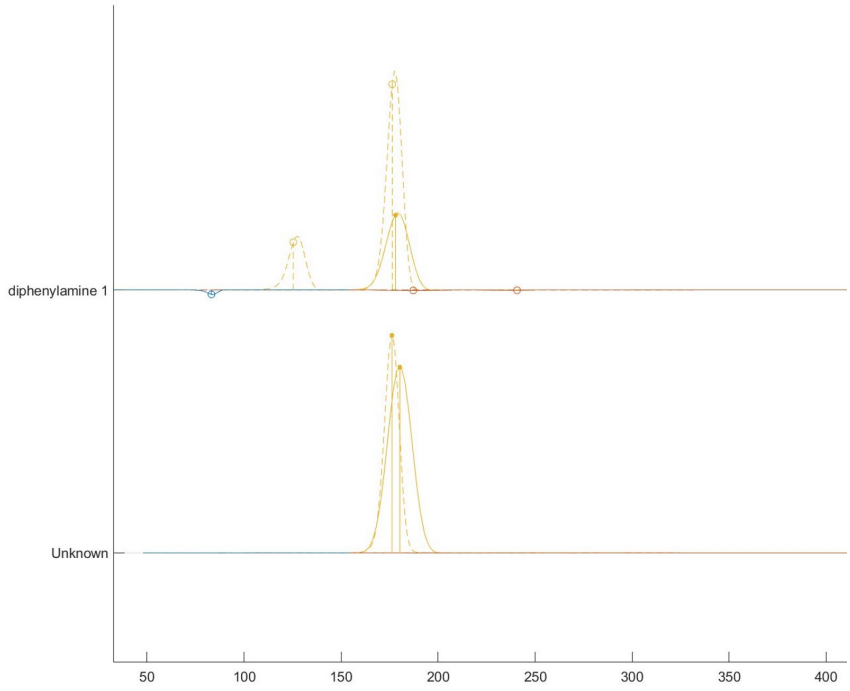

Figure 14. Mass spectra results from validation testing of DPA in Explosives Hunter showing reference spectra of the compound that alarmed: diphenylamine (top), and the diluted sample of DPA (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.2 Validation Testing of JDX Files in Chemical Warfare Hunter Mode

When doing preliminary testing of the targets, it became apparent that some targets fragmented better in the CWH mode than in EH mode. Due to this, a library of the targets was created in both modes. The aperture voltage ranges for Chemical Warfare Hunter Mode are 25V to 65V and collect in both positive and negative modes.

Mimicking the testing performed in EH mode, each target was tested in triplicate at three concentrations, ensuring that the SNR was above 25. The results were analyzed, and percentages were calculated (Table 7). To continue the experiment, a true positive rate of 80% or above, meaning at least seven out of nine samples, was required. The 908 Devices DataViewer software was used to analyze each event.

Table 7. Validation Testing of OGSR targets in Chemical Warfare Hunter Mode.

Chemical	**True Positive Red Alarm (Percent)**	**True Positive Yellow Alert (Percent)**	**False Positive Alarms (Percent)**
NQ	100%	N/A	N/A
EC	100%	N/A	Red Alarm - DBP (25%)
DBP	100%	N/A	N/A
DPA	100%	N/A	N/A
NG	100%	N/A	N/A

3.2.1 Nitroguanidine

As with Explosives Hunter, NQ had many peaks to choose from due to its adequate fragmentation at all voltages (Table 8). NQ had a 100% true positive red alarm

percentage, meaning all nine of the samples that were tested had a true positive result. This OGSR compound did well within this mission mode in comparison to the EH mode.

Table 8. Peaks chosen at various voltages for Nitroguanidine JDX file creation in Chemical Warfare Hunter Mode.

CID Voltage	**Ionization Mode**	**Required Peaks**	**Optional Peaks**
25 V	Negative	101.7 m/z	N/A
25V	Positive	103.0 m/z, 202.2 m/z	201.6 m/z
65V	Positive	N/A	100.2 m/z

Black powder was not a target in this mission mode so there was no possibility of a false alarm. Although all events alarmed for NG, the mass spectral data shown in Figure 15 was still analyzed, showing peak similarity between the sample that was tested in comparison to the JDX reference spectrum.

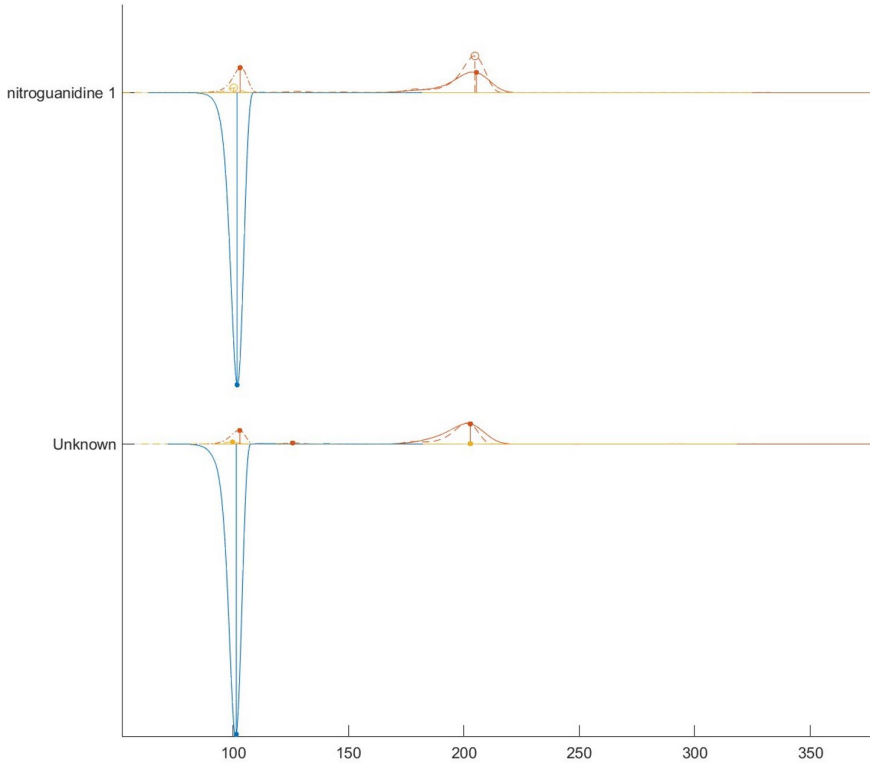

Figure 15. Mass spectra results from validation testing of NQ in Chemical Warfare Hunter showing mass spectra of the compound that alarmed: nitroguanidine (top), and the pure powder sample of NQ (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.2.2 Ethyl Centralite

Once again, EC did not adequately fragment (Table 9). EC did not generate any fragments in negative ion mode but fragmented slightly more at the higher voltages in positive ion mode. Due to this, it may be necessary to test EC at higher CID voltages and consider creating a mission mode specific to OGSR.

Table 9. Peaks chosen at various voltages for Ethyl Centralite JDX file creation in Chemical Warfare Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
25V	Positive	273.6 m/z	N/A
65V	Positive	N/A	94.1 m/z, 140.6 m/z

A red alarm for EC occurred in all the events, therefore the data was sufficient to continue further testing (Figure 16). There were red alarms for DBP as well as EC in a couple of the events (Table 7). This most likely occurred due to EC's JDX not being very specific, as well as EC and DBP having similar molecular weights.

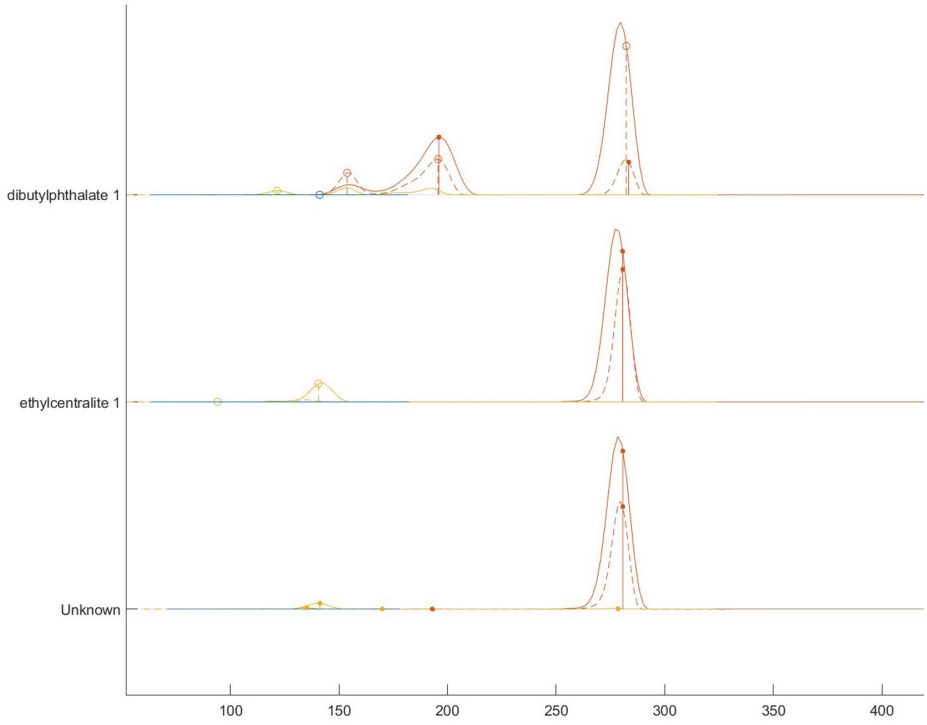

Figure 16. Mass spectra results from validation testing of EC in Chemical Warfare Hunter showing mass spectra of the compounds that alarmed: dibutyl phthalate (top), ethyl centralite (middle), and the diluted sample of EC (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.2.3 Dibutyl Phthalate

DBP had many peaks in positive ionization mode to choose from (Table 10). DBP had a 100% true positive red alarm, meaning all nine of the samples that were tested had a true positive result. This OGSR compound had a lot more fragmentation observed in this mission mode than EH mode. The mass spectral data seen in Figure 17 for DBP was analyzed, and there was peak similarity between the sample that was tested in comparison to the JDX reference spectrum.

Table 10. Peaks chosen at various voltages for Dibutyl Phthalate JDX file creation in Chemical Warfare Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
25V	Positive	276.3 m/z	149.0 m/z, 193.0 m/z, 275.2 m/z
65V	Positive	189.3 m/z	121.5 m/z, 152.2 m/z

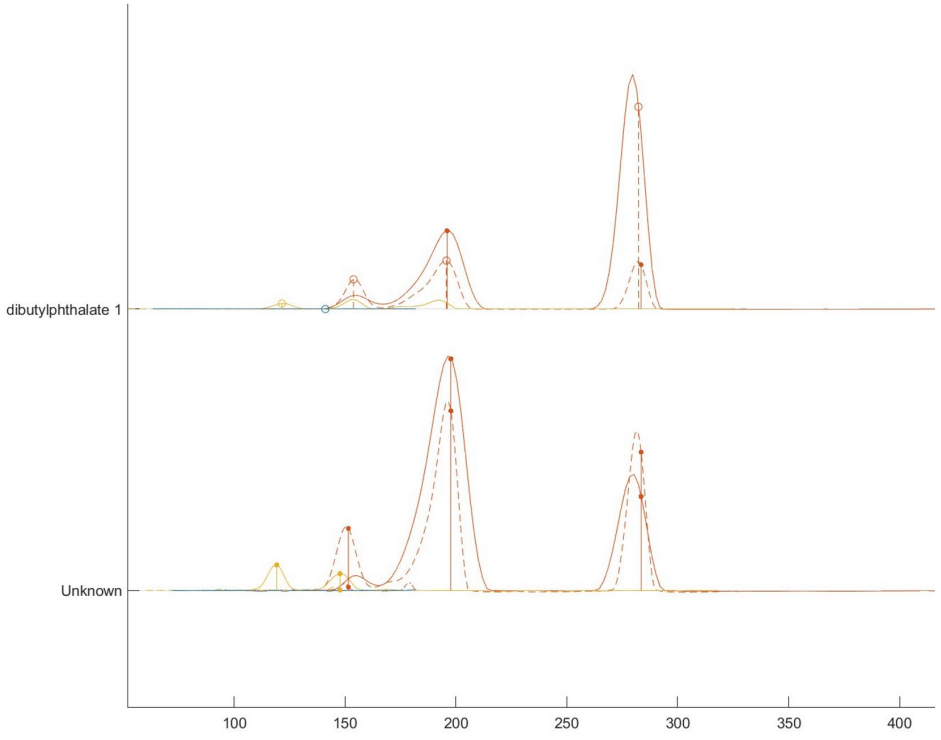

Figure 17. Mass spectra results from validation testing of DBP in Chemical Warfare Hunter showing reference spectra of the compound that alarmed: DBP (top), and the diluted sample of DBP (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.2.4 Diphenylamine

The aperture did not apply enough voltage to cause adequate fragmentation with DPA, so multiple peaks were chosen in a similar m/z range (Table 11). Although there was not a lot of fragmentation, DPA showed peaks at each voltage, increasing specificity.

Table 11. Peaks chosen at various voltages for Diphenylamine JDX file creation in Chemical Warfare Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
25 V	Negative	N/A	167.1 m/z
25V	Positive	168.6 m/z, 177.0 m/z	175.2 m/z, 193.5 m/z
65V	Positive	N/A	93.9 m/z, 173.8 m/z

As with the other targets, the mass spectral data was analyzed for DPA (Figure 18). Since there was not a lot of fragmentation, there was some concern about false positives of DPA when conducting the smokeless powder testing. This concern will be evaluated in future experimentation.

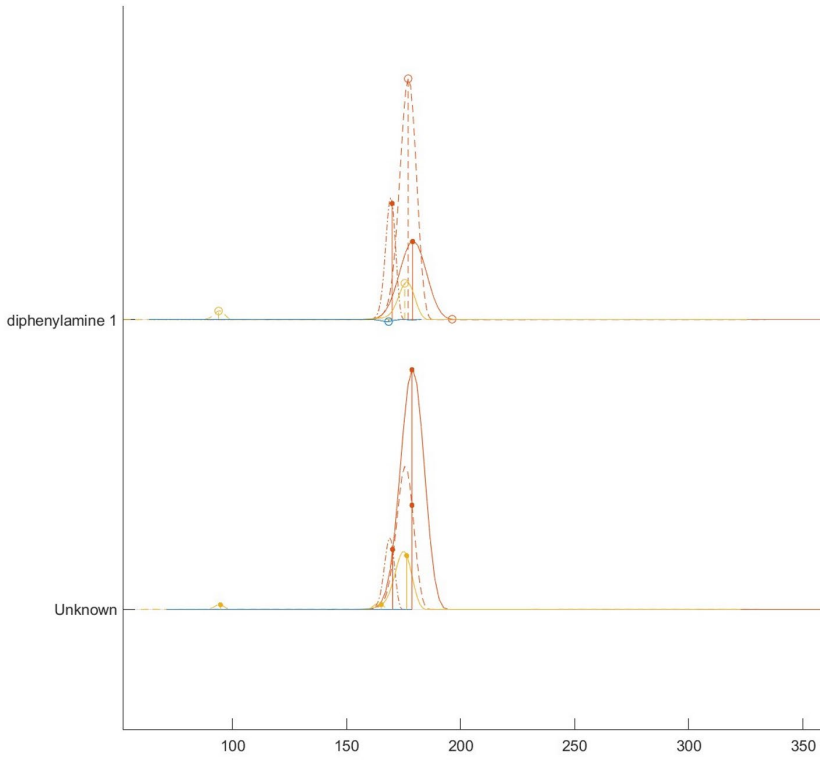

Figure 18. Mass spectra results from validation testing of DPA in Chemical Warfare Hunter showing reference spectra of the compound that alarmed: diphenylamine (top), and the diluted sample of DPA (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.2.5 Nitroglycerin

Due to Nitroglycerin not being a target in CWH, the same methods that were used with the previous targets were also utilized with NG to create a JDX file in this mode. NG did not show much fragmentation but there were enough peaks chosen to distinguish this OGSR component from the others tested in this study (Table 12). Every event had a red alarm for NG during the validation testing, and the mass spectral data seen in Figure 19, was compared to the JDX reference spectrum.

Table 12. Peaks chosen at various voltages for Nitroglycerin JDX file creation in Chemical Warfare Hunter Mode.

CID Voltage	Ionization Mode	Required Peaks	Optional Peaks
25V	Positive	196.1 m/z	N/A
65V	Positive	N/A	94.7 m/z, 120.5 m/z

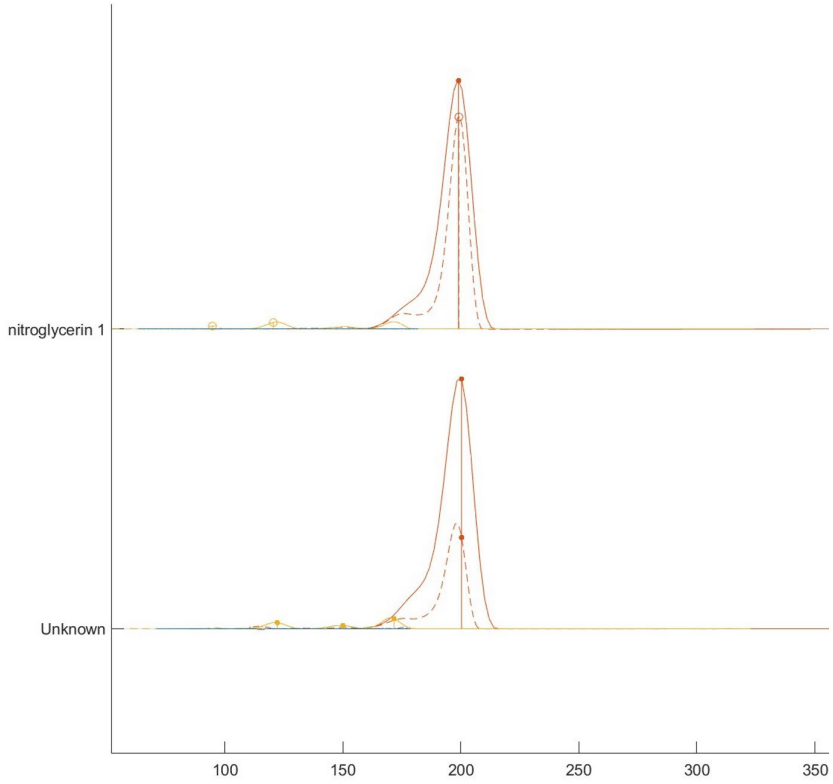

Figure 19. Mass spectra results from validation testing of NG in Chemical Warfare Hunter showing reference spectra of the compound that alarmed: nitroglycerin (top), and the diluted sample of NG (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.3 Smokeless Powder Results

For this part of the experiment, seven different brands of smokeless powder, burnt and unburnt, were tested in both Explosives Hunter and Chemical Warfare Hunter modes. These seven brands were tested due to the variability in morphology and size. Some brands had a rod-shaped morphology while others had a ball and disc shaped morphology. These brands can be found commonly in stores, and they all have various OGSR components. All of the brands chosen were double base, meaning they had NC and NG as OGSR components.

3.3.1 Unburnt Samples Analyzed using Explosives Hunter

Before testing, the Safety Data Sheet (SDS) for each brand was obtained and the OGSR components of each smokeless powder were determined. This was done to compare the results of the alarms and the true OGSR components. The OGSR components written on the SDS also have % weights next to each compound, which were used to help determine why a target may have or have not alarmed (Table 13).

When testing some of these powders, a suspected nitrate alert would occasionally result. This alert indicates that the device detected a nitrate ion at ~62 m/z. Although this alarm can alert users of an energetic threat material such as an explosive, it is not indicative of that energetic threat material. Since nitrate is a naturally occurring ion, additional testing would have to be conducted to determine if a sample contains an energetic threat material. All the brands tested here contained nitrocellulose at a percent weight greater than 50% so an alarm for a suspected nitrate was not unexpected.

Table 13. Results for Unburnt Smokeless Powder Testing in Explosives Hunter Mode.

Brand	**Ingredients (% wt)**	**True Positive Red Alarms (Percent)**	**True Positive Yellow Alerts (Percent)**	**False Positive Alarms (Percent)**
1 - *IMR 7828 Smokeless Powder* [28]	NC (80 - 100) DPA (0.5 - 1.5)	DPA: 100%	N/A	Suspect Nitrate: 100%
2 - *Winchester Western Ball Powder Smokeless Propellant 296* [29]	NC (50 - 100) NG (0 - 42) DPA (0 - 10) EC (0 - 10)	EC: 100%	NG: 33%	Suspect Nitrate: 66%
3 - *Hodgdon, Hornady Lever Evolution Rifle Powder* [30]	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 100%	NG: 66%	Suspect Nitrate: 33%
4 - *Hodgdon, Lil' Gun Shotgun Powder* [31]	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	NG: 100%	N/A	N/A
5 - *Winchester Ball Powder Smokeless Propellant 760* [32]	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 66%	EC: 33% DBP: 100%	N/A

6 - *Reloader 19 Smokeless Heavy Rifle Powder* [33]	NC (60 - 100) NG (5 - 18) DPA (1 - 2) EC (1 - 2)	N/A	DPA: 66% EC: 100%	Suspect Nitrate: 33%
7 - *Red Dot Smokeless Target Shotshell Powder* [34]	NC (60 - 96) NG (30 - 40) DPA (0.1 - 1) EC (0.1 - 1)	NG: 33%	NG: 66%	N/A

For each of the brands, there was at least one OGSR component that had a true positive red alarm or true positive yellow alert. However, some brands such as Brand 4 and Brand 7 only alarmed for one target, NG. For some brands such as Brands 1 and 5 there was consistency on the targets that alarmed, whether it was a red alarm or yellow alert. This could ensure confidence that the device is effective at detecting the same targets each time. On the contrary, Brands 2, 3, and 6 had varying results during the events. This could be problematic on scene because the user will most likely test the unknown sample once. If the device detects different targets each time, then it is hard to have certainty that targets are alarming accurately.

When conducting these experiments, it was also observed that the device never alarmed for more than 2 components even though many of the brands had 2-4 of the OGSR components loaded onto the device. The unknown sample shown in Figure 20 was Brand 1 of unburnt smokeless powder in EH mode. This sample produced many peaks, however only DPA and suspect nitrate alarmed. More testing would need to be conducted at various concentrations to determine the reason why some components such as NC

failed to alarm and why different results were observed across different events for some smokeless powders.

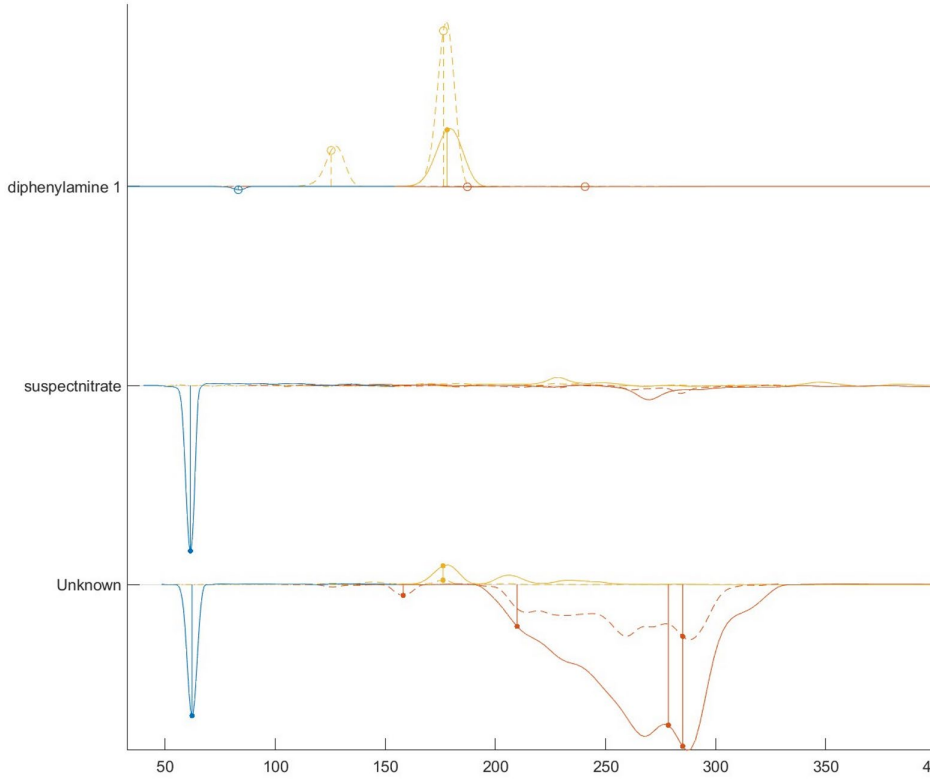

Figure 20. Mass spectra results from the unburnt smokeless powder testing of Brand 1 in Explosives Hunter mode showing reference spectra of the compound that alarmed: diphenylamine (top) and suspect nitrate (middle), and the diluted sample of Brand 1 (bottom). m/z is displayed on the X axis and peak intensity on the Y axis.

3.3.2 Unburnt Samples in Chemical Warfare Hunter

The CWH mission mode did not have a suspected nitrate target, so the goal for this mission mode was to observe if there were similar results between CWH and EH. As in EH mode, the % weight was documented to determine the accuracy between the reported values within the SDS and the device (Table 14). It was observed that there was

less accuracy between the SDS and the device's alarms compared to EH mode. Brands 3 and 6 did well, only having true positive alarms. Brands 4 and 5 both alarmed for DPA although that component was not a part of the OGSR components stated in those SDS. Brand 2 false alarmed for DBP, which was expected based on the validation tests conducted in this mission mode, but DPA was unexpected, and more testing will need to be conducted to determine why it alarmed for this target. There was still variation between events in this mission mode with Brands 1, 3, 4, and 6. As previously discussed, more testing will need to be conducted to determine the reason why this variation existed as well as why no more than 2 targets alarmed.

Table 14. Results for Unburnt Smokeless Powder Testing in Chemical Warfare Hunter Mode.

Brand	**Ingredients (% wt)**	**True Positive Red Alarms (Percent)**	**True Positive Yellow Alerts (Percent)**	**False Positive Alarms (Percent)**
1 - *IMR 7828 Smokeless Powder*	NC (80 - 100) DPA (0.5 - 1.5)	DPA: 100%	N/A	No Target Detected: 33%
2 - *Winchester Western Ball Powder Smokeless Propellant 296*	NC (50 - 100) NG (0 - 42) DPA (0 - 10) EC (0 - 10)	EC: 100%		DBP: 100%
3 - *Hodgdon, Hornady Lever Evolution Rifle Powder*	NC (50 - 100) NG (0 - 42) DBP (0 - 10)	EC: 100% DBP: 100%	N/A	N/A

	EC (0 - 10)			
4 - *Hodgdon, Lil' Gun Shotgun Powder*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 33%	N/A	DPA: 100%
5 - *Winchester Ball Powder Smokeless Propellant*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	N/A	N/A	DPA: 100%
6 - *Reloader 19 Smokeless Heavy Rifle Powder*	NC (60 - 100) NG (5 - 18) DPA (1 - 2) EC (1 - 2)	DPA: 100% EC: 33%	N/A	N/A
7 - *Red Dot Smokeless Target Shotshell Powder*	NC (60 - 96) NG (30 - 40) DPA (0.1 - 1) EC (0.1 - 1)	DPA: 100%	N/A	N/A

3.3.3 Burnt Residue Samples in Explosives Hunter

As previously mentioned, to prepare the burnt residue, five individual grains were added to a small porcelain bowl and carefully burned under a hood. Once the bowls were cooled off, 1 mL of acetone was added to the bowl, and the solution was transferred to a glass vial. For the testing of the burnt residue, the concentration of each brand was

calculated by dividing the weight of the powder by the total volume of acetone added. Three different concentrations per mission mode were tested. The burnt residue was tested because this will most likely be encountered on scene more than unburnt smokeless powder. Therefore, it is important to have an accurate and reliable method to detect these targets. As with the unburnt samples, the ingredients and % weight were documented (Table 15). However, since this was a residue, some of the components may have been consumed in the burning process.

Table 15. Results for Burnt Smokeless Powder Testing in Explosives Hunter Mode.

Brand	**Ingredients (% wt)**	**True Positive Red Alarms (Percent)**	**True Positive Yellow Alerts (Percent)**	**False Positive Alarms (Percent)**
1 - *IMR 7828 Smokeless Powder*	NC (80 - 100) DPA (0.5 - 1.5)	N/A	N/A	No Target Detected: 33% Suspect Nitrate: 66%
2 - *Winchester Western Ball Powder Smokeless Propellant 296*	NC (50 - 100) NG (0 - 42) DPA (0 - 10) EC (0 - 10)	N/A	EC: 100%	N/A
3 - *Hodgdon, Hornady Lever Evolution Rifle Powder*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 100%	N/A	N/A

4 - *Hodgdon, Lil' Gun Shotgun Powder*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	N/A	NG: 33%	Suspect Nitrate: 66%
5 - *Winchester Ball Powder Smokeless Propellant*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 66%	EC: 33% DBP: 33%	N/A
6 - *Reloader 19 Smokeless Heavy Rifle Powder*	NC (60 - 100) NG (5 - 18) DPA (1 - 2) EC (1 - 2)	N/A	N/A	No Target Detected: 33% Suspect Nitrate: 66%
7 - *Red Dot Smokeless Target Shotshell Powder*	NC (60 - 96) NG (30 - 40) DPA (0.1 - 1) EC (0.1 - 1)	N/A	NG: 100%	N/A

Similar to the results for the unburnt powders in Explosives Hunter, components listed in the SDS versus what alarmed was very accurate. The first observation with these results was that there were many more yellow alerts than red alarms. This could be due to it being a residue, so there was significantly less of each target present. It was also seen that Brands 1 and 6 had events where no target was detected, but a target alarmed during subsequent testing. This initial result would be concerning on scene due to it being a false negative. Brands 2 and 3 only alarmed for one of their components as opposed to two with the unburnt samples. This again can be attributed to the sample being a burnt residue.

3.3.4 Burnt Residue Samples in Chemical Warfare Hunter

As with the other samples, the % weight and alarms were noted (Table 16). Similar to the results of the unburnt samples, there was less consistency between the SDS and the device's alarms in CWH mode compared to EH mode. Brands 3 and 5 did well with 100% true positives. Once again, Brand 4 false alarmed for DPA, and Brand 2 alarmed for DBP. There was still variation between events in this mission mode with Brands 2, 4, and 7. No targets were detected during any of the events for Brands 1 and 6. More testing should be conducted to determine why there was so much variation between the alarms in the different mission modes and why there is variation between events for some brands.

Table 16. Results for Burnt Smokeless Powder Testing in Chemical Warfare Hunter Mode.

Brand	**Ingredients (% wt)**	**True Positive Red Alarms (Percent)**	**True Positive Yellow Alerts (Percent)**	**False Positive Alarms (Percent)**
1 - *IMR 7828 Smokeless Powder*	NC (80 - 100) DPA (0.5 - 1.5)	N/A	N/A	No Target Detected: 100%
2 - *Winchester Western Ball Powder Smokeless Propellant 296*	NC (50 - 100) NG (0 - 42) DPA (0 - 10) EC (0 - 10)	EC: 100%	N/A	DBP: 33%
3 - *Hodgdon, Hornady Lever Evolution Rifle Powder*	NC (50 - 100) NG (0 - 42)	EC: 100%	N/A	N/A

	DBP (0 - 10) EC (0 - 10)			
4 - *Hodgdon, Lil' Gun Shotgun Powder*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 33%	N/A	DPA: 100%
5 - *Winchester Ball Powder Smokeless Propellant*	NC (50 - 100) NG (0 - 42) DBP (0 - 10) EC (0 - 10)	EC: 100%	N/A	N/A
6 - *Reloader 19 Smokeless Heavy Rifle Powder*	NC (60 - 100) NG (5 - 18) DPA (1 - 2) EC (1 - 2)	N/A	N/A	No Target Detected: 100%
7 - *Red Dot Smokeless Target Shotshell Powder*	NC (60 - 96) NG (30 - 40) DPA (0.1 - 1) EC (0.1 - 1)	DPA: 33%	N/A	No Target Detected: 66%

4. CONCLUSION

The implementation of the MX908 Mass Spectrometer for the development of detecting OGSR targets in smokeless powder was demonstrated in this study. Currently, no on-site analytical technique for the detection of OGSR exists. As a result, method development for the creation of a technique that is both rapid and accurate is very important. The MX908 demonstrated the ability to detect the targets in the validation studies conducted. There were some issues with the fragmentation of EC specifically, causing the device to generate false positives when testing other samples in both the validation studies and smokeless powder testing. This target will need to be examined more closely in the future.

When conducting the validation studies, CWH mode performed better at fragmenting the target compounds while generating the least number of false positives. All target compounds in CWH mode had a true positive red alarm in 100% of the samples, with EC only having a false positive alarm in 25% of the samples. In EH mode, two targets, EC and DPA alarmed correctly for the intended compound in 100% of the samples with no false positives. DBP and NQ had a 100% true positive alarm and alert, with a few issues of false positives. DBP false alarmed for EC in about 90% of the samples. This was possibly due to similar molecular masses, or due to the fact that EC did not fragment well, causing the reference spectrum to be less specific than it is for other targets. The same thing can be said with NQ. When testing this target, there was a 90% false positive alarm for black powder. After looking closely at the mass spectral data, it could be seen that the JDX file for black powder was only looking for the

identification of one peak. Further testing on the individual components and how to prevent false positives is crucial for furthering method development.

Contrary to the validation testing, when testing the smokeless powders, EH mode had greater accuracy and no false positives. For unburnt smokeless powder, each brand had at least one organic compound alarm or alert in EH mode. During the testing of unburnt smokeless powder in CWH mode, all brands except for Brand 5 had at least one organic compound alarm or alert. Even though this was the case, there was still a lot of variation between events. Overall, the unburnt samples for both EH and CWH had more red alarms than the burnt residue samples. This was expected because as smokeless powder burns, some of the components are consumed. However, it is important to understand what is left over after the burning process so additional testing may be conducted.

4.1 Future Directions

To continue toward the objective of an on-site analytical detection method for OGSR, the next step would be to optimize a method that would become a designated hunter mode for OGSR. This mission mode would provide the best overall fragmentation and signal for all the OGSR targets, as well as a narrowed library. The mission mode would also need to be optimized to increase sensitivity to reduce the “No Target Detected” results for the burnt powder. Further validation testing would also need to be conducted using mixtures of the targets since OGSR can only be identified through a combination of individual components. Accuracy is very important, as we want to

eliminate false positives and false negatives as much as possible. More testing of the smokeless powders at different concentrations should be conducted as well. There was a lot of variation between events observed in this study. Testing of the burnt smokeless powder residue using GC-MS needs to be performed in the future. GC-MS analysis should be performed to determine what components remain after burning, and those results can be compared to the MX908's alarms. Lastly, a study to determine the persistence of OGSR on hands and articles of clothing can be conducted to determine persistence and transferability before conducting real-time testing using GSR evidence within the field.

LIST OF JOURNAL ABBREVIATIONS

Anal Bioanal Chem	Analytical and Bioanalytical Chemistry
Anal Chem	Analytical Chemistry
BioMed Res Int	BioMed Research International
Forensic Chem	Forensic Chemistry
For Sci Commun	Forensic Science Communications
For Sci Int	Forensic Science International
J Forensic Sci	Journal of Forensic Sciences
J Inj Violence Res	Journal of Injury and Violence Research
J Trauma Inj Infect Crit Care	Journal of Trauma: Injury, Infection, and Critical Care
Sens Actuators Rep	Sensors and Actuators Reports

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