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Explosive Residue Transfer from Various Explosive Ordinance Disposal (EOD) Render Safe
Procedures (RSP)

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Abstract

Before an improvised explosive device (IED) is sent to a laboratory for analysis, it needs to be rendered safe if it did not already initiate to ensure the safety of personnel. Render Safe Procedures (RSPs) include utilizing a percussion-actuated non-electric (PAN) disrupter or a fluid filled bottle disrupter. These disrupters utilize solid or liquid projectiles propelled by explosives to disrupt the container or fuzing system of the IED.

If the RSP fails, the IED will explode and only the residue on the IED fragments can be chemically analyzed to ascertain the identity of the explosive. However, since these RSPs also use explosives, they too can impart residue on the IED fragments. Compounds of analytical interest in smokeless powders used in the PAN disrupter include nitroglycerin (NG), diphenylamine (DPA), ethyl centralite (EC), and methyl centralite (MC). The bottle disrupter utilizes a pentaerythritol tetranitrate (PETN) detonation cord.

Before any testing was conducted, the bulk powder used in the shotgun ammunition and detonation cord was analyzed. The powders were then burned onto the various substrates to determine if the compounds would decompose. To test whether RSPs impart residue on IEDs, the disrupters were fired onto inert containers used in IED construction such as pipes and backpacks. These were later analyzed for post-blast residue. All the tests were performed in triplicate.

Instrumentation used in the analysis of the residues included a gas chromatograph/mass spectrometer (GC/MS), a liquid chromatograph/mass spectrometer (LC/MS), and a gas chromatograph with an electron capture detector (GC/ECD). Analysis of the smokeless powder in the PAN disrupter shotgun rounds showed the presence of NG, DPA, and EC. Only PETN was identified in the detonation cord. DPA was consumed when the powder was burned but all other analytes detected in the bulk powder were detected in the burn residue. Two of the three steel pipes rendered safe with the bird shot had detectable amounts of NG and EC. None of the PVC pipes had detectable amounts of NG, EC, or DPA. Trace amounts of PETN were detected on two out the three backpacks. Overall, forensic scientist should be aware that residues found on IED fragments of the backpacks and steel pipes rendered safe using these methods may have originated from the RSP and not the main charge of the explosive device.

Key Words: Explosives, Render Safe Procedure, Smokeless Powder, Pentaerythritol Tetranitrate

Introduction

Since the advent of the internet, the ability to access and exchange a variety of information has become easier. While much of this information is harmless and even helpful, some criminals have used it for nefarious purposes. One such use has been the making of improvised explosive devices (IEDs). Bombings can be commonly seen in the United States with motives ranging from property damage, personal revenge, or terrorism. In 2017 alone, the United States Bomb Data Center reported that 335 bombings occurred in the United States (1).

Each IED has two main components: a fuzing system and explosive (2). The fuzing system initiates the explosive and is a critical component to disrupt when rendering a device safe (2). In addition, the explosive and fuzing system can be inside of containers such as pipes, pressure cookers, bottles, or backpacks (2). These are commonly seen with low explosives which deflagrate and need to be confined in order to produce an explosion (2). Examples of low explosives include smokeless powders, flash powder, and black powder (2). Since high explosives detonate, they do not need to be placed into a container (2). Examples of high explosives include pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), nitroglycerine (NG), nitrocellulose (NC), and cyclotrimethylenetrinitramine (RDX) (2).

Both the explosive material and fuzing system can be forensically analyzed to help connect an individual to it. If the device remains intact, recovery of these components and explosives is fairly simple. However, in post blast scenes, collection can be tedious and challenging as the explosive laden fragments of the IED can be scattered across large distances. Explosives recovered at a scene can be divided up into two categories: bulk powder and trace residue. With bulk powder, enough material is present where there are few challenges to the interpretation of the data and a high amount of confidence with the conclusion. However,

with trace residue, the amount of explosives present is low in quantity. Thus interferants from the environment or from render safe procedures (RSP) can potentially complicate forensic analysis and the resulting data interpretation.

Render Safe Procedures and Disrupters

Before the fuzing system or powder can be analyzed at the laboratory, the IED must be rendered safe if it did not already explode or initiate. This ensures the safety of civilians, law enforcement, and the forensic scientist who will analyze its components and explosives. One tool utilized by bomb squads to render safe IEDs is the percussion-actuated non-electric (PAN) disrupter (3). The primary components of this disrupter include a barrel that accepts shotgun ammunition and a stand to mount and aim the barrel (3-4). Either water or a solid projectile can be propelled down the barrel (3-4). The disrupter can disable the circuitry of an electrical fuzing system by destroying the batteries, wires, and switches (3). It can also open containers for further examination by the bomb technicians to help them make further assessments on how to proceed with rendering the device safe (3). Opening the container also renders the device safe if a low explosive was used since the explosive would no longer be under confinement (3).

Another disruption device is a fluid filled bottle disrupter (5-6). One example of this disrupter is a plastic bottle that is filled with water and a detonation cord made of PETN (5-6). The water is used to produce a jet to disrupt the circuitry of the IED and can even be configured into a particular shape with the setup of the charge (5-6). Because water is the main substance performing the work, this disrupter is only used to disrupt soft skinned containers.

During the RSP, an IED can successfully be rendered safe or it could initiate in the process. Sufficient energy needs to be applied to perforate the container (7). However, the initiation of a device can occur due to the compression force of the disrupter imparting enough

kinetic energy to cause an increase in temperature and setting off the explosive (8). The rapid rise in pressure accompanied by the impact force from the solid projectile or water can also impart enough energy and lead to detonation (7). If this is performed properly, the container will rupture and the explosive will not initiate. The main charge can then be collected for forensic analysis. If an IED explodes, most of the time, only residue evidence will be left.

Smokeless Powder and Gunshot Residue

Smokeless powders constituted the fourth most common explosive used for the main charge of IEDs in the US for 2017 (behind pyrotechnics, black powder, and flash powder) (1). In addition to being commonly used as the main charge of an IED, smokeless powder is also used in the ammunition in some RSPs, such as the PAN disrupter. A multitude of compounds can be extracted from smokeless powder and analyzed with a wide variety of instrumentation (1). Energetics used in smokeless powder include: NC, NG, and nitroguanidine (NQ) (2, 9-17). The composition of energetics will depend on the type of smokeless powder. Single base smokeless powder will only have NC, double base will have NC and NG, and triple base will have NC, NG, and NQ (2, 9-12, 14-17). Various stabilizers are added to help extend the shelf life of the powder by preventing the breakdown of NC and NG (2, 9-15,16-19). These include diphenylamine (DPA), ethyl centralite (EC), and methyl centralite (MC) (2, 9-15, 17-19). MC and EC also act as deterrents that reduce the burning rate and flame temperature (2).

Analysis of these components in bulk smokeless powder present less of a challenge compared to residue. The powder can be extracted in an organic solvent such as methylene chloride or methanol (20-21). Residue analysis on the other hand can be more challenging since the explosives present are low in quantity. This type of analysis is what is required to assess the deposition of compounds by the RSP used in the field.

Since the PAN disrupter operates similarly to a firearm, the mechanism of how residue is deposited by the RSP is similar to the deposition of gunshot residue (GSR). When the propellant is burned in a round of ammunition, the pressure buildup causes the projectile to be expelled from the cartridge and exit out of the barrel (19). In addition to the physical bullet, vapors and particles escape too, referred to as the plume (19). As the plume travels, it deposits GSR onto nearby surfaces (20). The plume then starts to dissipate the further it travels (20). Fojtásek *et al.* (21) found that no GSR was detected 6 meters away from the shooters position in an open environment and 10 meters away from the shooters position in a closed environment. The difference in distances also show environmental factors play a role in the deposition of GSR. Inorganic gunshot residue (IGSR) arises from the bullet, jacket, and primer while organic gunshot residue (OGSR) arises from both the burned and unburned propellant found in the smokeless powder (9). These organic compounds often travel less distance than the heavier, metallic compounds (22). Because of this, organic compounds can be difficult to detect during the analysis of GSR as distance from the barrel increases.

Analysis of Smokeless Powder Residue

Residue first needs to be swabbed (preferred in the field) or rinsed off (preferred in the laboratory) of the deposition surface and then extracted using an organic or aqueous solvent such as acetone, methanol, acetonitrile, or water (9-11, 18, 23-25). Then the liquid extract from the swab or the extract from the direct rinse can be analyzed with a variety of analytical methods, one of the most common being gas chromatography (GC) with various detection systems. While an electron capture detector (ECD) and flame ionization detector (FID) can be used, the most common detection system is mass spectrometry (MS) since it can ascertain the structural information of the compounds as they are detected (9). Most previous studies have used non-

polar capillary columns that were between 15 m and 30 m long and contained stationary phases of either 100% dimethylpolysiloxane or 5% phenyl-methylpolysiloxane (12-16, 21). The temperature gradients varied while the quadrupole mass spectrometers utilize electron impact ionization (13-16, 21). Muller *et al.* (13) were able to detect NG, DPA, and EC with their method but did not address the detection of MC. This could possibly be due to MC not being commonly found in smokeless powders as Joshi *et al.* (12) found only 8% of powders contained MC and the smokeless powder database from SWGFEX (26) found MC was only in 5.9% of the 831 powders tested. EC, NG, and DPA are more commonly found in smokeless powders with 91.8% of the 831 powders in the database containing DPA, 62.8% containing NG, and 50.8% containing EC (26). However, Speers *et al.* (14) were able to detect DPA, EC and MC with their method.

Liquid chromatography with various detection systems are also commonly used to analyze smokeless powders. Common detectors used include ultraviolet (24), pendant mercury drop electrode (PMDE) (14), quadrupole trap (QTrap) (23, 27), quadrupole time of flight (QTOF) (11,17), or a triple quadrupole (QQQ) mass spectrometer (10, 18, 24-25). Most methods used reverse phase liquid chromatography with a C18 column but some have switched out the C18 column for a biphenyl column (10-11, 17-18, 23-25, 27-28). The mobile phases also varied with methanol, aqueous ionization aids, and acetonitrile being the most common (10-11, 17-18, 23-25, 27-28). Formic acid and ammonium acetate can be added to help with the ionization process (10-11, 17, 23, 25). While mass spectrometry can be used to determine mass information, the ionization mode needs to be switched if both stabilizers and energetics need to be detected (9). Taudte *et al.* (18) was able to detect DPA, EC, MC, and NG using a QQQ detector while switching between positive and negative ion modes. Gassner *et al.* (17) on the

other had was only able to detect DPA, EC, and MC with their QTOF and QTrap since they were only operating in positive ion mode.

Analysis of High Explosive Residue

Unlike smokeless powder, high explosives are not as prevalent in the United States due to the lack of accessibility. While PETN is not typically used as the main charge of an IED (only 6 seen in 2017), it is widely used in detonators, blasting caps, and detonation cord (1-2). However, it is also widely used in RSPs compared to other high explosives. PETN does require different analysis procedures for analysis compared to smokeless powder due to its thermal degradation and extensive fragmentation in GC/MS (9, 29). GC/ECD can be used for the separation and detection of PETN and other high explosives. The columns are usually shorter than typical GC/MS columns (6 m to 15 m) (28-30). In addition, 5% phenyl-methylpolysiloxane columns are used since RDX co-elutes with PETN on a 100% dimethylpolysiloxane column (30). The Environmental Protection Agency (EPA) was able to separate NG, TNT, PETN, RDX, cyclotetramethylenetetranitramine (HMX), and tetryl among other compounds with their method (30). Wash M. (29) was also able to separate out PETN from other high explosives using a similar method to the EPA's method.

In addition to GC/ECD, LC/MS has been used to analyze high explosives like PETN since there is little worry about thermal degradation (11, 24-25, 31-32). A UV detector cannot be used since PETN does not absorb UV light (31). Similar to smokeless powder, reverse phase LC with a C18 column is used with various mobile phases ranging from methanol, acetonitrile, and aqueous ionization aid (11, 24-25, 31-32). Benito *et al.* (11) and Taudte *et al.* (24) were able to separate out PETN from other high explosives like RDX, TNT, NG, and common compounds in smokeless powders like MC, EC, and DPA using LC/MS.

Goals and Objectives

While all of the methods above are valuable in identifying low explosive and high explosive residues that are present, sources other than the main explosive charge may have contributed to the residue left on the substrate. Most notably, the disrupters used to render IEDs safe utilize explosives. These explosives have the potential to leave their residue on the IED fragments. The PAN disrupter acts similarly to a firearm and can impart OGSR on a substrate. The high explosive from the fluid filled bottle disrupter can also be deposited on the fragments of the IED. The primary goal of this paper is to address the presence of residue in various RSP procedures used by bomb technicians on various substrates.

Research Materials and Methods

The project was divided into four different stages. The first stage involved developing a new method on the LC/MS to analyze the stabilizers EC, MC, and DPA along with the energetic compound NG. In the laboratory where this research was conducted, DPA was found to irreversibly bind to the column when the current method was used to separate out bulk smokeless powder standards. The second stage involved removing the explosives from the shotgun shells and detonation cord used in the RSPs to analyze the bulk powder. The third stage consisted of artificially burning the powder onto substrates and analyzing the residue left in order to determine if any of the compounds were fully consumed. This can help predict which compounds might be present in the residue after the powder is burned in the RSP. The final stage had mock IEDs rendered safe using three RSPs to determine if any residue is left on the container of a mock IED. The three disruption methods used were: a PAN disrupter utilizing a blank shotgun round and water column, a PAN disrupter utilizing a shotgun round filled with a solid projectile, and a Mineral Water Bottle disrupter using a detonation cord.

Chemicals, Materials, Instruments Used

The DPA standard was obtained from Acros Organics while the MC standard was obtained from Santa Cruz Biotechnology. The EC standard and 2,5-dichlorophenol internal standard were obtained from Aldrich. Both the NG standard and PETN standard was obtained from Cerilliant. The imidazole internal standard was obtained from. Structures of all of the analytes and internal standards are shown in Figure 1. The acetone used in dilutions was HPLC grade and from Fisher Chemical. The methylene chloride used in the bulk powder extraction was obtained from Fisher Scientific. Ammonium nitrate used as the LC ionization aid was obtained from. The analytical grade methanol used in the mobile phase was from Fisher Chemical. The analytical grade acetonitrile used in the mobile phase was from Fisher Scientific.

The LC/MS used in the analysis was Shimadzu LC-20AD Prominence in tandem with a Thermo Scientific LTQ XL. The GC/ECD used was an Agilent Technologies 7890A GC system. The GC/MS used was also an Agilent Technologies 7890A GC system coupled with an Agilent Technologies 5975C inert XL MSD. A VHX Digital Microscope from Keyence Corp was also used for the visualization of individual smokeless powder grains. The PAN disrupter used was made by Ideal Products Inc. The Mineral Water Bottle disrupter was produced by Cherry Engineering, Inc.

Instrumentation Methods

The method developed for the LC/MS to separate out the stabilizers DPA, EC, MC, energetic NG, and the internal standard imidazole utilized a gradient elution with a Phenomenex Kinetex® biphenyl 3.0 mm x 150 mm, 5 μ m column. The mobile phases were 3.125 mM ammonium nitrate ionization aid in deionized water, 100% methanol, and 100% acetonitrile. The methanol composition of the mobile phase was kept at a constant 10% throughout the whole

analysis while the acetonitrile and aqueous portions were varied. The summary of the gradient is shown in Table 1. The flow rate was 0.75 mL/minute with a total separation time of 9 minutes. Electrospray ionization (ESI) was utilized with the polarities being varied based on the analyte elution times. NG is detected under a negative polarity while imidazole, MC, EC, and DPA are detected under positive polarity. The times for the different ionization modes along with the mass ranges detected are shown in Table 2. The times had to be changed for some samples due to maintenance on the LC tubing. These changes are shown in Table 3. This method will be referred to as the biphenyl method throughout the paper

The LC/MS method for the analysis of PETN and other high explosives was already established by the FBI laboratory. An Xterra Waters C18 2.1 mm x 150 mm, 5 μ m column was used as the analytical column. An isocratic elution was used with the mobile phase being 60% methanol and 40% 3.125 mM ammonium nitrate in deionized water. The flow rate was 0.3 mL/min with a total separation time of 10 minutes. ESI was used throughout but two different analyses were completed with varying mass spectrometer methods. The first operated only in negative mode to scan for HMX, RDX, tetryl, PETN, and NG with a mass range of 200-400 m/z. This will be referred as the C18 single scan method throughout the paper. The second method operated in both positive scanning mode (for imidazole) and negative scanning mode (for PETN). This will be referred to as the C18 dual scan method throughout the paper. Table 4 and 5 summarizes the times for the different scanning modes and mass ranges with Table 4 corresponding to the analysis of the RSP residue extracts and Table 5 corresponding to the analysis of the burn test extracts and bulk powder extracts.

The GC/ECD previously established method for analyzing high explosives consisted of using a J&W DB-5ms column 6 m x 0.25 mm with a 0.25 μ m film thickness. The injector

temperature was 225°C using a 5:1 split ratio. The column temperature was held at 50°C for 1.5 minutes followed by a 25°C/min ramp to final temperature of 250°C. The carrier gas used was helium having a flow rate of 3.7 mL/minute. The ECD detector temperature was held at 275°C. The total analysis time was 10 minutes.

The previously established GC/MS method for analyzing smokeless powder utilized a J&W DB-5ms column 30 m x 0.25 mm with a 0.25 µm film thickness. The injector temperature was 170°C and used a 10:1 split ratio. The column was initially held at 45°C for 3 minutes. There was then a 15°C/min ramp to a temperature of 150°C followed another ramp of 40°C/min to a final temperature of 265°C. This final temperature was held for 9.875 minutes. The quadrupole mass spectrometer had a scan range of m/z 41-400.

Analytical Standards

Standards of the analytes and internal standards were analyzed on each of the instruments to determine their retention times and fragmentation patterns. Once individual standards were analyzed, mixtures of the standards were made to ensure separation was successful. The GC/ECD standard mixture was made up of 10 ppm NG, 10 ppm PETN, and 100 ppm 2,5-DCP. The GC/MS smokeless powder standard was made up of 50 ppm DPA, 50 ppm EC, 50 ppm MC, 500 ppm NG, and 100 ppm 2,5-DCP. The high explosive standard mixture analyzed on the C18 column was 10 ppm imidazole and 10 ppm PETN. The smokeless powder standard mixture analyzed on the biphenyl column was 10 ppm NG, 10 ppm DPA, 10 ppm EC, 10 ppm MC, and 10 ppm imidazole. Additional quality assurance/quality control (QA/QC) standards were run on the instruments daily to ensure they were in proper working order.

Bulk Powder Analysis

The two different shotgun rounds used in the PAN disrupter were disassembled and the powder was analyzed. One was a Remington NitroTurkey 12 Gauge 2 oz shot. The other was an

L-Tech Enterprises 12 Gauge EOD blank. A known double base smokeless powder standard (Hodgdon HS-7) was also analyzed with the smokeless powder standards since the smokeless powder standard did not contain NG. In addition, the extraction of the Hodgdon HS-7 powder acted as a positive control to ensure the methylene chloride extraction procedure was successful. Three samples of the smokeless powder within each shell were weighed out for analysis. About 23 mg of the Nitroturkey smokeless powder and three samples of about 15 mg of the L-Tech smokeless powder were weighted out and extracted in 600 μ L of methylene chloride for 2 hours. All extracts and negative controls were then filtered through a 0.2 μ m nylon filter. The concentration of the 2,5-DCP internal standard in all extracts was 100 ppm.

The powder from the detonation cord used in the Mineral Water Bottle was removed. Three samples of about 10 mg of powder were weight out and dissolved into 10 mL of acetone. This was diluted down to 10 ppm and the concentration of the imidazole internal standard was 10 ppm and 100 ppm for the 2,5-DCP internal standard. The samples were analyzed on the GC/ECD and LC/MS (C18 method).

All analytes detected on the GC/MS, GC/ECD, and LC/MS had their peak areas divided by the peak area of the internal standard spiked into the sample. The ratios calculated were then divided by the amount of powder used in each extraction. These calculations were performed to see if there was a consistent amount of the analytes present in each sample within each analysis completed.

Artificial Burn Residue Analysis

Pipe endcaps used for this part were rinsed out twice with acetone before powder was placed into them. The endcaps made from the same material used for each RSP was used in the burn test. The exception was with the Mineral Water Bottle test where PVC endcaps were used

since the powder could not be burned directly onto the backpack. Three samples of each powder weighing about 100 mg were placed in pipe endcaps: the L-Tech smokeless powder and detonation cord powder were placed in separate polyvinylchloride (PVC) endcaps while the Remington NitroTurkey smokeless powder was placed in steel endcaps. A butane torch was used to burn the powders. Three samples of the Remington NitroTurkey and the detonation cord powder were burned while nine samples of the L-Tech powder were burned due to an error with the internal standard for the first set of three and some discrepancies with the compounds detected in the next set of three. The powders were burned and 5 mL of acetone were used to extract the first set of L-Tech PVC samples and Remington NitroTurkey steel samples while 2 mL of acetone were used to extract the second set of L-Tech PVC samples and detonation cord PVC samples in order to concentrate the analytes present in the extract. All extracts were then filtered through a 0.2 μm nylon filter.

The Remington NitroTurkey steel extracts and detonation cord PVC extracts had to be diluted in acetone before being analyzed on the instrumentation. The Remington NitroTurkey extract was diluted 1:7.5. The detonation cord PVC burn extracts were diluted 1:25. The final internal standard concentrations were 10 ppm imidazole and 100 ppm 2,5-DCP. The L-Tech and Remington NitroTurkey samples were analyzed on the GC/ECD, GC/MS, and LC/MS (biphenyl column method) while the detonation cord was analyzed using the GC/ECD and LC/MS (C18 column). The same calculations were completed with the peak area as in the bulk powder analysis.

RSP Residue Setup

All of the mock devices used were not filled with explosives. Three trials were completed for each RSP. The PAN disrupter utilizing a water column propelled by the L-Tech blank was used to render safe a mock PVC pipe bomb. The PAN disrupter utilizing the Remington NitroTurkey round containing bird shot was used to render safe a mock steel pipe bomb. The Mineral Water Bottle disrupter was used against a backpack that was stuffed with paper and two PVC pipes to give it the weight of a mock IED. All test shots were conducted on an explosive's demolition range.

Each of the IEDs were placed in a steel drum so that it could catch the fragments as the device was being rendered safe. A clean steel drum was used in between each of the PVC mock IED and steel mock IED tests to prevent any residue contamination from the previous analysis. Only one steel drum was available for the mock backpack IED tests so a tarp to line the steel drum and was changed in between each sample to prevent contamination from previous analysis. A clean tarp was also placed on the ground for every test to prevent contamination from the soil and the previous shots residue. In addition to the pipes from each test being collected in different bags, the fragments on the tarp and steel drum within each test were separated. Each backpack was also collected in separate bags.

For the PVC IED, the barrel of the PAN was kept at about 6 inches standoff at a 90-degree angle, perpendicular to the pipe. Figure 2 illustrates the PVC pipe before and after it was rendered safe. For the steel IED, the barrel of the PAN was kept parallel to the pipe with the barrel pointed to the back endcap. The distances and angles were a little more varied with Table 6 summarizing the distances and angles. Figure 3 illustrates the steel pipe before and after it was rendered safe. For the backpack IED, the mineral bottle was placed on a sandbag stand for the

first backpack and an ammunition can for the other two backpacks in order to raise the bottle to the midpoint of the backpack. The standoff distance was about 6 inches.

RSP Residue Analysis

All extractions were performed in an explosive trace clean room. The steel pipes and PVC pipes were both rinsed with acetone; steel pipes were rinsed with 8 mL and the PVC pipe fragments were rinsed with 6 mL. Backpacks were vacuumed with a vacuum that had a fiberglass filter attachment. The fiberglass filter was extracted with 1.5 mL of acetone. For backpack 3, the filtered extract was accidentally added into a test tube that was already filled with clean acetone. The acetone was then dried down and the extract was reconstituted with 1 mL of acetone. In addition, a second extract of the initial filter from backpack 3 was completed. A second vacuuming was also performed on backpack 3 and the same extraction procedure for that filter was followed. All extracts were then filtered through a 0.2 μm nylon filter. The extracts were then directly spiked with the internal standards with final concentrations being 10 ppm for the imidazole and 100 ppm for the 2,5-DCP.

The PVC and steel pipe residue extracts were analyzed using GC/ECD, GC/MS, and LC/MS (biphenyl column) while the backpack residue extracts were analyzed using GC/ECD and LC/MS (C18 column). The same calculations that were completed with the other two parts were performed with each of the analytes with the exception that the ratios calculated were not divided by the weight of the powder used since this is an unknown factor.

Research Results and Discussion

Retention times for the standards analyzed on each instrument were determined. The internal standards were chosen based on the retention time of the analytes of interest. 2,5-DCP was detected on the GC/ECD and GC/MS but not the LC/MS. In contrast, the imidazole internal standard was detected on the LC/MS but not the GC/ECD and GC/MS. Imidazole did elute close

to HMX and RDX but this was not an issue since HMX and RDX were not expected to be present. However, since these high explosives are detected in negative mode, a second analysis was completed where the extract was analyzed only in negative mode in order to confirm the presence/absence of RDX and HMX. The 2,5-DCP did not coelute with any analyte of interest. For the GC/ECD analysis, 2,5-DCP, NG, and PETN were well resolved in the chromatogram as shown in Figure 5.

When the smokeless powder standard mixture was analyzed using the GC/MS 2,5-DCP, NG, DPA, MC, EC were successfully separated as shown in Figure 6. The mass spectrum in Figure 7 confirmed that the compound eluting at 9.486 minutes is 2,5-DCP. The molecular ion peak of m/z 163 is equal to the molecular mass of 2,5-DCP. The base peak of m/z 162 (M-H) accounts for the loss of hydrogen from the hydroxyl group. Figure 8 is the mass spectrum that confirms the compound that eluted at 10.981 minute was NG. The molecular ion peak cannot be seen, most likely due to the extensive fragmentation of NG, but the base peak of m/z 46 is equal to NO_2^+ , a possible fragment of NG. The mass spectrum in Figure 9 confirms that the compound that eluted at 12.428 minutes is DPA. This is due to the presence of the molecular ion peak and base peak of m/z 169 is equal to the molecular mass of DPA. The compound that eluted at 13.204 minutes was confirmed to be MC based on the mass spectrum in Figure 10. The molecular ion peak m/z 240 is equal to the molecular mass of MC and the base peak of m/z 106 is equal to the molecular mass of $\text{C}_6\text{H}_5\text{NCH}_3^+$. The final mass spectrum in Figure 11 is the compound that eluted at 13.363 minutes. This was confirmed to be EC based on the molecular ion peak of m/z 268 being equal to the molecular mass of EC and the molecular mass of the $\text{C}_6\text{H}_5\text{NCH}_2\text{CH}_3^+$ fragment being equal to the base peak of m/z 120.

Figures 12 and 13 illustrate a successful separation of high explosives HMX, RDX, tetryl, NG, and PETN utilizing the previously developed C18 single scan method. However, the corresponding mass spectrum in Figure 13 for each compound has a m/z base peak equal to the $[M+62]$. This is due to each of the compounds forming a nitrate adduct from the ammonium nitrate ionization aid used in the mobile phase. Imidazole was detected when the C18 dual scan method was used with its identity being confirmed by the mass spectrum in Figure 14. The m/z value in the mass spectrum was 69, corresponding to $[M+H]$ ion that is formed.

The developed method to analyze smokeless powder using LC/MS was successful with separating imidazole, NG, MC, EC, and DPA. All of the compounds were resolved in the TIC displayed in Figure 15 with the exception of EC and DPA. However, separation was achieved when the EICs for both compounds were extracted from the TIC with their corresponding mass spectra being completely resolved as shown in Figure 16. The base peaks in the corresponding mass spectrum for all of the compounds except NG have a m/z value of $[M+1]$. Similar to the C18 methods, NG forms a nitrate adduct from the ammonium nitrate ionization aid used in the mobile phase so the base peak has a m/z value equal to $[M+62]$. DPA also formed a hydrogen bond with acetonitrile leading to the m/z 211 peak seen in the mass spectrum.

PAN Disrupter Water Column

The powder removed from the L-Tech blank weighed approximately 2.8279 g. Other parts included what appeared to be a cardboard wad and two fibrous wads as shown in the disassembled shell displayed in Figure 17. Through GC/MS analysis, it was determined that the smokeless powder contained NG, DPA, and EC as seen in Figure 18. Each compounds identities were confirmed based on the corresponding mass spectra displayed in Figures 19-22. Based on the ratio calculations displayed in Table 7, there was very little variation between samples 1 and

2 while sample 3 had some slight variation in the relative abundance of NG and EC compared to samples 1 and 2.

The analysis of sample 4 of the burned L-Tech smokeless powder using GC/ECD shown in Figure 23 indicated that NG was present. NG was present in the four samples where it was identified through the GC/ECD analysis as summarized in Table 8. There was a large amount of variation between samples, with sample 5 being two orders of magnitude different from samples 4 and 6 and sample 7 being an order of magnitude different from sample 8.

The EIC and mass spectra in Figure 24 confirmed NG presence in the L-Tech smokeless powder burn residue sample 4 while also identifying EC. While there is a peak that appears in the EIC for MC, the retention time differs from the MC standard. In addition, there are extra peaks at high abundance present in the mass spectrum that differ from the mass spectra of the MC standard. As summarized in Table 9, four out of the six samples had NG present while five of the six had detectable amounts of EC present. In sample 5, a peak with the same retention time as NG was present in the GC/ECD chromatogram, but its identity could not be confirmed through LC/MS. the only evidence of residue being present in sample 5 was the detection of EC. No DPA was detected in any of the samples. There was also a greater amount of variation between samples in these extracts when compared with the bulk powder samples with some of the samples even differing by an order of magnitude.

None of the analytes of interest were detected in any of the other L-Tech smokeless powder burn tests through GC/MS analysis. This was most likely due to the higher limit of detection of the GC/MS when compared to LC/MS or GC/ECD. Figure 30 is an example chromatogram for sample 4, where the only compound of interest detected was 2,5-DCP internal

standard. This eliminated the possibility of instrumental error as a reason why none of the other analytes were detected.

In the residue analysis of the PVC pipe rendered safe using the PAN disrupter and water column, there were no compounds of interest detected in any of the extracts. There were no analytical peaks present in the EIC from the LC/MS analysis displayed in Figure 26. While the other chromatograms are not displayed, the internal standards were identified in each of the chromatograms; therefore, instrumentation error was ruled out as a reason why none of the analytes were detected.

PAN Disrupter Birdshot

The round disassembled, shown in Figure 27, consisted of large polymer pellets weighing 0.7980 g, small polymer powder weighing 0.8674 g, lead birdshot weighing 54.1021 g, and smokeless powder weighing 1.8844 g. The compounds detected in the Remington NitroTurkey smokeless powder through GC/MS analysis shown in Figure 28 are NG, DPA, and EC. The 2,5-DCP internal standard was also detected. The identities of each of the compounds in the smokeless powder were confirmed by the corresponding mass spectra that are displayed in Figures 29-32. Between bulk samples, most of the variation is between NG and EC; primarily with sample 3, as displayed in the summary of the calculations in Table 10. DPA does not vary greatly between samples with sample 1 being the only sample to differ by more than 10%.

Initially, NG was identified in the burn residue for the Remington NitroTurkey powder using GC/ECD analysis as seen in the example chromatogram for sample 1 in Figure 47. The ratio calculations summarized in Table 11 indicate the variation in the amount of NG detected was not as apparent in the GC/ECD results as it was for the L-Tech burn samples. This might be

attributed to the ease of burning the powder more evenly in the steel endcap, as melting the steel endcap with the torch was not a concern.

NG and EC were the only two analytes of interest detected in sample 1 using LC/MS analysis. While there appears to be a peak for the MC in the EIC displayed in Figure 34, that peak was also seen in the negative controls and blanks. This could possibly be due to noise from switching between positive and negative mode since it occurs right at the switch. The mass spectrum also indicated that it was not MC. Table 12 summarizes the calculated ratios for each of NG and EC detected in the Remington NitroTurkey powder burn residue. There is a wider amount of variation among the amount of NG in the samples than the EC. The variation among all of the burn samples also seems to be greater than that of the bulk powder samples. Similar to the L-Tech smokeless powder burn tests, no analytes of interest were detected when the samples were analyzed using GC/MS, with an example chromatogram being displayed in Figure 35.

NG was initially identified on 2 out of 3 pipes rendered safe using the PAN disrupter and Remington NitroTurkey round, with the chromatogram for pipe 1 being displayed in Figure 36. On pipe 1, NG is detected from the sample collected on the tarp but not on the sample collected in the barrel. The summarized ratio calculations in Table 13 indicate the amount of NG present in each sample varies widely when compared to the burn test samples and bulk powder extracts. Pipes 1, 2, and 3 all have NG relative concentrations that differ by an order of magnitude from each other, with pipes 1 and 3 differing by two orders of magnitude.

In the residue analysis, NG was detected on all three pipes rendered safe using the PAN disrupter and Remington NitroTurkey round, while EC was only detected in two out of the three samples using LC/MS analysis. An example EIC and its corresponding mass spectrum for pipe 2 recovered in the barrel is in Figure 37. The amount of each analyte detected varied extensively

among each sample as indicated by Table 14. While NG was detected on pipe 1, it was at a whole order of magnitude lower than the NG detected on pipe 2 and pipe 3. The GC/MS analysis could not confirm the presence of any of the analytes of interest on the pipes as shown in Figure 39. Despite the low amount of residue detected relative to pipes 2 and 3, the mass spectra confirmed the identity of NG with the m/z 289 peak being present as seen in Figure 38.

Mineral Water Bottle

The white powder removed from the detonation cord as shown in Figure 40 was analyzed utilizing GC/ECD with the resulting chromatogram for sample 1 displayed in Figure 41, indicating the presence of PETN. There is some variation between the analytes detected in sample 1 and the other two samples with the variation of analytes detected between samples 2 and 3 being minimal. Despite all solutions being diluted down to 10 ppm, a possible explanation for the variation seen in Table 15 is some variation in the pipetted volumes which had to be rounded in some cases.

The identity of PETN was confirmed when the extract was analyzed using LC/MS as indicated in the EIC and mass spectra shown in Figure 42. The calculated area ratios for each of the samples are summarized in Table 16. The in this analysis there was variation between sample 3 and samples 1 and 2 (which did not vary greatly). This discrepancy could possibly be from area not being as accurately calculated in the LC/MS analysis as the imidazole internal standard does not form a gaussian peak. Therefore, the parts of the peak that encompassed the area had to be guesstimated for each chromatogram which could lead to some inconsistencies due to human error. Further LC/MS analysis as seen in Figure 43, shows PETN was the only high explosive present within the detonation cord powder.

The PETN in the detonation cord powder did not completely degrade or decompose after the powder was burned as it was still initially identified in all three-burn test samples through GC/ECD analysis. Figure 44 is the chromatogram from sample 1 where the PETN peak is present. The values summarized in Table 17 indicate there is a higher amount of variation in the amount of PETN detected between each of the samples when compared to the bulk powder analysis, most likely due to uneven amounts of burning.

The presence of PETN was confirmed through LC/MS analysis. The PETN peak is still present in sample 1 as seen in the EIC displayed in Figure 45. However, even though PETN was detected in all three of the samples, there was much more variation in the amount of PETN present in each sample, summarized in Table 18. This was most likely due to more PETN being consumed by an inconsistent burning process in some of the samples. In addition to PETN being present, it appears there is a peak in the EIC for tetryl and NG but the retention times differ from the tetryl and NG standards; therefore, the peak cannot be identified as tetryl or NG. The C18 single scan method confirmed that HMX and RDX were also not present in the sample.

In the preliminary analysis of the RSP residue from backpacks rendered safe utilizing the mineral water bottle PETN was still able to be detected in some of the backpack samples after GC/ECD analysis. Figure 46 is the chromatogram for backpack 2, where a small PETN peak is present at 6.148 minutes. The presence of PETN was initially identified in backpacks 2 and 3, summarized in Table 19. Backpack 1 had no detectable amounts of PETN present.

Despite the initial screening using GC/ECD, the PETN detected using LC/MS would differ in some ways compared to the GC/ECD results. PETN was identified in two out of three backpacks with an example chromatogram and mass spectrum for the imidazole internal standard and PETN displaying in Figure 47. As indicated in Table 20, PETN residue was present in

backpacks 1 and 2 while PETN was absent in all of the residue extracts from backpack 3.

Despite not being detected in the GC/ECD, the determination that PETN is present on backpack 1 can be confirmed on LC/MS as LC and MS are two orthogonal techniques. Surprisingly, the dried down extract from backpack 3 had detectable amounts of PETN present in the GC/ECD chromatogram. This could possibly indicate that the compound detected in the GC/ECD analysis could have been another compound. Even though PETN was detected in the chromatogram of the dried down extract from backpack 3, it cannot be confirmed through any other analysis, therefore it will be excluded as a positive result. Similar to the LC/MS results, there is a higher amount of variation among sample that were rendered safe when compared to the burn residue and bulk powder analysis.

Discussion of Overall Trends

The widest amount of variation of concentration between samples was in the residue analysis and the least amount of variation was with the bulk powder analysis. This trend is explained by the fact that there is a wider array of factors that affect the deposition of residue compared to any of the other tests. In the bulk powder analysis, the only factor that would affect the variation would be systematic error such as the weighing of the powder or pipetting of the extracts. In the burn test, the extent to which the powder was burned affected the amount of residue left. Evaporation of acetone as the burned residue was being extracted led to variation in the volume of liquid extracted from each sample which could have also played a role in the variation. However, evaporation affected the variation seen in rendered safe pipe residue the most since the pipes were rinsed multiple times with the same aliquot of acetone that had to be replenished a few times. In addition, residue deposition onto the mock IEDs was affected by environmental factors such as the weather, particularly air currents which can affect the plumes

travel direction and therefore, affect where it is deposited. This was unseen in the other two tests that were performed in a controlled, inside environment. Inconsistencies in the setup of the RSP can also affect the deposition of residue on an IED. While the distances and angles of the shots were kept as consistent as possible, a minor deviation could have altered the trajectory of the RSP solid round or water.

Most of the compounds that were detected in the bulk analysis were also detected in the burn residue and RSP residue analysis. The only compound that was completely consumed was DPA. For the Remington NitroTurkey round, the lack of DPA can be explained by the lack of an abundance of DPA in the bulk powder when compared to the other compounds. For the L-Tech shotgun blank, the DPA could have thermally degraded when subjected to the high heat of the butane torch.

Conclusion

As summarized in Table 21, the PAN disrupter that utilized the L-Tech blank left no residue, while the PAN disrupter that utilized the Remington NitroTurkey round left NG and EC residue and the Mineral Water Bottle Disrupter left PETN residue. For the PAN disrupter that utilized the L-Tech shotgun blank and water, finding no residue was surprising. Instrumentation error was ruled out as the internal standard was present in all of the chromatograms. A possible explanation was that the water had potentially washed the residue away. Another explanation was that the residue did not adhere to the PVC pipe. Future research should test the L-Tech RSP on other substrates to see if substrate was the reason no residue was detected or whether it was the RSP itself. Since no DPA was detected in any of the residue cases, future research should also examine the degradation products of DPA such as benzene or aniline or reaction products

such as 2-nitrodiphenylamine, 4-nitrodiphenylamine, or N-nitrodiphenylamine to determine if the DPA was simply broken down by the high heat of the butane torch.

Residue was detected in the other two RSPs: the PAN disrupter that utilized the Remington NitroTurkey rounds and the Mineral Water Bottle disrupter. In each of these groups, two out of three samples had detectable residue present while one of the samples was free of residue. In addition, there was a large amount of variation in the amount of residue present after the RSP compared to the burn test and bulk powder analysis making it difficult to predict the amount of residue that is left by the RSP. Despite the large variation between samples and that only 67% of the samples had residue present, it is advised that examiners should be more conservative with their interpretation. Therefore, examiners should be aware that these render safe procedures could possibly leave residue on the devices. It is then recommended that any results should also include that the residue found could have come from the RSP. However, if analytes other than NG, DPA, EC for the PAN disrupter that utilized the Remington NitroTurkey round or PETN for the Mineral Water Bottle disrupter is detected, then it most likely originated from the main charge of the explosive.

Despite residue being left by two of the three RSPs, there is still room for future experimentation and improvement. The high amount of variation in residue left by the RSP was only based off of the two samples for each RSP. Future experimentation could test a greater number of samples to see if there is a more predictable pattern to the amount of residue left. There are also many other RSP used by bomb technicians. Residues from mock IEDs rendered safe using these other procedures should be analyzed. While future experimentation can give scientist a greater understanding on the amount of residue left by the RSPs, using the current information, forensic examiners will be aware which RSPs leave residue and the compounds that

constitute the residue. This allows for more accurate interpretation of the examination results that can ultimately affect the outcome of the case.

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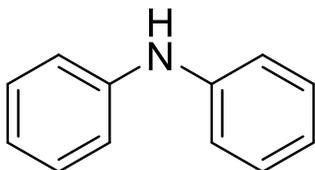
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Acknowledgements

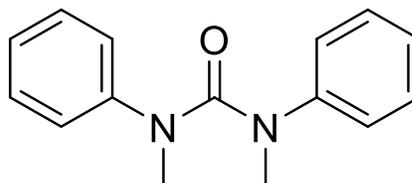
I would like to thank my committee, Supervisory Special Agent Bomb Technician Jason Miller, Associate Teaching Professor Eric Hazelrigg, and Associate Professor Dr. Christopher Ehrhardt for guiding me throughout my directed research. I would also like to thank Dr. Kirk Yeager with his support of this project. Finally, I would like to thank the Federal Bureau of Investigation Laboratory Division's Explosives Unit with providing the laboratory space, explosives demolition range, explosives expertise, equipment, and materials for this project.

Appendix

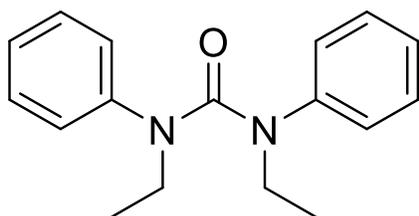
Diphenylamine (DPA)
MW: 169 g/mol



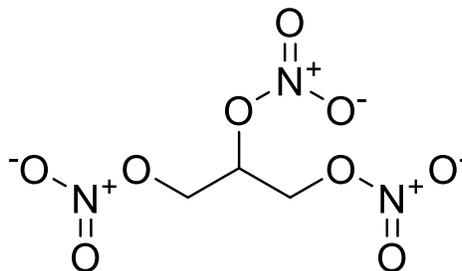
Methyl Centralite (MC)
MW: 240 g/mol



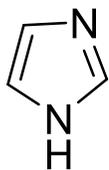
Ethyl Centralite (EC)
MW: 268 g/mol



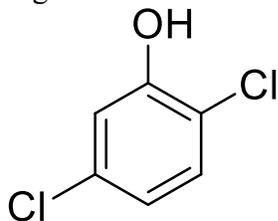
Nitroglycerine (NG)
MW: 227 g/mol



Imidazole
MW: 68 g/mol



2,5-Dichlorophenol (2,5-DCP)
MW: 163 g/mol



Pentaerythritol tetranitrate
(PETN) MW: 316 g/mol

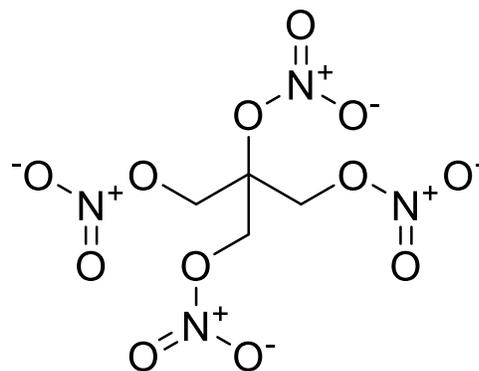


Figure 1: Structures and molecular masses for the analytes of interest and the internal standards

Table 1: Gradient for the separation of DPA, EC, MC, NG, and Imidazole

Time	Acetonitrile	Ammonium Nitrate	Methanol
0.00	30%	60%	10%
0.10	45%	45%	10%
1.50	45%	45%	10%
3.00	55%	35%	10%
5.00	60%	30%	10%
5.10	30%	60%	10%
9.00	30%	60%	10%

Table 2: Scanning modes, mass ranges, and times for the detections of DPA, EC, MC, NG, and Imidazole

Scan Time (Minutes)	Mode	Mass Range
0.00-1.15	+	65-71
1.15-2.55	-	150-300
2.55-9.00	+	150-300

Table 3: Scanning modes, mass ranges, and times for the detections of DPA, EC, MC, NG, and Imidazole after maintenance

Scan Time (Minutes)	Mode	Mass Range
0.00-1.41	+	65-71
1.41-2.55	-	150-300
2.55-9.00	+	150-300

Table 4: Scanning modes, mass ranges, and times for the detections of PETN and Imidazole for the RSP residue samples

Scan Time (Minutes)	Mode	Mass Range
0.00-2.00	+	65-72
2.00-10.00	-	200-400

Table 5: Scanning modes, mass ranges, and times for the detections of PETN and Imidazole for the RSP burn test and bulk samples

Scan Time (Minutes)	Mode	Mass Range
0.00-1.62	+	65-72
1.62-10.00	-	200-400



Figure 2: Before and after the water column was used to disrupt the PVC mock IED. The pieces inside the barrel and on the tarp were collected separately.



Figure 3: Before and after the birdshot was used to disrupt the steel mock IED. The pieces inside the barrel and on the tarp were collected separately.

Table 6: Standoff distances and angles for mock steel pipe IEDs

Steel Pipe	Distance (in)	Angle
1	12.75	11.40°
2	12.20	10.20°
3	17.50	11.25°



Figure 4: Before and after the water was used to disrupt the backpack mock IED. The barrel was lined with a clean tarp each time since there was only one barrel left for all of the backpack shots.

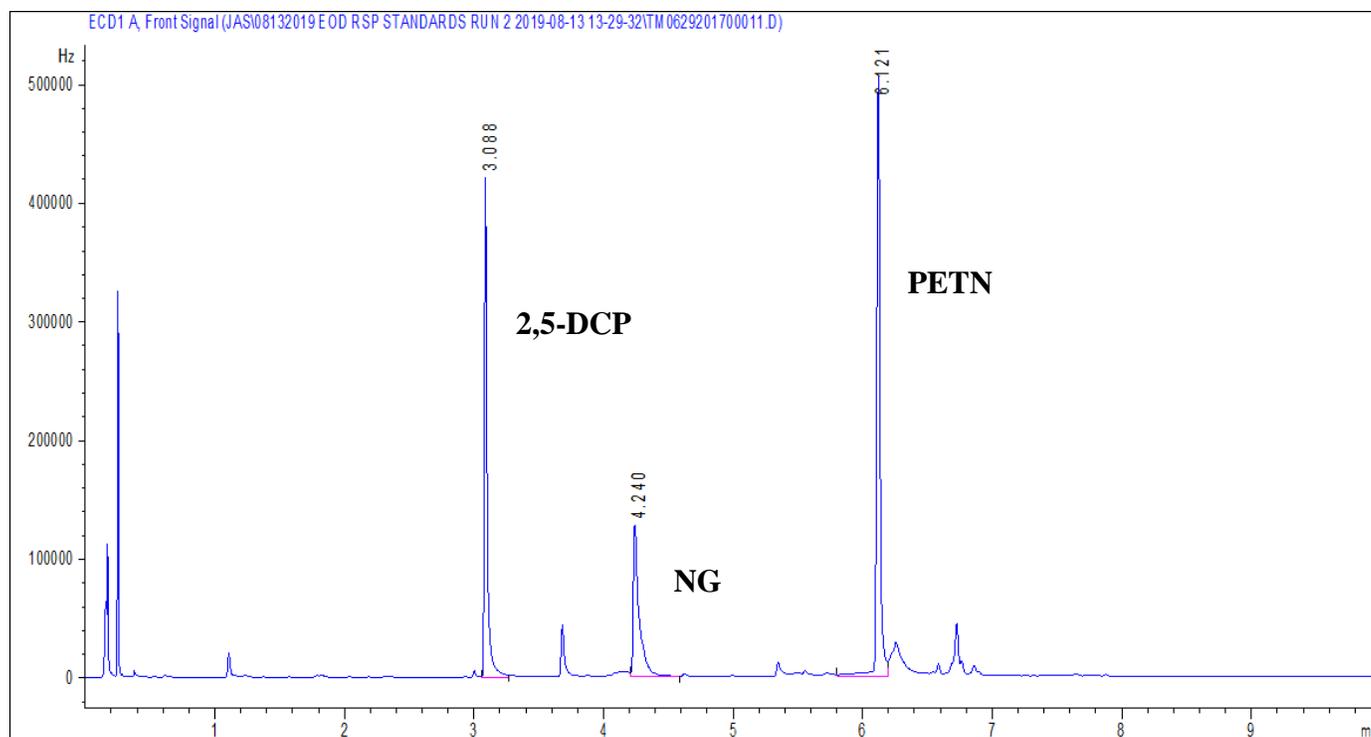


Figure 5: The chromatogram of the GC/ECD standard mixture. The internal standard 2,5-DCP eluted at 3.088 minutes. Analytes NG eluted at 4.240 minutes and PETN eluted at 6.121 minutes

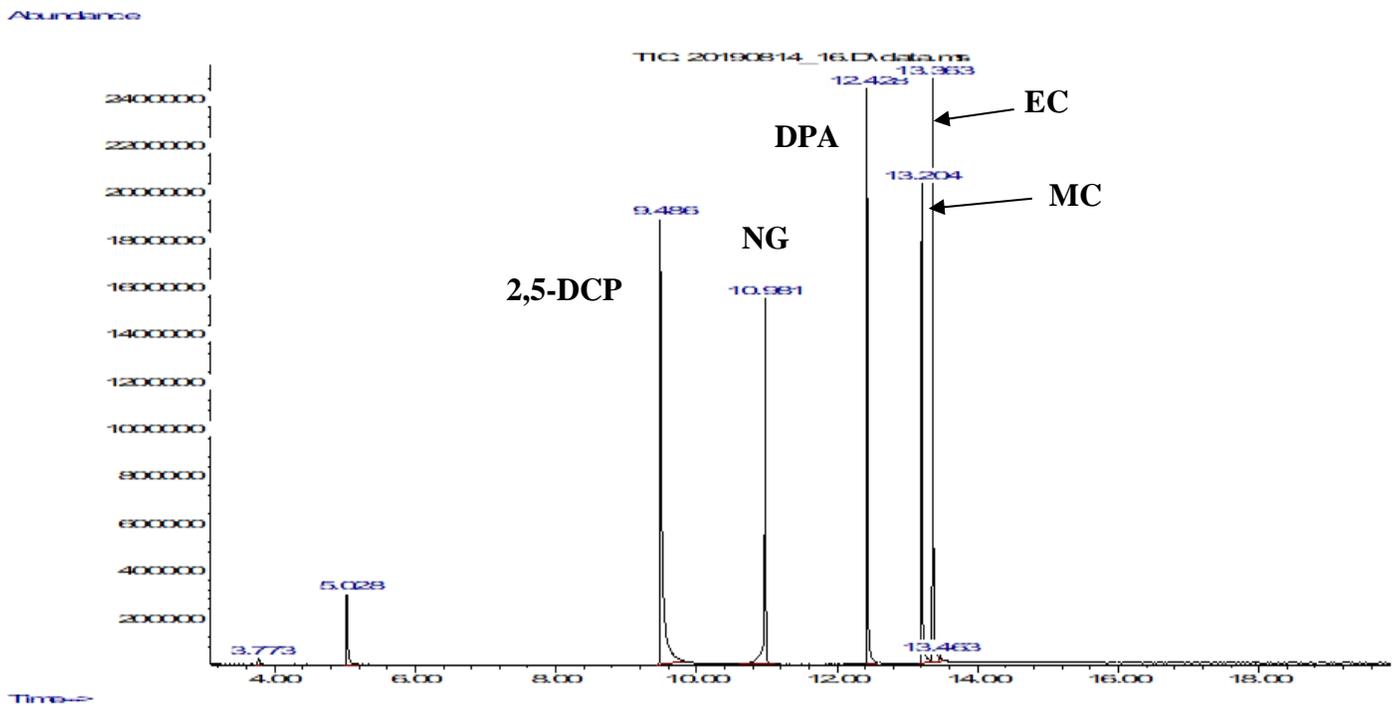
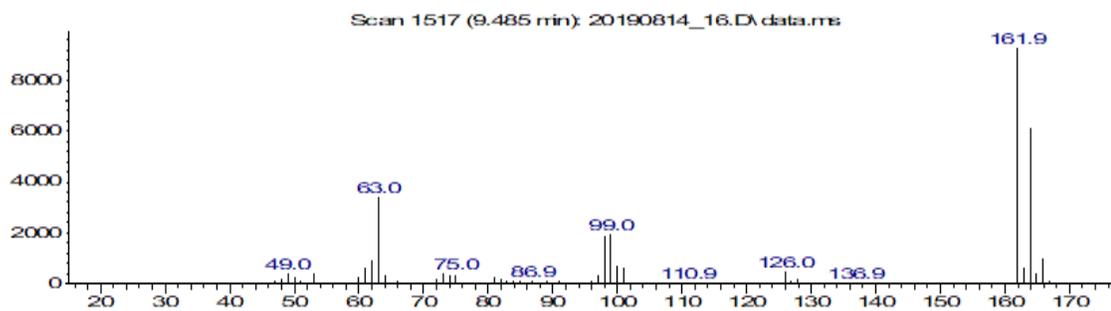
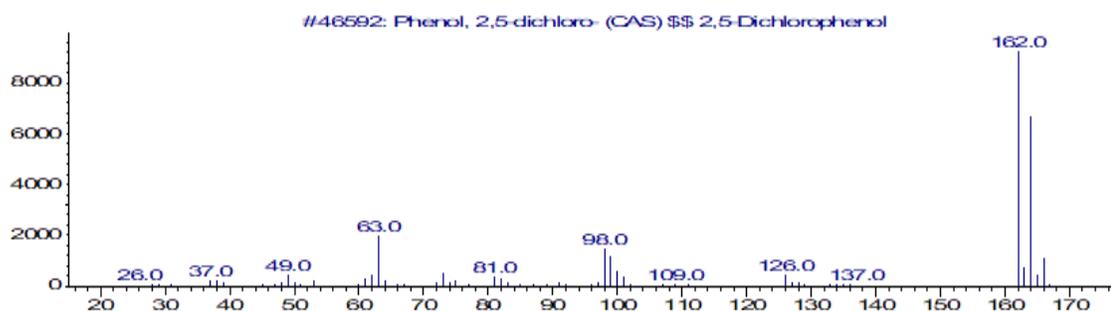


Figure 6: The chromatogram of the GC/MS standard mixture. The internal standard 2,5-DCP eluted at 9.486 minutes. Analytes NG eluted at 10.981 minutes, DPA at 12.428 minutes, MC at 13.204 minutes, and EC at 13.363 minutes.

Abundance



m/z->
Abundance



m/z->

Figure 7: The mass spectrum of the 2,5-DCP that elutes at 9.485 minutes in Figure 5. The base peak is 161.9 while the molecular ion peak is 163. The bottom mass spectrum from the library search also indicates that the compound is 2,5-DCP.

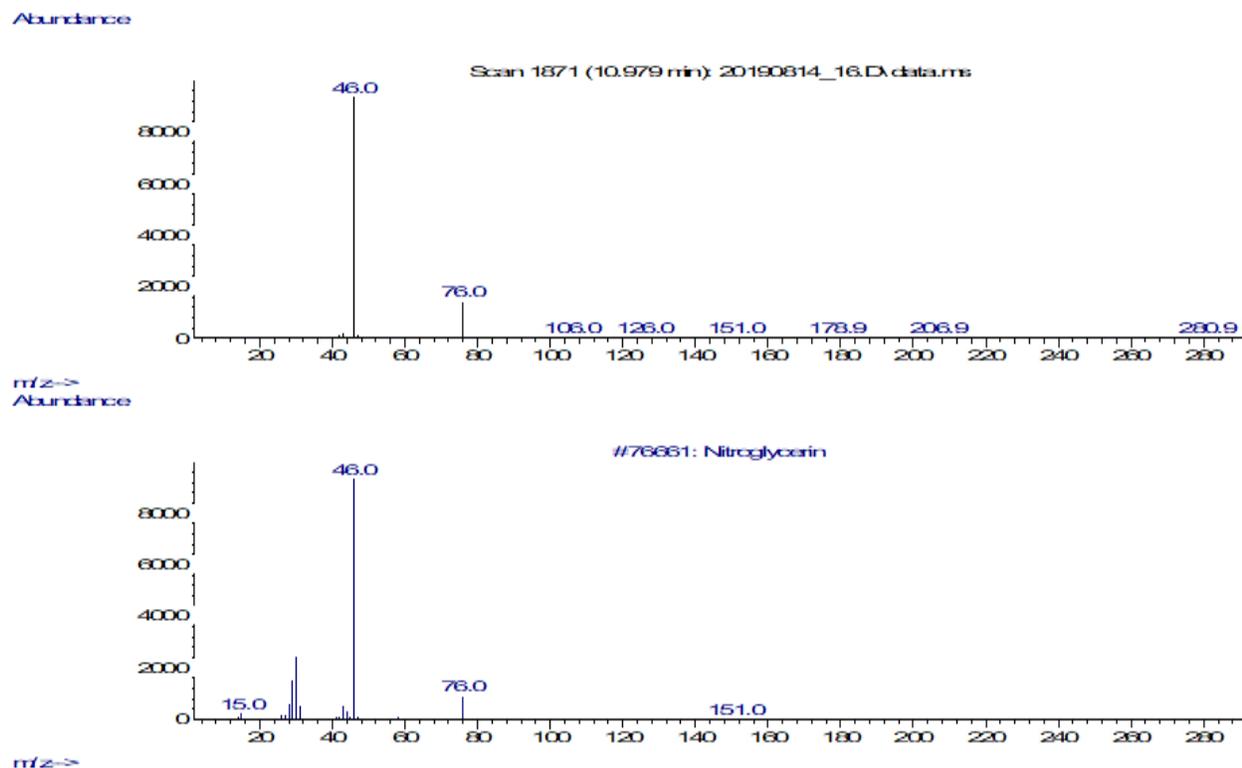


Figure 8: The mass spectrum of the NG that elutes at 10.979 minutes in Figure 5. The base peak is 46 while the molecular ion peak is not visible. The bottom mass spectrum from the library search also indicates that the compound is NG.

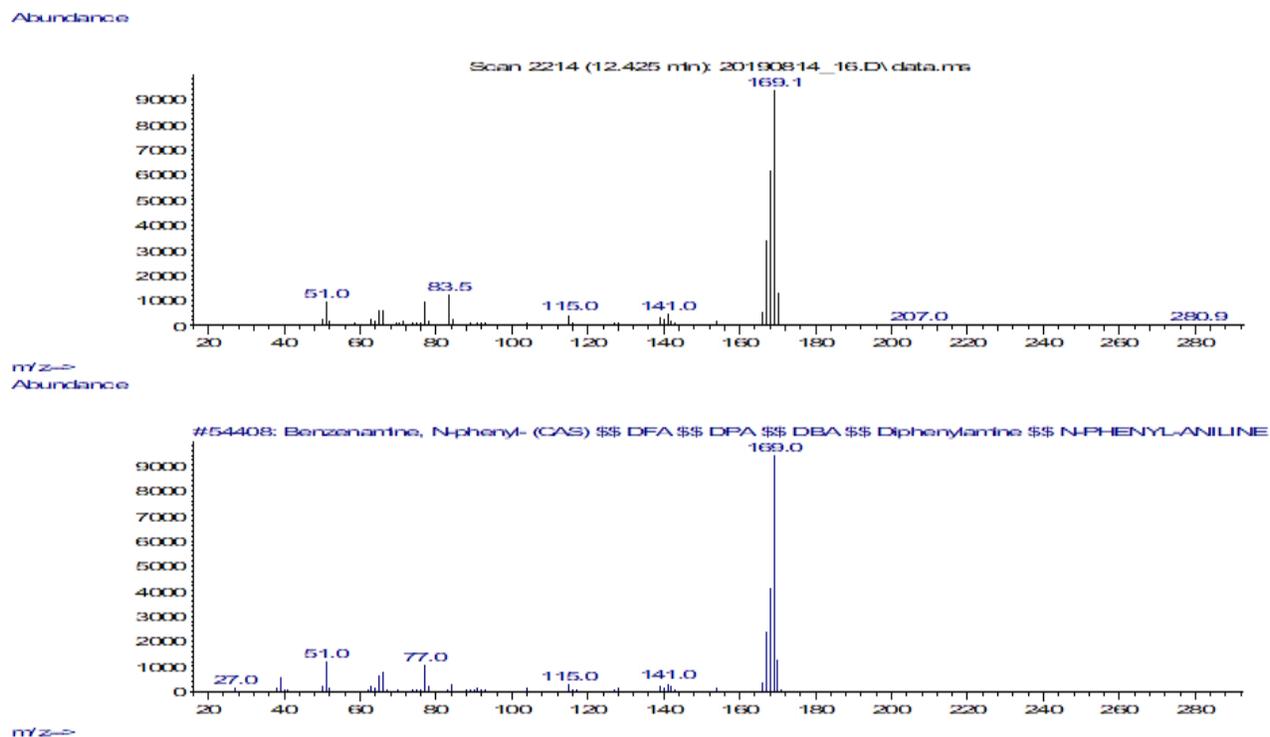


Figure 9: The mass spectrum of the DPA that elutes at 12.425 minutes in Figure 5. The base peak and molecular ion peak are 169. The bottom mass spectrum from the library search also indicates that the compound is DPA.

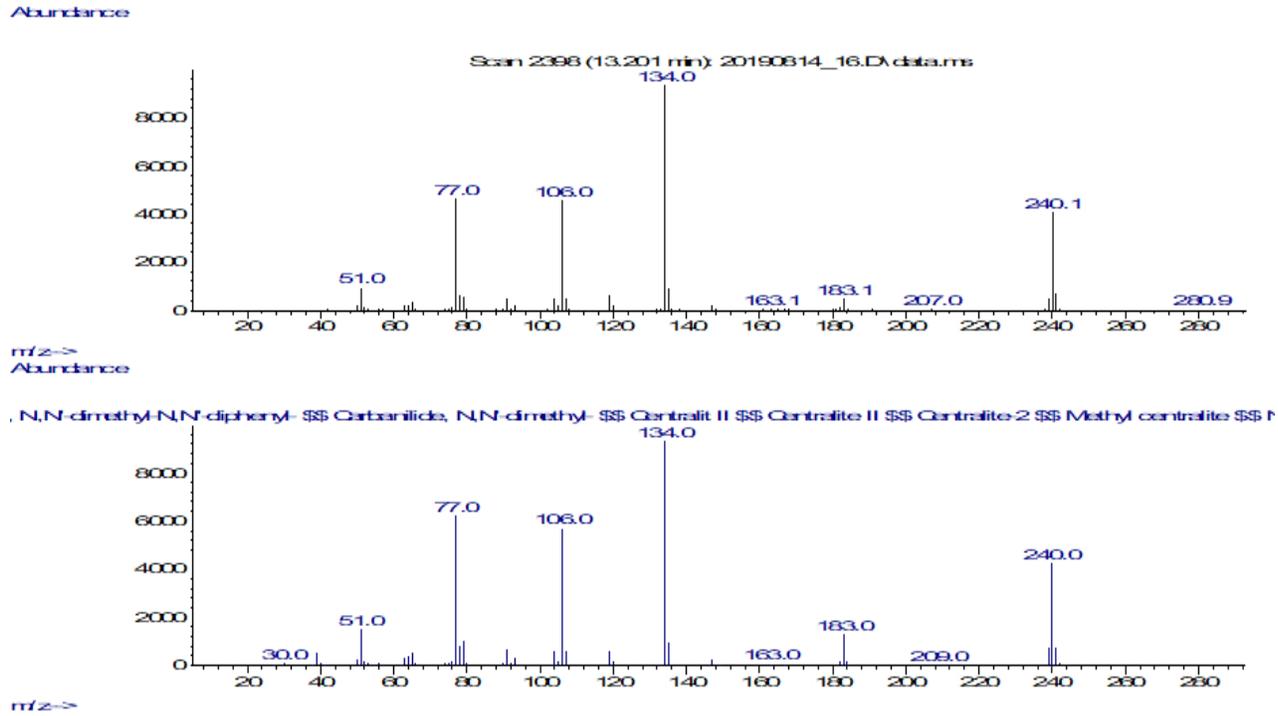


Figure 10: The mass spectrum of the MC that elutes at 13.201 minutes in Figure 5. The base peak is 134. The molecular ion peak is 240. The bottom mass spectrum from the library search also indicates that the compound is MC.

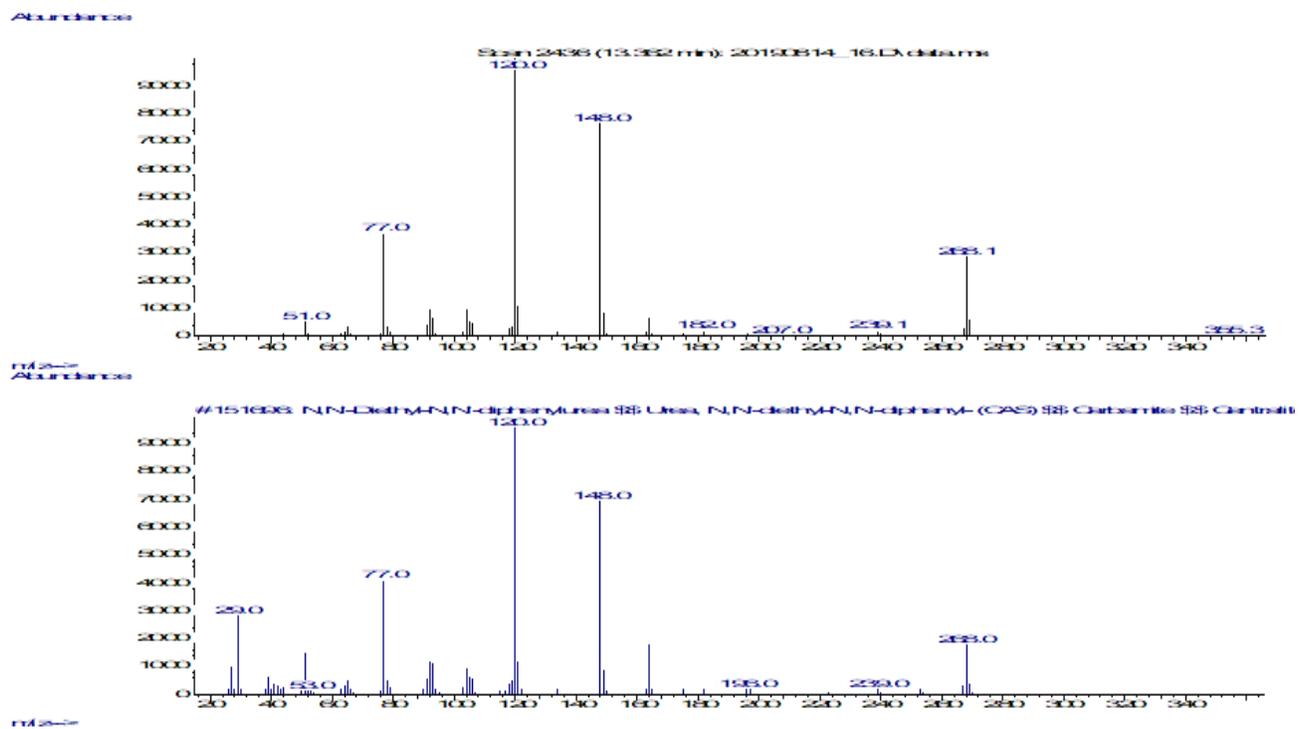


Figure 11: The mass spectrum of the EC that elutes at 13.363 minutes in Figure 5. The base peak is 120. The molecular ion peak is 268. The bottom mass spectrum from the library search also indicates that the compound is EC.

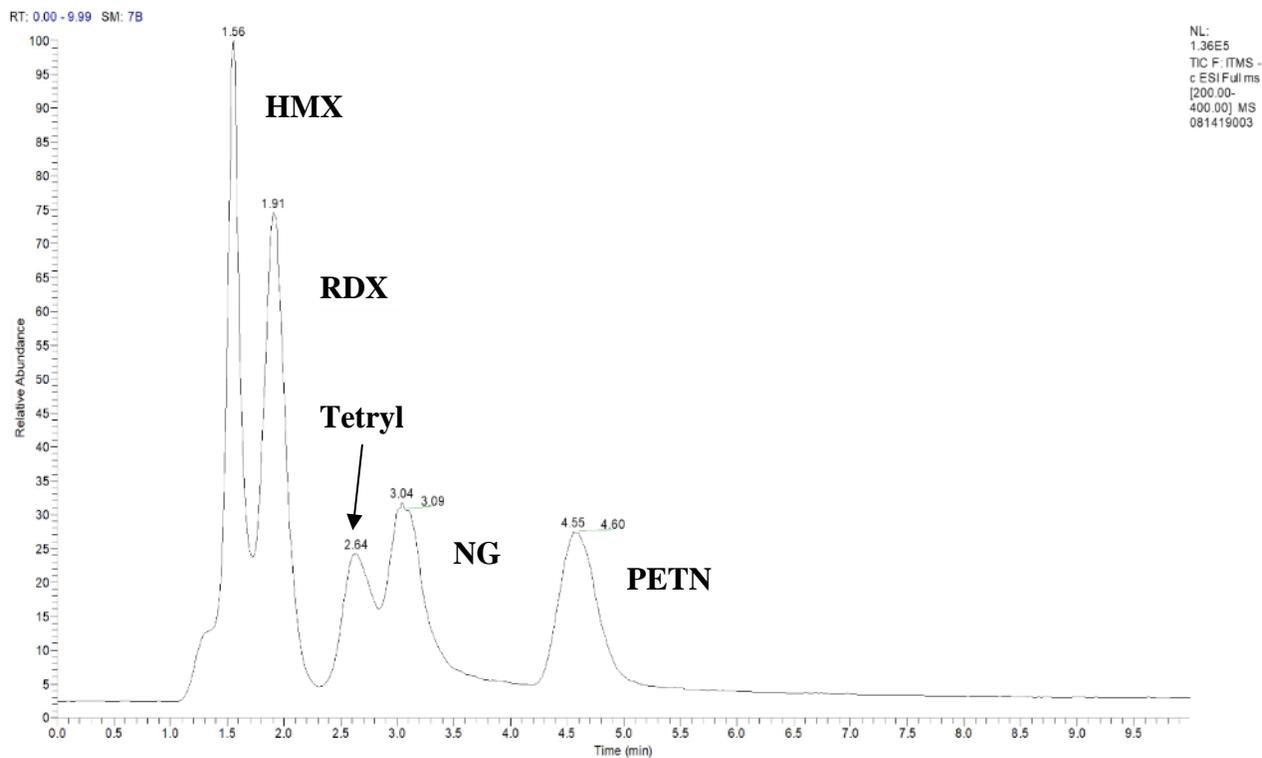


Figure 12: The TIC for the high explosive standard analyzed using the C18 single scan mode method. The explosives detected include HMX, RDX, Tetryl, NG, and PETN in that elution order.

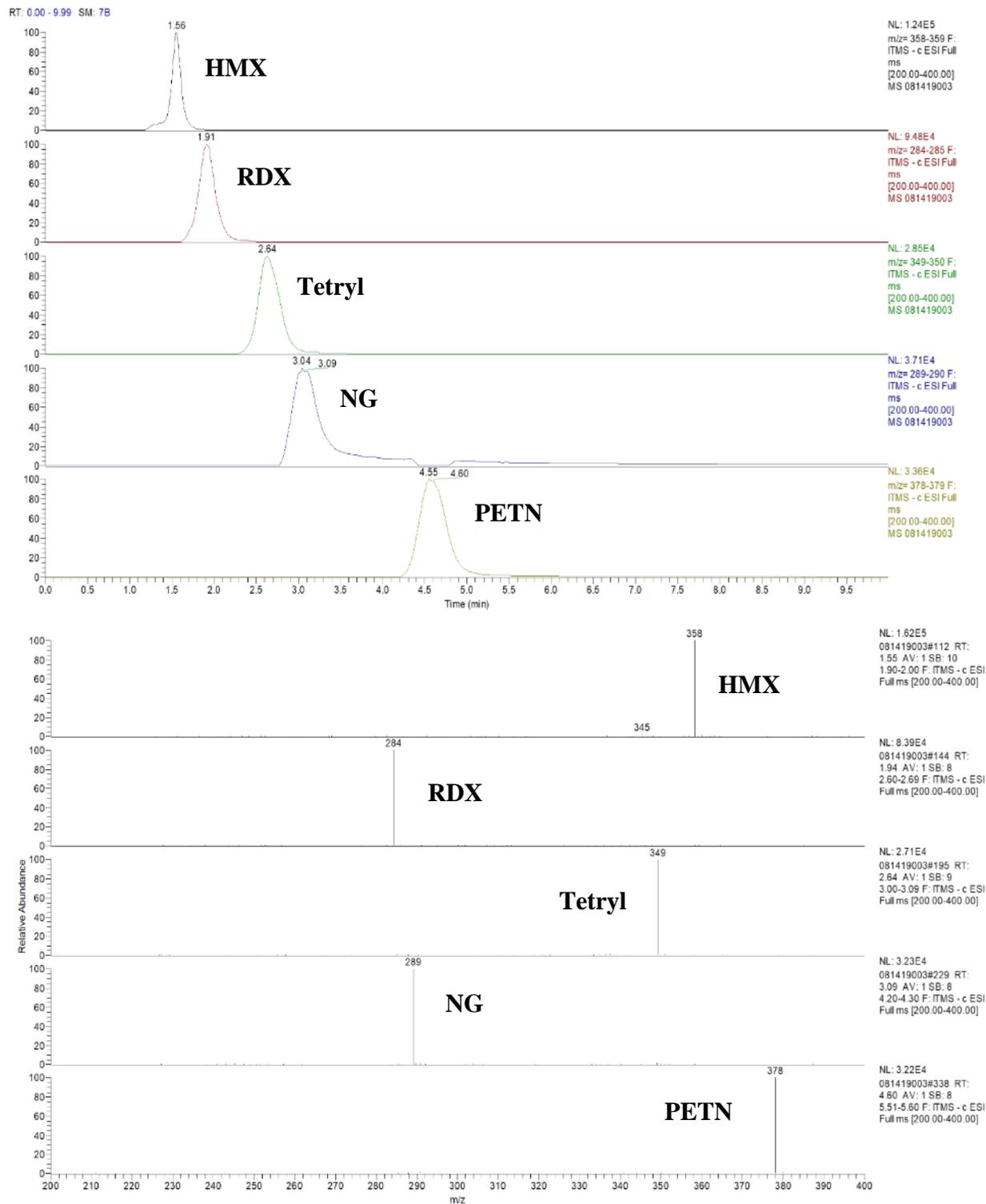


Figure 13: The EIC and corresponding mass spectra for the standards analyzed using the C18 single scan method. The first line is HMX, the second line is RDX, the third line is tetryl, the fourth is NG, and the fifth line is PETN.



Figure 14: The TIC and corresponding mass spectrum for the imidazole standard analyzed using the C18 dual scan mode method.

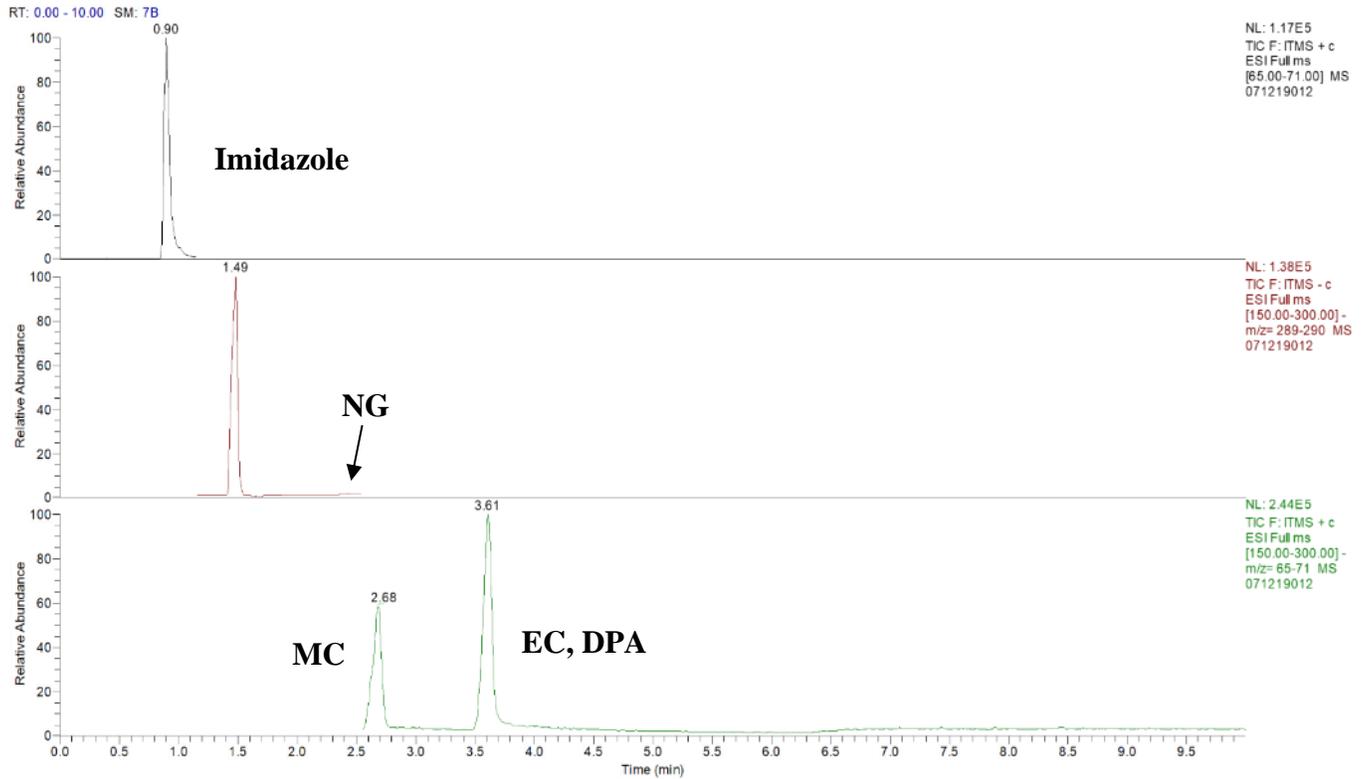


Figure 15: The TIC for the standards analyzed using the biphenyl column method. The first line is for the initial positive scan to detect imidazole, the second line is the second negative scan to detect NG, the third line the final positive scan to detect MC, EC, and DPA. The large peak in the NG scan overshadow the true NG peak, pointed out by an arrow. EC and DPA appear to co-elute in the TIC

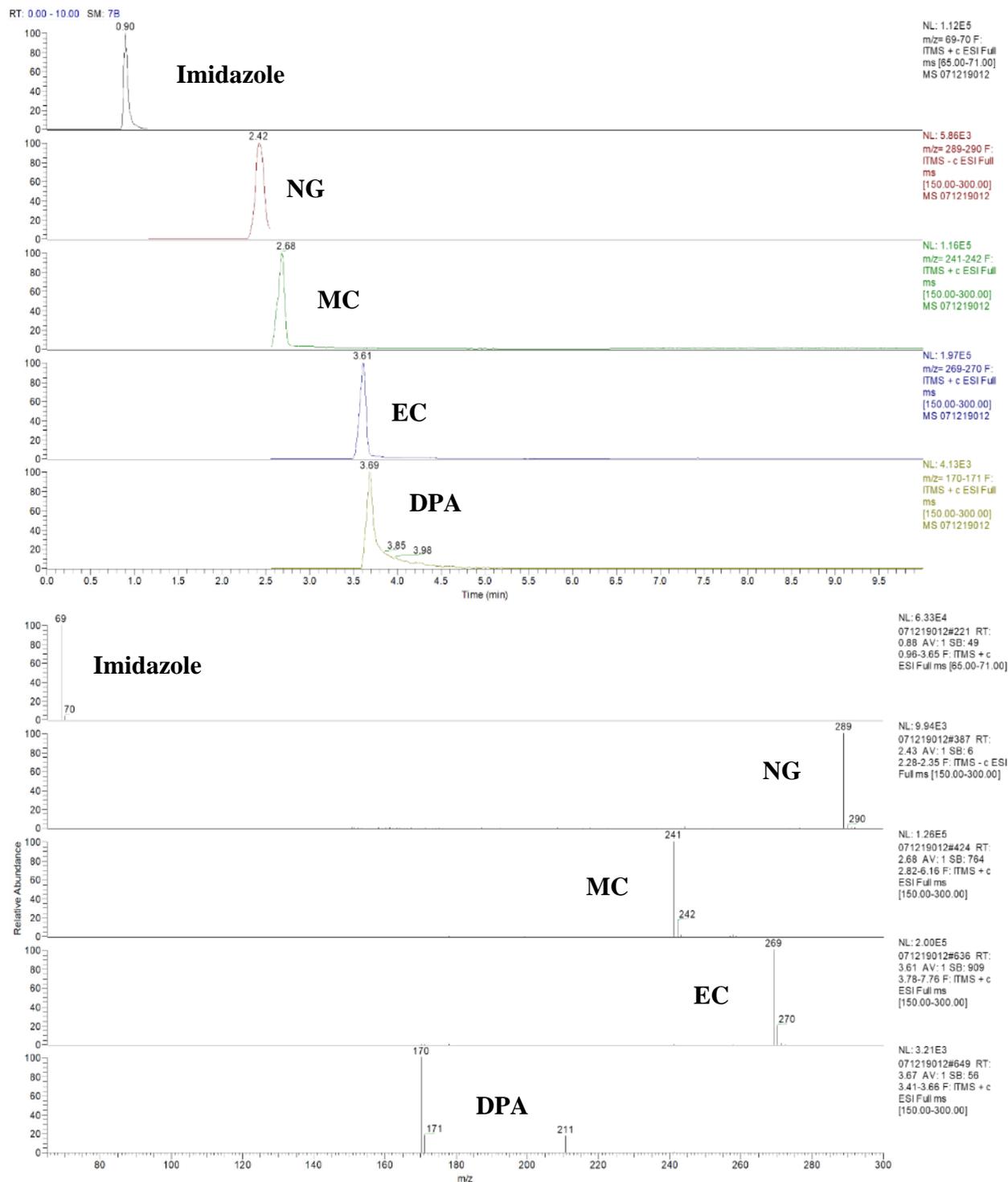


Figure 16: The EIC and corresponding mass spectrum for the standards analyzed using the biphenyl column method. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA.

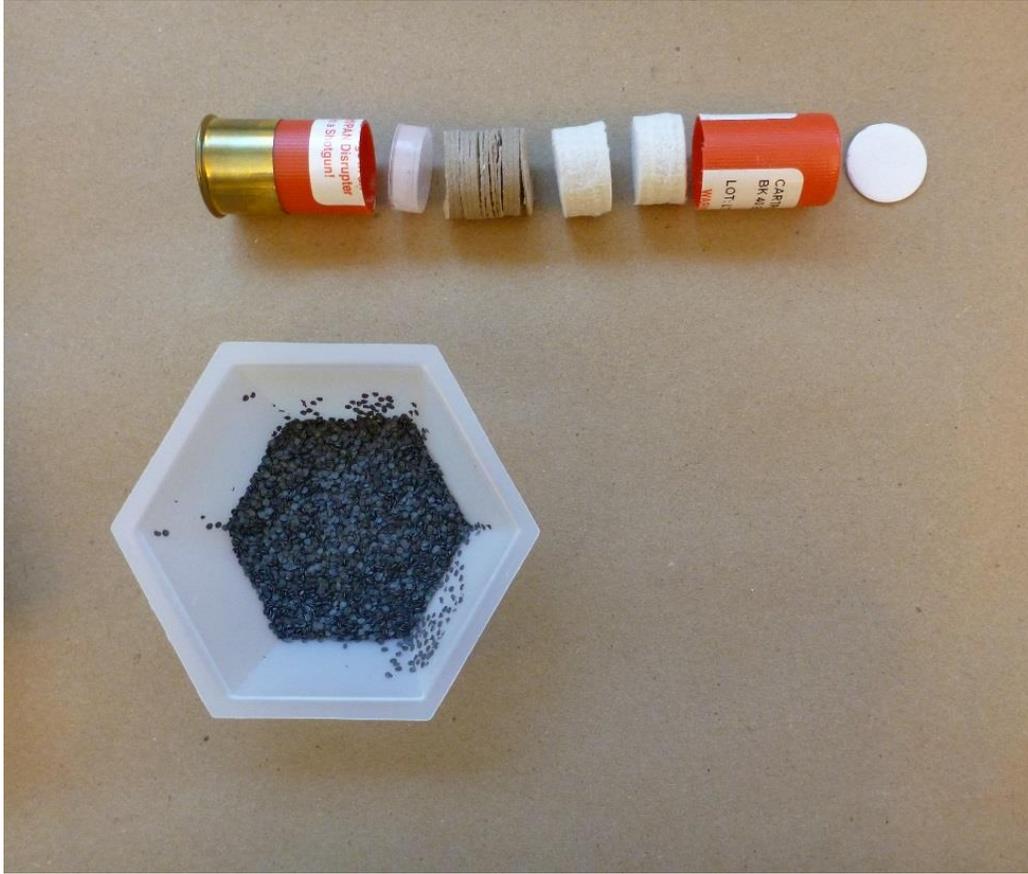


Figure 17: Disassembled L-Tech shotgun shell used in the PAN disrupter to propel water down the column.

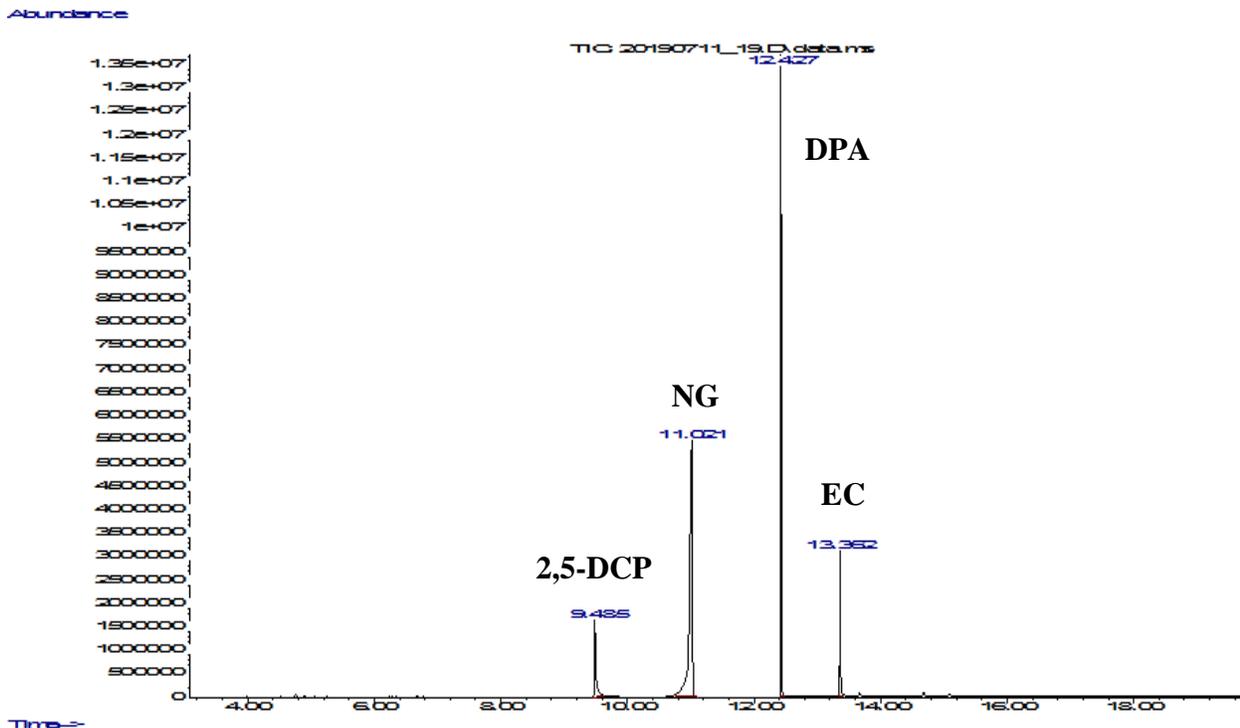


Figure 18: The chromatogram of the GC/MS analysis of the L-Tech bulk powder sample 1. NG, DPA, and EC were the compounds detected in addition to the 2,5-DCP internal standard.

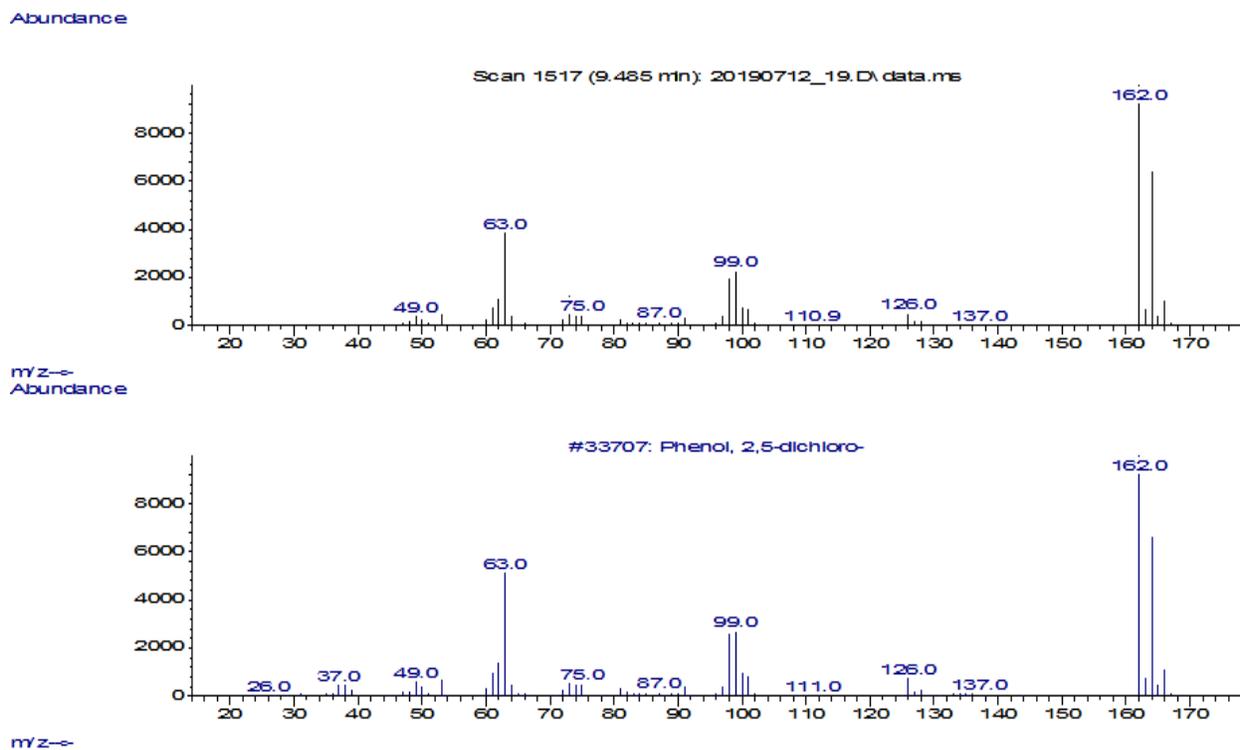


Figure 19: The mass spectrum of 2,5-DCP eluting at 9.485 minutes from Figure 18. The bottom mass spectrum is from the library search.

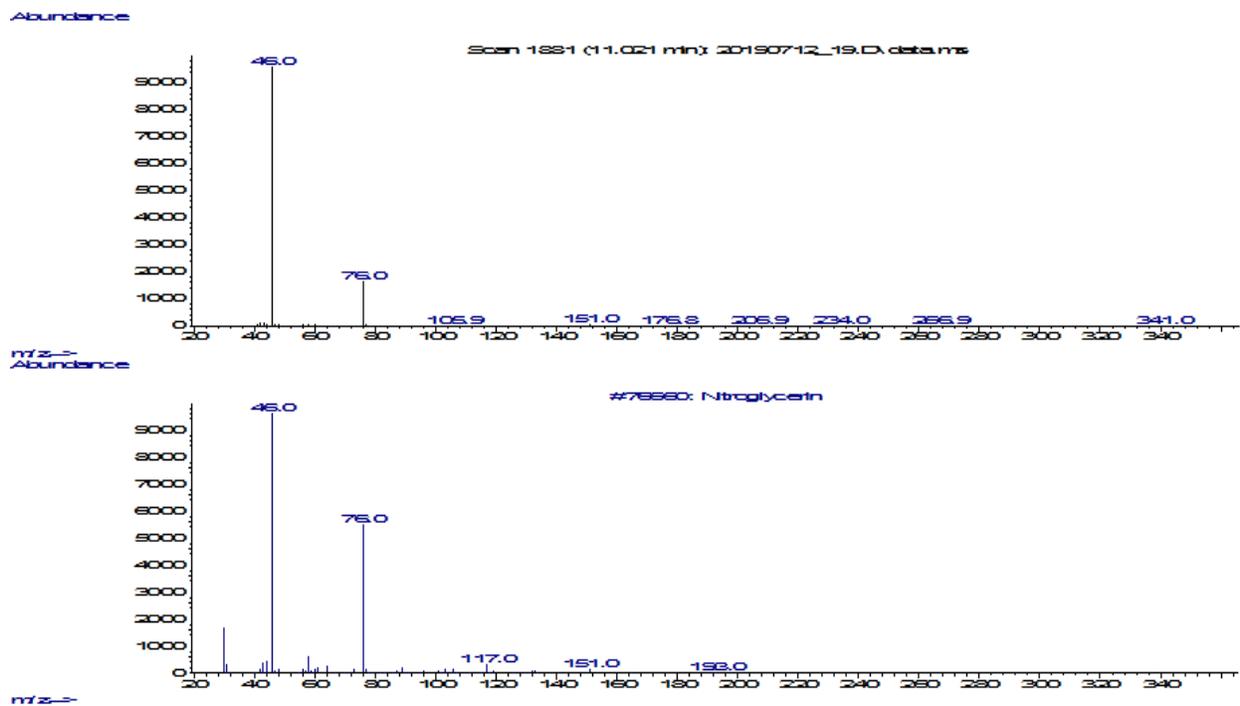
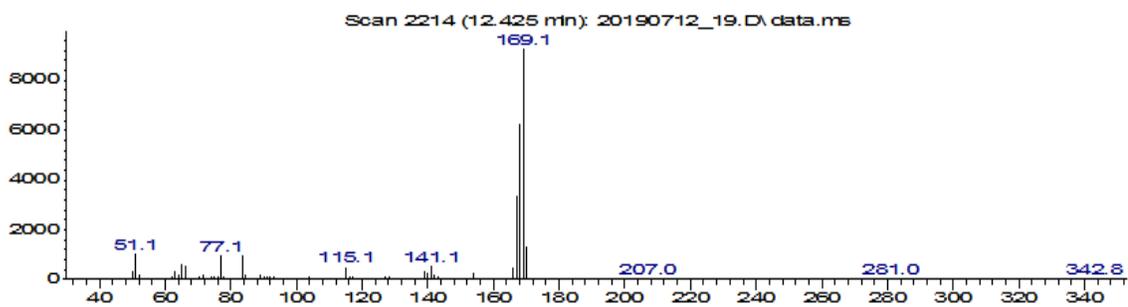
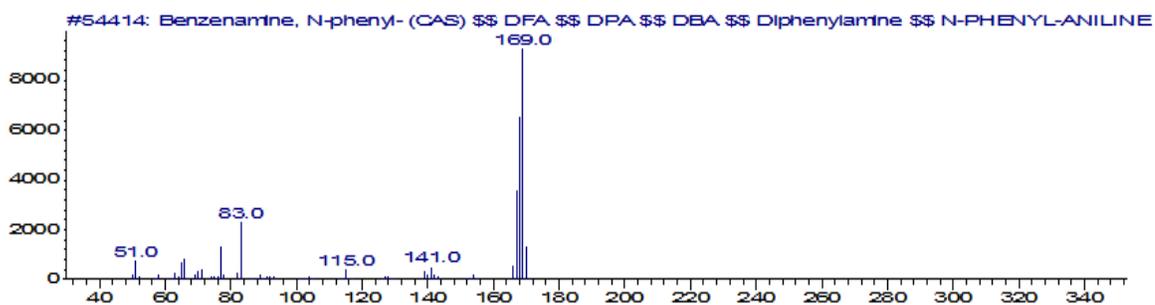


Figure 20: The mass spectrum of the NG eluting at 11.023 minutes from Figure 18. The bottom mass spectrum is from the library search.

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Abundance



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Figure 21: The mass spectrum of the DPA eluting at 12.425 from Figure 22. The bottom mass spectrum is from the library search.

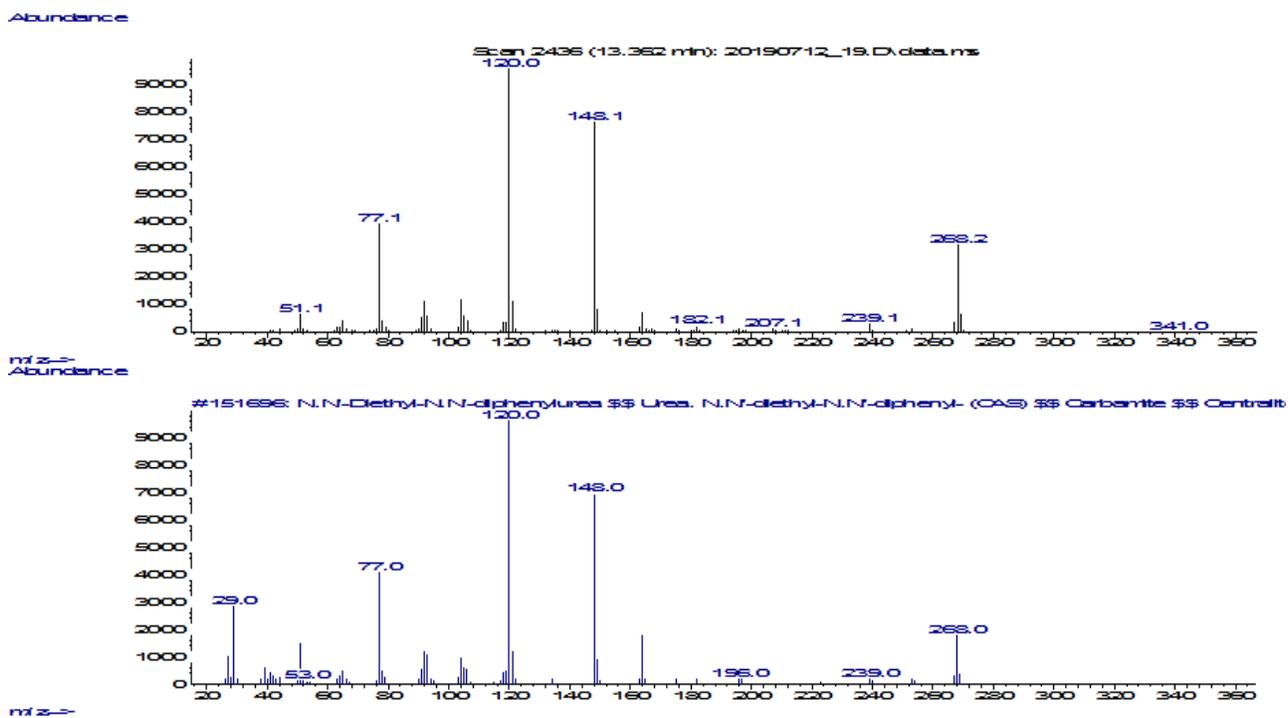


Figure 22: The mass spectrum of the EC eluting at 13.363 minutes from Figure 18. The bottom mass spectrum is from the library search.

Table 7: Peak area ratios for the compounds detected in the GC/MS analysis of the bulk L-Tech smokeless powder. These ratios were also normalized by dividing the initial ratio by the weight of the powder.

	Sample 1	Sample 2	Sample 3
Weight of Powder (g)	0.0153	0.0151	0.0155
NG/2,5-DCP Peak Area Ratio w/Powder	410.3	416.9	438.5
DPA/2,5-DCP Area Ratio w/Powder	207.2	208.8	223.9
EC/2,5-DCP Area Ratio w/Powder	57.9	56.5	65.2

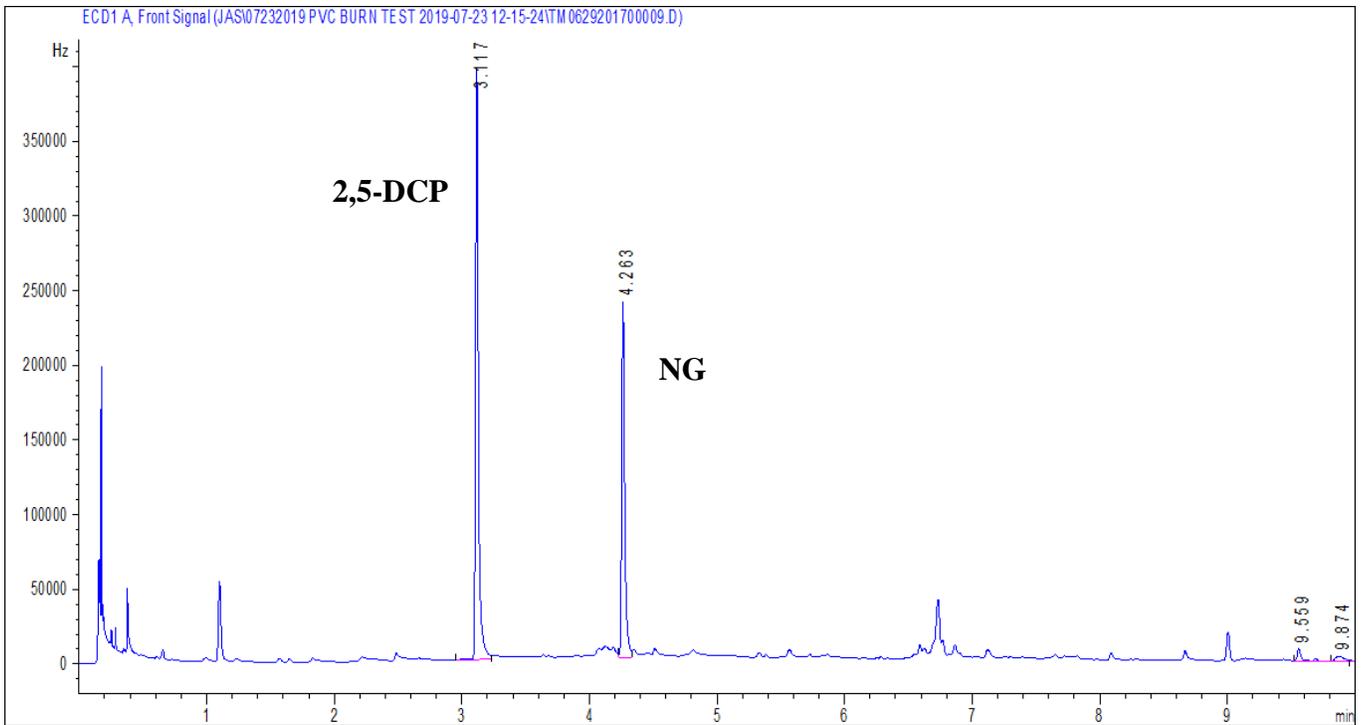


Figure 23: The GC/ECD chromatogram of sample 4 from the L-Tech smokeless powder burn extract from a PVC pipe endcap. NG is present, eluting at 4.263 minutes. 2,5-DCP eluted at 3.117 minutes.

Table 8: Peak area ratios for the nitroglycerine detected in the GC/ECD analysis of the extracted residue from the burned L-Tech smokeless powder. These ratios were normalized by dividing the initial ratio by the weight of the powder burned.

	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
Weight of Powder (g)	0.1005	0.1011	0.1008	0.1004	0.1008	0.1008
NG/2,5-DCP Peak Area Ratio w/Powder	6.267	0.040	1.748	0.568	2.026	0

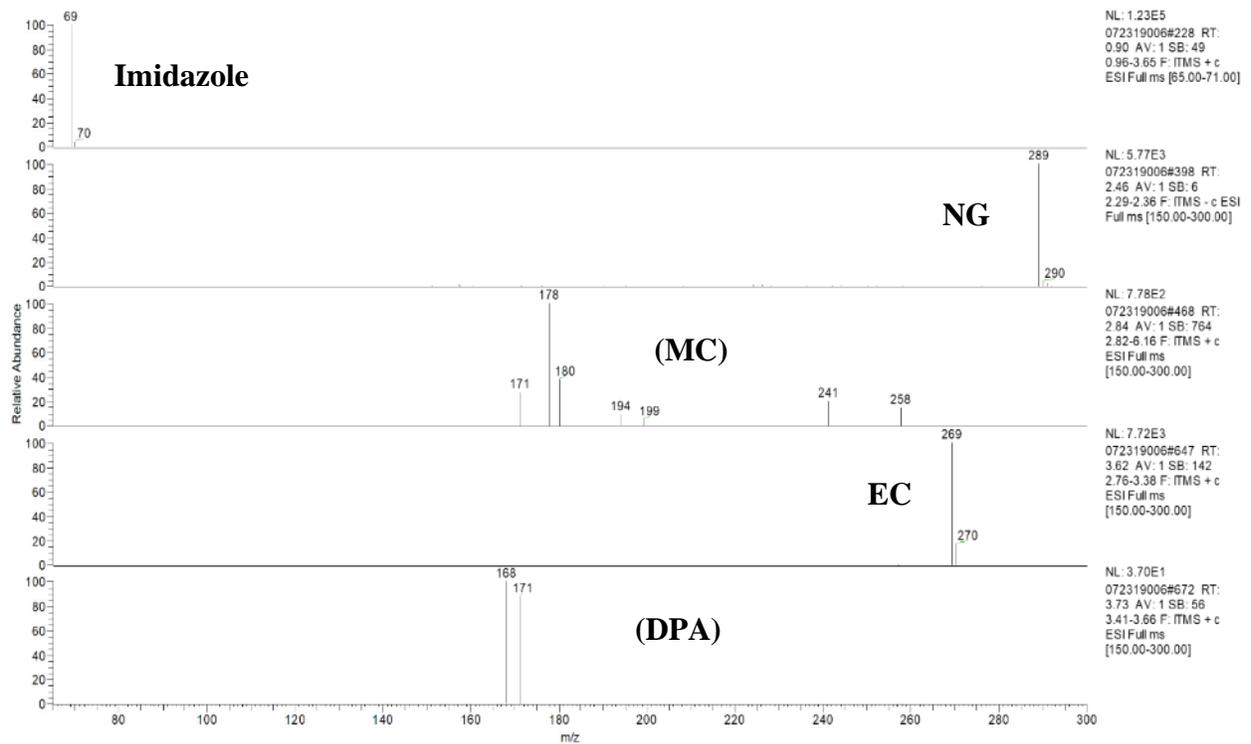
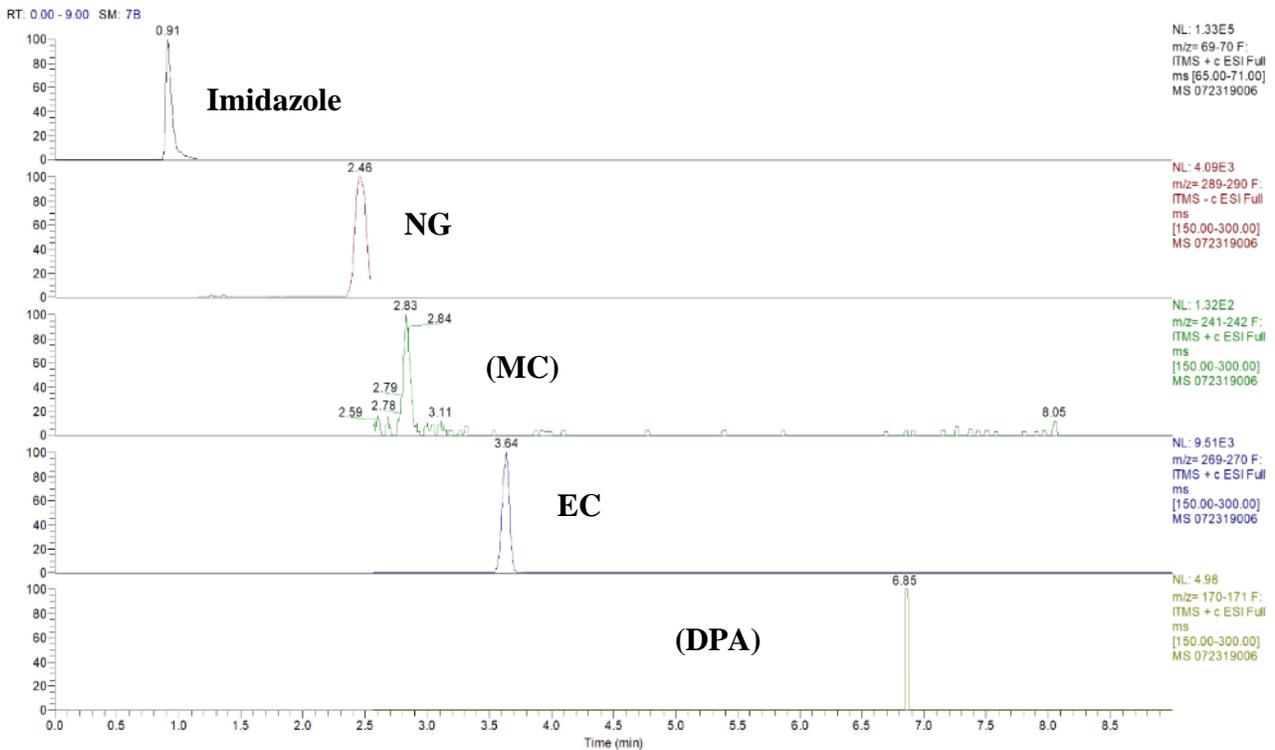


Figure 24: The EIC of extract resulting from L-Tech smokeless powder burn in a PVC endcap. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA. NG and DPA were the only analytes detected.

Table 9: Peak area ratios for the compounds detected in the LC/MS analysis of the extracted residue from the burned L-Tech smokeless powder. These ratios were normalized by dividing the initial ratio by the weight of the powder burned.

	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
Weight of Powder (g)	0.1005	0.1011	0.1008	0.1004	0.1008	0.1008
NG/Imidazole Area Ratio w/Powder	0.583	0	0.115	0.012	0.082	0
DPA/Imidazole Area Ratio w/Powder	0	0	0	0	0	0
EC/Imidazole Area Ratio w/Powder	0.881	0.0614	0.496	0.0420	0.0948	0

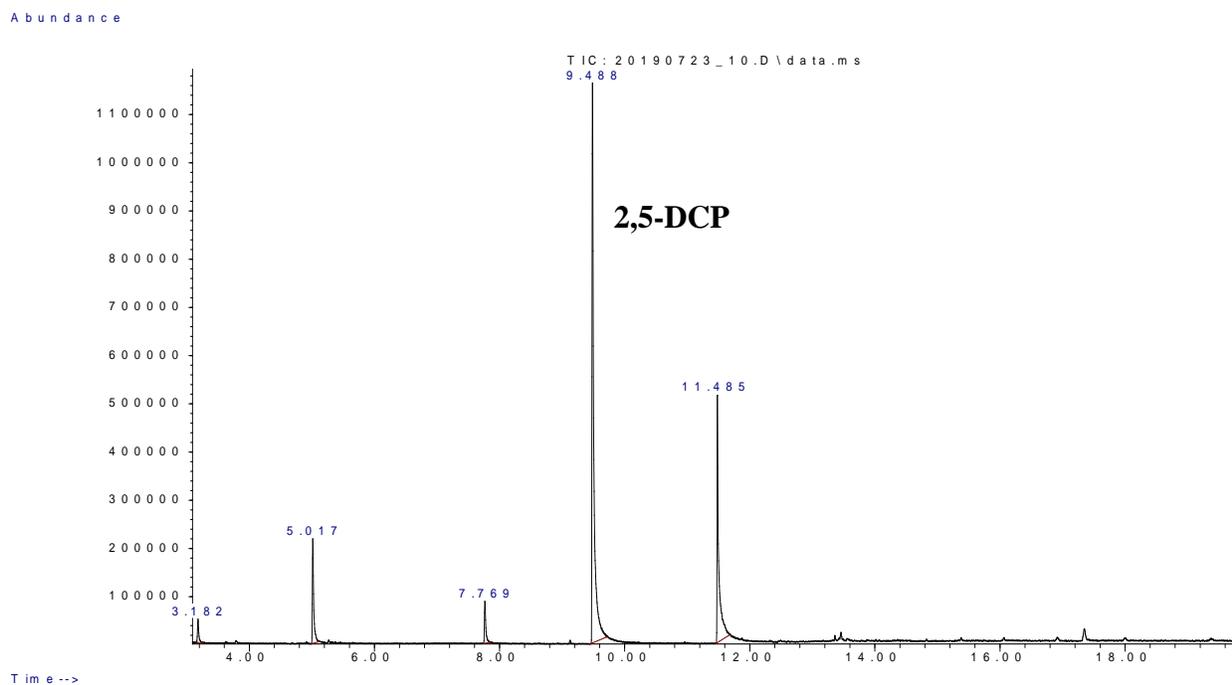


Figure 25: The chromatogram of the GC/MS analysis of sample 1 of the L-Tech burned smokeless powder extract. None of the analytes of interest were detected, only the internal standard 2,5-DCP was detected.

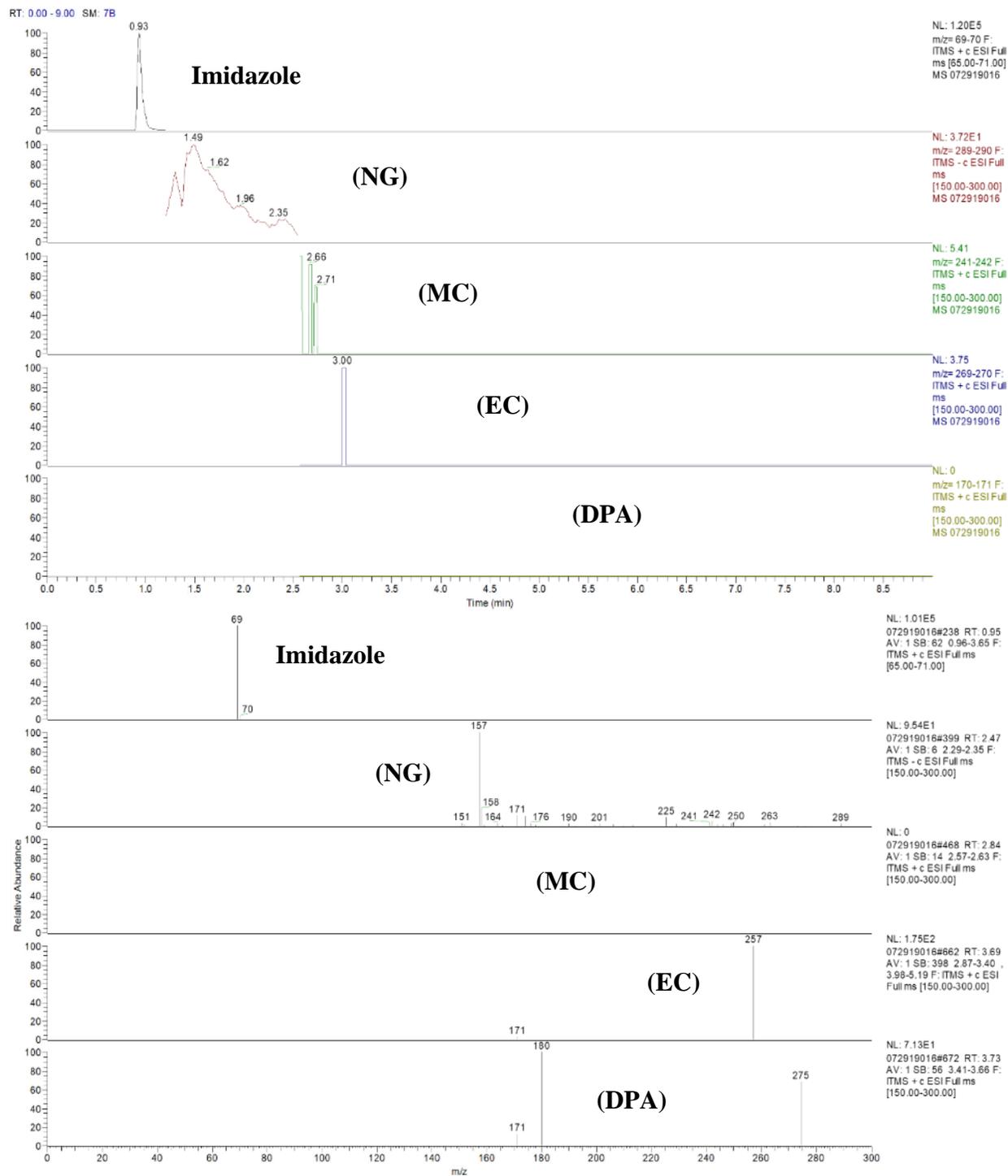


Figure 26: The EIC of the residue extract from pipe 2 recovered in the barrel that was rendered safe using the PAN disrupter, the L-Tech shotgun blank, and water. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA. None of the analytes of interest were detected but the imidazole internal standard was detected.



Figure 27: Disassembled Remington NitroTurkey shotgun shell used in the PAN disrupter that propels birdshot down the barrel.

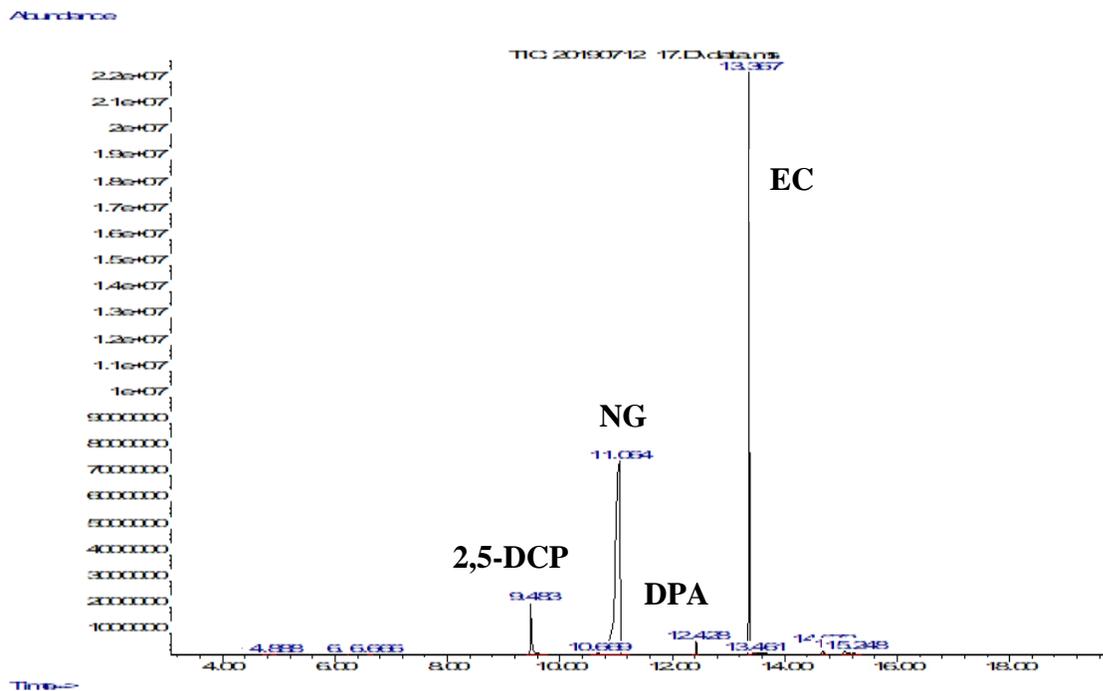


Figure 28: The chromatogram of the GC/MS analysis of sample 1 of the Remington NitroTurkey bulk smokeless powder. NG, DPA, and EC were the analytes detected in addition to the 2,5-DCP internal standard.

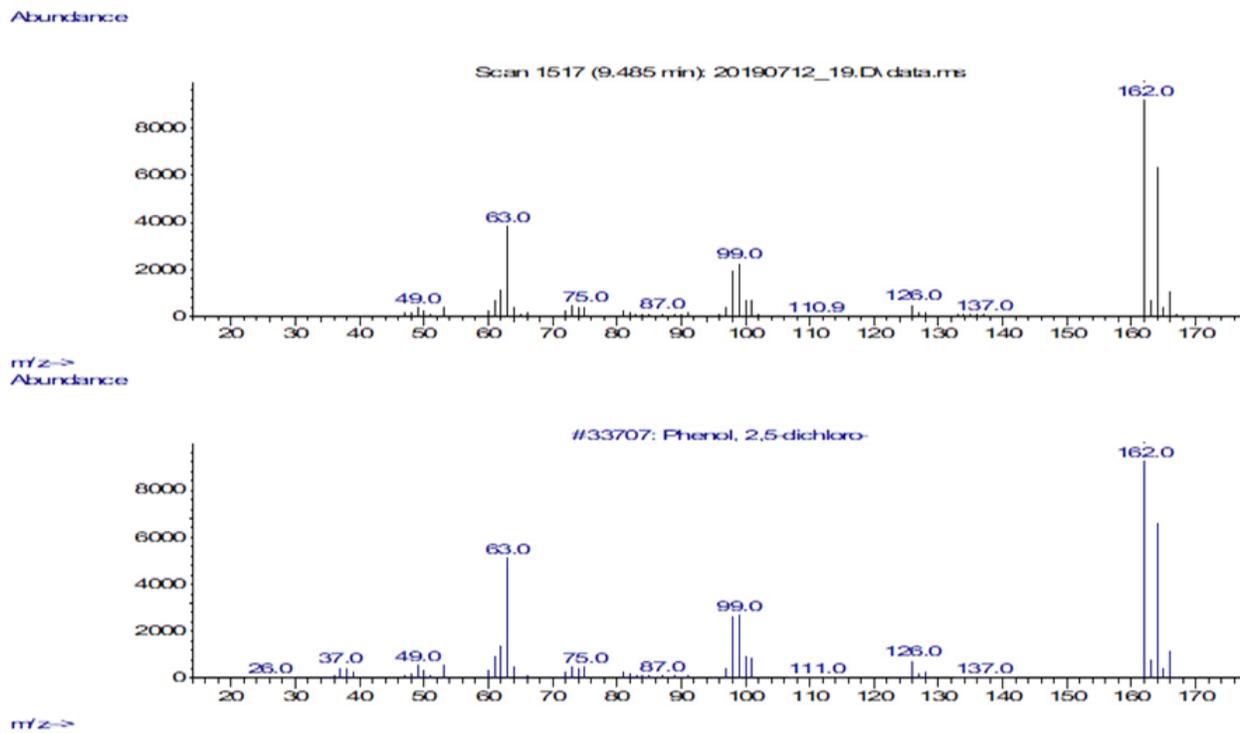


Figure 29: The mass spectrum of 2,5-DCP eluting at 9.483 minutes from Figure 28. The bottom mass spectrum is from the library search.

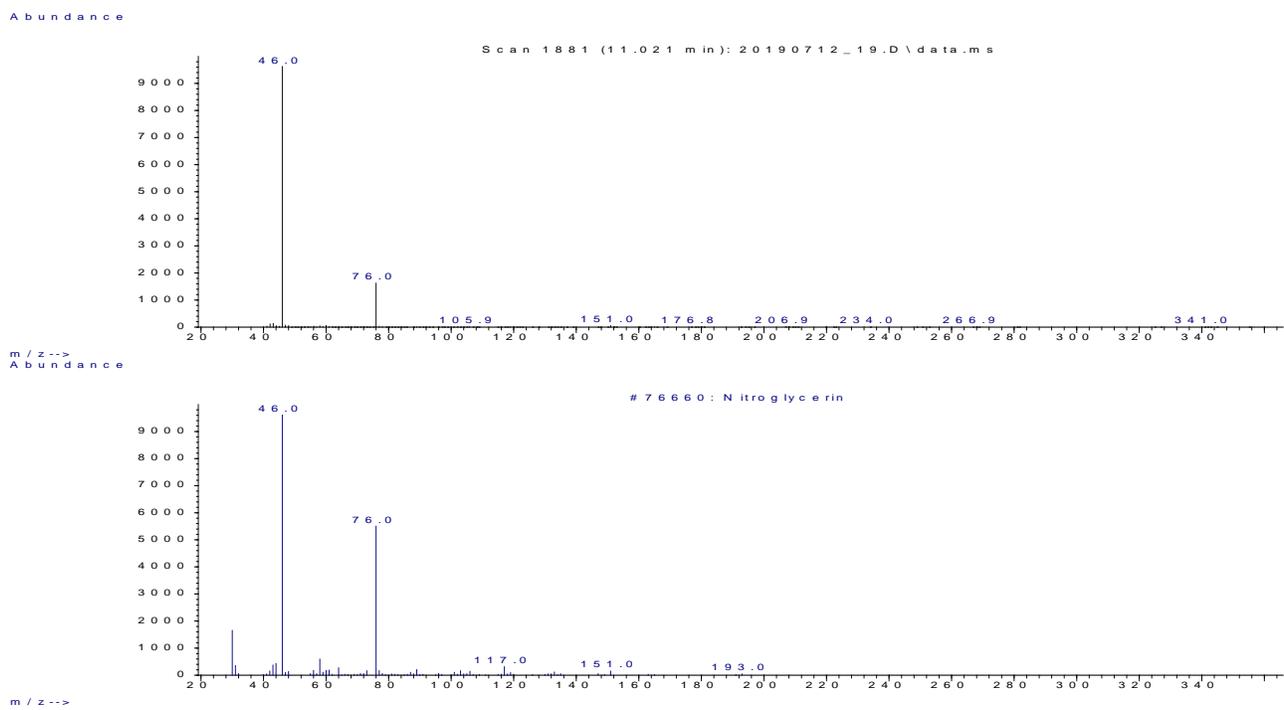
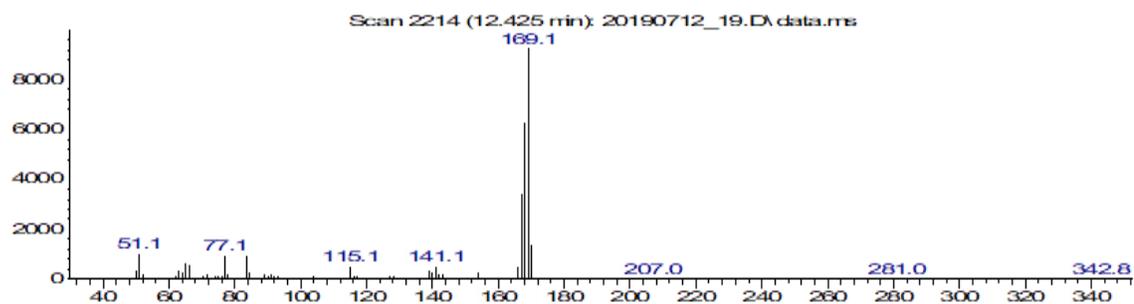
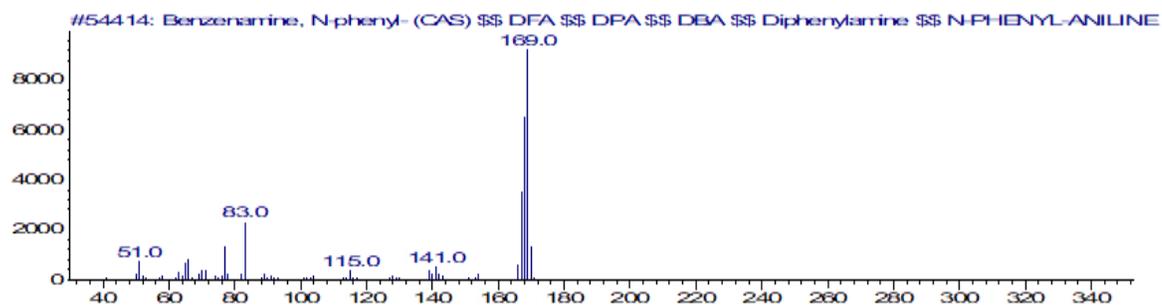


Figure 30: The mass spectrum of NG eluting at 11.064 minutes from Figure 28. The bottom mass spectrum is from the library search.

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Abundance



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Figure 31: The mass spectrum of DPA eluting at 12.428 minutes from Figure 28. The bottom mass spectrum is from the library search.

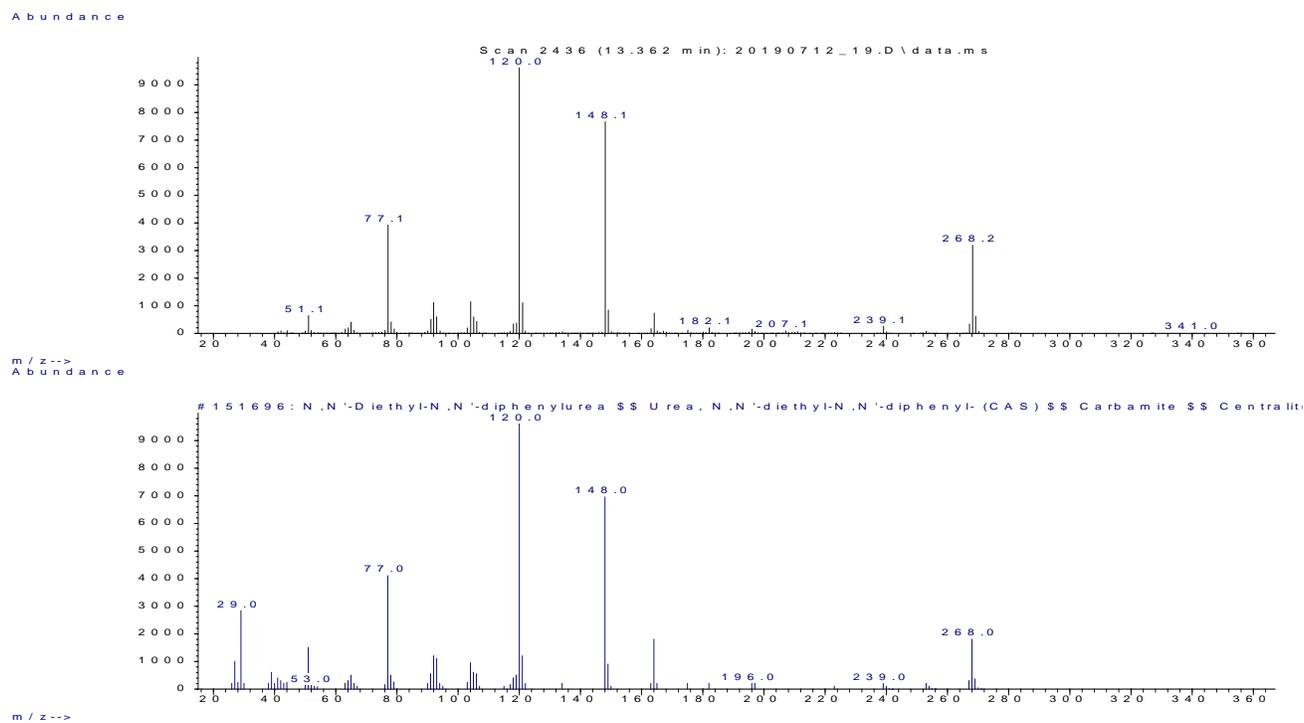


Figure 32: The mass spectrum of EC eluting at 13.367 minutes from Figure 28. The bottom mass spectrum is from the library search.

Table 10: Peak area ratios for the compounds in the GC/MS analysis of the bulk Remington NitroTurkey smokeless powder. These ratios were normalized by dividing the initial ratio by the weight of the powder.

	Sample 1	Sample 2	Sample 3
Weight of Powder (g)	0.0227	0.0224	0.0231
NG/2,5-DCP Peak Area Ratio w/Powder	639.159	641.124	560.962
DPA/2,5-DCP Area Ratio w/Powder	5.91234	5.19698	5.12736
EC/2,5-DCP Area Ratio w/Powder	252.949	283.322	214.884

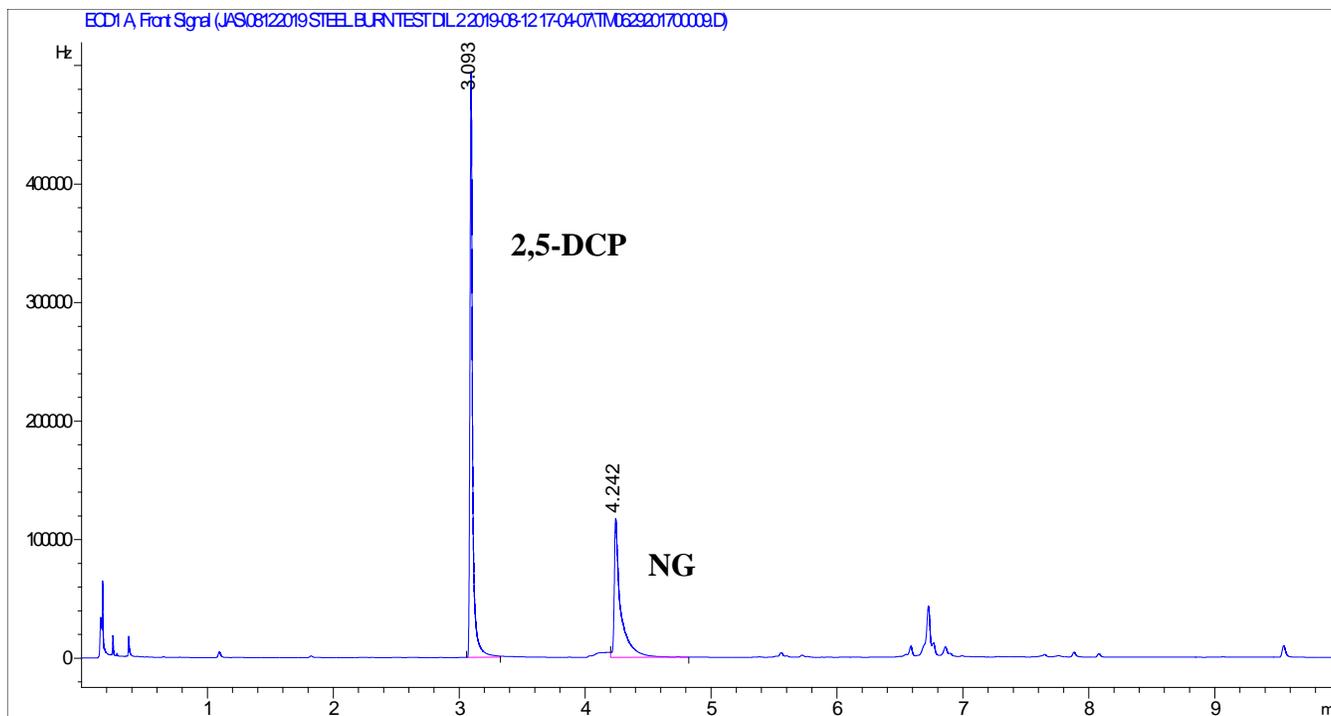


Figure 33: The GC/ECD chromatogram of sample 1 from the Remington NitroTurkey smokeless powder burn extract in a steel endcap. NG is present, eluting at 4.257 minutes. 2,5-DCP eluted at 3.095 minutes.

Table 11: Peak area ratios for the nitroglycerine in the GC/ECD analysis of the extracted residue from the burned Remington NitroTurkey smokeless powder. These ratios were normalized by dividing the initial ratio by the weight of the powder burned.

	Sample 1 Diluted	Sample 2 Diluted	Sample 3 Diluted
Weight of Powder (g)	0.01006	0.01005	0.01001
NG/2,5-DCP Peak Area Ratio w/Powder	56.63	58.74	53.10

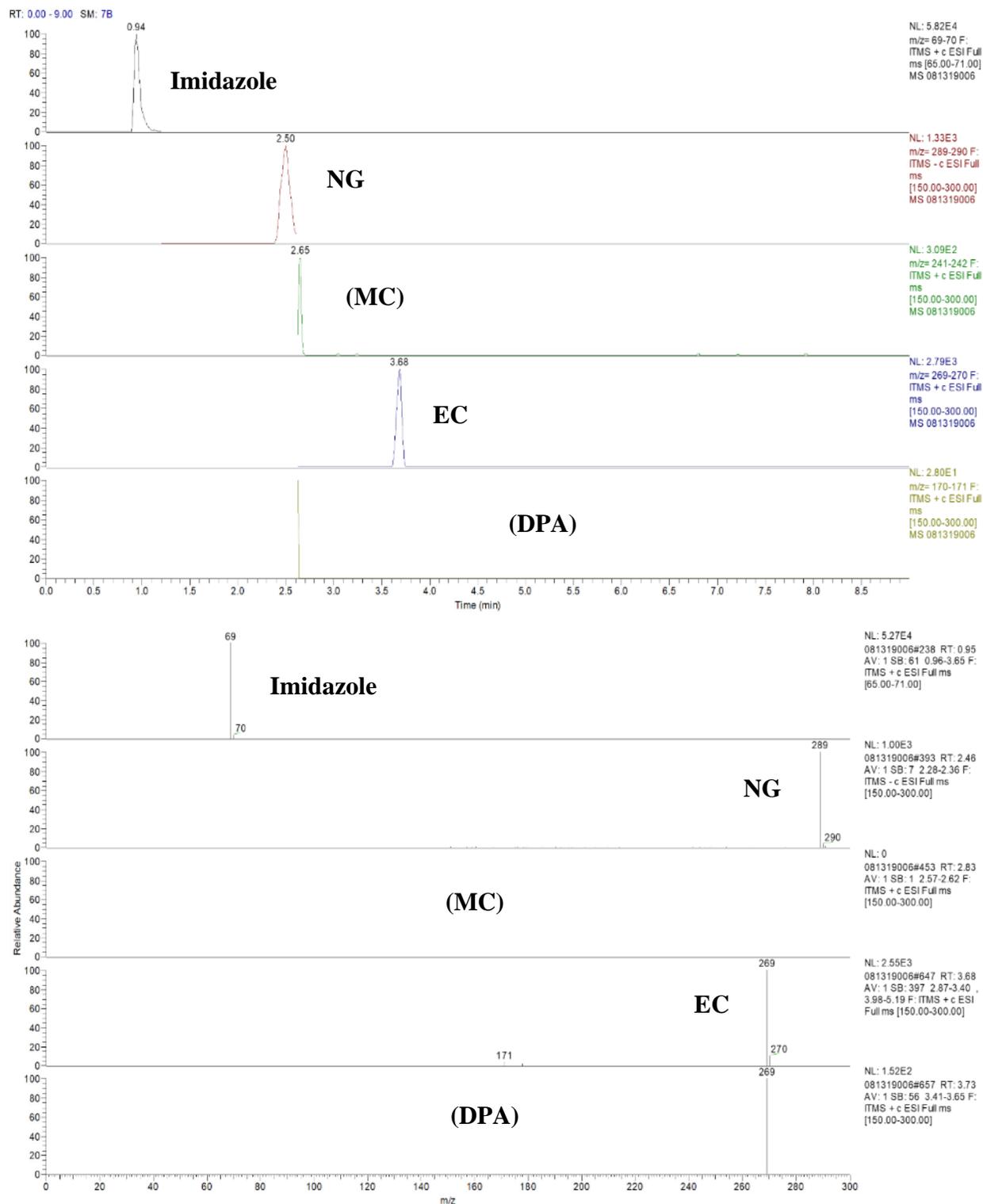


Figure 34: The EIC of extract resulting from the Remington NitroTurkey smokeless powder burned in a steel endcap. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA. NG and DPA were the only analytes detected.

Table 12: Peak area ratios for the compounds in the LC/MS analysis of the extracted residue from the burned Remington NitroTurkey smokeless powder. These ratios were normalized by dividing the initial ratio by the weight of the powder burned.

	Sample 1 Diluted	Sample 2 Diluted	Sample 3 Diluted
Weight of Powder (g)	0.01006	0.01005	0.01001
NG/Imidazole Area Ratio w/Powder	3.67	6.26	4.85
DPA/Imidazole Area Ratio w/Powder	0	0	0
EC/Imidazole Area Ratio w/Powder	4.43	5.03	4.13

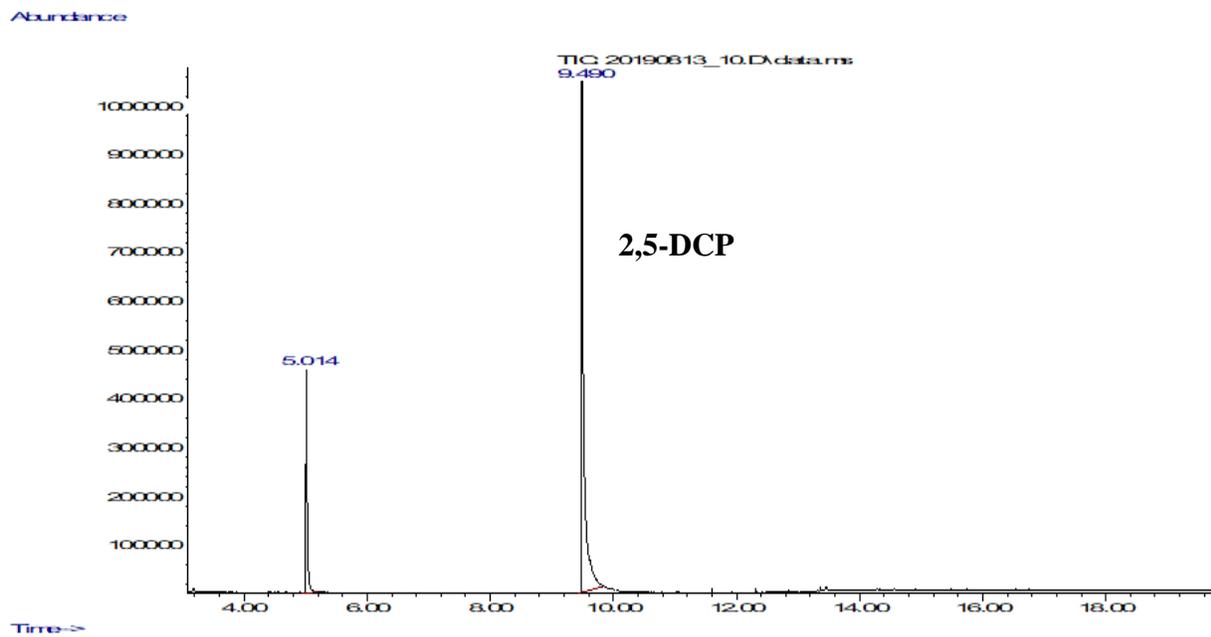


Figure 35: The chromatogram of the GC/MS analysis of the Remington NitroTurkey sample 1 burned smokeless powder extract. None of the analytes of interest were detected, only the internal standard 2,5-DCP was detected

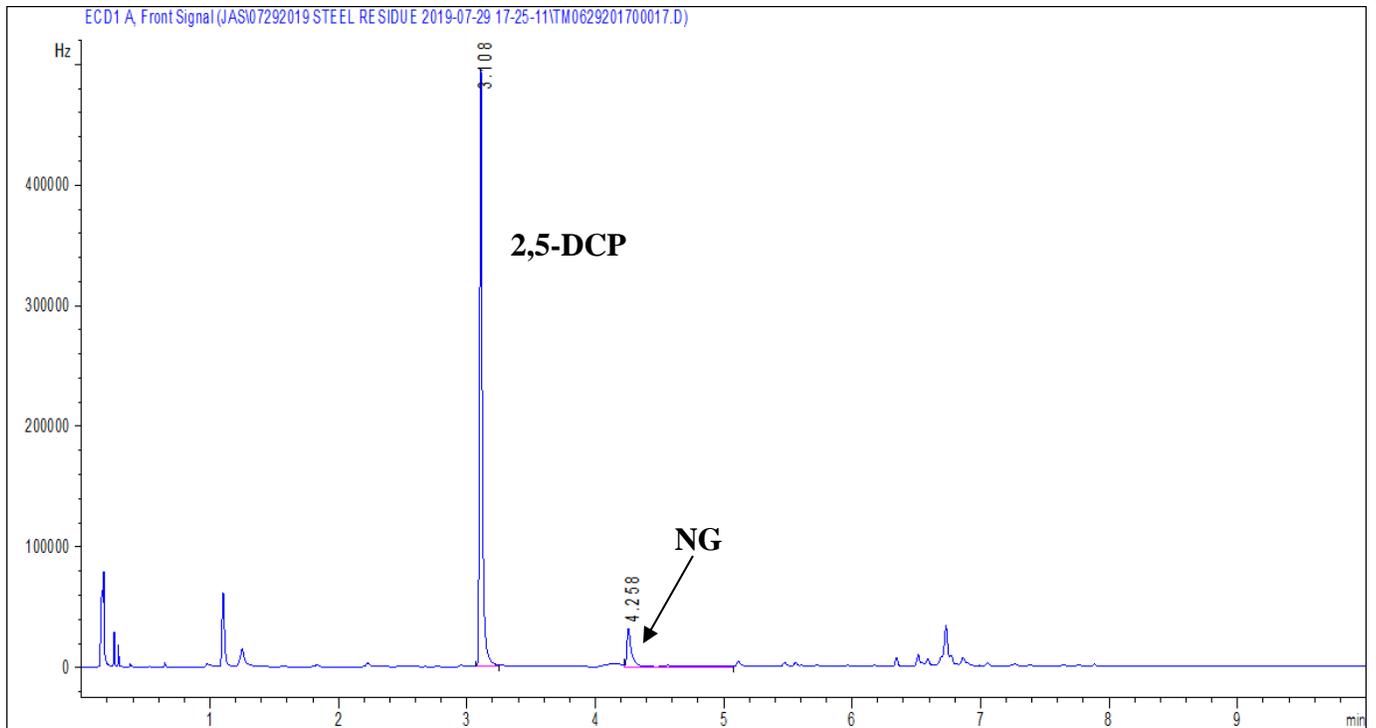


Figure 36: The GC/ECD chromatogram for the residue from pipe 2 recovered in the barrel rendered safe using the PAN disrupter and the Remington NitroTurkey shotgun round. NG eluted at 4.258 minutes. 2,5-DCP eluted at 3.111 minutes.

Table 13: Peak area ratios for NG in the GC/ECD analysis of the extracted residue from the steel pipes rendered safe using the PAN disrupter and Remington NitroTurkey shotgun round. Pieces from the same pipe were collected separately if they landed in the barrel or on the tarp.

	Steel Pipe 1 Barrel	Steel Pipe 1 Tarp	Steel Pipe 2 Barrel	Steel Pipe 3 Tarp	Steel Pipe 3 Tarp/Dirt
NG/2,5-DCP Peak Area Ratio	0	0.0083	0.1084	1.6674	0.0392

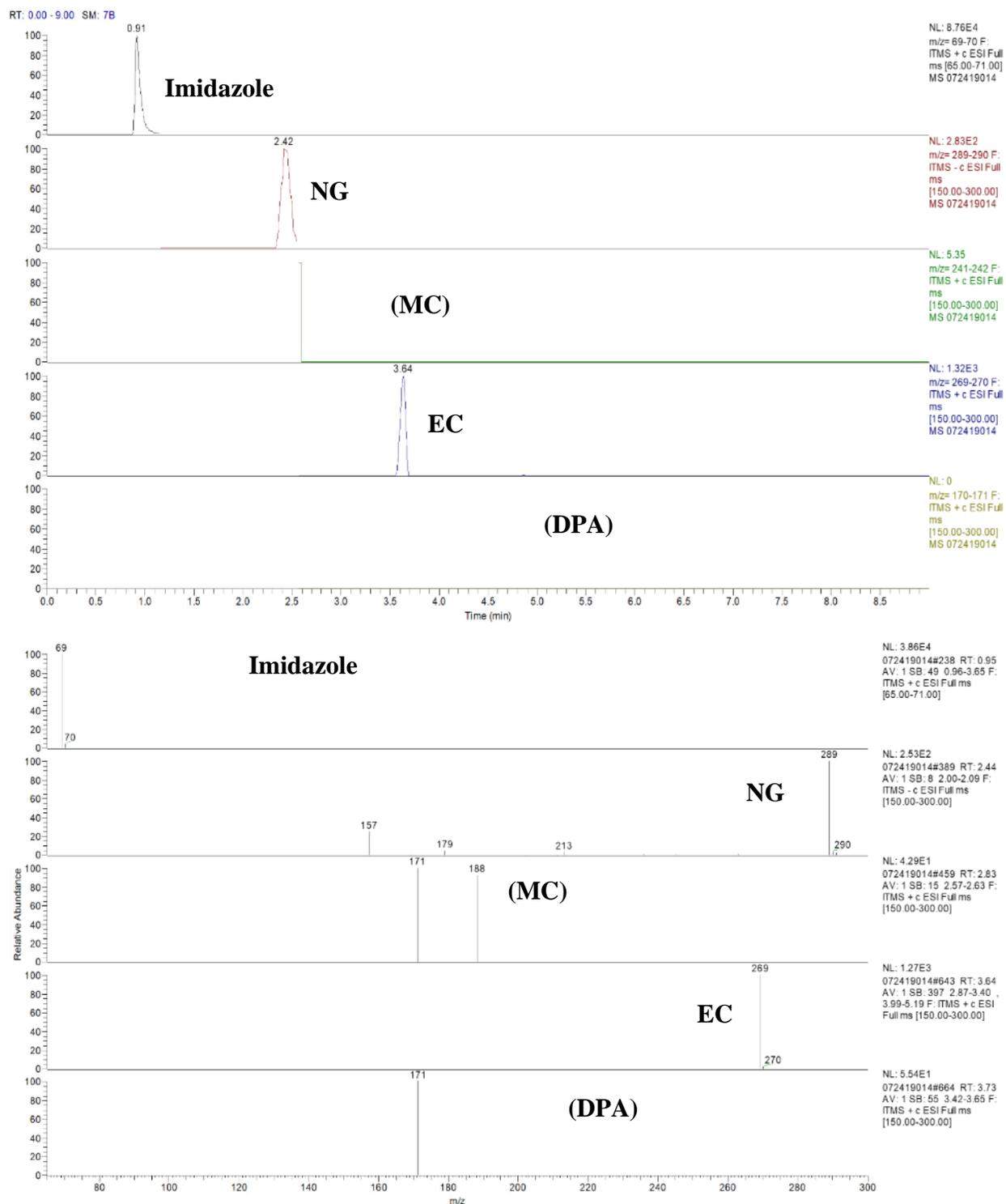


Figure 37: The EIC of the residue extract from pipe 2 recovered in the barrel that was rendered safe using the PAN disrupter and the Remington NitroTurkey shotgun round. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA. NG and EC were detected in addition to the imidazole internal standard.

Table 14: Peak area ratios for the compounds in the LC/MS analysis of the extracted residue from the steel pipes rendered safe using the PAN disrupter and Remington NitroTurkey shotgun round. Pieces from the same pipe were collected separately if they landed in the barrel or on the tarp.

	Steel Pipe 1 Drum	Steel Pipe 1 Tarp	Steel Pipe 2 Drum	Steel Pipe 3 Tarp	Steel Pipe 3 Tarp/Dirt
NG/Imidazole Peak Area Ratios	0.000532	0.000753	0.0105	0.0146	0.00233
DPA/Imidazole Area Ratio	0	0	0	0	0
EC/Imidazole Area Ratio	0	0	0.0138	0.0143	0.00377

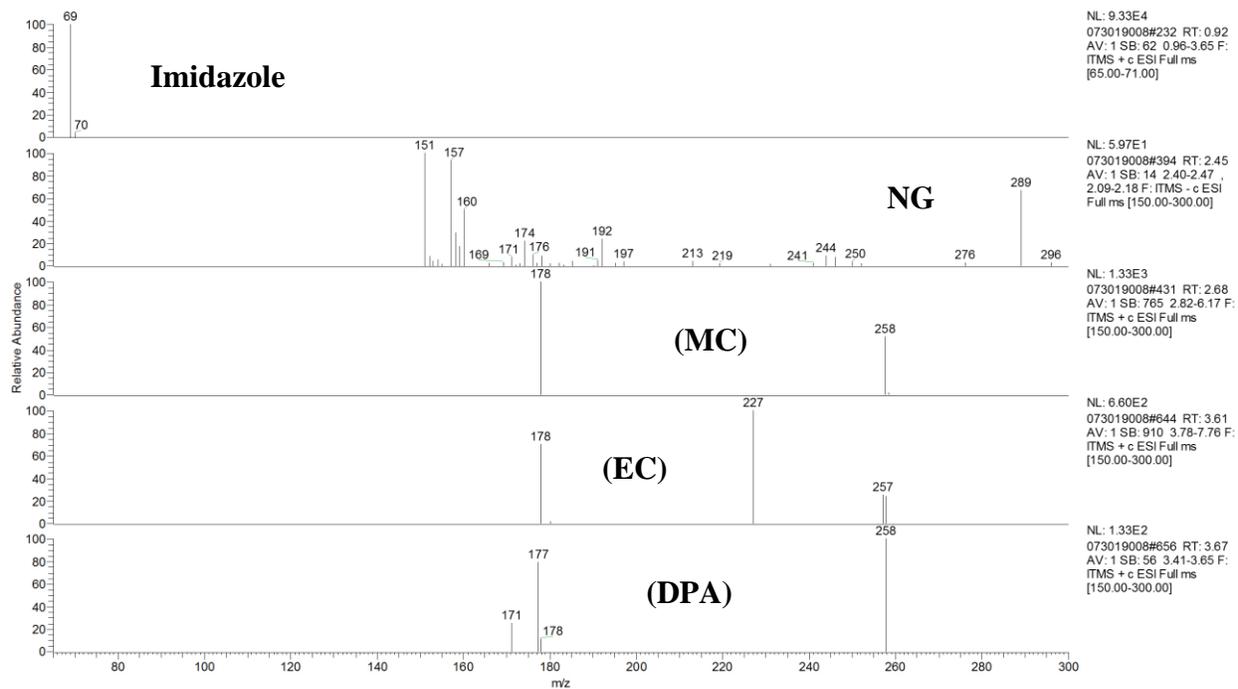
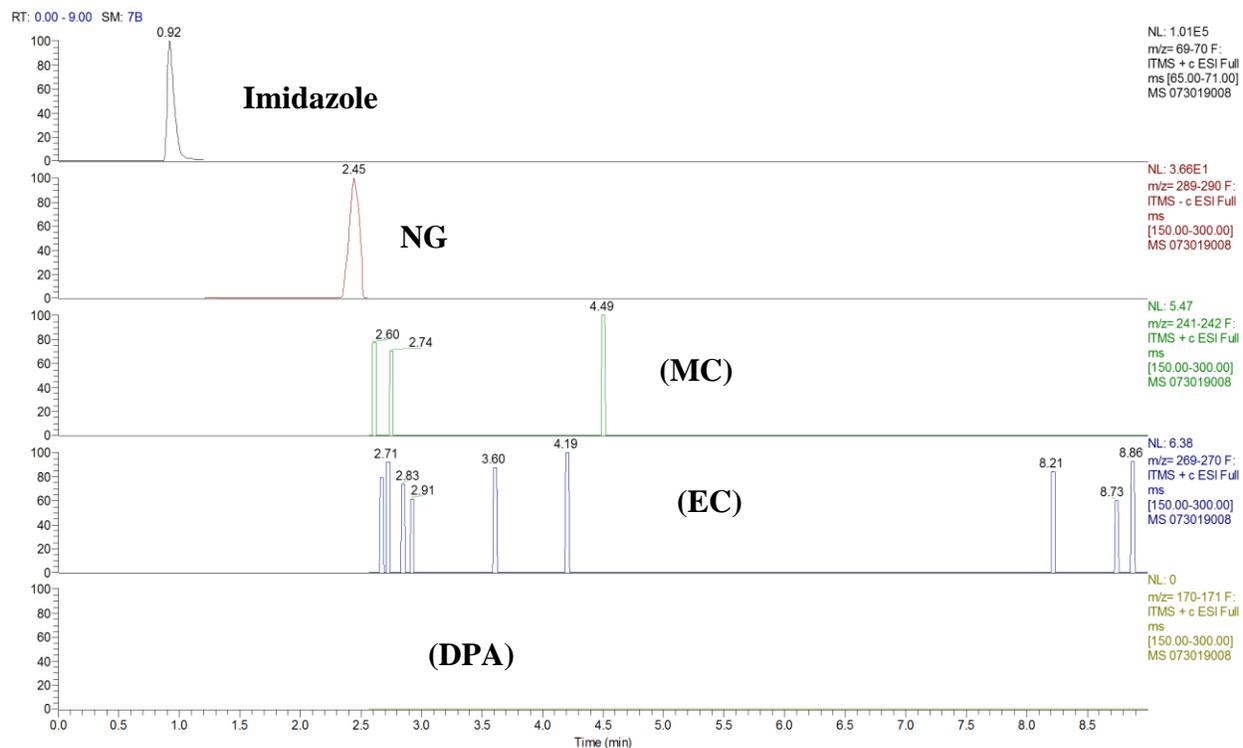


Figure 38: The EIC of the residue extract from pipe 1 recovered in the barrel that was rendered safe using the PAN disrupter and the Remington NitroTurkey shotgun round. The first line is imidazole, the second line is NG, the third line is MC, the fourth is EC, and the fifth line is DPA. NG was detected in addition to the imidazole internal standard.

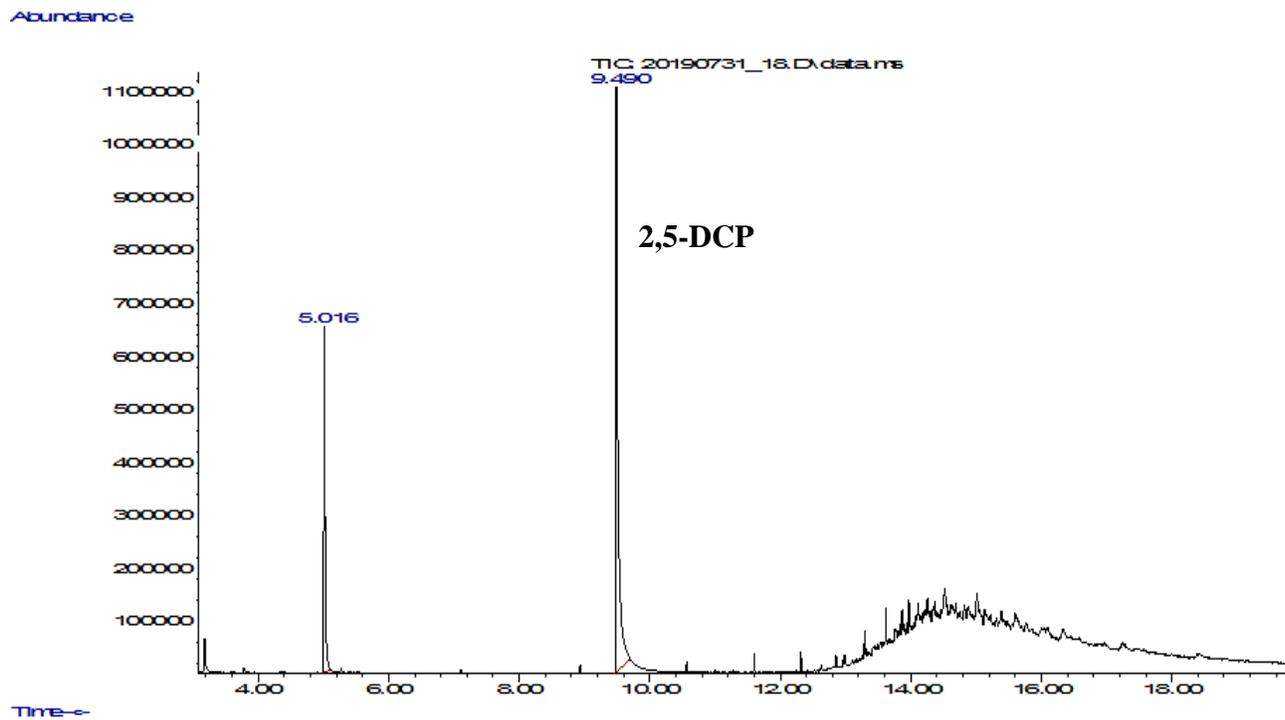


Figure 39: The GC/MS chromatogram for the residue from pipe 2 recovered in the barrel rendered safe using the PAN disrupter and the Remington NitroTurkey shotgun round. No analytes of interest were detected. 2,5-DCP eluted at 9.490 minutes.



Figure 40: Detonation cord utilized in the Mineral Bottle. A small amount of the high explosive powder used in the cord was collected into the metal tray. The ends are taped to prevent the cord from losing powder.

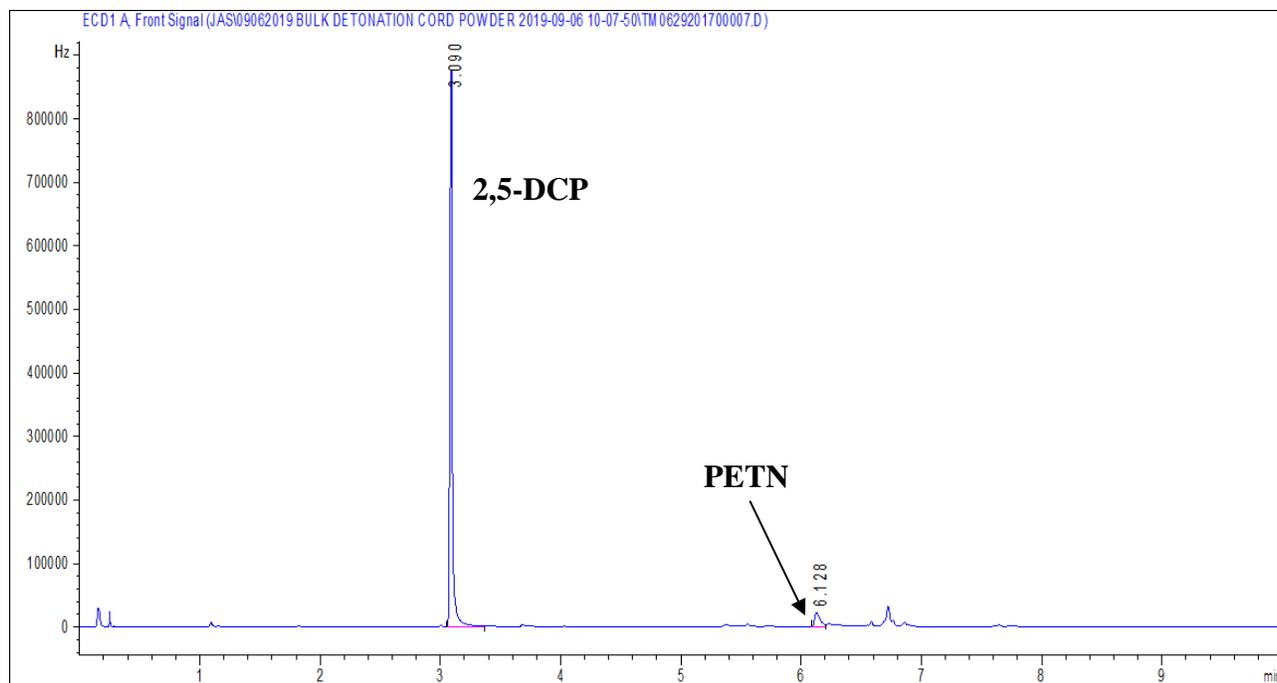


Figure 41: The GC/ECD chromatogram for the bulk detonation cord powder sample 1. PETN eluted at 6.128 minutes. 2,5-DCP eluted at 3.090 minutes.

Table 15: Peak area ratios for the PETN detected using the GC/ECD for the analysis of the bulk detonation cord powder.

	Sample 1	Sample 2	Sample 3
PETN/2,5-DCP Peak Area Ratio	0.05463	0.06946	0.06926

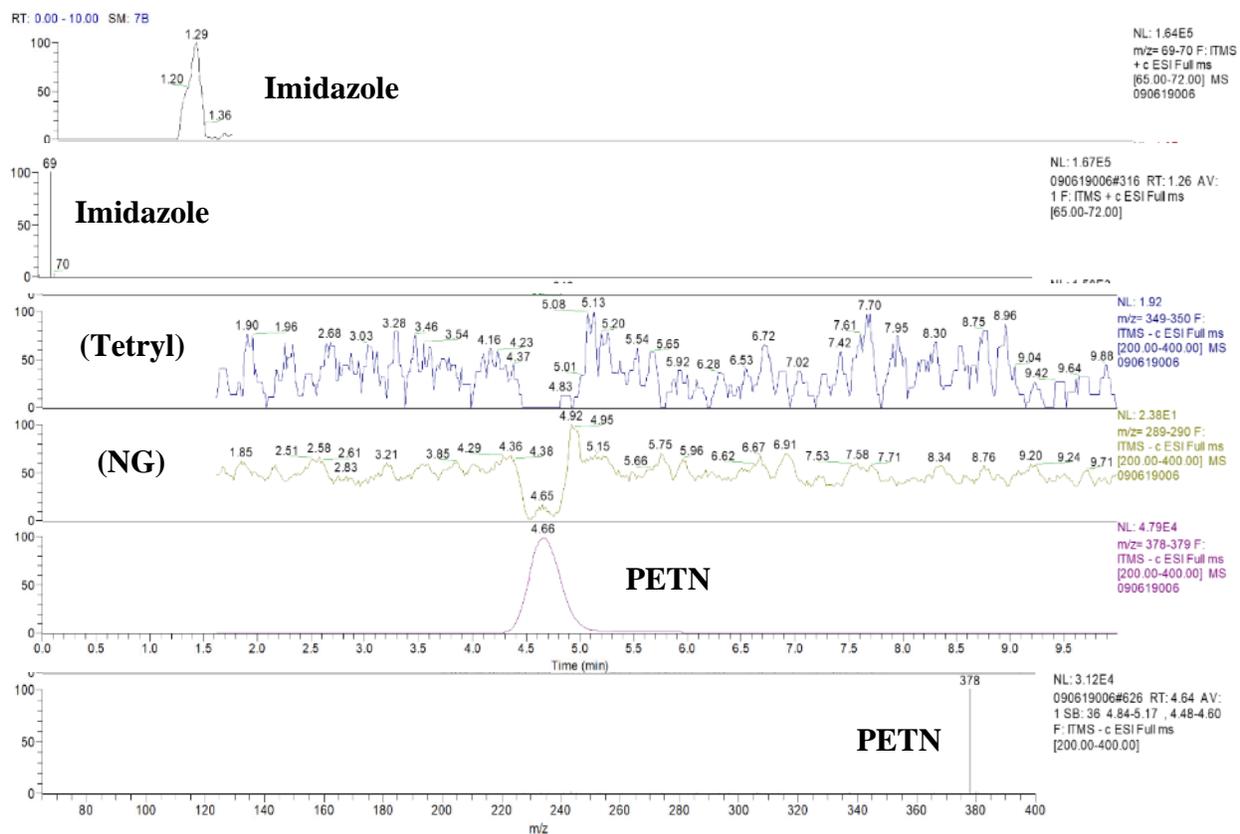


Figure 42: The EIC of the bulk detonation cord powder from sample 1. The first line is imidazole with its corresponding mass spectra, the second line is Tetryl, the third line is NG, the fourth is PETN, with its corresponding mass spectra. PETN was detected in addition to the imidazole internal standard.

Table 16: Peak area ratios for the PETN detected using the LC/MS for the analysis of the bulk detonation cord powder.

	Sample 1	Sample 2	Sample 3
PETN/Imidazole Peak Area Ratio	0.698	0.703	0.906

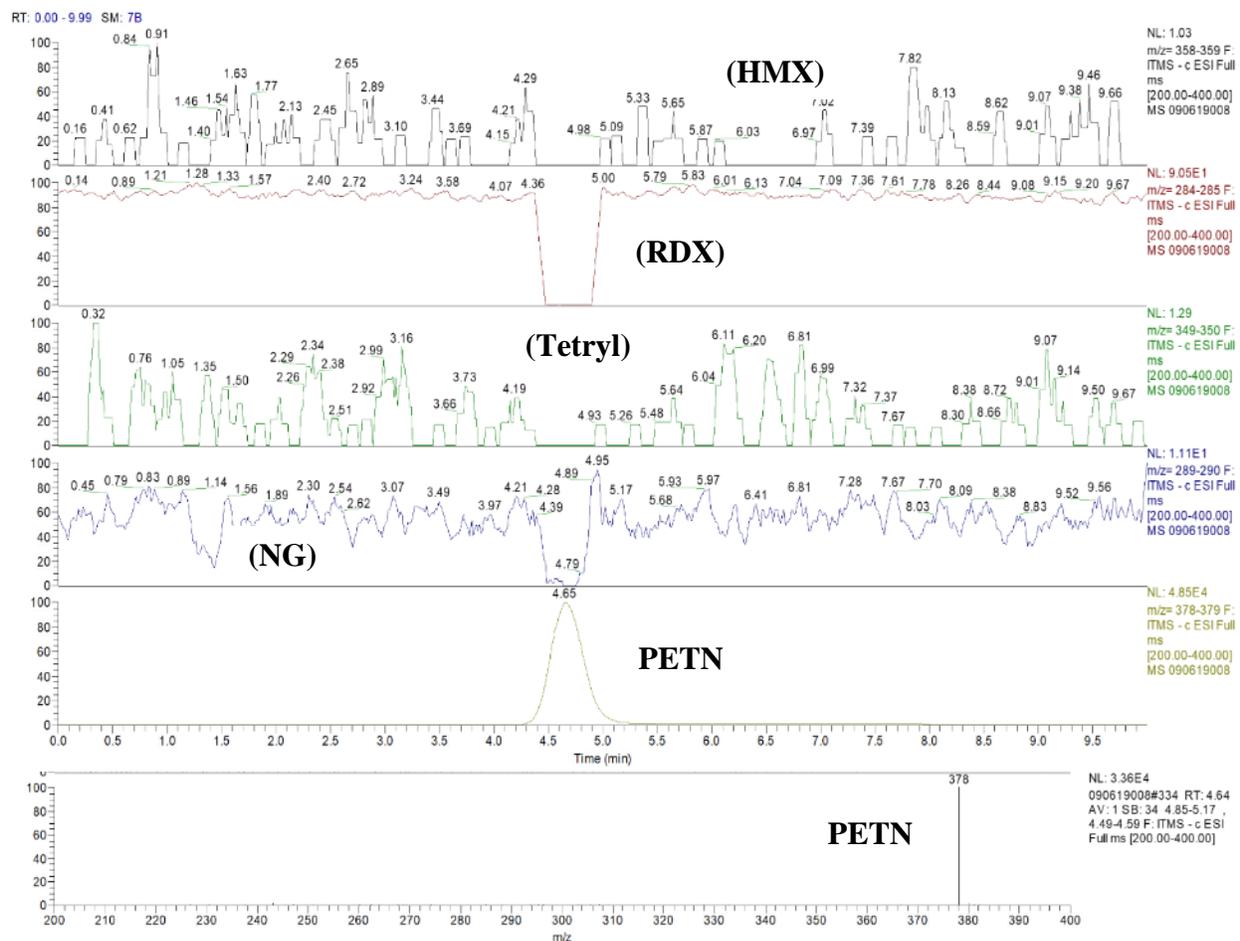


Figure 43: The EIC of sample 1 of the bulk detonation cord powder. The first line is RDX, the second line is HMX, the third is tetryl, the fourth is NG, and the fifth line is PETN. Only PETN was detected. The corresponding mass spectra confirms PETN’s identity.

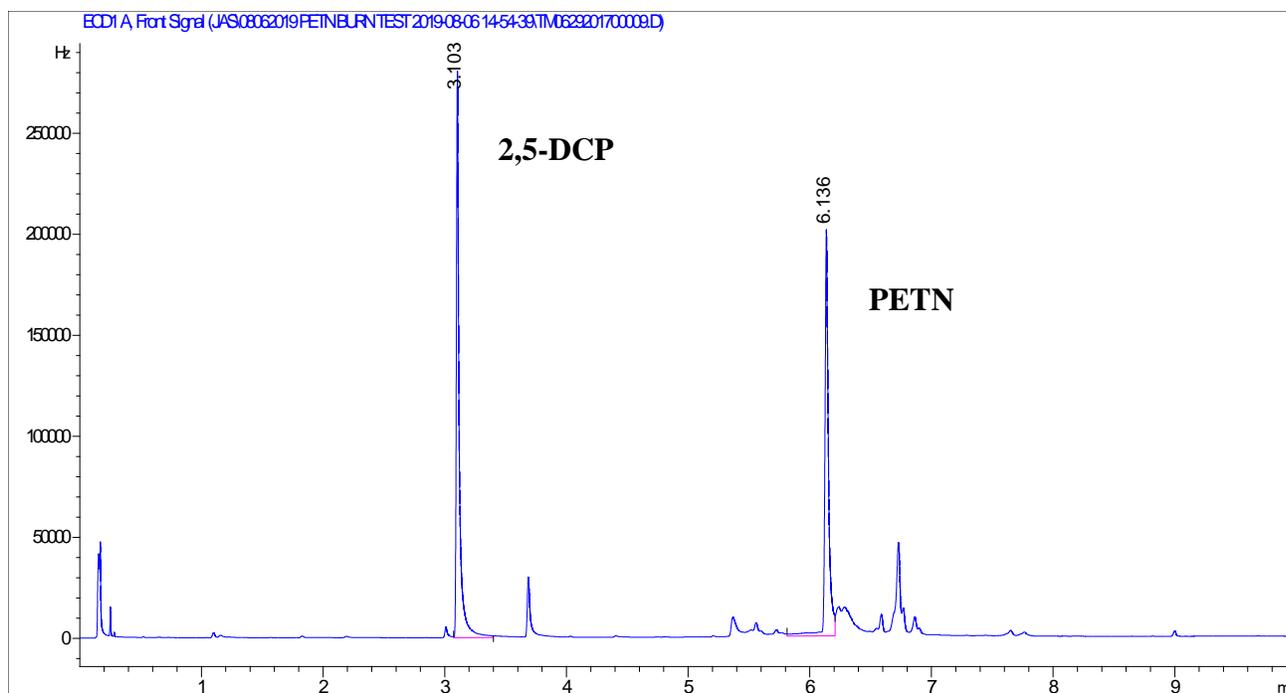


Figure 44: The GC/ECD chromatogram for sample 1 of the the burned detonation cord powder residue. PETN eluted at 6.136 minutes. 2,5-DCP eluted at 3.103 minutes.

Table 17: Peak area ratios for the PETN detected using the GC/ECD for the analysis of the residue from the burned detonation cord powder.

	Sample 1	Sample 2	Sample 3
Weight of Powder (g)	0.01003	0.01000	0.01005
PETN/2,5-DCP Peak Area Ratio w/Powder	89.35	67.01	34.58

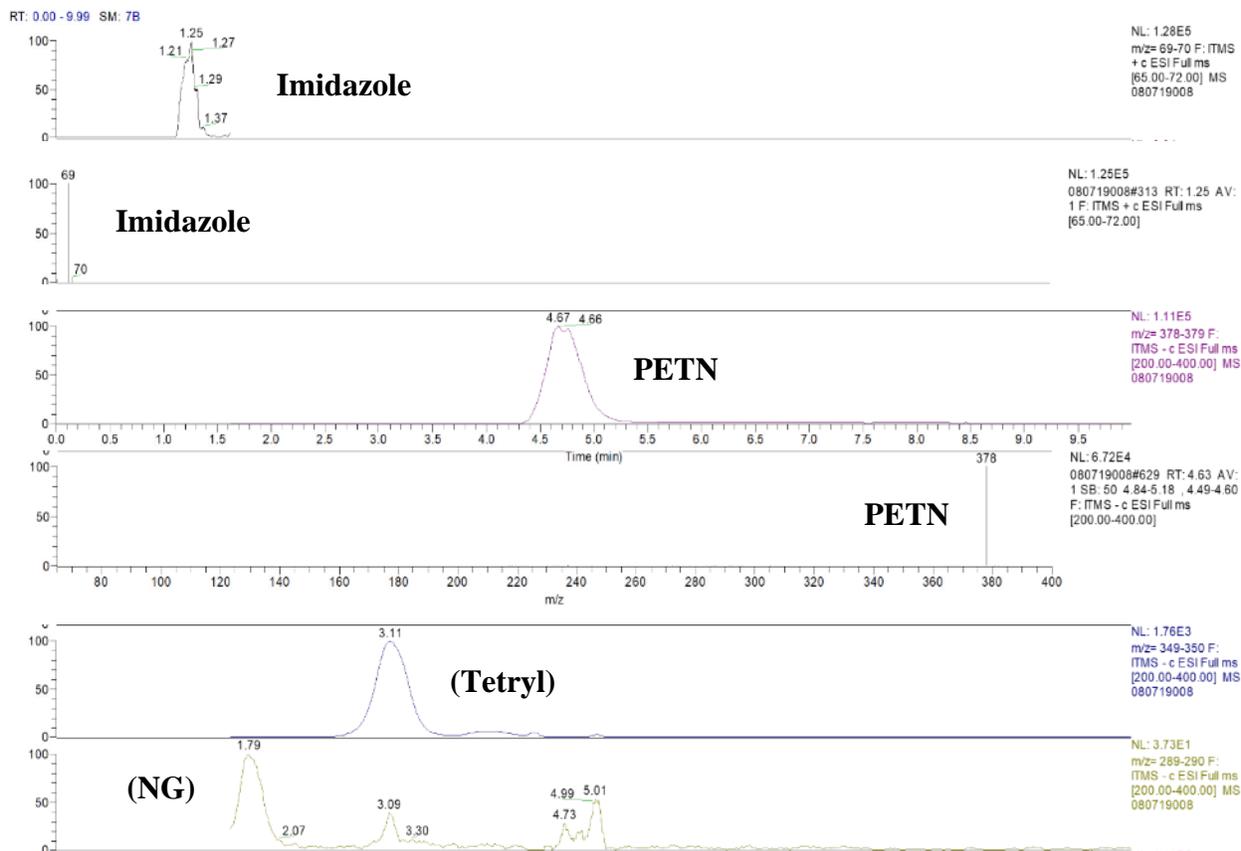


Figure 45: The EIC and mass spectrum of the residue from the burned detonation cord powder from sample 1. PETN was detected in addition to the imidazole internal standard. The EIC for Tetryl and NG had peaks present but the retention times did not match the corresponding standards

Table 18: Peak area ratios for the PETN detected using LC/MS for the analysis of the burned detonation cord powder residue.

	Sample 1	Sample 2	Sample 3
Weight of Powder (g)	0.01003	0.01000	0.01005
PETN/Imidazole Area Ratio w/Powder	274	201	181

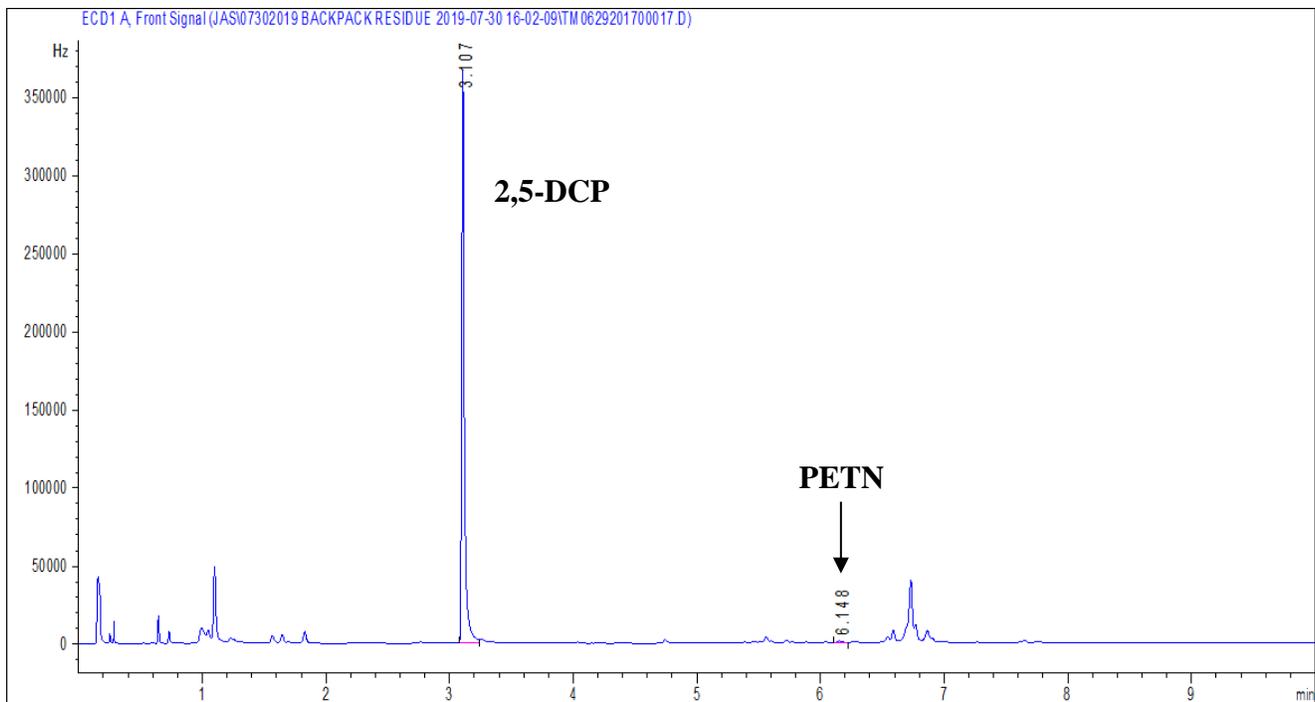


Figure 46: The GC/ECD chromatogram for the residue extract from backpack 2. PETN eluted at 6.148 minutes. 2,5-DCP eluted at 3.107 minutes.

Table 19: Peak area ratios for the PETN detected using the GC/ECD for the analysis of the residue from the backpacks. There was an error with the initial extraction from backpack 3. A second extraction of the first filter was performed along with a second vacuuming

	Backpack 1	Backpack 2	Backpack 3 Dried Down 1st Extract	Backpack 3 1st Filter 2nd Extract	Backpack 2nd Extract
PETN/2,5-DCP Peak Area Ratio	0	0.00653	0.00355	0	0

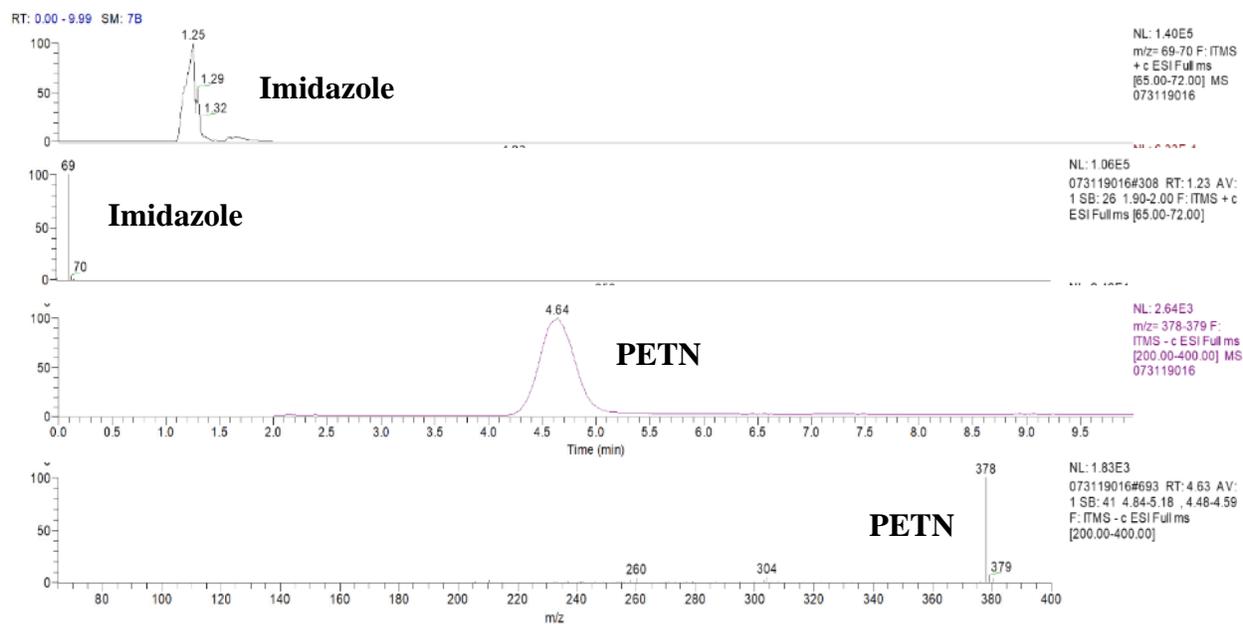


Figure 47: The EIC and mass spectrum of the residue from backpack 2. The first line is imidazole, the second line is PETN. PETN was detected in addition to the imidazole internal standard.

Table 20: Peak area ratios for the PETN detected using the LC/MS for the analysis of backpack residue. There was an error with the initial extraction from backpack 3. A second extraction of the first filter was performed along with a second vacuuming

	Backpack 1	Backpack 2	Backpack 3 Dried Down 1st Extract	Backpack 3 1st Filter 2nd Extract	Backpack 3 2nd Extract
PETN/Imidazole Peak Area Ratio	0.0201	0.0727	0	0	0

Table 21. Summary of compounds detected in the bulk powder (top) and compounds detected in the RSP residue (bottom).

RSP (Bulk Powder)	NG	EC	DPA	PETN
PAN (NitroTurkey)	Yes	Yes	Yes	No
PAN (L-Tech)	Yes	Yes	Yes	No
Mineral Water Bottle	No	No	No	Yes

RSP (Residue)	NG	EC	DPA	PETN
PAN (NitroTurkey)	Yes	Yes	No	No
PAN (L-Tech)	No	No	No	No
Mineral Water Bottle	No	No	No	Yes

Vita

Joseph Stein graduated from West Virginia University with Bachelor of Science Degrees in Chemistry and Forensic and Investigative Science with Emphasis in Chemistry in 2018. While attending West Virginia University, he worked on two research projects. One was on developing a method to detect both organic and inorganic gunshot residue using gas chromatography-mass spectrometry (GC-MS) and inductively coupled plasma-mass spectrometry (ICP-MS). The other project was developing a liquid chromatography-mass spectrometry (LC-MS) to analyze metabolites. Starting at West Virginia University and continuing while at Virginia Commonwealth University, Joseph has interned at the FBI Laboratory Division's Explosives Unit for the past three years where he completed his thesis. He is also a teaching assistant with the Virginia Commonwealth University's Forensic Science Department, mainly assisting with the microscopy and scientific crime scene investigation courses.