Identifying the Brand of Ammunition from Gunshot Residue

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Abstract

The analysis of gunshot residue (GSR) in forensic science can be used to link suspects to crimes, and link multiple crimes together, as well as providing police with intelligence. In the UK one of the most popular calibres of ammunition for target shooting is .22 Long Rifle (.22 LR). Limited research has been carried out to date on organic residues from this calibre, with most research focusing on inorganic residues or on other calibres more common in the USA and Europe. This research establishes a complete approach for collecting, sampling and analysing propellant and organic gunshot residue, and develops a bespoke, automatic interpretation method to allow fired cartridge cases to be linked back to unfired propellant through a database. The software was developed in Python and is available as Open-Source Software.

Unfired propellant and spent cartridge cases from three brands of .22 LR ammunition (Winchester “Pistol”, Eley “Contact”, and Geco “Rifle”) were analysed using an established method of solid-phase microextraction (SPME), gas chromatography (GC) and mass spectrometry (MS). SPME and GC-MS have previously been shown to be effective for analysis of gunshot residue. It has been possible to distinguish propellant and GSR samples from different brands, and link samples from the same brand together, based on the chromatograms and compounds identified by mass spectrometry.

The chemical compositions of the propellant and GSR from these brands are outlined. Possible further optimisations for the method to improve detection for different calibres of ammunition are also detailed.

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Glossary

.22 LR	.22 Long Rifle rimfire cartridge; 0.22” calibre
2-NDPA	2-nitrodiphenylamine, a derivative of diphenylamine
4-NDPA	4-nitrodiphenylamine, a derivative of diphenylamine
ACP	Automatic Colt Pistol, a type of cartridge
DNT	2,4-Dinitrotoluene, sometimes 2,4-DNT
DPA	Diphenylamine
EC	Ethyl Centralite
EIC	Extracted Ion Chromatogram
FTIR	Fourier-Transform Infra-Red Spectrometry
Ga.	Gauge (of a shotgun)
GC	Gas Chromatography
GSR	Gunshot Residue, also called Firearm Discharge Residue (FDR) or Cartridge Discharge Residue (CDR)
Hygroscopicity	How well a material absorbs moisture
IED	Improvised Explosive Device
IMS	Ion mobility spectrometry
MS	Mass Spectrometry
NC	Nitrocellulose
NG	Nitroglycerine
NIST	The National Institute of Standards and Technology
OGSR	Organic Gunshot Residue
PDMS/DVB	Polydimethylsiloxane / Divinylbenzene; a coating that may be used on SPME fibres
PETN	Pentaerythritol tetranitrate
S&W	Smith and Wesson
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis

SIM	Selective Ion Monitoring
Spl.	Special, a type of cartridge
SPME	Solid-Phase Micro Extraction
TIC	Total Ion Chromatogram
TNT	Trinitrotoluene
UK	United Kingdom
US	United States (of America)
Win.	Winchester

Definitions compiled from AFTE (2013), Murray *et al.* (2013), Barnes (2014), Linstrom and Mallard (2017) and Lucideon Limited (2018). Abbreviations of compounds not listed here are given in Appendix A (Page 45).

1. Introduction

Calibres of ammunition used in research are primarily those designed for handguns. By far the most popular calibre is 9 mm Parabellum, also called 9 mm Luger, and has been used in research by Reardon, MacCrehan and Rowe (2000), Brożek-Mucha and Zadora (2003), Burleson *et al.* (2009), Dalby and Birkett (2010), Arndt *et al.* (2012), and Hofstetter *et al.* (2017). Handguns are commonly used in crime in the United Kingdom (UK) and the United States (US) (*The Trace*, 2016, *BBC News*, 2018; Wright, 2017), and the 9 mm Parabellum cartridge is popular with police and military around the world (Sweeney, 2003; Barnes, 2014)

There has also been limited research involving rifle and shotgun ammunition by Dalby (2011), Tarifa and Almirall (2015), and Wilson, Tebow and Moline (2003). The most comprehensive study of organic compounds in propellant from different ammunition types was by Dalby (2011), although that study only analysed a few brands for each calibre.

Research involving small calibre rimfire ammunition appears to be fairly limited. Wrobel, Millar and Kijek (1998) developed a classification system for ammunition, Berg (1964) developed a classification system for firing pin impressions on 0.22” calibre cases to determine the type of firearm used, and Wallace and McQuillan (1984) analysed nail gun blanks for inorganic GSR. Dalby (2011) analysed propellant and organic gunshot residue (OGSR) from Vostok and Remington .22 Long Rifle ammunition. Lucas *et al.* (2016) analysed inorganic residues from suicides involving 0.22” calibre firearms.

1.1. .22 Long Rifle

First introduced in the 1800s, .22 Long Rifle (.22 LR) is one of the most popular calibres for target shooting in the UK and around the world (Whiting, 2010; Windham, 2013; Mike George, 2017). The .22 BB cap, .22 Short, .22 Long, and .17 HMR cartridges are all related to .22 LR and use similar cartridge cases (Barnes, 2014). Figure 1-1 shows a cross-section of a .22 LR cartridge.

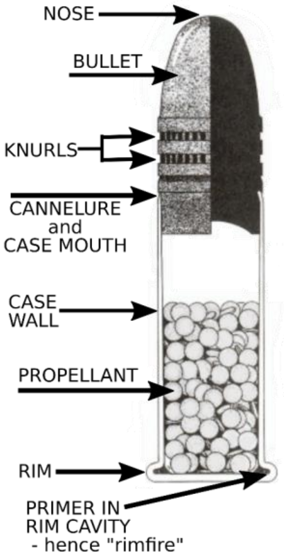

Figure 1-1: Cross-section of a .22 LR cartridge. Adapted from (ELEY Ltd, 2014)

1.2. Components of a Cartridge

A modern rifle or pistol cartridge contains several components: a primer, smokeless powder propellant, a bullet and a cartridge case (Wallace, 2008). These are shown in Figure 1-1.

The *primer* contains a small amount of an impact-sensitive high explosive which, in rimfire ammunition like .22 LR, is situated in a groove inside the rim of the cartridge case. When the trigger of a firearm is pulled, a firing pin strikes the primer and causes it to detonate (Warlow, 1996). Hot gases and particles produced by the detonation of the primer ignite the main *propellant* charge inside the cartridge, which burns slower than the primer and releases gases to increase the pressure in the case and propel the bullet down the firearm's barrel (Meng and Caddy, 1997; Wallace, 2008).

The *bullet* is usually made from lead, which may be coated with copper or alloyed with harder metals such as antimony. .22 LR bullets are often uncoated (Meng and Caddy, 1997; Wallace, 2008). The bullet is seated slightly inside the cartridge case mouth, which is crimped into the *cannelure* of the bullet to make a tight fit (ELEY Ltd, 2014). Cartridge cases are often made from brass, but can be made from other metals such as steel, which is common in Russian ammunition (Schwoeble and Exline, 2000; Wallace, 2008).

Paraffin, tallow, beeswax and several other long-chain hydrocarbons are added to the *cannelure* and *knurls* on the rear of the bullet to lubricate the bullet as it passes along the barrel (Wallace, 2008; Barnes, 2014). A comprehensive list of lubricants and their ingredients is available in Schneider and Hurst (2016).

1.3. Gunshot Residue

Gunshot residue (GSR) consists of gases, vapours, particulates and residues produced when a firearm is discharged, which originate from burned, unburned and partially burned propellant granules; residues from the primer; metals from the projectile; and lubricant from the cartridge (AFTE, 2013, p. 59; Hofstetter *et al.*, 2017). Residues remaining in the firearm after previous firings will also contribute to the GSR. The propellant is the largest contributor to GSR (Wallace, 2008). Analysis of GSR can aid in determining its source and link individuals to shooting events (Meng and Caddy, 1997; Reardon, MacCrehan and Rowe, 2000; Hofstetter *et al.*, 2017).

Brozek-Mucha and Zadora (2003) developed a method to identify the brand and calibre of four different types of handgun ammunition from the metals present in GSR when analysed by SEM-EDX. The method allowed 7.65 mm Browning and 9 mm Parabellum cartridges to be differentiated, but not 7.62 mm Tokarev or 9 mm Makarov. The metals examined were limited to those present in the ammunitions' primers, but the authors suggested that Makarov and Tokarev ammunition could be differentiated through analysis of organic residues from the propellant.

Meng and Lee (2007) determined the metallic elements present in the primer and GSR of 25 different handgun cartridges: 9 mm Parabellum, .40 S&W, .32 S&WL and .38 Spl..

Some of the cartridges had non-corrosive or lead-free primers, and the analysis was carried out by SEM-EDX. The authors found that the major elements in the GSR tallied with those present in the primer, and elements other than lead, barium and antimony were present in different combinations. Many of the different types of cartridge could be differentiated, including those that had the same headstamp

1.4. Compounds in Primers

Primers consist of at least three compounds performing different functions:

- Fuels, such as antimony sulfide, which burn rapidly and ignite the propellant
- Oxidisers, such as barium nitrate, which give up oxygen to allow the fuel to burn
- Initiators, such as lead styphnate, which are shock sensitive and start the reaction

Due to health hazards, these compounds are being replaced by non-toxic compounds, such as 2-diazo-4,6-dinitrophenol, TNT or PETN in place of lead styphnate, and zinc peroxide in place of barium nitrate. Primers containing these compounds are manufactured by CCI, Fiocchi, and Dynamit Nobel (under the Sintox® brand) (Hagel and Redecker, 1986; Schwoeble and Exline, 2000; Wallace, 2008).

GSR particles containing lead, barium and antimony are referred to as “inorganic GSR”. Heavy-metal-free or non-toxic primers may not produce inorganic GSR (Schwoeble and Exline, 2000; Benito *et al.*, 2015). Particles of lead, barium and antimony may also be absent in the GSR from .22 LR cartridges (Taudte *et al.*, 2014).

1.5. Compounds in Smokeless Propellant

Smokeless powder propellants are complex mixtures of multiple chemicals, and the compounds detected will be both those added during manufacture and the decomposition products of those compounds (Espinoza and Thornton, 1994; Meng and Caddy, 1997; Bender, 1998). Additionally, batches of propellant which are below specification may be “reblended” with other additives to manufacture new batches of propellant (Heramb and McCord, 2002).

Ethyl centralite (EC), 2,4-dinitrotoluene (DNT) and diphenylamine (DPA) are some of the most characteristic OGSR compounds (Mach, Pallos and Jones, 1978). A more comprehensive list of additives is available in Appendix A. Many minor additives were listed in only one or two literature sources, and reference mass spectra are not available for every compound (NIST Mass Spec Data Center and Stein, no date).

The composition of individual propellant granules can vary considerably, and analysing single granules of fired or unfired propellant is not recommended (Reardon, MacCrehan and Rowe, 2000; Wallace, 2008). Reardon, MacCrehan and Rowe (2000) used capillary electrophoresis to analyse organic compounds in reloading powders from a variety of manufacturers. They found that, while some powders had similar compositions, others varied in the concentration of nitroglycerine and the stabilisers present.

Smokeless powders are available in a variety of colours, and this can aid identification of the propellant (Heramb and McCord, 2002; Wallace, 2008).

Dalby (2011) analysed standards of many of the compounds present in smokeless powder. However, he was only able to identify the combustion products by searching their mass spectra against the NIST database. Dalby focused on compounds that had previously been reported as combustion products in literature, such as in Weyermann *et al.* (2009), but many of the cartridges analysed did not show obvious peaks for these compounds.

1.5.1. Energetics

Nitrocellulose (NC) is used as the main explosive in all smokeless propellants, functioning as both the oxidiser and fuel for the explosion (Bender, 1998). Propellants containing only nitrocellulose are called “single base”, and are mainly used in rifle cartridges, with occasional use in some revolver cartridges (Meng and Caddy, 1997).

Nitroglycerine (NG) may be added to form a “double base” propellant, with increased performance. Nitroglycerine is a high energy oxidising plasticiser which also softens the propellant and reduces its hygroscopicity (how well the propellant absorbs moisture) (Heramb and McCord, 2002; Dalby, 2011). Double base propellants typically contain between 5% and 44% nitroglycerine, and are used in both revolver and pistol cartridges and in shotgun shells (Warlow, 1996; Meng and Caddy, 1997; Wallace, 2008). Rimfire cartridges may be single or double based (Dalby, 2011; Eurenco, 2013).

Nitrocellulose and nitroglycerine cannot be used as a propellant in their original form because they react too violently. Instead, they are colloided – dissolved in alcohol or ether to form a plastic-like material of microscopic particles in suspension. This material can then be extruded into various shapes and cut up to produce powder granules. The shape of the extruded material and the manner in which it is cut produces a variety of differently shaped granules (Warlow, 1996; Heramb and McCord, 2002; Dalby, 2011).

1.5.2. Plasticisers

Plasticisers are added to reduce the volume of solvent required to colloid the nitrocellulose (see section 1.5.1) (Bender, 1998). Examples of plasticisers include phthalates, triacetin, and resorcinol (Meng and Caddy, 1997; Taudte *et al.*, 2014).

1.5.3. Moderants

Propellant granules may be coated with moderants such as phthalates, centralites, and natural resins. This reduces the burning rate and temperature to improve performance (Heramb and McCord, 2002; Wallace, 2008). Additionally, powders that burn at a lower temperature are preferred to reduce corrosion of the barrel, but faster-burning powders have reduced muzzle flash (Ball, 1931).

1.5.4. Flash Suppressors

Nitrotoluenes, nitroguanidine and triacetin may be added as flash suppressors, which produce nitrogen gas to dilute the muzzle gases and reduce the brightness of the flash (Meng and Caddy, 1997; Taudte *et al.*, 2014)

1.5.5. Stabilisers

Stabilisers react with the decomposition products of nitrocellulose – nitric acid, dinitrogen tetraoxide, and nitrous acids – to prevent further decomposition (Espinoza and Thornton, 1994; Meng and Caddy, 1997; Heramb and McCord, 2002). Stabilisers do not usually make up more than 2% of the propellant (Wallace, 2008). Examples of stabilisers include diphenylamine, phthalates, centralites, and resorcinol (Warlow, 1996; Meng and Caddy, 1997; Heramb and McCord, 2002)

Diphenylamine (DPA) is a common stabiliser in single base propellants and has several sites that can be nitrated to form a variety of derivatives. Not all sites are nitrated on every derivative, and some of these are listed in Table 1-1. Nitrated derivatives can continue to act as stabilisers until all sites are nitrated, forming 2,2',4,4',6,6'-hexanitro-DPA. (Espinoza and Thornton, 1994)

Different nitration products form depending on the storage conditions; after a prolonged period at high temperatures there may be no unreacted DPA remaining (Espinoza and Thornton, 1994; Taudte *et al.*, 2014). Reardon, MacCrehan and Rowe (2000) recommended measuring the concentration of diphenylamine and its derivatives together.

Table 1-1: Nitration products of diphenylamine.

2,2-dinitro-DPA	2-nitro-DPA
2,2'-dinitro-DPA	4-nitro-DPA
2,4-dinitro-DPA	*N*-nitroso-2-nitro-DPA
2,4'-dinitro-DPA	*N*-nitroso-4-nitro-DPA
4,4-dinitro-DPA	2,4,6-trinitro-DPA
4,4'-dinitro-DPA	4-nitroso-DPA
Pieric acid (2,4,6-trinitrophenol)	

(Levitsky, Norwitz and Chasan, 1968; Espinoza and Thornton, 1994; Bender, 1998)

2- and 4-NDPA may also be added as stabilisers during the manufacture of the propellant (Wallace, 2008; Dalby, 2011).

1.5.6. Environmental Sources of OGSR Compounds

Some of the compounds in propellant are also present in the environment, and examples of these are shown in Table 1-2. Their value for identifying gunshot residue is limited, but these compounds may prove useful to distinguish smokeless powder and GSR samples from different sources (Goudsmits, Sharples and Birkett, 2016).

Table 1-2: Environmental sources of OGSR compounds

Compound	**Environmental Source**
Diphenylamine	Growth regulator for picked fruit (Espinoza and Thornton, 1994; EPA, 1998)
Dibutyl Phthalate	Solvent in some deodorants (Davidson, 2017)
Nitrocellulose (NC)	Lacquers, paint and celluloid film (Morelato *et al.*, 2012)
Nitroglycerine (NG)	Cardiac stimulant (Meng and Caddy, 1997)
Breakdown products of NC and NG	Industrial explosives (Fernández de la Ossa *et al.*, 2011; Benito *et al.*, 2015)

Some industrial tools, such as nail guns, are operated by blank firearm cartridges, including .22 LR blanks (Hilti United Kingdom, no date; Wallace and McQuillan, 1984). The cartridges are manufactured by some of the companies who manufacture cartridges for firearms, including Eley, Winchester, and Dynamit Nobel (Wallace and McQuillan, 1984; Olin Winchester Ammunition, 2017). Wallace and McQuillan (1984) demonstrated that GSR produced by blank cartridges could be identified by SEM-EDX analysis, due to the lack of lead only particles that would have originated from the bullet. However, it is unclear whether analysis of organic GSR could be used to distinguish blank and live cartridges.

Population studies and sampling of police vehicles have not detected any of the main additives in propellants (Goudsmits, Sharples and Birkett, 2016; Hofstetter *et al.*, 2017).

1.5.7. Morphology of Smokeless Powder

The morphology of smokeless powder granules under a low-power microscope can indicate whether the powder is single or double base. Single base powders may have a tube or cylinder shape, with disc and ball-shaped granules common for double base propellants. However, some single base propellants may be disc or ball-shaped, and vice versa (Bender, 1998; Heramb and McCord, 2002). Some ball-shaped propellants are passed through rollers to produce flattened balls, but these can be difficult to distinguish from non-flattened balls. The shape of the propellant can also aid in identifying the manufacturer of the propellant (Selavka, Strobel and Tontarski, 1989).

1.6. Relationship Between Propellant and OGSR

Dalby (2011) found that most of the compounds present in unfired powder samples are not present in the OGSR in the fired cartridge cases. There was large variability in the relative abundances of compounds in the fired cases and these bore no relation to the unfired powder samples. Some compounds were detected in large concentrations in some cartridge cases from one ammunition type while going completely undetected in the other. Surface coatings, such as moderants, may be lost from propellant granules when fired (Wallace, 2008).

Dalby (2011) found that most variation between repeat samples is due to differences in powder composition between cartridges, with some attributable to the extraction and analysis. One cause of inter-sample variation may be the manual adsorption and desorption of the solid phase microextraction (SPME) fibre (Dalby, 2011).

The 16 different ammunition types tested by Dalby (2011) all had distinct compositions, and although some produced OGSR with distinct compositions many of the samples did not contain any detectable compounds. It was also possible to link cartridges from the same box of ammunition together. Bender (1998) found that the additives present in Hercules Unique® (now Alliant Unique®) and Herco® powders were too similar to distinguish them based on the presence of additives alone. The 9 mm Geco ammunition tested by Hofstetter *et al.* (2017) mainly contained DPA and N-nitrosoDPA, both of which were the main chemicals present in the GSR produced by the ammunition. 2-NDPA and 4-NDPA were also present.

Reardon, MacCrehan and Rowe (2000) loaded the same reloading powder into 9 mm Parabellum, .38 Spl. and .45 ACP cartridges. They found that the amount of OGSR produced varied considerably between cartridges, but there was no relationship between the amount of OGSR and the cartridge's calibre. There appeared to be a relationship between the composition of residues and the unfired powder, but this was discounted after testing two additional propellants.

1.7. Chemical Analysis of Gunshot Residue

1.7.1. Packaging of Fired Cartridge Cases

When recovering a spent cartridge case for analysis of OGSR, it is advantageous if the concentration of volatile compounds remains the same when the casing is analysed as when it was recovered (Wilson, Tebow and Moline, 2003).

Wilson, Tebow and Moline (2003) evaluated three different methods of sealing fired shotgun cartridges to prevent the loss of volatile compounds, and found that sealing the entire shell in a glass vial with an SPME-compatible lid was the most effective. The concentration of naphthalene was measured as a proxy for the various volatile compounds in GSR, and the concentration remained almost constant for nearly four weeks after firing. This method of packaging has been used in research by Burleson *et al.* (2009), Weyermann *et al.* (2009) and Dalby (2011).

OGSR compounds may adsorb onto the glass vial if the fired cartridges are stored for a prolonged period before analysis, causing a decrease in the measured concentration (Conrad, 1989; Gallidabino and Weyermann, 2016),

1.7.2. Solid-Phase Microextraction

Solid-phase microextraction (SPME) is a rapid sampling and sample preparation technique that can be used to analyse a range of samples, both in the laboratory and in the field (Chen and Pawliszyn, 2007; Hübschmann, 2015). The fused silica fibres are coated with a polymer such as divinylbenzene (DVB) and can be immersed in liquid samples or exposed to gaseous and headspace samples for extraction of analytes. The analytes diffuse onto the fibre's coating. Fused silica is also used to manufacture gas chromatography columns (Hübschmann, 2015).

A variety of polymer coatings exist and are optimised for extraction of different molecules based on size and polarity (Hübschmann, 2015). Dalby and Birkett (2010) reviewed seven SPME fibres against their ability to extract 30 compounds commonly found in smokeless propellant. Four different centre-fire ammunition brands in three different calibres were examined. GC-MS was used to identify the compounds detected by each fibre, with solvent extraction used to provide a baseline against which the fibre's performance was evaluated. The authors concluded that 65 µm PDMS/DVB fibres were the most suitable. These fibres are recommended for analysis of volatile compounds, amines, and nitro-aromatic compounds, with a molecular mass between 50 and 300 (Merck KGaA, 2018)

Weyermann et al. (2009) evaluated the performance of three SPME fibres, two of which were in common with Dalby and Birkett. For reference standards, they found the optimal extraction time to be 40 minutes with an 85 µm polyacrylate fibre. This fibre is recommended for analysis of polar semi-volatile compounds. However, when tested with fired cartridge cases, only diphenylamine was extracted.

Dalby (2011) and Weyermann et al. (2009) found that extraction carried out at higher temperatures (80°C) allowed for the extraction of more compounds than extractions carried out at lower temperatures (40°C) or room temperature. Andrasko and Ståling (1999) also encountered difficulty with extractions at room temperature. Dalby (2011) also determined that the optimal extraction time was 35 minutes, with the sample incubated for 10 minutes before extraction.

Sampling and injection into the gas chromatograph can be automated or carried out manually. Internal standards can be used with SPME to improve the standard deviation of the analysis, and there is no need for a solvent, which helps to minimise background noise (Chen and Pawliszyn, 2007; Hübschmann, 2015).

1.7.3. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography (GC) is a technique that allows for separation of complex mixtures of compounds (McCord and Bender, 1998). An inert carrier gas sweeps the mixture along several metres of a packed- or capillary-column containing a solid stationary phase. The column passes through an oven which allows the temperature to be controlled and varied during the analysis (McCord and Bender, 1998; Higson, 2003). The differing boiling points and affinity of the compounds for the stationary phase cause separation of the mixture (Stafford, 1992). Some compounds with similar structures may co-elute when analysed by GC, such as centralites (Wallace, 2008), and cresols (Dalby, 2011).

Analysis of explosives is commonly carried out with fused silica columns, 0.25 mm or 0.32 mm in diameter, coated with (5%-Phenyl)-methylpolysiloxane (PMS) (McCord and Bender, 1998). Examples include Agilent J&W's DB-5 and HP-5 columns (Agilent Technologies, 2017a, 2017b), which have been used in research by Burleson *et al.* (2009); Dalby and Birkett (2010); Joshi, Rigsby and Almirall (2011); and Almirall *et al.* (2017). In this project, a Supelco SLB-5 column was used, which has a silphenylene polymer stationary phase with an equivalent polarity to DB-5 columns (Sigma-Aldrich Inc., 2006). Green, Vetter and Baron (2017) used an SLB-5 column for analysis of organic residues from smokeless powder IEDs.

A variety of detectors can be used with GC to identify and quantify the compounds as they elute from the column (Dalby, 2011). Mass spectrometry (MS) works by splitting gaseous molecules into charged fragments and separating them based on the mass/charge ratio (m/z). The charged fragments produce a “mass spectrum” that can be used to both identify the compound and quantify its concentration In GC-MS a mass spectrum is produced for every compound that elutes from the column (Higson, 2003).

Alternative detectors for analysis of OGSR compounds include thermal energy analysers (TEA), and nitrogen phosphorous detectors (McCord and Bender, 1998; Burleson *et al.*, 2009). They can be used for rapid screening but are limited to detecting compounds with nitro groups, such as NG and TNT (Wallace, 2008).

Chromatography is the primary technique to detect organic compounds in GSR (Wallace, 2008), but gas chromatography is limited to volatile compounds (McCord and Bender, 1998). High-performance liquid chromatography (HPLC), thin layer chromatography combined with UV analysis, and liquid chromatography-mass spectrometry (LC-MS) can be used to analyse non-volatile compounds (Espinoza and Thornton, 1994; Wallace, 2008; Benito *et al.*, 2015). LC-MS can detect at least 17 compounds found in propellant.

1.7.4. Other Techniques

Other techniques that can be used for the analysis of smokeless propellant and organic GSR include infrared spectroscopy (FTIR) and ion mobility spectrometry (IMS). FTIR can be used to detect nitrocellulose – which cannot be analysed by GC-MS – and some minor constituents (Kee *et al.*, 1990; Lindblom, 2002). IMS can detect at least six different additives and can distinguish shooters from non-shooters (Arndt *et al.*, 2012; Bell and Seitzinger, 2016). IMS is routinely used in airport security to quantitatively detect explosives (Eiceman, Karpas and Hill, 2014).

Almirall *et al.* (2017) described a novel approach to extracting volatile compounds in organic GSR using “capillary microextraction of volatiles” (CMV), a device developed in 2014 by Fan & Almirall that functions in a similar manner to SPME. Analysis of samples was carried out by GC-MS with a DB-5 column. While the authors successfully extracted organic compounds from gunshot residue with this technique, they noted that it requires further optimisation to enhance the extraction performance.

1.8. Transfer and Persistence of OGSR

Hofstetter *et al.* (2017) found substantial variability in the amount of OGSR transferred by individual cartridges from the same brand of ammunition. The research also demonstrated that the concentration of GSR decreased with increasing distance from the ejection port of the firearm. Other factors affecting GSR deposition include wind, rain, humidity and temperature, with less GSR detected when firing takes place outdoors. The texture of clothing and skin moisture also have a bearing on the deposition of GSR (Wallace, 2008).

Many studies sampled GSR from shooters’ hands after discharging a handgun, including Brożek-Mucha and Zadora (2003), Tarifa and Almirall (2015), Bell *et al.* (2017), and Hofstetter *et al.* (2017). Wallace (2008) and Lucas *et al.* (2016) had limited success with detecting GSR on shooters’ hands and forearms following the discharge of a bolt action rifle, which he attributed to the closed breech of these firearms. The breech and muzzle of handguns are also closer to the shooter’s hands than they are in rifles, which help to improve deposition of GSR onto the hands. Wallace (2008) and Lucas *et al.* (2016) also encountered difficulty in detecting GSR from .22” calibre firearms.

For these firearms, the only remaining sources of GSR are the cartridge case and residues that exit the muzzle. It is therefore advantageous for this research to examine the residues remaining on .22” calibre cartridge cases fired by a bolt-action rifle, where the transfer of residues to the shooter will be negligible.

1.9. Criminal Use of Firearms and Propellant

1.9.1. .22 Long Rifle Firearms

Firearms chambered in .22 LR are occasionally used by criminals (Averty, 2017, Parker, 2017; “Episode 13”, 2018). UK firearms legislation makes it more likely that a legally held firearm will be a rifle than a handgun (*Firearms Acts 1967-1997*). Between April 2015 and March 2016 rifles[1] were involved in 48 offences. Although this was less 1% of all firearm offences, rifles were discharged in 17 of those incidents. These led to two deaths and one serious injury, along with 7 cases of property damage (Wright, 2017). Between April 2016 and March 2017 the number of offences increased, with rifles being fired in almost half of the incidents they were involved in, resulting in 1 death, 5 serious injuries, and 14 cases of property damage (Flatley, 2018).

Firearms chambered for .22 LR have been used in some notable crimes in the UK. In 2010 Derrick Bird killed twelve people and injured eleven others with a 12 ga. shotgun and a bolt-action CZ 452 rifle chambered for .22 LR, both legally held (Whiting, 2010). The rifle was a similar design to the CZ 455 used in this project. Derrick Bird used two different brands of ammunition: RWS (manufactured by RUAG), and CCI (now manufactured by Vista Outdoor) (Whiting, 2010; Vista Outdoor, 2017).

In June 2016 MP Jo Cox was killed by Thomas Mair with a knife and stolen bolt-action .22 LR rifle using Eley Ammunition. (*Telegraph & Argus*, 2016; Cobain and Taylor, 2016). Around 600 licenced firearms

Table 1-3: Recent firearm offences that may involve .22 LR firearms.

Type of Firearm	**No. offences**	
	15-16	**16-17**
Rifles	48	61
Unidentified firearms	666	844
Converted imitation handgun	12	9
Other converted imitation	6	2
Converted air pistol	12	15
Reactivated handgun	1	0
Other reactivated weapon	1	2
Unknown Handgun	1,727	2,231
Total	2,473	3,164

Excerpt from Wright (2017) Table 3.02 and Flatley (2018) Table 2.

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[1] Rifles as categorised by the Police and the Office for National Statistics. Includes rifles chambered in calibres other than .22 LR. Police do not categorise incidents by the calibre of weapon involved.

and shotguns are reported lost or stolen in England and Wales each year (Home Office, 2017). The numbers of recent incidents that may involve firearms chambered in .22 LR are shown in Table 1-3.

Several improvised firearms utilise .22 LR ammunition (Duerr, 1997; Warlow, 2007). Air weapons can be converted to fire live ammunition, deactivated firearms may be reactivated, or an entire firearm may be manufactured in a clandestine workshop (Foggo and Bamber, 2003; Warlow, 2007). Converted and reactivated firearms of all types and calibres are involved in under 1% of firearms incidents, totalling 242 offences over the last 10 years. The types of firearm involved are broken down in Table 1-3.

In many incidents, the exact classification of the firearm(s) involved remains unknown and, as such, the number of converted and reactivated firearms involved in crimes may be higher (Wright, 2017).

1.9.2. Improvised Explosive Devices

Analysis of smokeless propellant is not solely limited to firearm crime, as it is frequently used in improvised explosive devices (IEDs) in North America. Examples of such bombings include the 1996 Centennial Olympic Park Bombing in Atlanta, Georgia which killed two people and injured hundreds (*BBC News*, 1996; The National Academies and The Department of Homeland Security, 2005), and in the pressure cooker bombs detonated at the Boston Marathon in 2013.

The majority of bombings in North America in 2012 involved low explosives like smokeless powder, which can be readily obtained (Heramb and McCord, 2002; Girard, 2017). Analysis of smokeless powder from bombing sites may identify the brand of the propellant, and lead to intelligence on its origin.

1.10. Aims and Objectives

The aim of this project was to determine if the brand and calibre of ammunition can be identified from the chemical compositions of gunshot residue and unfired propellant.

The objectives of this project were to:

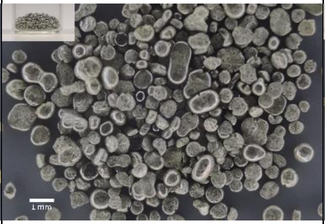
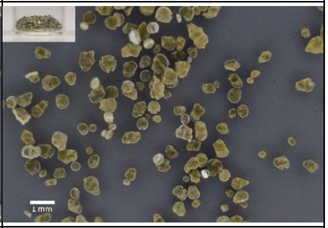
1. Validate the method developed by Dalby and Birkett (2010)
2. Determine the composition of volatile compounds present in fired and unfired propellant
3. Differentiate samples of propellant and GSR based on the chemical composition
4. Establish a relationship between GSR and propellant samples, and hence identify the brand of ammunition

2. Materials and Methods

2.1. Unburned Propellant Powders

Boxes of .22 Long Rifle (LR) ammunition for three brands – Winchester Pistol, Geco Rifle, and Eley Contact – were provided by Marlow Rifle and Pistol Club. For each brand, six cartridges from the same box were disassembled and the propellant weighed into individual 2 mL screw-top GC vials with silicone/PTFE septa (Chromacol Ltd.), as used by Dalby and Birkett (2010) and Almirall *et al.* (2017). Table 2-1 shows the mass of the propellant samples. The propellant morphologies were classified based on the criteria in Selavka, Strobel and Tontarski (1989). Larger images of the propellants are available on the enclosed disc (Appendix B, Page 51).

Table 2-1: Information about the .22 Long Rifle cartridges used in this research.

Brand	**Eley Contact .22 LR**	**Winchester Pistol .22**	**Geco .22 LR Rifle**
Image			
Colour	Pale green	Light grey	Shades of olive green
Shape	Cylinders	Mixture of flakes and balls, irregular shapes	Mixture of flakes and balls, irregular shapes
Width	Width ≈ 0.5 mm Length 0.5-1.5 mm	Balls ≈0.4 mm Flakes ≈1.17 mm	Balls ≈0.42 mm Flakes ≈0.67 mm
Propellant Mass	0.06 g ± 0.01 g $\bar{x}$ = 0.058g, σ = 0.008367	0.08 g (one sample 0.07 g) $\bar{x}$ = 0.078g, σ = 0.004082	0.09 g ± 0.01 g $\bar{x}$ = 0.088g, σ = 0.008367
Fired case storage time	22 days (case 4,5,6) 28 days (case 7,8,9)	5 days	5 days (case 2,3,4,5) 11 days (case 6,7)
Notes	Lot 3L17-40041 Manufactured 7/7/17	Batch ACDITE62	Manufactured 2008-14 (Huegel, 2014)

2.2. Firing Procedure

The firing was carried out with two Česká Zbrojovka CZ 455 bolt-action rifles chambered for .22 LR. Ten cartridges from the same box were fired for each brand of ammunition. The firing procedure was based on Dalby (2011), with the cases from the first two cartridges fired discarded to prevent any carry-over of GSR from other ammunition fired in the rifle previously.

Six of the fired cases were collected and placed into 4 mL screw-top GC vials with silicone/PTFE septa (Chromacol Ltd, Welwyn Garden City) within 30 minutes of being fired. The remaining cases were recovered in plastic tubs. The vials were stored at approximately 20°C for several days before analysis; the exact storage times are shown in Table 2-1. The method for packaging the fired cases was based on that developed by Wilson, Tebow and Moline (2003).

2.3. GSR Standard Mixture

A standard mixture containing seven compounds that may be present in GSR was used to confirm that these compounds were being extracted by the SPME fibre and correctly detected and identified by the GC-MS system. The retention times for these compounds and the smallest peak area that could be correctly identified were also determined.

The composition of the standard mixture is shown in Table 2-2. Camphor and ethyl centralite were purchased from Sigma-Aldrich (Gillingham, UK). 2-nitrotoluene, 3-nitrotoluene and 4-nitrotoluene were purchased from Aldrich (Steinheim, Germany). Diphenylamine was purchased from Arcos Organics (New Jersey, USA). Nitrobenzene was purchased from EJ Payne (Longton, Stoke-On-Trent, UK). Standards were made in analytical grade methanol from Arcos Organics.

Table 2-2: Composition of the 100 mg/mL standard mixture

Compound	**Concentration (mg/mL)**
2-nitrotoluene	100.02
3-nitrotoluene	99.50
4-nitrotoluene	85.30
Camphor	110.00
Diphenylamine	92.20
Ethyl centralite	100.60
Nitrobenzene	99.60

The standard mixture was diluted to the following concentrations: 80, 60, 40, 25, 20, 10, 5, 1 and 0.1 µg/mL. This was based in part on the methods used by Dalby and Birkett (2010) and Weyermann *et al.* (2009). 1 µL of each of these dilutions, together with the original 100 µg/mL mixture, were injected into the GC-MS for analysis.

Additional 20 µl aliquots of the 20 µg/mL standard were placed into 2 mL and 4 mL GC headspace vials. These were left in a fume cupboard to allow the solvent to evaporate, sealed and stored for 9 days, before undergoing SPME extraction.

2.4. SPME Extraction

Samples were incubated in an oven at 80°C for 10 minutes before analysis. A 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fibre (Supelco, Bellefonte, Pennsylvania, USA) was then inserted into each vial and heated for a further 35 minutes at 80°C. After extraction, the SPME fibre was removed and immediately inserted into the injection port of the GC-MS. The fibre was then conditioned in the injection port for 10 minutes at 250°C to ensure the sample was clean before the next sample was analysed. The extraction conditions and choice of fibre were based on the findings of Dalby and Birkett (2010) and the method used by Dalby (2011).

2.5. GC-MS Analysis

The GC-MS was a PerkinElmer Clarus 500 GC-MS, fitted with a Supelco SLB-5 GC column (30 m × 0.32 mm × 0.25 µm). Before analysis of SPME-extracted samples took place, both a column blank and an SPME fibre blank were run. For liquid extractions, a vial containing a sample of the methanol used to prepare the samples was placed into the autosampler and 1 µL injected and analysed by the GC-MS.

The existing method developed by Dalby (2011) was modified to work with the equipment available for this research. A slightly different temperature profile was used, as shown in Figure 2-1. Dalby's method used a greater ramp rate (20°C/min) to give a shorter run time of 32 minutes, and a higher final temperature of 300°C.

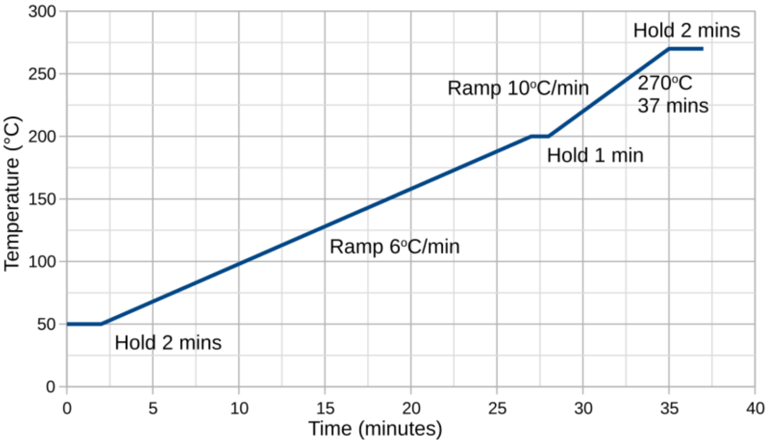


Figure 2-1: Annotated temperature program graph for the GC-MS method

The carrier gas used was helium with a flow rate of 1.5 mL per minute. The injector temperature was 250°C. For SPME-extracted samples, splitless injection was used, but 45 s after injection the injector split was turned on. For liquid-extracted samples, 1 µL of the sample was injected by the chromatograph's liquid autosampler. A split of 67% was used, and each injection was carried out twice.

The scan range of the mass spectrometer was set to 50-500 for the five samples of Eley Contact propellant. After further method development, this was changed to 45-500 for the remaining samples to improve detection of nitroglycerine, which has major ion fragments at m/z 46 and m/z 30 (NIST Mass Spec Data Center and Stein, no date). An Extracted Ion Chromatogram (EIC) was then generated for each sample at m/z 46.

2.6. Data Analysis

A bespoke, automatic, data analysis method was developed for interpretation of the GC-MS results. Called "GunShotMatch", the method incorporates some existing elements from literature, but also introduces some novel approaches. GunShotMatch was written in Python 2.7, making use of several open-source libraries. The basic operation of the program is described below. Full details are available in Appendix C (Page 55), and the source code is available on the enclosed disc (Appendix B, Page 51).

GunShotMatch took the output from TurboMass (PerkinElmer, Waltham, Maryland) for the 80 largest peaks present in each chromatogram. Possible hits for each peak were identified automatically by TurboMass by searching the NIST database (NIST MS Search 2.0). Any hits with a match probability below 450 were excluded from the search results. GunShotMatch then identified peaks in common between samples from the same source and determined the most likely compound responsible for the peak. The software allows for a slight variation in retention time of ± 0.1 minutes between the samples.

The mass spectra for peaks at the same retention time were compared with the NIST MS Search program to determine if the compounds were similar. Peaks with an average match factor below 650 were excluded from the output and were not analysed further. Peaks that appeared to be column-, septum- or fibre-bleed, such as those that contained "siloxane" in their name, were also excluded (English, 2013).

GunShotMatch automatically generated descriptive statistics – mean, standard deviation and %RSD (percent relative standard deviation) – for the peak areas, match factors and retention times. Kolmogorov-Smirnov and Shapiro-Wilk tests for normality are possible with the program, but were not used for this project because of the small sample sizes ($n \leq 6$) (Ghasemi and Zahediasl, 2012).

A sub-program, "GSM Compare", was used to compare the profiles for different propellants, or for the unfired and fired samples of the same propellant. Where there were peaks within 1 minute of each other in the two samples being compared, and the peaks corresponded to the same compound, a Student's t-test was undertaken for the retention time and peak area, with an α level of 0.01. A Welch's t-test was also carried out for the peak area to accommodate for samples with unequal variances (Ahad and Yahaya, 2014). The t-tests were computed using the SciPy "stats" module for Python (The Scipy community, 2016, 2017b).

Data points more than two standard deviations from the mean were classified as outliers. This method is less effective with non-normal distributions and small sample sizes (Leys *et al.*, 2013), so two alternative classifications were considered, using the inter-quartile range (National Institute of Standards and Technology, 2017) and the Median Absolute Deviation (Leys *et al.*, 2013; Rosenmai, 2013). However, these were not used due to problems rendering the error bars on a graph. The results of the different methods for detecting outliers are shown in Appendix D.

3. Results and Discussion

3.1. Compositions of Unfired Propellant and Gunshot Residue

The analysis primarily focused on additives that were previously reported in literature, such as Weyermann *et al.* (2009), and Taudte *et al.* (2014). The complete list is available in Appendix A. 20 of these compounds were detected in the unfired propellants, with diphenylamine (DPA) the only additive detected in all three propellants. Ethyl centralite (EC), 2-nitro-DPA and 4-nitro-DPA were detected in all propellants apart from Eley Contact. DPA and its nitrated derivatives are common stabilisers for smokeless propellants (Wallace, 2008). The compositions of the propellants are shown in Figure 3-1.

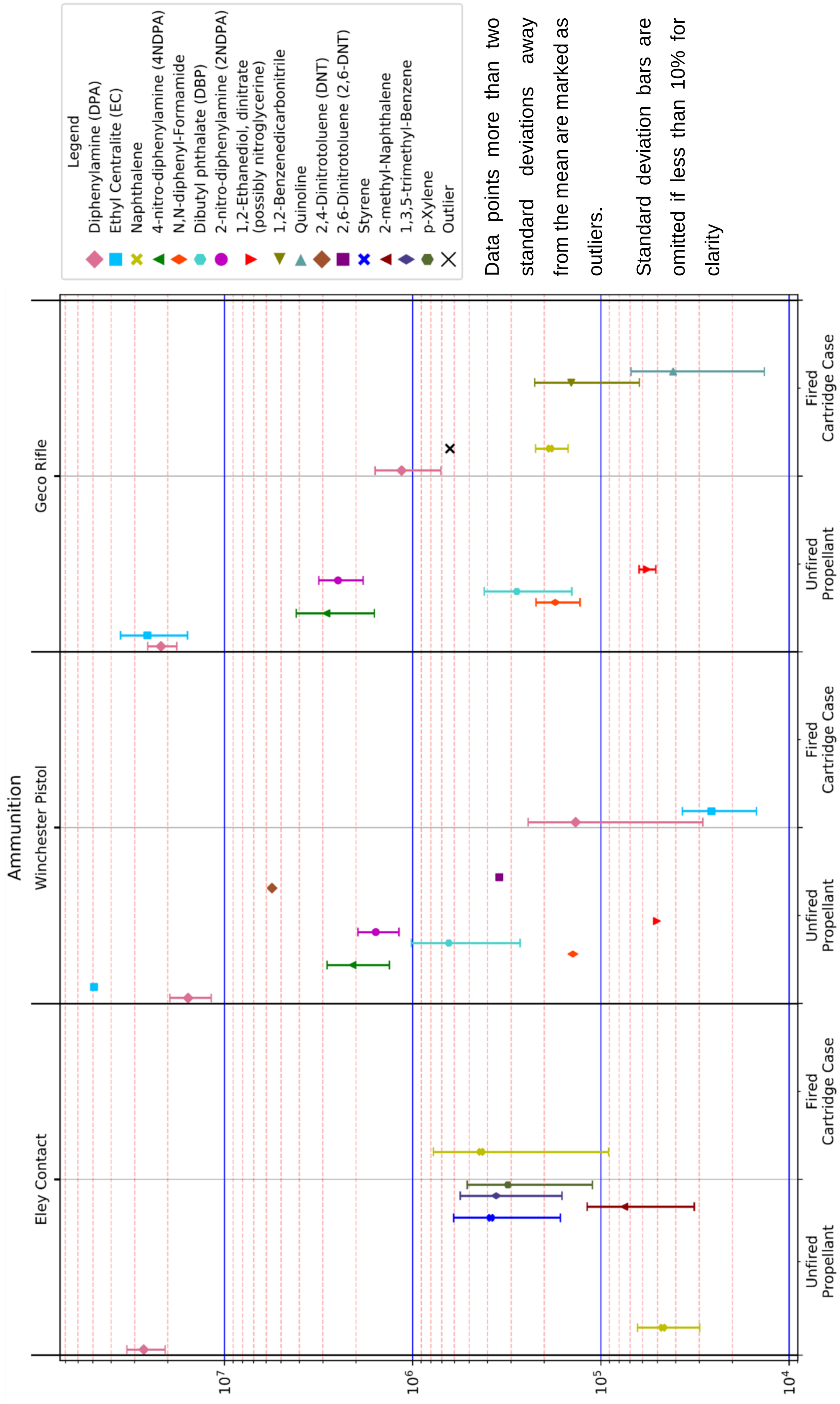
The morphology of the propellants may help to identify the manufacturer (Selavka, Strobel and Tontarski, 1989). Links to searches made in the Smokeless Powders Database (National Center for Forensic Science and University of Central Florida, 2006) for propellants with similar compositions to those analysed here can be found in Appendix G.

Many compounds exhibited substantial variation in peak areas between samples of the same propellant, such as p-xylene in Eley Contact (64%) and dibutyl phthalate in Geco Rifle and Winchester Pistol (49% and 58%). However, the peak areas were generally in the same order of magnitude for each compound. There was no apparent correlation between the peak areas and the mass of the samples. For some compounds, such as DNT and NG in Winchester Pistol propellant, the standard deviation was less than 10%. With outliers classified as being more than 2 standard deviations away from the mean, the only outlier identified was for naphthalene in the GSR from Geco Rifle ammunition.

The peak areas generally increased and decreased in tandem between samples of the same propellant. This may be due to the varying mass of the samples (± 0.01 g) or slight variations in the composition of the propellant granules (Wallace, 2008).

DPA, EC and 2,4-dinitrotoluene (DNT) are some of the most characteristic organic GSR compounds (Mach, Pallos and Jones, 1978). DPA was the primary additive in Eley Contact propellant, and was detected in the fired Winchester Pistol and Geco Rifle cartridges. EC was the primary additive in the Winchester and Geco propellants, although DPA was another major additive. EC was only detected in the fired Winchester cartridges, although the identification was poor, and was not detected in the Geco cartridges. Kee *et al*. (1990) also encountered difficulty with detecting EC in fired samples. DNT was not detected in any fired cases.

The complete lists of compounds identified by GunShotMatch were also analysed when determining relationships between the fired and unfired samples.



Data points more than two standard deviations away from the mean are marked as outliers.

Standard deviation bars are omitted if less than 10% for clarity

Figure 3-1: Composition of fired and unfired propellant samples from .22 LR ammunition

Most of the compounds detected in the unfired propellant samples were not detected in the fired cartridges cases. This mirrors the results of Dalby's 2011 analysis of a variety of calibres and brands of ammunition. Table 3-1 shows the numbers of compounds detected in the propellant and GSR samples.

Table 3-1: Numbers of compounds detected

	Eley	Win.	Geco
Compounds previously reported in literature	6	9	7
Total number of compounds detected	20	17	19
Compounds with more than one peak detected	3	0	0
Compounds in both propellant and GSR	3	2	1

3.1.1. Winchester Pistol

The propellant is a mixture of irregularly shaped ball and flake granules. The ball-shaped granules suggest a double base composition, containing nitrocellulose (NC) and nitroglycerine (NG), and NG was detected in the propellant. While the propellant was a similar shape to the Geco Rifle propellant, they were different colours and sizes.


Figure 3-2: Winchester Pistol Headstamp

Winchester have been manufacturing .22" rimfire ammunition since 1877 (Huegel, 2015; McKune, 2017). They were purchased by Olin in 1931 and merged into Olin's existing ammunition business (Olin Corporation, 2018). Olin currently produce 23 different types of .22 LR ammunition for a variety of uses (Winchester, 2018).

The Winchester "Pistol" ammunition used in this project was manufactured and marketed by "Winchester Australia" (Huegel, 2013, p. 115), a subsidiary of Olin who manufacture much of the rimfire ammunition sold by Winchester in Europe and North America (*Sporting Shooters' Association of Australia*, 2016). However, it does not appear that the ammunition used in this experiment is still manufactured (Winchester Australia, 2014),

It is possible that the same propellant is used in several different types of rimfire and centerfire ammunition sold by Winchester, including discontinued types sold under the "Olin" and "Western" brands. Reloading powders are also sold under the Winchester brand (Wolfe and Polacek, 2016).

A search of the Smokeless Powder database (National Center for Forensic Science and University of Central Florida, 2006), which contains entries for many reloading powders available in the United States, identified some propellants with a similar chemical composition and morphology as the Winchester Pistol propellant. Some of these propellants were sold under the "Winchester" brand, and Winchester 785 was the most similar. However, none of the propellants contained both ball and flake-shaped granules.

Several other Winchester reloading powders have a similar morphology to that found in the Winchester Pistol ammunition, including Winchester 748, “680”, “630P”, and “231” (Selavka, Strobel and Tontarski, 1989; Wolfe and Polacek, 2016). Winchester 680 is the most similar – a flattened ball powder with an average diameter of 0.37 mm. Some of the flattened balls have elongated elliptical shapes. However, the flake granules present in the Winchester Pistol propellant are not present in Winchester 680 (Simpson, 1984). Manufacturers may blend multiple propellants or batches together to achieve the optimal burning characteristics for the .22 LR ammunition (Heramb and McCord, 2002), and this could be the case here.

DPA and EC were the main additives in the Winchester Pistol propellant, and were the only compounds detected in the fired cartridge cases; the other 7 additives present in the propellant were not detected. The peak areas of both additives decreased from the unfired propellant to the GSR. While EC was the primary additive in the propellant, DPA gave the largest peak for the fired cartridge cases. The peak area of DPA decreased significantly by a factor of ≈115 ($t(9) = 8.877, p = 0.00001$), and the peak area of EC decreased significantly by a factor of ≈1906 ($t(9) = 32.191, p = 0.00000$).

No other compounds were in common between the fired and unfired samples, including those that have not previously been reported in literature.

3.1.2. Geco Rifle

Figure 3-3: Geco Rifle Headstamp

The propellant is a mixture of irregularly shaped ball and flake granules. The ball-shaped granules suggest a double base composition, NG was detected in the propellant. Although the propellant had a similar morphology to the Winchester propellant they were different colours and sizes. The propellant is reported to be clean burning (*Geco 22LR 40gr Rifle 500 Rnds*, 2018).

Geco ammunition is manufactured by RUAG (RUAG Group, 2018). Two different types of .22 LR ammunition are available: Geco Semi-Auto, and Geco Rifle (RUAG AMMOTEC, 2018). RUAG also sell .22 LR ammunition under the RWS and Norma brands, with at least 17 different types of cartridge available, alongside reloading powders (Norma Precision AB, 2014; RUAG Ammotec, 2015; RUAG AMMOTEC, 2016). It is possible that some of these cartridges are loaded with the same propellant. RUAG also sell reloading powders under the Norma brand (RUAG Ammotec UK Ltd, 2018). One of these may be used in the Geco Rifle ammunition. Several propellants in the smokeless powder database have a similar chemical composition to the Geco Rifle propellants, but none were identified with a similar morphology. However, there were several propellants with either flattened ball or flake shaped granules, and the Geco Rifle propellant could be a mixture of these

Diphenylamine was the primary additive detected in the fired Geco Rifle cases, and the peak area decreased significantly by a factor of ≈19 from the unfired samples to the fired cases ($t(9) = 13.291$, $p = 0.00000$).

None of the other six additives present in the unfired propellant were detected in the fired samples. However, naphthalene, 1,2-benzenedicarbonitrile, and quinoline were detected in the fired cartridge cases, but not in the unfired samples. If these three compounds were present in the unfired samples, the peak areas were too small for the automated method to detect them. They may also be combustion or decomposition products, although none of these compounds have a similar structure to the additives in the unfired propellant. Further research is required to determine the origin of these compounds.

At 25.573 minutes "1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester" **(1)** was detected in the unfired propellant, and "1,2-Benzenedicarboxylic acid, diheptyl ester" **(2)** was detected in the fired cases. GunShotMatch indicated a better confidence for **(2)**; it was identified as a possible match in more of the repeats and had a higher average match factor than **(1)**. These are both phthalate compounds with similar structures and spectra, which are reproduced in Appendix E.4. It is possible that the same compound is responsible for the peaks in both the fired and unfired samples. Assuming that the peaks do correspond to the same compound, there is a significant increase in peak area by a factor of ≈1.5 from the unfired propellant to the fired cases ($t(9) = -3.487$, $p = 0.00687$).

3.1.3. Eley Contact

The cylindrical shape of the propellant in Eley Contact ammunition suggests that it is single base (Heramb and McCord, 2002; Wallace, 2008), and as expected NG was not detected in any samples, both automatically and following manual examination of the chromatograms.

Figure 3-4: Eley Contact Headstamp

Eley have been manufacturing ammunition since 1828, and first produced .22 LR cartridges in 1860. Eley currently manufacture 16 different types of .22 LR ammunition for target shooting and hunting (ELEY Ltd, 2018b). and the ammunition is popular with target shooters across the world (ELEY Ltd, 2018a, 2018c). It is possible that some, if not all, of the cartridges produced by Eley use the same propellant.

The only propellant in the smokeless powders database with a similar chemistry and morphology as the Eley Contact propellant was Rottweil P 805. However, the two propellants were different colours and Rottweil also contained dipentyl phthalate, which was not detected in the Eley propellant.

Naphthalene was the only additive detected in the cartridge cases from Eley Contact ammunition that had previously been reported as an additive and was present in the unfired propellant (Gallidabino *et al.*, 2014). The peak area of naphthalene increased from the unfired propellant to the GSR by a factor of ≈9. However, the peak areas for the cartridge cases varied substantially, giving a large standard deviation of over 70%. An independent samples t-test indicated that there may be no significant difference in the actual peak areas ($t(8) = -2.819$, $p = 0.02252$).

The five other main additives detected in the unfired propellant were not detected in the GSR. This may be due to the longer storage time of these samples before analysis, or the lower mass of propellant in each cartridge of Eley Contact compared to Winchester Pistol and Geco Rifle. OGSR compounds may adsorb onto the glass vial if the fired cartridges are stored for a prolonged period before analysis (Conrad, 1989; Gallidabino and Weyermann, 2016), and this may have affected the detection of other compounds.

Methyl 2,2-dimethyl-3-hydroxypropionate **(3)** and dodecane, 2,6,10-trimethyl- **(4)** were also detected in both fired and unfired samples of Eley Contact propellant. The identification of **(3)** was poor in the fired cases, but the peak area decreased significantly by a factor of ≈5 between the unfired and fired samples ($t(8) = 8.011$, $p = 0.00004$). The peak area of **(4)** roughly doubled from the unfired to fired samples, and this change is statistically significant ($t(8) = -3.972$, $p = 0.00411$).

1-iodo-tridecane was also detected in the fired and unfired samples, but as multiple peaks with a difference in retention time of between 4 and 10 minutes. This difference was substantially greater than the inter-sample variation of the retention times, which was below 1 minute for all other compounds. Therefore, the multiple peaks seen for 1-iodo-tridecane may have been caused by several different compounds with similar structures. The spectra for the three compounds contained the same main fragments at m/z 58, 72 and 86. A comparison of the spectra with NIST MS Search indicated that the spectra were similar, with an average match factor of 814 ($\sigma = 87.175$).

Multiple peaks may be caused by a difference in polarity between the solvent and the stationary phase of the gas chromatograph’s column (de Zeeuw, 2013), but since no solvent was used during this analysis it is unclear what the actual cause may be.

3.2. Distinguishing Samples

Based on the composition of the unfired propellant samples (Figure 3-1), they can all be distinguished based on the compounds that had previously been reported in literature. The full list of compounds, provided suitable standards are analysed, may allow these propellants to be distinguished from other samples with a similar composition.

The propellants from Geco Rifle and Winchester Pistol cartridges were the most chemically similar. 12 compounds were detected in both propellants, of which 9 had peak areas that did not exhibit a significant difference between the propellants. There was a statistically significant difference between the peak areas of 2-Anilino-2-phenylpropionitrile ($t(9) = -5.207$, $p = 0.00056$) and phenazine ($t(9) = 5.482$, $p = 0.00039$) between the two propellants, but neither of these compounds have been previously listed as additives in smokeless powder (See Appendix A). Ethyl centralite, which is a common additive (Mach, Pallos and Jones, 1978), was present in both samples but with statistically different peak areas ($t(9) = -5.494$, $p = 0.00038$).

2,4- and 2,6-dinitrotoluene were only detected in the Winchester propellant. Both have previously been listed as additives (Hofstetter *et al.*, 2017), but DNT is a common additive and therefore its value in distinguishing samples is minimal (Mach, Pallos and Jones, 1978). 9 other compounds (5 in Geco and 3 in Winchester) were only detected in one of the propellants, and could be used to distinguish the propellants, but the identification of these compounds is not conclusive, and they have not previously been reported as being present in smokeless powder.

The three brands of ammunition produced GSR with different compositions. Naphthalene was detected in Eley Contact and Geco Rifle GSR, and DPA was detected in both Winchester Pistol and Geco Rifle. No other compounds that had been previously been reported in literature were detected in the Eley ammunition. DPA and EC are common additives (Mach, Pallos and Jones, 1978), and therefore their value to distinguish GSR from different sources is limited.

Unlike the unfired propellants, the only compounds in common between the Winchester and Geco GSR samples were 4-(Prop-2-enoyloxy)octane **(5)**, 6-ethyl-2-methyl-decane **(6)** and DPA. The peak areas for **(5)** and **(6)** were similar between the two brands, but there was a significant difference in the peak areas of diphenylamine ($t(9) = 4.989$, $p = 0.00075$).

The only compound in common between the Geco and Eley GSR samples was acenaphthylene, with a similar peak area in both brands ($t(9) = -0.176$, $p = 0.86397$). 2,6,10-trimethyl-dodecane was the only compound detected in the GSR from both

Winchester and Eley ammunition. There was a difference in peak area between the brands, but this was not significant ($t(8) = -1.914$, $p = 0.09191$).

The smokeless powders database (National Center for Forensic Science and University of Central Florida, 2006) only identifies a limited selection of additives in smokeless powder, although this includes the main additives from all five propellants analysed in this project. A wider range of compounds, such as those identified by GunShotMatch, may help to distinguish some of these samples if they originated from different sources.

3.3. SPME Extraction

In this research, the SPME fibre was conditioned for 10 minutes after each sample was analysed to reduce carry-over to the next sample. This is a shorter time than was used by Dalby and Birkett (2010), and was chosen to keep the extraction and analysis times as close to each other as possible to improve sample throughput. However, some carry over was experienced between samples, and although the peak areas for those compounds are low, this may contribute to an increase in peak area in subsequent samples.

Because fibre blanks were run between each lot of samples, the potential for carry over was limited to between samples of the same lot. There was also some variability in the extraction times (± 1 minute). The use of an autosampler would help to ensure that extraction times remained consistent and allow the fibre to be conditioned for a longer period without requiring the operator’s attention.

3.4. Analysis of Fired Cases

The method used for analysis of the fired cases was based on Wilson, Tebow and Moline (2003) and Dalby (2011). Dalby’s method additionally froze the samples at −22°C within 12 hours of firing to prevent loss of volatiles, and then placed the cases into headspace vials for analysis. It is unclear what advantage, if any, this has over Wilson, Tebow and Moline’s method. In this project, the samples were placed into headspace vials within half an hour of firing but were not frozen. Freeze drying has been shown to improve detection of volatile organic compounds (VOCs) in urine samples by headspace-SPME-GC-MS (Aggio *et al.*, 2016) but, as GSR samples are not liquids, without further research it is unclear whether freezing the cartridge cases would improve sensitivity.

Since the composition of individual propellant granules can vary considerably (Reardon, MacCrehan and Rowe, 2000; Wallace, 2008), the few unburned or partially burned granules remaining inside the cartridge case may not be representative of the overall propellant composition. This may account for some of the difference in composition between the fired and unfired samples of the same ammunition.

Dalby (2011) used 14 mL headspace vials for extraction of some fired cartridge cases (p142). Dalby used a variety of calibres of ammunition, such as .22 LR and 7.62×51 mm NATO. While a 14 mL vial is a similar volume to a 7.62×51 mm cartridge case, it is substantially larger than a .22 LR case.

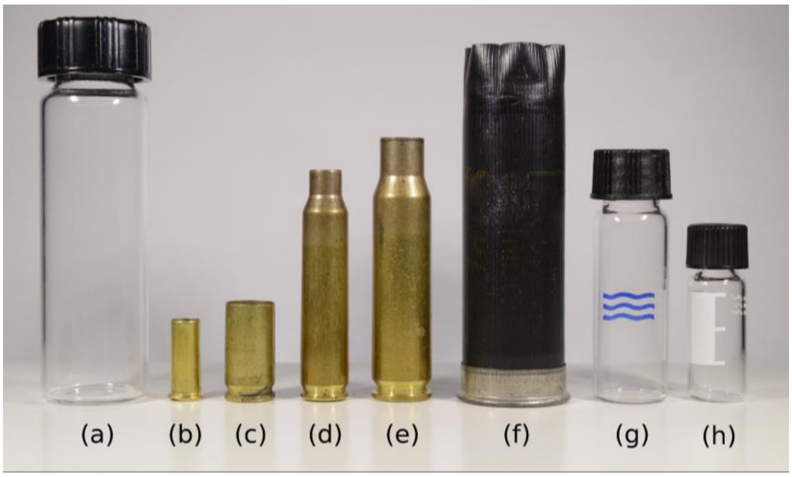


Figure 3-5: Comparison of various fired cartridge cases and headspace vials.
(a) 14 mL vial; (b) .22 LR; (c) 9×19 mm; (d) 5.56×45 mm; (e) 7.62×51 mm; (f) 12 gauge; (g) 4 mL vial; (h) 2 mL vial.

Figure 3-5 shows a comparison of these vials and cartridge cases. Wilson, Tebow and Moline (2003, p. 1301) recommended that the vial be "just large enough to fit a shell" or cartridge case. The substantially larger volume of the vials used by Dalby compared to the cartridge cases may have contributed to the author's difficulty in extracting compounds from fired cartridge cases. Almirall *et al.* (2017) were unable to recover OGSR compounds from the headspace of a 1 litre container, and the authors attributed that to the larger volume of the container. They were able to successfully extract compounds from the headspace of 15 mL vials.

A 2 mL GC vial is a more appropriate size for a .22 LR cartridge case, but the neck of the vial is too narrow for the cartridge to fit inside. As a result, 4 mL vials – which have a wider neck – were used in this experiment. This does, however, leave a larger volume of air inside the vial. Where a vial with a larger volume is necessary to physically fit the cartridge case, it may be beneficial to consider the use of a non-absorbent block below the case to reduce the headspace inside the vial.

3.5. Data Analysis Method

Data analysis was initially carried out manually, and the manual method was used as the basis for GunShotMatch. The automated approach removed subjectivity when matching peaks at similar retention times between samples: the software stringently matches peaks only if they are within 6 seconds of each other.

The automated method also substantially decreased the time taken to analyse the data. For five samples of the same propellant, the analysis can be completed within 20 minutes on a high-end computer, compared to several hours by hand. However, the software does not decide whether two samples of propellant or GSR could have originated from the same source; it merely provides the necessary information to the operator.

Many of the parameters for GunShotMatch can be customised, allowing it to be tailored for analysis of minor additives in other samples, such as cutting agents in drugs or ingredients in paint and alcohol (Maldaner *et al.*, 2015; allnex group, 2017; Ellis *et al.*, 2017; Metrohm UK and Ireland, 2018).

3.5.1. Accuracy of Identification

GunShotMatch cannot make a positive identification for compounds without a standard also being run. As such, not every compound identified will necessarily be present in the propellant. GunShotMatch can only identify that a compound is in common between repeat analyses of propellants; the limitations of mass spectrometry and the database searching algorithm still apply. The compound must also be present in the NIST Mass Spectra database to be correctly identified from its mass spectrum (McLafferty *et al.*, 1998, 1999; Ausloos *et al.*, 1999).

Not every compound listed in Appendix A has an entry in the database. The presence of these compounds in the propellant samples could be confirmed by analysing standards for these compounds, but that is outside the scope of this research project.

3.5.2. Detection of Nitroglycerine

Using GunShotMatch for automated analysis of the chromatograms (Section 2.6) did not indicate nitroglycerine (NG) as being present in the top 80 peaks of any of the propellants analysed. NG is present in double base propellants commonly used in revolver, pistol and ammunition (Warlow, 1996; Meng and Caddy, 1997; Wallace, 2008). A manual examination of the chromatograms identified that it consistently eluted at ≈15.95 minutes across all the propellants, with a standard deviation of 0.082%.

The Extracted Ion Chromatograms (EIC) for m/z 46 indicated large, sharp peaks at 15.95 minutes for NG in the Geco and Winchester propellants, although the confidence of the identifications varied. NG was not detected in any fired cartridge cases. Dalby (2011) detected nitroglycerine at 15.06 minutes. The difference in retention time may be due to the different temperature profile used in this project.

Green, Vetter and Baron (2017) found that extracted ion chromatograms improved the detection and identification of DPA and EC in Alliant Bullseye® propellant from detonated IEDs.

For Geco 1, Geco 2, Winchester 2 and Winchester 3, NIST MS Search identified nitroglycerine as a possible match, but it was not within the top 5 results. Only the top 5 potential matches for each peak are exported to GunShotMatch, and this will affect the software's ability to correctly identify nitroglycerine. However, GunShotMatch will still indicate that *a* compound is in common between samples of the same propellant.

GunShotMatch identified the peaks at 15.95 minutes in the Geco and Winchester propellants as 1,2-Ethanediol, dinitrate, which was a commonly suggested compound for the peak in the other samples.

1,2-Ethanediol, dinitrate and nitroglycerine both contain nitrate groups and produce mass spectra with the same major ion fragments. The structures and spectra for these compounds are reproduced in Appendix E.3. Analysis of a standard containing nitroglycerine would be required to conclusively determine the identity of the peak at 15.95 minutes, but that is outside the scope of this research.

Nitroglycerine has also been reported to decompose at temperatures above 50°C (Sokoloski and Wu, 1981; Dalby, 2011). The temperature at which extraction took place (80°C) may have resulted in decomposition of nitroglycerine and affected detection.

3.6. Standard Mixture

Analysis of the GSR standard mixture indicated that the smallest peak area that could be reliably detected and identified correctly was 10^5. The retention times for the compounds, which are shown in Table 3-2, were generally consistent, in most cases within ± 6 seconds.

Table 3-2: Retention times and match factors for the standard mixture

Compound	**Average Retention Time**	**%RSD**
2-nitrotoluene	11.439	0.09
3-nitrotoluene	12.346	0.13
	12.821	0.24
4-nitrotoluene	12.346	0.13
	12.821	0.24
Camphor	11.140	0.09
Diphenylamine	21.539	0.30
Ethyl centralite	26.000	0.03
Nitrobenzene	9.664	0.09

Data based on 60, 80 and 100 mg/mL standards

EC was identified as N,N'-diethyl-N,N'-diphenyl-oxamide **(7)** in the more dilute standards (<10 mg/mL). The two compounds have similar structures and similar mass spectra; **(7)** contains an oxamide group ($(CONH_2)_2$) whereas EC contains a urea group ($CO(NH_2)_2$) (Linstrom and Mallard, 2017). Spectra and structures for these compounds are reproduced in Appendix E.

An alternative hit listed for the peaks corresponding to DPA was 2-p-Tolylpyridine. This compound was also listed as a possible hit for DPA in all three unfired propellants. It has a similar structure to DPA and both compounds produce similar mass spectra (Linstrom and Mallard, 2017). The structures and mass spectra are reproduced in Appendix E.

Two consecutive peaks were present at 12.328 minutes and 12.768 minutes that both listed 3-nitrotoluene and 4-nitrotoluene as possible hits. These are highlighted in grey on Table 3-2. The compounds have similar structures, differing only in the position of the nitro group. From this standard mixture, it was not possible to distinguish the two compounds and determine which compound corresponds to which peak.

All compounds were successfully extracted and correctly identified following extraction with the SPME fibre. Double peaks at similar retention times were occasionally exhibited, such as for camphor at 11.053 and 11.176 minutes in SPME Standard A. However, double peaks were not always present for the same compound.

3.7. Effect of analysis on other evidence types

Latent fingermarks and DNA may be deposited on cartridge cases when loading ammunition into the magazine of the firearm (Fieldhouse, Oravcova and Walton-Williams, 2016; Fan *et al.*, 2017). The intense temperatures encountered during firing – which may reach 1800°C inside the cartridge case – may degrade fingermarks and DNA, making recovery difficult (Polley *et al.*, 2006; Fan *et al.*, 2017). The method used in this project requires the fired cartridge case to remain sealed inside a vial following collection until extraction is complete, so there is no opportunity to recover DNA or fingerprints before heating the sample. It is therefore important that the method for analysis of GSR used in this project does not cause further degradation.

Smith (2017) showed that fingermarks on brass began to degrade after heating for 30 minutes at 200°C. Heating at lower temperatures did not cause degradation. It does not, therefore, seem that the analysis for OGSR will cause further degradation of fingermarks.

Karni *et al*. (2013) found that DNA begins to degrade at 130ºC, but their study only heated the DNA for less than 10 minutes. The method employed in this project heats the cartridge cases for 45 minutes at 80°C. Further research is required to determine whether, in practice, this method has any effect on the recovery of DNA from fired cartridge cases. The police may have to decide which evidence type – OGSR or DNA – they wish to recover from a fired cartridge case. This is similar to recovery of a fingermark or DNA from latent mark at a crime scene – only one evidence type can be recovered, not both (Fieldhouse, Oravcova and Walton-Williams, 2016).

3.8. Further Research

3.8.1. Improvements to method

Several improvements could be made to the method used in this project before further analysis. Selective Ion Monitoring (SIM) could be used to improve detection of OGSR compounds, based on Dalby (2011) and Green, Vetter and Baron (2017). An Extracted Ion Chromatogram (EIC) at m/z 46 could be incorporated into the automated method to improve detection of nitroglycerine, along with analysis of a standard. The EIC would target compounds that elute at around 16 minutes.

3.8.2. Standards

To confirm the identification of compounds, a wider range of standards would need to be analysed, including those compounds that have not previously been reported in literature, but which were tentatively identified in the propellant and GSR samples.

3.8.3. Database

The method used in this research could be used to develop a database of the chemical and physical properties of smokeless powder and the GSR it produces. Dalby (2011) found that the GSR found on targets may have a different composition to both the propellant and the GSR in fired cartridges cases, and therefore it may be advantageous to also include the chemical composition of GSR that exits the muzzle of the firearm. A database already exists of reloading powders (National Center for Forensic Science and University of Central Florida, 2006), but this does not have data for gunshot residue or propellants used in commercially made ammunition.

Wrobel, Millar and Kijek (1998) developed a classification system for .22” calibre cartridges, based on chemical and physical characteristics, and produced a database for 70 different types of cartridge. The authors found that, while no single factor allowed for differentiation of all samples, the combination of characteristics was unique for every sample, and ammunition types produced by the same manufacturer could also be distinguished. These criteria, as shown in Table 3-3, could be incorporated into the database of propellant and GSR to aid the differentiation of fired and unfired cartridges. Analysis of inorganic GSR could also be included, as this is also capable of differentiating different types of ammunition (Meng and Lee, 2007)

Table 3-3: Classification criteria developed by Wrobel, Millar and Kijek (1998)

Headstamp and physical features of cartridge
Propellant shape, size and colour
Projectile shape and type (e.g. hollow point)
Position of cannelures on projectile
Elemental composition of cartridge components

4. Conclusion

The aim of this project was to examine whether it is possible to determine the brand and calibre of ammunition that produced the gunshot residue (GSR) from the chemical composition of the GSR and unfired propellant. The existing chemical analysis method developed by Dalby and Birkett (2010) was effective for the analysis of "Winchester Pistol", "Geco Rifle" and "Eley Contact" brands of .22 Long Rifle ammunition. The analysis demonstrated that three brands could be distinguished based on their propellants. The three brands also produced GSR with different chemical compositions.

However, this project only analysed a very small sample of the .22 Long Rifle ammunition available, and only a single calibre of ammunition. Even taking into account the 16 different brands analysed by Dalby (2011), further analysis is required to verify whether every brand and calibre uses a different propellant and produces distinct gunshot residues.

The automatic data analysis software "GunShotMatch", developed alongside this project, allowed for the compounds in the propellant and GSR samples to be rapidly identified from the GC-MS results, and shows potential for use in a database of propellant and GSR samples, alongside other criteria such as the colour and shape of the propellant and the dimensions of the cartridge.

There was no consistent relationship between the composition of the propellant and GSR from the same brand of ammunition; the concentration of compounds increased in one brand while decreasing in another. However, the GSR could still be linked back to the propellant and brand of ammunition using a database.

The method requires minor alterations to improve the detection of nitroglycerine, and analysis of a wider range of standards is required to confirm the identification of compounds detected in the propellant and GSR samples.

However, even without modification, it has been possible with the method used in this research to distinguish "Winchester Pistol", "Geco Rifle" and "Eley Contact" .22 Long Rifle ammunition based on the chemical compositions of their propellants and gunshot residues.

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Appendix A: Compounds in Smokeless Powder and OGSR

Compound	CAS	Abbreviation	Functions
Dipropyl adipate	106-19-4		Plasticiser
2-Furaldehyde	98-01-1		
Benzaldehyde	100-52-7		
3,5-Dinitroaniline	618-87-1		Stabiliser Moderant
Aniline	62-53-3		
N-methyl-p-nitroaniline	100-15-2		Stabiliser
2,4-Dinitroanisole	119-27-7	DNAN	Energetic
Benzene	71-43-2		
Benzonitrile	100-47-0		
Benzophenone	119-61-9		
Benzothiazole	95-16-9		
Benzylnitrile	140-29-4		
Ethylbenzene	100-41-4		
1,2-Dicyanobenzene	91-15-6		
1,3-Dicyanobenzene	626-17-5		
1,4-Dicyanobenzene	623-26-7		
1,2,3-Trimethylbenzene	526-73-8		
1,2,4-Trimethylbenzene	95-63-6		
1,3,5-Trimethylbenzene	108-67-8		
1,3-Dinitrobenzene	99-65-0	1,3-DNB	Energetic
1,3,5-Trinitrobenzene	99-35-4		Energetic
Nitrobenzene	98-95-3		Energetic
Borneol	507-70-0		
Camphor	76-22-2		Plasticiser
D-Camphor	464-49-3		
DL-Camphor	21368-68-3		
L-Camphor	464-48-2		
Butyl centralite		BC	Plasticiser Stabiliser
Ethyl Centralite (N,N-diethyldiphenylurea)	85-98-3	EC	Plasticiser Stabiliser Moderant
Methyl centralite	611-92-7	MC	Plasticiser Stabiliser Moderant
Dinitrocresol	534-52-1		Stabiliser
m-Cresol	108-39-4		Stabiliser
o-Cresol	95-48-7		Stabiliser
p-Cresol	106-44-5		Stabiliser
2-Nitrodiphenylamine	119-75-5	2-NDPA	Stabiliser Nitration Product

Appendix A: Compounds in Smokeless Powder and OGSR

Compound	CAS	Abbreviation	Functions
4-Nitrodiphenylamine	836-30-6	4-NDPA	Stabiliser Nitration Product
Diphenylamine	122-39-4	DPA	Stabiliser
2,2'-dinitro-DPA	18264-71-6	2,2’-DNDPA	Nitration Product
2,4-dinitro-DPA	961-68-2	2,4-DNDPA	Stabiliser Nitration Product
2,4'-dinitro-DPA	612-36-2	2,4’-DNDPA	Nitration Product
4,4'-dinitro-DPA	1821-27-8	4,4’-DNDPA	Stabiliser Nitration Product
2,2',4,4',6,6'-hexanitro-DPA	131-73-7		Nitration Product
2-nitrosodiphenylamine		2-nDPA	
4-nitroso-DPA	156-10-5	4-nDPA	Stabiliser Nitration Product
N-nitroso-2-nitro-DPA	21565-15-1		Nitration Product
N-nitroso-4-nitro-DPA	3665-70-1		Nitration Product
N-nitroso-DPA	86-30-6	N-nDPA	Stabiliser Nitration Product
N-nitroso-2,2’-dinitro-DPA			Nitration Product
N-nitroso-2,4'-dinitro-DPA			Nitration Product
N-nitroso-4,4'-dinitro-DPA			Nitration Product
N-nitroso-2,2’,4-trinitro-DPA			Nitration Product
2,2',4,4'6-pentanitro-DPA			Nitration Product
2,2',4,4'-tetranitro-DPA			Nitration Product
2,4,4'-trinitro-DPA			Nitration Product
2,4,6-trinitro-DPA			Nitration Product
Fluoranthene	206-44-0		
1,2-Dinitroglycerin	621-65-8	1,2-DNG	Energetic
1,3-Dinitroglycerin	623-87-0	1,3-DNG	
Nitroglycerin	55-63-0	NG	Energetic Plasticiser
Diethylene glycol dinitrate	693-21-0		
Ethelyne glycol	107-21-1		
Ethylene glycol dinitrate	628-96-6	EGDN	Energetic
Hexylene glycol	107-41-5		
Gum Arabic			
Gum tragacanth			
Karaya gum			
2-Ethyl-1-hexanol	104-76-7		
2-Ethylhexanal	123-05-7		
1-Methylnaphthalene	90-12-0		
1-Naphthalenecarbonitrile	86-53-3		
1,4-Dimethylnaphthalene	571-58-4		
2-Ethylnaphthalene	939-27-5		
2-Methylnaphthalene	91-57-6		

Appendix A: Compounds in Smokeless Powder and OGSR

Compound	CAS	Abbreviation	Functions
2-Naphthalenecarbonitrile	613-46-7		
2,6-Dimethylnaphthalene	581-42-0		
Naphthalene	91-20-3		Moisture Displacer
2-Naphthol	135-19-3		
Nitrocellulose (“Gun cotton”)	9004-70-0	NC	Energetic
Nitroguanidine	556-88-7	NQ	Energetic Flash Suppressor
4-Methylbiphenyl	644-08-6		
Biphenyl	1486-01-7		
Biphenylene	259-79-0		
N,N-diphenylformamide	607-00-1		
N,N’-Diphenyl urea	102-07-8	Akardite I	Stabiliser
N’-Ethyl-N,N’-Diphenyl urea		Akardite III	Stabiliser
N’-Methyl-N,N’-Diphenyl urea	13114-72-2	Akardite II	Stabiliser
Diamyl phthalate	131-18-0	DAP	Plasticiser
Dibutyl phthalate	84-74-2	DBP	Moderant Plasticiser Flash Suppressor
Diethyl phthalate	84-66-2	DEP	Plasticiser
Dimethyl phthalate	131-11-3	DMP	Plasticiser
Dioctyl phthalate	117-84-0		Moderant
Monomethyl phthalate	4376-18-5		
1-(5-tetrazolyl)-4-guanyltetrazene hydrate		Tetrazene	Sensitiser
Cyclonite (Hexahydro-1,3,5-trinitro-1,3,5-triazine)	121-82-4	RDX	Energetic Primer
Diazodinitrophenol	4682-03-5	DDNP	Primer
Isoquinoline	119-65-3		
Quinoline	91-22-5		
2-Nitrotoluene	88-72-2	2-NT	Energetic Flash Suppressor
3-Nitrotoluene	99-08-1	3-NT	Energetic Flash Suppressor
4-Nitrotoluene	99-99-0	4-NT	Energetic Flash Suppressor
Toluene	108-88-3		
2-amine-4,6-dinitrotoluene	35572-78-2	2-ADNT 2-A-4,6-DNT	Flash Suppressor
4-amine-2,6-dinitrotoluene	19406-51-0	2-ADNT 4-A-2,6-DNT	Flash Suppressor

Appendix A: Compounds in Smokeless Powder and OGSR

Compound	CAS	Abbreviation	Functions
2,3-Dinitrotoluene	602-01-7	2,3-DNT	Energetic Stabiliser Moderant Flash Suppressor
2,4-Dinitrotoluene	121-14-2	DNT 2,4-DNT	Energetic Stabiliser Moderant Flash Suppressor
2,6-Dinitrotoluene	606-20-2	2,6-DNT	Energetic Stabiliser Moderant Flash Suppressor
3,4-Dinitrotoluene	610-39-9	3,4-DNT	Energetic Stabiliser Moderant Flash Suppressor
2,4,6-Trinitrotoluene	118-96-7	TNT	Energetic Sensitiser
m-Tolunitrile	620-22-4		
o-Tolunitrile	529-19-1		
p-Tolunitrile	104-85-8		
Candelilla Wax			
Paraffin Oil			
o-Xylene	1330-20-7		
p-Xylene	106-42-3		
Pentaerythritol Tetranitrate	78-11-5	PETN	Energetic Sensitiser
1,3-Benzenediol	108-46-3	Resorcinol	Plasticiser Stabiliser
1,3-Diacetyloxypropan-2-yl acetate	102-76-1	Triacetin	Plasticiser Flash suppressor
2,4,6-Trinitrophenylmethylnitramine	479-45-8	Tetryl	Sensitiser
Acaroid resin			
Anthracene	120-12-7		
Carbazole	86-74-8		
Charcoal	7440-44-0		
Chrysene	218-01-9		
Dextrin			
Dimethyl senacate	109-43-3		Plasticiser
Graphite	7782-42-5		Lubricant
Indene	95-13-6		
Indole	120-72-9		
Nonanal	124-19-6		

Appendix A: Compounds in Smokeless Powder and OGSR

Compound	CAS	Abbreviation	Functions
Octogen (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)	2691-41-0	HMX	Energetic
Oxamide	471-46-5		
Pentaerythritol dioleate	25151-96-6		
Petrolatum			
Phenanthrene	85-01-8		
Phenol	108-95-2		
Picric acid	88-89-1		By-product of Nitration
Pyrene	129-00-0		
Starch			
Styrene	100-42-5		
Tetracene	92-24-0		
Triphenyl bismuth	603-33-8		
Urethane	51-79-6		Plasticiser

Compiled from Harrison and Gilroy (1959); Levitsky, Norwitz and Chasan (1968); Espinoza and Thornton (1994); Meng and Caddy (1997); Bender (1998); Hopler (1998); Heramb and McCord (2002); National Center for Forensic Science and University of Central Florida (2006); Wallace (2008); Dalby and Birkett (2010); Arndt et al. (2012); AFTE (2013); Taudte *et al*. (2014); Benito *et al*. (2015) and Goudsmits, Sharples and Birkett (2015).

Appendix B: Software and Data DVD

The source code for GunShotMatch, the complete results, raw data, draft versions of the thesis and notes are provided on the disc below and are available online at:

dominic.davis-foster.co.uk/GSR

A table of contents for the disc is provided overleaf.

```
dotRAW Files      # Directory containg .RAW files produced by TurboMass
                  # for every sample.

Draft Versions    # Directory containing draft versions and notes.

Cartridge Case Collection Instructions
            # Procedure for collecting propellant and GSR samples,
            # together with form for recording information about samples

GunShotMatch      # Directory containing GunShotMatch,
│                 # results and raw data.
│
├─── box whisker plot groups0.2.py        # Program to plot graphs.
│
├─── box whisker plot0.2.py               # Older version of program to
│                                         # plot graphs.
├─── Charts       # Directory containing charts for results
│
├─── comparison_list.txt      # List of profiles to compare against
│                             # each other.
├─── config.ini         # GunShotMatch configuration.
│
├───CSV     # Directory containing raw GC-MS data from TurboMass.
│
├─── csv_rename.py      # Program to rename TurboMass CSV files into
│                       # something logical.
│
├─── Custom Legend.py         # program to produce custom legends for
│                             # graphs.
│
├─── ELEY_CASE_SUBTRACT_20180329105043.tar.gz
│           # Results for Eley fired cartridge cases.
├─── ELEY_CASE_SUBTRACT_v_WINCHESTER_CASE_SUBTRACT_COMPARISON_
│           20180330202141.xlsx
│                 # Comparison of Eley and Winchester fired cases.
├─── ELEY_SHOTGUN_SUBTRACT_20180329091836.tar.gz
│           # Results for Eley Hawk propellant.
├─── ELEY_SUBTRACT_20180329102613.tar.gz
│           # Results for Eley Contact propellant.
├─── ELEY_SUBTRACT_v_ELEY_CASE_SUBTRACT_COMPARISON_20180313200407.xlsx
│           # Comparison of fired and unfired Eley Contact.
├─── GECO_CASE_SUBTRACT_20180329114204.tar.gz
│           # Results for Geco fired cartridge cases.
├─── GECO_CASE_SUBTRACT_v_ELEY_CASE_SUBTRACT_COMPARISON_
│           20180330204907.xlsx
│                 # Comparison of Geco and Eley fired cases.
├─── GECO_CASE_SUBTRACT_v_WINCHESTER_CASE_SUBTRACT_COMPARISON_
│           20180330154453.xlsx
│                 # Comparison of Geco and Winchester fired cases.
├─── GECO_SUBTRACT_20180329110848.tar.gz  # Results for Geco propellant
│
├─── GECO_SUBTRACT_v_GECO_CASE_SUBTRACT_COMPARISON_20180329162940.xlsx
│           # Comparison of fired and unfired Geco Rifle.
├─── GECO_SUBTRACT_v_WINCHESTER_SUBTRACT_COMPARISON_20180323093318.xlsx
│           # Comparison of Winchester and Geco propellant.
│
```

```
│
├─── GSMatch0.8.1c.py   # The main GunShotMatch program
│
├─── GSM_Compare0.2.1.py      # Program to compare profiles for two
│                             # propellants or GSR samples.
│
├───lib     # Directory containing ancillary parts of GunShotMatch
│    ├─── CAS.txt                  # List of CAS numbers for compounds.
│    │                             # previously reported in literature.
│    ├─── default.ini               # Default configuration.
│    ├─── gsmatch.ini               # Part of GunShotMatch.
│    ├─── GunShotMatch logo256.png  # GunShotMatch Logo.
│    ├─── GunShotMatch logo32.png   # GunShotMatch Logo.
│    ├─── hashes.ini                # Part of GunShotMatch.
│    ├─── import_timer.py           # Import benchmark for third party
│    │                              # modules.
│    ├─── ini_fragment              # Part of GunShotMatch.
│    ├─── ini_fragment2             # Part of GunShotMatch.
│    ├─── latex requirements.txt    # List of required LaTex plugins.
│    └─── procedure to search NIST database.txt
│                                   # Details of NIST MS Search API.
│
├───Licences      # Contains licence information for GunShotMatch.
│    ├─── gpl.txt # GNU General Public Licence v3.
│    └─── MIT.txt # MIT Licence.
│
├───MS Comparisons      # Contains PNG and PDF images of mass spectra
│    │                  # for the compounds detected in each propellant
│    │                  # and GSR sample.
│    ├─── ELEY_CASE_SUBTRACT  # Eley Contact fired cartridge cases.
│    ├─── ELEY_SHOTGUN_SUBTRACT     # Eley Hawk Olympic propellant.
│    ├─── ELEY_SUBTRACT             # Eley Contact propellant.
│    ├─── GECO_CASE_SUBTRACT        # Geco Rifle fired cartridge cases.
│    ├─── GECO_SUBTRACT             # Geco Rifle propellant.
│    ├─── UNIQUE_SUBTRACT           # Alliant Unique propellant.
│    ├─── WINCHESTER_CASE_SUBTRACT  # Winchester Pistol fired cartridge
│    │                              # cases.
│    └───WINCHESTER_SUBTRACT        # Winchester Pistol propellant.
│
├─── outlier_comparison.py          # Program to evaluate methods of
│                                   # outlier detection
│
├─── Outlier_Comparisons.py         # Results of evaluation of different
│                                   # outlier detection methods
│
├─── Spectra_CSV  # Contains GC-MS data in CSV format as produced by
│                 # OpenChrom.
│
├─── SPME Standards_TARGETS_COMBINED.CSV
│           # Results for standards extracted by SPME.
├─── Standard Set 1_COMBINED.CSV
│           # Complete results for first set of standards (liquid).
├─── Standard Set 1_TARGETS_COMBINED.CSV
│           # Results for first set of standards (liquid).
├─── Standard Set 2_COMBINED.CSV
│           # Complete results for second set of standards (liquid).
│
```

```
├─── Standard Set 2_TARGETS_COMBINED.CSV
│          # Results for first set of standards (liquid).
│
├─── standards.py       # Version of GunShotMatch tailored to analysis
│                       # of standards.
├─── UNIQUE_SUBTRACT_20180329160532.tar.gz
│          Results for Alliant Unique propellant.
├─── UNIQUE_SUBTRACT_v_ELEY_SHOTGUN_SUBTRACT_COMPARISON_
│          20180313200908.xlsx
│                # Comparison of Unique and Eley Hawk propellants.
│
├──utils         # Contains modules used by GunShotMatch.
│    ├─── DirectoryHash.py           ├─── DirectoryHash.pyc
│    ├─── helper.py                  ├─── helper.pyc
│    ├─── MassSpectraPlot.py         ├─── MassSpectraPlot.pyc
│    ├─── outliers.py                ├─── outliers.pyc
│    ├─── pynist.py                  ├─── pynist.pyc
│    ├─── terminalsize.py            ├─── terminalsize.pyc
│    ├─── timing.py                  ├─── timing.pyc
│    └─── __init__.py                └─── __init__.pyc
│
├─── WINCHESTER_CASE_SUBTRACT_20180329095020.tar.gz
│          # Results for Winchester fired cartridge cases.
├─── WINCHESTER_SUBTRACT_20180329093211.tar.gz
│          # Results for Winchester propellant.
└─── WINCHESTER_SUBTRACT_v_WINCHESTER_CASE_SUBTRACT_COMPARISON_
           20180329161821.xlsx
                 # Comparison of Winchester fired and unfired.

Notes       # Directory containing further notes produced during research
├─── British Library.docx          # Contains notes on journal
│                                  # articles read at British Library.
│
├─── Calibres and Brands.docx      # Contains notes on the calibres
│                                  # and brands of ammunition used in
│                                  # research previously.
│
├─── Cut from Project.docx       # Contains parts of the writeup that
│                                # were cut from the final version.
│
├─── Literature Review Table.docx
│
├─── ONS firearms 1516 excerpts.ods   # Excepts from Office for
│                                     # National Statistics data on
│                                     # firearm crime.
└─── Raw Notes

Raw Data
├─── Appendices
├─── Temperature Program graph
└─── Propellant Measurements.xlsx
```

Appendix C: Detailed information about GunShotMatch

C.1. Introduction

GunShotMatch is a bespoke automated analysis program for Organic Gunshot Residue (OGSR). The aim of the program is to find peaks that are in common between samples originating from the same source. This allows the additives present in the propellant and OGSR to be distinguished from both background contamination and combustion and degradation products that are not consistently produced. The program produces descriptive statistics for the samples and produces a variety of charts automatically.

GunShotMatch is Free and Open Source software licenced under the GNU General Public Licence V3.0. Portions of the software are licenced under other open source licences. Full details of the copyright and licencing can be found in Appendix F (Page 75).

GunShotMatch is written in Python 2.7, an open-source programming language available for Windows, Mac and Linux (Python Software Foundation, 2018). Python has previously been used for a variety of scientific applications, including proteomics, analysis of mass spectra (O'Callaghan *et al.*, 2012; Goloborodko *et al.*, 2013; Röst *et al.*, 2014), DNA analysis (Van Neste *et al.*, 2014; Bailey *et al.*, 2017), document analysis (Talbot-Wright *et al.*, 2016), and drug trafficking investigation (Rhumorbarbe *et al.*, 2016; Broséus *et al.*, 2017). Python can also perform a variety of statistical tests on data, similar to SPSS or MATLAB (The Scipy community, 2017a, 2017b).

C.2. Preparation

Before processing by GunShotMatch, the "strip" function of Turbomass Version 5.4.2 (PerkinElmer, Waltham, Maryland) is used to subtract a fibre blank from the samples. This helps to minimise peaks caused by column-, fibre- and septum-bleed (English, 2013). Turbomass is then used to generate a report of the top 80 peaks present in each sample. A copy of the report template is available on the enclosed disc (Appendix B (Page 51).

The parameters used by TurboMass to integrate the chromatograms and determine the peak area are shown in the box to the right.

Smooth: Off

Peak Detect
- Join = 30
- Raise = 5
- Detect shoulders = off
- Reduce = 50
- Draw vertical = 90

Threshold absolute area = 4

Peak to peak noise amplitude = 1500

Integration parameters used by TurboMass

CSV files containing the raw GC-MS data are also required. These are currently produced using OpenChrom (Wenig and Odermatt, 2010) from the TurboMass .RAW files. It is planned to incorporate this functionality into GunShotMatch in the future. A conversion is also possible using a proprietary program provided by PerkinElmer with TurboMass.

C.3. Combine Functions

The report produced by Turbomass consists of two CSV files – one for the GC data and another for the MS data. The program automatically renames the CSV files, extracts the relevant data and combines the data into a single CSV file. Takes CSV files for GC and MS data from TurboMass and combined them into a single CSV file. The format is shown in Figure C1. The CSV files also contain the instrument parameters, sample number, mass spectrometer scan number and peak height. This information is currently excluded from the output, but could be included.

Retention Time	Peak Area		Lib	Match	R Match	Name	CAS Number	Notes
21.349	55216784	Page 49 of 80						
		1	mainlib	877	896	Diphenylamine	122-39-4	
		2	mainlib	860	864	1-Methyl-3,3-diphenylurea	13114-72-2	
		3	mainlib	858	935	2-p-Tolylpyridine	4467-06-5	
		4	mainlib	847	847	[1,1'-Biphenyl]-2-amine	90-41-5	
		5	mainlib	842	933	4-(4-Methylphenyl)pyridine	4423-10-3	

Figure C1: Format for the CSV file containing GC and MS data

The CSV data also is appropriately spaced so that 5 lines are allocated for the hits, even if fewer than 5 hits were identified. At this stage the data has not been changed. With minor alterations to the code, it can be used to merge data for other reports with between 1 and 98 peaks.

This functionality is provided by the functions `GCMScombine()` and `getRTlist()`

C.4. Spacer and Merge Functions

The combined CSV data for a batch of samples from the same source – such as five samples of Alliant® Unique propellant – are spaced so that peaks with the same retention time appear on the same lines when the all the data is placed side-by-side. The program obtains a list of the top 80 peaks from all the samples to determine the required spacing. With minor alterations, the code could support reports with fewer peaks, or target only the 30 largest peaks across the samples.

The program provides the above as three functions: `single_spacer()`; `batch_spacer()`, which is a wrapper for `single_spacer()`; and `get_top_80()`, which obtains the information on the top 80 peaks. A final function, `Merge()`, combines the separate spaced CSV files together to form a single CSV file.

C.5. "Jigsaw" Function

Although the Spacer function ostensibly aligns peaks with the same retention time on the same line, this only works when the retention times are *exactly* the same. Peaks corresponding to the same compound may be present on two or more consecutive clusters of rows. For the samples analysed in this project, in most cases the difference was within ± 6 seconds.

Figure C2 shows a representation of this phenomenon and the intended result of processing. This step can be performed in three ways:

1. Open LibreOffice (an open-source alternative to Microsoft® Office) to allow the user to edit the output manually. This is the slowest and most subjective approach.
2. Suggest to the user which clusters should be merged together. This is based on the retention times being within ± 6 seconds.
3. Automatically perform this operation without any user input. This is the fastest and least subjective approach, but will fail where anomalous results are detected. At worst, this should only cause a minor additive to be omitted from the output results.

The data is not changed in any way, just moved around. Where a peak is not present in every sample the rows are omitted from the output. Any peaks rows that appear to be column-, fibre-, or septum-bleed are also deleted. The criteria for this is if any of the Hit names contains “silox”, “silane”, or “TMS” (short for “tetramethylsilane”).

“Ethyl [5-hydroxy-1-(6-methoxy-4-methyl-3-quinolinyl)-3-methyl-1H-pyrazol-4-yl]acetate” is also excluded because it presents itself as lots of peaks with no relation between retention times. It shows up in almost every sample and isn’t a compound of interest. The source of this compound is currently unknown.

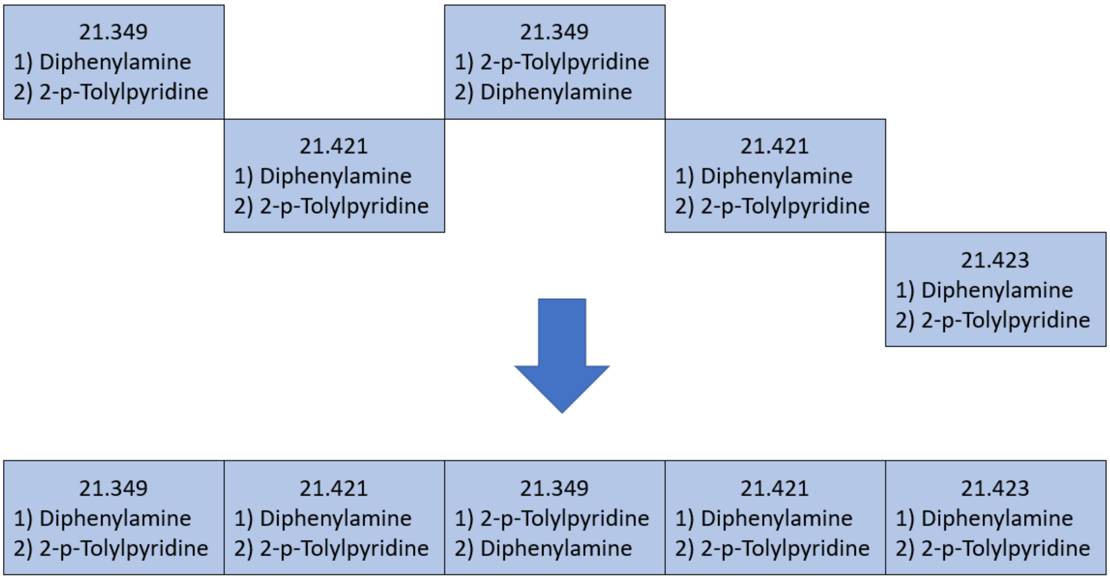


Figure C2: Representation on the "jigsaw" functionality of GunShotMatch

A side effect of excluding *-bleed compounds in this way is that any compounds in the analyte that also meet the criteria will be excluded too. An improvement would be to exclude *-bleed based on retention time as well as name, using data from a blank run.

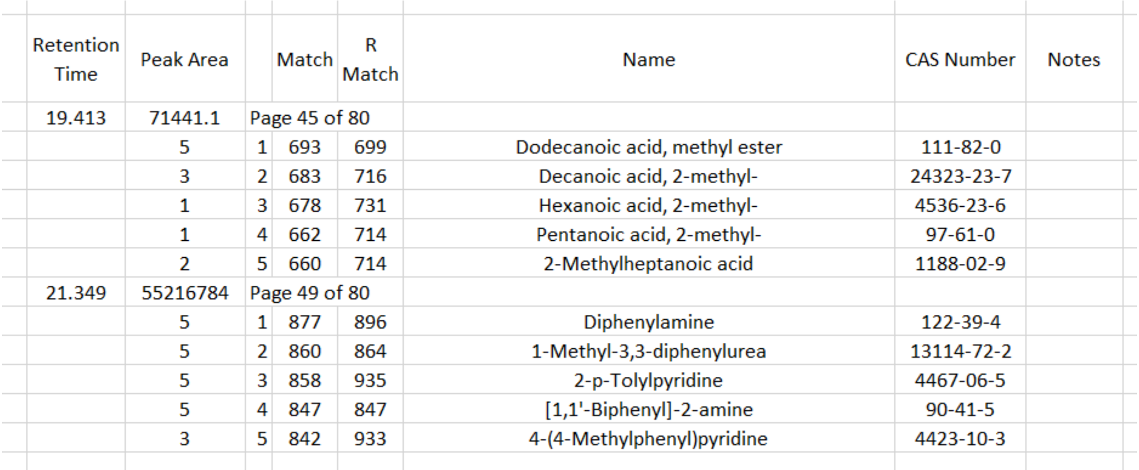
The criteria for excluding *-bleed can be customised in the code, as can the threshold for including a peak when it does not show up in every sample. However, changing this value causes incompatibility with later functions, but may be useful in certain circumstances.

The function `jigsaw()` provides the two automated approaches to this step. The function `open_lo()` opens the file in Libre Office to allow the user to perform this step manually.

C.6. Final Processing

C.6.1. Match Counter

The `counter()` function counts the number of times a particular compound appears as a hit for a specific peak. For example:



Retention Time	Peak Area		Match	R Match	Name	CAS Number	Notes
19.413	71441.1	Page 45 of 80					
	5	1	693	699	Dodecanoic acid, methyl ester	111-82-0	
	3	2	683	716	Decanoic acid, 2-methyl-	24323-23-7	
	1	3	678	731	Hexanoic acid, 2-methyl-	4536-23-6	
	1	4	662	714	Pentanoic acid, 2-methyl-	97-61-0	
	2	5	660	714	2-Methylheptanoic acid	1188-02-9	
21.349	55216784	Page 49 of 80					
	5	1	877	896	Diphenylamine	122-39-4	
	5	2	860	864	1-Methyl-3,3-diphenylurea	13114-72-2	
	5	3	858	935	2-p-Tolylpyridine	4467-06-5	
	5	4	847	847	[1,1'-Biphenyl]-2-amine	90-41-5	
	3	5	842	933	4-(4-Methylphenyl)pyridine	4423-10-3	

Figure C3: Examples of Match Counter output. Note that the Hits have not yet been sorted into order.

C.6.2. Statistics

Based on the number of times a compound appears as a hit for each peak, and the average match factor, the program lists the top 5 (if possible) possible compounds that the peak corresponds to.

The mean, standard deviation and %RSD are then calculated for the following variables:

i. Match Factor
ii. Reverse Match Factor
iii. Hit Number
iv. Retention Time
v. Peak Area

The output XLSX file has a sheet showing all this data (“Matches”), and a sheet showing just the top match for each peak (“Statistics”). A separate sheet (“Statistics – Lit Only”) shows only those compounds previously reported as being present in propellant or GSR (see Appendix A).

C.6.3. NIST Comparison

GunShotMatch then takes the spectra for each peak shown in the “Statistics” sheet from every sample analysed and compares them by making calls to the NIST MS Search Program.

NIST .MSP files are produced for each spectrum, and these are converted into a custom NIST library with the NIST Library Conversion Tool `LIB2NIST.exe` (free of charge from

http://chemdata.nist.gov/mass-spc/ms-search/Library_conversion_tool.html)

The .MSP spectra are passed in sequence to the search program, which returns the hits it has found in the database.

i. This is the same procedure used by Chromatography Data Systems to search the NIST Database
ii. The software is available for free from chemdata.nist.gov/mass-spc/ms-search/
iii. The instructions for the API calls are available in the manual (http://chemdata.nist.gov/mass-spc/ms-search/docs/Ver20Man_11.pdf)

The software finds all permutations for the samples being analysed (e.g. 1 and 2, 1 and 2, 2 and 3) and finds the relevant matches from the output from NIST MS Search.

The software then calculates the average match and lists this in the “Statistics” sheet.

Any peaks with an average match below 650 are excluded from the results, but are shown in the “Statistics Full” spreadsheet.

C.6.4. Charts

GunShotMatch includes the following graphs in the output, both for all compounds and for only those reported in literature as being present in propellant or GSR:

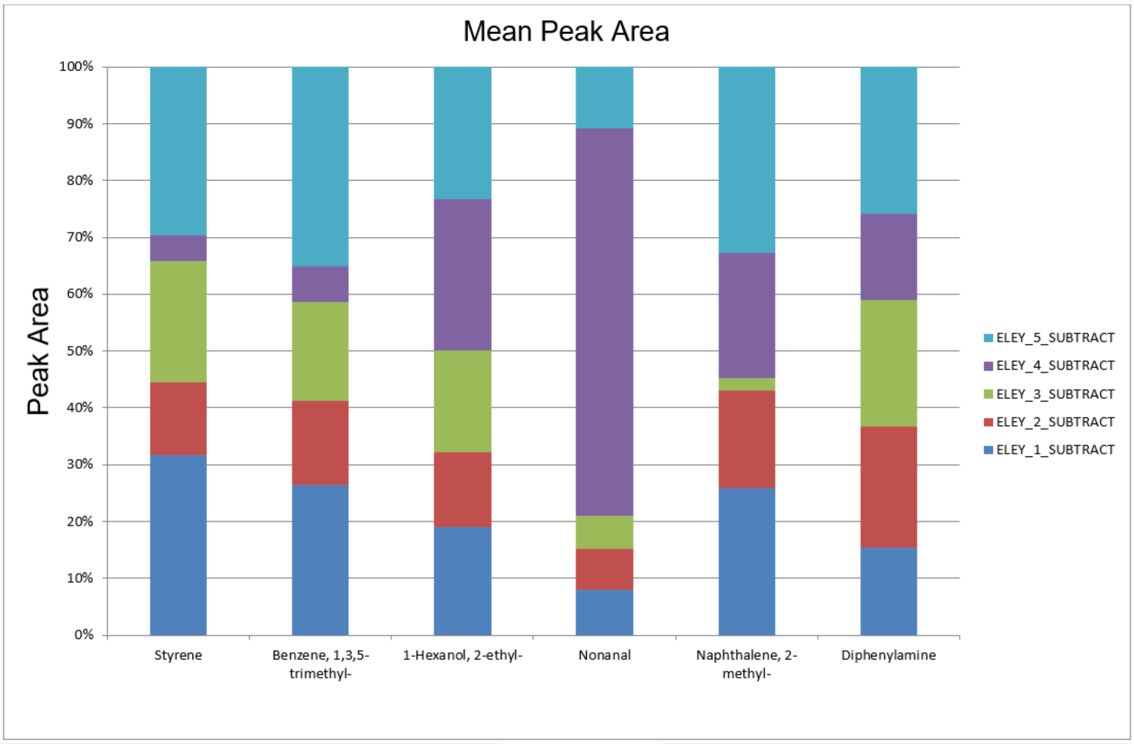
a. Mean Peak area and Log(Mean Peak Area) (stacked bar)
b. All Samples - Peak Areas (stacked bar)
c. All Samples - Log(PA) (stacked bar)
d. Radar Log(Peak Area)
e. All samples Log(PA) line (only for compounds reported in literature)

Generation of the XLSX file and the graphs is provided by the `finalXLSX()` function.

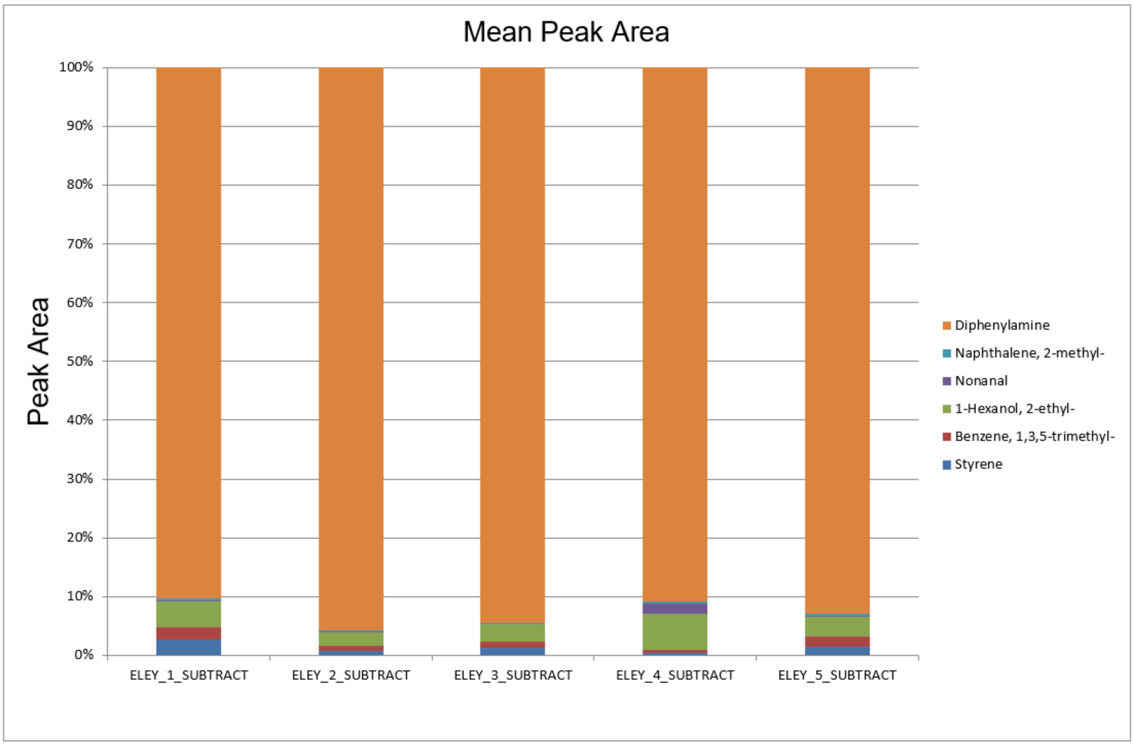
Appendix C: Detailed information about GunShotMatch

The stacked bar charts can be viewed in two different ways:

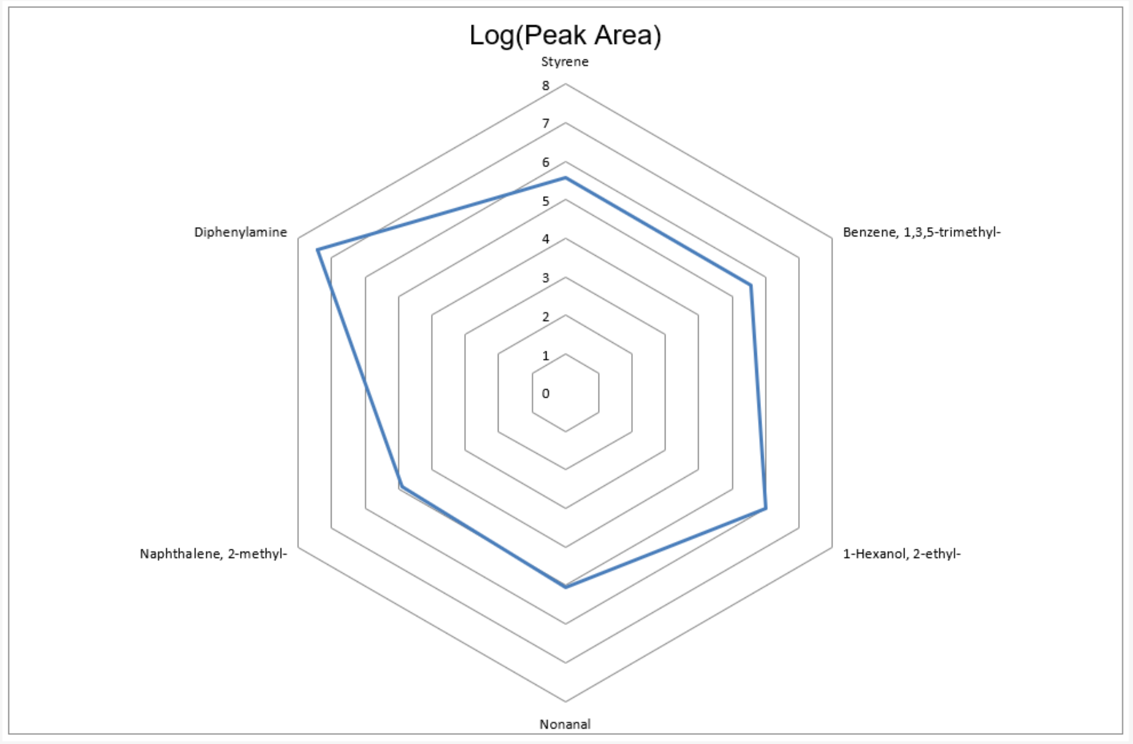
> By compound, with the samples stacked



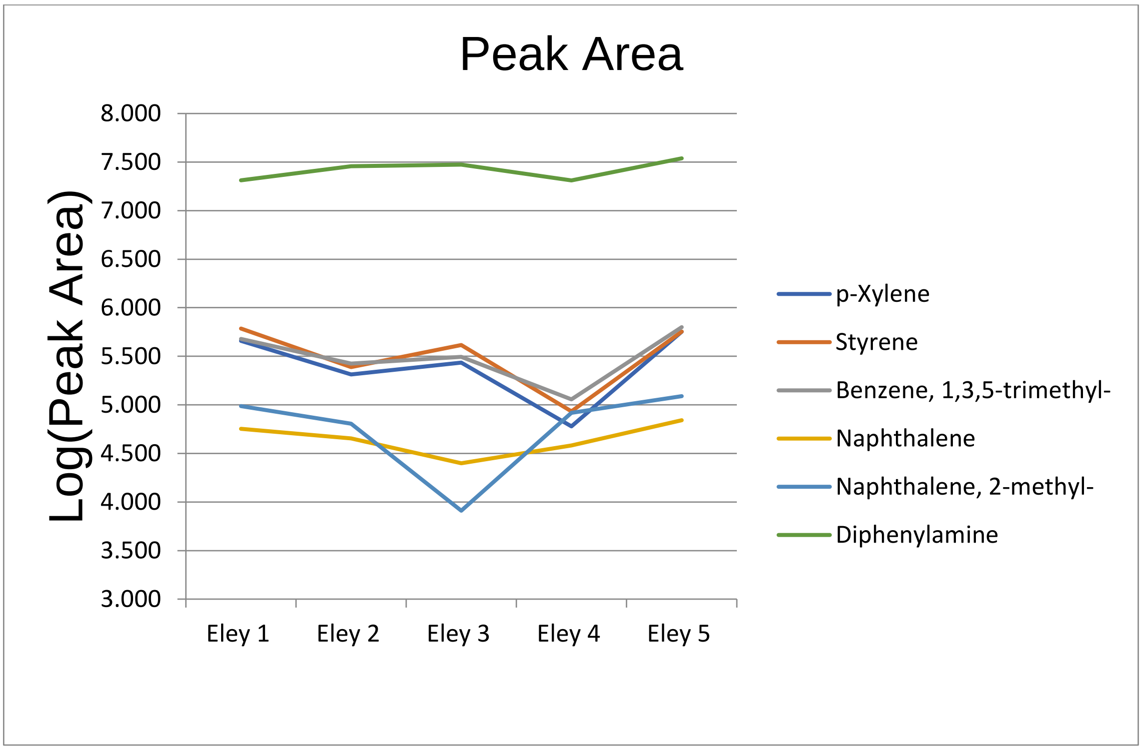
> By sample, with the compounds stacked



The software also produces a Radar Chart for Log(Mean Peak Area) for the compounds reported in literature. This could be combined with pattern recognition software to compare propellant and GSR from different sources, but further work is required to implement this.



Finally, a line chart is produced for the compounds reported in literature to allow trends to be visualised between the samples.



C.7. Final Output

All the data is neatly packaged into a single XLSX spreadsheet, and is bundled into a tar.gz file (a bit like a .zip file) with the .MSP spectra, and PNG & PDF images of the spectra.

A sub-program, “GSM_Compare”, is used to compare two propellants or GSR samples, based on the following criteria:

1. The number of peaks with similar retention time and identity in both samples
2. A t-test for the retention times
3. A t-test and Welch’s t-test for the peak areas
4. The mass spectra of those compounds, compared using NIST MS Search in the same manner as in the main program

The matching is carried out with the complete list of compounds detected, not just those compounds previously reported in literature.

References

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Appendix D: Evaluation of Outlier Detection Methods

Three different methods for classifying outliers were considered:

- Outliers are data points where the Median Absolute Deviation is greater than three (Leys *et al.*, 2013; Rosenmai, 2013) “MAD”
- Outliers are data points more than three times the interquartile range above the upper quartile or below the lower quartile (National Institute of Standards and Technology, 2017) “IQR”
- Outliers are data points more than two standard deviations from the mean (Leys *et al.*, 2013) “STD”

The results of these three methods are shown below and are also available on the enclosed disc (Appendix B, Page 51).

Merged cells indicate that the same outliers were identified with multiple criteria. “All” indicates that the same outliers were identified for all three criteria.

Eley Propellant		Outliers	List	Mean	%RSD	Median
Benzene, 1,3,5-trimethyl-	All		476312.7, 266285.7, 312642.6, 113947.8, 630875.9	360012.9	49.45%	312642.6
Diphenylamine	All		20567004, 28729476, 29759626, 20473082, 34545996	26815036.8	20.52%	28729476.0
Naphthalene	All		56529.9, 45282.2, 25054.6, 38068.4, 69483.5	46883.7	32.50%	45282.2
Naphthalene, 2-methyl-	MAD	8132.4	97363.5, 64064.1, 82878.9, 122905.3	91803.0	23.41%	90121.2
	IQR		97363.5, 64064.1, 8132.4, 82878.9, 122905.3	75068.8	51.41%	82878.9
	STD					
p-Xylene	All		455311.9, 205584, 272594.2, 60055.7, 566347.8	311978.7	57.62%	272594.2
Styrene	All		610725.9, 245438.2, 411877, 85752.1, 570243.2	384807.3	51.32%	411877.0

Eley Cartridge Cases		Outliers	List	Mean	%RSD	Median
Naphthalene	All		926356.4, 614083.2, 379835.3, 129301.9, 119535.8	433822.5	70.64%	379835.3

Appendix D: Evaluation of Different Outlier Detection Methods

Geco Propellant		Outliers	List	Mean	%RSD	Median
1,2-Ethanediol, dinitrate	All		57607.7, 53290.5, 50390, 65629.6, 57511.5	56885.9	9.05%	57511.5
Benzenamine, 2-nitro-N-phenyl-	All		1628653.2, 2423974.8, 3256083.5, 2128501.5, 3020533.5	2491549.3	23.71%	2423974.8
Benzenamine, 4-nitro-N-phenyl-	All		1209065, 1952027.8, 4151133.2, 3083157, 3987381	2876552.8	39.75%	3083157.0
Dibutyl phthalate	All		129497.3, 228295.2, 476927.3, 207863, 357062.7	279929.1	43.82%	228295.2
Diphenylamine	All		25890406, 18090972, 23460378, 23950766, 17313574	21741219.2	15.66%	23460378.0
Formamide, N,N-diphenyl-	All		131530.3, 175876.7, 228085.1, 126794.1, 212421.7	174941.6	23.47%	175876.7
N,N'-Diethyl-N,N'-diphenylurea	MAD	42236988	16993880, 21424230, 20460232, 27289890	21542058.0	17.20%	20942231.0
	IQR		16993880, 21424230, 42236988, 20460232, 27289890	25681044.0	34.72%	21424230.0
	STD					

Geco Cartridge Cases		Outliers	List	Mean	%RSD	Median
1,2-Benzene dicarbonitrile	MAD	34580.3	49246.4, 172008.8, 175413.3, 210144.9, 221046.5	165572.0	36.97%	175413.3
	IQR		49246.4, 172008.8, 175413.3, 210144.9, 34580.3, 221046.5	143740.0	51.62%	173711.1
	STD					
Diphenylamine	All		1434395.2, 532138.8, 1230531, 1765613, 825829.2, 1082193.1	1145116.7	34.89%	1156362.1
Naphthalene	All	633378.1	235230.5, 134767, 187932.9, 196473.1, 175286	185937.9	17.47%	187932.9
Quinoline	All		13376.5, 28178, 45679, 70117.4, 13449.2, 77061.3	41310.2	61.37%	36928.5

Appendix D: Evaluation of Different Outlier Detection Methods

Winchester Propellant		Outliers	List	Mean	%RSD	Median
1,2-Ethanediol, dinitrate	All		54362.4, 44699.4, 57540.3, 47212.8, 51683, 47369.5	50477.9	8.86%	49526.3
Benzenamine, 2-nitro-N-phenyl-	All		1400772, 960360.8, 1384135.9, 1850898.1, 1889762.4, 1928704	1569105.5	22.45%	1625835.1
Benzenamine, 4-nitro-N-phenyl-	MAD	3379990	2137397.5, 1259626.6, 1666002.6, 1627232.8, 2461235.8	1830299.1	23.00%	1666002.6
	IQR		2137397.5, 1259626.6, 1666002.6, 1627232.8, 2461235.8, 3379990	2088580.9	33.22%	1901700.1
	STD					
Benzene, 1-methyl-2,4-dinitro-	All		5527593.5, 5455115.5, 5154389.5, 5830137, 5571435.5, 5959182	5582975.5	4.66%	5549514.5
Benzene, 2-methyl-1,3-dinitro-	All		339829.6, 312150.9, 323209.8, 391738.4, 352276.5, 361428	346772.2	7.51%	346053.1
Dibutyl phthalate	MAD	52380	1171939.1, 462795.5, 614880.6, 783635.2, 766507.6	759951.6	31.12%	766507.6
	IQR		1171939.1, 52380, 462795.5, 614880.6, 783635.2, 766507.6	642023.0	53.08%	690694.1
	STD					
Diphenylamine	All		16816804, 21070192, 18677694, 11270476, 13333774, 12476673	15607602.2	22.58%	15075289.0
Formamide, N,N-diphenyl-	MAD	129260.5, 121156	148921.5, 145786.7, 151140.2, 148880.3	148682.2	1.28%	148900.9
	IQR		148921.5, 129260.5, 145786.7, 121156, 151140.2, 148880.3	140857.5	8.11%	147333.5
	STD					
N,N'-Diethyl-N,N'-diphenylurea	All		48126712, 44261972, 47635364, 50310068, 51875536, 53819152	49338134.0	6.28%	49218390.0

Winchester Cartridge Cases		Outliers	List	Mean	%RSD	Median
Diphenylamine	All		188558.1, 279730.8, 38671.5, 21666.7, 152610.4	136247.5	70.58%	152610.4
N,N'-Diethyl-N,N'-diphenylurea	All		28566.4, 33077.2, 16873.4, 12381.7, 38527.7	25885.3	37.94%	28566.4

Appendix E: Mass Spectra Comparisons for Selected Compounds

E.1. Diphenylamine and 2-p-Tolylpyridine

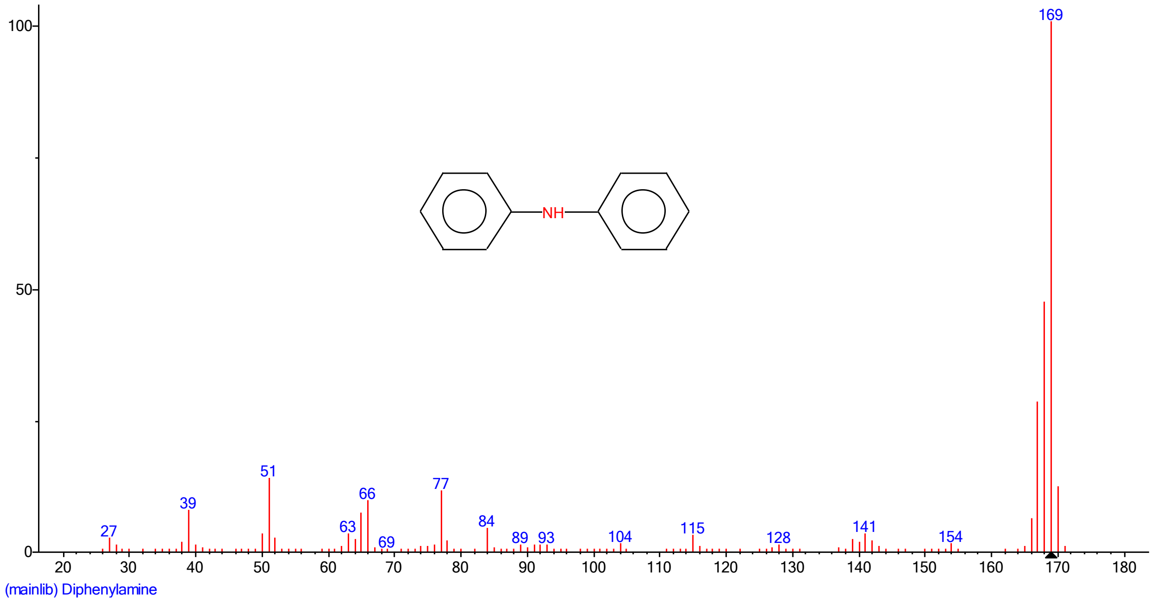
E.2. Ethyl Centralite and N,N’-diethyl-N,N’-diphenyl-oxamide

E.3. Nitroglycerine and 1,2-Ethanediol, dinitrate

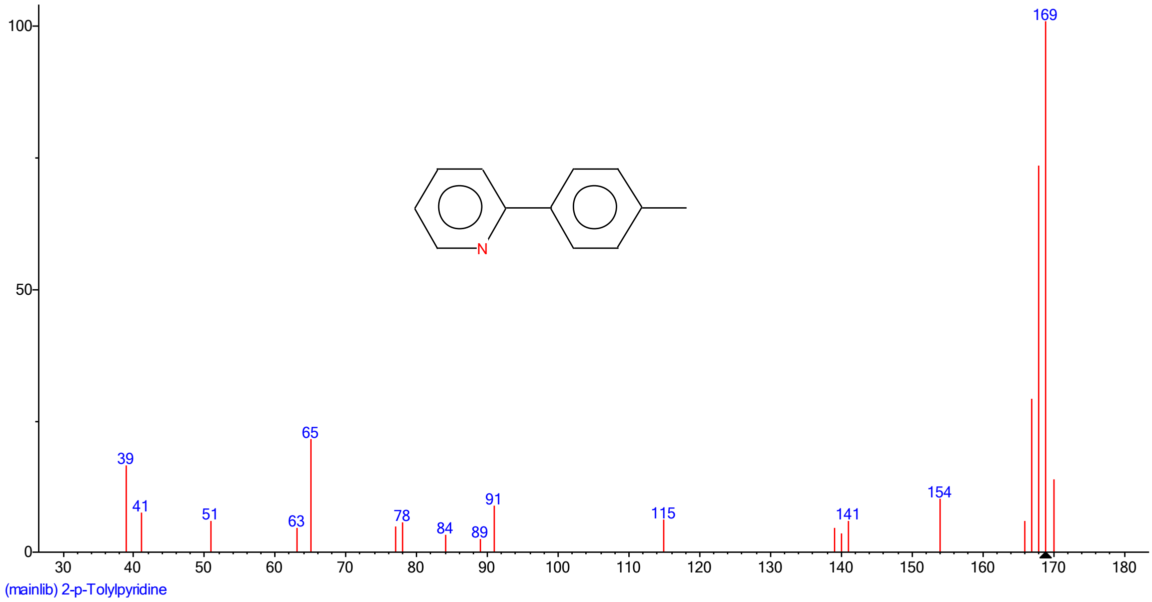
E.4. 1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester and 1,2-Benzenedicarboxylic acid, diheptyl ester

Spectra and structures were generated using NIST MS Search version 2 using data from NIST Mass Spec Data Center and Stein (no date)

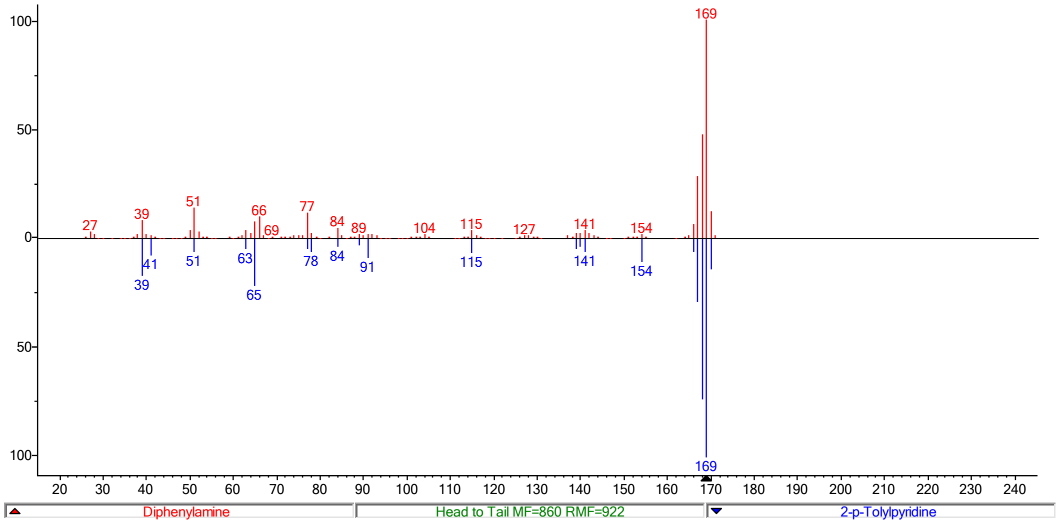
E.1. Diphenylamine and 2-p-Tolylpyridine



^ Diphenylamine

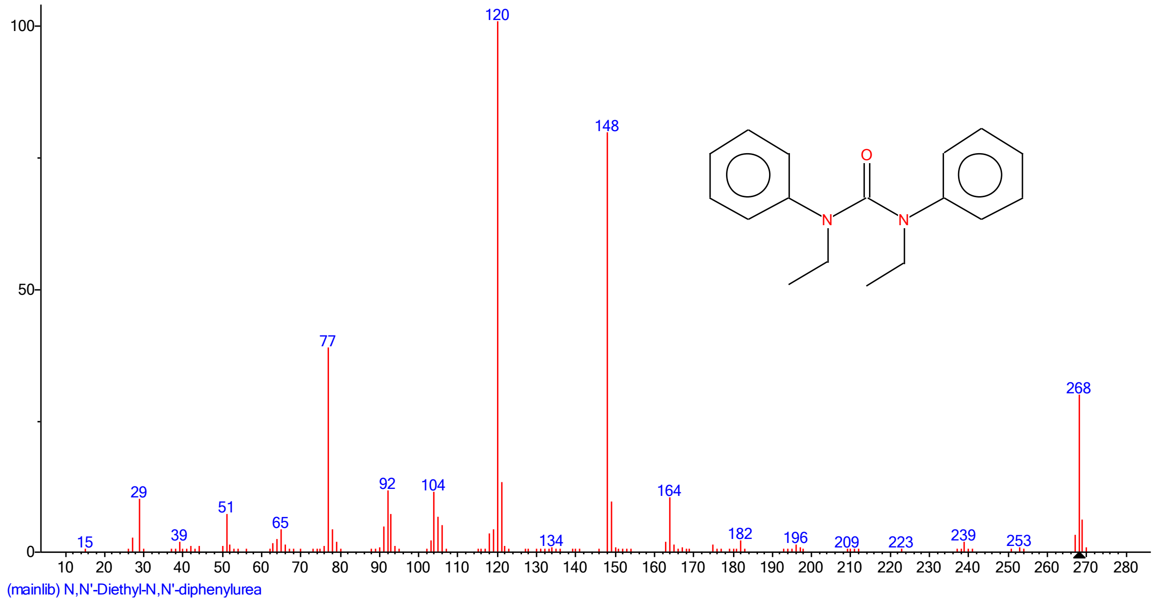


^2-p-Tolylpyridine

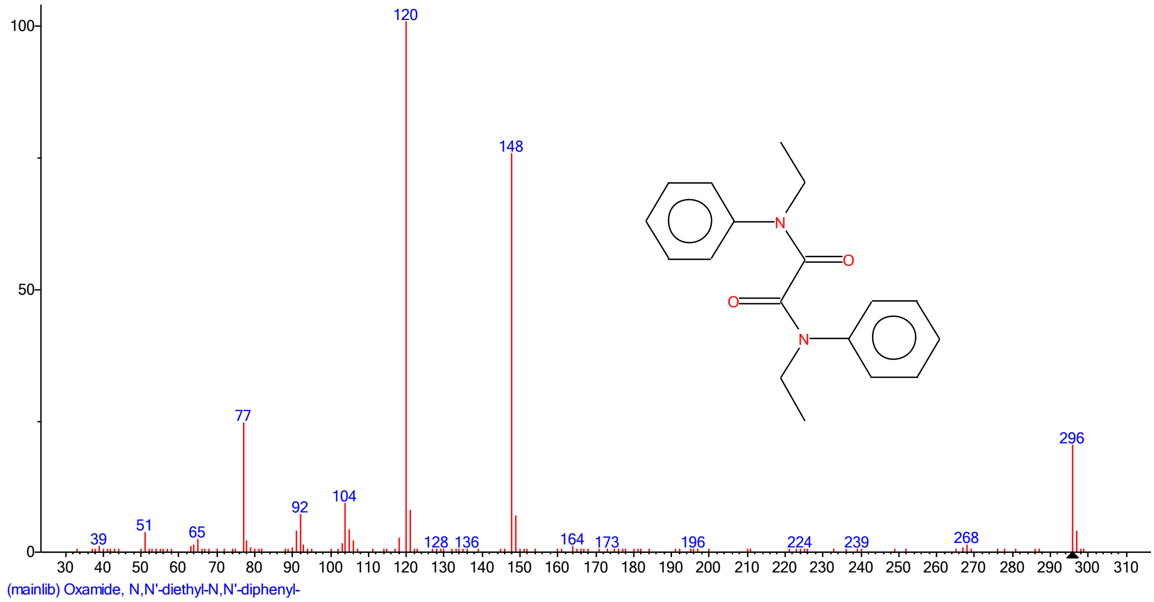


^ Head to Tail

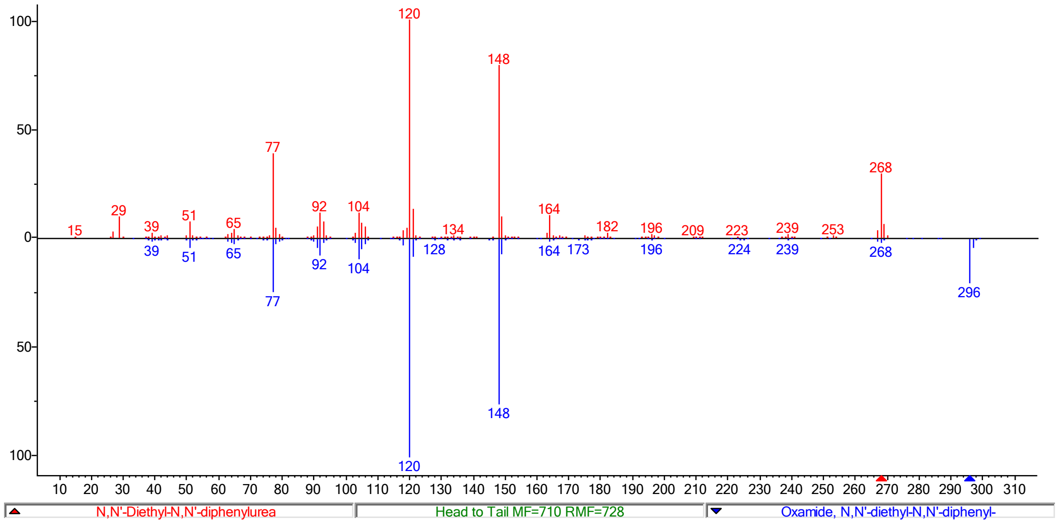
E.2. Ethyl Centralite and N,N’-diethyl-N,N’-diphenyl-oxamide



^ Ethyl Centralite (N,N’-diethyl-N,N’-diphenylurea)

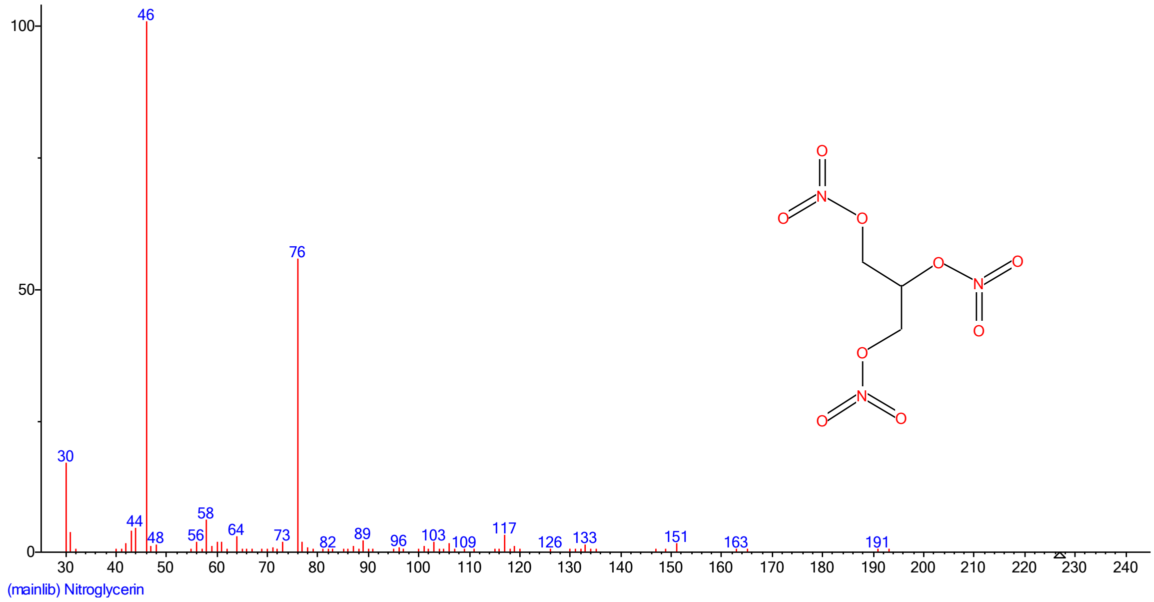


^ N,N’-diethyl-N,N’-diphenyl-oxamide

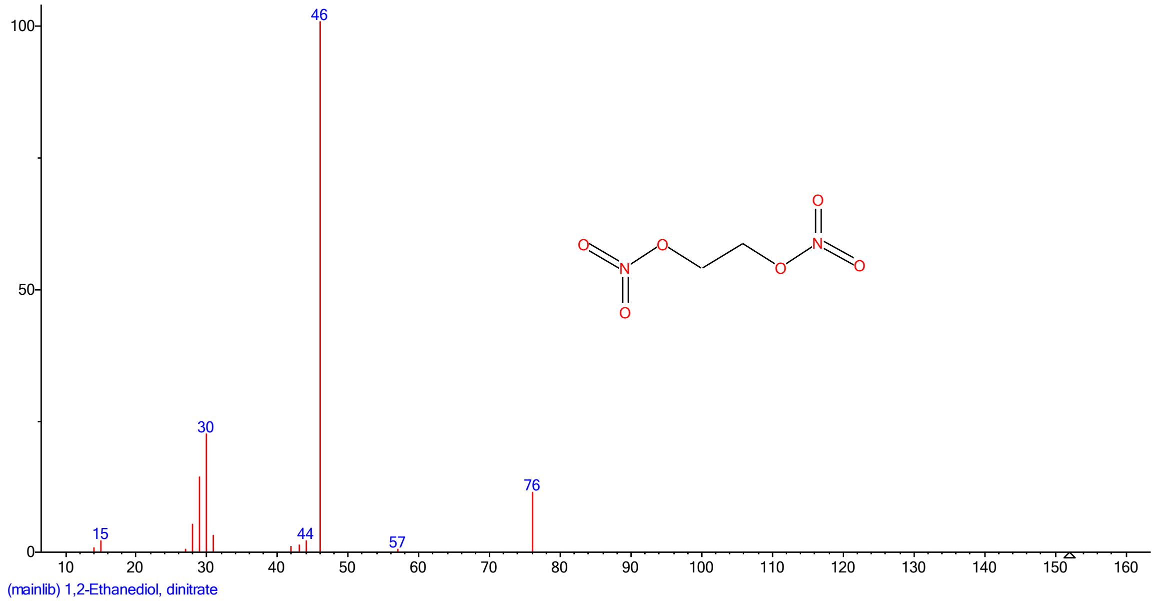


^ Head to Tail

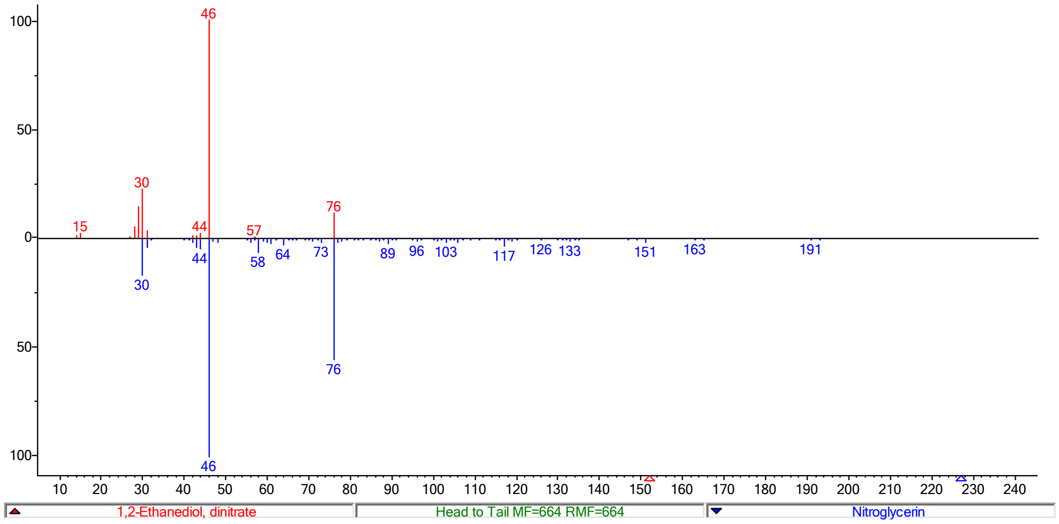
E.3. Nitroglycerine and 1,2-Ethanediol, dinitrate



^ Nitroglycerine

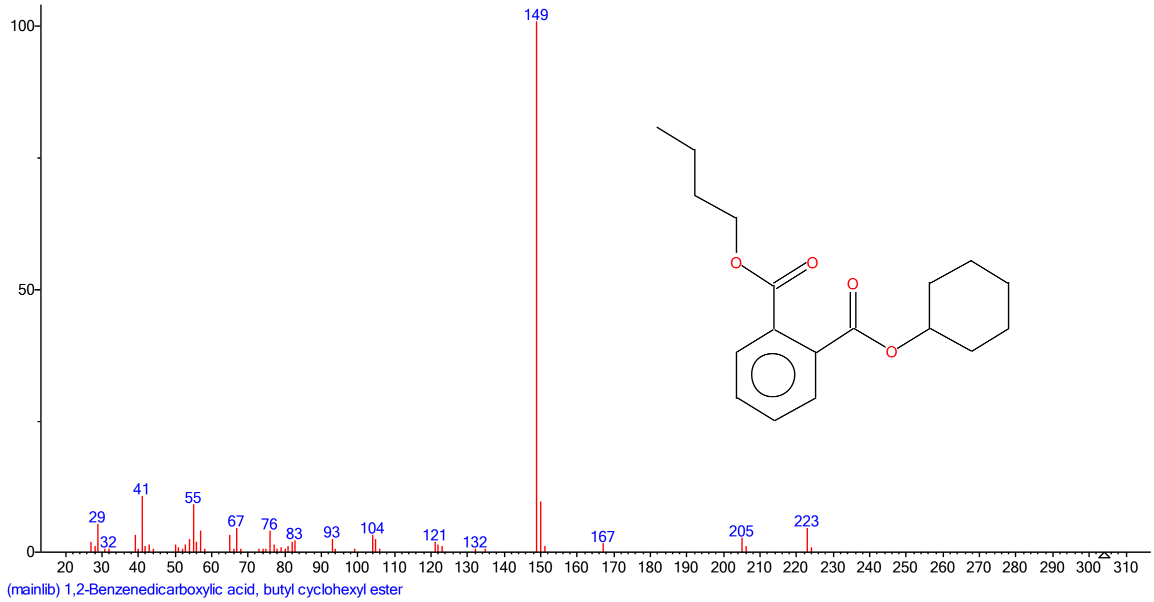


^ 1,2-Ethanediol, dinitrate

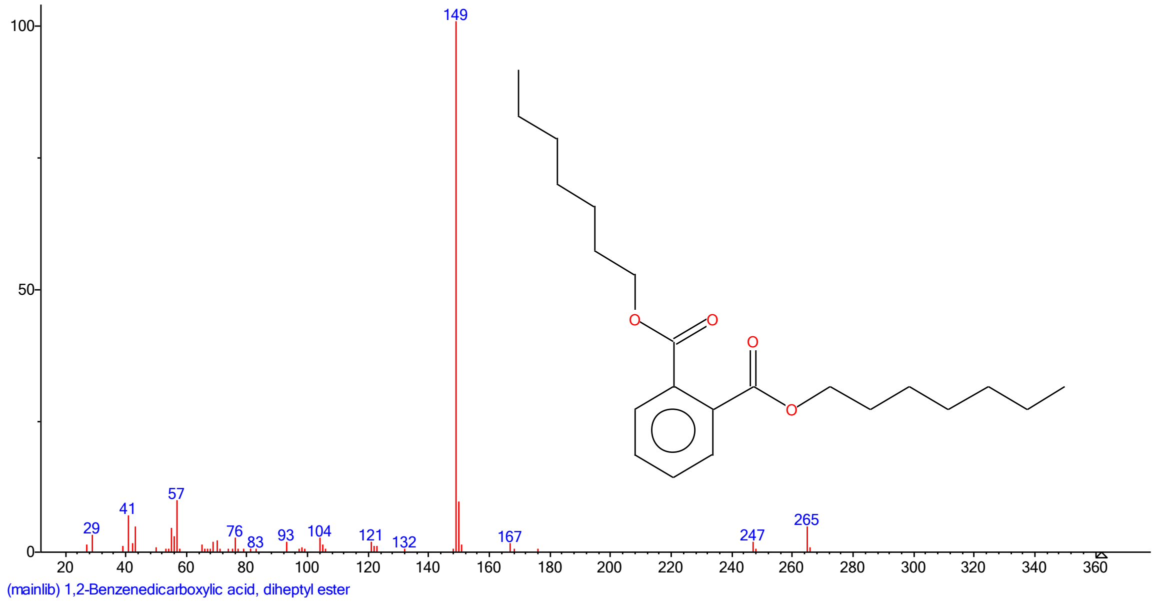


^ Head to tail

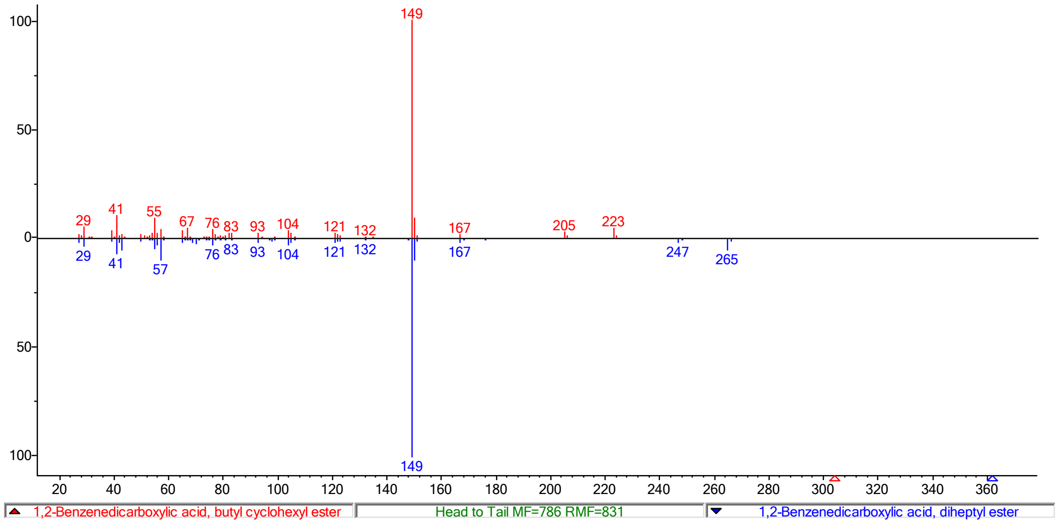
E.4. 1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester and diheptyl ester



^ 1,2-Benzenedicarboxylic acid, butyl cyclohexyl ester



^ 1,2-Benzenedicarboxylic acid, diheptyl ester



^ Head to tail

Appendix F: Licence and Copyright

Except where stated otherwise, the main GunShotMatch Program (*GSMatch0.8.1c.py*) and the sub-programs *GSM_Compare.0.2.1.py*, *csv_rename.py*, *standards.py*, *box whisker plot0.2.py*, *box whisker plot groups0.2.py*, *Custom Legend.py*, and *outlier_comparison.py* are Free and Open Source software licenced under the GNU General Public Licence V3.0. Copyright 2017, 2018 Dominic Davis-Foster

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The function `RepresentsInt()` Copyright 2009 Triptych.

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Appendix G: Searches of Smokeless Powders Database

Eley Contact

http://www.ilrc.ucf.edu/powders/search.php?s_reference=&s_content_source=&s_source_reference=&s_product_use=&s_distributor=&s_product_name=&s_date_obtained=&s_lot_number=&s_date_analyzed=&s_manufacturer=&s_date_manufactured=&s_notes=&s_shape_id=7&s_color_id=&s_luster_id=&s_dia_min=&s_dia_max=&s_dia_avg=&s_dia_tol=&s_length_min=&s_length_max=&s_len_avg=&s_len_tol=&s_chemical[]=3&s_other_comp[]=3&display_image=1&image_size=400

Winchester Pistol

http://www.ilrc.ucf.edu/powders/search.php?resultPage=1&resultPageSize=50&s_reference=&s_content_source=&s_source_reference=&s_product_use=&s_distributor=&s_product_name=&s_date_obtained=&s_lot_number=&s_date_analyzed=&s_manufacturer=&s_date_manufactured=&s_notes=&s_shape_id=&s_color_id=2&s_luster_id=&s_dia_min=&s_dia_max=&s_dia_avg=&s_dia_tol=&s_length_min=&s_length_max=&s_len_avg=&s_len_tol=&s_chemical[]=1&s_chemical[]=2&s_chemical[]=3&s_chemical[]=4&s_chemical[]=6&s_chemical[]=10&display_image=1&image_size=400

Geco Rifle

http://www.ilrc.ucf.edu/powders/search.php?resultPage=1&resultPageSize=50&s_reference=&s_content_source=&s_source_reference=&s_product_use=&s_distributor=&s_product_name=&s_date_obtained=&s_lot_number=&s_date_analyzed=&s_manufacturer=&s_date_manufactured=&s_notes=&s_shape_id=&s_color_id=2&s_luster_id=&s_dia_min=&s_dia_max=&s_dia_avg=&s_dia_tol=&s_length_min=&s_length_max=&s_len_avg=&s_len_tol=&s_chemical[]=1&s_chemical[]=3&s_chemical[]=4&s_chemical[]=6&s_chemical[]=10&s_chemical[]=11&display_image=1&image_size=400