(Wrobel, Millar and Kijek, 1998)

Email and ask if he still has the database

Harald.Wrobel@police.vic.gov.au

Software for database https://winworldpc.com/product/paradox/50-for-windows

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Can samples of gunshot residue be used to determine the ammunition that produced it?

Glossary

.22 LR	.22 Long Rifle rimfire cartridge; 0.22” calibre
Cal	Calibre (of a rifle)
Ga	Gauge (of a shotgun)
FTIR	Fourier-Transform Infra-Red Spectrometry
GC	Gas Chromatography
GSR	Gunshot Residue, also called Firearm Discharge Residue (FDR) or Cartridge Discharge Residue (CDR)
IGSR	
OGSR	
IR	Infra-Red (Spectrometry)
MS	Mass Spectrometry
PDMS/DVB	Polydimethylsiloxane / Divinylbenzene; a coating that may be used on SPME fibres
SPME	Solid Phase Micro Extraction
TOF	Time of Flight (Mass Spectrometry)
UK	United Kingdom
Hygroscopicity	How well a material absorbs moisture
IED	Improvised Explosive Device
TAC	Tandem Air Cartridge

Abbreviations of compounds not listed here are given in Appendix (?)

Units and Measurements

1 inch (”) equals 2.54 millimetres (mm)

1 grain (gr) equals 64.7989 milligrams (mg)

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 by Reardon, MacCrehan and Rowe (2000), Brożek-Mucha and Zadora (2003), Burleson *et al.* (2009), Weyermann *et al.* (2009), Dalby and Birkett (2010), Arndt *et al.* (2012), Benito *et al.* (2015), Tarifa and Almirall (2015), Bell and Seitzinger (2016), and Hofstetter *et al.* (2017). Handguns are commonly used in crime in the UK and the US (*The Trace*, 2016; Office for National Statistics, 2017a), and the 9 mm Parabellum cartridge is popular with police and military around the world (Chang, Yew and Abdullah, 2015; Eger, 2017; Mears, 2017).

There has also been limited research involving rifle and shotgun ammunition by Dalby (2011), Tarifa and Almiral (2015), and Wilson, Tebow and Moline (2003). The most comprehensive study of the smokeless powder and OGSR from different ammunition types was by Dalby (2011), although this study only looked at a few different brands for each calibre.

Research involving small calibre rimfire ammunition appears to be limited to Wrobel, Millar and Kijek's 1998 classification system for ammunition, and analysis of nailgun blanks for IGSR by Wallace and McQuillan (1984). Berg (1964) developed a classification system for firing pin impressions on .22" calibre cases, with an aim of being able to determine the type of firearm used, and Dalby (2011) also analysed powder and OGSR from two brands of .22 Long Rifle (.22 LR) ammunition – Vostok and Remington. A few papers also cover wound characteristics from .22 LR ammunition (DiMaio, Petty and Stone, 1976; Fackler, Bellamy and Malinowski, 1988; Hollerman *et al.*, 1990).

1.1. .22 Long Rifle

First introduced in the 1800s, .22 Long Rifle is one of the most popular calibres for target shooting in the United Kingdom (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.

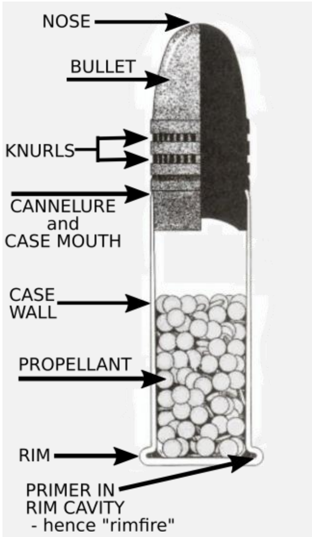


Figure 1-1: Cross-section of a .22 LR cartridge. Adapted from (ELEY Ltd, 2014)

Commercially produced .22 LR cartridges contain around 6.9 gr of propellant (Wallace, 2008), but reloaded ammunition may require up to 11.7 gr of powder, depending on projectile mass and desired velocity (Alliant Powder, 2017a).

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). The *primer* consists of a small amount of an impact-sensitive high explosive. In rimfire ammunition, like .22 LR, it is located in a groove inside the rim of the cartridge case, whereas in centerfire ammunition the primer is encased in a metal primer cup at the base of the cartridge. 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 *propellant*, which is the main charge inside the cartridge. The propellant burns slower than the primer and releases gases to increase the pressure in the case. This propels the bullet down the gun's barrel, together with unburned and partially burned propellant granules (Meng and Caddy, 1997; Wallace, 2008). The smokeless powder does not burn completely.

The *bullet* – which strictly speaking refers only to the projectile – is made from soft lead, but it may be coated with another metal such as copper to prevent too much lead from being stripped from the bullet by the rifling and fouling the barrel (Wallace, 2008). The lead may also be alloyed with harder metals such as antimony and tin to achieve the same effect (Meng and Caddy, 1997). Unjacketed bullets are only used in low power firearms, such as those in .22" calibre, that have a muzzle velocity below 1200 feet per second. 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 (Wallace, 2008). Russian manufacturers of .22" calibre ammunition often use steel cases (Schwoeble and Exline, 2000).

Paraffin, tallow, beeswax and several other compounds – mainly long chain hydrocarbons – are added to the *cannelure* and *knurls* on the rear of the bullet to provide lubrication as the bullet passes along the barrel. This helps prevent lead being stripped from the bullet by the rifling and accumulating inside the barrel (Wallace, 2008; Barnes, 2014; Merriam-Webster, 2017). A comprehensive list of lubricants and their ingredients is available in Schneider and Hurst (2016)

1.3. Gunshot Residue (GSR)

The Association of Firearm and Toolmark Examiners Glossary (2013, p. 59) defines gunshot residue as *"[t]he total residues resulting from the discharge of a firearm. It includes both gunpowder and primer residues, carbonaceous material, metallic residues from projectiles, fouling, and any lubricant associated with the projectiles."* Wallace (2008) also includes gases, vapours and particulates in the definition. The largest contributor of OGSR is the propellant, and burned, unburned and partially burned granules will be present (Wallace, 2008; Hofstetter *et al.*, 2017). Some OGSR will also originate from the firearm itself, as a result of previous firings (Wallace, 2008).

Analysis of gunshot residue 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 ammunition from the populations of different metals present in GSR when analysed by SEM-EDX. Four types of handgun ammunition were tested, and the method allowed 7.65 mm Browning and 9 mm Luger to be differentiated, but 7.62 mm Tokarev and 9 mm Makarov differentiated from the other cartridges. The metals examined were limited to those present in the ammunitions' primers. The authors suggested that including metals from the projectile and case, and organic residues from the propellant, could be used to differentiate Makarov and Tokarev ammunition.

Meng and Lee (2007) determined the metallic elements present in the primer and resultant GSR of 25 different handgun cartridges. The cartridges were 9 mm Parabellum, .40 S&W, .32 S&WL and .38 Spl, with both non-corrosive and lead-free primers, and analysis was carried out by

SEM-EDX. They found that the major elements in the GSR tallied with those present in the primer, and many elements other than lead, barium and antimony were present in different combinations, allowing many cartridges to be differentiated, including those that had the same headstamp but which originated from different types of ammunition.

1.4. Compounds in Primers

Primers consist of at least three compounds fulfilling different roles:

- Fuels, such as antimony sulfide, which burn rapidly and ignite the propellant
- Oxidisers, such as barium nitrate, which readily 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 in place of lead styphnate, and zinc peroxide in place of barium nitrate. Primers with this composition are manufactured by CCI, Fiocchi, and Dynamit Nobel (Sintox® brand) (Hagel and Redecker, 1986; Wallace, 2008; Benito *et al.*, 2015). TNT and PETN are alternative replacements for lead styphnate (Warlow, 1996; Schwoeble and Exline, 2000; Wallace, 2008).

GSR particles containing lead, barium and antimony are referred to as "Inorganic GSR" (IGSR). Heavy metal free or non-toxic primers may not produce inorganic GSR (Schwoeble and Exline, 2000; Benito *et al.*, 2015).

1.5. Compounds in smokeless propellant

Smokeless propellants are complex mixtures of multiple chemicals, and the compounds detected will be both those added by the manufacturer and the decomposition products of those compounds. Additionally, batches of propellant which are below specification may be used in the manufacture of new batches of propellant (called "reblending") (Espinoza and Thornton, 1994; Meng and Caddy, 1997; Bender, 1998; Heramb and McCord, 2002).

Dalby (2011) analysed standards of many of the compound 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 (e.g. Weyermann, 2009, Tables 1,3 and 4). However, many of the cartridges analysed did not show obvious peaks for these breakdown products.

Table 1-1 shows examples of some of the additives in smokeless propellant, together with their functions. Mach, Pallos and Jones (1978) believe ethyl centralite (EC), 2,4-dinitrotoluene (2,4-DNT) and diphenylamine (DPA) to be the three most characteristic OGSR compounds.

Appendix A lists compounds that have been reported in literature to be present in smokeless propellant or GSR. While there is generally agreement between the sources, many minor additives are listed in only one or two sources. The NIST Mass Spectra Database does *not* contain spectra for every one of these compounds.

Reardon, MacCrehan and Rowe (2000) analysed organic compounds in reloading powders from a variety of manufactures by capillary electrophoresis. They found that, while some powders contained similar compositions of NG, DPA and *N*nDPA, others varied in the concentration of nitroglycerine and the stabilisers present. The composition of individual powder particles from the same batch was found to vary considerably, and the authors cautioned against analysing single particles, as they may not represent the composition of a bulk sample of the powder.

Dalby (2011) analysed standards of many of the compound 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 (e.g. Weyermann, 2009, Tables 1,3 and 4). However, many of the cartridges analysed did not show obvious peaks for these breakdown products.

Table 1-1 Categories of Smokeless Propellant Additives

	Functions	Examples	Environmental Sources
Energetics	Main explosive charge [4]	• Nitrocellulose • Nitroglycerine • Nitroguanidine [4, 9]	Nitrocellulose - lacquers, paint, celluloid film [7] Nitroglycerine - cardiac stimulant [12]
Plasticisers	Reduce volume of solvent – alcohol or ether – required to colloid nitrocellulose [3, 4]	• Phthalates [4, 9] • Triacetin [4, 12] • Resorcinol [6] • Centralites [4, 9]	Dibutyl phthalate is used in some deodorants[13]
Moderants	Coating applied to granules [4] • Lower burning rate and temperature • Improves performance • Reduces corrosion	• Phthalates[4] • Centralites[4] • Natural resins	Trees and other plants
Stabilisers	Limit decomposition of nitrocellulose and nitroglycerine over time [3, 4, 5]	• Diphenylamine • Phthalates • Centralites [1, 4, 9]	Diphenylamine - plant growth regulator in picked fruit [2]
Flash Suppressors	Produce nitrogen gas to dilute muzzle gases and reduces the brightness of the flash[4, 5]	• Nitrotoluenes[10] • Nitroguanidine [4] • Triacetin[12]	- Mining explosives [10] - Polyurethane foam [11] - Waste from the production of azo dyes [8, 11]

1: (Warlow, 1996) **2:** (EPA, 1998) **3:** (Bender, 1998) **4:** (Heramb and McCord, 2002)
5: (Wallace, 2008) **6:** (Heard, 2008) **7:** (Morelato *et al.*, 2012) **8:** (Freeman, 2012)
9: (Taudte *et al.*, 2014) **10:** (Thompson and Innes, 2014) **11:** (EPA, 2014)
12: (Tarifa and Almirall, 2015) **13:** (Davidson, 2017)

1.5.1. Diphenylamine

Diphenylamine is a common stabiliser in single base propellant (Meng and Caddy, 1997). Stabilisers act as nitrate scavengers, which react with the decomposition products of nitrocellulose – nitric acid, dinitrogen tetraoxide, and nitrous acids. These would otherwise catalyse further decomposition (Espinoza and Thornton, 1994; Heramb and McCord, 2002;

Wallace, 2008). Stabilisers do not usually make up more than 2% of the propellant (Wallace, 2008).

Diphenylamine has several sites that can be nitrated, although not all sites will be nitrated on every molecule initially. A wide variety of derivatives can form, and some of these are shown in Table 1-2. These nitration products can still act as stabilisers until all sites have been nitrated to form 2,2',4,4',6,6'-hexanitro-DPA (Espinoza and Thornton, 1994; Taudte *et al.*, 2014). 2- and 4-NDPA may also be added as a stabiliser during the manufacture of the propellant (Wallace, 2008; Dalby, 2011).

Different nitration products will be present depending on the conditions the cartridges or powders have been stored at. After a prolonged period at high temperatures, there may be no unreacted DPA remaining (Espinoza and Thornton, 1994). Reardon, MacCrehan and Rowe (2000) recommended measuring the concentration of the diphenylamine and its derivatives together.

Table 1-2: Nitration products of diphenylamine.

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

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

1.5.2. Energetics

Nitrocellulose is used as the main explosive in all smokeless propellants, functioning as both the oxidiser and fuel for the explosion – the nitrate ester group oxidises the atoms in the hydrocarbon chain (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 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.

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 (Warlow, 1996). The shape of the extruded material and the manner in which it is cut produces a variety of differently shaped granules (Heramb and McCord, 2002; Dalby, 2011).

Smokeless propellant is readily recognisable under a low power microscope. The morphology of powder granules under a low-power microscope can indicate whether the powder is single or double base (Bender, 1998; Heramb and McCord, 2002).

1.5.3. Dyes

Organic *dyes* are added to some propellants to allow for identification (Heramb and McCord, 2002). Chemical codes or isotopic labelling can also be incorporated into the propellant to facilitate easier identifciation of gunshot residue (National Research Council, 1998a; Reardon, MacCrehan and Rowe, 2000).

1.5.4. Environmental sources of OGSR compounds

Many of the compounds in propellant are also present in the environment, such as in azo dyes and tea leaves, and so cannot be used to detect gunshot residue. However, they may prove useful to differentiate smokeless powder and GSR samples from different sources (Goudsmits, Sharples and Birkett, 2016). Table 1-1 shows some of the environmental sources of these compounds. While diphenylamine is used as a plant growth regulator for picked fruit, its nitrated derivatives are rarely encountered except in propellant (Espinoza and Thornton, 1994).

Some industrial tools, such as nail guns, are operated by blank firearm cartridges, including .22 LR blanks. (Hilti United Kingdom, no date). 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). It has been demonstrated that GSR produced by the two types of cartridge can be distinguished under SEM-EDX (Wallace and McQuillan, 1984). It is unclear whether the same is true for organic GSR.

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

1.6. Relationship between Propellant and OGSR

Dalby 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 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. Dalby found that most variation between 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 SPME fibre (Dalby, 2011).

The 16 different ammunition types tested by Dalby (2011) all had distinct compositions, and some produced OGSR with distinct compositions, although many of the GSR 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 are 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, 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. The authors found no relationship between the amount of OGSR and the cartridge's calibre, but there was a general relationship between the composition of residues and the unfired powder. However, after testing two other powders the authors could not determine any universal relationship between fired and unfired powder,

Wallace (2008) found considerable variations in the compositions of single smokeless powder granules from a single round. Therefore, when comparing fired unfired granules, he advised caution with any interpretation based on the composition of the granules if only a small number of granules are available for comparison. Additionally, some surface coatings may be lost from propellant granules when fired (Wallace, 2008). Kee et al. (1990) could not detect ethyl centralite in fired granules. This may be because it is only present as a surface coating on the granules, or it may be thermally unstable.

Meng and Caddy (1997) note that analysis of organic compounds in GSR is not a recent development: Bratin *et al.* (1981) used HPLC with electrochemical detection to identify nitro-containing explosives in GSR, and Dahl, Cayton and Lott (1987) used a similar technique to identify stabilisers. Even before then, HPLC and mass spectrometry had been used for analysis of explosives since 1977 (Vouros *et al.*, 1977).

1.7. Classification of cartridges

Wrobel, Millar and Kijek (1998) developed a classification system for .22" calibre cartridges, based on chemical, physical and ballistic characteristics of the case, bullet, propellant, and complete cartridge. The authors are based in Australia, where .22" firearms are most common. At the time the research was published there was little data on the chemical or physical composition of propellants used in rimfire ammunition. The aim was to be able to determine the brand and batch of ammunition based on this classification system. The characteristics used for classification are shown in Table 1-3.

Table 1-3 Classification criteria developed by Wrobel, Millar and Kijek (1998)

Headstamps
Propellant shape, size and colour
Projectile shape and type (e.g. hollow point)
Position of cannelures on projectile
Physical features of cartridge
Elemental composition of cartridge components
Ballistics info - velocity and accuracy of projectile

A database of seventy different types of cartridge was produced using the classification system. The authors found that, while no single factor allowed for differentiation of all samples, the combination of several different characteristics gives a unique "fingerprint" for each cartridge type. It was also possible to differentiate ammunition types produced by the same manufacturer.

1.8. Chemical Analysis of Gunshot Residue

1.8.1. SPME

<small section on theory>

"Lorem ipsum dolor sit amet, consectetur adipiscing elit, sed do eiusmod tempor incididunt ut labore et dolore magna aliqua. Ut enim ad minim veniam, quis nostrud exercitation ullamco laboris nisi ut aliquip ex ea commodo consequat. Duis aute irure dolor in reprehenderit in voluptate velit esse cillum dolore eu fugiat nulla pariatur. Excepteur sint occaecat cupidatat non proident, sunt in culpa qui officia deserunt mollit anim id est laborum."

Dalby & Birkett (2010) reviewed seven SPME fibres against their ability to extract over 30 compounds commonly found in smokeless propellant. Four different centre-fire ammunition brands in three different calibres were examined and GC-MS was used to identify the compounds detected by each fibre. Solvent extraction was used to provide a baseline to evaluate the fibres' performance against.

65µm PDMS/DVB fibres were determined to be the most suitable for extraction of OGSR compounds, able to identify 27 of the 30 standards used in their study, and the authors believe that the fibre should perform well with other ammunition types containing these 27 compounds.

Weyermann et al. (2009) also evaluated 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 85µm polyacrylate fibre. However, when tested with fired cartridges, only diphenylamine was extracted. The authors therefore used an alternative liquid extraction method, which could extract 32 different compounds from GSR samples.

Dalby (2011) originally performed extractions at 40°C, but switched to 80°C part way through the experiment after further method development. The optimal extraction time was determined to be 35 minutes, with the sample heated for 10 minutes before extraction.

1.8.2. 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 several different methods of preventing the loss of volatiles from fired shotgun shells: placing a cork in the end of the shell; placing a Teflon-coated cork in the end of the shell; and sealing the entire shell in a glass vial with SPME compatible lid. The concentration of naphthalene was measured as indicative of all volatile compounds in GSR.

The latter method was found to be the most effective method of preventing loss of volatiles. Unlike shells plugged with a cork, and the control left in the open air, almost no naphthalene was lost from the glass vials. There was a slight drop in concentration over the first two days while the naphthalene equilibrated with the air in the vial, but after this, the concentration of volatiles inside the sealed vials remained constant for almost four weeks after firing.

The initial drop can be compensated for by multiplying the peak height by the ratio of *volume of vial outside casing : volume of vial* (Wilson, Tebow and Moline, 2003).

This method has been used in research by Burleson *et al.* (2009), Weyermann *et al.* (2009) and Dalby (2011).

1.8.3. GC-MS

<small section on theory of GC>

"Lorem ipsum dolor sit amet, consectetur adipiscing elit, sed do eiusmod tempor incididunt ut labore et dolore magna aliqua. Ut enim ad minim veniam, quis nostrud exercitation ullamco laboris nisi ut aliquip ex ea commodo consequat. Duis aute irure dolor in reprehenderit in voluptate velit esse cillum dolore eu fugiat nulla pariatur. Excepteur sint occaecat cupidatat non proident, sunt in culpa qui officia deserunt mollit anim id est laborum."

Fused silica columns coated with either methyl-silicone or (5%-Phenyl)-methylpolysiloxane are commonly used for analysis of explosives. The columns are usually 0.25 mm or 0.32 mm in diameter (McCord and Bender, 1998). Agilent J&W's DB-5 and HP-5 columns are both 5% PMS (Agilent Technologies, 2017a, 2017b), and these have been used in research by Burleson *et al.*, (2009); Dalby and Birkett, (2010); Joshi, Rigsby and Almirall, (2011); Tarifa and Almirall, (2015) and Almiral *et al.* (2017), as well as for the Smokeless Powders Database (National Center for Forensic Science and University of Central Florida, 2006). In this project, a Supelco SLB-5 column was used, which has a silphenylene polymer stationary phase. The manufacturers say this phase is of an equivalent polarity to (5%-Phenyl)-methylpolysiloxane (Sigma-Aldrich Inc., 2006; Sigma-Aldrich Inc. and Merck KGaA, 2017)

Chromatography is the primary technique to detect organic compounds in GSR (Wallace, 2008), but Gas Chromatography is limited to volatile compounds only (McCord and Bender, 1998). Walsh (2001) described an application of wide bore gas chromatography columns for analysis of nitrate explosive residues in soil, which are not normally used for this purpose. A similar technique, utilising solid phase extraction, was described by Walsh and Ranney (1998) to detect explosives in water.

<small section on theory of MS>

"Lorem ipsum dolor sit amet, consectetur adipiscing elit, sed do eiusmod tempor incididunt ut labore et dolore magna aliqua. Ut enim ad minim veniam, quis nostrud exercitation ullamco laboris nisi ut aliquip ex ea commodo consequat. Duis aute irure dolor in reprehenderit in voluptate velit esse cillum dolore eu fugiat nulla pariatur. Excepteur sint occaecat cupidatat non proident, sunt in culpa qui officia deserunt mollit anim id est laborum."

Another detector that can be coupled to a gas chromatograph for analysis of OGSR compounds is a thermal energy analyser (TEA), also called a chemiluminescence detector (McCord and Bender, 1998; Wallace, 2008). It can be used for rapid screening but is limited to detecting chemicals with nitro groups (Wallace, 2008).

Ethyl and methyl centralite may co-elute when analysed by gas chromatography (Wallace, 2008). m-cresol and p-cresol have also been reported to coelute, but at a different retention time to the centralites (Dalby, 2011).

1.8.4. Other Techniques

In addition to GC-MS, there are several other techniques that can be used to analyse organic compounds within smokeless propellant and organic GSR. Some of these techniques are shown in Table 1-4. Ion mobility spectrometry is usually used in airport security and customs to quantitatively detect explosives and narcotics (Eiceman, Karpas and Hill, 2014).

Table 1-4 Alternative techniques for analysis of smokeless propellant

<table>
<tr><td>2D TLC with UV analysis
- can detect DPA and its nitrated derivatives
- Espinoza and Thornton (1994)</td><td>Ion mobility spectrometry
- can detect at least six different compounds
- can distinguish shooters from non-shooters
- Arndt et al. (2012); Bell and Seitzinger (2016)</td><td>Infrared spectroscopy
- can detect nitrocellulose and minor constituents of smokeless powder
- Kee et al. (1990); Lindblom (2002)</td></tr>
<tr><td rowspan="4">LC-MS
- can detect at least 17 different compounds
- Benito et al. (2015)</td><td>HPLC with a UV absorbance detector</td><td>Raman spectroscopy</td></tr>
<tr><td>Molecular luminescence spectroscopy</td><td>NMR</td></tr>
<tr><td>UV Spectroscopy</td><td>Polarography</td></tr>
<tr><td colspan="2" align="right">Wallace (2008)</td></tr>
</table>

Almiral *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. Unlike in previous research, Almiral *et al.* (2017) used cryofocusing – that is, cooling to -10°C in under 5 minutes – on the CMV device to cause condensation of volatile compounds from the air. Analysis of samples was carried out by GC-MS with a DB-5 column. While the authors successfully extracted VOCs from gunshot residue with this technique, they noted that it requires further optimisation to enhance the extraction performance.

Duarte *et al.*, (2018) analysed inorganic components of Brazilian ammunition using Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry. Unlike Meng and Lee (2007), who only identified the elements present in primers, Duarte *et al*. determined the concentration of these elements, alongside the concentrations of carbon, oxygen and nitrogen in the propellant. The authors did not attempt to use the results to differentiate the three types of cartridge they tested using this method.

1.9. Transfer and persistence of OGSR

Hofstetter et al., (2017) examined the transfer of organic gunshot residues to an individual after discharging a firearm, and the prevalence of chemically similar residues in the general population that have not handled firearms. They found substantial variability in the amount of OGSR transferred by individual cartridges of the same brand of ammunition. The research also demonstrated that the concentration of organic gunshot residues decreased with increasing distance from the ejection port of the firearm. Other factors affecting GSR deposition include the weather conditions – wind, rain, humidity and temperature – with less GSR detected when firing takes place outdoors. The surface texture (for clothing) and skin moisture (for bare skin) also have a bearing on the deposition of GSR (Wallace, 2008).

Many studies sample 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) had limited success in casework with detecting GSR on shooters' hands and forearms following the discharge of a bolt action rifle. He attributed this to the closed breech of these firearms. The breech and muzzle of handguns are closer to the shooter's hands than they are in rifles, which help to improve deposition of GSR onto the hands.

Wallace also had only limited success with .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.

1.10. Criminal use of Firearms and Propellant

1.10.1. .22 Long Rifle Firearms

Firearms chambered in .22 LR are occasionally used by criminals (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*). Excluding air weapons, firearms are primarily used as a threat or as a blunt instrument and not fired (Office for National Statistics, 2017b). Between April 2015 and March 2016 rifles[1] made up less than 1% of offences but were fired 17 times out of 48 offences, resulting in two deaths and one serious injury. 7 incidents resulted in property damage. The majority of offences involving rifles were for possession of weapons (Office for National Statistics, 2017a, 2017b).

Incidents of armed robbery are on the increase while overall robbery is falling, with rifles involved in 8 incidents. Armed robberies mainly occur in shops and on public highways (Office for National Statistics, 2017a, 2017b).

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

Firearms chambered for .22 LR have been used in some notable crimes in the UK. In 2010 Derrick Bird murdered twelve people and injured eleven others with a 12 ga shotgun and a bolt-action .22 LR rifle, both legally held (Whiting, 2010). In June 2016 MP Jo Cox was murdered by Thomas Mair with a knife and bolt-action .22 LR rifle. The stock and barrel had been shortened after the firearm was stolen from its licenced owner the previous year (*Telegraph & Argus*, 2016; Cobain and Taylor, 2016). Each year around 600 licenced firearms and shotguns are reported lost or stolen in England and Wales (Home Office, 2017).

Several improvised firearms utilise .22 LR ammunition (Duerr, 1997; Warlow, 2007). The Tandem Air Cartridge system (TAC) of air weapons consists of a brass cartridge with a similar shape and size as a pistol cartridge, containing a .22" air pellet and a quantity of compressed air. A firing pin released the compressed air and fired the pellet. (Saxby, 1984; Warlow, 2007).

Table 1-5 Firearm offences in 2015-16 that may include firearms chambered in .22 LR.

Type of Firearm	No. offences
Rifles	48
Unidentified firearms	666
Converted imitation handgun	12
Other converted imitation weapon	6
Converted air pistol	12
Reactivated handgun	1
Other reactivated weapon	1
Unknown handgun	1,727

Excerpt from Office for National Statistics (2017a) Table 3.02.

It transpired that the air weapons could be readily converted to fire .22 LR cartridges, in a variety of ways. This included manufacturing an adapter the size of a TAC cartridge, inside which a .22 LR cartridge could be inserted and fired from the air weapon. The barrel diameter could also be enlarged to allow conventional handgun cartridges to be fired (Foggo and Bamber, 2003; Warlow, 2007). These firearms were banned in 2003, but despite an amnesty at the time it is believed that large numbers are still in circulation, and are encountered by the police over 10 years later (*Hansard*, 2004, *Wiltshire Times*, 2014; British Association for Shooting and Conservation, 2005; Averty, 2017; Parker, 2017).

In the year ending March 2016, converted and reactivated firearms of all types and calibres were involved in under 1% of firearms crimes, totalling 242 offences over the last 10 years. However, in many incidents, the exact classification of the firearm(s) involved in an incident remains unknown, and as such, the number of converted and reactivated firearms involved in crimes may be higher (Office for National Statistics, 2017a). The number of times reactivated firearms are encountered by police is shown in Table 1-5.

1.10.2. Improvised Explosive Devices

Analysis of GSR is not solely limited to firearm crime. Single and double base powders are frequently used in improvised explosive devices (IEDs) in North America, since they can be readily obtained and used as the explosive charge without modification (Bender, 1998; Heramb and McCord, 2002; Beveridge, 2013). Based on data from the Federal Bureau of Investigation (1997), the National Research Council (1998b) estimate that smokeless and black powders were used in a third of bombings in 1995 in the US. In 2012 the majority of bombings involved low explosives like smokeless powder (Girard, 2017).

Smokeless powders have been used in 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 (Girard, 2017).

1.11. Aims and Objectives

The aim of this project was to determine whether or not it is possible to determine the brand and calibre of ammunition that produced the GSR.

The objectives of this project were to:

1. Validate the method developed by Dalby and Birkett (2010) and optimise it for the available equipment and timescales
2. Determine the composition of volatile compounds present in OGSR and unfired propellant
3. Differentiate samples of propellant and GSR based on the chemical composition
4. Link GSR samples to propellant, and hence to the brand of ammunition
5. <identify source of propellant before manufacturer>

1.12. Limit of Detection – move to introduction and method

Dalby (2011) determined the limit of detection (LOD) of some of the main compounds present in smokeless powder with his method. To do this, he examined the peak areas in 10 blank runs at the retention times previously identified for the compounds. While Dalby determined the LOD in terms of concentration, in this project it was determined in terms of peak area only. If any compounds were detected with peak areas below the LOD, they were ignored.

2. Materials and Methods

2.1. Unburned Propellent Powders

A bulk sample (~5g) of Alliant Unique® smokeless propellant, and boxes of .22 LR ammunition for three brands – Winchester Pistol, Geco, and Eley Contact – were provided by Marlow Rifle and Pistol Club. The Eley Contact ammunition had been previously been donated by the manufacturer to review its shooting performance. The Winchester Pistol and Geco ammunition had been left over at the end of a batch several years before. The Alliant Unique powder is used by the chairman to produce handloaded ammunition.

Propellent from three Eley Hawk Olympic 12 ga shotgun cartridges were provided by Merlijne le Haen as part of a separate research project in collaboration with Cleveland and Durham Specialist Operations Unit. The cartridges had been seized from a former shotgun certificate holder.

For each brand, six cartridges from the same box were pulled and approximately 100 mg of each powder was 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). Where the amount of powder in a cartridge was less than 100mg, the entire contents of the cartridge was used. For the Alliant Unique, five 100 mg aliquots were weighed into individual 2 mL vials. 100 mg aliquots were also taken from each of the shotgun propellant powders. The mass of each powder sample is shown in Table 2-1.

Table 2-1 Mass of propellant samples

	Sample Propellant Mass (g)					
	1	2	3	4	5	6
Alliant Unique	0.10	0.10	0.10	0.10	0.10	
Winchester Pistol	0.08	0.08	0.08	0.08	0.07	0.08
Eley Contact	0.06	0.05	0.05	0.06	0.07	
Geco	0.08	0.08	0.09	0.10	0.09	
Eley Hawk Olympic	0.10	0.10	0.10			

The Alliant Unique® propellant was used to optimise the method and ensuring that the GC/MS gave consistent results over time. It was also used to assess whether variation seen between cartridges from the same box of ammunition was due to a difference in chemical composition, or to variability in the instrument and method. This powder was analysed five times throughout the experiment. This propellant is a disc-shaped reloading powder designed for centerfire rifle cartridges and shotgun shells (Wootters, 1969).

Table 2-2 shows information about the powder samples used, including the shape and size of granules.

2.1.1. Alliant Unique

Unique is a double base powder with a long shelf life (Wootters, 1969). Wootters reported a nitroglycerine content of around 40%, but VanDenburg Jr (2011) reports a concentration of around 20%. A previous data sheet lists a concentration of between 4% and 40% (Alliant Powder, 2002). The most recent data sheet, which covers several different types of propellant, reports three ranges of concentration: 4-10%, 30-30%, and 30-40% (Alliant Powder, 2017b). It is unclear which of these corresponds to Unique. The manufacturer was unable to shed any light on this.

Unique propellant is widely used and is suitable for all ammunition types (rifle, pistol and shotgun), but the speed at which the powder burns makes it unsuitable for jacketed rifle bullets (Wootters, 1969).

Wootters (1969, p. 165) described Unique powder as being "…in the form of gray [sic], round flakes, about .065" in diameter and .006" in thickness". Since manufacture switched to Alliant the thickness appears to have increased to between .008" and .009". However, despite the change in size, the burning rate has remained constant over time (VanDenburg Jr, 2001).

The propellant has been noted to leave a residue in barrels after firing (Wootters, 1969). The manufacturer now claims that the propellant is cleaner burning, suggesting a change of formulation has occurred (Alliant Powder, 2010).

BAE Systems took over operation of the Radford Army Ammunition Plant in 2011 and Alliant production moved to Lewiston, Idaho (Williams, 2016; BAE Systems, 2017).

Table 2-2 Information about the cartridges and propellants used in this research.

Brand	Alliant Unique®	Eley Contact .22 LR	Winchester .22 LR	Geco .22 LR	Eley Hawk Olympic 12ga
Type	Bulk Powder	Individual Powders	Individual Powders	Individual Powders	Individual Powders
Photograph					
Description	Flat discs				
Primary components	Nitrocellulose Nitroglycerin Rosin, Diphenylamine Ethyl centralite	Paraffin wax lubricant Composition of propellant not listed	Nitrocellulose Lead styphnate		Nitrocellulose
Fired case storage time	N/A	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)	N/A
Notes	Formerly sold as Hercules and DuPont	Lot 3L17-40041 Manufactured 7/7/17	Batch ACDITE62		
Reference	(Alliant Powder, 2017b)	(ELEY Ltd, 2016, 2018c)	(Olin Winchester Ammunition, 2015)		(Maxam Outdoors, 2012, 2016; Eley Hawk Ltd, 2016)

2.2. Firing Procedure

The firing was carried out with two Česká zbrojovka CZ 455 bolt-action rifles chambered for .22 Long Rifle. As shown in Section 1.10, this calibre of firearm is occasionally encountered in crimes. The CZ 455 is a similar design to the CZ 452 used by Derrick Bird in a mass shooting in 2010 (Whiting, 2010).

Ten cartridges were fired from the same box for each brand of ammunition. Before firing, the cartridge cases were labelled using a permanent marker pen with a number corresponding to the order in which they were fired. The length and mass of the cartridges were measured before firing, and the cases from the first two cartridges fired were discarded to prevent any carry-over of GSR from other ammunition fired in the rifle previously. This is based on the method used by Dalby (2011), except in this research only the first two cases were discarded, not the first three. Six of the 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 method for packaging the fired cases is based on the method developed by (Wilson, Tebow and Moline (2003)

The vials were stored at approximately 20°C for several days before analysis. The dates and times firing and analysis took place were recorded, and the storage times are shown in Table 2-2.

2.3. Solvents and Standards

Camphor and ethyl centralite were purchased from Sigma-Aldrich (Gillingham, Dorset, 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 purchased from Arcos Organics.

Camphor and ethyl centralite were purchased and opened in January 2018. All other standards were already available and had been opened previously.

2.4. GSR Standard Mixture

A standard mixture containing seven compounds that may be present in GSR was made in analytical grade methanol. The composition of the standard mixture is shown in Table X-X. The standard mixture was then used to confirm that these compounds are correctly detected and identified by the GC-MS system, identify the retention times for these compounds, and determine the smallest peak area that can be correctly identified.

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 mixtures, 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 for the solvent to evaporate, before being sealed and stored for 9 days before undergoing SPME extraction and GC-MS analysis following the methods described in Sections 2.5 and 2.6.

2.5. SPME Extraction

2.5.1. Extraction Conditions

Before extraction was carried out on a set of samples, the SPME fibre was conditioned in the injection port of the GC-MS for 10 minutes at 250°C and a blank run carried out to ensure the fibre was clean.

Samples were incubated in an oven at 80°C for 10 minutes before analysis (Dalby, 2011). A 65µm polydimethylsiloxane/divinylbenzene SPME fibre (Supelco, Bellefonte, Pennsylvania, USA) was then inserted into each vial and heated for 35 minutes at 80°C. After extraction, the SPME fibre was removed and immediately injected into the sample port of the GC-MS.

After injection, the fibre was left in the injection port for a further 10 minutes to condition, before being inserted into the next vial.

The extraction conditions and choice of fibre were based on the findings of Dalby and Birkett (2010) and the method used by Dalby (2011). Dalby and Birkett found 65 µm polydimethylsiloxane/divinylbenzene o be the optimum coating, performing well for extraction of 27 different compounds, including toluenes, nitroglycerine, diphenylamine and its derivatives.

2.6. 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, a column blank was run with the gas syringe in the injection port. 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 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 mins, and a higher final temperature of 300°C.

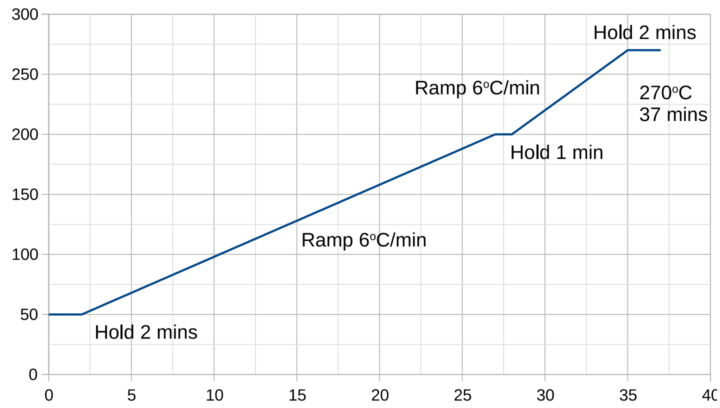


Figure 2-1 Annotated temperature program graph for the GC-MS method

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.

2.7. Data Analysis

A bespoke data analysis method was developed for interpretation of the GC-MS results. The method incorporates some existing elements from literature, but also introduces some novel approaches.

A program, "GunShotMatch", has been developed to automate this analysis. GunShotMatch is Free and Open Source Software written in Python 2.7, making use of several open-source libraries. Full details of the program are available in Appendix B. The basic operation of the program is described below.

GunShotMatch takes the output from TurboMass 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, <supplier name>). Any matches with a match probability below 450/650 were excluded from the search results.

"GunShotMatch" then identifies peaks in common between samples from the same source and determines the most likely compound responsible for the peak. The software allows a slight variation in retention time of +/− 0.1 minutes for peaks between the samples.

Any peaks where the matches appear to be column-, septum- or fibre-bleed, such as those that contain "siloxane" in their name, are automatically excluded.

GunShotMatch makes use of the NIST MS Search program to compare the mass spectra for matching peaks to verify that the compounds are indeed similar. The average of this value for each peak is shown in the output, alongside the average peak area, retention time, hit ranking and match factor. The Standard deviation and %RSD are also shown.

The method for GunShotMatch was developed from a completely manual approach that functioned on broadly the same lines. The automated approach allowed many subjective steps to be removed, and 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.

Many of the parameters for GunShotMatch can be customised, allowing it to be tailored to other applications.

A second program, "GSM Compare", is used to compare the output from GunShotMatch for samples from different propellants.

3. Results and Discussion

Most significant finding first

- identification of compounds in propellant and GSR and peak areas before and after firing
- Similarities and differences
    - % loss
- Linked to aims

Compare and contrast

Link results together

Link back to sources from introduction

Ensure introduction contains material relevant to points raised in discussion and doesn't omit any information

3.1. Composition of Unfired Propellant

Analysis of the propellant and GSR samples primarily focused on compounds that were previously reported in literature. Across the five propellant samples, twenty different compounds were identified 41 times. These are shown in Figure 3-2.

Diphenylamine was the only additive detected in all five propellants. Ethyl centralite, 2-nitro-DPA and 4-nitro-DPA were detected in all propellants apart from Eley Contact.

Many compounds exhibited substantial variation in peak area between samples of the same propellant, up to 60% for some compounds. For most peaks the peak areas were the in same order of magnitude. None of the peaks were more than two standard deviations away from the mean peak areas. For some compounds in certain propellants, the standard deviation was less than 10%. The standard deviations are shown in Figure 3-2.

The peak areas generally increase and decrease in tandem between samples. This may be due to the varying mass of the samples (+/- 0.01g) or slight variations in the composition of the propellant granules.

Diphenylamine was the primary additive in Eley Contact and Aliant Unique propellant. Ethyl centralite was the primary additive detected in Winchester Pistol and Geco propellant, although DPA was the second major additive. 2,4-dinitrotoluene was the primary additive in the Eley Hawk Olympic shotgun propellant. As well as acting as a stabiliser, 2,4-DNT can also act as an energetic and flash suppressor. Diphenylamine and ethyl centralite are both stabilisers.

The five sample of Eley Contact propellant and the first three samples of Alliant Unique used a mass spectrometer scan range of 50-???, but nitroglycerine has a major ion fragment at m/z 46, and substantial fragment at m/z 30 (NIST Mass Spec Data Center and Stein, no date). This may have affected the detection of nitroglycerine in these samples. For the remaining samples the scan range was changed to 45-???? to improve detection.

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

The disc shape of the Alliant Unique propellant granules suggests that it may be a double base propellant, and nitroglycerine has been listed as an additive previously (Wootters, 1969;

VanDenburg Jr, 2001; Heramb and McCord, 2002). However, nitroglycerine was not detected in any samples, including the two samples analysed with the larger scan range.

Table 3-1 shows the numbers of compounds detected in the unfired propellant samples.

Table 3-1 Number of compounds detected in unfired propellant samples

	Alliant Unique	Eley Contact	Winchester Pistol	Geco	Eley Hawk Olympic
Number of compounds previously reported in literature	6	6	9	7	13
Total number of compounds detected	15	20	17	19	32
Number of compounds with more than one peak detected	0	3	0	0	1

The numbers of compounds detected in the Eley Hawk propellant may be higher than for the other samples because of the lower number of samples analysed for this propellant. As more samples of each propellant are analysed, GunShotMatch is able to eliminate more compounds that are not detected in all samples, reporting only the main additives.

GunShotMatch cannot make a positive identification for compounds without a standard also being run. As such, not all every compound identified will necessarily be present in the propellant. GunShotMatch can only identify that compounds are in common between repeat analyses of propellants; the limitations of automatic Mass Spectrometric identification still apply. 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.

3.1.1. Alliant Unique

Shape of propellant

<look for nitroglycerine manually>

Composition

History

Alliant Unique has been produced for over 100 years by several manufacturers: Laflin & Rand of Haskell, New Jersey; Dupont; Hercules; Alliant Techsystems; and currently Vista Outdoor. The formulation is reported to have remained broadly unchanged between these manufacturers (VanDenburg Jr, 2001, 2011). However, since the late 1990s, when manufacture switched to Alliant at the US Army's Radford Ammunition Plant in Virginia, the consistency of the powder has improved, and less reblending of below-spec batches occurs (VanDenburg Jr, 2001). Alliant's parent, Vista Outdoor, and also manufacture ammunition under the Federal, CCI and American Eagle brands, amongst others (Vista Outdoor, 2017).

3.1.2. Eley Contact

Shape of propellant

<comment on shape of propellant.>

Composition

Diphenylamine had a %RSD of 20.5%, which is similar to that found in Alliant Unique. With the exception of 2-methyl-naphthalene, the peak areas for all six compounds appear to increase and decrease in tandem between samples.

History

Eley have been manufacturing ammunition since 1828, and first produced .22 LR cartridges in 1860. Eley became part of Nobel Industries in the early 1900s (later Imperial Chemical Industries, and then IMI) before being sold off in 1993 (Grace's Guide Ltd, 2015, 2017; ELEY Ltd, 2018d). Production is still carried out in the UK, and the ammunition is popular with target shooters across the world (ELEY Ltd, 2018a, 2018d). Eley manufacture 16 different types of .22 LR ammunition for target shooting and hunting (ELEY Ltd, 2018b)

.22 LR Eley ammunition, although not this specific range, was used by Thomas Mair to shoot Jo Cox MP in June 2016 (*Telegraph & Argus*, 2016).

3.1.3. Winchester Pistol

Shape of propellant

Composition

History

Winchester ammunition is now manufactured by Olin, an American chemical manufacturer (Olin Corporation, 2018b). Winchester currently manufacture 23 different types of .22 LR ammunition for a variety of uses, alongside .22 Short and .22 Long cartridges. However, it does not appear that the ammunition used in this experiment is still manufactured (Winchester, 2018). Olin started manufacturing ammunition in 1898 as the Western Cartridge Company. Olin purchased Winchester in 1931 (Olin Corporation, 2018a). Ammunition was also sold under the "Western" brand. Winchester have been manufacturing .22" rimfire ammunition since 1877 http://22box-id.com/USA/Winchester.pdf (McKune, 2017)

3.1.4. Geco

Shape of propellant

Composition

History

Geco ammunition is manufactured by RUAG https://www.ruag.com/en/products-services/land/hunting-sports-ammunition/geco. Two different types of .22 LR ammunition are available: Geco Semi Auto, and Geco Rifle.

https://geco-munition.de/en/ammunition/rimfire-cartridges.html#!0/93/23

Geco S/A and Rifle reported to be clean burning, wih parrafin wax lubricant on S/A http://www.rimfirecentral.com/forums/showthread.php?t=520470; https://murphysammo.com/products/geco-22lr-40gr-rifle-500-rnds

3.1.5. Eley Hawk Olympic

Shape of propellant

Composition

History

http://www.maxamcomponents.com/en/outdoorsbrand/componentes/products/powders

Here are the links relating to Eley Hawk ammunition and its propellant.
http://www.clay-shooting.com/news/1st-prize-eley-hawk-1st-select-reviewed-by-richard-atkins/
https://www.maxam.net/en/fundacion/sala_prensa/history_articles/long_standing_quality_heritage
https://www.eleyhawkltd.com/about-us

And here is the article that covers the shapes of propellant granules:

https://archives.fbi.gov/archives/about-us/lab/forensic-science-communications/fsc/april2002/mccord.htm

The relevant part is near to Figure 1.

3.2. Analysis of Fired Cases

The research by Hofstetter *et al.*, (2017) into the persistence of OGSR was carried out with the ventilation in the range turned off. This will have helped with the deposition of GSR particles onto the shooter. For this project is was not possible to switch the ventilation off during firing. However, this should not have any impact on the residues remaining within the cartridge cases.

The method for analysing the fired cases is based on Wilson, Tebow and Moline (2003) and Dalby (2011). Dalby's method additionally froze the samples at -22ºC 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 <discuss this impact>.<would freezing improve sensitivity?>. For fire accelerants, neither the *Scenes of Crime Handbook* (Scenesafe and The Forensic Science Service, 2008) or Baxter (2015) recommend freezing fire debris to prevent loss of volatiles; however, the Office of Fire Prevention and Control in New York (2010) do recommend freezing fire debris.

Dalby (2011) used 14 mL headspace vials for extraction of some fired cartridge cases (p142); the author does not state the volume of vials used for all extractions. Dalby used a variety of calibres of ammunition, ranging from .22 LR to 7.62x51 mm NATO. While a 14 mL vial is a similar volume to a 7.62x51 mm cartridge case, it is substantially larger than a .22 LR case. A comparison of these cartridge cases and vials is shown in Figure 3-1.

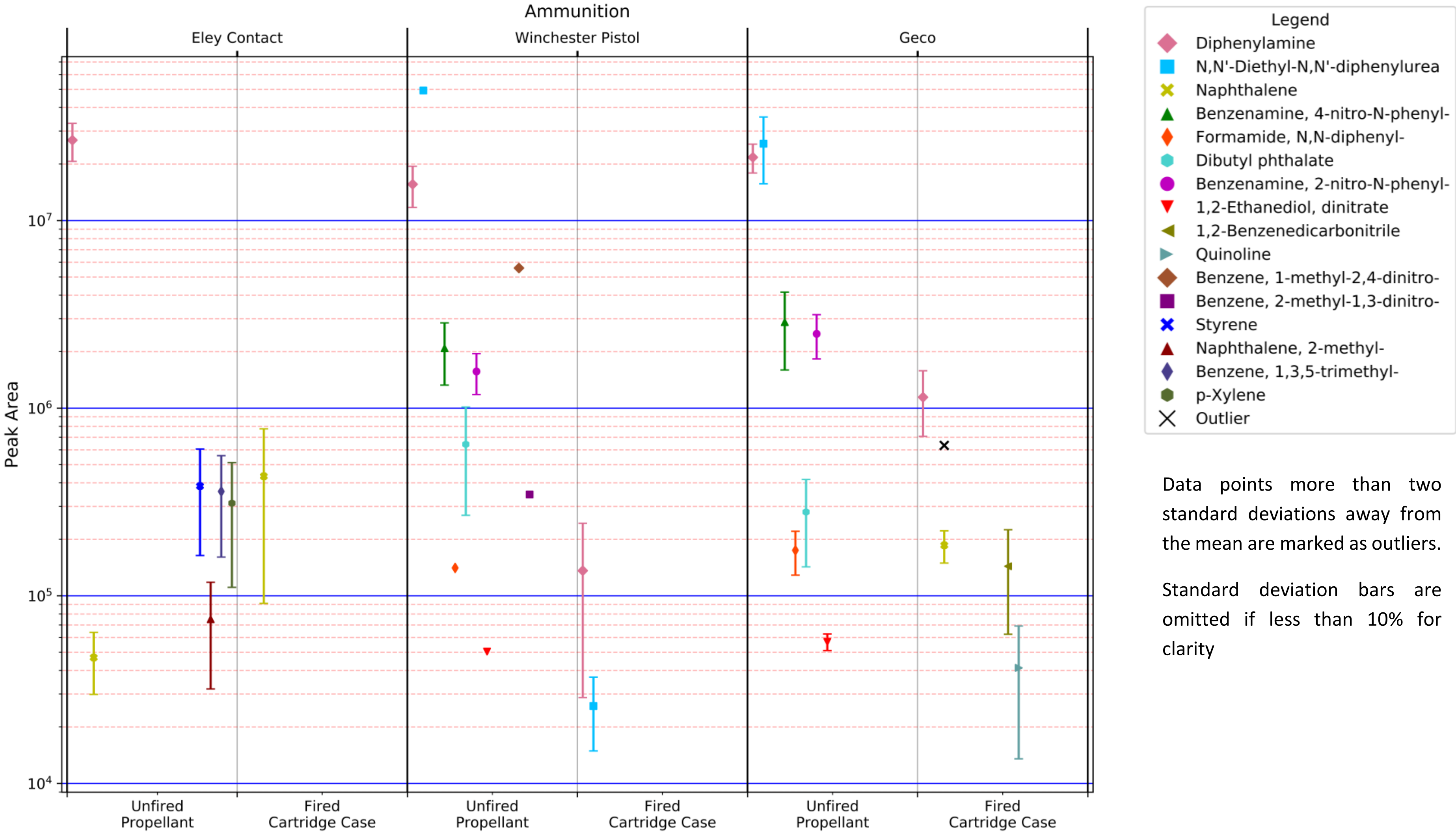
Figure 3-1 Comparison of various fired cartridge cases and headspace vials. From left to right: 14 mL vial; .22 LR; 9x19 mm; 5.56x45mm; 7.62x51mm; 12 gauge; 4 mL vial; 2 mL vial.

Wilson, Tebow and Moline (2003, p. 1301) recommended that the vial be "just large enough to fit a shell" or, in this project, a 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. Almiral *et al.* (2017) were unable to recover OGSR compounds from the headspace of a 1 litre container, and the authors attributed it 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 larger volume of vial 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 fill some of the volume inside the vial.

Dalby (2011) used samples of unfired powder, rather than OGSR, to develop his analytical method. Dalby noted that the loss of volatiles from OGSR samples over time has been reported in literature (Weyermann *et al.*, 2009).

Weyermann et al. (2009) performed SPME extractions at room temperature and at 80^{o}C, which allowed for five additional compounds to be detected. Dalby (2011) also found that a higher temperature was optimal for SPME extraction, and noted that Andrasko and Ståling (1999) had encountered difficulty with their room-temperature extractions.



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 3-2 Composition of unfired propellant samples

3.3. Distinguishing Samples

Compare all samples together

Similarity to other propellants

3.4. Composition of GSR

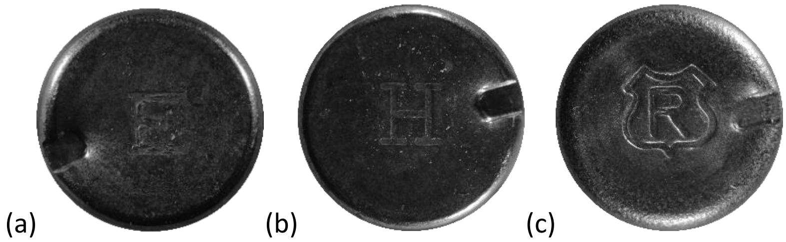


Figure 3-3 Headstamps from the fired cartridge cases.
(a) Eley Contact. (b) Winchester Pistol. (c) Geco

Compounds in GSR

Mach Et Al 1978 list EC, 2,4-DNT and DPA as most characteristic GSR compounds. However, Goudsmits, Sharples and Birkett report that DPA is widely encountered in the environment.

Of these, only DPA was positively identified in the GSR from Winchester ammunition, with a poor identification of EC

Similarity between prop and GSR with graph to show loss

Similarity to other GSRs

3.5. Accuracy of Identification

3.6. Automated Method

3.7. Effect of analysis on DNA recovery

It may be useful during the course of the investigation into a shooting event to recover and sequence DNA from the fired cartridge cases. The high temperatures sustained during the firing of a cartridge are likely to degrade any DNA deposited on the casing when the magazine was loaded (Fan *et al.*, 2017). The flame temperature of smokeless powder burning inside the casing may reach 1800°C (Schaefer, 2016).

Polley *et al.* (2006) encountered difficulty with recovering DNA from fired cartridge cases in sufficient quantities to successfully profile. After analysing fired casings using the method used in this project, it is likely that the chances of DNA recovery may be further reduced as a result of DNA degradation when the casing is heated. Karni *et al*. (2013) found that DNA begins to degrade at 130^{o}C, 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^{o}C. Further research is required to determine whether, in practice, this method has any effect on the recovery of DNA from fired cartridge cases.

Because the case must remain sealed inside a vial following collection until extraction is complete, there is no opportunity to recover DNA before heating the sample. 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).

4. Conclusion

Results in context of field and relevance to practitioners

What small changes required to improve this in the future?

Links back to introduction, where research's context in field was established

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Possibly useful sources

(Zitrin, 1998) Chapter 9 in (Beveridge, 1998)

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Analysis by GC/MS with total ion chromatogram

Chapter has info on HPLC and IC, which may be useful for discussion on alternative techniques

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(Espinoza and Thornton, 1994) Provides detail on the mechanisms involved in nitration reactions of DPA. Other lists of decomposition products in powder in references in p369 (Bender, 1998)

Other citations to hide

(Fan and Almirall, 2014)

(Duerr, 1997)

(*Hansard*, 2004, *Wiltshire Times*, 2014; British Association for Shooting and Conservation, 2005; Averty, 2017)

Citations to replace

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