THE ANALYSIS OF ORGANIC BALLISTIC MATERIALS

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A thesis submitted in partial fulfilment of the requirements of Nottingham Trent University for the of Doctor of Philosophy

July 2011

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Declaration of Originality

This is to certify that I am responsible for the work submitted in this thesis. The original work is my own, except as specified in the acknowledgements and in the references. Neither the thesis nor the original work contained therein has been previously submitted to any institution for a degree.

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Acknowledgements

My thanks go to all those who have advised, guided and supported me throughout the length of this project. Special thanks go to my partner Danielle and my parents, for if it were not for them this work would never have reached completion.

In dedication to Lucy Hudson who passed away during the period of this project.

Abstract

Both gas chromatography/mass chromatography (GC/MS) and solid phase microextraction (SPME) methodologies have been developed for the extraction and analysis of compounds encountered in relation to unburned propellant powders from firearm ammunitions. These methods allowed the detection of 27 compounds that may be present in organic gunshot residues (OGSR)

The developed methodologies were applied to the analysis of unburned propellant and OGSR from spent ammunition cartridges and fabrics subjected to firearm discharges. Throughout the study a total of 16 ammunition types where investigated.

Work carried out on the suitability of various SPME fibre types showed that 65µm PDMS/DVB was the most appropriate type for extracting the compounds of interest.

Extractions carried out on unburned propellant powders showed that all of the ammunitions analysed produced different chromatographic results. All of the ammunitions in the analysed population could be differentiated from one another; it was determined to be highly unlikely that false matches could occur.

Extractions from spend cartridges showed that some of the compounds originating from the precursor propellants remained, with many compounds being lost during discharge. In some examples, however, all compounds in the unburned propellant were extracted from spent cartridges cases. The amount of variability of compound abundances between spent cases of the same ammunition types was shown to be much greater than the variability between unburned propellant samples. It was, therefore, concluded that firearms discharges are likely to be non-reproducible events, with varying amounts of non-combusted materials remaining in each case. These results were considered to have implications when carrying out “time since discharge” back calculations on cases.

The collection and extraction of shot fabric samples were carried out using Nylon evidence bags, traditionally used for the collection of fire/arson materials. Results from this work showed that for some ammunitions it was possible to link extracts from fabrics to spent cartridge cases and unburned propellant powders, by matching compounds present in the originator propellant to residue extracts. For other ammunition types it was shown to be possible to link fabric extracts to spent cases directly, by matching the compounds present in both.

Abbreviations

2-NDPA	-	2-Nitrodiphenylamine
2,3 DNT	-	2,3 Dinitrotoluene
2,4 DNT	-	2,4 Dinitrotoluene
2,5 DNT	-	2,5 Dinitrotoluene
2,6 DNT	-	2,6 Dinitrotoluene
3NT	-	3-Nitrotoluene
3,4 DNT	-	3,4 Dinitrotoluene
4-NDPA	-	4-Nitrodiphenylamine
AAS	-	Atomic absorption spectroscopy
AES	-	Atomic emissions spectroscopy
AKII	-	Akardite II
Ag	-	Silver
Al	-	Aluminium
AM	-	Analyte molecule
Ammo	-	Ammunition
Au	-	Gold
ASTM	-	American Society for the Testing of Materials
Ba	-	Barium
^{o}C	-	Degrees celsius
^{o}C/min	-	Degrees celsius per minute
ca.	-	Approximately
Ca	-	Calcium
CAMPH	-	Camphor
CAR	-	Carboxen
CE	-	Capillary electrophoresis
Cl	-	Chlorine
Cu	-	Copper
Co	-	Cobalt
CW	-	Carbowax®
CZE	-	Capillary zone electrophoresis
CDR	-	Cartridge discharge residue
DBP	-	Dibutylphthalate
DEP	-	Diethylphthalate
DIBP	-	Diisobytlphthalate

DC - Direct current

DNG - Dinitroglycol

DNT - Dinitrotoluene

DPA - Diphenylamine

DVB - Divinylbenzene

EC - Ethyl centralite

ECD - Electron capture detector

EDX - Energy dispersive X-ray

EI - Electron impact ionisation

e.g. - *exemplia gratia* (for sake of an example)

et al. - *et alii* (and others)

FDR - Firearm discharge residue

Fe - Iron

FED - Federal

GC - Gas chromatography

GC/MS - Gas chromatography with mass spectrometric detection

GC-TEA - Gas chromatography- thermal energy analysis

GFAAS - Graphite furnace atomic absorption spectroscopy

GSR - Gunshot residue

HPLC - High performance liquid chromatography

HPLC-API-MS - High performance liquid chromatography-atomic pressure Ionisation- mass spectrometry

HPLC-TSI-MS - High performance liquid chromatography-thermospray Ionization - mass spectrometry

HPLC-PMDE-electrode High performance liquid chromatography-pendent mercury drop

ICP - Inductively coupled plasma

ICP-AES - Inductively coupled plasma- Atomic emissions spectroscopy

ICP-MS - Inductively coupled plasma – mass spectrometry

IMS - Ion mobility spectroscopy

K - Potassium

L&B - Lellier and Bellot

LC - Liquid chromatography

LC-ESI-MS - Liquid chromatography-elect spray ionisation- mass spectrometry

LOD - Limits of detection

Ni - Nickel
MAG - Magtech
MC - Methyl centralite
MECE - Miceller electrokinetic capillary electrophoresis
MC-ICP-MS - Multiple collector inductively coupled plasma – mass spectrometry
MEKS - Miceller electrokinetic capillary chromatography
MRM - Multiple reaction modelling
MS - Mass spectrometry
N-NDPA - N-nitrosodiphenylamine
Na - Sodium
NAA - Neutron activation analysis
NAPH - Naphthalene
NC - Nitrocellulose
NG - Nitroglycerin
OGSR - Organic gunshot residue
Pb - Lead
p/s ratio - ratio of propellant:total amount of stabiliser
UV - Ultra violet detector
µg - Micrograms
µg mL^{-1} - Micrograms per millilitre
µL - Microlitres
µm - Micrometres
Mg - Magnesium
mg - Milligrams
mins - Minutes
P - Phosphorus
PA - Polyacrylate
PDMS - Polydimethylsiloxane
PETN - Pentaerythritol tetranitrate
PRIVI - Privi Partizan
RDA - Regularized discriminant analysis
RDX - cyclotrimethylenetrinitramine
REM - Remington
RF - Radio frequency
rpm - Revolutions per minute

S	-	Sulfur
SEM	-	Scanning electron microscope
SEM-EDX	-	Scanning electron microscopy-energy dispersive x-ray
SF-HR-ICP-MS	-	Sector field-high resolution- inductively coupled plasma – mass spectrometry
Si	-	Silicon
SIM	-	Single/selective Ion Monitoring
Sb	-	Antimony
SPE	-	Solid phase extraction
SPME	-	Solid phase Microextraction
Sn	-	Tin
Sr	-	Strontium
Temp.	-	Temperature
Ti	-	Titanium
TOF-SIMS	-	Time of flight – secondary ion mass spectrometry
TNT	-	2,4,6 Trinitrotoluene
UK	-	United Kingdom
VP	-	Variable pressure
WIN	-	Winchester
WDX	-	Wavelength dispersion X-ray dispersion
Zn	-	Zinc

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1. Introduction

1.1 Aims

As is shown in the following review of literature (section 2) there is a need for further work to be carried out in the area of OGSR analysis (defined on page 5). Currently inorganic residue materials are analysed much more frequently than organic compounds, although the latter might provide additional useful information within a forensic investigation context (Dalby *et al*. 2010).

The primary aim of this project was to develop a GC/MS methodology for the analysis of organic compounds present in the propellant powders of firearm ammunitions. This methodology was then to be applied to the analysis of unburned propellant powders in order to determine the levels of variability between propellants from different ammunition types. The significance of finding variability would be that powders could be linked to ammunitions by their chemical compositions.

A further aim, following the investigation of unburned propellant powders was to analyse materials produced by firearm discharges. This was carried out in order to assess the potential for linking these materials to the originating ammunition. Spent cartridge cases and shot fabric samples were assessed.

2. Literature review

2.1 Introduction

Between 2006/2007 there were 9,650 reported incidents involving firearms in England and Wales (excluding air rifles), 566 of which involved serious or fatal injuries. Firearms were discharged in 40% of these reported incidents. Despite a drop in the number of incidents involving firearms in the last three years, the general trend appears to show a rise in their numbers (Figure 1). A variety of firearm types were used in reported incidents and these are summarised in Figure 2 (Povey *et al*. 2008). Despite firearm offences accounting for only 0.2% of the total crime volume in England and Wales in 2006/07 (Povey *et al*. 2008), the gravity of their nature means that they must not be overlooked and it must be seen as paramount that forensic evidence involved in such cases is as reliable and accurate as practicable.

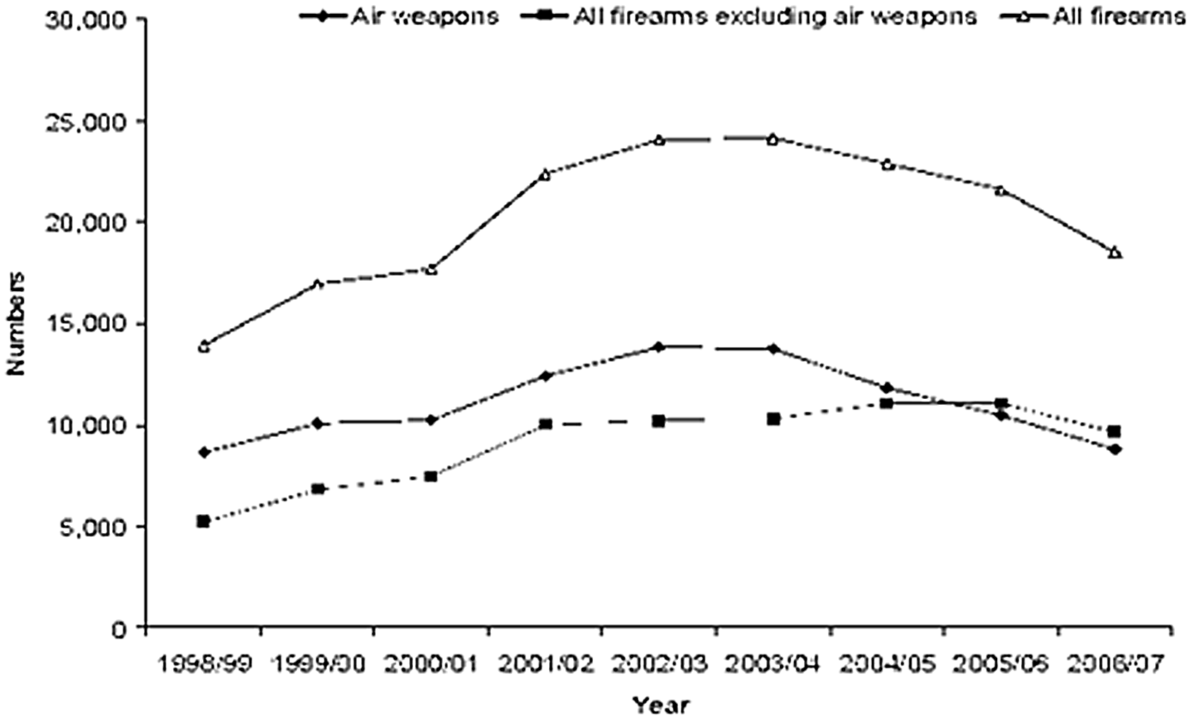


Figure 1: Government statistics for the number of reported incidences involving firearms in England and Wales 2006/2007 (Povey et al. 2008).

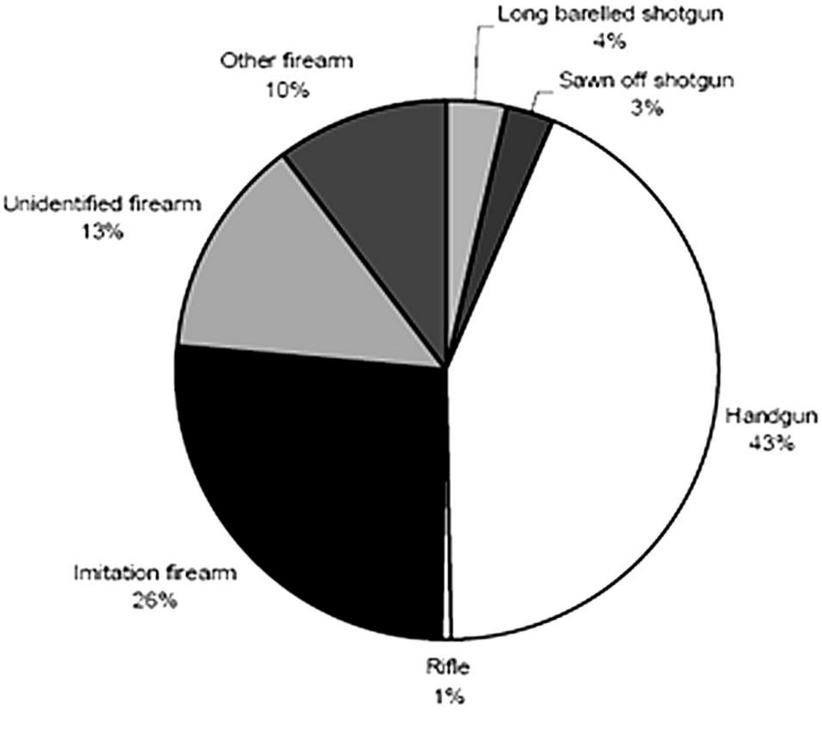


Figure 2: Government statistics of the types of firearms used in reported incidents in England and wales 2006/2007 (Povey et al. 2008).

Mejia (2005) raised a number of questions about the methods currently used for the analysis of gunshot residues (GSR); which methods of analysis are most effective? How can false negative or positive results be best minimised? Is it actually possible to state with certainty that a person has discharged a firearm?

Ronald Singer, former president of the American Academy of Forensic Sciences thinks not, stating "None of what we do can establish if anybody discharged a firearm." (Mejia, 2005).

Aleksandar (2003) comments “In my ten years of very intense practice… I still haven’t met the method on the basis of which with absolute reliability, as a court expert working on identification activities of eventual shooters, I could confirm that the suspect 100% fired from the firearm on that occasion.”

High profile cases in the UK such as the Gill Dando murder trial (o’Neill, 2007) have brought the evidential value of GSR analysis further into question. Therefore, a review of techniques used for the analysis of GSR and their effectiveness is valuable, relevant and timely. This review covers the formation and distribution of GSR, the collection, preparation and analysis of GSR samples and discusses factors that may affect the interpretation of any given GSR sample.

2.2 What is gunshot residue?

GSR, which may also be known as cartridge discharge residue (CDR) or firearms discharge residue (FDR) are particles produced during the discharge of a firearm. When a cartridge/round is fired in a firearm, combustion products from both the primer and the propellant will be released at the same time (Warlow, 1996).

Gunshot residues are composed of unburned and partially burnt propellant powder, particles from the ammunition primer, smoke, grease, lubricants and metals from the cartridge as well as the weapon itself (Morales and Vazquez (2004), Romolo and Margot (2001)). Organic compounds mainly originate from propellant and firearm lubricants, taking the form of unburned and partially burned gunpowder particles, some products of their transformation and hydrocarbons. Inorganic residues such as nitrates, nitrites and metallic particles originate from the primer and propellant as well as the cartridge case, the projectile jacket or its core and from the weapon barrel itself (Brozek-Mucha, 2007). These combustion materials from the primer, propellant and other sources escape from weapon openings and vaporized materials solidify into particulates. These particulates are usually of sizes ranging from 0.5 – 10µm in diameter (Warlow, 1996) although sizes of up to 100µm have been reported (Schwoeble and Exline, 2000).

2.2.1 Organic compounds present in GSR

Organic compounds are predominantly found in a cartridge’s propellant powder, and the primer mixture, but can also originate from every part of the ammunition used (Meng and Caddy, 1997). Table 1 contains a list of organic compounds that may contribute to the composition of organic GSR (OGSR).

The original propellant type used in firearms was black powder. The first recorded European recipe for black powder was produced by Roger Bacon in 1250 (Warlow, 1996). Black powder is typically composed of 75% potassium nitrate (saltpetre), 15% sulphur, and 10% charcoal (fuel) (Meng and Caddy (1997), Wallace (1990)). Today black powder is hardly ever used as a firearm propellant; however, it may still be encountered, usually linked to persons involved in military re-enactments.

Smokeless powders have long since replaced black powder as the main propellant used in firearms. Single base powders are based around nitrocellulose as an explosive, while double base powders contain both nitrocellulose (NC) and nitroglycerine (NG), with NG increasing the energy potential of a powder. In triple base powders a portion of NC and NG is replaced by nitroguanidine (Meng and Caddy, 1997).

All smokeless powders, in addition to explosive ingredients, contain a number of additives, including; stabilizers, plasticizers, flash inhibitors, coolants, moderants, surface lubricants, and anti-wear additives. A particular propellant powder will contain one or more of these additives depending on its intended use (Meng and Caddy (1997), Gunaratnam and Himberg (1994), Maloney and Thornton (1982), Laza *et al*. (2007), Davis (1944), Espinoza and Thornton (1994), Druet and Asselin (1988) and Curtis (1990)).

Table 1: Organic compounds that may contribute to GSR (Warlow (1996), Meng and Caddy (1997), Oommen and Pierce (2006), Gunaratnam and Himberg (1994), Harrison and Gilroy (1959), Maloney and Thornton (1982), Wolten et al. (1977), Laza et al. (2007), Cascio et al. (2004), MacCrehan et al. (1998), Wallace (1990), Northrop (2001) (i), Northrop (2001) (ii))

Compound	**Source of compound**
2,4,6-Trinitrotoluene (TNT)	Propellant powder/primer mix
2,4-Dinitrodiphenylamine (2,4-DPA)	Propellant powder
2,3-Dinitrotoluene (2,3-DNT)	Propellant powder
2,4-Dinitrotoluene (2,4-DNT)	Propellant powder
2,6-Dinitrotoluene (2,6-DNT)	Propellant powder
2-Nitrodiphenylamine (2-NDPA)	Propellant powder
4-Nitrodiphenylamine (4-NDPA)	Propellant powder
Akaridte II (AKII)	Propellant powder
Butyl phthalate	Propellant powder
Butylcentralite (N,N-Dibutylcarbanilide)	Propellant powder
Camphor	Propellant powder
Carbanilide	Propellant powder
Carbazole	Propellant powder
Charcoal (major carbon)	Black powder
Cresol	Propellant powder
Dextrin	Primer mix
Diazodinitrophenol	Primer mix
Diazonitrophenol	Primer mix
Dibutyl phthalate	Propellant powder
Diethyl phthalate	Propellant powder
Dimethyl phthalate	Propellant powder
Dimethylsebacate	Propellant powder
Dinitrocresol	Propellant powder
Diphenylamine (DPA)	Propellant powder
Ethyl centralite (N,N-Diethylcarbanilide)	Propellant powder
Ethyl phthalate	Propellant powder
Ethylene glycol dinitrate	Propellant powder
Gum Arabic	Primer mix
Gum tragacanth	Primer mix
Karaya gum	Primer mix
Methyl cellulose	Propellant powder
Methyl centralite (N,N-Dimethylcarbanilide)	Propellant powder
Methyl phthalate	Propellant powder
Nitrocellulose (NC)	Propellant powder/primer mix
Nitroglycerine (NG)	Propellant powder/primer mix
Nitroguanidine	Propellant powder
Nitrotoluene	Propellant powder
N-nitrosodiphenylamine (N-NDPA)	Propellant powder
Pentaerythritol tetranitrate (PETN)	Propellant powder/primer mix
Picric acid	Propellant powder
RDX (Cyclonite)	Propellant powder
Resorcinol	Propellant powder
Rubber cement	Primer mix
Sodium Alginate	Primer mix
Starch	Propellant powder
Tetracene	Propellant powder/primer mix
Tetryl	Propellant powder/primer mix
Triacetin	Propellant powder

This list is not exhaustive. Some of the substances present may now be obsolete from production but are included as obsolete ammunition may still be in circulation.

2.2.2 Inorganic compounds present in GSR

Inorganic components predominantly derive from primer mixtures. The particular type of primer used in a cartridge will generate materials of interest due to variations in formulation compositions from manufacturer to manufacturer. The history of primer formulation development can be found elsewhere (Warlow, 1996). The first example of a 'modern' primer formulation was produced in 1921, containing lead styphnate, barium nitrate and antimony trisulphate (Warlow, 1996).

The most recent major development in primer manufacture has been the introduction of numerous types of lead (Pb) and heavy metal free primers. These primer types have been produced in response to increased concerns over health problems relating to airborne pollution and exposure to high levels of heavy metals, such as those found in 'modern' primer mixtures (Martiny *et al*., 2008). There is currently a large number of manufacturers producing completely lead free ammunition (Torre and Mattutino, 2003), while others produce cartridges with lead free primers but not lead free bullets. The compounds used in lead free primers differ from manufacturer to manufacturer (Martiny *et al*., 2008).

Further inorganic constituents may originate from the cartridge case, primer cup, bullet (including jacket) and the barrel of the firearm (Wolten *et al*., 1977). Table 2 contains a list of inorganic compounds that may contribute to the composition of inorganic GSR.

Table 2: Inorganic compounds that may contribute to GSR (Warlow (1996), Oommen and Pierce (2006), Harrison and Gilroy (1959), Wolten et al. (1977), Wallace (1990), Beijer (1994), Harris (1995), Pillay (1974))

Compound	**Source of compound**
Aluminium	Primer/case
Aluminium sulfide	Primer mix
Antimony	Case / bullet
Antimony sulfide	Primer mix
Antimony sulfite	Primer mix
Antimony trisulphide	Primer mix
Arsenic	Case
Barium Nitrate	Primer mix/propellant powder
Barium Peroxide	Primer mix
Bismuth	Case
Boron	Primer mix
Brass	Case
Bronze	Bullet
Calcium carbonate	Propellant powder
Calcium silicide	Primer mix
Chromium	Bullet
Copper	Bullet jacket/primer cup/case
Copper thiocyanate	Primer mix
Cupro-nickel	Bullet jacket
Gold	Primer mix
Ground glass	Primer mix
Iron	Rust inside barrel, bullet
Lead	Bullet
Lead azide	Primer mix
Lead dioxide	Primer mix
Lead nitrate	Primer mix
Lead peroxide	Primer mix
Lead stifnate (styphnate)	Primer mix
Lead thiocyanate	Primer mix
Magnesium	Primer mix
Mercury	Primer mix
Mercury fulminate	Primer mix
Nickel	Case
Nitrate	Black powder
Phosphorus	Case
Potassium chlorate	Primer mix
Potassium nitrate	Propellant powder/primer mix
Prussian blue	Primer mix
Red brass	Bullet jacket
Silicon	Primer mix
Sodium nitrate	Primer mix
Sodium sulphate	Propellant powder
Steel	Bullet core/case
Strontium nitrate	Primer mix
Sulphur	Primer mix/ black powder
Tin	Primer mix
Titanium	Primer mix/ Lead free primer mix
Tungsten	Bullet
Yellow brass	Bullet jacket/case
Zinc	Primer cup
Zinc peroxide	Primer mix
Zirconium	Primer mix

This list is not exhaustive. Some of the substances present may now be obsolete from production but are included as obsolete ammunition may still be in circulation

2.3 The formation of GSR particles

Inorganic GSR particles form during the discharge of a firearm. As the firing pin strikes the primer cap the primer mixture is ignited, creating an environment of rapid temperature and pressure increases within the cartridge. This increase in temperature melts the primer mixture and within a few milliseconds the vaporisation points of lead (Pb), barium (Ba) and antimony (Sb) are exceeded (Pb 1620ºC, Ba 1140ºC, Sb 1380ºC). The effects of supersaturation cause vapour from particles to condense back onto the liquefied primer surface as droplets. There has been evidence to suggest that inorganic GSR particles of materials originating solely from the primer (primer GSR) are formed even before the propellant is ignited (Basu, 1982).

As the primer mix ignites the propellant powder a second rapid increase in pressure and temperature occurs and the bullet is expelled from the firearm barrel. During this process the particles involved are subjected to extreme temperature and pressure followed by rapid cooling. Particles form as liquid droplets which subsequently solidify (Basu, 1982).

Wolten and Nesbitt (1980) suggested that GSR particles formed from inorganic substances can be divided into two categories; "primer particles" and "bullet particles". Primer particles were shown to contain oxides, sulphides and salts in which the anion contained oxygen (oxysalts), such as barium meta-antimonate and basic lead sulphate (lanarkite). It was reported that primer ingredients are initially compounds and, therefore, cannot be expected to be reduced to elements in the oxidising environment of the primer ignition. Elemental particles should, therefore, originate from bullet materials (Wolten and Nesbitt, 1980).

Basu (1982) further divided inorganic GSR particles originating from the primer (with a lead styphnate, barium nitrate and antimony trisulphate mixture) into three categories (Table 3), each formed differently depending on how they interact during firearm discharge. Categories II and III are larger sized particles which are thought to travel slower through the propellant ignition front than category I particles and are, therefore, subjected to a second, greater increase in pressure and temperature. This causes these particles to pass through various metastable states as a result of boiling, fragmenting or etching until a stable shape is again reached (Basu, 1982).

Table 3: *Inorganic primer residue particle types proposed by Basu (1982)*

Particle Category	Mechanisms of formation
I	Most commonly found type on the hands of a person who has previously discharged a firearm. Small spheroid particles that may have small nodules/ bulges upon their surfaces. Nodules are usually of single elemental composition which may originate from the primer or bullet and may be non-specific (not Pb, Ba or Sb). Believed nodules are captured by the main particle mass when a degree of cooling has occurred and the particle is solidifying. The main body of these particles contain a uniform and concurrent mixture of Pb, Ba and Sb. Sizes ranging from 2-10µm diameter. Generally solid with no space in the core. Particles likely homogenous due to thermal agitation and Brownian motion. Particles are formed prior to the ignition of the propellant mix and due to their smaller size travel through the propellant ignition detonation front much faster than larger particles leaving unaffected. Represented 68% of the total GSR on a firer's hands.
II	25% of all particles found. Inhomogeneous and have a discontinuous distribution of Pb, Ba and Sb. Heterogeneity produced by a final irregular distribution of lead, barium and antimony which may reflect the way in which the particle grows. Particles often have air central cavities which suggest they have been subjected to some form of disturbance during formation, which may explain elemental distribution.
III	The least commonly found. They consist of a Pb crust, which surround a homogenous core of Ba and Sb. It is believed that the Ba and Sb core is in the process of solidifying when it captures Pb vapours from burnt residues and the etched bullet (caused by barrel rifling as the bullet travels down the barrel). The Pb coating may also take on a peeled orange appearance in certain conditions.

Burnett (1989) suggested an alternative reason for the formation of irregular inorganic GSR particles (Basu's category II type), reporting the observation of particles still being molten upon impact onto target materials. Particles were observed to be splattered or flattened on target impact causing sometimes drastic modification of spherical form. This occurred especially at muzzle to target distances between 20 and 30cm (although observed between 10 and 70cm). Larger particles (> 2µm diameter) which came into contact with a target within 40cm of the muzzle were often molten on impact (9mm semi automatic pistol). At distances greater than 50cm it was shown that particles may shatter or adhere to the target surface (Burnett, 1989).

OGSRs are not formed in a manner like inorganic materials but instead are compounds mainly originating from propellant and firearm lubricants, taking the form of unburned and partially burned gunpowder particles, some products of their transformation and hydrocarbons. (Brozek-Mucha, 2007).

2.4 GSR collection techniques

The areas from which GSR may be collected are wide ranging. Skin, vehicles (seats and seat backs, doors, windows, dashboards, headliners, interiors and exteriors), the surroundings of an incident, doors, windows, body parts, clothing and any surfaces in the immediate vicinity of a firearm discharge may all be sample targets(Schwoeble and Exline, 2000). There are numerous techniques that can be used for GSR sample collection and selecting the most appropriate one is important in ensuring maximum collection efficiency.

2.4.1 Tape lifts

Tape lifts are the most commonly used procedure for the collection of inorganic residues from skin surfaces (Romolo and Margot, 2001). It has also been applied to sample collection from hair (Zeichner and Levin, 1993) and other mediums (Shaffer and Yi (1999), Wrobel *et al*. (1998)).

Wrobel (1998) compared the efficiency of a number of different adhesives for the collection of inorganic GSR particles. Fifteen assorted adhesives were investigated, with a variety of criteria being used to assess the suitability of each adhesive. Eight double sided tapes, three adhesive tabs, two adhesive liquids, a glue stick and a carbon conductive cement were all tested. Out of all the adhesives tested Sellotape 404 double sided tape was the medium chosen as the best performer.

Shaffer and Yi (1999) compared tape/sticky lifts to swabs (isopropanol as solvent) for the collection of inorganic GSR for scanning electron microscope (SEM) analysis. Results showed that tape lifting was much more effective than swabbing. The average lifting efficiency for tape was 389 particles in total, with 126 being classified as “unique” (defined in section 2.6.1, page 34). The average for swabbing was 60 particles in total with only 3 particles classified as “unique”.

DeGaetano (1992) compared three techniques developed for the sampling and analysis of inorganic GSR by SEM with energy dispersive X-ray detection (EDX); tape lift (3M brand adhesive), glue lift (Basu and Ferriss, 1980), and a centrifugal concentration technique (Ward, 1982). The number of particles of inorganic GSR found on the collection surface in

1 hour was used as an indicator of the lift efficiency of each medium. Of the three techniques tape lifts were reported to be the most effective, being cheap, having good collection efficiency and performing well in the SEM. A shelf life of at least 6 weeks was reported and samples were shown to be able to withstand being in the high temperatures that may be expected in a crime scene vehicle, for at least 12 hours without being effected. However, a number of problems were reported with tape lifts including the large surface area to be searched (dependent on tape size), the requirement to carbon coat samples prior to analysis (something which can now be avoided by using carbon coated adhesives) and the collection of debris that may mask particles. The sample concentration technique tested, which theoretically should reduce the search area (by repeated centrifugal concentration thorough high density liquid), was shown to produce highly variable results and be less efficient than tape lifting.

Zeichner *et al*. (1989) also found concentration techniques problematic, concluding that the build up of debris on filter surfaces was to such a degree that direct observation of a tape or glue lift was preferable.

Wallace and Keely (1979) reported a successful concentration technique. Samples were suspended in non polar solvent as particles and subjected to a two stage filtration process firstly removing extraneous materials and secondly retaining small particles including any inorganic GSR. Particles from sizes 0.5 to 2 µm were captured on the second filter. Recovery levels as high as 90% for Pb and 91% for barium were shown. However, as GSR particles maybe as large as 100µm in diameter (Schwoeble and Exline, 2000), potentially helpful particles may be lost using this method. This must be seen as a drawback to this particular concentration technique.

Zeichner and Eldar (2004) reported a technique for extracting OGSR from tape stubs following SEM-EDX analysis. Extraction with an aqueous (0.1% w/v sodium azide)/ethanol mix (80/20) at 80ºC for 15 minutes, followed by further extraction with methylene chloride and concentration by evaporation was shown to be the optimal procedure for gas chromatography with thermal energy analysis (GC-TEA) and ion mobility spectrometry (IMS). However, tests on single base powder showed variable results, with recovery levels for NG and dinitrotoluene (DNT) ranging from 30 to 90%.

Plasma ashing of tape samples has been reported to be successful for reducing organic material (skin cells etc) that may be present on the surface of a tape lift, making GSR particles easier to analyse (Sild and Pausak, 1979). However, Varetto (1990) argued that a combination of contamination by the electron beam of the SEM and oxygen plasma ashing was required to destroy the cells of the skin epidermis, leaving only thin filaments. Plasma ashing alone was reported to be ineffective.

Zeichner (2001) reported that in fact skin debris posed little threat to impeding the analysis of inorganic GSR particles using SEM. Particles completely covered in skin cells that could not be detected by the secondary electron image, were detected without problem by the backscatter electron image and EDX detector. Although morphological information could not be gained, Zeichner argued that the ASTM (American Society for the Testing of Materials) considered morphology a secondary criterion for GSR identification. This must though be seen as problematic, as particles from ulterior environmental sources have been shown to have elemental compositions that may be easily mistaken for GSR (Twibell *et al*. (1982), Thompson *et al*. (1999), Lloyd and King (1990)), in such situations it is the morphological information that is of key importance in correctly determine a particles origin.

Collecting samples from clothing using tape lifts may also create problems with fibres and other debris. This detritus is likely to be non conductive and may hold charge during SEM analysis. Carbon/gold coating of the sample may, therefore, be required which involves extra time and expense (Mastruko, 2003).

The collection of inorganic GSR particles from hair has been reported as important due to the longevity of particle retention when compared to hands (Metropolitan Police Forensic Science Laboratory, 1980). Tape lifts have been reported to be unsuitable for GSR collection from hair (Metropolitan Police Forensic Science Laboratory, 1980). However, Zeichner and Levin (1993) reported that tape lifting was an acceptable method for use on hair (both curly and straight) and no significant difference between tape stubs and more complicated hair comb swab and solvent damp cloth were observed. Maximum collection efficiency was reported at 200-300 dabs (60-120 dabs for hands).

2.4.2 Vacuum lifts

Vacuuming is used primarily for the collection of GSR from clothing. Speers *et al*. (1994) reported the successful application of a vacuum collection technique for both organic and inorganic residues from items of clothing. Residues were collected from clothes following only one firearm discharge. More organic than inorganic residues were seen. Solid phase extraction was used to clean up and concentrate samples in order to maximise the high performance liquid chromatography-pendent mercury drop electrode (HPLC-PMDE) and gas chromatography-mass spectrometry (GC-MS) systems being used. Recovery levels from the vacuum filters used were in the region of 57-78% depending on the compound of interest. Debris and garment fibres present on the filter were reported as a possible cause of reduced extraction efficiency.

Zeichner *et al*. (2003) investigated the vacuum collection of OGSR with two different types of vacuum filter, fibre glass and Teflon. Four solvents (acetone, methylene chloride, ethyl acetate and chloroform) were also tested for their ability to extract residue collected on the filters. No significant differences between the solvents in their extraction efficiency of the propellant components were found. Collection levels were highly variable, with between 30-100% yields for the same solvent. Methylene chloride was chosen due to the advantage of not dissolving/extracting NC (which is not volatile enough to be analysed by GC-MS (Zitrin, 1986)). Teflon filters were shown to have greater collection efficiency. The use of tape lifts on clothing for the collection of inorganic GSR, followed by vacuum lifting to collect organic residues was shown to be an effective technique (Zeichner *et al.*, 2003).

Andrasko and Pettersson (1991) reported the use of a double filtration vacuum system. A pre-filter with a pore size of 20µm allowed the separation of residue particles from debris and fibres. Residues were collected on the second filter (0.8µm), and concentrated onto a tape stub for SEM analysis. As with previously discussed concentration methods the range of filters used in this study could potentially lead to the loss of inorganic GSR particles larger than 20µm.

Mastruko (2003) reported that vacuum lifts from clothing collect particles from the surface of the material but also the depth of the clothing. This was determined to be problematic as it increased the difficultly of interpreting sample analysis, as particles from other shoots (for example a hunter or sports shooter) may be present. In this respect tape lifting is advantageous as it only lifts particles settled on the surface of a material. However, Andrasko and Petterson (1991) reported that tape lifting was not very suitable for the collection of GSR from clothing as the loss of tape stickiness restricted the area that could be sampled and also fibres and other unwanted particles were transferred to the tape making analysis using SEM more difficult.

2.4.3 Swabbing

Twibell *et al*. (1982) assessed the efficiency of 8 solvents for the collection of NG from hands followed by GC analysis. Solvent efficiency was determined based on the amount of NG removed from the hands, the amount of interfering material removed from the hands and the stability of NG within the solvent. Aqueous solvents showed the best recoveries, when thin layer chromatography was used for partial purification. However, NG was degraded by micro organisms that grew in the solutions. Ethanol was determined to have performed best, with the most complete, stable and consistent recovery.

Organic solvents are commonly used for the collection of explosive residues as such residues are readily dissolved in them. However, this causes the problem that many other compounds are also dissolved causing interference issues. Thompson and Miller (1999) reported that this matrix of interfering compounds may be removed by using water as an extraction agent and adding an additional step, solid phase extraction (SPE). Water extraction followed by SPE was reported to be an effective process for treating organic explosive residues on cotton swabs for subsequent analysis by liquid chromatography (LC) or GC-MS and fast GC-thermal energy analysis (TEA). When compared to a solvent extraction (acetone) and direct injection method, the water/SPE was shown to be just as effective at recovering organic explosives. Water/SPE also gave much greater selectivity in most cases.

Lloyd and King (1990) reported a method by which swabs used to collect explosives and firearm residues were extracted and cleaned up by SPE in the containers issued for the return of samples to the laboratory. Recovery over the range 63-75% was reported. Inorganic GSR particulates also remained on the swab after organic compounds had been extracted and could be subsequently recovered for characterisation by SEM by sonication in an organic solvent followed by membrane filtration of the extract. This method was reported to reduce the possible problems of sample loss due to transfer and minimize the chances of cross contamination.

Reardon and MacCrehan (2001) compared supercritical fluid extraction (SFE) and ultrasonic solvent extractions (USE) in order to determine whether a reliable quantitative extraction technique for smokeless powders could be achieved. SFE was shown to be unsuitable for quantitative extraction of double base powders, although it has been shown as successful with regard to single base powders. Even after optimisation of the extraction process, yields of below 90% with smokeless powder standards were recorded. NG was also shown to readily react with stabilisers under the conditions of SFE. 2-butanol:methanol (1:3) was reported as the most efficient solvent for USE. The most desirable extraction time was determined to be 15 minutes (handgun powders). For ball type rifle powders, 75 minute extractions were recommended. No significant differences between temperature of 0 and 50ºC were reported and so 25ºC was selected.

2.4.4 Glue lifts

Glue lifts have been applied to the collection of GSR from hands (Basu and Ferriss (1980), Basu *et al*. (1997)). Basu and Ferriss (1980) reported that glue lifting was a very usable technique for the collection of GSR from the surface of hands. When compared to tape lifts, glue lifts required less dabs on the skin surface and collected less debris due to the glue being less tacky than tape lifts. This increased the speed of SEM analysis. The glue also contained no elements of high atomic numbers that could potentially interfere with the GSR particle analysis with a SEM.

In contradiction, DeGaetano *et al*. (1992) reported glue lifts to be an ineffective lifting medium. However, a different type of glue lifting planchet was used to that of Basu and Ferriss (1980) which could potentially have led to the different results.

2.4.5 Nasal collection

Schwartz *et al*. (1995) reported the development of a technique for the collection of airborne inorganic GSR particles from human nasal mucus. Samples were collected on a 5x5 piece of substrate by normal nose blowing. SEM-EDX was used for sample analysis. Inorganic GSR particles were recorded at times greater than 48-hours post firing. This collection method must be seen as promising in terms of determining whether a person has been in the vicinity of a firearm discharge. However, it may not be of value in trying to determine whether a person actually discharged a firearm, as airborne GSR particles have been shown to take relatively long periods of time to settle (Fojtasek and Kmjec, 2005).

2.4.6 Collection of GSR from hair

Smoke plumes exiting the breach of a weapon during discharge frequently extend posterior to the face and head (MacCrehan and Layman, 2003), with potentially useful GSR being deposited in the hair. A number of methods for the collection of GSR from hair have been reported including a swab and comb method and tape lifting (Zeichner and Levin (1993), Tugcu *et al*. (2006)).

MacCrehan *et al*. (2003) used a fine toothed comb to collect residue samples from head hair. Nearly intact grains of incompletely burned propellant powder residues approaching mm diameters were recovered from handgun firings. Particles smaller than the gaps in the teeth of the comb were also recovered with this method. Difficulties with curly hair were reported due to the fine teeth of the comb. 20 positive results from 23 tests were reported for human hair wig tests. Tests on shooters show NG positive results for all three different shooters tested. NG and ethyl centralite (EC) were found on the collections from rifles and revolvers. When compounds from unfired powders, exemplar residues (taken from the inside of a cartridge) and residues collected from the hair were compared it was reported that there was an amount of variation between the unburned powder and hair combed residue but that the exemplar and the combed residue were in good agreement. It was concluded that although EC was detected in some of the residue samples there was not an effective enough extraction for it to be reliably detected using capillary electrophoresis (CE). It was also concluded that a more effective protocol for hair residue collection and analysis would be required to enable reliable detection of stabilisers such as EC that are present in OGSR.

2.5 GSR analysis

2.5.1 Colour/spot testing

Colour/spot tests are most commonly used for the estimation of firing distances (Schwoeble and Exline, 2000). However, they can also be used as a rapid test for the presence of GSR and the determination of bullet holes/entrance wounds (Tugcu *et al.*, 2006). Such tests have been in use since 1933, when the dermal nitrate or paraffin test was introduced (Romolo and Margot (2001), Meng and Caddy, (1997)). Table 4 contains a list of some of the most common colour/spot tests used for GSR detection.

The main problem that arises from using spot/colour tests is their presumptive nature. However, despite this they are still used in case work in some countries (e.g. Brazil) for determining the presence of GSR (Martiny *et al.*, 2008).

Table 4: Colour/spot tests that have been applied to GSR (Romolo and Margot (2001), Schwoeble Exline (2000), Meng and Caddy, (1997), Harrison and Gilroy (1959), Beijer (1994), Tugcu et al. (2006), Lloyd (1987), Hawley (1981), Walker (1940), Steinburg (1984), Tschirhart et al. (1991), Dahl (1952), Bartsch (1996)).

Test Name	**Compounds Detected**	**Additional Notes**
Dermal nitrate/paraffin test	Nitro groups	False positive results may be found by reaction with compounds present in tobacco, leguminous plants, fertilisers, pharmaceuticals, fingernail polish urine and as a result of striking a match, tires and outer garments, solid rocket fuels, pesticides and dyes, pharmaceuticals, veterinary medicines and the storage preservation of apples. Chlorates, dichromates, iodates, bromates, permanganates and higher metal oxides may all cause reactions that may lead to false positives. Aleksandar tested 250 persons that had not handled firearms using the dermal-nitrate test. 117 of them produced positive results (46.8%).
Walker test/Griess test	Nitrites	Tests specific for nitrites but not for GSR
Modified Griess test	Nitrites	Test specific for nitrites but not for GSR
Harrison and Gillroy test	Pb, Ba and Sb.	Reported as much more successful than the dermal nitrate test as it produced much fewer numbers false positive results Test specific for Pb, Ba and Sb but not GSR
Alizarin red S (ARS)	Ca and other metal ions, including Pb and Ba present in primer residues	None specific and will stain many heavy metal ions including Fe, Ba, Sr, Be, Cd, La, Pb and U
Sodium Rhodizonate Test	Pb	Test specific for Pb but not GSR
Marshal and Tewari test	Nitrites	Test specific for nitrites but not GSR
Lunge	NC	Test specific for NC but not GSR
Zincon reagent	Zn and Ti	Applied to Pb free ammunition. Will also react with copper. Test not specific to GSR.

2.5.2 Inorganic GSR analysis

2.5.2.1 Neutron activation analysis

Neutron activation analysis (NAA) has been used as a bulk analysis method for various elements which can be found in inorganic GSR. Ba and Sb are the two main elements identified using this method (Rudzitis *et al*. (1973), Rudzitis and Wahlgren (1975), Ruch *et al*. (1964), Krishnan (1974)). However, Cu and Au (Pillay *et al.*, 1974), Ag, Ni and Co (Capannesi and Sedda, 1992) have also been analysed. Capannesi and Sedda (1992) used NAA to examine the trace elements present in lead core, jacketed bullet fragments. With this method as many as 13 trace elements could be analysed. As the elements present in bullets can become part of inorganic GSR this NAA method could theoretically be used for GSR analysis. NAA has also been used for the determination of firing distances (Krishnan, 1967) and the determination of GSR on the hands of shooters (Pillay *et al*. (1974), Rudzitis and Wahlgren (1975), Krishnan (1974), Krishnan (1967), Kilty (1975)).

The levels of compounds in samples are usually compared to hand blanks in order to determine if elevated levels of the compounds of interest are present. Ruch *et al*. (1964) reported average levels on hands of non firearm firers (130 samples) of Ba and Sb to be 0.05-0.10µg and 0.01-0.03µg respectively. A smaller study (14 samples) by Pillay *et al*. (Pillay *et al.*, 1974) reported Ba and Sb levels at 0.061µg and 0.036µg and Cu and Au levels as 1.085µg and 0.020µg. Kilty (1975) determined the average Sb and Ba as 0.01µg and 0.32µg respectively, although daily fluctuations in concentration levels, especially with Ba were reported.

A number of problems have been reported with NAA; the technique cannot be applied to Pb analysis, samples must be irradiated, which requires a nuclear reactor as a neutron source, trained personnel are required to carry out the analysis procedure (Romolo and Margot, 2001) and it is also an expensive and time consuming technique (Schwoeble and Exline, 2000).

2.5.2.2 Atomic absorption spectrometry

Conventional atomic absorption spectrometry (AAS) has been reported sensitive enough for the detection of Pb in GSR samples, but inadequate for Ba and Sb. However, the introduction of electro thermal atomisers (carbon rod, tantalum and graphite tube furnace) made flameless AAS suitable for the analysis of Ba and Sb in GSR samples (Romolo and Margot, 2001). Samples are most commonly collected using cotton tipped swabs and 5% nitric acid (Cooper *et al*. (1994), Koons *et al*. (1987)).

Flameless AAS has been reported as a successful technique for the analysis of inorganic GSR as it is both readily available and cost effective (Can *et al.*, 2003). It has an advantage over NAA, having excellent sensitivity for Ba and Sb and can be used to detect other elements of interest including Pb (Koons, 1993).

AAS has been applied to the determination of shooting distances, based on concentration patterns of Pb around bullet holes, (Krishnan, 1974) and the detection of GSR on collection swabs taken from hands by the determination of Sb and Ba concentrations (Koons, 1993).

Ravreby (1982) reported the use of flame and flameless AAS for the analysis of residues collected from bullet holes. Elements originating from the bullet, case, primer and firearms were analysed (Cu, Zn, Pb, Sb, Ni, Fe, Ba, K, Sr (from the paint on the bullet tips of tracer rounds) and tin). The results provided a means for identifying the type of ammunition used.

Reed *et al*. (1990) applied AAS to the analysis of GSR on the hands of 112 suicide cases. With threshold levels set at 0.2µg for Sb and 0.3µg for Ba positive results were found in 38% of cases. The most important factor in obtaining good results was reported to be the condition of the hands being sampled. Dry, clean hands sampled at the scene, or protected by paper bags during transport provided the most GSR consistent results. Time delays, weapon characteristic and body location were all secondary considerations.

Cooper *et al*. (1994) used flameless AAS for the analysis of Sb and Ba levels on the hands of persons in close proximity to firearm discharges, using porcine skin as a substitute. Threshold levels were set at 0.05 µg mL^{-1} for Sb and 0.50 µg mL^{-1} for Ba. In most cases levels of Sb and Ba were only slightly elevated at a distance of 1 foot from discharge.

Koons (1987) discussed a number of problems associated with AAS. Incomplete extraction of Sb from collection swabs was shown to be an issue; even with an optimized method only 60-70% was extracted, compared to a nearly complete extraction of Pb and Ba. Further problems arising from the extraction process included variable absorbance-time profiles for Sb and the enhancement of Ba absorbance caused by various matrix constituents. Heavily soiled swabs that potentially prevented effective extractions were also reported as problematic. Ashing methods have been proposed to overcome this problem; however, Koons *et al*. (1987) also reported good recoveries from soiled swabs using a 10% nitric acid sample digestion method.

The worth of AAS in term of GSR analysis was further brought into question by Aleksandar (2003), who criticised the method on the basis of the large number of false negative results it has been shown to produce (about 40%).

2.5.2.3 Inductively coupled plasma

Inductively coupled plasma (ICP) is a bulk analysis technique that is usually used to analyse trace amounts of Pb, Ba and Sb in primer residues (Schwoeble and Exline, 2000).

Koons (1988) reported the use of ICP with atomic emissions spectroscopy (AES) for the analysis of Ba levels in swabs. The method was determined more successful than the previously used AAS due to the lack of interference from common swab constituents, a wide linear dynamic range and good precision and accuracy (limits of detection for barium, defined as three times the baseline noise level were determined to be $0.002 \mu g mL^{-1}$ for AAS and $0.0008 \mu g\ mL^{-1}$ for ICP-AES. Relative standard deviations of multiple measurements of the same solution having a barium concentration of $0.05\ \mu g\ mL^{-1}$ were reported as 5 to 10% for AAS and less than 1% with ICP-AES).

Koons (1998) also reported the use of ICP - MS for the analysis of residues originating from primers. This method was chosen due to superior detection limits in comparison to ICP-AES and graphite furnace-AAS (GFAAS) (0.052, 0.020, and 0.14 ng mL^{-1} for Sb, Ba, and Pb respectively) and faster analysis times than GFAAS. The use of MS allowed the detection of several isotopes for each of the elements of interest (Pb, Ba, Sb). ICP-MS was reported as potentially useful in several areas; the determination of levels of additional elements which may be associated with the handling of a firearm or ammunition component, or elements which maybe present in specific ammunitions, such as Sn in some non toxic primers, Co in Nyclad™ bullets, or Cu, Ni or Zn in jacketed bullets. ICP-MS also provided the possibility of some sourcing of primer derived Pb by isotope distribution (Koons *et al.,* 1998).

Steffen *et al*. (2007) reported the use of ICP-MS in conjunction with SEM-EDX. Following SEM analysis GSR particles on the adhesive stub were dissolved using 2% v/v HNO_3 in nanopure water. Pb isotope ratios were determined for 8 lead based primer ammunitions. Ratio comparisons were shown to be promising and some of the lead based primers could be distinguished from one another. However, such a method was not recommended for everyday case work, being both destructive and time consuming.

Zeichner *et al*. (2006) investigated lead isotope ratios in inorganic GSR using multiple-collector ICP-MS. (MC-ICP-MS). Lead isotope levels were reported as potentially useful in specific types of scenarios, for example in a shoot out situation where several firearms and ammunition are discharged. It was reported to be possible to link a bullet hole to the firearm that discharged the bullet. However, problems were reported with “lead memory”. Even after thorough cleaning of a firearm, some amounts of Pb from previous firings remained, and contributed to the residues of following discharges. This memory was reported to lower the levels of association between residues collected from the firearm barrel and residues from the fired ammunition (bullet and case).

Sarkis (2007) employed sector field, high resolution-ICP-mass spectrometry (SF-HR-ICP-MS) to determine the levels of Pb, Ba and Sb in residue samples, allowing identification of these elements at concentrations as low as 1ng mL^{-1}. Ternary graphs were used to better visualise the results and allow direct comparisons between the relative percentages of the 3 compounds of interest in different samples. Such graphs were reported to provide strong evidence concerning the origins of sample components on hands (GSR or environmental).

2.5.2.4 Scanning electron microscopy

SEM equipped with an X-ray detector (wavelength dispersion (WDX), or energy dispersion (EDX)) is the most commonly used method of analysing inorganic GSR (Romolo and Margot, 2001).

The advantage that SEM and X-ray detection has over bulk analysis techniques is the ability to analyse individual particles of inorganic GSR both morphologically and chemically. Bulk elemental techniques are problematic as the total sample levels of specific compounds (usually Pb, Ba and Sb) must be above pre determined thresholds for a positive result to be concluded. Therefore, due to the small levels of GSR that are often encountered in case work, many cases involving such analysis techniques are determined inconclusive. A further problem with bulk analysis lies with the fact that the elements being analysed are not exclusively found in GSR and, therefore, elevated levels of such compounds on the hand of a suspect must not be taken as conclusive evidence that they have discharged a firearm (Wolten *et al.*, 1979).

Aleksandar (2003) comments that the ability of SEM-EDX to morphologically and chemically analyse samples makes it possible to determine that particles could have only originated from the discharge of a firearm and no other way. Despite this SEM-EDX cannot determine whether a person discharged a weapon on any given occasion.

Brozek-Muncha (2007) used SEM-EDX to examine the differences between inorganic airborne and cartridge case residues. Both similarities and differences were observed in the two residue types. It was reported that the composition of a residue is influenced by two main factors:

1. The direction of movement of the expanding products of burning propellant at the stage of internal ballistics.

2. The kind of materials that were applied to construct the gun and ammunition.

Lebiedzik and Johnson (2002) reported the use of specific morphological and elemental indicators within inorganic GSR particles to differentiate between the firearm used to discharge a round, the case and bullet material of the ammunition and ultimately differentiate one type of ammunition from another. 21 elements, within 60 types of ammunition were assessed by individual particle analysis using SEM, with automated image analysis and X-ray micro analysis. In ideal conditions it was reported possible to differentiate between residues produced by firearms with barrels made of stainless steel, carbon steel and titanium. Ammunition calibre could be estimated and information on the materials used for the bullet and case of a cartridge could be determined.

Brozek-Muncha and Jankowicz (2001) compared the residues collected from the hands of 6 different shooters using 6 different lead based ammunition types. Purely visual inspections of the results allowed differentiation between three ammunition types. Statistical comparison approaches to the results were also evaluated. The Wilcoxon rank sum method was shown to be unsuitable for such an application. T-kendall rank correlation coefficients and the R Spearmen methods proved suitable for the evaluation of mutual relationships among frequencies of occurrence of certain chemical classes of primer residue. One ammunition type could be distinguished from the others and two other ammunition types could be differentiated from one another. It was concluded that further research would be required in order to determine the most suitable statistical analysis method for such applications.

Steffen *et al*. (2007) reported the use of chemometric classification of inorganic GSR. Residues from 8 lead based and 7 lead free primer ammunitions were analysed. Regularized discriminant analysis (RDA) presented the ability to enter unknown samples into a distribution model consisting of various classes. Differentiation of lead based primers was achieved and successful classification rates varied from 51-86%, with a misclassification risk of 9%. Problems in classification occurred due to the very similar qualitative compositions of lead based primers, which were inorganically consistent. Therefore, only the semi-qualitative information gained from the EDX could be used for classification purposes. Lead free primers proved much easier to classify as both qualitative and quantitative differences could be used for classification. The risk of misclassification was determined to be as low as 2.4%, with particles being correctly assigned 90-100% of the time.

Miyauchi *et al*. (1998) used SEM-EDX to analyse smokeless powders from 20 different ammunition types. Cu, Si, K, S, Al, Ca, Fe, Cl, Ba and Zn were all found. It was suggested that propellant powders may contribute to inorganic residues to a greater degree than was previously thought.

Collins *et al*. (2003) reported the analysis of glass fragments in inorganic GSR in .22 calibre ammunitions. Particles containing glass fragments were found on the hands of shooters, with sizes varying from 2-100µm. Particles were described as having morphologies indicative of the fusion of Pb and Ba compounds with glass of varying viscosities. Such particles were reported to provide a further area of interest which may allow discrimination between inorganic GSR and environment sources of GSR like particles. Only break linings were determined to be a potential source of similar particles.

One of the biggest drawbacks to SEM analysis was the tedious and time consuming task of manual particle searching within samples. The introduction of automated GSR search programmes has eliminated such a problem, reducing the total search time for a sample, freeing the SEM operator to do other tasks and reducing the number of potential human error sources (White and Owens, 1987).

Germani (1991) investigated the effects of changing SEM-EDX variables on search results, in an attempt to compile a set of standard settings for the analysis of inorganic GSR particles. It was reported that no one set of standard operating procedures could be determined, as the required search parameters between different samples are likely to be variable. For example a sample collected from a suspected shooter a number of hours after firearm discharge is likely to contain smaller sized particles than a sample collected immediately and a search programme would need to be tailored accordingly.

Zeichner and Levin (1995) reported the success rates in case work of inorganic GSR analysis using SEM-EDX on samples from hands, hair and clothing over a period of 6 years. The overall success rate for finding GSR was reported at about 10%, which was determined to increase the probative value of positive results, as it diminished the danger of accidental sample contamination leading to positives. In 39% of positive cases only 1 particle of inorganic GSR was discovered.

The analysis of the inorganic GSR can provide a great deal of information. However, in some cases where inorganic residues are not present in a sample, or are only present in relatively low levels, OGSR components may be used. Even when inorganic residues are present at large enough levels to be useful, the analysis of OGSR may provide complementary and additional information that may strengthen the probative value of a sample (Meng and Caddy, 1997) and potentially provide additional means of differentiating between GSR and environmentally sourced residues.

2.5.3 OGSR analysis

The analysis of OGSR up until the year 1997 has been reviewed in detail previously (Meng and Caddy, 1997). Therefore, work up until 1997 will be briefly covered, while more attention will be directed towards work published after this point. Techniques covered previously where no additional noteworthy articles were found during the compilation of this review are not included.

2.5.3.1 Gas chromatography

GC coupled with a number of different detectors has been applied to OGSR analysis, including flame ionisation, Thermal energy analysis (TEA), electron capture (ECD), and MS. TEA has been most commonly used for OGSR analysis.

Andrasko *et al*. (2003) reported the use of GC-TEA and GC-MS for the detection of various constituents and degradation products from smokeless powders in the barrels of firearms after test shootings. GC-TEA was employed for the analysis of samples and GC-MS was used to identify some of the compounds of interest.

Zeichner (2003) assessed the value of GC-TEA and GC-MS alongside ion mobility spectrometry (IMS) for the analysis of OGSR. GC-TEA showed a good level of sensitivity for the compounds of interest. Limits of detection were; 0.2ng for NG, 0.05ng for 2,4 DNT and 0.05ng for 2,6 DNT. The considerably lower sensitivity of GC-TEA for NG compared to DNT was reported as being due to thermal decomposition of the NG in the GC column, creating a non linearity of the NG peak height as a function of concentration, in particular when approaching the limit of detection. An increase in column length (15-30m) yielded two peaks for NG, a second smaller peak being determined as 1,2-GDN, a thermal decomposition product of NG. This decomposition was reported as a drawback to sensitivity. However, the presence of two peaks increased the probability of identifying NG using GC-TEA. Two GC-MS systems were used to analyse standard mixtures, details of which can be found elsewhere (Zeichner *et al.*, 2003). Neither of these systems were optimized for explosive analysis, however, limits of detection for the compounds of interest were reported at several nanograms. Not one case work example which was found positive for NG by GC-TEA could be confirmed by GC-MS. It was, therefore, reported that GC-MS was not sensitive enough for the majority of real life cases. IMS was shown as a good complimentary technique for GC-TEA for the detection OGSR.

Kirkbride *et al*. (1998) reported the use of GC-MS for the detection of explosive compounds, many of which may be found in firearm ammunition. As reported by Zeichner (2003) the limits of detection for many of the compounds were several nanograms (NG 10ng, TNT 10ng, RDX 10ng, PETN 0.5ng).

A potentially useful method for the combined analysis of inorganic and organic GSR by SEM-EDX, and GC-TEA and IMS has been reported (Zeichner and Eldar, 2004). Samples were collected onto aluminium stubs and inorganic analysis carried out by SEM-EDX. Samples were then extracted from the stub with a water/ethanol mixture (80/20) at 80ºC with sonication for 15 minutes, followed by further extraction with methylene chloride and concentrated by evaporation for analysis of OGSR by GC-TEA and IMS(Zeichner and Eldar, 2004).

Gas chromatography techniques suffer from the inability to analyse nitrocellulose, as it is not sufficiently volatile. Its introduction (as a major component) to a GC column may also accelerate the deterioration of the column’s performance (Zeichner *et al.*, 2003). Nitrate esters which are frequently found in GSR are also incompatible with the usual condition of GC systems due to their thermal instability. Such compounds will decompose on improperly prepared columns. PETN has been reported to suffer particularly from this (Meng and Caddy, 1997). It has also been reported that GC is unsuitable for the analysis of stabilizers such as N-nitrosodiphenylamine (N-NDPA) because the temperatures involved in such systems may cause denitrosation to diphenylamine (Meng and Caddy (1997), Espinoza and Thornton (1994)).

2.5.3.1.1 GC combined with solid phase microextraction

Solid phase micro-extraction (SPME) has been commercially available since 1993 (Lord and Pawliszyn, 2000). The technique is a variation of solid phase extraction (SPE), allowing the collection of trace and ultra-trace levels of analytes from liquid, gaseous or solid samples (via headspace) by concentrating them onto a fused-silica optical fibre coated with a layer of polymeric substances such as polydimethylsiloxane (PDMS). These coatings range in thickness between 5 and 100µm. Coatings are attached to a supporting injection device that resembles a microsyringe. Extraction is an equilibrium process, affected by temperature, analyte, sample component concentration and the volume/thickness of the polymeric coating. A major advantage of SPME is that no solvents are required to carry out extractions; this is both economically and environmentally advantageous (Fifield and Kealey, 2000). SPME has been applied to a number of areas within the forensic arena including fire arson investigation (Pert *et al.*, 2006), explosives (Furton *et al*., 2000) and ballistic materials (Andersson and Andrasko (1999), Andrasko and Stahling (2003), Andrasko and Stahling (2000), Andrasko *et al*. (1998), Andrasko and Stahling (1999), Weyermann (2009), Burleson *et al*. (2009)). The SPME work carried out to date on ballistic materials has generally focussed on "time since discharge" back calculations based on the loss of compounds from spent cartridge cases or firearm barrels over time. These authors have applied a number of different SPME fibre types, chosen using a variety of selection criteria (Weyermann (2009), Burleson *et al*. (2009), Joshi *et al*. (2009)).

Furton *et al*. (2000) investigated the suitability of 6 different SPME fibre types for the recovery of explosives and ignitable liquid residues from forensic specimens. It was determined that the 65µm polydimethylsiloxane/divinylbenzene gave the highest overall recoveries. 65µm polydimethylsiloxane/divinylbenzene fibres were also determined to be the most suitable for recovery of nitro-aromatics by Jonsson *et al*. (2007), while Calderara *et al*. (2003) reported the 65µm polydimethylsiloxane/divinylbenzene fibres to be the most appropriate for the recovery of organic explosives (some of which may be found in ammunition).

2.5.3.2 High performance liquid chromatography

High performance liquid chromatography (HPLC) has been applied to OGSR analysis with various types of detector. NG, 2,4-DNT and DPA have been analysed with electrochemical detection (Bratin *et al.*, 1981). Lloyd (1986) applied PMDE to the analysis of NG and DPA and size exclusion chromatography/PDME for NC.

Speers *et al*. (1994) reported the use of HPLC-PMDE and GC-MS in the analysis of organic propellant powder residues combined with SEM-EDX for the analysis of inorganic residues. HPLC-PMDE was used to detect NG and 2,4-DNT (GC-MS for DPA, EC,MC). The analysis of residues for organic components was shown to yield more positive results than inorganic analysis. The combined analysis of both kinds of residue was reported to produce the most useful/powerful results. HPLC-PMDE and GC-TEA have also been used in conjunction with one another (King, 1993).

Laza *et al*. (2007) reported the use of LC-MS/MS for the quantitative analysis of common propellant powder stabilizers in OGSR. Residues where collected from the hands of shooters with cotton swabs (ethanol, water 75/25% v/v). A SPE technique was used for the concentration and purification of the samples. Diphenylamine (DPA), N-nitrosodiphenylamine (N-NDPA), 4-nitrodiphenylamine (4-NDPA), 2-nitrodiphenylamine (2-NDPA), Akardite II (AKII), Methylcentralite (MC) and Ethylcentralite (EC) were all resolved from standard mixtures using multiple reaction monitoring (MRM), allowing the presence of precursor ions in the samples to be determined and, therefore, the identification of the corresponding target compounds. The limits of detection were reported to be 0.29, 0.27, 0.34, and 0.21 nmolL^{-1} for DPA, N-NDPA, 4-NDPA, and 2-NDPA, respectively. EC as well as MC had a limit of detection of 0.07 nmolL^{-1} and a limit of detection of 1.3 nmolL^{-1} was determined for AK II. Converted into the equivalent amount of target compounds injected onto the column, the limits of detection were of 5, 6, 20, 27, 32, 34, and 115 µg injected onto the column for EC, MC, 2-NDPA, N-NDPA, 4-NDPA, DPA, and AK II, respectively. The method was determined to be very sensitive for the centralites (EC and MC) and poor AKII results were linked to problems with recovery levels during SPE. The analysis of samples collected from the hands of shooters confirmed that the method was suitable for routine analysis of OGSR. However, it was reported that further investigation into the longevity of OGSR components on the hands of shooters was required before the true value of such a technique could be truly determined.

Xu *et al*. (2004) developed a combination of three HPLC- atomic pressure ionisation (API)-MS systems for the analysis of 21 nitroaromatics, nitramines and nitric esters, some of which may be found in firearm ammunition. Limits of detection for most compounds were reported to be between 0.012 and 1.2ng. The method was also determined to be superior to a previously developed HPLC-thermospray ionization (TSI)-MS, allowing a greater screening range and an increase in selectivity by a factor of ten. The HPLC-API-MS method was reported as specific, stable and reproducible.

Mathis and McCord (2003) reported the application of a reverse-phase LC-electospray ionisation (ESI)-MS for the comparison of organic additives in several smokeless powders. The method was determined useful in the analysis of compositional variations in smokeless powders.

Cascio *et al*. (2004) compared HPLC and micellar electrokinetic capillary chromatography (MEKC) for their ability to analyse OGSR. Results indicated that both reverse phase HPLC and MEKC with UV detectors were capable of resolving standard mixtures of organic components of smokeless powders. Statistical analysis using the Spearman's rank correlation test showed the separate patterns from the two systems were highly correlated. Due to the broader range of analytes detected, better suitability for diode array detection and lower operation costs MEKC, diode array UV detection looked particularly interesting as a screening technique.

2.5.3.3 Capillary electrophoresis

Capillary electrophoresis (CE) is an important analytical technique, which can provide rapid, high resolution separations of complex mixtures. Although electrically neutral compounds such as those found in OGSR cannot be separated by conventional CE, micellar electrokinetic capillary electrophoresis (MECE) permits the separation of such substances (Meng and Caddy, 1997).

Reardon *et al*. (2000) reported the use of CE for the analysis of NG, DPA and N-NDPA and EC in 7 reloading propellant powders (1 single base and 6 double base). Both bulk samples and single particles were analysed. Compositional variations between particles were shown to be significant in some cases. Due to potential blending in finished propellant powders it was reported that individual particles may not be sufficient in representing the sample bulk. The ratio of propellant/total amount of stabilizer (p/s) was shown to be a more robust way of linking residues to powders. In 5 out of 6 of the double base powders the p/s ratio of ten particles taken from the bulk were in agreement with the p/s of the bulk. 49 out of 60 particles analysed gave reliable comparisons to bulk samples. It was also reported that the combination of quantitative and qualitative information with details of particle size, shape and colour could help associate unknown powders or OGSR with a known sample.

MacCrehan *et al*. (2002) also used the propellant to stabilizer ratio in order to associate handgun fired OGSR with unfired propellant powders. Out of 7 powders analysed 4 could be easily differentiated. However, when visual examinations of particle morphologies were combined with the results of the P/S ratios all 7 of the powders could be reliably differentiated. It was reported that a much larger sample of ammunitions would, however, need to be evaluated before such observations could be considered as generally acceptable.

Northorp (Northrop (2001) (i), Northrop (2001) (ii)) assessed the application of MECE to case work. SEM and MECE were used together to provide information on both inorganic and organic substances present within propellant powders and residue samples. Samples were collected on adhesive stubs and analysed using SEM before being extracted with methanol for MECE analysis. The limits of detection for 13 characteristic organic gunpowder components (2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT, 2-NDPA, 4-NDPA, Dibutylphthalate (DBP), Diethylphthalate (DEP), DPA, EC, MC, NG, N-NDPA) ranged from 0.9-3.8pg for standard solutions. One hundred commercial propellant powders were analysed in order to create a reference library. It was concluded that the detection of characteristic organic gunpowder components was a strong indication of OGSR with little or no likelihood that they resulted from environmental exposure. MECE found detectable residues on all ammunition types examined except for .22 calibre. Levels of OGSR were also shown to vary between firings carried out under the same conditions, leading to the conclusion that residue deposition mechanisms and collection efficiency significantly affected the outcome of OGSR analysis. In case work both inorganic and organic compounds were identified on some samples collected from the hands of suspect shooters and the clothing of victims. MECE was concluded to be a potentially valuable tool in the examination of OGSR.

CE has also been applied to the analysis of inorganic GSR. Hopper and McCord (2005) reported the use of capillary zone electrophoresis (CZE) for the analysis of inorganic ion profiles from smokeless powders. Seven smokeless powders were analysed in both unburned and burnt states. Results demonstrated that ionic profiles could be used for characterising smokeless powders.

Romolo *et al*. (2003) reported the worth of CE for the detection of nitrate and nitrite ions in GSR. The used method proved simpler, cheaper and faster than the traditional approaches to GSR analysis based on AAS, AES, ICP-MS, or SEM. Hair and skin samples from a victim shot in the head were also successfully analyzed for the presence of nitrites and nitrates. This preliminary study indicated that CE offered a sound potential for forensic GSR investigation as a screening technique prior to more expensive and time consuming analytical methods. It was also reported that CE could be useful in the detection of residues produced by lead free ammunition, where the evidential value of analytical results obtained with SEM can be poor (Romolo *et al*., 2003)

Morales and Vazquez (2004) developed a CE method for the simultaneous detection of both inorganic and organic substances in GSR, with 11 organic and 10 inorganic compounds being analysed. The method did suffer from poor detection limits for some compounds, including Ba and Sb. A pre concentration method did, however, allow OGSR to be detected. It was concluded that two separate runs for inorganic and organic residues might be a better option, or alternatively the analysis of inorganic compounds with CE and organic compound with another technique, for example GC.

2.5.3.4 Other techniques that have been applied to GSR analysis

Tong *et al*. (2001) reported the use of a tandem MS/MS method for the quantitative analysis of DPA and its nitrated derivatives in smokeless gunpowders. Detection limits for DPA, N-NDPA and 4-NDPA were 1.0, 0.5, 2.5ngml^{-1} respectively. The method was determined highly selective and sensitive.

Meng and Caddy (1994) reported the use of a fluorescence method for the detection of EC in GSR. The limit of detection for EC in spiked swabs and standard solutions was 5ng and 1ng respectively. Three out of six test firing were determined to contain EC. One of these swabs was collected 180 minutes following firearm discharge.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been applied to both organic and inorganic GSR analysis. Cumbaros *et al*. (2001) reported TOF-SIMS analysis as a useful method of detecting inorganic residues. The technique was determined to have a number of advantages over SEM-EDX including; lower detection limits, the elimination of signal overlaps, the ability to analyse both organic and inorganic compounds, near surface depth profiling allowing elemental distribution to be monitored as a function of depth and elemental and compound mapping from raw data. However, it was reported that due to a lack of high resolution imaging capabilities, such as those provided by SEM back scatter electron detection, SEM-EDX should still be considered the method of choice for routine detection and counting of potential GSR particles.

Mahoney *et al*. (2001) applied TOF-SIMS to the analysis of both organic (such as EC, DBP and NC) and inorganic substances (such as potassium nitrate, potassium perchlorate and sulphur) in smokeless and black powders (and black powder substitutes). However, because of the high-vacuum conditions inside the instrument the technique was reported to be unsuitable for more volatile components such as NG.

X-ray microfluorescence has been reported as an applicable method for the analysis of inorganic GSR (113-115). However, despite several advantages over SEM-EDX being reported (larger potential scanning area (20x20cm) and direct visualisation of target materials e.g. fabrics), the inability to analyse particles smaller than 10µm led to the conclusion by Flynn (Flynn *et al*., 1998) that X-ray microfluorescence could not replace SEM-EDX as the method of choice for inorganic residue analysis. Berendes (2006) reported that although X-ray microflourescence could not replace other commonly used techniques in GSR investigation it does offer a good supplement, especially with non toxic primer residues.

Niewohner and Wenz (1999) applied focused ion beam systems to gunshot residue investigation. It was reported that scanning ion microscopy allowed particles to be cross sectioned, revealing interior morphologies that could be used for the identification of ammunition manufactures. Some particles were shown to be solid throughout, in which case such cross sectional information was not useful. However, where morphological details were present, different ammunition types produced characteristics that could be used to differentiate between them. However, the study only investigated four types of ammunition, and although each of these ammunitions did produce unique interior morphologies an investigation of a much larger number of ammunition types would be required to confirm the true worth of such analysis.

Pun and Gallusser (2008) reported the worth of macroscopic observations of the morphological characteristics of propellant powders, investigating 181 cartridges of different calibres. The colour and shape of the powder grains were shown to be an effective way of linking partially burnt powders from discharged rounds back to unburned samples. On these observations alone a number of potential ammunitions matches for any residue sample could be determined. The correct source ammunition was always within those selected as possibilities for any given sample. However, a quantity of particles was required for accurate analysis of both colour and shape. In real situations, factors such as weapon type, spatial distribution of GSR and problems with contamination arising from previously discharged cartridges were all reported as potential hindrances to the successful application of such observations.

2.6 Environmental sources of GSR like particles and their influence on GSR classification and analysis

2.6.1 Environmental sources of inorganic GSR like particles

The possibility that there could be other sources of GSR like particles is very important. If it were found that any other process or activity could produce particles with indistinguishable morphological and/or compositional characteristics to those of GSR then the weight of such particles as forensic evidence would be greatly reduced.

The analysis of GSR with bulk analysis techniques such as NAA or AAS does not take into account the morphology of individual particles being analysed and, therefore, the possibility of false positive results is much greater. The three elements most commonly analysed using these techniques are Pb, Ba and Sb, which may be picked up from a number of environmental sources. Pb particles can be found in the emissions of leaded petrol, plumbing materials, battery plates, solder, glass and paints. Sb is found in several alloys, often with Pb, and its oxides are used as a fire retardant in cotton and polyester blend fibres. Ba is found in paint, car grease and barium sulphate from paper (Romolo and Margot, 2001).

The application of SEM and X-ray detectors allows the morphology and elemental composition of individual particles to be determined. Wolten *et al*. (1977) produced a list of particle types that were considered unique (characteristic) and consistent to inorganic GSR particles based on particle composition (Table 5), size and morphology. In the majority of cases 70-100% of particles analysed were spheroid, with smooth or fuzzy surfaces, scaly or covered with smaller spheres. The remaining (rarely above 30% depending on ammunition) particles had irregular morphologies. The vast majority of particles had diameters less than 5µm.

Table 5: *Classification of inorganic GSR particles (Wolten et al., 1977).*

Unique	**Characteristic**
Pb,Sb,Ba	Pb,Sb
Ba,Ca,Si with trace S	Pb,Ba
Sb,Ba	Pb
	Ba if S is absent or only trace levels

The above particles may also contain the following Si,Ca,Al,Cu,Fe,S,P(rare), Zn (only if Cu>Zn), Ni (rare and only with Cu and Zn), K Cl and Sn (in obsolete ammunition).

A number of studies have since been published that have investigated whether or not inorganic GSR particles of such compositions are indeed unique to firearm discharge, these are outlined below.

Wolten *et al*. (1979) carried out SEM-EDX analysis on samples taken from the hands of people working in areas that were considered to be possible sources of GSR like particles. Areas with the most potential for producing GSR like particles were described as critical occupations. These were made up of industrial and commercial operations involving metals or compounds of Pb, Ba and Sb. Sectors that involved melting and/or vaporisation of such elements were of particular interest. An overview of their results is presented in Table 6. The possibility of particles being created in some of the areas investigated that were of similar morphological and compositional structures to inorganic GSR was observed. It was reported that such particles would be classified as indicative of GSR using the "formal" classification system presented in the Aerospace report (Wolten *et al*., 1977). Such particles were seen in residue samples collected from stud guns. It was concluded that individual particles should be considered within the context of all other particles within the sample in which they are found if the potential for misinterpretation was to be minimised. The occupation of the person from which a sample is taken was also considered as potentially relevant to the interpretation of samples (Wolten *et al*., 1979). None of the samples analysed contained particles of Pb, Ba and Sb or Ba and Sb, which were still considered to be unique to GSR (Wolten *et al.*, 1977). The results of this study showed the possibility that particles from other sources could be confused with GSR. This must be seen as an important finding, especially if a sample being analysed has only a small number of particles present.

Table 6: Results of investigations into environmental sources of Inorganic GSR like particles (Wolten et al, 1979).

Vocation/activity	Findings
Stud Guns	Two particles consistent with GSR particles were found in samples from one brand of stud gun cartridge (Remington); these were small spheroid particles containing Ba, Pb, Zn and Cu. It was only the abundance of larger non GSR like particles that lead to sample being determined as not GSR. 13 particles consistent with GSR were found in samples collected from Omark brand cartridges. A typical composition of these particles was Cu and Zn (3:1) with Pb, Fe and Ba (major) and Si, K, Cu, Ca and Zn (minor). Again it was only the abundance of non GSR like particles that meant samples were not determined to be GSR.
Cap Guns	No GSR like particles were found in these samples. Sb was seen but there was no Pb or Ba present. Both crystalline (Sb, S (major) Cl and P (minor)) and spheroid (Cl, Ca and P and Ca, P, Zn and K (major) Sb, Cl and S (minor)) morphologies seen.
Blanks	No GSR particles found with two blank types Winchester .22 with black powder and Winchester Western .38 with smokeless powder.
Lead smelting	Pb and Sb particles were found in samples, 50% were spheroid and 50% irregular (determined not consistent with GSR). None of the samples were determined to be GSR.
Car brake mechanics	2 particles consistent with GSR (Pb and barium with other element associated with GSR). The first contained Fe, Cu, S, Si, Ba and Pb. The second, Pb, Fe, Cu, Si, Ba and Cl. The elemental proportions were, however, determined not to be that of GSR and the particles were dismissed.
Pb acid battery assemblers	Particles consistent with GSR were found. These included the following 1.Pb and Sb 2. Pb, Sb, Fe, Si, Zn 3. Pb, Ca, Ba, Fe and Zn. 4. Pb, Fe and Ba. 5. Pb, Cu, Si and Zn. 6. Pb, Ca, Ba, Fe and Zn. However, by taking into account all particles present, samples were discounted as GSR. The size distribution of particles was also deemed inconsistent with GSR samples
Car mechanics, exhaust fitters and environmental lead.	Nothing relating to GSR particles was found.

Wallace and McQuillan (1984) carried out a more detailed study of particles produced by stud guns, analysing (SEM-EDX) the primer and residue compositions of 6 types of stud gun ammunition. All of the particles found were between 1-12μm in diameter and both spherical and irregular morphologies were observed. Morphologies were consistent with vaporising or melting of the compounds involved. No crystalline structures were seen in any of the collected particles (which would indicate the particles would have been created in an environment not consistent with those involved in a firearm discharge (Wolten *et al*., 1977)). It was concluded that the physical characteristics of the samples analysed were indistinguishable from GSR. The results from Wallace and McQuillan (1984), together with their past experience led to a conclusion that the original classification system for inorganic GSR particles (Table 5) should be modified to take into account particles generated from cartridge operated tools (Table 7). This classification system was stated to be only applicable to brass cased, Pb, Ba and Sb primed and Pb, Ba primed ammunition types. A simplified version of this system was adopted in the ASTM standard guide for inorganic GSR analysis by SEM/EDX (ASTM (1995), ASTM (2001)).

Table 7: Inorganic GSR classification system proposed by Wallace and McQuillan (1984).

Unique	**Indicative**[*]
Pb, Sb, Ba	Ba, Ca, Si[†]
Sb, Ba	Pb, Sb
	Pb, Ba
	Sb (with or without S)
	Ba[2]
	Pb
	Pb, Sb and Ba absent[‡, §]

*. Indicative particles listed in order of decreasing significance

†. S absent or acceptable as trace only when Ba present at a major level.

‡. Any of the above may also include some or all of the following: Al, Ca, S, Si at major, minor or trace levels; Cl, Cu, Fe, K, Zn (only if Cu also present and Zn:Cu < 1) at minor or trace level; Mg, Na, P at trace levels only.

§. Particles containing no Pb, Sb or Ba may be considered indicative if they are composed entirely of the elements in 3 above and are accompanied by other types of indicative particles.

Wallace and McQuillan (1984) also suggested that the term GSR should be reworked with relation to the classification system, suggesting the term “primer residues” should be adopted as this would incorporate all percussion-activated charges based on Pb, Ba,Sb compounds, therefore, including cartridge based tools.

In addition to this proposed change Wallace and McQuillan (1984) also suggested a number of other considerations that should be taken into account when analysing inorganic GSR. Spent cartridges, they argued may be used for chemical composition comparisons but not for morphological checks, as particles found inside cartridge cases will be different from those ejected from the firearm. The analysis of inorganic GSR by comparing samples collected from hands or other sources to cartridge cases/ammunition is a move away from a “formal” approach in which samples are interpreted following the rules of a formal general interpretation system, to a “case by case” or “specific” approach (an approach concluded as the most appropriate for GSR analysis wherever possible by Romolo and Margot (2001)). Further more, individual particles within a sample should be considered in relation to all the others that are present. The fewer the number of particles that are present in a sample the more difficult it is to discriminate between tool and gunshot residues (Wallace and McQuillan, 1984).

Zeichner and Levin (1997) agreed with Wallace and McQuillan (1984) that GSR like particles could be found in residues from cartridge operated tools.

Garofano *et al*. (1999) followed on and expanded upon the work of Wolten *et al*. (1979), investigating the same vocations/activities that were flagged as potential sources of GSR like particles. 175 samples from the hands of persons undertaking these activities of interest were analysed using SEM-EDX. Their results corroborated those of Wolten *et al*. (1979) and confirmed that particles of Pb, Ba and Sb were unique to inorganic GSR (although they were found in samples collected from stud gun operators). However, Garofano *et al*. (1999) found particles of Sb and Ba in samples relating to car repair and maintenance activities. Even taking into account the morphology of these particles there were some that were hard to distinguish from genuine inorganic GSR Sb, Ba particles. It was, therefore, suggested that Ba, Sb particles (with iron present) no longer be classed as unique to inorganic GSR (Wolten *et al*. (1977), Wolten *et al*. (1979), Wallace and McQuillan (1984)) and instead be seen as characteristic (unless found with Pb, Ba and Sb particles in which case they would still be seen as unique). Ba and Sb particles in the absence of Fe should be seen as boarder line particles. Garofano *et al*. (1999) also concluded that both the elemental and the morphological compositions of the particles being analysed are important if a correct interpretation of a particle's source is to be achieved.

Mosher *et al*. (1998) investigated the possibility of fireworks and pyrotechnic devices producing particles that resembled inorganic GSR. Residues from pyrotechnic devices only available to professional display organisers as well as those available to the general public were analysed with SEM-EDX. Results showed that it was possible to find firework residue particles that could be mistaken for inorganic GSR. Samples collected from the hands of the professional firework display organisers contained some Sb and Ba particles that were morphologically (at least externally) similar to inorganic GSR particles (spheroid, non crystalline and between 0.5-5μm in diameter). Such particles could be classified as unique to GSR using the original guidelines (Wolten *et al*., 1977). Other Sb and Ba particles, with irregular morphologies and much larger in size (up to 40μm) were also present. These particles, although not considered typical of GSR could still be classified as such under the original formal classification system (Wolten *et al*., 1977).

The analysis of the fireworks available to the general public showed that all of the unburned powders contained both Pb and Ba, with two also containing Sb. Residue samples indicated that the fireworks without antimony could produce Pb and Ba particles (seven were found), which had been reported in inorganic GSR produced from some .22 calibre rim fire primer units (Meng and Caddy, 1997). Residues from one of the firework types that also contained Sb had particles that consisted of Pb, Ba and Sb, an elemental composition classified as unique to GSR (Wolten *et al*., 1977). Many of these particles were irregular shaped and between 10 and 35µm in size and containing other elements. These other elements and the morphology of the particles would, it was determined, allow a trained GSR examiner to differentiate such particles as coming from some form of pyrotechnic device. However, a few particles contained Mg, which had been reported as being present in some inorganic GSR particles were reported (Wallace, 1990). Therefore, a potential for such particles to be wrongly identified as GSR has been shown to exist. There was also two Pb, Ba and Sb particles found that did not contain Mg, which had the potential to be mistaken for GSR.

Torre *et al*. (2002) carried out an investigation into car brake linings and their potential for producing inorganic GSR like particles. It was argued that; Sb, Ba particles should not be considered unique (as suggested by Wallace and McQuillan (1984)) as they can be found readily in urban areas rich in metallic particulates such as those exposed to road traffic. Brake linings appeared to be an obvious source of GSR like particles, as many contain lead sulphide, antimony sulphide and barium sulphate in different combinations and, while breaking, disks can reach temperatures in excess of 600ºC, reaching up to 1500ºC in friction spots on the surface, similar temperature to those that occur during a firearm discharge (Torre *et al*, 2002). The results of tests on 40 different types of brake discs showed that it was possible to obtain Pb, Ba and Sb particles from the wear of brake linings. Such particles were subdivided by Torre *et al*. into two groups, “clean” and “unclean”. “Unclean” particles contained the three elements of interest, but with other elements or concentrations of elements that were inconsistent with inorganic GSR. “Clean” particles were described as those collected from car front brakes and new brake linings composed of Ba, Sb or Pb, Sb, Ba, that were of a similar size to inorganic GSR with elements and elemental concentrations that were consistent with inorganic GSR. Such particles as these were found mainly in new break linings, while those collected from car front breaks often had iron present within them at major levels. Results were in agreement with other recent publications in that Sb,Ba particles could not be considered “unique” to GSR (Garofano *et al*., 1999), further more the observation of “clean” Pb, Ba, Sb particles also suggested that such particles could not be considered “unique” to GSR. The only two compositions that were not found were; “clean” Ba, Sb particles with no S, or S at trace levels and “clean” Pb, Sb, Ba particles with Ba and/or Sb levels higher than lead. These particle types could still in theory be considered “unique”, however, it was suggested that the “unique” classification be dropped all together in favour of the “more prudent” "consistent" categorisation. It was reported that in order to discriminate between primer discharge residue and environmental particles, analysis of particle morphology must be re-evaluated (Torre *et al.* (2002), Garofano *et al.* (1999)). Particles identical to primer discharge residue in elemental composition maybe found, but never of a typical shape. The only reliable particle, would be of the "ideal" morphology, spherical or globular, with a surface either perfectly smooth, pitted with craters, or coated with rounded and smooth nodules, but never, even in part dusty or rough (Torre *et al.*, 2002). Torre at al (2002) agreed with Wallace and McQuillan (1984) suggesting that the term GSR should be dropped and replaced by either "primer discharge residue" or "residues of the detonation of a mixture of Pb, Ba and Sb compounds". Finally it was concluded that if ammunition which was recovered from a suspect/scene is not available for comparison to residue samples then any conclusions should be drawn with extreme caution (Torre *et al*., 2002).

Cardinetti *et al*. (2004) used X-ray mapping techniques to analyse a number of non-firearm sources of possible inorganic GSR like particles. Break lining samples from 42 different makes and models of car were taken. Hand (palm and back) samples from car electricians, motor mechanics and pyrotechnic and firework operators were also collected. A number of different genuine firearm cartridge residues where also analysed to re-evaluate compositions and morphologies that may be encountered. Results confirmed that it was possible to find particles containing Pb, Sb and Ba and Sb, Ba in non-firearm related samples. Two particles containing Pb, Sb, Ba were found in samples collected from car brake linings, along with 214 Sb, Ba particles. Each of the samples collected from the hands of workers contained Sb, Ba particles. The analysis of residue from within cartridge cases showed that it was also possible to find irregular particles in GSR samples, which could in theory lead to false negative results for actual inorganic GSR. It was reported that X-ray mapping techniques, which can analyse the internal elemental structures of particles, could reduce the probability of mistakes in inorganic GSR analysis occurring, because true GSR particles and those from other environmental sources have very different internal element distributions. Inorganic GSR particles showed homogenous elemental distribution, where as environmental particles, which had been created under much lower temperatures and pressures showed a layered structure of individual elemental plaques (Cardinetti *et al.*, 2004).

The findings of Cardinetti *et al*. (2004) are interesting; however, there are two areas which may be problematic. Firstly, tested residues were taken from inside cartridge cases, which although valid in some respects (chemical comparisons) may not accurately represent the particles that may leave a firearm during a discharge (Wallace and McQuillan 1984). Secondly, it is stated that by looking at the internal structures of particles it is possible to differentiate GSR from environmental particles by analysis of internal elemental distributions. However, work carried out by Basu (1982) showed that a number of different internal structures maybe found among GSR particles, including ones in which elements are layered. Therefore, it may not be possible to accurately determine the source of a particle using this method.

2.6.2 EnvironmentalsSources of organic compounds found within organic GSR

If the analysis of the organic compounds present in gunshot residue is to improve the evidential value of GSR analysis it must be determined to what extent these compounds of interest could come from other sources.

Lloyd (1987) listed a variety of environmental sources of the stabilizer compound DPA; the surface of apples, tires and outer garments were all shown to be possible sources. Solid rocket fuels, pesticides, dyes, pharmaceuticals and veterinary medicines are also formulations know to contain DPA (Hawley, 1981).

Direct swabbing of the skins of apples, pears, bananas and citrus fruit have been reported to produce chromatogram peaks at the same retention time (HPLC) as DPA (Leggett and Lott, 1989). Grapefruit, oranges and pears have also been reported to produce peaks at the same retention time as EC. Items of clothing, shoe polish and many rubber products all produced interfering peaks (Leggett and Lott, 1989). Leggett and Lott (1989), therefore, commented that HPLC analysis of organic compound is not an infallible method of determining the presence of OGSR in any given sample.

2.6.3 *Inorganic GSR from ammunitions with lead free/non-toxic primers*

Another aspect of residue analysis that must be taken into account is ammunition types that do not have primers which contain Pb, Ba and Sb compounds. A number of studies into GSR produced by lead free/non toxic ammunitions have been published and their findings are summarized in Table 8.

Table 8: Elemental compositions of residues from various lead free/non toxic ammunitions (Oommen and Pierce (2006), Gunaratnam and Himberg (1994), Martiny et al. (2008), Harris (1995)).

Ammunition	Primer composition	Residue particles
Sintox (.375 Mag)	Diazodinitrophenol (DDNP), tetracene, zinc peroxide, titanium metal powder, nitrocellulose.	Zn-Ti Zn-Pb Ti-Zn-Pb-Ba
CCI Blazer® Lead free (.38 SPL+P)	Tetracene, DDNP , smokeless powder, strontium nitrate	Sr Sr-Ba
Winchester Winclean™ (9mm and .45ACP)	Copper and zinc (primer cup), DDNP, potassium nitrate, boron, nitrocellulose (MSDS contents)	Cu-Zn K-Al-Si-Na Al-Na,Ca or Mg
Remington/UMC LeadLess™ (9mm and .45ACP)	Copper and zinc (primer cup), DDNP, barium, tetracene (MSDS contents)	Cu-Zn Al-Si-K (trace Na) Al-Si-K (Na or Ca)
Federal Ballisticlean™(9mm and .45ACP)	Copper and zinc (primer cup), tetracene, barium nitrate, aluminium, nitrocellulose, nitroglycerine	Cu-Sn Al,Si,Ba,K (Na)
Speer lawman Cleanfire™(9mm and .45ACP)	Copper, Zinc, nickel, DDNP, tetracene, Strontium nitrate, nitrocellulose, nitroglycerine	Cu Cu-Zn Sr-Al/Si or Cl
Cleanrange 1st generation (9mm Luger)	DDNP, tetracene, nitrocellulose, strontium nitrate, Gum tragacanth (patent claim)	Sr (plume) Sr-Na-K-Fe (hand residue)
Cleanrange 2nd generation (9mm Luger, 0.40S&W, .380 AUTO and .38SPL)	DDNP, tetracene, nitrocellulose, potassium nitrate, aluminium powder, ground glass, Gum tragacanth (patent claim)	Al,Si,Ca (plume) Al-K-Si-Ca-Fe (S in .38 SPL) (hand residue)

Gunaratnam (1994) analysed the inorganic residue particles formed by Sintox lead free ammunition (cal .375 Magnum) with SEM-EDX. Characteristic particles were reported to contain Zn and Ti, with spheroid morphologies. Morphology was determined as the only way of truly discriminating such particles from environmental sources (irregular particles could not be used). However, a much smaller number of spheroid particles were found in residue samples than in those collected from cartridges with Pb,Sb,Ba based primers. Ti and Zn are found in paint pigments, but never as major elements and never with inorganic

GSR characteristic spherical morphologies. However, scenarios involving burning paint and the particles formed have not been fully investigated (Gunaratnam and Himberg, 1994).

Harris (1995) analysed GSR from CCI Blazer lead free ammunition using SEM-EDX. The only significant metallic element found in the residue particles was Sr. Particles were mostly 0.5-10μm (some up to 35μm) and spherical, as would be expected from Pb,Ba,Sb primers. Traces of Ba were seen in some residues, even though not stated by the manufacturer as being included, however, natural deposits of Sr are often found in association with Ba. It was reported that Sr particles with spherical morphologies could result from exposure to flares and fireworks, limiting the evidential value of such particles.

Oommen and Pierce (2006) analysed a number of lead free ammunition types with SEM-EDX, reporting different elemental compositions for each (Table 8). Similarities were observed between Federal Ballisticlean™ and sparkler pyrolysis residues, although it was determined that a trained analyst should not have problems differentiating them. K, Ca, Mg and Na salt, present in some of the residues are soluble in water and, therefore, would be expected to be dissolved by human sweat. These elements would not be expected to persist on shooters' hands for as long, as those elements that are not water soluble.

Martiny *et al*. (2008) characterised the inorganic GSR elements present in Magtech Cleanrange® ammunition (SEM-EDX). Two varieties of 9mm Luger, .40S&W, .380 Auto and .38 special types were analysed. None of the residue particles analysed could be considered unique to GSR using the ASTM formal classification system (ASTM, 2001). Cleanrange® produced predominantly irregular shaped particles, which would also be considered atypical using formal classification. The elements present in residues for Cleanrange® may also be found in association with automobile components, lubricants and combustibles. For this reason it was reported that elemental compositions of primer resides from Cleanrange® products cannot be used to confirm firearm discharge. The use of alternative analysis techniques, for example organic residue analysis, was reported to be a potential means of improving the evidential value of residues from such ammunitions.

Lead free and non toxic ammunitions are problematic when it comes to determining whether residues originated from firearm discharge or environment sources using a "formal approach" (Romolo and Margot, 2001). Therefore, a "case by case" assessment procedure would be more appropriate for such cases as these (Romolo and Margot (2001), Garofano *et al*. (1999), Brozek-Mucha (2003)). Additional research into possible environmental sources of particles like those produced by lead free and non toxic ammunitions is also required before the evidential value of such particles can be truly determined (Oommen and Pierce, 2006).

2.7 The effects of changing ammunition types on the composition of GSR.

The effects of changing ammunition types in any given firearm have been shown to produce inorganic particles of exceptional compositions. Such particles may differ greatly from the “classic” criteria for the identification of inorganic GSR (using a “formal” identification approach) (Schwoeble and Harrison, 2006). Even the thorough cleaning of a firearm has been shown not to remove all traces of previous residues and lead to a kind of memory effect within the firearm barrel (Harris (1995), Zeichner *et al*. (2006)). Therefore, a “case by case” basis for analysis should be adopted where possible if the potential misinterpretation of the evidence is to be minimized.

Lebiedzik and Johnson (2002) reported that in cases where a variety of ammunition types are fired by one firearm, descriptive indicators (21 elements) may be difficult to interpret due to the combined influence of ammunitions (Lebiedzik and Johnson, 2002).

Torre and Mattutino (2003) collected samples of lead free and non toxic GSR by swabbing the insides of spent cartridges; these were compared to samples collected from hands and targets. Variable pressure (VP) SEM-EDX was used for analysis. Results showed that previous shots of lead based ammunition within a given firearm could influence the composition of residues produced from subsequently discharged lead free rounds. Due to the poor evidential value of the results obtained from solely using this technique on lead free and non toxic GSR it was recommended that further analysis techniques should be employed to gain as detailed a picture of composition of any given GSR sample as possible.

MacCrehan *et al*. (2001) reported that compositional analysis of residues from firearms in which ammunition types had been changed showed only trace amounts of organic compounds (from propellant powder) from previous firings in the first shot and non in subsequent shots.

2.8 Distribution and transfer of GSR following a firearm discharge

Once a firearm has been discharged it is essential to understand the distribution of GSR in relation to the shooter and their surroundings, not only in terms of sample collection but also minimisation of contamination/secondary transfer within samples which could potentially lead to an inaccurate conclusion as to whether a subject has been involved in handling or discharging firearms. An understanding of these processes may also aid in the accurate interpretation of analysis results (Romolo and Margot, 2001).

Schwoeble and Exline (2000) investigated the evolution of residue plumes from a number of different weapon types (pistols, revolvers, rifles and shotguns), using high speed photography. A great amount of variation in plume evolution patterns between firearms was described (Table 9). Blow back or drift of residue plumes towards the chest, shoulder, face and hair of the shooter was observed. Cartridge ejection was shown to be a factor in the dispersion of GSR (contradictory to Wolten *et al*. (1977)). Ejection plumes were then shown to spread out in all directions and, therefore, be subject to the influences of any air turbulence in the vicinity of discharge (Schwoeble and Exline, 2000).

Table 9*: Characteristic residue distribution plume patterns by firearm type (Schwoeble and Exline, 2000)*

Firearm	**Residue Distribution**
Smaller calibre semi automatic weapons (high/forward cartridge ejection).	Sometimes plumes concentrations to the front of the fingers, but in most cases the plumes tend to follow in the direction of the ejected cartridge
Larger calibre revolvers	Widespread plumes
Larger calibre semi automatic pistols	Smaller more compact plumes (compared to larger revolvers)
Shotguns and rifles	Consistent area of plume concentration in the crook of the support arm

Schwoeble and Exline (2000) also investigated inorganic GSR particle fall out. Rates were shown to vary widely, based upon the physical characteristics (size, shape and particle density) of particles.

Carreras *et al*. (1998) also used fast photography to examine the ejection of residues from the muzzle end of; a 9mm parabellum, a 9mm short gun, a .38 revolver and a 7.62 carbine rifle. Residues leaving a firearms muzzle were divided into three categories: Primary -

residues leaving the barrel prior to the projectile, secondary – residues leaving the barrel at the same time as the projectile, and tertiary – residues leaving the barrel after the projectile. This process will affect the amount of residue available for collection dependent on muzzle to target distance. At close ranges the gunpowder combustion residues reach the target and cause soiling. The characteristics and the amount of GSR on a target are dependent on the distance of the shot. Contact wound shots may yield little or no external GSR as the residues are forced into the bullet hole (Carreras *et al*., 1998).

Basu *et al*. (1997) investigated the evolution of inorganic GSR from the rear of firearms, described as "trigger blast". It was demonstrated that deposits of residue on the hands of shooters came almost exclusively from GSR emanating from the rear of the firearm (as suggested by Wolten *et al*., (1977) and not the muzzle (overlap of muzzle and trigger residues was observed in unclean firearms). This was shown to occur in both open and closed breach weapons. Residues on hands were deposited by blasting due to firearm discharge and not from the deposition of airborne particles. These results were in agreement with Schlesinger (1990) who reported that wind velocity has no effect on the deposition of residue particles on the hands of a shooter. Therefore, for a non firing individual to have residue present on their hands they would have to be in very close proximity to a weapon discharge. It was also hypothesised that deposits of GSR that have been found on forward facing portions of shooters' bodies could also be deposited by the firearm discharge blast and not the fallout of airborne particulates (Basu *et al*., 1997).

Fojtasek *et al*. (2003) investigated the distribution of GSR particles surrounding a pistol shooter. Experiments carried out in a closed environment showed that "unique" (Pb, Sn, Ba, Si, Ca and Pb, Sn, Sb, Ba (Walten *et al*., 1979)) inorganic GSR particles could be found at distances up to 10m from the shooter. The maximum quantity of residue particles were found at 45º to the right in front of the shooter (several 1000 particles were found in this area), however, several hundred particles were also found in front of the shooter and to their right. In an open environment distribution patterns were the same, but particle concentrations were 10 times lower in magnitude. This demonstrates a significant influence of climatic conditions on the amount of residue that might be available for collection. There were no particles found after a distance of 6m (Fojtasek *et al.*, 2003). There was no indication of any observable differences in the distribution of particles with different sizes as a function of distance. The majority of the particles were less than 3µm in diameter.

Gerard *et al*. (2006) reported that GSR can travel much further than suggested by Fojtasek *et al*. (2003), detecting inorganic GSR at distances up to 18m. These particles were reported to have been carried such distances in association with the projectile. It was also demonstrated that inorganic GSR could spread outward laterally from the firearm to at least a distance of 3m.

Work carried out by Bergman *et al*. (1988) demonstrated that inorganic GSR particles can be consistently found on the bottom of discharged bullets, including those which have been severely deformed on impact or undergone other severe conditions. Many of these particles were shown to have a strong adhesion to the bullet, even after 20 minutes in an ultrasonic bath, only “loose” particles were removed. The high temperatures and pressures in the firearm on discharge appeared to cause particles to fuse to the base of the bullet. Such particles may prove very useful in determining which weapon a specific bullet was discharged from during an incident involving multiple shooters, especially if said bullet is greatly deformed, rendering visual comparisons to test firings difficult/impossible (Bergman *et al.*, 1988).

Fojtasek and Kmjec (2005) carried out an investigation of inorganic GSR deposition rates. A 9mm and a 7.65mm pistol and a .38 special revolver were tested. Results showed that each weapon type had a different time period of maximum deposition. Time periods were dependant on the firearm and the calibre of the ammunition used. With a pistol discharge the possibility of airborne contamination was reported to exist within *ca*. 8 min after discharge. With a revolver the time could be as long as 10 min after discharge. The relationship between particle size and deposition time was also investigated. As would be expected (Schwoeble and Harrison, 2006) larger particles (6-10µm) were deposited first, followed by those with smaller diameters (1-5µm). Different firearms and ammunitions produced varying levels of “unique” particles in different size ranges (the 9mm produced most “unique” particles in the 1-5µm range while the 7.65 were in the range 6-10µm).

Andrasko and Pettersson (1991) investigated the possibilities of non firing persons, present in locations where a firearm discharge had occurred being contaminated with inorganic GSR. A summary of the results from the experiments can be seen in table 10. Contamination was shown to be possible when a person walked through the particle cloud of a firearm discharge and not just as a consequence of staying close to a shooter. This conclusion is particularly important when considering the evidential value of any given GSR sample.

Table 10: *Contamination experiments and particles found (Andrasko and Pettersson, 1991).*

Experiment	Particles found
Walking into a contaminated area. Subject walked in a shooting room in which no shooting had occurred that day. The floor was cleaned every second day	2 particles observed in lower part of the coat
Clothing hung in a shooting gallery: coat hung 2m behind shooter who fired over 300 rounds (.22)	Hundreds of GSR and bullet particles observed
Clothing present in the same room as a shooter. Two persons (A 1m to right and B 4m behind) in a room with a shooter. Four 357 magnum shots fired. Subjects then walked across area in front of the shooter while leaving the room	A: 6 particles found B: 8 particles found

The papers above present evidence to suggest that there is a real possibility that contamination of persons in or entering a room/location where a firearm has been discharged could occur.

2.9 Shooter activities post firearm discharge and effects on GSR Loss

It is of importance to understand the potential longevity of GSR particles on hands, other skin, clothing and other materials from which samples maybe collected. Not only is this information useful when determining whether a sample should be taken (in cases where the subject is suspected of discharging a firearm days, weeks or months prior to apprehension), but also in interpreting the results of any given sample analysis.

GSR deposits on a person are continuously lost as a result of normal activities and as a consequence of this it is very difficult to generalise a time period during which GSR may be retained (Meng and Caddy, 1997).

Inorganic GSR retention on the hands of shooters has been shown to vary greatly following normal activities. Maximum recovery times ranging from one to 48 hours have been reported for particles on shooters hands (Harrison and Gilroy (1959), Mastruko (2003), Krishnan (1974), Kilty (1975), Walten *et al*. (1979), Andrasko and Maehly (1977), Heard (1997), Jalanti *et al*. (1999), Murdock (1984), Krishnan (1977), Nesbitt *et al*. (1977)). Rapid decreases in particle numbers have been shown to occur within 1-3 hours post discharge (Kilty (1975), Andrasko and Maehly (1977), Murdock (1984), Nesbitt *et al*.

(1977)). The rapid loss of inorganic GSR particles from hands is a great disadvantage in terms of collection, but on the other hand increases its value if found, as this indicates a very short time frame between firearm discharge and sample collection (Mastruko, 2003).

Specific everyday actions have been shown to radically affect the amount of inorganic GSR on shooters hands. Kilty (1975) investigated the effects of various activities on inorganic GSR levels on hands using bulk analysis (antimony and barium). Washing hands with soap and water then drying on a paper towel effectively removed all traces of inorganic GSR. Rinsing hands for three seconds under low pressure water removed substantial amounts of residue, as did wiping hands on clothing (Kilty, 1975), bringing levels close or equal to those levels found on the hands of non shooters (Nesbitt *et al.*, 1977). Rubbing the hands together transferred residue from one hand to the other and placing hands in pockets removed residues (Kilty, 1975), however, residues could be subsequently detected within the pocket (Nesbitt *et al.*, 1977).

Lloyd (1986) reported that NG could be detected up to 7 hours post firing on a shooters hands, face and throat, whereas it could be detected on clothes worn without restrictions for up to 5 hours only. Douse (1986) reported contradictory results showing a 0.5 hour detection limit for NG on skin. Northrop (2001 (part II)) reported that recoverable organic gunshot residues may not persist on skin for more than 1h.

The longevity of GSR on clothing has been reported to be generally much greater than on skin. Particles have been found days or even weeks after firearm discharge (Mastruko, 2003). Jane *et al.* (1983) reported that clothing removed and stored post firing as opposed to clothing that was continually worn retained organic residues (NG, NC and DPA) for a much longer period of time (residue found on the stored cloths the following day, the worn garments retained residue for up to 6 hours). Residues deposited on a cotton sheet placed 1m in front of a revolver that discharged 5 rounds remained detectable for up to two months, if the sheet was undisturbed. These experiments suggest that the loss of GSR is caused by physical activity rather than compound degradation (Jane *et al.*, 1983). Further evidence for this theory was provided by Douse (1986), who reported that inorganic GSR particles may be found on the hands of suicides for up to 48 hours and potentially longer, A much greater time period than would normally be expected on a shooters hands. Inorganic GSR particles have even been recovered from the garments of a badly decomposed male who was discovered after being outside for 2 months, further strengthening the case for physical activity being the major cause of particles loss from a subject.

Zeichner and Levin (1995) reported the detection of inorganic GSR in samples collected from hair up to 24 h post discharge, if the hair was not washed. However, this time was seen to be greatly reduced in case work, where inorganic GSR was reported to persist on hands and hair for about the same period of time (hands 2.7h and hair 3.3h). However, other factors such as shootings occurring outside and wind affecting the deposition rate of GSR in hair were suggested as potential reasons for this (Zeichner and Levin,1995).

Machine washing or brushing of clothing has been reported to decrease considerably the amount and the density of inorganic GSR remaining on clothing (Vinokurov *et al.*, 2001).

2.10 Studies into contamination relating to the arrest and transfer of suspects

Gialamas *et al*. (1995) investigated the levels of GSR that were present on the hands of firearm carrying US police officers at the end of their shifts. Of the 43 officers that were tested only 3 of them had any “unique” particles on their hands, about 7% of the total. None of the officers were found to have more than one unique particle present on their hands. There were no GSR particles found on 25 of the officers in the study (about 58%). Gialamas *et al*. (1995) commented that although the potential for secondary transfer contamination was present, the low empirical numbers of GSR particles found on these non-shooting officers suggest the potential for this occurrence was relatively low. However, it must be taken into account that, GSR particles are lost from the surface of the hands relatively rapidly (depending on activities undertaken), therefore, taking samples at the end of shift may not be the most representative method of assessing transfer potential.

Pettersson (2003) showed that around 25% of samples collected from a selection of Swedish police vehicles contained 6 or more inorganic GSR particles. Samples collected from crime scene investigators also showed positive results in 25% of cases. One sample had as many as 16 inorganic GSR particles (none had handled a firearm for at least 12 hours previous to being sampled).

Berk *et al*. (2007) also looked at the possibility of secondary transfer within the police. 201 samples were collected from law enforcement vehicles and detention facilities in order to assess the probability of inorganic GSR present in these locations being transferred to those persons in detention. Both “unique” and “consistent” inorganic GSR particles were recorded. Out of the 201 samples 173 had no unique particles, while the other 23 contained 56 (2 tactical vehicles, 34 table type surfaces, 20 restraining bars). A second collection of samples suggested that there was no accumulation of particles over time. A blank study of persons reputed to have had no primary contact with firearms also presented one case of a “unique” particle being found. Berk *et al*. (2007) stated that although the possibility of unique GSR particles being transferred did exist the low number of unique particles observed suggested the potential for secondary transfer was relatively low.

Berk *et al*. (2007), Pettersson (2003) and Gialamas *et al*. (1995) have shown that the potential for secondary GSR transfer does exist within the police. Berk *et al*.(2007) and Gialamas *et al*.(1995) both also commented that the potential for this occurring was relatively low. However, the possibility of even one particle of GSR being transferred to a person who is to be tested for GSR must be seen as important, as such a small quantity of GSR has been used in court as evidence of a person discharging a firearm (o’Neill, 2007). A survey in 1990 by DeGaetano *et al*. (1990) showed that 41% of laboratories (two surveys of 200 US labs, 1st 51.0% response, 2nd 71.5% response) considered 1 “unique” particle to be conclusive evidence of GSR. Technically the presence of one “unique” particle (SEM-EDX) does confirm the presence of GSR; however, it is the opinion of the expert as to the particles significance that is of paramount importance (Degaetano and Siegel, 1990). Another survey of 50 labs by Singer *et al*. (1996) showed only one lab considered finding 1 particle of GSR enough to indicate a person had discharged or been in the vicinity of the discharge of a firearm (one indicated 2 particles were sufficient and all other stated that their criteria were under review or that interpretation was dependent on the particle type found). Even though it would seem that there has been a general move away from one particle being seen as much of a significant indicator, the existence of a secondary transfer potential of one particle must still be seen as relevant to the interpretation of analysis results. However, the level of significance such a particle holds as a piece of evidence is in the hands of the expert witness and it is an expert’s interpretation of any given sample that is of primary importance.

2.11 Summary

A review of various aspects of GSR has highlighted a number of areas worthy of consideration. The use of a “formal” classification system has been shown to be problematic. The introduction of numerous lead free and non toxic ammunitions as well as ammunitions which do not produce “characteristic” or “indicative” residues, combined with the potential for the misinterpretation of particles from environmental sources means that such an approach must be applied with great care. Particles produced by firearms through which numerous different ammunition types have been discharged may also produce particles which do not fit into a “formal” system.

The adoption of a “case by case” approach to GSR analysis must be seen as preferable. This is in agreement with Romolo *et al*. (2001). The comparison of samples collected from a victim, suspect or crime scene to firearms, bullets or cartridge cases has been shown to be an effective approach within a “case by case” framework. The application of statistical evaluation and the construction and utilization of databases have also been shown to be promising approaches to the evaluation of results.

The analysis of both inorganic and organic residues has been shown as a promising method of gaining as much information about any given sample as possible. A combination of these techniques with microscopic or even macroscopic analysis of particle/grain morphologies would be even more favourable. Therefore, this must be seen as the most ideal approach to sample analysis. Having as much information as possible must be seen to increase the probability of the accurate interpretation of results and also increase the evidential value of any given sample.

With regard to the analysis of trace elements/compounds within both organic and inorganic residues, the development of increasingly sensitive and selective analytical techniques has increased the analyst’s ability to gain a truer picture of the composition of such residues. With a large number of potential substances that maybe present in ammunition, further research in to the applicability of such analytical techniques to the analysis of GSR is required.

The interpretation of the results of any sample analysis by an expert witness is incredibly important. A further study into the guidelines which are applied to the interpretation of GSR by independent laboratories/experts would be incredibly valuable in terms of assessing the levels of consistency within the field.

2.12 Project aims summary

The findings of the preceding literature review suggest that both inorganic and organic residue materials are important in forensic investigations. However currently the analysis of OGSR has not been as thoroughly investigated as inorganic residue analysis. Therefore the aims of this research project were to;

1. Develop a GC/MS methodology for the analysis of compounds found in unburned ammunition propellant powders.

2. Develop a solid phase microextraction (SPME) protocol for the collection and analysis of the compounds found in unburned propellant powders.

3. To apply the developed methodologies to the extraction and analysis of a number of unburned propellant samples, from different ammunition types, to determine their chemical compositions. The aim of these analyse being to determine if it was possible to differentiate between the ammunition types based on their compositions.

4. To apply the developed SPME and GC/MS methods to the extraction and analysis of spent cartridge cases in order to determine whether it was possible to link the residues in the cases to unburned originator powders.

5. To use the developed methodologies to extract residues from shot fabric materials. This was carried out in order to determine whether it was possible to link these residues to those extracted from spent cartridge cases and to the originator propellant powders.

3 The development of a gas chromatographic method for the analysis of compounds found in association with unburned ammunition propellant powders and organic gunshot residues

3.1 Introduction

3.1.1 General principles of chromatography

Chromatography can be generally defined as a separation process based on the differential distribution of sample components between a moving (mobile phase) and a stationary phase (Levine, 2003). Figure 3 shows a basic schematic of a chromatographic system.

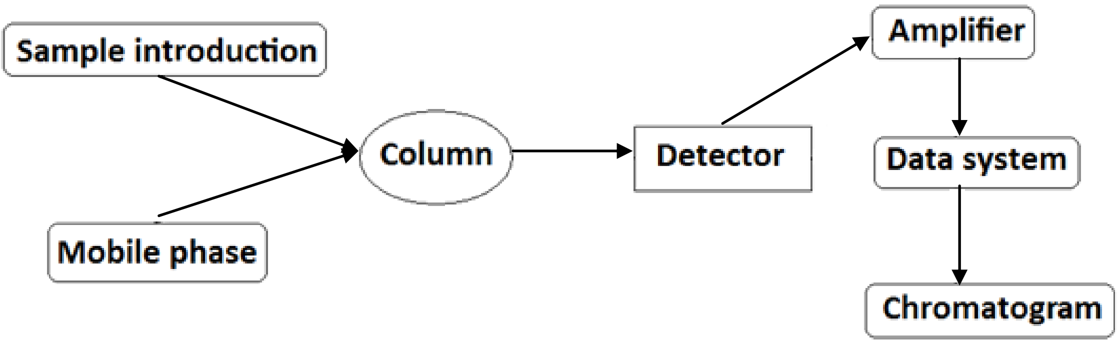


Figure 3: Schematic of a chromatographic system.

A typical chromatographic system consists of the following components;

- Sample introduction: The Sample that is to be separated by the chromatographic system is introduced onto the column using a method such as an injector.

- Mobile phase: This is the medium used to carry the sample introduced to the front of the column through the system. This might be a gas or liquid depending on the type of chromatography employed.

- Column: The element of the chromatographic system that separates the introduced sample into its component parts.

- Detector: Equipment that responds to changes in the system caused by the separated solutes as they move through the environment of the detector

- Amplifier and data system: Transforms the signals produced by the detector into a useable format, the chromatogram

•Chromatogram: A graphical representation of the data produced by the detector.

3.1.2 Chromatographic separation

Figure 4 illustrates the chromatographic separation of a mixture (containing solutes A and B). As solutes A and B move though the column (under influence of the mobile phase) if A has a greater affinity for the stationary phase than B it will be retarded to a greater degree. This will lead to solute B eluting from the column before solute A and, therefore, separation is achieved (Harris, 2007). At any given point a molecule of solute is either stationary, absorbed into or adsorbed onto the stationary phase or travelling along the column length at a given velocity in the mobile phase (Miller, 2005).

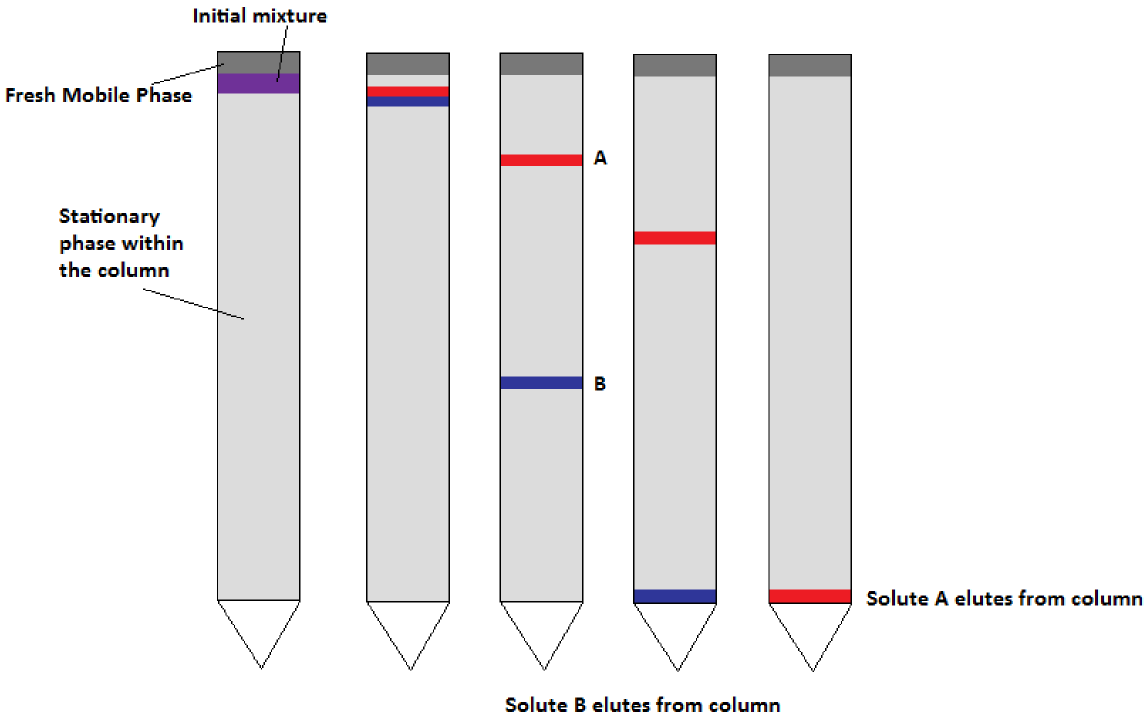


Figure 4: Visual representation of chromatographic separation.

3.1.3 Types of chromatographic separation

Table 11 contains a summary of a number of categories of chromatography based on the mechanisms of solute and stationary phases.

Table 11: Descriptions of chromatographic separation techniques (Harris 2007, Fifield and Keeley 2000)

Separation type	**Description**
Surface adsorption	Involves a solid stationary phase and a liquid mobile phase. The solute is adsorbed onto the stationary phase's solid particles. The more strongly the solute is adsorbed the slower it will travel through the column. Relative polarities of both the stationary phase and the solute determine the rate of movement of the solute through the column
Partition	A liquid stationary phase is bonded to solid surface, typically silica SiO_2 based (as in the inside of a GC column). Solute equilibrates between solid phase and mobile phase which is flowing gas in GC. The movement of the solute is determined solely by its relative solubility in the two phases or by its volatility if the mobile phase is a gas.
Ion Exchange chromatography	Anions are covalently attached to a permeable polymeric solid phase (usually a resin in this type of chromatography). The solid phase contains fixed charged groups and mobile counter ions which can exchange with ions of the Solute as it is carried through the structure.
Molecular exclusion	In gel filtration or gel permeation chromatography molecules are separated by size. Separation occurs based on the variation in the extent to which solute molecules can diffuse through an inert but porous stationary phase. Larger solutes move though more quickly. Pores are small enough to not interact with larger particles but capture smaller ones.
Affinity	Most selective kind of chromatography. Specific interactions between one kind of solute molecule and a second molecule that is conveniently bonded to the stationary phase.

Note: both partition and surface adsorption may occur simultaneously depending on nature of the mobile and stationary phase, solid support and solute (Harris 2007, Fifield and Kealey 2000).

3.1.4 The chromatogram

The chromatogram is a graph showing a detectors response as a function of elution time. Retention time t_r is the time from a compound's injection onto the column until it reaches the detector. Retention volume V_r is the volume of mobile phase required to elute a particular solvent from the column. Non-retained mobile phase travels through the column in the fastest possible time t_m or volume V_m . The adjusted retention time/volume $t'_{r/}$ V'_r is the additional time/volume, beyond that of the unretained mobile phase and is calculated by subtracting the non-retained mobile phase time/volume from the recorded time/volume of compound peak RT (Harris, 2007). This is graphically represented in figure 5

$$t'_r = t_r - t_m$$

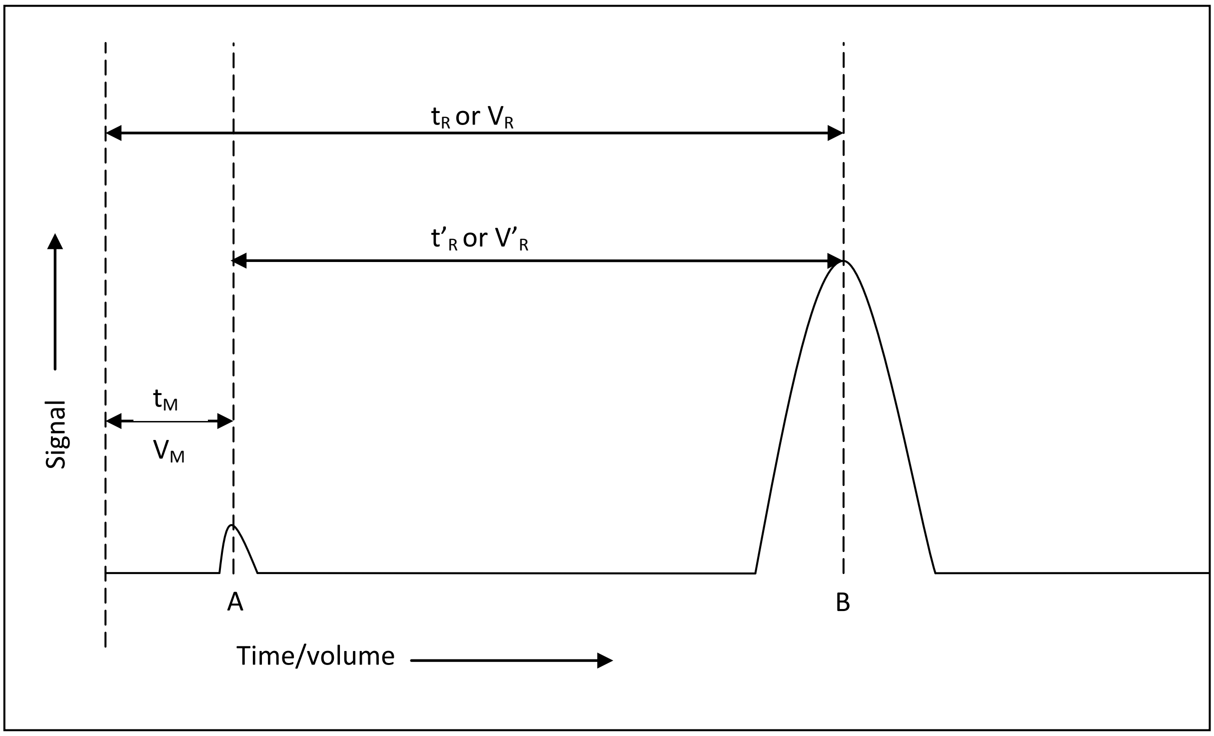


Figure 5: Schematic of gas chromatogram showing the measuring of retention times and volumes

The amount of time that any given analyte takes to travel through a column is spent going through the interstitial space in the column (assuming other volumes in connections between the columns and the detector and the like are negligible) and interacting with the stationary phase (not moving downstream). Thus the total time or volume can be broken into two parts, interspatial volume of the column occupied by the mobile phase and through which every analyte must pass (V_M), and the mobile phase that flows while the analyte is immobile ($K_C V_S$)

$$V_R = V_M + K_C V_S$$

Where:

V_R = total volume

V_M = mobile phase volume

V_S= stationary phase volume

K_C = is a partition coefficient called the distribution constant

3.1.5 Gas chromatography

GC has become the premier technique for the separation and analysis of volatile compounds and is the most widely used in the world. It is a great complimentary technique for high performance liquid chromatography (HPLC), which can be used for non volatiles not suitable for GC analysis. GC can be generally used up to 350°C (high temperature GC up to 450°C has been used) and an upper molecular weight limit of 600 Daltons (HPLC being used for higher molecular weight compounds). Table 12 summarises the advantages and disadvantages of gas chromatography (Miller, 2005).

Table 12: Advantages and disadvantages of gas chromatography (Miller, 2005).

Advantages	**Disadvantages**
1. Efficient, selective and widely applicable	1. Samples must be volatile
2. Easily combined with MS	2. Not suitable for thermally labile samples
3. Fast	3. Difficult for large samples
4. Inexpensive and simple	
5. Easily quantitated and automated	
6. Requires only small sample sizes	
7. Non destructive detectors available	

3.1.6 Components of gas chromatography

A schematic of a generic gas chromatography system can be found in Figure 6. The element of this system are discussed below

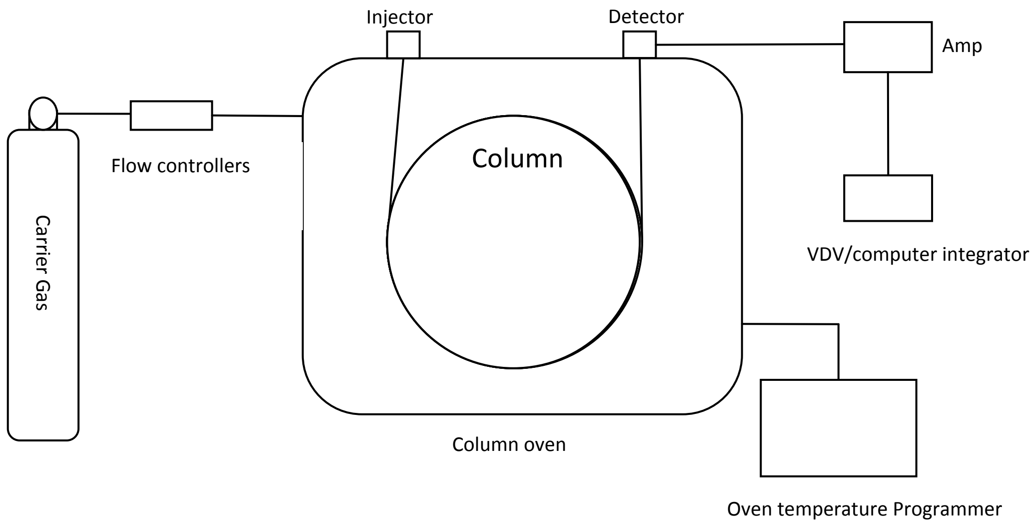


Figure 6: Schematic of a typical gas chromatography system.

3.1.6.1 Sample introduction

Samples are introduced into the GC system via a heated injection port. Injection is most commonly carried out through a self sealing rubber septum using a microsyringe. Usually there is the option of using split or spiltless injection. A schematic of a typical split injection port system is presented in figure 7. On-column injection may also be considered.

3.1.6.1.1 Split injection

As the sample is vaporised in the injection port only a fraction (0.2-2%) (Harris, 2007) of the vapour is allowed to enter onto the column. The rest is carried out through a split or purge valve. The advantages of this method are that it is simple, allows small volumes to enter the column as required for capillary columns and the flow rate up to split point is fast and so provides high resolution separation. “Neat” samples can be introduced with large split ratios. Dirty samples can be introduced by putting a plug of deactivated glass wool in the liner to trap non volatiles. For samples with analyte concentrations of greater than 0.1% split injection is usually preferable (Harris, 2007). However, split injections are not preferred for trace analysis as only a fraction of the sample is getting onto the column (Miller, 2005)

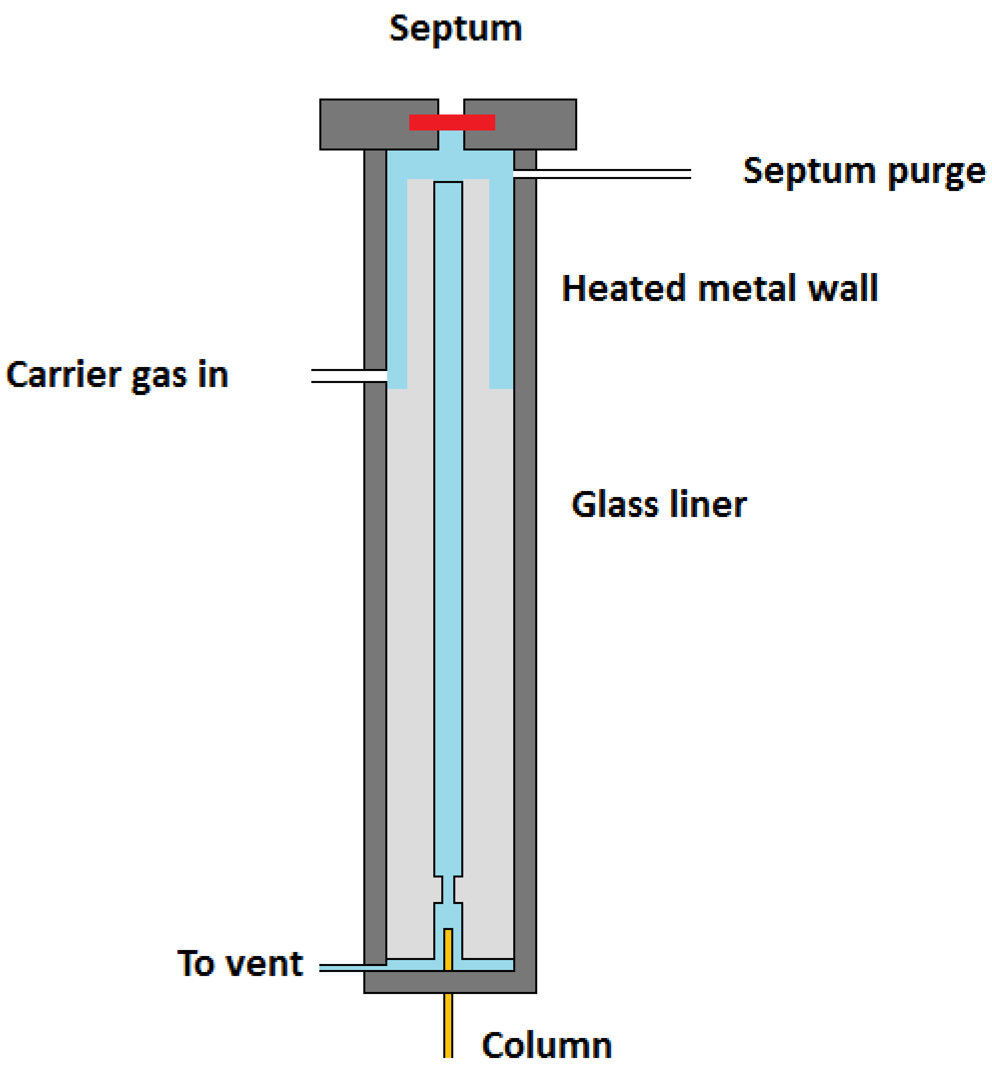


Figure 7: Schematic of a typical injection port.

3.1.6.1.2 Splitless injection

For trace analysis Splitless or on-column injection methods are preferable. Splitting can also discriminate against high molecular weight solutes, therefore, making the proportion of the sample entering the column unrepresentative of the whole. This should also be considered when selecting which injection method to apply.

With splitless injection, the whole of the injected sample is vaporised and carried onto a relatively cold column. This allows the volatile solvent to travel thorough the column while the solutes remain condensed at the front of the column, being refocused into a narrow band with residual solvent. The big advantage of splitless injection is the increased sensitivity compared to a split mode. Typically 20 to 50 times more sample enter the column (Harris, 2007).

3.1.6.1.3 On column injection

On-column injection is generally used for samples that decompose above their boiling points and is preferred for quantitative analysis. This type of injection is achieved by having the injection syringe needle precisely aligned with the column. The sample is introduced directly onto the column and not via a hot injector. A low initial temperature is used to condense the sample in the column, raising this temperature then initiates the chromatography (Harris 2007).

On-column injection does not provide as good a resolution as split or splitless methods. However, it is more preferable for trace analysis and provides good quantification (Miller, 2005).

3.1.6.2 Mobile phase/carrier gas

With Gas chromatography the mobile phase is a gas, referred to as the carrier gas. The most common carrier gases are nitrogen, helium and hydrogen. Often chosen for their inertness as their only purpose is to carry the analyte vapours through the column (Harris, 2007).

3.1.6.3 The column

The injected sample is moved through the injection port and onto the column by the carrier gas. The column contains the stationary phase that is usually a non volatile liquid held on a solid support. The sample is then moved through the column by the carrier gas (Miller, 2005).

Separation of the analytes in the column is based on differences in boiling point, solubility and adsorption. There are two categories of stationary phases; gas-liquid chromatography and gas-solid chromatography. In gas-liquid chromatography the stationary phase is a high boiling point liquid and with such a phase sorption is the key cause of separation. In gas-solid chromatography the stationary phase is solid and adsorption plays a key role in separation (Fifield and Kealey, 2000).

The vast majority of gas chromatographic analysis is carried out using capillary open tubular columns made of fused silica and coated with polyimide. Open tubular columns offer high resolutions, short analysis times and greater sensitivity than alternative column types (such as packed columns) (Harris, 2007). Figure 8 is a diagram of a typical open tubular capillary column.

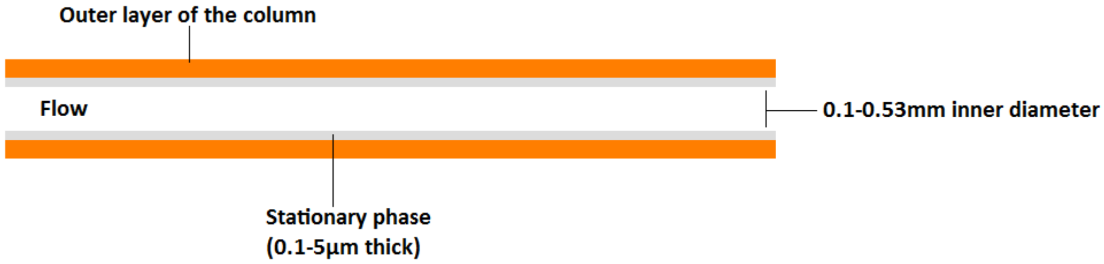


Figure 8: Schematic of a typical open tubular capillary column (Harris, 2007).

Open tubular column lengths vary from 15-100m. It is the unrestricted flow of carrier gas through the centre of capillary columns that allows them to be made so long. Columns have inner diameters of between 0.1-0.53mm (Harris, 2007). Packed columns may also be used with GC. These columns do not have high resolving powers but they are cheap, robust and have high sample capacities, allowing simple injection systems to be used. The resolving power of capillary columns is far greater than that of packed columns, up to 150,000 plates per 25 metres, compared to a few thousands for a 2m packed column (Fifield and Kealey, 2000).

There are a large number of types of stationary phase coatings available for open tubular columns (Table 13). However, modern open tubular columns are so efficient, and auxiliary techniques such as mass spectral (MS) detection so effective, that they have removed the necessity to spend time finding the best stationary phase. The polarity of the coating should though be taken into consideration and be similar to that of the compounds of interest to be analysed (Grant, 1996).

Table 13: Common stationary phases in capillary GC (Grant 1996).

Stationary phase	**Identity**	**Polarity**	**Maximum temp. (°C isothermal)**
OV101,OV1,SP2100,SPB1,HP-1,AT-1,DC200, SE30, CPSIL5CB,007-1,DB1,BP-1,RTx-1,BP-1	Poly(methylsiloxane)	Low	300-350
OV73, SE52,SBP-5,BP-5,007-2,DB-5,HP-5,RTx-5, CPSIL8CB,AT-5	95% Dimethyl 5% phenyl Poly (methylsiloxane)	Low	300
007-1701,db-1701,BP-10,AT-1701,CPSIL19CB,SBP-1701,RTx-1701	86% Dimethly, 7% phenyl 7% Cyanopropyl polysiloxane	Low/medium	275
OV-202,OV-210,OV-215,SP-2401	Poly(methyl-trifluoropropylsiloxane)	Low/medium	275
DB-225,BP-225,CPSIL43CB,HP-225,OV-225,RTx-225,SP2300,AT-225, 007-225	50% Dimethyl, 25% phenyl, 25% Cyanopropyl Polysiloxane	Medium	200
007-CW,DB-WAX,supelco-10, HP-20M,stabilwax, CPWAX52CB	Polyethylene glycol	Medium	250
BP-21,DB23,FFAP,DBFFAP, Nukol,CPWAX58CB,AT-1000,BP-21	Polyethyleneglycol Nitroterephthalic acid Ester (‘free fatty acid phase’)	Medium/high	250
007-23,DB-23,SP-2330, RTx-2330, CPSIL88,AT-SILAR, BPX-70	100% Cyanopropyl	High	225

3.1.6.3 .1 In column band broadening and the Van Deemter equation

Van Deemter and his co-workers suggested a kinetic approach to rate theory in chromatography. Identifying several effects which contribute to band broadening within columns (Miller, 2005). This work has led to many improvements in column design originating from the knowledge of how to optimise the column parameters presented in the Van Deemter equation (Karasek and Clement ,1988).

The Original equation expressed band broadening in terms of plate height, *H,* as a function of the linear gas velocity.

$$H = A + \frac{B}{u} + Cu$$

Where;

A is eddy diffusion/multiple paths

B is longitudinal molecular diffusion

C is mass transfer in the stationary liquid phase

u is the linear velocity

By minimising these three constants the amount on band broadening within a column can be reduced (Miller, 2005).

Eddy Diffusion/multiple paths (A)

This is more relevant to packed rather than open tubular columns. Some paths for molecules through a packed column are longer than others. Therefore, a number of molecules entering a column at the same time will elute at different times based on the paths they take though the column (Miller, 2005). This term is, however, a very simplistic representation of what is a combination of numerous complex effects (Harris, 2007).Term A can be defined as;

$$A = 2\lambda d_p$$

d_p= diameter of particles packed in the column

λ= the packing factor

Longitudinal molecular diffusion (B)

The equation governing this term is

$$B = 2\psi D_M$$

Where;

D_M= diffusion coefficient for the solute in the mobile phase

ψ= obstruction factor that allows for the nature of packed beds.*

*As open tube column such as those used for this investigation are not packed the equation for this term does not include ψ.

A small value for the diffusion coefficient is desirable as this will lead to less band broadening. This can be achieved in GC by using carrier gas with larger masses such as nitrogen. However, such a choice of carrier gas is usually undesirable for other reasons. A larger linear velocity will also minimise the contribution of term B to overall band broadening. As high velocities are usually preferable in GC methods, term B tends not to be an important contributor to overall band spreading (Harris (2007), Miller (2005)).

Mass transfer (C)

Term C addresses the transfer of solute into and out of the stationary phase. It is represented by the following equation

$$C = \frac{8}{\pi^2}\frac{k}{(1+k)^2}\frac{d_f^2}{D_s}$$

Where;

d_f = average film thickness of the liquid stationary phase

D_s = the diffusion coefficient

k = retention factor

In order to minimise the effects of term C on band broadening, film thickness should be small and the distribution coefficient large. Rapid diffusion through thin films allows solute molecules to stay closer together (Miller, 2005).

In capillary GC column mass transfer in the mobile phase must also be considered. This extended Van Deemter equation includes two C terms, C_s (mass transfer in stationary phase)and C_m (mass transfer in mobile phase), which makes the equation

$$H = A + \frac{B}{u} + (C_M + C_S)u$$

C_M is represented by the equation

$$C_M = \frac{(1 + 6k + 11k^2)d_c^2}{96(1 + k)^2 D_M}$$

Where;

d_c = diameter of the column

k = retention factor

There is a range of mobile phase velocities across the diameter of the column because of the frictional resistance at the walls. Smaller diameter columns minimise broadening because the mass transfer is relatively small. Larger diffusion coefficients (D_M) promote mixing and, therefore, decrease broadening (Miller, 2005).

3.1.6.4 Column oven

Chromatographic retention properties are critically dependent on the columns temperature. Therefore, it is essential that this parameter is accurately controlled. This function is performed by the column oven. Most ovens are electrically heated with forced air circulation by a fan. The usual temperature range is from ambient to 400-500°C (Grant, 1996). By manipulating the temperature programme of any given sample analysis the separation of analytes can be modified.

3.1.6.4.1 Temperature programming

The effect of column temperature on chromatographic retention is pronounced in that there is an inverse exponential relation with the distribution constant/partition coefficient. As temperature is increased retention times are decreased. Temperature programming, which is a form of gradient elution uses this relationship to improve the resolution of mixtures and shorten the overall analysis time by speeding up the elution of high boiling point compounds (Fifield and Kealey, 2000). An increase in temperature will increase the rate at which analytes migrate towards the end of the column, whereas the opposite is true of a temperature decrease. Slowing the rate at which analytes travel through a column will increase the time period during which interactions may occur between analytes and the column stationary phase and may, therefore, improve separation (Harris, 2007).

3.1.6.5 Detectors

On leaving the end of the column the sample is then introduced into the detector. The purpose of a detector is to monitor the carrier gas as it leaves the column and to respond to any changes in its composition as analytes are eluted (Fifield and Kealey, 2000). There are numerous detector types that can be paired with gas chromatography and these are summarised in Table 14.

Table 14: Detectors that maybe coupled to gas chromatographs (Fifield and Kealey, 2000).

Detector	Minimum detection quantity (gs^{-1})	Linear range	Temperature limit (°C)	Remarks
Thermal conductivity (TCD)	10^{-9}	10^{4}	450	Non – destructive, temperature and flow sensitive
Flame Ionisation (FID)	10^{-12}	10^{7}	400	Destructive, excellent stability
Electron Capture (ECD)	10^{-13}	10^{2} -10^{3}	350	Non – destructive, easily contaminated, temperature sensitive
Phosphorus	10^{-14}	10^{5}	400	Similar to flame ionisation
Nitrogen	10^{-13}	10^{5}	400	Similar to flame ionisation
Flame photometric (FPD)				
(P compounds)	10^{-12}	10^{4}	~250	Signal approximately proportional to square of S concn.
(S compounds)	10^{-10}	-	~250	

3.1.7 Gas Chromatography/mass spectrometry (GC/MS)

3.1.7.1 Definition

GC-MS is an established technique for the analysis of complex mixtures, holding a prime position in analytical chemistry because of its combination of sensitivity, wide range of applicability and versatility. Alone chromatography is excellent at separating out the components of a given mixture, but it does not allow the definitive identification of said components with any degree of certainty. This is because the only criterion that can be used is retention time and any number of compounds could potentially elute at any given time. Therefore, MS acts as a complimentary technique to GC, providing additional information about the chemical structures of analytes. (Johnstone and Rose, 1996).

Open tubular (OT) columns are well suited for use in system where GC is coupled to MS due to the flow rate of 1-2mL/min. A direct interface is used, that is the end of the column is extended from the GC directly into the ion source of the MS. Due to the low flow rate and the high vacuum pumping the conditions required by the MS can easily be maintained (Harris, 2007).

3.1.8 Basic principles of MS

Analytes eluting from the end of the GC column are ionised and fragmented by a variety of means. Analysis is carried out on the range of mass fragments that are produced (Fifield and Kealy, 2000). Ionic species are easier to manipulate than neutral ones as they can be affected by magnetic and electrostatic fields. Ions are separated by a mass analyser based on their mass to charge ratio *m/z*. The ion current generated is plotted versus *m/z* ratio to produce a mass spectrum. This spectrum is characteristic of the original analyte and can be used for both qualitative and quantitative analysis. Usually the charge of the ion is +/- 1 and, therefore, the *m/z* ratio is equal to the molecular weight for that ion (Miller, 2005). Separation occurs down to a difference of <1 Dalton (Levine, 2003). Figure 9 shows a schematic of a basic MS system.

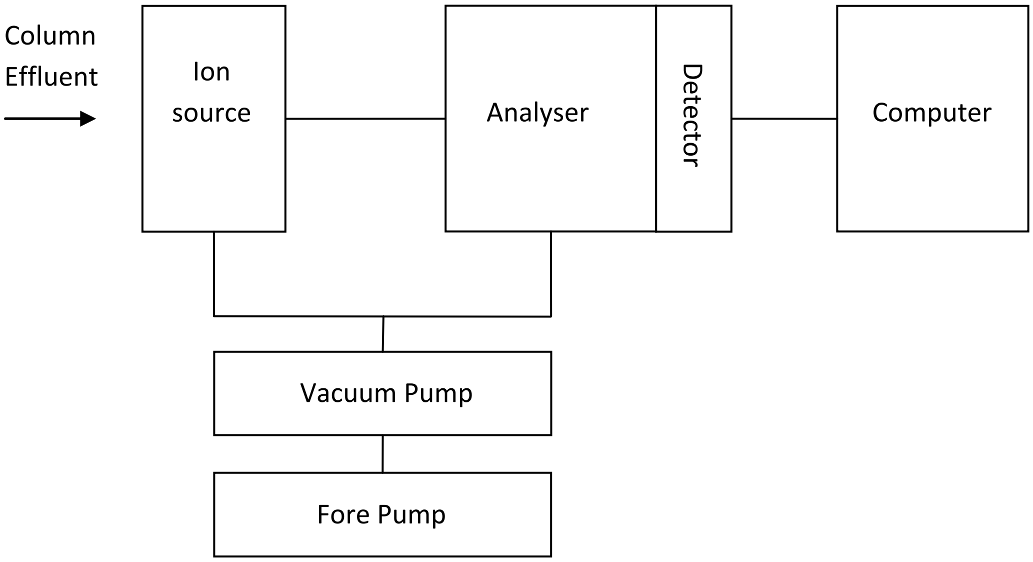


Figure 9: A schematic of mass spectroscopy system.

3.1.9 Components of MS

3.1.9.1 Ion Sources

There are several ion sources available on the market and the following table provides an overview of the most common. Both negative and positive ions are produced in most sources but negative ions are more commonly used. Table 15 contains details of ions sources available.

Table 15: Ions sources commonly available for various chromatographic systems (Miller, 2005)

Chromatographic system	Ionization method	Upper Mass Limit (Daltons)	Molecular ion (M) or fragmentation (F)
Gas chromatograph	Electron impact (EI)	1,000	F
	Chemical ionisation (CI) (both negative and positive (NCI/PCI)	1,000	M
High performance liquid chromatography	Particle beam	10,000	F
	Thermospray ionisation (TSI)	2,000	M
	Electrospay ionisation (ESI)	200,000	M
	Atmospheric pressure ionisation (API)	10,000	M
	Atmospheric pressure photoionisation (APPI)	10,000	M
	Atmospheric pressure chemical ionisation (APCI)	10,000	M
Other	Fast atom bombardment (FAB)	10,000	F
	Matrix-assisted laser desorption ionization (MALDI)	500,000	M

As Electron impact ionisation system has been used in this project, its principles will be outlined in more detail below.

3.1.9.1.1 Electron impact ionisation (EI)

EI is the oldest and most common ionisation method. In the EI ion source electrons are emitted from a heated filament (usually tungsten at 70eV) and bombard the vaporised analyte molecules (AM), causing ionisation and the loss of an electron.

$$AM + e^- \rightarrow AM^+ + 2e^-$$

(Where AM is the analyte molecule and e^- is an electron). The molecular ion (AM^+) has a mass to charge ratio (*m/z*) of the molecular mass and is, therefore, named the molecular ion. Depending on the structure of the molecular ion and the amount of energy it has absorbed, it may travel through the analyser unchanged, or it might fragment into smaller fragments (Miller, 2005).

EI is considered a hard ionisation technique (for example in comparison to chemical ionisation) and can produce molecular ions with sufficient excess energy to cause fragmentation by the ejection of a neutral particle (N), creating a fragment ion ($A^{+\bullet}$ or A^+). A neutral molecule gives a radical cation and the fragment ion may be either a cation or a radical cation (contains one or more unpaired electrons). The ejected neutral molecule maybe a radical or a neutral molecule, as below;

$$M - e^- \rightarrow M^{+\bullet} \rightarrow A^+ + N^\bullet$$

or

$$M - e^- \rightarrow M^{+\bullet} \rightarrow A^{+\bullet} + N$$

If the fragment ion has sufficient excess internal energy remaining, then further decomposition may occur, leading to the formation of new fragment ions (B^+ and C^+, etc.) until there is insufficient excess internal energy in any of the ions for further decomposition to occur.

$$M^{+\bullet} \overset{N^\bullet}{\overset{\uparrow}{\longrightarrow}} A^+ \overset{N_a}{\overset{\uparrow}{\longrightarrow}} B^+ \overset{N_b}{\overset{\uparrow}{\longrightarrow}} C^+ \longrightarrow \text{etc.}$$

This series of decompositions when elucidated from a mass spectrum is known as a fragmentary pathway. However, a given molecular ion may decompose along more than one pathway. All of these pathways combined form a fragmentation pattern that is characteristic of a given analyte. These pathways must be considered in context to the specific energy (excess energies of the ions) and times (time between ion formation and detection) as it is these parameters that can alter them. Ions created by the source will continue through the analyser while free radicals are pumped off in the vacuum (Johnstone and Rose, 1996). Figure 10 shows a schematic of a EI source.

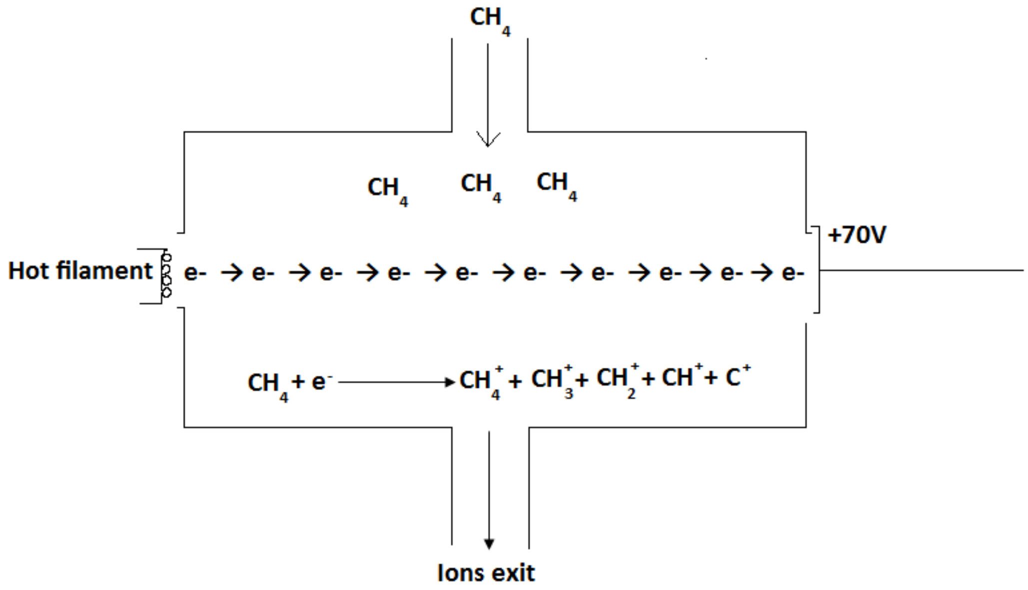


Figure 10: Schematic of an electron impact ion source (ionising methane) (Karasek and Clement, 1988).

An EI spectrum is scaled relative to the most abundant peak (the base peak). The pattern of ions which specific compounds produce has been thoroughly studied and the identification of compounds from the interpretation of mass spectra is possible for many compounds. Figure 11 shows an annotated example of a mass spectra (Harris, 2007).

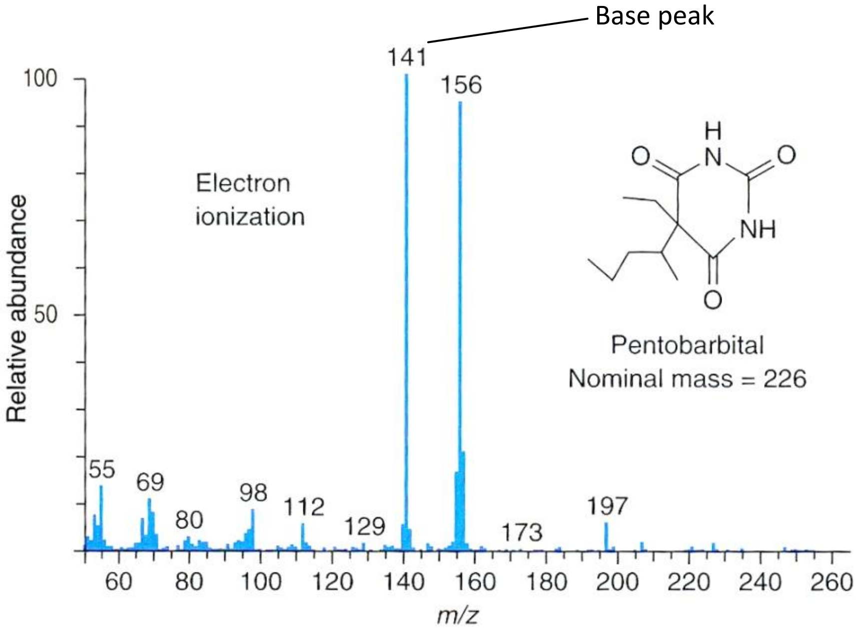


Figure 11: Example of a mass spectrum (Harris, 2007).

3.1.9.2 Analysers

Following ionisation the analyte travels into the mass analyser. The most common analyser methods and their attribute are summarised in Table 16.

Table 16: Types and specifications of MS analysers (Miller, 2005)

Analyser Type	Upper Mass range	Resolution
Sectors (magnetic and electric)	10^4	10^2 -10^5
Quadrupole	10^4	10^2 -10^4
Ion trap	10^5	10^3 -10^4
Time of flight (TOF)	$\geq 10^5$	10^3 -10^4
Fourier transform ion cyclotron resonance (FT-ICR)	$\geq 10^4$	10^4 -10^6

3.1.11 Aims

The aim of work presented in this section was to develop a GC/MS methodology that would allow the separation and detection of 27 compounds reported in the literate to be present in unburned ammunition (page 7).

3.2 Materials and methods

3.2.1 Solvents and standards

Diethyl phthalate, Carbazol, Triacetin, 3,4 – Dinitrotoluene, 3 – Nitrotoluene, 2,4 – Dinitrotoluene, 2,6 – Dinitrotoluene, 2,3 – Dinitrotoluene, Diphenylamine, N – Nitrosodiphenylamine, 4 – Nitrodiphenylamine, 2 – Nitrodiphenylamine, m-Cresol, o-Cresol, p-Cresol, Dimethyl phthalate, Dibutyl phthalate, 2-Nitrotoluene, 4-Nitrotoluene, Dimethyl sebacate, 2,4-Dinitrodiphenylamine,Urethane, Camphor, 2,3-Dimethyl-2,3-Dinitro butane, were sourced from Sigma Aldrich (St. Louis, MO, USA). Tetryl, Nitroglycerin, and Ethyl Centralite were purchased from LGC Standards (Middlesex, UK). Structural information on these compounds can be found in section 9.

Working standard mixtures were prepared in analytical grade methanol purchased from Fisher Scientific (Leicester, UK).

3.2.2 Production of the standard mixture

1000µgmL^{-1} standards of each of all of the compounds were either bought in at this concentration or made up from pure solid standards by dilution in methanol. All of the compounds were then mixed together and diluted with methanol to a concentration of 25µgmL^{-1}. This standard mixture was then used to assess changes made to the existing chromatography method.

3.2.3 Gas chromatography

The GC was an Agilent Technologies 6890N and the MS was an Agilent 5975MS. A J&W Scientific HP5-MS (30M x 0.25mm x 0.25µm) column was used. Run conditions were as follows; thermal desorption of the SPME fibres was carried out using an injector temperature of 250°C with splitless injection. A SPME/direct inlet linear was purchased from Sigma Aldrich in order to minimise band broadening. The initial oven temperature was 50°C, a temperature ramp of 9,8,7 and 6°C per minute to 200°C were investigated and are discussed below. After reaching 200°C temperature was raised by 20°C per minute until 300°C was reached. The carrier gas was Helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England).

3.3 Results and Discussion

3.3.1 Chromatograms

Out of the 28 compounds present in the mixture 27 of these were represented on the final chromatogram. N-nitrosodiphenylamine is thermally labile and has been reported to break down into DPA in the injector port of the GC system, it is denitrosated to diphenylamine in the heated zones of the chromatograph (Via and Taylor, 1992). Therefore, N-nitrosodiphenylamine is represented by DPA in the DPA peak. This explains why in the compound mixture analysis the DPA peak is much larger than any other compound.

3.3.2 Temperature programmes

Chromatograms from runs carried out using the first developed method (temperature increase to 200°C at 9°C per minute) contained 25 peaks representing 27 compounds (Figure 12). Four compounds were seen to co-elute based on information gained from running each of the compounds separately and recording their retention times. The data provided by the NIST mass spectral database made it possible to discriminate between the two compounds in each of the co eluting peaks.

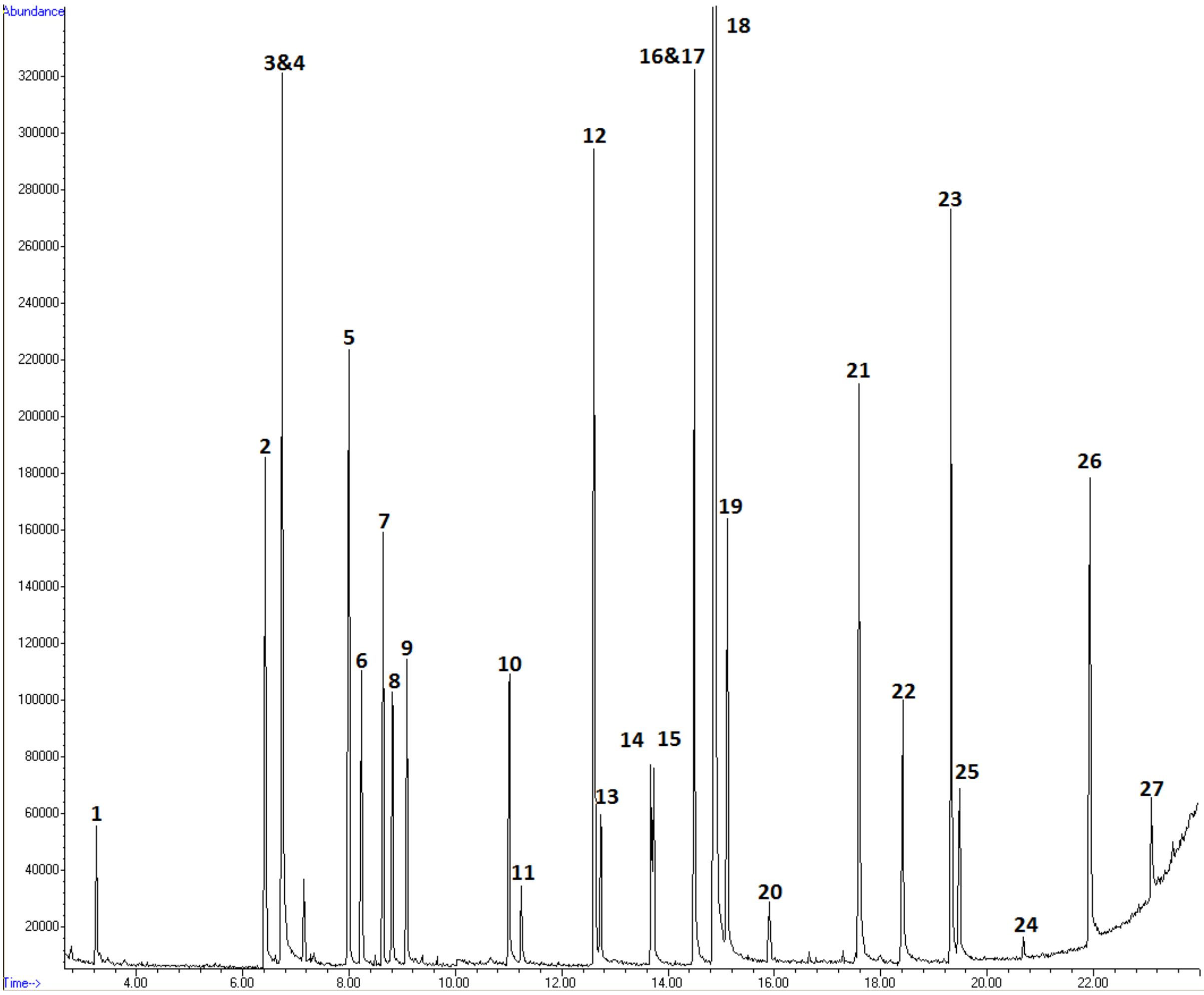


Figure 12: chromatogram from analysis of standards using initially developed GC methodology; 1. urethane, 2. O cresol, 3&4. M cresol & P cresol, 5. Camphor, 6. 2-Nitrotoluene, 7. 2,3 – dimethyl – 2,3 – dinitrobutane , 8. 3-Nitrotoluene, 9. 4-Nitrotoluene, 10. triacetin, 11. Nitroglycerin, 12. Dimethylphthalate, 13. 2,6 – Dinitrotoluene, 14. 2,3 – Dinitrotoluene, 15. 2,4 – Dinitrotoluene, 16&17. 3,4 – Dinitrotoluene & Diethylphthalate, 18. Diphenylamine (including n-nDPA), 19. Dimethylsebacate, 20. 2,4,6 Trinitrotoluene, 21. Carbazole, 22. Ethyl centralite, 23. Dibutylphthalate, 24. 2 – Nitrodiphenylamine, 25. Tetryl, 26. 4 – Nitrodiphenylamine, 27. 2,4 – Dinitrodiphenylamine

Chromatograms produced from the GC methods involving temperature programmed increases of 8 and 7°C produced slightly improved resolutions but no additional compounds were separated. However, the method with 6°C incremental increases allowed the separation of 3,4 – Dinitrotoluene and Diethylphthalate (Figure 13). The two compounds were not base line separated, however, the method was deemed to be suitable for this research project as it was concerned with qualitative and not quantitative analysis. P and M cresol were not separated physically but as stated above could still be discriminated by reference to the NIST MS database.

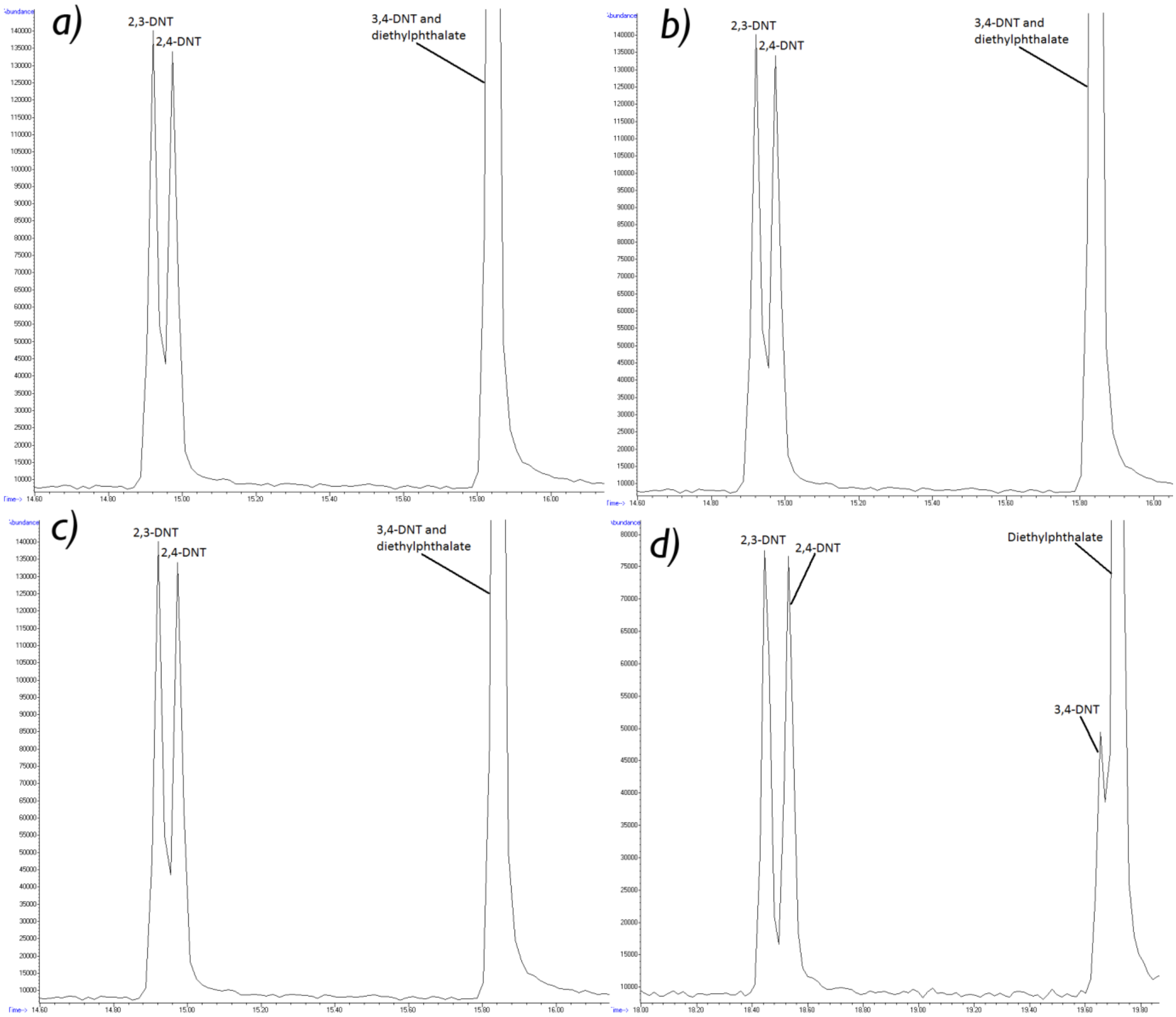


Figure 13:comparison of separations of 2,3-DNT 2,4-DNT, 3,4-DNT and diethylphthalate: a) 9°C per min, b) 8°C per min. c) 7°C per min and d) 6°C per min.

Figure 14 is a full chromatogram of the method containing 6°C incremental increases. This method was used for all GC analysis throughout the project. Figure 15 contains an example mass spectra used by the NIST database to identify the peaks in the chromatogram (along with retention time data from single compound standard runs).

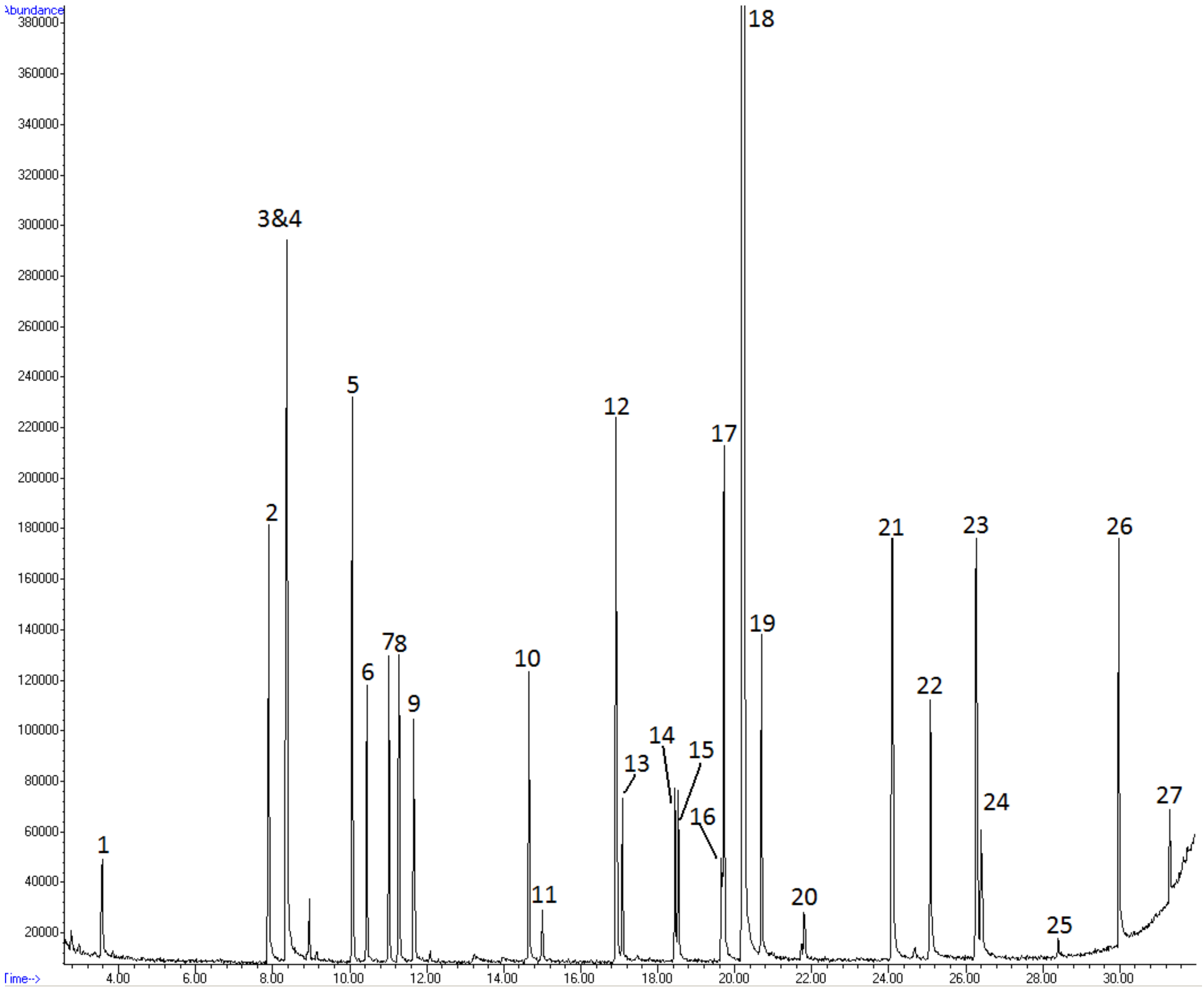


Figure 14: chromatogram from analysis of standards using improved GC methodology; 1. urethane, 2. O cresol, 3&4. M cresol & P cresol, 5. Camphor, 6. 2-Nitrotoluene, 7. 2,3 – dimethyl – 2,3 – dinitrobutane , 8. 3-Nitrotoluene, 9. 4-Nitrotoluene, 10. triacetin, 11. Nitroglycerin, 12. Dimethylphthalate, 13. 2,6 – Dinitrotoluene, 14. 2,3 – Dinitrotoluene, 15. 2,4 – Dinitrotoluene, 16. 3,4 – Dinitrotoluene, 17. Diethylphthalate, 18. Diphenylamine (including n-nDPA), 19. Dimethylsebacate, 20. 2,4,6 Trinitrotoluene, 21. Carbazole, 22. Ethyl centralite, 23. Dibutylphthalate, 24. 2 – Nitrodiphenylamine, 25. Tetryl, 26. 4 – Nitrodiphenylamine, 27. 2,4 – Dinitrodiphenylamine

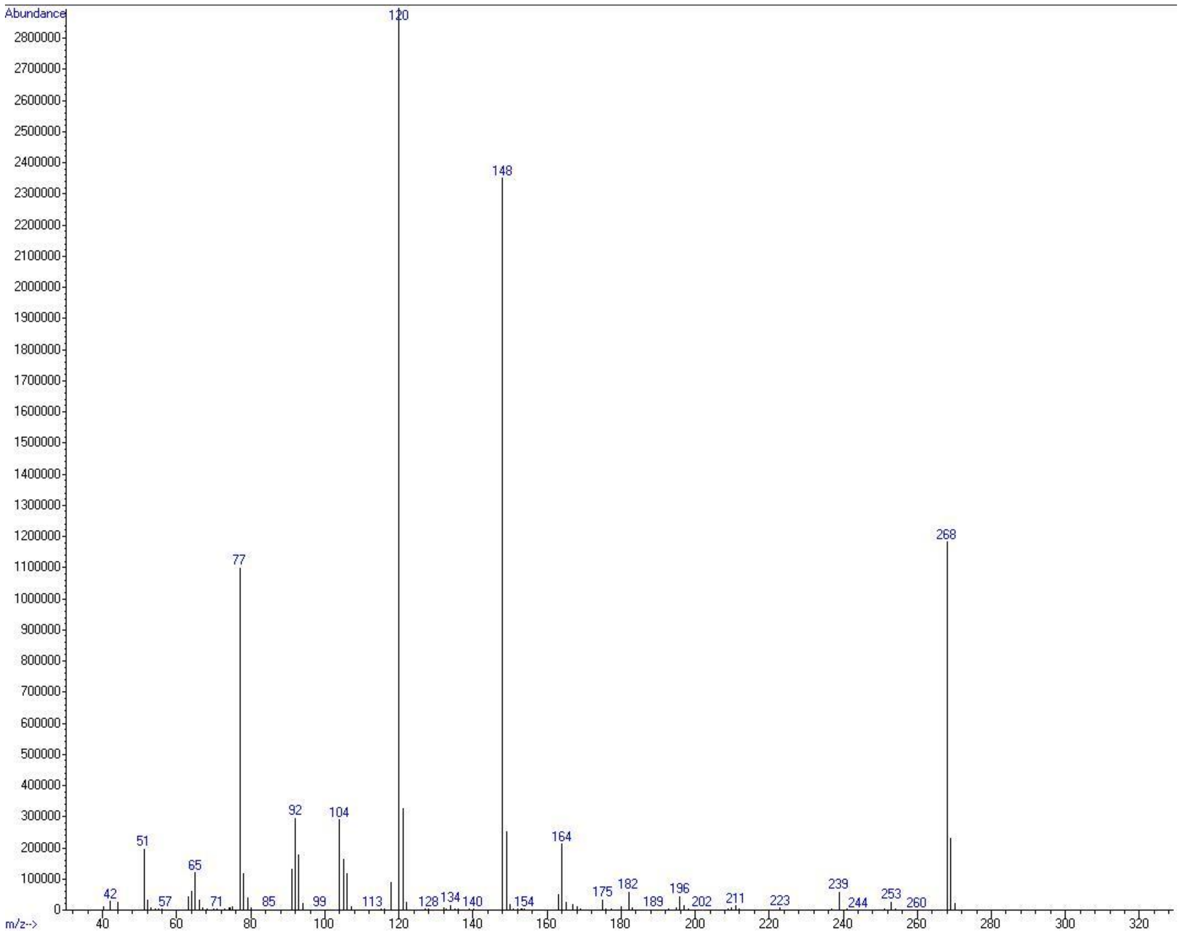


Figure 15: Example mass spectrum for ethyl centralite

3.3.3 Compound retention times

Table 17 contains a list of all the compounds recorded in the final chromatograms. These times were based on the average of the retention times recorded for three consecutive analyses of the same 28 compound mixture sample.

Table 17: Retention times and standard deviations for compounds using the developed GC methodology

Compound	Mean retention time (n=3)	Standard deviation (n=3)
Urethane	3.63	0.0231
O cresol	7.94	0.0032
M cresol	8.42	0.0049
P cresol	8.40	0.0030
Camphor	10.08	0.0010
2-Nitrotoluene	10.47	0.0006
2,3 – dimethyl – 2,3 – dinitrobutane	11.04	0.0021
3-Nitrotoluene	11.31	0.0000
4-Nitrotoluene	11.69	0.0006
Triacetin	14.70	0.0006
Nitroglycerin	15.04	0.0000
Dimethylphthalate	16.95	0.0017
2,6 – Dinitrotoluene	17.10	0.0010
2,3 – Dinitrotoluene	18.49	0.0026
2,4 – Dinitrotoluene	18.56	0.0055
3,4 – Dinitrotoluene	19.70	0.0061
Diethylphthalate	19.75	0.0006
Diphenylamine (including n- nDPA)	20.24	0.0011
Dimethylsebacate	20.71	0.0021
2,4,6 Trinitrotoluene	21.84	0.0070
Carbazole	24.13	0.0015
Ethyl centralite	25.10	0.0006
Dibutylphthalate	26.31	0.0078
2 – Nitrodiphenylamine,	26.44	0.0038
Tetryl	28.43	0.0101
4 – Nitrodiphenylamine	30.00	0.0006
2,4 – Dinitrodiphenylamine	31.31	0.0015

3.4 Conclusions

The developed GC/MS methodology was shown to be suitable for the analysis of 27 of the 28 compounds reported in the literature to be present in unburned propellant powders in firearm ammunitions. A method suitable for the analysis of this number of compounds associated with propellant powders has not been seen in the literature before. Due to the large number of compounds separated the technique should be suitable for a large variety of different ammunition types. The developed method would also be potentially useful for the analysis of explosive materials and particularly improvised explosive devices (IEDs), both of which may contain many of the compounds analysed here.

The next stage of this investigation was to combine the developed GC/MS method with SPME for the extraction of the compounds of interest from unburned propellant powder samples from a variety of ammunition types. This is investigated in sections 4 and 5.

As it has been reported in the literature that unburned propellant powder particles can exit the muzzle end of a firearm during discharge (Meng and Caddy, 1997) it must be seen as reasonable to hypothesise that this method would also be applicable to the analysis of materials containing OGSR. This is investigated in sections 6 and 7.

4 The Analysis of the OGSR by solid phase microextraction

4.1 Introduction

4.1.1 Basic Principles of solid phase microextraction

Solid phase microextration (SPME) was first introduced by Supelco in 1993 (Lord *et al*., 2000), it is a variation of solid phase extraction (SPE) which allows the extraction of trace and ultra-trace levels of analytes in liquid, gaseous or solid samples (via headspace)(Fifield and Kealey, 2000) by concentrating them onto a thin, solid rod of fused silica (although flexible cores are now available in the form of Supelco 'Stableflex' products), coated with an absorbent polymer. These fused silica supports are of the same type as used in the production of GC columns and are very stable, even at high temperatures (Wercinski, 1999). Polymeric coatings range in thickness between 5 and 100µm (Fifield and Kealey, 2000). Coatings are attached to a supporting injection device that resembles a microsyringe (Figure 16).

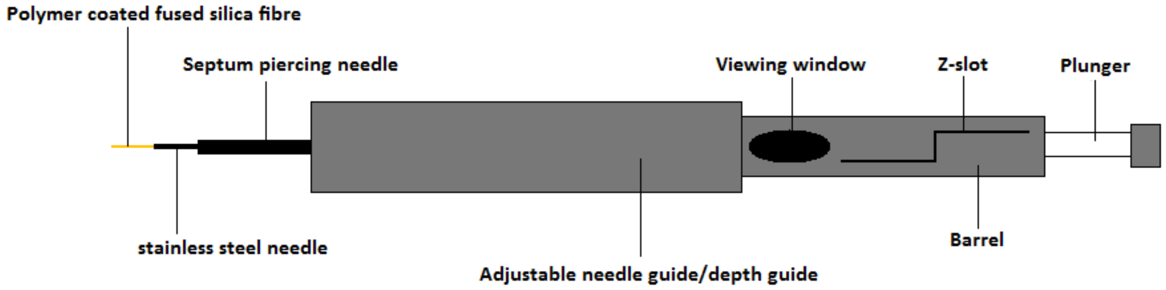


Figure 16: Schematic diagram of an SPME syringe setup (adapted from Fifield and Kealey, 2000).

4.1.2 SPME extraction

Figure 17 shows a step by step diagram of a typical SPME extraction procedures.

SPME extraction consists of two processes;

1) Analytes partition between the sample and fibre coating, and

2) The concentrated analytes desorb from the coated fibre into the analytical instrument.

To perform an extraction, an aqueous sample containing organic analytes or a solid sample containing volatile organic analytes is placed in a vial, and then sealed. To sample, the SPME protective sheath is pushed though the seal of the vial and the plunger is lowered to expose the fibre to the sample headspace. Analytes are subsequently extracted onto the fibre coating from the sample matrix. The fibre is then withdrawn (after a predetermined extraction time) back into the protective sheath. The syringe is then removed from the vial and inserted in to the injection inlet of a GC (or HPLC-when samples fibres are subjected to a solvent extraction prior to analysis). The injector must be at a high temperature to desorb the analytes from the fibre when it is exposed to the inside of the liner. Analytes are then refocused on the GC column. After desorption the fibre is again withdrawn into its protective sheath and the the syringe withdrawn from the GC injector.

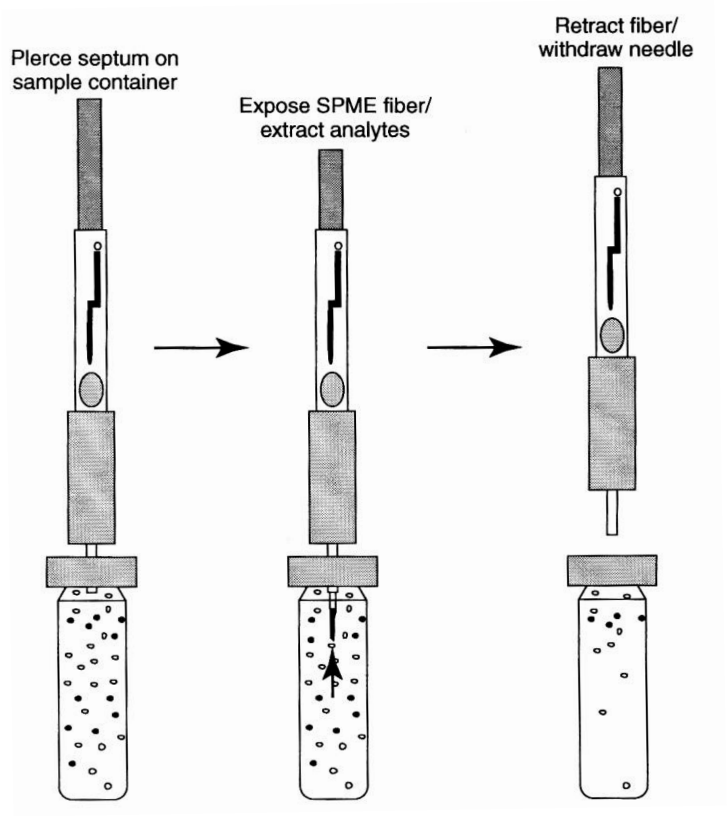


Figure 17: Diagrammatic depiction of the SPME extraction process (Miller, 2005).

4.1.3 Equilibrium

SPME is an equilibrium based technique affected by temperature, analyte concentration and the volume/thickness of the polymeric coating (Fifield and Keely, 2000). Analytes are not completely extracted from the matrix. With a system involving a liquid or solid, the sample is placed within a closed vial and equilibrium is reached between three phases; the liquid or solid and the headspace, the headspace and the SPME fibre and fibre coating and the aqueous/solid phase (Wercinski, 1999).

Typically an extraction is considered complete when an analyte’s concentration has reached a distribution equilibrium between the sample matrix and the fibre coating. This means that once equilibrium is reached the extracted amount is constant within the limits of experimental error and is independent of further increases in extraction time (Wercinski, 1999).

The distribution of the analyte amongst the three phases after equilibrium is represented by the following equation.

$$C_oV_s = C_h^{\infty}V_h + C_s^{\infty}V_s + C_f^{\infty}V_f$$

Where C_o is the initial concentration of the analyte in the aqueous/solid phase and C_h^{∞}, C_s^{∞} and C_f^{∞} are the equilibrium concentrations of the analyte in the headspace, aqueous/solid phase and the fibre. V_h, V_s and V_f are the volumes of the headspace, aqueous/solid solution and fibre coating respectively (note this equation applies to a sample involving headspace sampling). If direct sampling from a liquid is employed then the headspace value; $C_h^{\infty}V_h$, is removed from the equation (Wercinski, 1999)).

4.1.4 Extraction theory

SPME can be applied as a direct immersion or headspace sampling technique. Each of these methods are governed by a number of equations. As this project only applied headspace sampling the equations for direct extraction have not been included and maybe found elsewhere (Wercinski, 1999).

4.1.5 Headspace extraction

The equations covering the equilibrium process between the three phases of interest (fibre, headspace and liquid/solid sample are as follows:

$$K_{fh} = \frac{C_f}{C_h} \qquad K_{hs} = \frac{C_h}{C_s} \qquad K_{fs} = \frac{C_f}{C_s}$$

Where $C_{f,}C_h$ andC_s represent the concentration of the analyte in the fibre, headspace and solid/aqueous phase respectively and K_{fh}, K_{hs}, K_{fs}, represent the partition coefficients between the fibre and the headspace phases, the headspace and solid/aqueous phases and the fibre and the solid/aqueous phases. Therefore, the amount of analyte absorbed by an SPME fibre can be expressed as follows:

$$n_f = \frac{K_{fs}V_fV_sC_o}{K_{fs}V_f + K_{hs}V_h + V_s}$$

The three denominators represent the capacity of the three phases; fibre ($K_{fs}V_f$), headspace ($K_{hs}V_h$) and the sample (V_s).These equations show that as long as the volumes of the fibre, headspace and sample are kept constant the location of the fibre (within a specific medium e.g, headspace, or immersed in the liquid sample) does not affect the amount of analyte extracted. (Wercinski, 1999).

4.1.6 Fibre coatings

An SPME fibre consists of a stable inner silica based rod coated with a polymeric material which acts as a sorbent. Different sorbents will extract different groups of analytes; therefore, many different fibre coatings have been developed. Table 18 contains a summary of a number SPME coatings and their inherent properties.

Table 18: Properties of SPME fibre types (Sigma 1 (2011), Sigma 2,(2011))

Fibre Coating Type	**Coating Stability**	**Property**	**Polarity**	**Recommended analyte type**
PDMS 100µm	Non bonded	Absorbant	NP	Volatiles (MW 60-275)
PDMS 30µm	Non bonded	Absorbant	NP	Non-polar volatiles (MW 80-500)
PDMS 7µm	Bonded	Absorbant	NP	Non-polar high MW (MW 125-600)
Polyacrylate 85µm	Crosslinked	Absorbant	P	Polar semi-volatiles (MW 80-300)
DVB/CAR/PDMS 50/30µm	Highly crosslinked	*Adsorbant*	BP	Trace compound analysis (MW40-275)
PDMS/DVB 65µm	Highly crosslinked	*Adsorbant*	BP	Volatiles, amines, nitro-aromatics(50-300)
CAR/PDMS 85 µm	Highly crosslinked	*Adsorbant*	BP	Gases, low molecular weight (MW 30-225)

4.1.7 *Bond classifications*

There are three categories of fibre coating stability: nonbonded, bonded and crosslinked. Non bonded are stabilised but do not contain any crosslinking agents (linking one polymer chain to another). They are not solvent resistant and tend to swell, but can withstand some polar solvents such a methanol and acetonitrile. They have less thermal stability than bonded fibre coatings.

Partially crosslinked fibre coatings contain crosslinking agents such as vinyl groups. Crosslinking tends to occur only within the coating and not between the coating and the fused silica core. These coatings have better thermal stability and resistance to solvents compared to non bonded phases.

Bonded fibre coatings also contain crosslinking agents, the diffence being that the crosslinking is not only between the fibre but also the fibre and the fused silica core. These fibre types are resistant to most organic solvents and have good thermal stability. However, the thicker the fibre coating the harder it is to bond, therefore, the only fully bonded phase is the 7µm PDMS.

4.1.8 Fibre coating thickness

The thickness of any given fibre will have an effect on its extraction characteristics. A thicker fibre has a larger phase volume and can, therefore, retain more analyte. For retention of volatile compounds with low molecular weights a thicker film is a better choice. Smaller phase volumes are, however, more suitable for larger molecules as they can migrate more readily in the thinner coatings (Wercinski, 1999). Thicker coatings result in longer extraction times. An extraction time of around 30 minutes is usually the practical limit for setting an extraction time. Therefore, with the larger fibres an equilibrium within the extraction system might not have been reached. If equilibrium is not reached before the fibre is withdrawn then slight changes in variables such as time and temperature can dramatically change the results leading to poor reproducibility. Detection limits are lowest with thicker fibres but equilibrium times can be up to several hours (Fifield and kealey, 2000). Using thinner fibres may help improve reproducibility and precision.

4.1.9 *Adsorption and absorption*

These are the two extraction mechanisms applicable to SPME fibre types. Adsorption is the process in which a substance sticks to a surface, whereas absorption is the process in which a substance is taken inside another (Harris, 2007). In SPME extraction both of these processes begin with the adsorption of an analyte at the extraction phase-matrix interface. Following this analytes diffuse into the bulk of the extraction phase. If the diffusion coefficient of the analytes in the extraction phase are high then the analytes partition fully between the two phases and the absorbative effect is accomplished. If on the other hand the diffusion coefficient is low the analyte will remain at the interface and adsorption results. The main advantage of absorption extraction is a linear isotherm over a wide range of analyte and interference concentrations, since the property of the extraction does not change substantially until the extraction amount is one percent weight of the extraction phase. Adsorption on the other hand has a highly non-linear isotherm for high analyte concentrations when the surface coverage is substantial. This causes a problem in equilibrium based extraction techniques as the response of the fibre for the analyte at high sample concentrations will depend on the concentrations of both analytes and interferences.

4.1.10 Fibre coatings and properties

4.1.10.1 polydimethylsiloxane, polyacrylate and carbowax

The most common SPME fibre type is the non polar PDMS type. Polyacrylate (PA) and Carbowax are more polar.

PA is rigid and solid at room temp and unlike most phases, therefore, takes longer to extract anayltes than others. Higher temperatures are also required to desorb analytes from the fibre. The medium is quite solvent resistant.

Carbowax has been used as a moderately polar coating for GC phases. The medium will swell and dissolve in water.

Both Carbowax and PA are easily oxidised at temps above 220°C and carrier gas for GC must be free of oxygen.

4.1.10.2Porous particle blends

4.1.10.2.1 Divinylbenzene

The ability of pores to adsorb analytes and physically retain them can lead to tighter retention of the analytes that fit into pores. Therefore, generally this type of medium is better suited to trace extractions (ppt/ppb/ppm) with low distribution constants. DVB has a pore distribution of mainly mesoporous (pore diameter 2-50nm) with some macro (pore diameter >50nm) and micro pores (pore diameter <2nm). Mesopores are ideal for trapping C_6-C_{15} analytes but can also trap larger molecules. As DVB is solid it must be mixed with other compounds. Mixing with Carboxen increases the fibre’s overall polarity and ability to extract a wider molecular weight range. PDMS/DVB provides slightly better retention of small molecules than PDMS alone and has been shown to have greater affinity for some polar compounds.

4.1.11 Aims

The aim of the work presented in this section was to determine which (from 7 different types) was the most appropriate SPME fibre for the extraction of the compounds of interest (page 80) found in unburned propellant powders. The ability of the chosen fibre to extract the compounds of interest from single particles of unburned powder was also investigated.

4.2 Materials and methods

4.2.1 Solvents and standards

See section 3.2.1 (page 79).

4.2.2 Solid phase microextraction

Seven SPME fibre types; 65µm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 7µm Polydimethylsiloxane (PDMS), 30 µm Polydimethylsiloxane (PMDS), 100µm Polydimethylsiloxane (PDMS), 85µm Carboxen/Polydimethylsiloxane (CAR/PDMS), 50/30µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and 85 µm Polyacrylate (PA) were purchased from Supelco (Bellefonte, PA, USA). Fibres were conditioned prior to use as recommended by the manufacturer. Table 18 (page 85) shows the characteristics of the fibres being assessed.

4.2.3 Propellant powders

Propellant powders from four ammunition types (9mm Magtech, 5.56mm Magtech, 7.62mm Lapua and 7.62mm Federal) were supplied by Nottinghamshire Police. Cartridges had their bullets pulled and the propellant powders were collected into 8mL headspace vials for analysis.

4.2.4 Solvent extraction of unburned propellant powders

100mg of unburned propellant powder from three cartridges from each of the ammunition types were extracted with 2mL of methanol, samples were placed in an ultrasonic bath for 1 hour. None of the powders were completely dissolved; the 9mm Magtech ammunition left a fine powder on the bottom of the tube, while the other three ammunitions remained as small white pellets. The samples were then placed in a centrifuge for 15 minutes at 13,000RPM, the supernatant was removed and filtered through a 0.22µm PTFE filter before being injected into the GC-MS.

4.2.5 SPME extraction of 100mg samples of unburned propellant powders

100mg of each of the 4 ammunition types were extracted three times by each of the 7 fibre types. Extractions were carried out in an oven at 40°C, a temperature high enough to volatilise the compounds of interest in to the headspace of the sample vial. Nitroglycerin is also known to begin to decompose at temperatures above 50°C and this was not desired

(Sokoloski and Wu, 1981). Extracts were carried out for 35 minutes and the fibres introduced to the injection port of the GC-MS immediately following extraction.

Following each injection fibres were conditioned for 20 minutes in the GC injection linear at 250°C in order to ensure no carryover of the compounds of interest occurred. Blank fibre runs were carried out between every extraction in order to show that the fibres were clean before each powder extraction.

4.2.6 The extraction of single particles of unburned propellant powder

The fibre determined to be the most suitable was then used to extract single particles of unburned propellant powder from the 4 ammunition types. In order to determine the most suitable extraction time for single particles of unburned powder 1 particle from each ammunition type was extracted for time periods of 5, 15, 25,35,45 and 55 minutes. Peak areas for extracted compounds were recorded.

4.2.7 GC/MS equipment and conditions

The GC was an Agilent Technologies 6890N and the MS was an Agilent 5975MS. A J&W Scientific HP5-MS (30M x 0.25mm x 0.25µm) was used. Run conditions were as follows; thermal desorption of the SPME fibres was carried out using an injector temperature of 250°C with splitless injection. A SPME/direct inlet linear was purchased from Sigma Aldrich in order to minimise band broadening. The initial oven temperature was 50°C, rising to 200°C by 6°C per minute, at 27 minutes the temperature was raised by 20°C per minute until 300°C at 32 minutes. The total run time was 32 minutes. The carrier gas was Helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England).

4.3 Results and Discussion

4.3.1 The comparison of solvent and SPME extractions of unburned propellant powder samples

Comparisons of solvent and SPME extracts from the same types of ammunition showed high levels of similarity. All of the compounds of interest extracted using solvents were extracted by the SPME fibre. Figure 18 shows chromatograms from solvent and SPME extracts of 100mg of unburned Magtech 5.56mm calibre ammunition. In the SPME extraction of ammunitions containing DPA, 4-NDPA was also sometimes seen. This is due to the degradation of DPA (Laza, 2007). The fact that 4-NDPA was not seen in the solvent extractions is likely to be because there was no pre-concentration employed on the samples and the levels of 4-NDPA were below the limits of detection of the equipment used. Due to the selective nature of SPME fibres the relative abundances of extracted compounds varied from solvent to SPME methodologies, but as it was qualitative and not quantitative analysis (the presence, or not of a compound rather than its actual quantity) that was the basis of this study these differences were determined to not be detrimental to the application of SPME extraction.

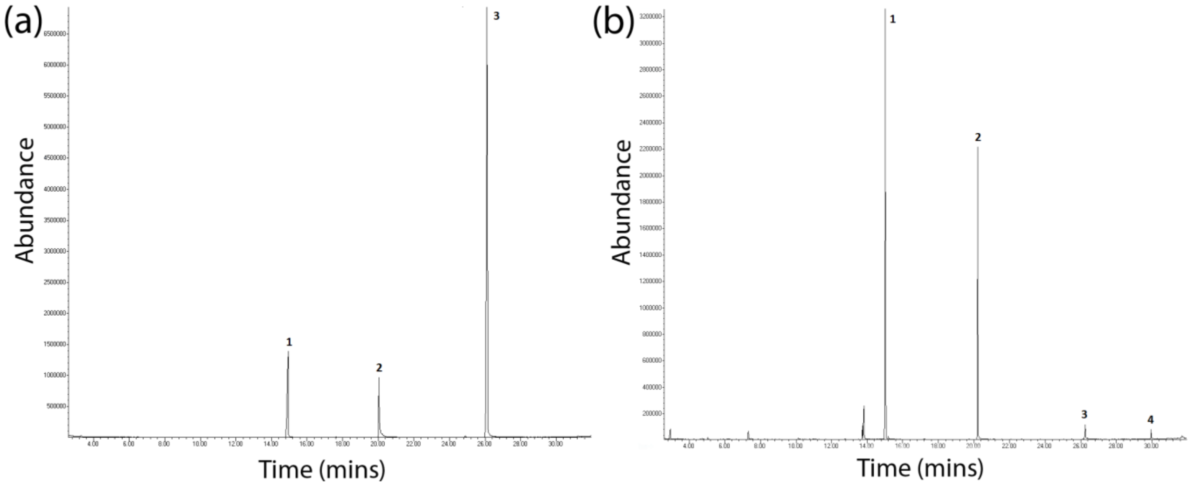


Figure 18: Chromatograms from extractions of 100mg samples of Magtech 5.56 propellant powders, a) solvent extraction, b) SPME extraction (1. Nitroglycerin , 2. diphenylamine, 3. dibutyl phthalate, 4. 4-nitrodiphenylamine).

4.3.2 The use of unburned powder samples

The use of unburned propellant powders to determine the most suitable SPME fibre type for potentially extracting compounds associated with OGSR was chosen for a number of reasons. Although it might have been preferable to use OGSR samples, the loss of materials from such samples over time has been reported to occur (Andrasko and Stahling (2000),Weyermann *et al*. (2009)). Therefore, using such samples for the selection of the most suitable fibre type would most likely yield irreproducible results. This would obviously be biased to the fibres used to carry out the initial extractions on any sample, with the compounds present for extraction diminishing with time. The amount of variability of the compounds of interest between different samples was also not known and, therefore, carrying out extractions across different samples was determined to be unsuitable. Second the use of a blown down standard mixture was decided against due to the varying amounts of each compound which are found in real samples. The levels of NG in one ammunition are unlikely to be the same in another. Furton *et al*. (2000) reported that lower molecular weight hydrocarbons reach optimal relative recoveries much earlier than molecules of higher molecular weights. It can, therefore, be extrapolated that with ammunitions having variable amounts of compounds of varying molecular weights the extraction profiles are likely to be different compared to homogenous standard mixtures of compounds all at the same concentration. It was also not known whether the structures (rod, ball, flake etc) of different propellant powders would also affect compound recoveries, something which could not be taken into account using blown down standards. It has also been reported that when a firearm is discharged both unburned and partially burned powder granules are propelled from barrel along with the projectile (Meng and Caddy, 1997). Therefore, it is reasonable to say that using unburned powders can be justified as these unburned and partially burned residue particles will have structures identical to, or similar to the non fired unburned particles. Moreover, Newlon and Booker (1979) reported that there was no difference between the chemical compositions of partially burned powders, residues taken from barrels of fired weapons and unburned propellant powders from 40 powders tested.

4.3.3 Comparison of SPME fibre types

Figure 19 (a-d) shows the mean peak areas of compounds extracted from the four unburned propellant powders used to determine the suitability of the 7 SPME fibre types tested (raw data for these calculations can be found in appendix II) . It was determined that overall the most suitable fibre type for the extract of the compounds present in the unburned powders was the 65µm PDMS/DVB type. This was based on the comparisons of the average peak areas of the compounds recovered and the relative standard deviations calculated for each fibre type. The 65µm PDMS/DVB fibre extracted the greatest amount of NG in all powder samples. For the other compounds extracted the 65µm PDMS/DVB provided either the highest extraction amount or extracted levels very close to the leading fibre type.

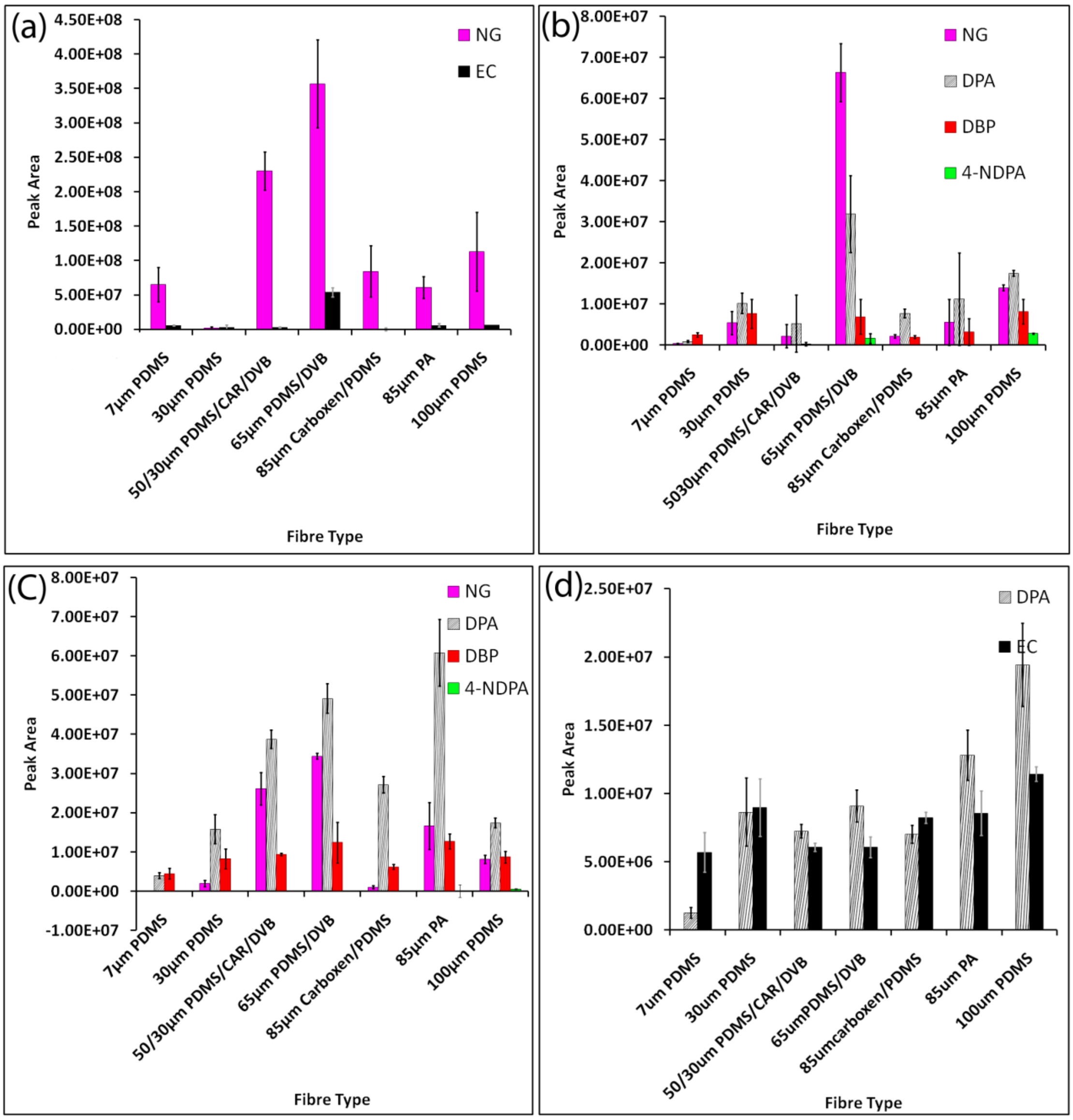


Figure 19: Average peak areas for compounds extracted from 4 ammunition types by the 7 SPME fibre types. a) Magtech 9mm, b) Magtech 5.56, c) Federal 7.62, d) Lapua 7.62(errors bars taken from mean relative standard deviation figured (Table 19)

Average relative standard deviations were calculated for each fibre type by taking the means of all relative standard deviations from each of the compounds extracted by each fibre. This allowed the fibres that performed the best over the entire range of compounds to be determined. The 65 µm PDMS/DVB was shown to have the third lowest relative standard deviation (Table 19). However, there was only a 3% difference between the lowest average relative standard deviation and that of 65 µm PDMS/DVB fibre type. Neither 85µm CAR/PDMS nor the 100µm PDMS fibre types performed as well as the 65 µm PDMS/DVB in terms of extracting the compounds of interest. As it is qualitative rather than quantitative information that was more important in this study the relative standard deviation figures were determined to not be as significant as the extraction yield data. Therefore, it was concluded that the most suitable fibre type was 65 µm PDMS/DVB.

Fibre	**Average relative standard deviation**
85µm carboxen/PDMS	17.9
100µm PDMS	18.1
65µm PDMS/DVB	20.9
7µmPDMS	26.6
30µm PDMS	28.9
85µm PA	36.0
50/30µm DVB/CAR/PDMS	47.2

Table 19: Average relative standard deviation figures for the 7 fibre SPME fibre types

It was shown that despite 65µm PDMS/DVB being the most appropriate fibre overall it was not always the best performer for every compound in every propellant powder. The extraction of powders using SPME is a complex process and some unexpected occurrences were observed. For example the same compound found in different propellant powders was not always extracted in the highest abundances by the same fibre. DPA was recovered in three of the ammunitions, with the 65µm PDMS/DVB extracting the greatest amounts in the Magtech 5.56mm ammunition, while the 100µm PDMS performed best with the Lapua 7.62mm ammunition, with the 85µm PA extracting the greatest levels in the Federal 7.62mm powders. It is therefore, suggested that the structural composition of different ammunitions and the ratios of compounds present may both influence the extraction process. For example the use of deterrents and other coatings such as graphite on particle surfaces may affect the levels of some compounds entering the headspace. Reference to the relative abundances of extracted compounds from the four ammunition types (Figure 19) show variations, suggesting the partition coefficient values are different in the extraction systems for each powder analysed (Newlon and Booker, 1979). It has also been reported that higher concentrations of a competitive interface compound can dislodge other analytes from fibres (Lord and Pawliszyn, 2000). A combination of these factors may explain this variation in which different fibres perform best for any given compound between different propellant powder samples.

The ammunitions that were used in this investigation only contained a limited number of compounds, however, the inherent characteristics of the 65 µm PDMS/DVB fibre, for example its bipolar character and suitability for extracting volatiles, amines & nitro aromatics (Sigma 2, 2011) suggest that it should be the most suitable fibre across most other ammunition types. Research by Furton *et al*. (2000) into SPME extractions of explosives concluded that the 65µm PDMS/DVB was the most suitable overall for a number of additional compounds that may also be found in firearm ammunitions including nitrotoluenes, dinitrotoluenes and trinitrotoluene.

4.3.4 Evaluating the effects of extraction time on single particles of propellant powders

In OGSR samples there will obviously be variable amounts of the compounds of interest and depending on these amounts, the volume of headspace from which compounds of interest will be extracted and the volume of the sample being analysed, the optimum extraction time will vary. Although it would be impossible to account for all the potential variability from sample to sample, extracting from one particle of propellant powder was an attempt to mimic lower amounts of sample that might be found in relation to OGSR. As stated previously both unburned and partially burnt propellant powder particles may be found in association with firearm discharges (Meng and Caddy, 1997). Pun and Gallusser (2008) showed that partially burnt powder particles can be found in various stages of decomposition exiting the barrel of firearms following discharge. The SPME extraction of partially burned particles has been shown to be possible by Burleson *et al*. (2009).

Results for single particles extracted across the range of times (5-55mins) showed a great level of variation between individual particles from the same ammunition type and between different ammunition types.

Extractions of compounds from the same ammunition type but different individual particles showed the potential for orders of magnitude differences in extraction abundances to occur. For example two sets of extractions of 9mm Magtech ammunition carried out consecutively on two separate particles from the same cartridge yielded abundance levels for 35 minute extractions of 8,417,107 and 380,380 for NG. This suggests that on a particle to particle basis extraction efficiency maybe highly variable.

The optimum extraction time for particles was also shown to vary from particle to particle within the same ammunition type. Figure 20 shows extractions of two different particles of the same Magtech 5.56mm ammunition taken from the same cartridge. It can be seen that in the first set of particle extractions the levels of both NG and DPA reach equilibrium within the extraction system at 35 minutes (and in the case of NG begin to drop after 45mins) and this would therefore, be determined as the optimum extraction time. However, in the second set of extractions the levels of DPA and NG extracted continue to increase with time up to the last extraction of 55 minutes suggesting this would be a more suitable time for this particle.

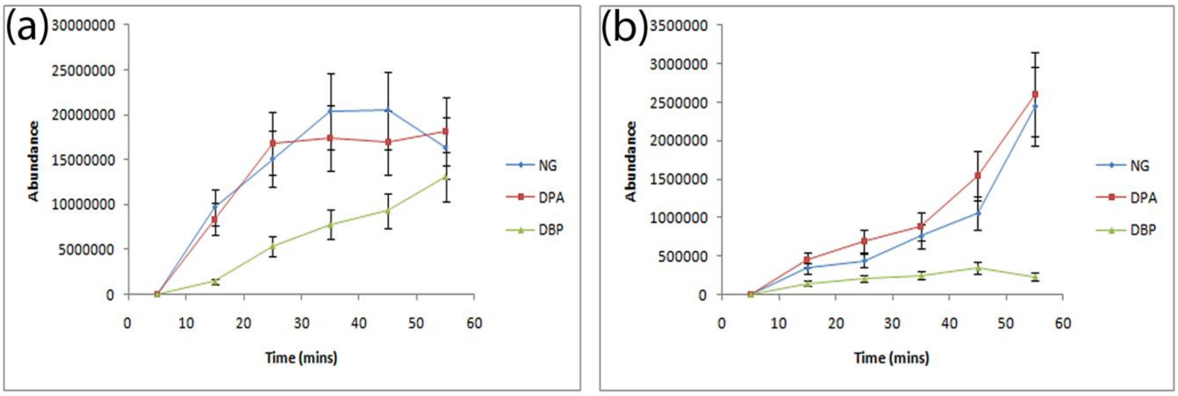


Figure 20: Extractions of two different single particles of Magtech 5.56 ammunition collected from the same cartridge.

Extractions from single particles of Magtech 9mm and 5.56mm ammunition types proved successful. It was determined that despite variation between particles an extraction time of 35 minutes was suitable, providing good extractions and having a time similar to that of the GC/MS analysis (32 minutes), something stated as preferable by Wercinski (1999).

Extractions from single particles of the two 7.62mm ammunition types proved to be less effective than those of the smaller calibre ammunition types. With Lapua 7.62mm no DPA was extracted from the individual particles, even after 55 minute extractions. This compound was known to be present in this ammunition type by reference to the extracts from 100mg samples. When this particle was subsequently cut in half, DPA was detected in extraction of 25 minutes and above. These findings are illustrated in Figure 21. By exposing the inner core of the powder particle and increasing the surface area, extraction efficiency was shown to increase. However, extracts from single particles of Federal 7.62mm ammunition exhibited none of the compounds which were previously determined to be present in the ammunition (by analysis of 100mg of the propellant powder), even at the maximum tested extraction time of 55 minutes. Cutting these particles into pieces had no effect and still no compounds of interest were extracted. These finding would suggest that the shape of a particle, together with the internal and external morphologies and compositions may affect the success of SPME extractions.

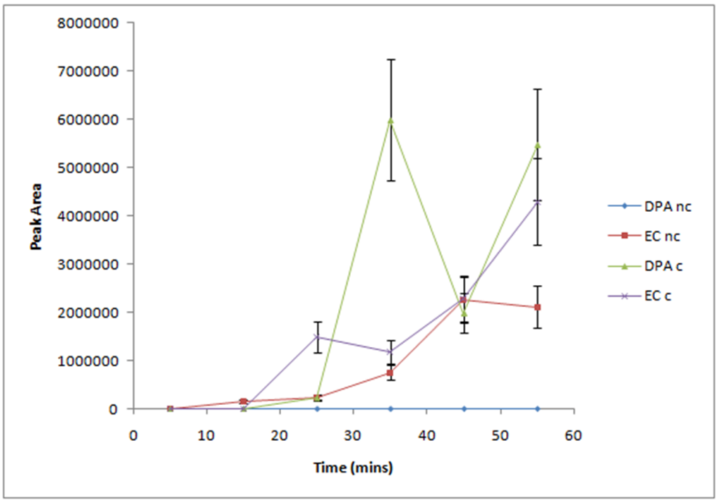


Figure 21: Lapua 7.62 single particle extracts from cut (c) and non-cut (nc) particles.

These results show that the specific type of ammunition being analysed can have an effect on SPME extractions. No one extraction time was shown to be universally optimal for all ammunition types, or even between individual particles of the same ammunition. However, with the exception of the Federal 7.62mm ammunition, an extraction time of 35 minutes was determined to be suitable, yielding peaks for all of the compounds determined to be present in the ammunitions in this study.

4.4 Conclusions

The most suitable SPME fibre for the extraction of the compounds found in relation to unburned propellant powders and, therefore, potentially OGSR was determined to be the 65µm PDMS/DVB fibre type, performing well across all of the compounds present in the ammunition investigated. Such a detailed investigation into the suitability of such a large number of SPME fibre types for the application of propellant powder analysis has not been reported before in the literature.

Results from extraction optimization work have shown that no one extraction time was universally optimal for all compounds being extracted. However, a 35 minute extraction time was determined to be suitable, allowing detection of the compounds of interest. Issues experienced with extracting compounds from the 7.62mm ammunition types suggest that the shape of a particle, its internal and external morphologies and compositions may influence the effectiveness of SPME extractions.

The results of this study may also be useful to those investigating improvised explosive devises (IEDs) in which smokeless propellant powders have been used (MacCrehan and Bender, 2009).

5 The analysis and comparisons of unburned propellant powders

5.1 Introduction

5.1.1 Firearm ammunition

Firearm ammunition is very variable but in general consists of the following:

- Projectile
- Case
- Propellant
- Primer

Figure 22 show in more nomenclature common to firearm cartridges.

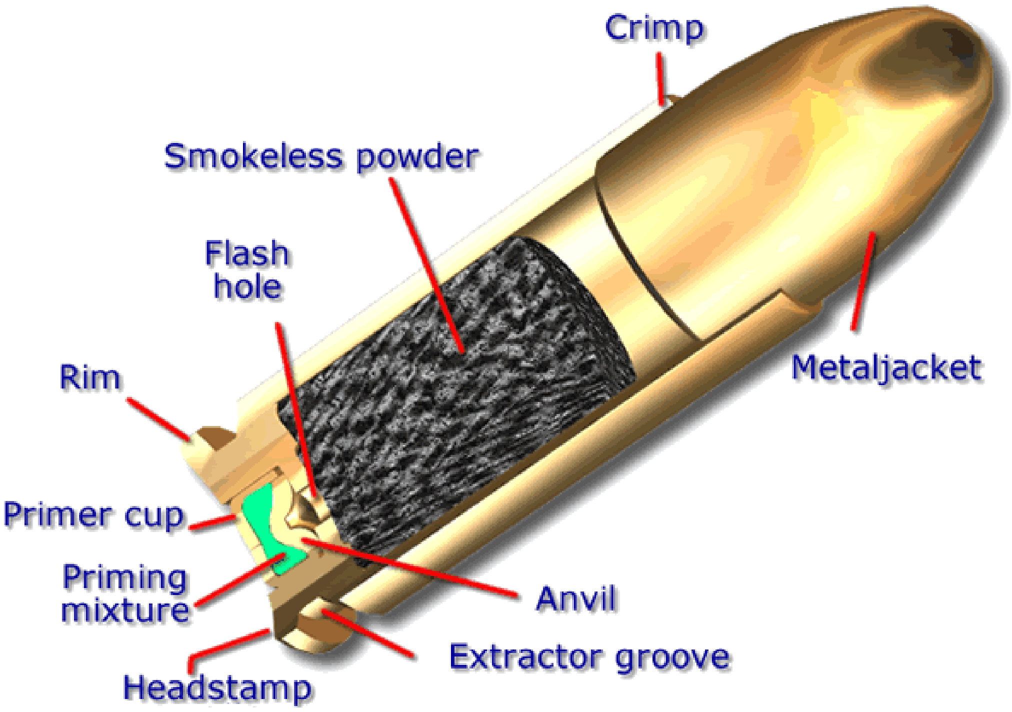


Figure 22: Diagram of a typical small arms cartridge (firearmsid.com, 2011).

5.1.1.1 Projectile

The projectile is the object that is propelled out of the barrel of the firearms when a cartridge is discharged; it commonly takes the form of a bullet. This investigation has not been concerned with projectiles and, therefore, no more detail is provided here. However, more information can be found elsewhere (Warlow, 2008, Wallace, 2008, Heard 2008).

5.1.1.2 Cartridge case

This is designed to house the primer, propellant, and to securely retain the bullet in the neck of the case (Wallace, 2008). The vast majority of cartridge cases are made from Brass (approximately 70% copper and 30% zinc), however, other materials such as steel (coated with zinc, brass, gilding metal, copper, lacquer or blackened), copper, nickel plated brass, cupronickel (approximately 80% copper and 10% zinc) and aluminium are also used (Wallace, 2008). Cases come in a large variety of shapes and sizes information on this may be found elsewhere (Barnes and Skinner, 2006).

5.1.1.3 Primer

Primers consist of the primer cup, which holds the primer mixture and the mixture itself. The formulation of the primer mixture is responsible for the majority of the compounds found within inorganic gunshot residue particles (Meng and Caddy, 1997).

A priming composition is designed to provide a sudden blast of flame that serves to ignite the propellant within the cartridge case. The mixture must generate a relativity large amount of hot gases and solid particles without the development of a detonating wave (Wallace, 2008).

Most mixtures consist of a blend of one or more initial detonating agents, with oxidizing agents, fuels, sensitizers and binding agents. The intended effect of these additions is to reduce the initial detonation in to a rapid combustion (Wallace, 2008). Table 20 contains a list of compounds commonly used in primer mixtures while Table 21 contains a list of some modern primer formulations.

Table 20: Compounds commonly used in the manufacture of primer mixtures (adapted from Wallace, 2008)

Function	**Compounds**
Explosive	Azides, fulminates, diazos compounds, nitro or nitroso compounds
Oxidisers	Barium nitrate, potassium chlorate, lead dioxide and lead nitrate
Fuels	Antimony sulphide, gum Arabic, calcium silicide, nitrocellulose, carbon black, lead thiocyanate and powdered metals such as aluminium, magnesium, zirconium, or their alloys
Frictionators	Ground glass and aluminium powder
Sensitizers	Tetracene, TNT and PETN
Binders	Gum Arabic, gum tragacanth, glue, dextrin, sodium alginate, rubber cement and karaya gum

Table 21: Examples of chemical compositions from 5 (A,B,C,D,E) modern primer formulations (adapted from Warlow, 1996).

Component	**Composition (%)**				
	A	**B**	**C**	**D**	**E**
Lead styphnate	36	41	39	43	37
Barium nitrate	29	39	40	36	38
Antimony trisulphide	9	9	11	0	11
Calcium silicide	0	8	0	12	0
Lead dioxide	9	0	0	0	0
Tetrezine	3	3	4	3	3
Zirconium	9	0	0	0	0
Pentaerythritol tetranitrate	5	0	0	0	5
Nitrocellulose	0	0	6	0	0
Lead peroxide	0	0	0	6	6

5.1.1.4 Propellant

Small arms ammunition propellants can be defined as explosive materials which are formulated, designed, manufactured and initiated in such a manner as to permit the generation of large volumes of hot gases at highly controlled, predetermined rates (Wallace, 2008).

It is very important that the energy/weight/bulk relationship of a propellant and the rate of delivery of energy must be matched to the system (space in case and barrel, bullet weight, pressure requirements and required bullet velocity). Due to the vast array of small arms available with different ballistic specifications a wide range of propellant powders is required (Wallace, 2008).

Burning rates are incredibly important. This can be controlled by the size and shape of the individual grains of the propellant and the application of moderants (surface coatings). Figure 23 shows some common propellant shapes (Pun and Gallusser, 2008) and figure 24 shows macroscopic images taken of propellants from all (except Samson 9mm) ammunitions analysed during this research project.

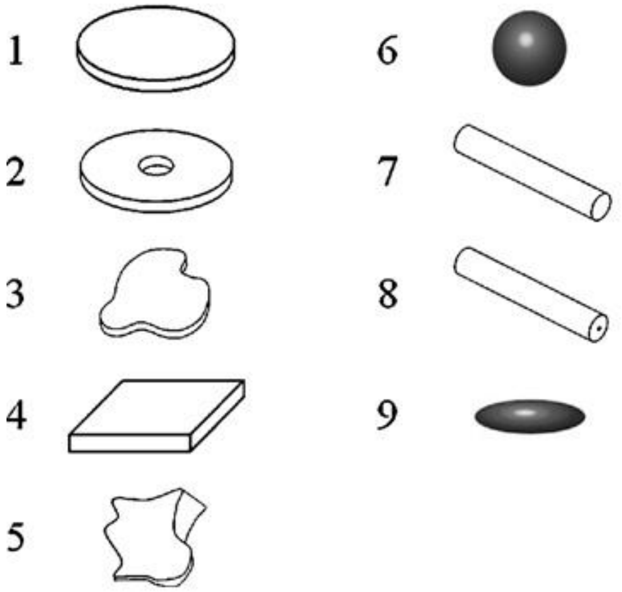


Figure 23: Some examples of propellant particle shapes; 1. Disc flake, 2. Perforated disk flake, 3. Irregular flake, 4. Quadrilateral flake, 5. Grain, 6. Ball, 7. Stick, 8. Single perforated stick, 9. Flattened ball.

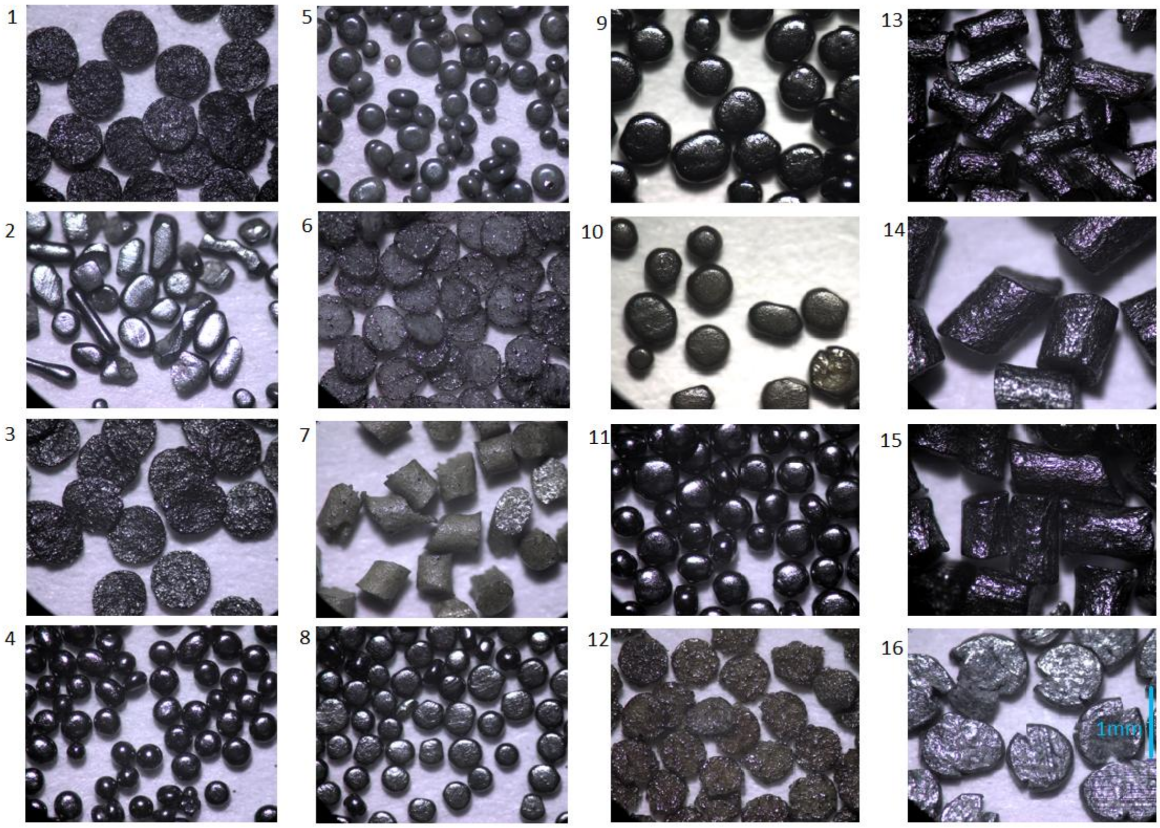


Figure 24: Maroscopic images of the propellant powers analysed during this project; 1. Remington .22lr, 2. Lellier and Bellot .357 Magnum, 3. Winchester .38 Special, 4. Eley .410, 5. Vostok .22LR,6. Magtech .357 Magnum, 7. Geco .38 Special, 8. Winchester .410, 9. Magtech 5.56mm, 10, Federal 7.62x51mm, 11. Nato 7.62x51mm, 12. Magtech 9mm, 13. Privi Partizan 7.62x39mm, 14. Lapua 7.62x51mm, 15. Privi Partizan 7.62x51mm, 16. Winchester 9mm.

Modern propellants (smokeless powders) for small arms almost exclusively contain nitrocellulose as the major oxidising ingredient. Various other ingredients may also be added for specific purposes. Table 22 contains a list of some compounds that maybe found in propellants.

Table 22: Compounds added to propellants and their desired effects (adapted from Wallace, 2008 and Heard 2006)

Compound Type	Desired effect
High energy plasticiser such as nitroglycerin,	Increase performance
Fuel type plasticisers such a phthalates, polyester adipate or urethane resorcinol, triacetin, dimethyl sebacate and 2 nitrodipheylamine	Improve the physical and processing characteristics
Organic crystalline chemicals such as nitroguanidine	Moderate ballistic characteristics
Stabilisers such as diphenylamine, 2-nitrodiphenylamine, dinitrotoluene , centralites, calcium carbonate or acardites	Increase chemical stability by combining with decomposition products
Inorganic additives such as chalk, graphite, potassium sulphate, potassium nitrate, barium nitrate	Improve ignitability, facilitate handling and minimise muzzle flash
Gelatinisers such as dinitrotoluene, dibutylpthalate and carbamate (centralite)	Slow rate of propellant burning
Powdered metals	Change in thermal characteristic such as conductivity
Colour taggants	Aid the identification of specific products

MacCrehan (2006) stated that “the accurate analysis of additives in smokeless powder is often an integral part of investigations of improvised explosive devices (IEDs) and in the evaluation of organic gunshot residues (OGSR)”. To this end a number of smokeless powders (propellant) have been analysed using the methods devloped in sections 3 and 4.

The aim of this investigation was to determine whether, by comparsion of the relative abundances of compounds extracted from samples of unburned propellants using SPME headspace extraction, it was possible to differentiate one propellant from another.

5.1.2 Aims

The aim of the work presented in this chapter was to assess the applicability of the developed methodologies to the extraction and analysis of a larger number of unburned propellant powder samples. It was investigated as to whether the comparison of the powder extracts would allow discrimination between each powder type.

5.2 Materials and Methods

5.2.1 Solid phase microextraction

65µm polydimethylsiloxane/ divinylbenzene fibres were purchased from Supelco (Bellefonte, PA, USA) Fibres were conditioned prior to use as recommended by the manufacturer.

5.2.2 Solvents and standards

See section 3.2.1(page 79).

5.2.3 Ammunitions

16 different ammunitions were analysed. Nottinghamshire Police provided propellant samples from Magtech 9mm, Magtech 5.56mm, Federal 7.62x51 and Lapua 7.62x51 ammunition. Key Forensic Services provided propellant samples from Vostok .22LR Remington .22LR, Eley .410 shotgun, Winchester .410 shotgun, Privi Partizan 7.62x51, Nato 7.62x51, Privi Partizan 7.62x39, Geco .38 special, Winchester .38 special, Magtech .357Magnum, Sellier and Bellot .357 Magnum and Winchester 9mm.

5.2.4 Collection of unburned propellant powders

Samples of unburned propellant were collected from unfired rounds by pulling their bullets and collecting the powders in vials. 100mg of each of the propellant samples was subsequently weighted out from three cartridges taken from the same box of ammunition. However, the Remmington .22LR ammunition only contained an average of 80.1mg of propellant. Samples were stored in the freezer at -22°C prior to analysis.

5.2.5 The extraction of unburned propellants

Each of the 100mg samples was placed in the lab oven at 80°C and heated for 10 minutes prior to extraction commencing in order to allow time for volatiles and semi volatiles in the solid propellant to volatilise into the headspace. The temperature of the extractions was increased from 40°C based on further temperature tests carried out (section 7.3.2, page 158). Following this equilibrium period the SPME syringe was pushed through the rubber septum of the headspace vial and the plunger depressed to expose the fibre surface to the headspace in the vial. Extraction was carried out for 35 minutes, after which the SPME fibre was immediately introduced to the injection port of the GC-MS system.

5.2.6 GC-MS equipment and conditions

The GC was an Agilent Technologies 6890N and the MS was an Agilent 5975MS. A J&W Scientific HP5-MS (30M x 0.25mm x 0.25µm) was used. Run conditions were as follows; thermal desorption of the SPME fibres was carried out using an injector temperature of 250°C with splitless injection. A SPME/direct inlet linear was purchased from Sigma Aldrich in order to minimise band broadening. The initial oven temperature was 50°C, rising to 200°C by 6°C per minute, at 27 minutes the temperature was raised by 20°C per minute until 300°C at 32 minutes. The total run time was 32 minutes. The carrier gas was Helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England).

A number of compounds were seen in the propellant extracts for which standards were not available. For these compounds matches were made using the data generated for the in the NIST database. Many of these compounds have been reported to be present in propellants (Table 1).

5.2.7 Calculation of limits of detection (LOD)

LOD figures for the compounds that were found in the propellant for which standards were held were calculated using a statistical approach. 10 blank runs were used and peak heights recorded at the retention times where compound peaks were observed in standard runs. Mean peak height values and standards deviations were then calculated. LOD figures were generated by taking the mean values and adding 3 standards deviations then dividing this figure by the gradient generated from calibration graphs. Limit of quantitation (LOQ) values were also calculated in the same manner but using the mean plus 10 standard deviations.

5.2.8 Assessment of the performance of the SPME fibre

A single SPME fibre was used to extract the same 100mg sample of Magtech 5.56 ammunition after every10 extracts that the fibre was used for. These results were used to determine the degradation of the SPME fibre with increasing numbers of extraction. It was an attempt to indicate at what point the fibre began producing irreproducible extractions.

5.3 Results and discussion

5.3.1 LOD and LOQ

Table 23 contains all the calculated LOD and LOQ figures for the compounds that were found in the propellants analysed. For compounds for which standards were held the LOD and LOQ were also calculated in terms of analyte amount (µg).

Table 23: Limits of detection (LOD) and quantitation (LOQ) for compounds found in the analysed propellant powders

Compound	Mean retention time	LOD (µg)	LOD of quantitation (µg)
Naphthalene (NAPH)	14.55	/	/
Dinitroglycol (DNG)	10.97	/	/
CAMPHOR	10.06	0.54	0.89
3 nitrotoluene (3NT)	11.31	0.75	1.30
Nitroglycerin (NG)	15.06	1.89	2.96
2,6 dinitrotoluene (2,6 DNT)	17.10	25.28	43.05
2,3 dinitrotoluene (2,3 DNT)	18.49	0.38	0.65
2,4 dinitrotoluene (2,4 DNT)	18.61	0.96	1.67
2,5 dinitrotoluene (2,5 DNT)	17.93	/	/
Diphenylamine (DPA)	20.26	0.39	0.67
Methyl centralite (MC)	24.11	/	/
Ethyl centralite (EC)	25.08	0.44	0.76
Dibutylphthalate (DBP)	26.32	0.62	1.09
Diisobutylphthalate (DIBP)	25.38	/	/
2 nitrodiphenylamine (2NDPA)	26.48	0.83	1.47
4 nitrodiphenylamine (4NDPA)	30.05	2.14	3.58

5.3.2 Analysis of the propellant powders

5.3.2.1 The use of mean values

Table 24 contains figures for what has been called “relative distribution”, a figure representing the spread of abundances (peak area) between the three extracted powders for each of the ammunitions (3 separate cases). These figures were calculated as follows

$$relative\ distribution = \frac{range}{mean} \times 100$$

The results of these calculations show that some propellants have much more widely distributed compound abundances. It has also been observed that within one ammunition/propellant type some compounds may show relatively small relative distributions while others are much higher. For example in the Vostok .22LR ammunition the relative distribution of DPA is 8 where as for DBP it is 81. Based on these figures it might seem unsound to apply mean values for the comparisons of the ammunitions. However, as figures 25 and 26 demonstrate all ammunitions were compositionally different to such degrees that it would be highly unlikely to mistake one of the ammunition types investigated for another.

Table 24: Relative distribution figures for analysed propellants.

AMMO	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22LR	123.64	/	/	/	13.11	/	/	/	/	44.44		15.18	/	/	24.32	30
VOSTOK 22LR	43	/	/	/	51	/	/	/	/	8	20	11	81	/	18	10
L&B 357MAG		/	/	/	11.97	/	/	/	/	30.95		9.20	95.55	/		5.32
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	18	13	/	/	/
GECO 38SPL		/	/	/	/	/	/	/	/	18.89	/	15.75	47.31	/	/	/
WIN 38 SPL	/	/	/	/	18.22	/	/	/	/	/	/	3.78	/	/	/	/
ELEY 410	47.11	/	/	/	13.43	/	/	/	/	15.88	/	22.72	11.12	27.099	115.68	144.35
WIN 410	28.86	/	/	/	10.37	/	/	/	/	10.71	/	2.27	31.90	/	12.10	24.44
MAG 556CBC	/	/	/	/	20.18	/	/	/	/	54.22			122.86			142.93
PRIVI 762X39	/	/	63.07	/	/	/	/	/	/	31.38	/	47.39	/	/	/	/
FED 762X51	/	/	/	/	4.18	/	/	/	/	13.65	/	/	74.20	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	13.65		74.20	/	/	/	/
NATO 762X51	/	/	/	/	25.63	/	/	/	/	27.53	/	7.83	2.94	/	14.91	11.20
PRIVI 762X51	/	/	16.32	/	/	1.718	51.28	6.88	16.32	5.76	/	17.16	7.24	/	/	/
MAG 9MM	/	/	/	53.677	19.61	/	/	/	/	/	/	83.64	/	/	/	/
WIN 9MM	/	/	/	/	39.79	/	/	/	/	28.07	/	69.60	95.55	/	245.72	55.22

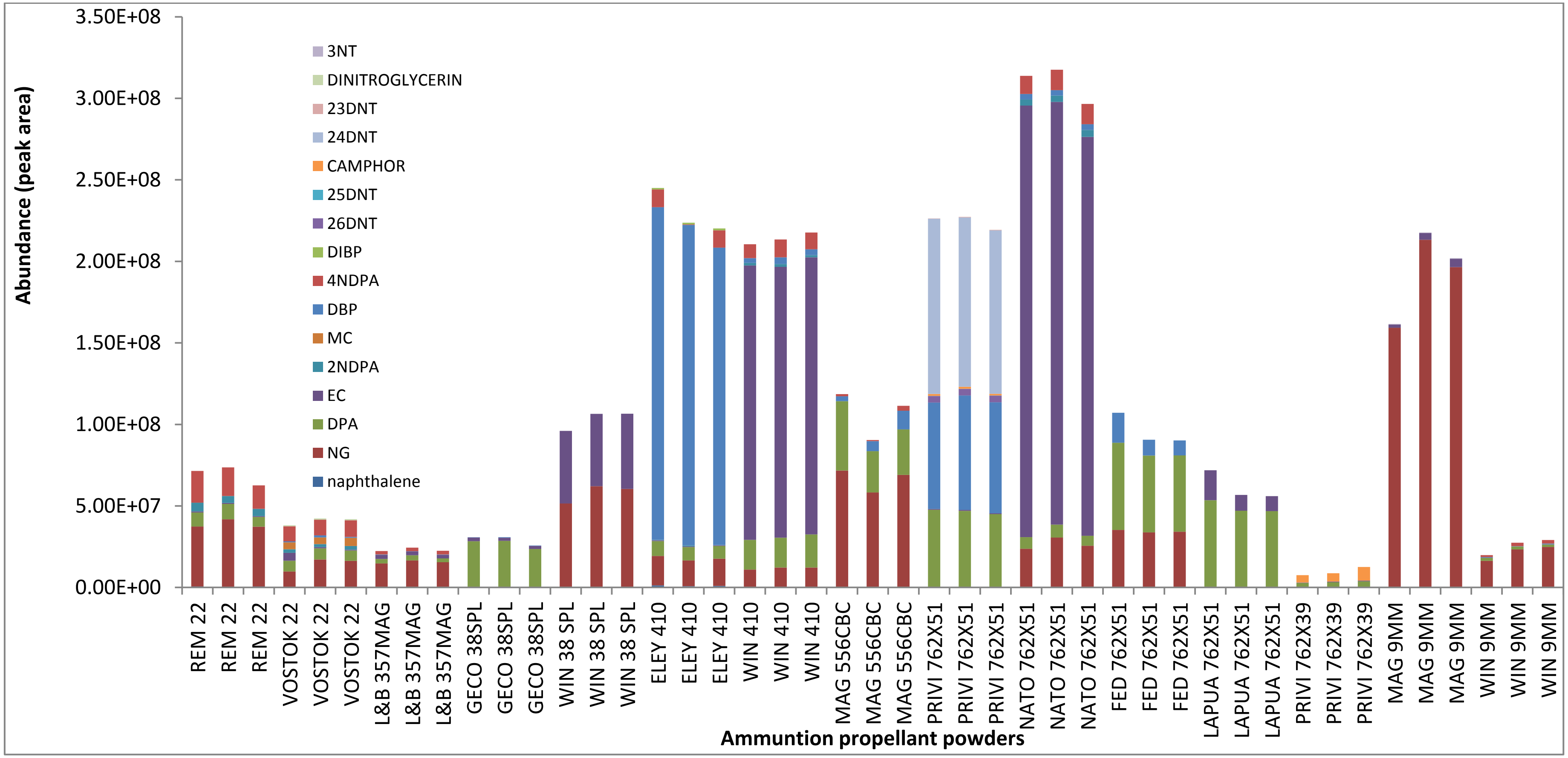


Figure 25: Compounds extracted from unburned propellant powders from 3 cartridges of each ammunition type (each 3 taken from the same box of ammuntion). Magtech .357mag extracts are not included here as the abundances of compounds extracted were much greater than those presented here. See figure26 for this data.

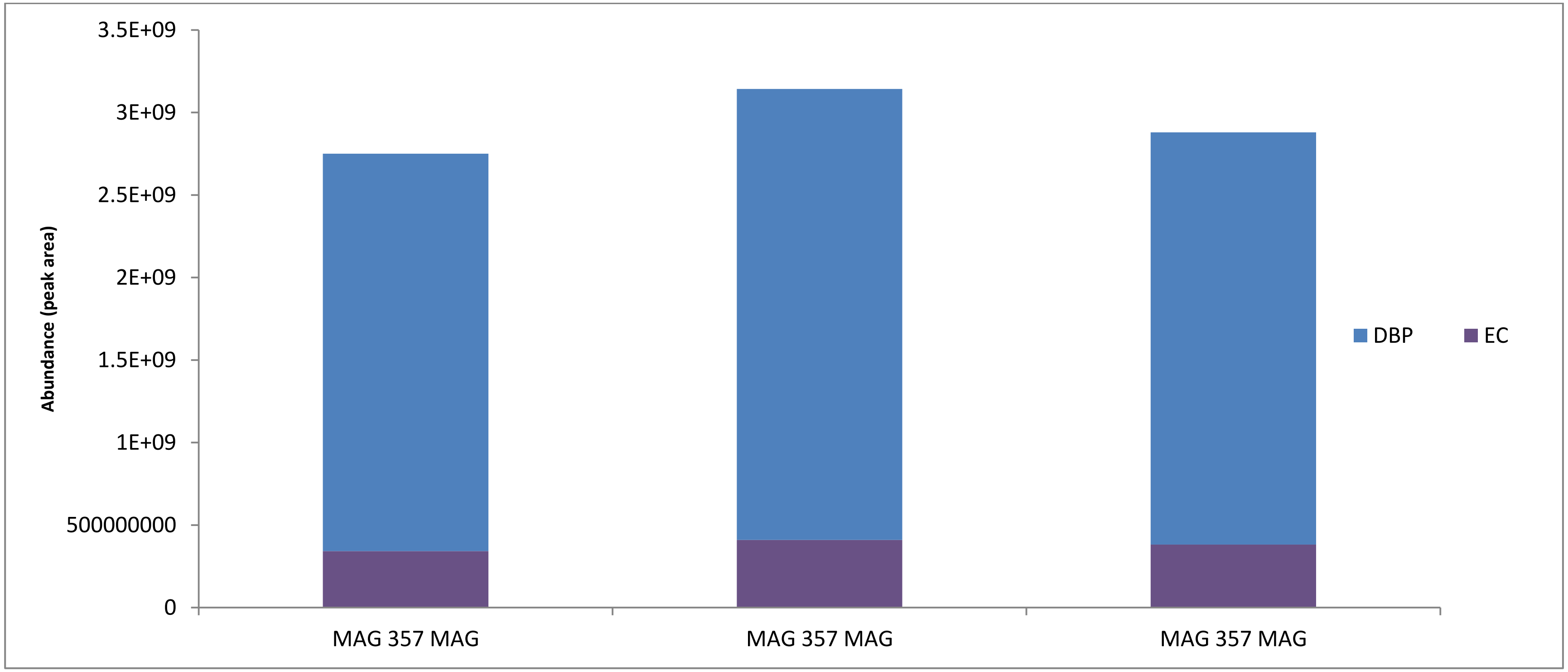


Figure 26: Abundances of compounds extracted from unburned propellant from Magtech .357mag ammunition

5.3.2.2 Inter sample variation

In order to assess whether the variations in compound distribution was due to different amounts of the compounds of interest in the 3 different samples taken from three cartridges or whether it was related to the methodology, three extracts were carried out on the same sample of Remington .22 ammunition. Table 25 shows the results of these extracts compared to those from the extracts from three separate powder samples. It is shown that the relative distributions calculated for the extracts from the single sample are less than those of the three separate powder extracts. This suggests that some of the variation seen may be due to variation between cartridges/propellants.

The most important point is that even with some relatively large relative distribution figures being calculated for some compounds in some propellants it is still possible to differentiate between all of the individual propellant extracts and categorize them based on the original source ammunition. Therefore, the use of mean values for propellant comparisons must be seen as applicable to the data.

The fact that manual adsorption and desorption were used in the sampling procedure may have had some effect on the precision of the method. Ideally an automated sampling system would be used for these processes.

Table 25: Comparison of relative distribution data from 3 extracts of one 100mg samples of Remington .22 ammunition and 3 extracts of 3 separate 100mg sample of Remington .22 ammunition from separate cartridges

	NAPH	**NG**	**DPA**	**EC**	**2NDPA**	**4NDPA**
3 extracts from one sample	23.11	5.93	13.57	6.68	13.52	4.76
3 extracts from 3 samples	123.64	13.11	44.44	15.18	24.32	30.00

5.3.2.3 Comparison of propellant extracts

Figure 27 shows the average relative abundances of the compounds extracted from each of the propellant powders (Appendix III (section 11) contains the raw data for all of the extracted samples). Therefore, the potential exists to link an unknown propellant sample from one of these 16 ammunitions to its originator, there is also the possibility of being able to link extracts from OGSR samples originating from these 16 propellants back to the parent ammunition.

Naphthalene was determined to be present in 4 of the ammunition extracts (by reference to the NIST MS database). These were the Eley and Winchester .410 and Remmington and Vostok .22LR. Naphthalene has been shown by Weyermann (2009) to be produced during the discharge of firearm ammunitions as a by-product of propellant degradation. However, Zayed *et al*. (2010) referenced naphthalene as a stabiliser and it may, therefore, be that these ammunitions had naphthalene present as a primary stabilizing ingredient. However, the Vostok .22LR ammunition was manufactured in the USSR and was, therefore, at least 20 years old. The other .22LR and .410 ammunitions are known to be at least 10 years old. These four ammunitions were the oldest of all those analysed and there is, therefore, a greater potential for the naphthalene to be the product of propellant degradation.

The degradation of propellant powders over time has been previously documented (Laza, 2006) and this is something in the context of which the analysis of these unburned powder samples should be evaluated. The occurrence of derivatives of DPA in aged propellant powders depends on the temperature of storage. Therefore, the presence of amounts of 2 and 4-NDPA (Reemmington .22LR, Vostok .22LR, Lellier and Bellot .357mag, Eley .410, Winchester .410, Magtech .357Mag, Nato 7.62x51, Winchester 9mm) in some powders suggest that these propellants might have undergone some form of degradation. However, Wallace (2008) references 2-NDPA as a stabilizing ingredient of some propellant powders. As with the presence of Naphthalene in some of the powders it is not possible from the results collected here to say with any certainty whether the presence of these compounds is due to degradation, or inclusion as an ingredient in the original powders. However, the fact that the degradation of propellant is known to occur means that this must be considered if, for example a database of propellant profiles was to be used to link unknown samples to catalogued propellants.

It has been shown in this work that the profiles of propellants from individual cartridges originating from the same box of ammunition can be linked to each other (in this sample population of 16 propellants). This, therefore, means that the potential must exist to be able to differentiate between OGSR from each of these ammunitions, if unburned material exits the muzzle end of firearms, or remain in the spent cartridge cases (These elements are investigated in sections 6 and 7). More research is required looking into the similarities and differences in ammunition propellant of the same types but from different boxes and indeed differently manufactured batches. It must though be stated that this problem is not exclusive to this SPME method but rather to all techniques used for the analysis and comparison of propellants.

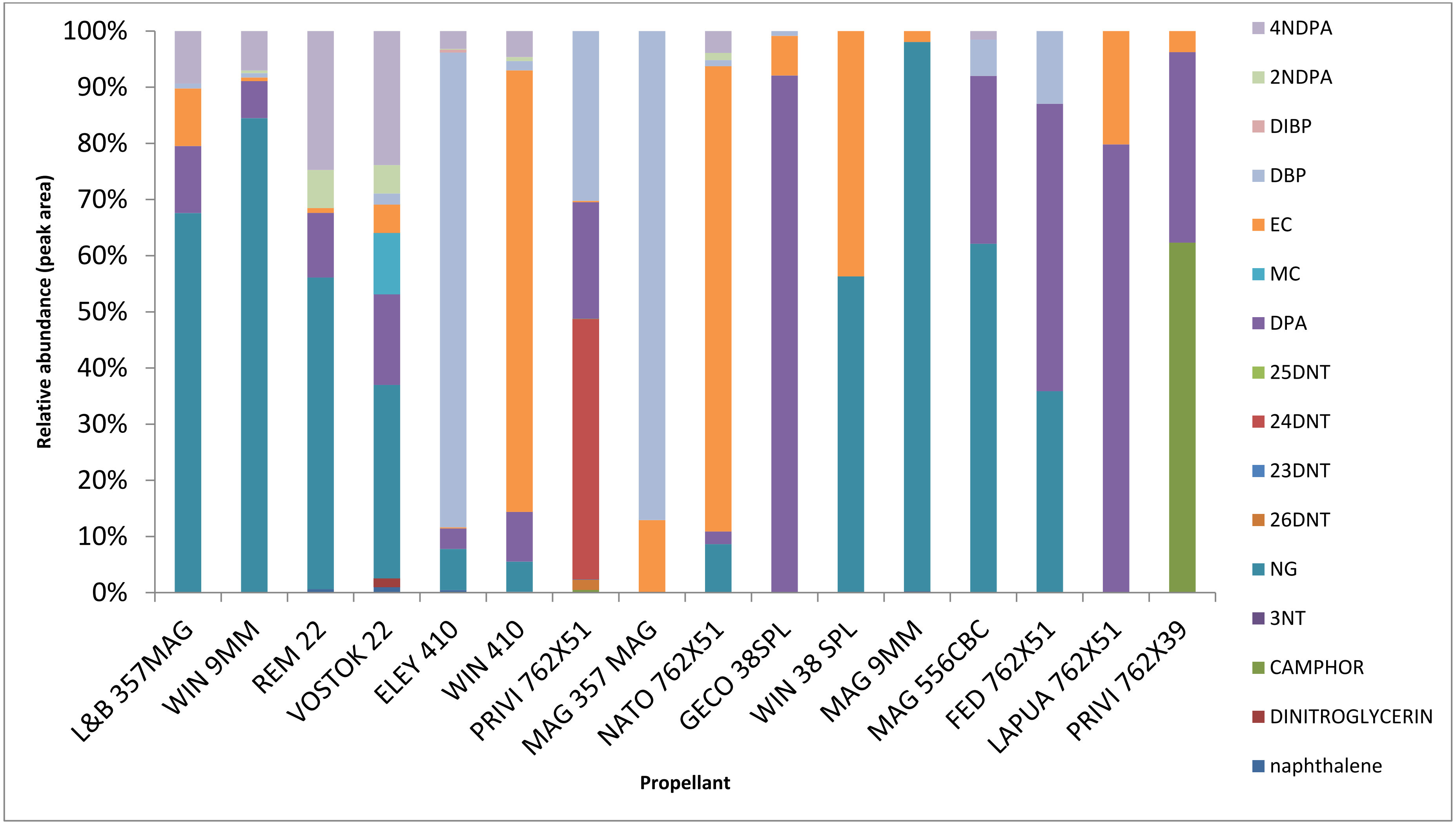


Figure 27: Average relative abundance of compounds present in propellant powder.

5.3.3 The effect of carrying out extractions on fibre performance

Figure 28 shows the peak areas of the compounds extracted by the same 65µm PDMS/DVB in ten extract increments (2 fibres tested). Over the range of extractions of the first fibre (0-30) the levels of all four of the propellant compounds remained relatively constant. A second fibre (0-60 extractions) was also used with the same 100mg Magtech 5.56mm reference sample.

A comparison of these two data sets shows that for NG and DBP the amounts extracted by each of the fibres were very similar. The amounts of DPA and 4-NDPA extracted were, however, less for the second fibre. With an increase in the number of extractions the amounts of DPA and 4-NDPA reduced. These observations are unlikely to be because of fibre degradation as this is not seen with the extracts carried out by fibre 1. It is, therefore, more likely that some form of degradation occurred with the sample due to the repeated extractions carried out. However, beause only two fibres were tested more work in this area needs to be carried out before the hypothesised conclusions can be more fully discussed.

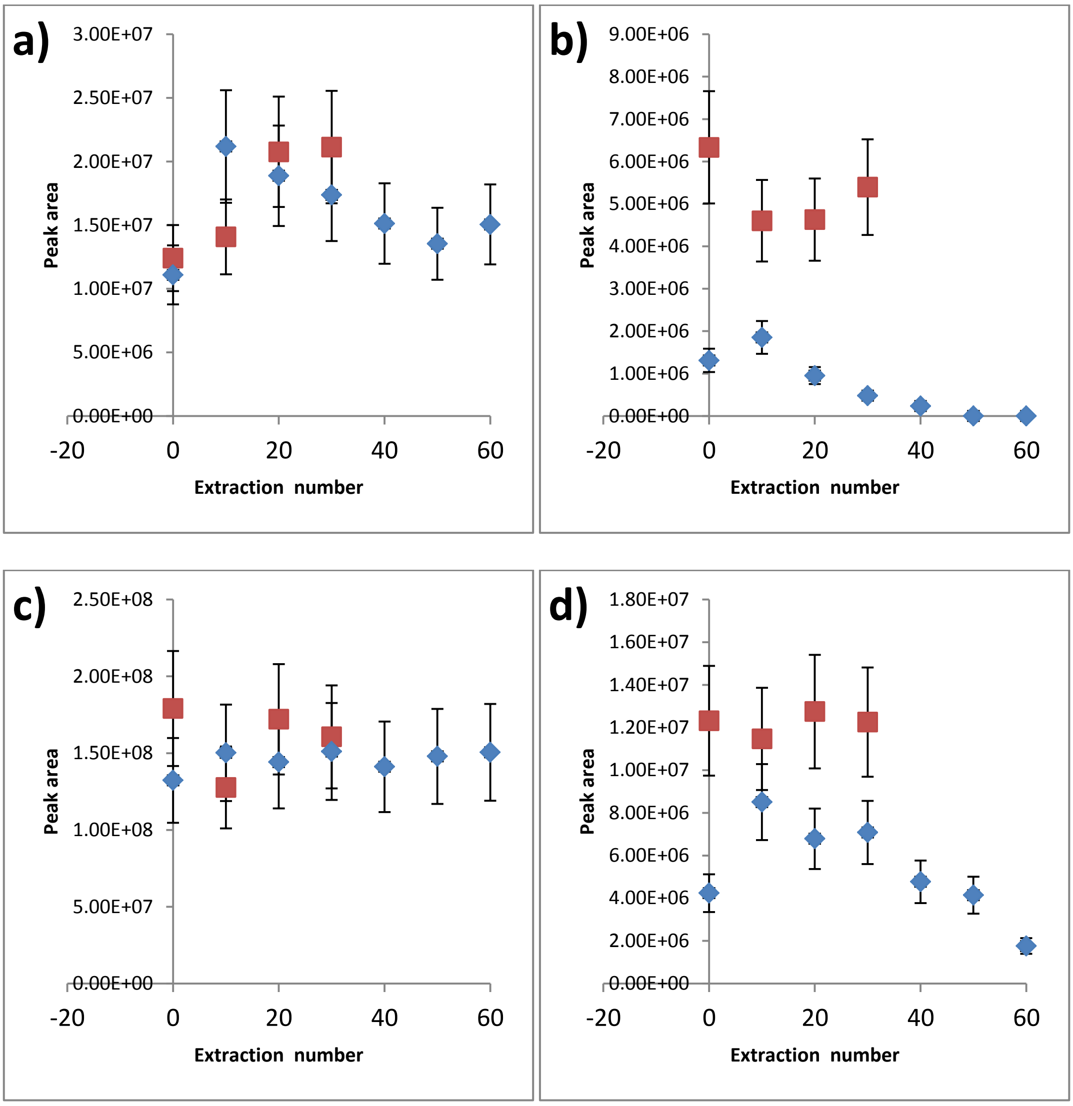


Figure 28: compounds extracted from a single 100mg sample of Magtech 5.56 propellant taken at ten extract intervals, a)NG, b) DPA, c)DBP, d)4-NDPA. 🟥 fibre 1 🔷 fibre 2. Error bars based on average relative standard deviation for fibre type (Table 19)

The degradation of DPA and 4-NDPA is discussed in detail in Laza (2006). As propellant powders age N- and C-nitrosation of DPA occurs. The rapidity of these processes is increases with temperature. Figure 29 illustrates the degradation pathways that may occur. However, if degradation was occurring over the time period of heating during extraction it would be logical to expect the presence of 2-NDPA and also the subsequent nitrosations and denitrosations products (n-NDPA would not be seen as it is thermally labile and degrades into DPA in the GC injector). This was, however, not the case. A possible cause for this might be that the DPA and 4-NDPA degraded into a number of products that were each below the LOD of the system.

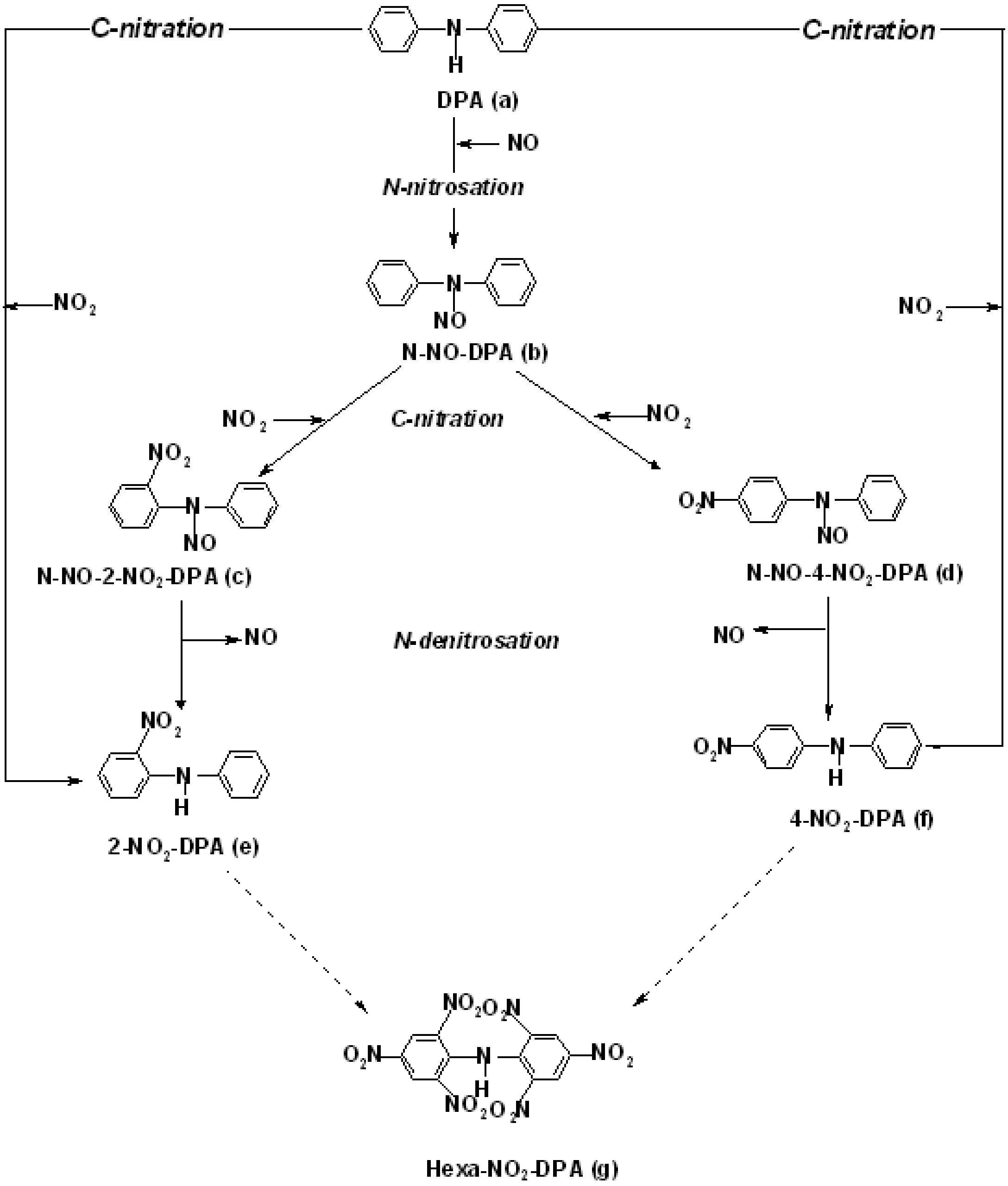


Figure 29: Degradation pathways of DPA (Laza, 2006)

Alternatively it might be possible that the SPME fibre had degraded and become less able to extract less polar compounds such as DPA and 4-NDPA. If this were the case it would be the polydimethylsiloxane (PDMS) component of the fibre that would be degrading as this is a non polar coating.

These results indicate that the 65µm PDMS/DVB SPME fibres can carry out at least 30 extractions without any determental degradation to the fibre.

5.4 Conclusions

The methods developed in sections 3 and 4 have been shown to be applicable to the analysis of a number of propellants. The SPME extraction technique has been shown to provide results that allowed all of the 16 propellant analysed to be differentiated from each other. Such an in depth study of compositions of unburned propellant powders has not been found previously published in the literature.

Investigations into the performance of the 65µmPDMS/DVB based on the number of extractions carried out have shown that fibres can carry out at least 30 extractions without any noticeable degradation occurring. It is feasible that a larger number of extracts might be possible before noticeable degradation occurs, however, more work in this area is required using reference materials or standard spiked substrates.

The most important finding is that all of the 16 ammunitions tested could be differentiated. This, therefore, means that there is potential for the OGSR produced by these ammunitions to be used to determine the source of any given residue sample. It is this potential that is investigated in the following sections.

5.5 Future work

More work on the affects of multiple extractions by fibres would be useful in order to assess with more certainty a threshold value for the life of a fibre before extraction performance begins to decline. MacCrehan and Reardon (2002) and MacCrehan and Bedner (2005) have shown the worth of using reference materials for method testing/quality assurance. The use of such reference materials as the US National Institute of Standards and Technology (NIST) RM 8107 (Additives in Smokeless Powder) would be something to assess. It is important to determine a threshold for fibre performance as drop in performance is very undesirable when attempts are being made to compare one sample to another.

6. The analysis of spent cartridge cases

6.1 Aims

To date no study has investigated the variation of compounds present within spent cartridge cases from a number of different ammunition types across a number of calibres following cartridge discharge. The aim of this study was to assess the repeatability of the compounds deposited in cartridge cases immediately following discharge. This must be seen as of key importance if subsequent “time since discharge calculations” are to be carried out. It was also of interest how many of the compounds detected in unburned powders were found in the spent cartridges.

6. 2 Materials and methods

6.2.1 Solvents and standards

See section 3.2.1(page 79)

6.2.2 Solid phase microextraction

65µm polydimethylsiloxane/divinylbenzene fibres were purchased from Supelco (Bellefonte, PA, USA). Fibres were conditioned prior to use as recommended by the manufacturer.

6.2.3 Propellant powders

See section 5.2.3 (page 108)

6.2.4 Collection of spent cartridge cases

Cartridges from the same 16 ammunition types from which propellants were collected were discharged by members of the Nottinghamshire Police and Key Forensic Services. Cases were collected immediately following discharge and placed in sealed glass vials. Upon return to the laboratory samples were stored in a freezer at -22°C prior to analysis. All cases were in freezer storage within 12 hours of discharge.

6.2.5 SPME extraction of unburned propellant powders

See section 5.2.5 (page 108)

6.2.6 SPME extraction of spent cartridge cases

Spent cases were placed in headspace vials and subjected to extractions of 35 minutes. Cartridge cases extracted in the early stages of the research project (Magtech 9mm, Magtech 5.56, Lapua 7.62x51, Federal 7.62x51, Winchester 9mm) were done so at a temperature of 40°C as it was reported in the literature that nitroglycerin begins to degrade at 50°C (Sokoloski and Wu, 1981). However, due to the evolutionary nature of such a long term study, further method development work carried out for alternative sample types (fabric extracts) indicated that 80°C was more suitable and, therefore, cartridge cases extracted after this point were done so at an oven temperature of 80°C. However the 40°C extracts have been included in this section for completeness. Samples were placed into the laboratory oven 10 minutes before extractions began in order to allow time for compounds to volatilise into the headspace. Fibres were introduced into the GC system immediately following extraction to minimise loss of the compounds of interest.

6.2.7 GC-MS equipment and conditions

See section 5.2.6 (page 109)

6.2.8 Analysis of products of combustion

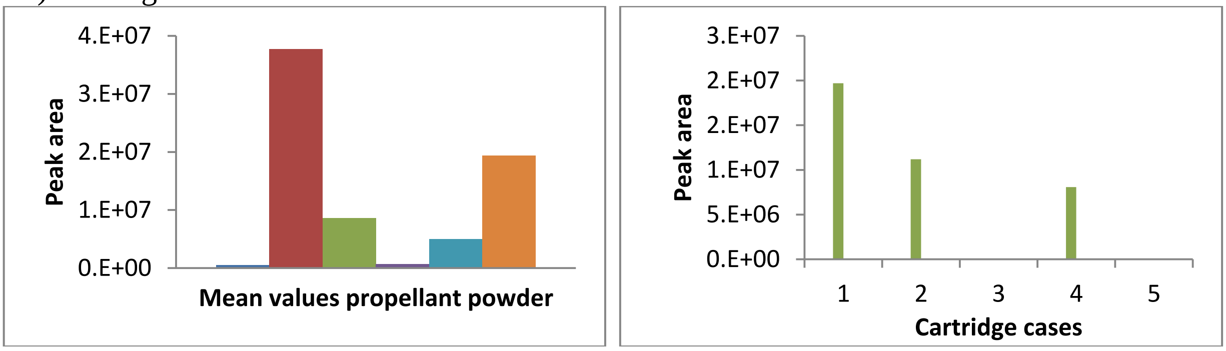
Breakdown products from combustion were only identified by the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England). No standards were held for the products of combustion from cartridge discharges and it was, therefore, not possible to identify these compounds with the same degree of certainty as compounds for which standards were run. Due to this it was decided that only compounds identified by the NIST database that had previously been reported to be combustion products (Weyermann, 2009) would be used for investigating the reproducibility of extracted abundances of breakdown product compounds. 3 of the 16 ammunitions examined were investigated for product of combustion compounds, these were seen to contain the most obvious peaks for breakdown products. It was decided that as the products of combustion were not the main area of interest of the study, and that many of the chromatograms did not show any discernable peaks for breakdown products, 3 ammunition types would provide enough results for discussion.

6.3 Results and discussion

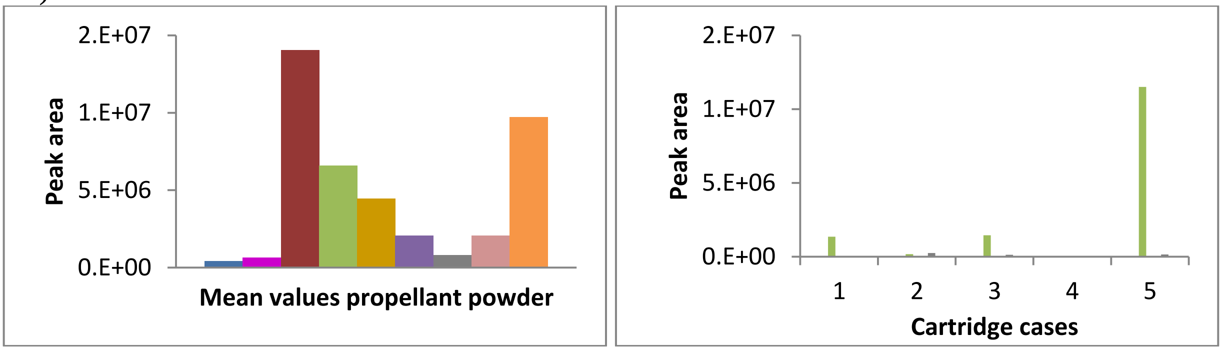
6.3.1 Comparing SPME extractions from unburned propellant powders and spent cartridge cases

Figure 30 contains mean data values for extracted unburned propellant powder samples and extract data from all discharged cartridge cases. Extracts were carried out on spent cases for two reasons; to examine the variability of compounds present in spent cases, and to determine the compounds that remained in the cases in order to see if they could be linked back to unburned powders and residues found on other surfaces.

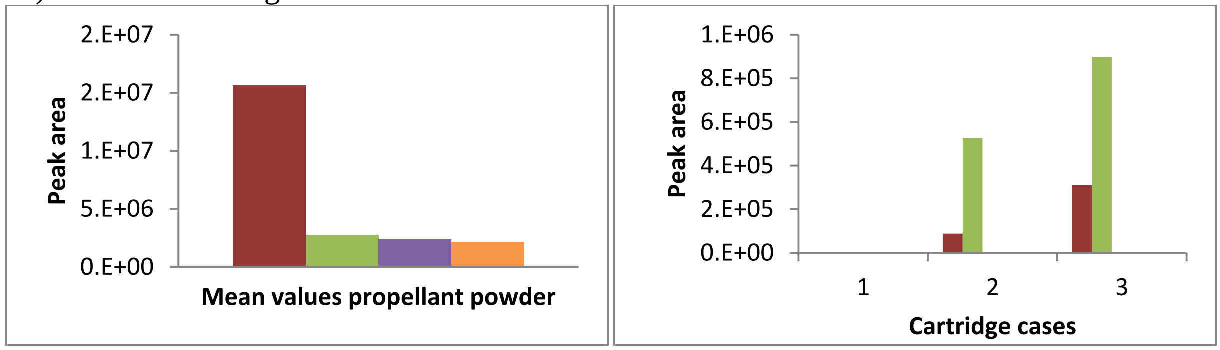
a) Remington .22LR



b) Vostok .22LR



c) L and B .357Mag



d)Magtech .357Mag

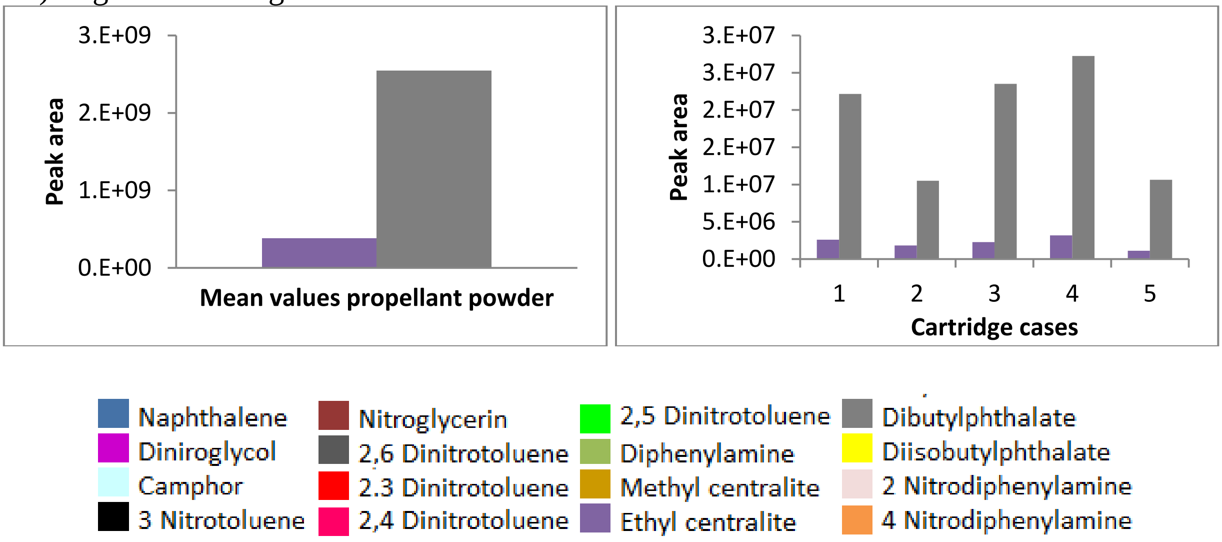
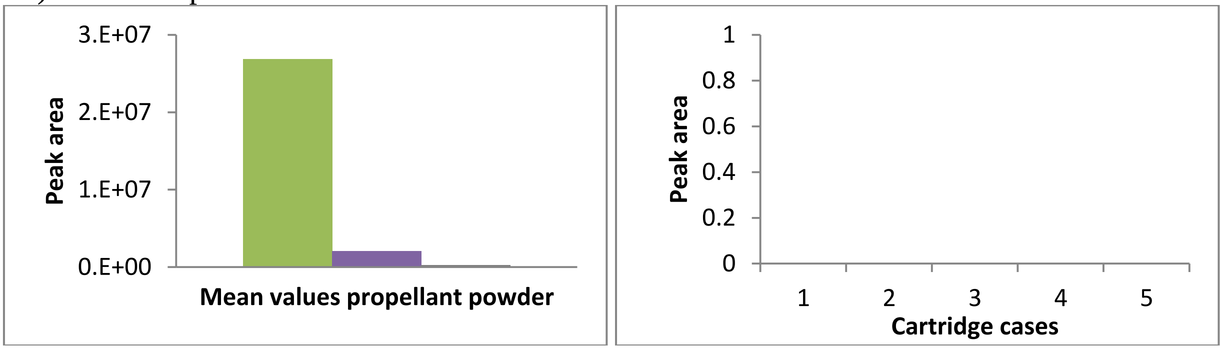
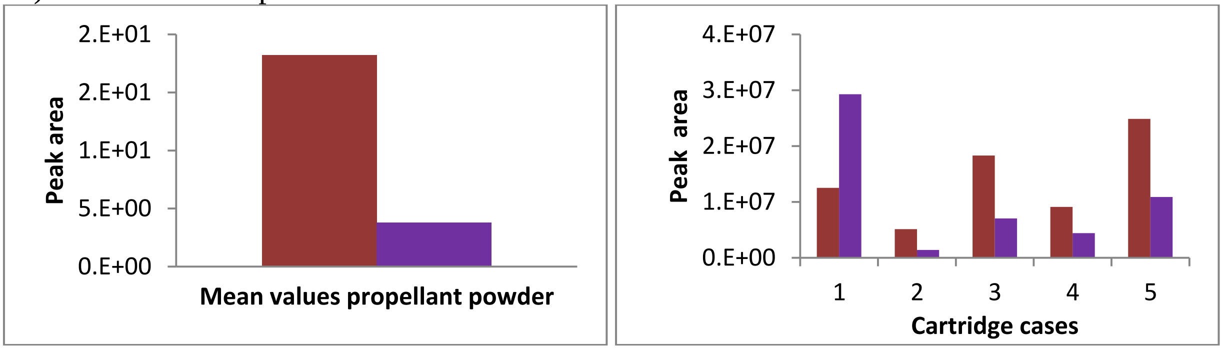


Figure 30: Mean compound abundances (peak area) for unburned propellants and extracts from spent cartridge cases.

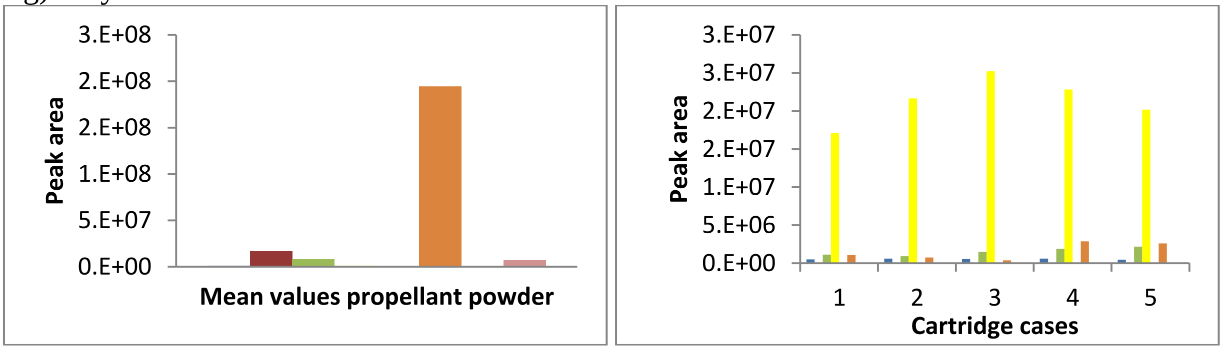
e) Geco .38Spl



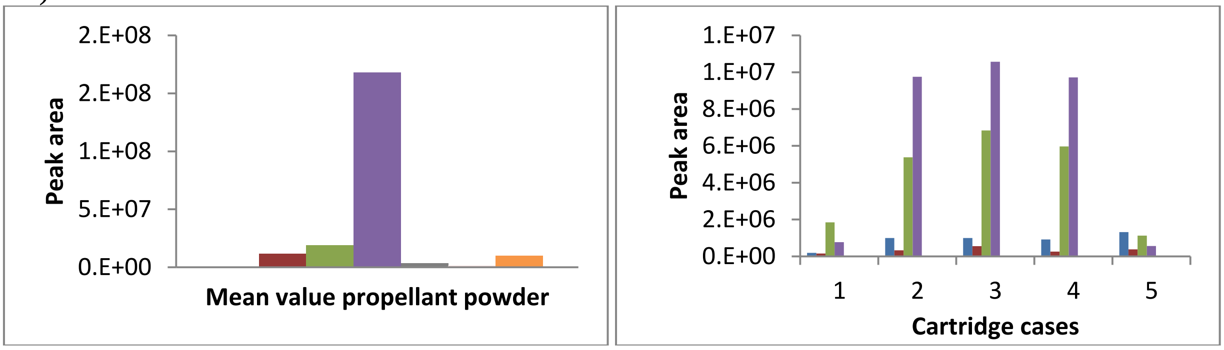
f) Winchester .38spl



g) Eley .410



h) Winchester .410



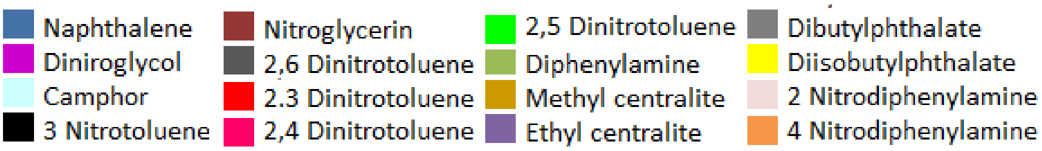
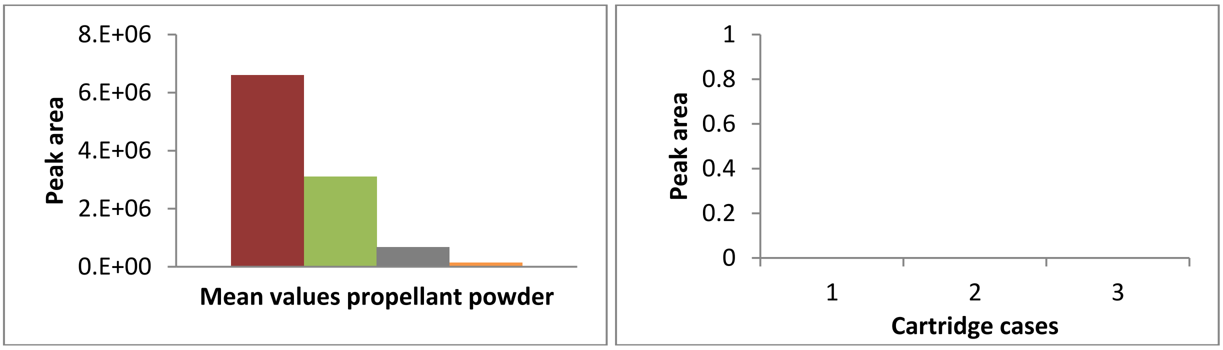
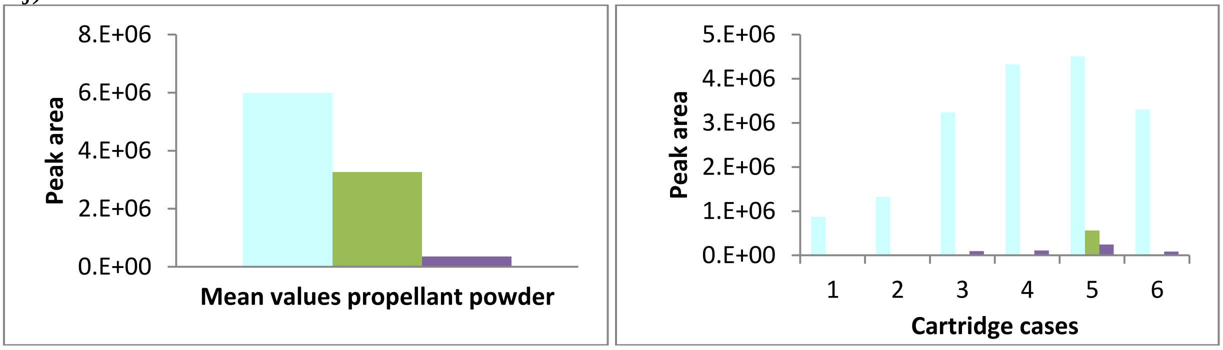


Figure 30 continued: Mean compound abundances (peak area) for unburned propellants and extracts from spent cartridge cases.

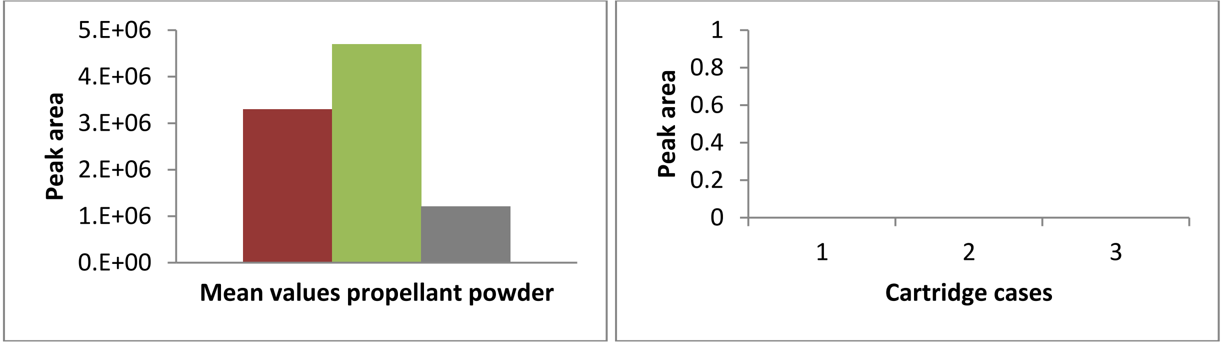
i) Magtech 5.56 (cases extracted at 40°C)



j) Privi Partizan 7.62x39



k)Federal 7.62x51 (cases extracted at 40°C)



l)Lapua 7.62x51 (cases extracted at 40°C)

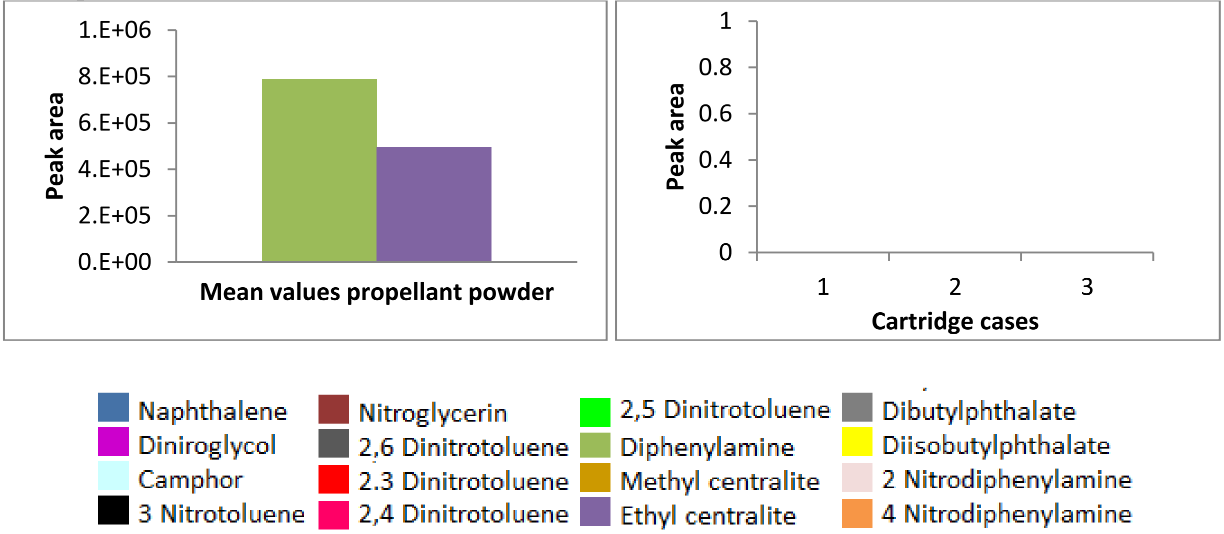
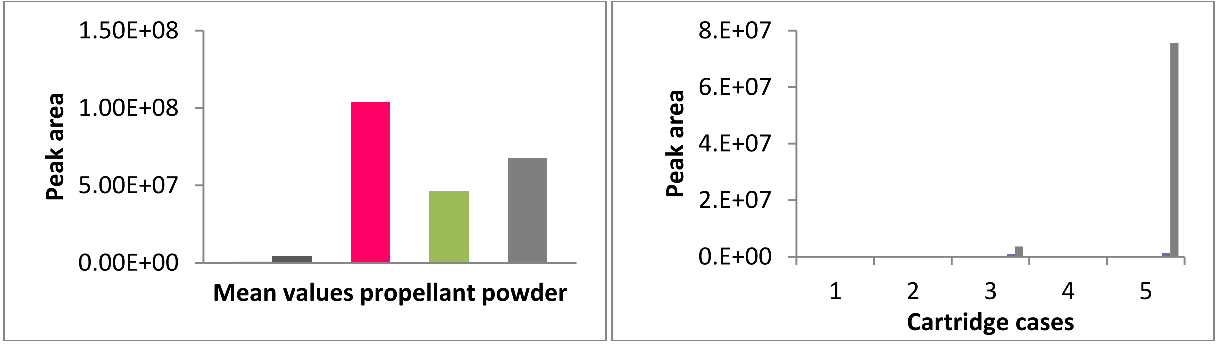
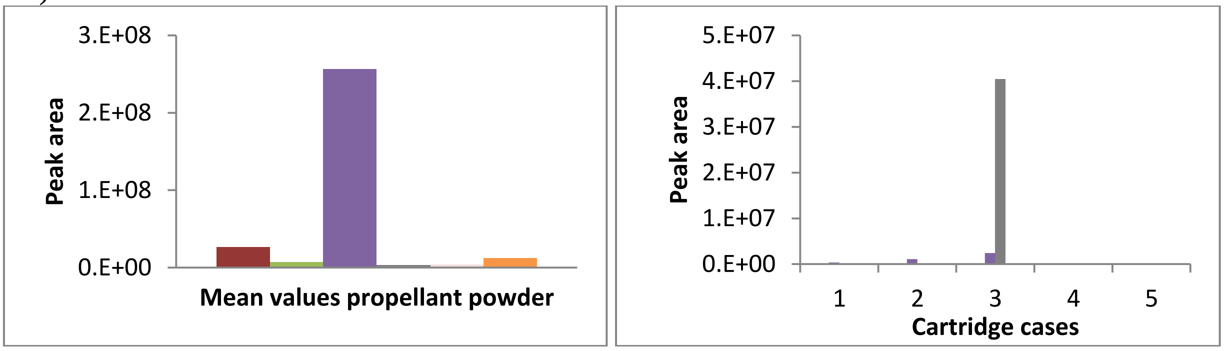


Figure 30 continued: Mean compound abundances (peak area) for unburned propellants and extracts from spent cartridge cases.

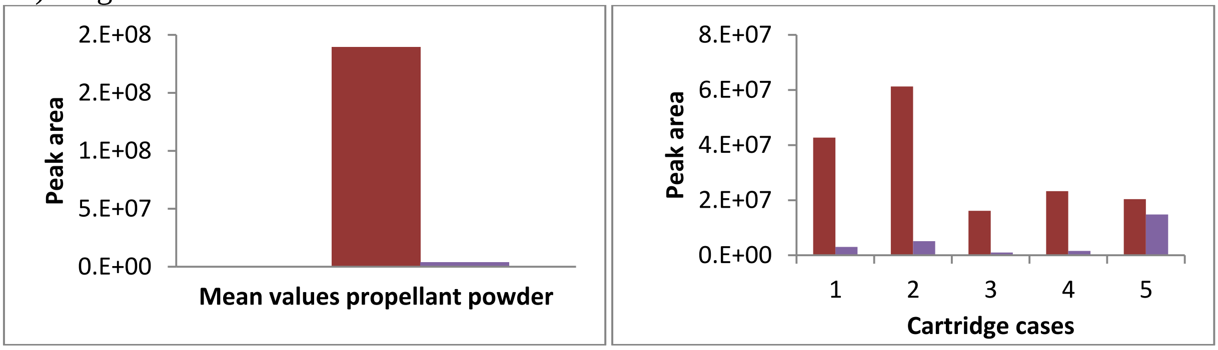
m)Privi Partizan 7.62x51



n) NATO 7.62 x 51



o) Magtech 9mm



p) Winchester 9mm

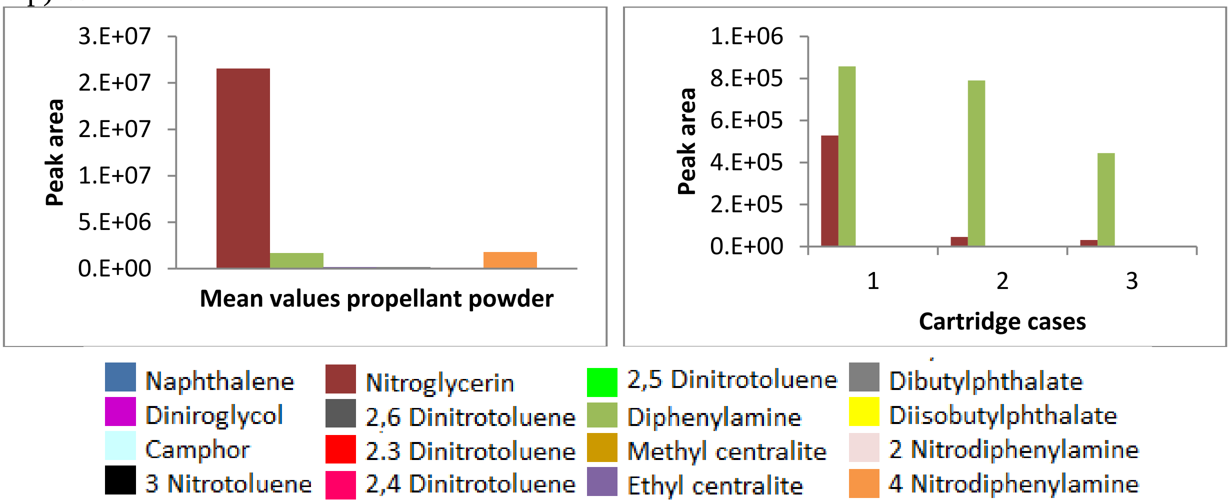


Figure 30 continued: Mean compound abundances (peak area) for unburned propellants and extracts from spent cartridge cases.

By reference to figure 30 it is clear that most of the compounds that are originally found in the unburned powders are not preserved in the spent cases. Table 26 illustrates the compounds that were present in the original unburned powders and those remaining in the spent cases. Only two of the 16 ammunition’s cartridge cases contained all of the compounds in the original propellant, the Magtech .357mag and the Winchester .38spl(ringed in red on the table). These two ammunitions were the most simple in terms of initial propellant composition, containing only two compounds (NG and EC for the Winchester 38spl and EC and DPA in the Magtech .357Mag). It is reasonable to suggest, therefore, that as these propellants contained greater amounts of fewer compounds this could be responsible for the observed result. However, further work with more “simple” propellant powders is required in order to determine this.

The compounds extracted from the spent cases were not present in the same relative abundances as were seen in the unburned powder. Figure 31 shows example chromatograms of extracts from unburned propellant and an extracted cartridge case from the Magtech .357mag ammunition. Based on the relative abundance data collected from these extracts it would not be possible to directly link the spent cartridge cases to a propellant type. With industry loaded cases this is of relatively little importance as the fact that the cartridge case must be held before such extracts can be made means that any manufacturer details can be obtained from the cases. However, in situations where cartridge cases have been hand loaded by an individual such residue information may be useful as a discriminative technique for narrowing down the types of reloading powder that might have been used. For example if a case was to contain camphor, as in the Privi Partizan 7.62x39 ammunition it would, in the case of the 16 propellants tested, narrow the potential propellant to one.

Table 26: Compounds present in unburned propellants (red) and spent cartridge extracts(blue)

AMMUNITION	NAPH	DNG	CAMPH	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22LR	🟥				🟥					🟥		🟥			🟥	🟥
Case 1										🟦						
Case 2										🟦						
Case 3																
Case 4										🟦						
Case 5																
VOSTOK 22LR	🟥	🟥			🟥					🟥	🟥	🟥	🟥		🟥	🟥
Case 1										🟦						
Case 2										🟦		🟦				
Case 3										🟦		🟦				
Case 4																
Case 5										🟦		🟦				
L&B 357MAG					🟥					🟥		🟥	🟥			🟥
Case 1																
Case 2					🟦					🟦						
Case 3					🟦					🟦						
MAGTECH 357 MAG												🟥	🟥			
Case 1												🟦	🟦			
Case 2												🟦	🟦			
Case 3												🟦	🟦			
Case 4												🟦	🟦			
Case 5												🟦	🟦			
GECO 38SPL										🟥		🟥	🟥			
Case 1																
Case 2																
Case 3																
Case 4																
Case 5																
WIN 38 SPL					🟥							🟥				
Case 1					🟦							🟦				
Case 2					🟦							🟦				
Case 3					🟦							🟦				
Case 4					🟦							🟦				
Case 5					🟦							🟦				

Table 26 continued: Compounds present in unburned propellants (red) and spent cartridge extracts (blue)

AMMUNITION	NAPH	DNG	CAMPH	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
ELEY 410	🟥				🟥					🟥		🟥	🟥	🟥	🟥	🟥
Case 1										🟦			🟦	🟦		
Case 2										🟦			🟦	🟦		
Case 3										🟦			🟦	🟦		
Case 4										🟦			🟦	🟦		
Case 5										🟦			🟦	🟦		
WIN 410	🟥				🟥					🟥		🟥	🟥		🟥	🟥
Case 1	🟦				🟦					🟦		🟦				
Case 2	🟦				🟦					🟦		🟦				
Case 3	🟦				🟦					🟦		🟦				
Case 4	🟦				🟦					🟦		🟦				
Case 5	🟦				🟦					🟦		🟦				
MAG 556CBC					🟥					🟥			🟥			🟥
Case 1																
Case 2																
Case 3																
Case 4																
Case 5																
PRIVI 762X39			🟥							🟥		🟥				
Case 1			🟦													
Case 2			🟦									🟦				
Case 3			🟦									🟦				
Case 4			🟦									🟦				
Case 5			🟦							🟦		🟦				
Case 6			🟦									🟦				
FED 762X51					🟥					🟥			🟥			
Case 1																
Case 2																
Case 3																
Case 4																
Case 5																

Table 26 continued: Compounds present in unburned propellants (red) and spent cartridge extracts (blue)

AMMO	NAPH	DNG	CAMPH	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
LAPUA 762X51										🟥		🟥				
Case 1																
Case 2																
Case 3																
Case 4																
Case 5																
NATO 762X51					🟥					🟥		🟥	🟥		🟥	🟥
Case 1												🟦				
Case 2												🟦				
Case 3												🟦	🟦			
Case 4																
Case 5																
PRIVI 762X51			🟥			🟥	🟥	🟥	🟥	🟥		🟥	🟥			
Case 1																
Case 2																
Case 3												🟦	🟦			
Case 4																
Case 5												🟦	🟦			
MAG 9MM				🟥	🟥							🟥				
Case 1					🟦							🟦				
Case 2					🟦							🟦				
Case 3					🟦							🟦				
Case 4					🟦							🟦				
Case 5					🟦							🟦				
WIN 9MM					🟥					🟥		🟥	🟥		🟥	🟥
Case 1					🟦					🟦						
Case 2					🟦					🟦						
Case 3					🟦					🟦						

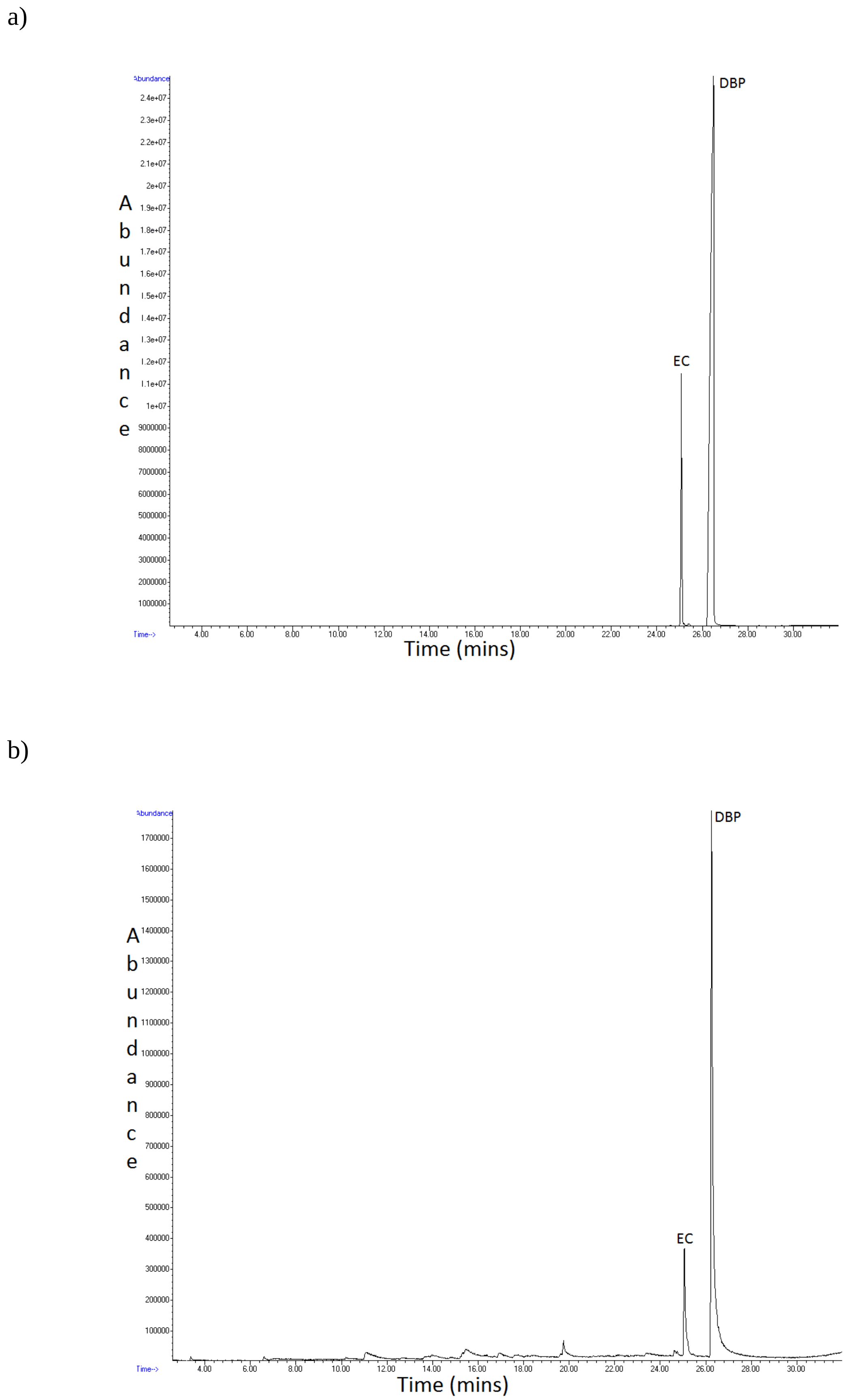


Figure 31: Comparison on samples of; a) unburned Magtech .357Mag propellant and b) an extracted spent cartridge case.

6.3.2 Extractions from pistol and revolver cases

Andrasko and Ståling (1999) reported that they found extractions from spent pistol and revolver cartridges difficult due to the relatively small amounts of OGSR deposited in such cases. Andrasko and Ståling (1999) extracted their cases at room temperature whereas the cases in this investigation were extracted at either 40°C or 80°C. It would seem from this study that the application of a higher extraction temperature is more suitable for these smaller calibre cases. All bar one of the pistol and revolver ammunition types were seen to contain some compounds found in the preceding unburned powders.

6.3.3 Cartridge case extracts and their applicability to "time since" discharge back calculations

A number of authors have published work which uses the loss of compounds from spent cartridge cases over time to determine a time period since the cartridge was fired (Weyermann *et al*. (2009) Andrasko and Ståling (1999)). It must be seen as important that if these back calculations are to be wholly useful the amounts of any compound remaining in spent cartridges must be reproducible from case to case. If this is not so then any calculations made could well be flawed.

Table 27 contains "relative distribution" figures (as described in section *5.3.2.1 (page 111)*) for the compounds extracted from the cartridge cases. Figures calculated for the same compounds extracted from the samples of unburned propellants are also included for comparison. By reference to these values in Table 27 and also the graphical representations of cartridge case extracts (figure 30) it can be seen that the abundances of compounds extracted from cartridge cases are very variable. In some ammunitions (DPA in Remington .22LR , DPA and EC in Vostok .22, NG and DPA in Lellier and Bellot .357 Mag, EC and DBP in Privi 7.62x51, EC and DPA in Nato 7.62x51 and DPA and EC in Privi 7.62x39) a compound that is present in one of the cartridges is not seen at all (below LOD) in another. This lack of reproducibility in the cartridge cases is much greater than the figures calculated for the unburned powders. This suggests that the variability in the case extracts is likely to be due to non-reproducible mechanisms taking place during firearm discharge. The implication of these finding is that great care must be taken if any time since discharge calculations are to be undertaken. Taking DPA as an example (Weyermann *et al*. (2009) having suggested its worth for back calculations), in four ammunitions (Remington .22, Vostok .22, Lellier and Bellot .357Mag, Privi 762x39) it is present in a number of case extracts but undetected in others. Therefore, if the loss of this compound is to be used for back calculation caution must be applied. The presence of DPA in a case would suggest the cartridge had been relatively recently discharged, however, the lack of DPA does not suggest that the cartridge had not been fired recently (Weyermann *et al*. (2009), measured the loss of this compound over 30 hours).

These results have shown that a number of test cases must be produced for any ammunition in order to determine the relative distributions for compounds between cases. This would help assess the value of any time since discharge calculations.

In this study no actual time since discharge calculations were carried out. It was the intent of this piece of work to assess the initial levels of compounds found in discharged cartridges and interpret these results in terms of the potential consideration these results might raise for carrying out such back calculations. The extractions in this study were carried out on cartridges stored at -22°C prior to analysis in the hope of representing as closely as possible analysis occurring directly following cartridge discharge.

Table 27: Relative distribution figures for compounds extracted from cartridge cases (black) and unburned propellants (red). (Overleaf).

AMMUNITION	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22	/	/	/	/	/	/	/	/	/	252.68	/	/	/	/	/	/
REM 22	/	/	/	/	/	/	/	/	/	44.437	/	/	/	/	/	/
VOSTOK 22	/	/	/	/	/	/	/	/	/	397.20	/	/	235.24	/	/	/
VOSTOK 22	/	/	/	/	/	/	/	/	/	8	/	/	81	/	/	/
L&B 357MAG	/	/	/	/	233.63	/	/	/	/	189.18	/	/	/	/	/	/
L&B 357MAG	/	/	/	/	11.97	/	/	/	/	30.95		/	/	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	94.17	88.97	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	18	13	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
GECO 38SPL		/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
WIN 38 SPL	/	/	/	/	141.20	/	/	/	/	/	/	262.81	/	/	/	/
WIN 38 SPL	/	/	/	/	18.22	/	/	/	/	/	/	3.78	/	/	/	/
ELEY 410	/	/	/	/	/	/	/	/		81.57	/	/	161.43	37.93	/	/
ELEY 410	/	/	/	/	/	/	/	/	/	15.88	/	/	11.119	27.099	/	/
WIN 410	127.22	/	/	/	118.13	/	/	/	/	134.92		159.44	/	/	/	/
WIN 410	28.86	/	/	/	10.37	/	/	/	/	10.71	/	2.27	/	/	/	/
MAG 556CBC	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
MAG 556CBC	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
PRIVI 762X39	/	/	124.06	/	/	/	/	/	/	/	600	266.84	/	/	/	/
PRIVI 762X39	/	/	63.07	/	/	/	/	/	/	/	/	47.39	/	/	/	/
FED 762X51	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
FED 762X51	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
NATO 762X51	/	/	/	/	/	/	/	/	/	/	/	269.38	500	/	/	/
NATO 762X51	/	/	/	/	/	/	/	/	/	/	/	7.83	2.94	/	/	/
PRIVI 762X51	/	/	/	/	/	/	/	/	/	/	/	294.69	477.23	/	/	/
PRIVI 762X51	/	/	/	/	/	/	/	/	/	/	/	17.16	7.24	/	/	/
MAG 9MM	/	/	/	/	138.10	/	/	/	/	/	/	280.79	/	/	/	/
MAG 9MM	/	/	/	/	19.61	/	/	/	/	/	/	83.64	/	/	/	/
WIN 9MM	/	/	/	/	246.69	/	/	/	/	59.17	/	/	/	/	/	/
WIN 9MM	/	/	/	/	39.79	/	/	/	/	28.07	/	/	/	/	/	/

6.3.4 The analysis of propellant breakdown products extracted from spent cartridge cases

Both Andrasko and Ståling (1999) and Weyermann *et al*. (2009) reported the applicability of some breakdown products from cartridge discharges for time since discharge back calculations. Andrasko and Ståling (1999) used Naphthalene and an unknown compound named TEA-2 to calculate time since discharge of a number of cartridge case types. Weyermann *et al*. (2009) listed 6 compounds that were considered suitable for carrying out back calculations, these were Benzonitrile, phenol, 2-ethyl-hexanol, naphthalene, 1,2 dicyano-benzene and diphenylamine. In this investigation no standard solutions for these compounds (except DPA) were held and it was not the primary concern of the project to investigate products of combustion. However, as a large number of breakdown product peaks were seen in the chromatograms of some of the extracted cases it was determined to be something worthy of discussion.

Figure 32 shows an example of an annotated chromatogram from an SPME extract of a spent cartridge from Winchester 9mm ammunition. As with the compounds seen in unburned propellant powders remaining in spent cartridges it was of interest whether the abundances of breakdown products were reproducible between cases. Table 32 contains products of combustion relative distribution data for 3 ammunition types assessed. The results of these calculations show that the abundances of these compounds between spent cases are variable and this will in turn have implications for the relevance of any time since discharge back calculations that may be carried out using these compounds. Also abundances of Phenanthrene (in Magtech 9mm) Naphthalene (in 9mm Winchester) and Biphenyl (in 9mm Winchester) were not detected in some of the spent cases. This finding means that the lack of a breakdown compound in any given cartridge cannot be taken as a sign of case age. It is the presence of these compounds that are significant in that they may indicate a recently discharged case. However, as this area was not the main focus of this study and only a small number of extractions have been investigated more work is required in this area.

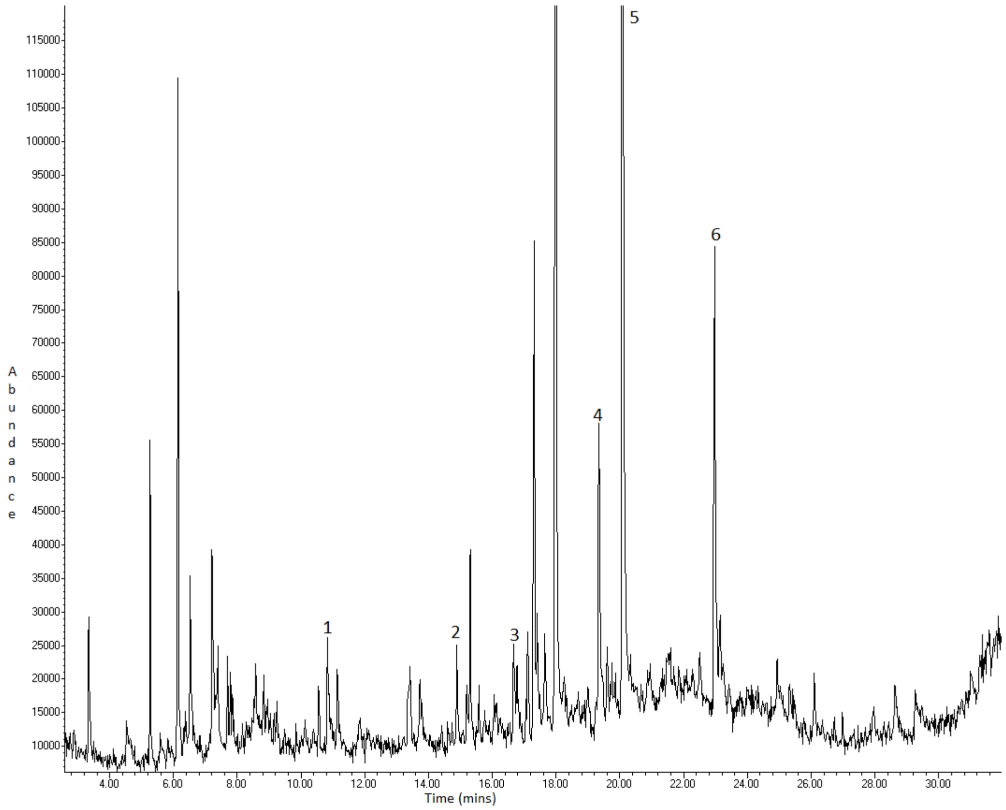


Figure 32: extract from a spent Winchester 9mm cartridge; 1. Naphthalene, 2. Nitroglycerine, 3. Biphenyl, 4. Fluorene, 5. Diphenylamine, 6. Phenanthrene.

Table 32: Relative distribution figures for products of combustion found in spent cartridge cases

Ammunition	Benzonitrile	Naphthalene	Biphenyl	Flourene	Phenanthrene
MAG 357Mag	43.40	141.56	226.04	/	/
WIN 9mm	/	300	163.01	91.24	52.65
MAG 9mm	/	/	/	/	199.26

Andrasko and Ståhling (1999) and Weyermann (2009) used different extraction and analysis methodologies and different SPME fibre types in their research and, therefore, it is not possible to compare these finding directly with those reported in their papers.

6.4 Conclusions

The developed method has been shown to be suitable for the extraction of compounds of interest (originating from unburned propellants and products of combustion) from cartridge cases from a wide range of calibre and firearm types. Such an investigation into spent cartridge case extracts from a large number ammunition types, using an elevated extraction temperature and the 65µm PDMS/DVB SPME fibre has not been previously published.

The comparisons of spent cartridge extracts to unburned powders have shown that it would not be possible to link extracts from cases to powders in most cases. The results of case extracts may, however, be useful as a discriminatory technique.

An investigation into the reproducibility of compounds deposited in spend cartridges has shown that there is a great level of variability. These findings suggest that any attempt to apply time since discharge back calculations to cartridges must be approached with caution. A number of test spent cartridges must be assessed in order to determine the variability between cases for any given ammunition type. With some ammunition types it was seen that a compound present in one case might be missing from another. Therefore, only the presence of the compounds could potentially be used to estimate how long ago a discharge had occurred (being present would indicate a recent discharge). For example, if DPA is extracted from a cartridge case it would suggest that the firing had occurred recently. However, the lack of a compound cannot be taken as a sign of there being a longer time since discharge as it has been shown to be possible to extract no compounds from a cartridge, even when extraction takes place very soon after discharge.

6.5 Future work

Only 16 ammunition types have been evaluated in this investigation, which in the context of the number of ammunition types that exist is a small population sample. Future work in this area would be to expand the number of ammunitions investigated.

7 The application of nylon bags to the extraction of organic gunshot residues from fabrics

7.1 Introduction

7.1.1 The principles of head space analysis

The procedure of headspace extraction involves suspending an adsorbent material, either a porous polymer or carbon, in the headspace of a sample, thus allowing the volatiles in the vapour to adsorb or absorb onto/into the material. The compounds collected on this sampling medium can then be extracted by solvent or thermal desorption allowing analysis to take place (Waters and Palmer (1993), ASTM (2001), Caddy *et al*. (1991), Jackowaki (1997), Newman *et al*. (1996))

One of the main advantages of using this technique is that the original sample from which extracts are taken can be stored for re-analysis, as extractions are performed in a closed system, avoiding depletion of the sample or introducing any potential sources of contamination.

Recovery of sample analytes depends largely on temperature and time (Bertsch and Ren, 2000). Generally, temperatures above ~60^{o}C are required to ensure recovery of the higher boiling compounds. However, excessive heating, as well as longer sampling times, will result in poorer yields of more volatile components, which become preferentially replaced by the heavier molecules (Newman *et al*,1996).

7.1.2 Aims

The aim of this study was to apply nylon evidence collection bags and SPME to the collection and extraction of OGSRs from samples of clothing fabrics. Initial work was carried out in order to determine which fabric types retained the greatest amount of residues. Further work was concerned with determining any differences between residues produced by different ammunitions types. It was also investigated whether residues extracted from fabrics could be matched to unburned powders or to spent cartridge cases.

7.2 Materials and Methods

7.2.1 Solid phase microextraction

65µm polydimethylsiloxane/ divinylbenzene fibres were purchased from Supelco (Bellefonte, PA, USA) Fibres were conditioned prior to use in the manners recommended by the manufacturer.

7.2.2 Solvents and standards

See section 3.2.1 (page 79)

7.2.3 Ammunitions

Twelve different ammunitions were used, these are summarised in Table 29

Table 29: Ammunitions analysed and firearms used to discharge them.

Firearm	Ammunitions
Glock 17 (pistol)	Samson (Israeli Military Industries) 9mm
	Winchester 9mm
Tikka T-3 (rifle)	Privi Partizan 7.62x51
	Nato 7.62x51
Uberti Colt Army (revolver)	Lellier and Bellot .357 mag
	Geco .38spl
	Winchester .38spl
	Magtech .357mag
BSA (shotgun)	Eley .410 extra long
	Winchester .410 X super High Brass Game Load
CZ 29990 (rifle)	Remington .22LR
	Vostok .22LR

7.2.4 Capturing of high speed video of firearm discharges

An Olympus i-Speed 3 camera was used to capture the discharges of several firearm types (Table 30). These firearms were provided by Key Forensic Services and the Nottinghamshire Police. Figures 33 and 34 show the set up of the camera and lights used to make the recordings.

Table 30: Firearms provided by the Nottinghamshire Police and Key Forensic Service

Firearm manufacturer, model and type	Firearm calibre
Heckler and Koch G36C (carbine)	5.56mm
Walther p99 (pistol)	9mm
Glock 26 (Pistol)	9mm
Smith and Wesson .357 (revolver)	.357
Gorosabel s/s (Shotgun)	12 bore

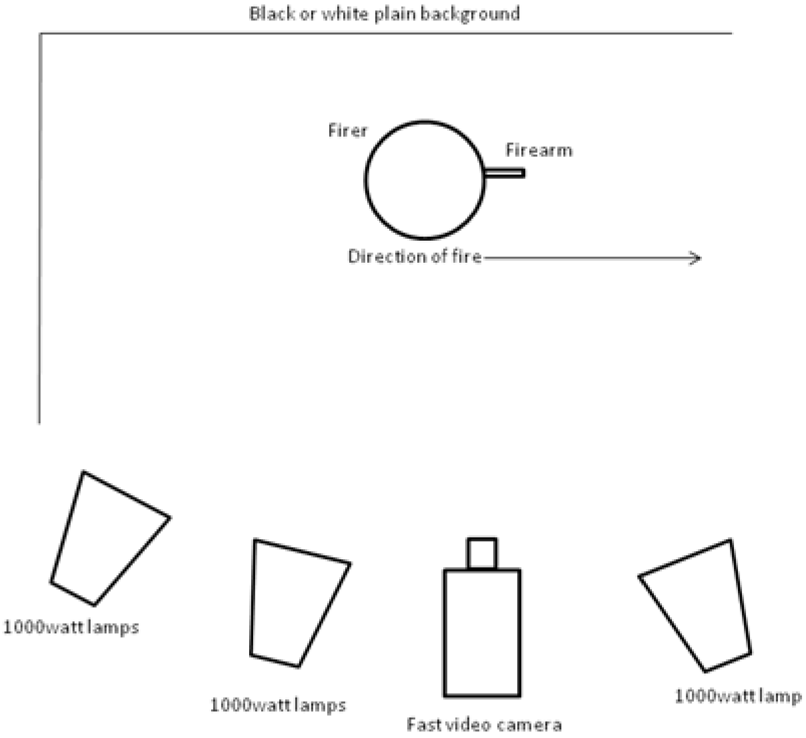


Figure 33: Set up of the Olympus fast photography fast video system.

Figure 34: Photograph of the Olympus fast video set up.

7.2.5 Collection of unburned propellant powders

Samples of unburned powder were collected from unfired rounds of each of the ammunition types by pulling their bullets and collecting the powders in headspace vials for analysis.

7.2.6 The extraction of OGSR from spent cartridge cases

Cartridges were fired though the firearms listed in Table 30. Three rounds were cycled through each firearm before any sample cartridges in order to reduce any memory/carry over of materials from previously used ammunitions. Spent cartridge cases were collected from Key Forensic Services and placed into individual vials (14mL). Cases were stored at -22°C until being analysed in order to minimise the loss of any volatile materials. Cases were extracted within the vials. Nylon evidence collection bag material was used to seal vials allowing headspace analysis to be carried out. An extraction temperature of 80°C and a time of 35 minutes were used. Samples were placed in the oven 10 minutes before extractions were carried out in order to allow the compounds of interest to enter the headspace. SPME fibres were immediately injected into the GC-MS system following extraction.

7.2.7 Collection of OGSR on fabric samples

20x20cm Swatches of five different materials (Table 31) were cut from garments of clothing. Samples were pinned to a ballistic rubber wall, with a piece of white paper in between fabric and wall. This paper was intended to prevent any residues transferring from the wall to the fabric. Swatches were shot from a distance of 20cm with single rounds of ammunition and then placed into to nylon evidence bags immediately following discharge. Nylon bags were swan-necked at both ends and stored in at -22°C as above prior to analysis. 3 swatches of each of the fabrics were shot by each of the ammunitions types.

Table 31: Fabric types assessed

Fabric	**Materials**
T-shirt	100% cotton
lab coat	67:33% polyester:cotton
Fleece	100% polyester
Grey jumper	80:20% lambs wool:nylon
Brown jumper	100% acrylic

7.2.8 Analysis of blank fabric samples

Control swatches were taken for each of the fabric types investigated. These were sealed in nylon bags as described above. These fabrics were never exposed to any environment in which firearms were handled, stored or discharged.

7.2.9 Collection of particles from fabric samples

Once SPME extracts had been carried out on fabric samples they were removed from their nylon bags and the materials adhered to their surfaces were removed by scraping the surface of the fabrics with a clean spatula. Fabrics were held at roughly a 45° angle to lab work top surface, a piece of paper was placed underneath the fabric and then a spatula was used to scrape downwards from the top to the bottom of the fabric. This method allowed some of the materials adhered to the fabric surfaces to be collected onto the paper surface. These “scrapings” were then collected into 14mL headspace vials. SPME extractions were carried on these samples in the same manner as for nylon bagged samples. This method allowed these collected particulates to be analysed separately to the fabric.

7.2.10 GC-MS equipment and conditions

The GC used was an Agilent Technologies 6890N and the MS was a 5975MS. A J&W Scientific HP5-MS (30M x 0.25mm x 0.25µm) was used. Run conditions were as follows. Thermal desorption of the SPME fibres was carried out using an injector temperature of 250°C, with splitless injection. An SPME/direct inlet linear was purchased from Sigma Aldrich in order to minimise band broadening. The initial oven temperature was 50°C, rising to 200°C by 6°C per minute, at 27 minutes the temperature was raised by 20° per minute until 300°C at 32 minutes. The total run time was 32 minutes. The carrier gas was helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS Ltd., Manchester, England).

For this series of analyses it was determined that selective/single ion monitoring (SIM) was required as the levels of the compounds of interest being detected were very low. Details about SIM can be found in section 3.1.10 (page 78). Table 32 contains details of the compounds of interest and the ions monitored for each. For each of the compounds the dwell time was 30ms.

Table 32: Selected ions for SIM analysis

Compound	**Ion (m/z)**
Naphthalene	Not analysed using SIM
DNG	Not analysed using SIM
Camphor	Not analysed using SIM
3-NT	Not analysed using SIM
NG	46
2,6-DNT	165
2,3-DNT	165
2,4-DNT	165
2,5-DNT	165
DPA	169
MC	134
EC	120
DBP	149
DIBP	149
2-NDPA	167
4-NDPA	214

7.3 Results and discussion

7.3.1 High speed video recording of firearm discharges

High speed video equipment was used to record a number of different firearm types discharging. This was done in order to assess the potential for partially burnt and potentially unburned propellant materials to exit the barrel end of firearms.

7.3.1.1 Revolver close shot

Figure 35 shows a number of still frames taken from the fast video footage of a revolver being discharged with close up framing. Upon discharge a plume of burning residue flashed from the chamber of the firearm, this plume spread and can be seen to impact upon the hands of the firer. Some larger pieces of burning propellant powder were also recorded travelling in the direction of the firer. These largely organic propellant particles maybe potential sources of information if they could be collected and analysed. The fact that these particles are travelling in the direction of the shooter (hands and clothing) means that it may indeed be possible to collect them. However, as these particles are burning it maybe that the full number of compounds present in unburned propellant particles would not remain in these particles. At the barrel end of the weapon an amount of smoke was recorded prior to and following a flash of burning material. After the flash of burning materials a number of particles of propellant powder, unburned or partially burnt were recorded leaving the barrel. Some of these are seen in Figure 37 Some of these were subsequently recorded falling back towards the ground. It may also have been possible that particles such as these may have fallen on the shooter outside the frame of the shot.

7.3.1.2 Revolver long shot

Figure 36 shows a number of still frames taken from the fast video footage of a revolver being discharged at a greater distance. Looking at the region in front of the barrel of the firearm a plume of burning materials was recorded travelling in the direction of the discharge. Ahead of this plume front a number of individual particles of burning propellant powder were recorded also travelling away from the shooter. After the plume front has disappeared from view a number of propellant particles can be seen exiting the barrel end of the firearm. These unburned, or partially burnt, particles “twinkled” as they rotated and reflect the fast video systems lights.

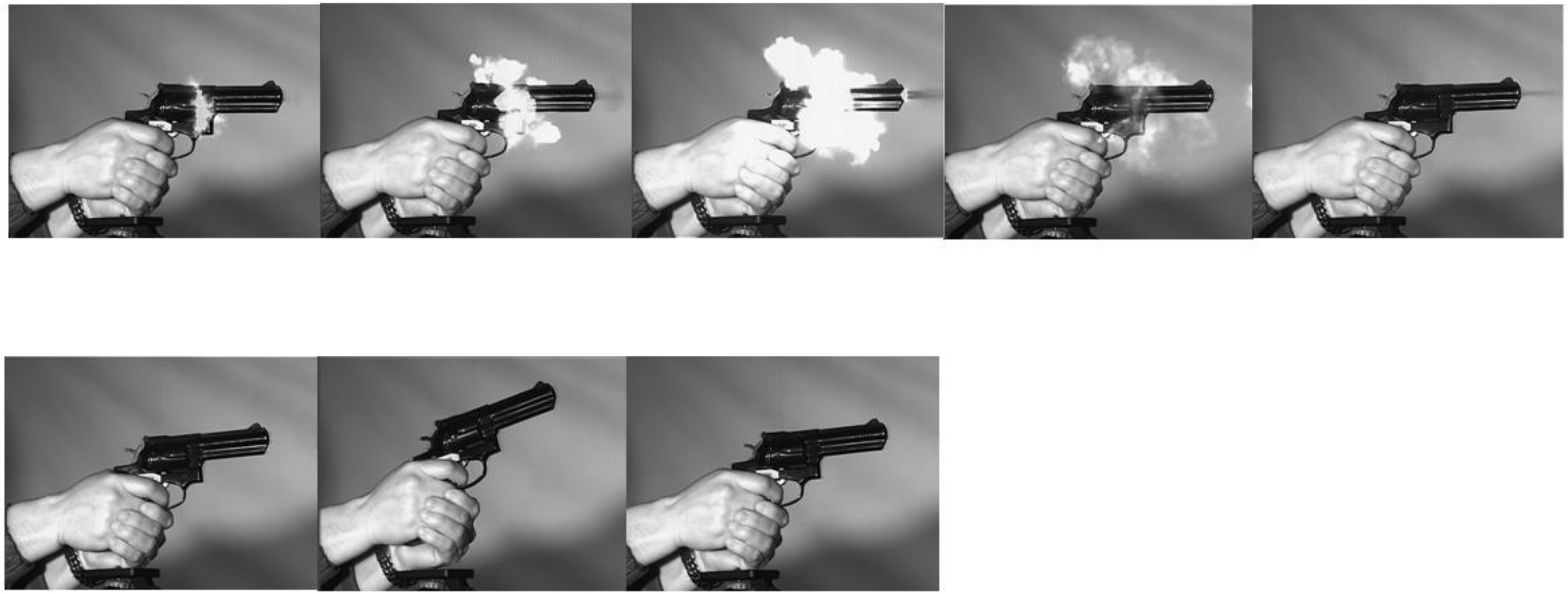


Figure 35: Still frames taken from fast video footage of a revolver discharge. Settings of the fast video equipment were; frame rate 10000 fps, exposure time 100usec total record time 3604 frames.

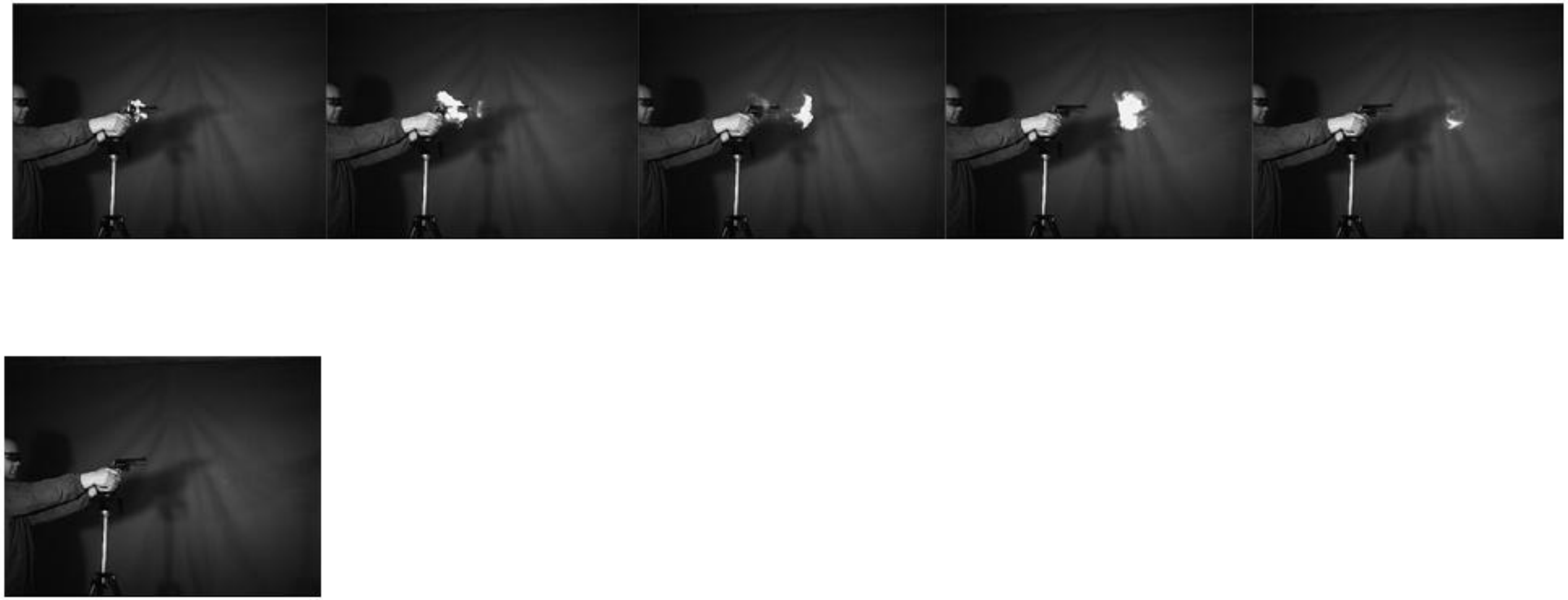


Figure 36: Still frames taken from fast video footage of a revolver discharge (wider framing). Settings of the fast video equipment were; frame rate 10000 fps, exposure time 100usec.

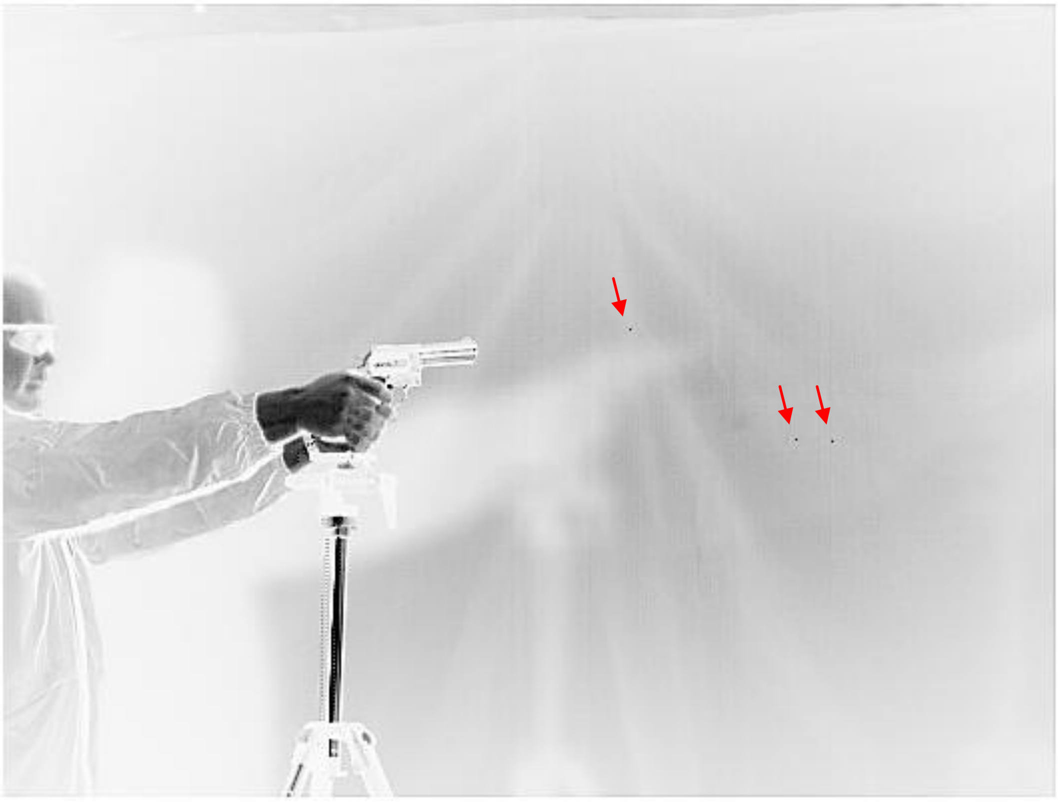


Figure 37: Inverted black and white freeze frame from fast video recording of revolver discharge. Small particles of partially burnt/unburned particles are highlighted with red arrows (particle locations enhanced for printed version).

7.3.1.3 Glock 26 pistol close shot

Figure 38 shows a number of still frames taken from the fast video footage of a Glock 26 pistol being discharged with a close framing. Upon discharge and prior to the bullet leaving the firearm a plume of combusted products leave both the barrel end of the firearm and also the ejection chamber. Following the burning plume front from the barrel end of the weapon a large number of unburned/partially burned propellant power particles were recorded leaving the firearm. These particles may potentially, therefore, be found in the environment surrounding a firearm discharge as well as on any victim that maybe involved in a close quarters shooting. Upon the ejection of the cartridge case from the firearm a single particle of unburned propellant powder was recorded travelling in the direction of the shooter, which could potentially impact clothing or hair and become lodged, such a particle could then be collected for analysis. As the ejected cartridge case spins through the air having hit the edge of the ejection port particles of unburned propellant powder exit the spent cartridge and travel in the direction of the hands and torso of the shooter (Figure 39). Again these particles could potentially be found on the shooter and collected for analysis.

Figure 38: Still frames taken from fast video footage of a Glock 26 discharge (close framing). Settings of the fast video equipment were; frame rate 10000 fps, exposure time 100usec.

Figure 39: inverted black and white freeze frame from fast video of Glock 26 discharge. Particles of propellant materials are highlighted with red arrows.

7.3.1.4 Walther P99 pistol close up

Figure 40 shows a number of still frames taken from the fast video footage of a Walther P99 pistol being discharged. Following the main burning residue plume leaving the barrel end of the weapon a large amount of both burning and potentially unburned propellant powder particles were seen exiting the barrel end of the weapon. This was very similar to what was recorded for the Glock 26 pistol. During the ejection of the cartridge case a number of small particles of propellant powder were also recorded exiting the ejection port. As with the Glock pistol these particles have the potential to become entangled on the clothing of the shooter and could, therefore, potentially be recovered for analysis.

At these distances it was very difficult to show the observed particles in still images and, therefore, it was decided to record a video of just the barrel end of the Walther p99 in an attempt to better record the levels of partially or unburned particles exiting the firearm during discharge. Still frames from this recording can be seen in figure 41. A single frame from this sequence is presented in figure 42. The images are presented in inverted black and white in order the help highlight the particles exiting the firearm.

Figure 40: still frames taken from fast video footage of a Walther P99 discharge (close framing). Settings of the fast video equipment were; frame rate 10000 fps, exposure time 100usec.

Figure 41: still frames taken from fast video footage of a Walther P99 discharge (very close framing). Settings of the fast video equipment were; frame rate 30000 fps, exposure time 100usec.

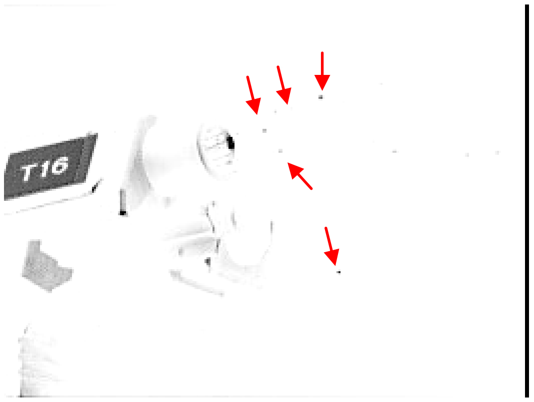


Figure 42: Still from high speed video recording of Walther P99 pistol discharge. Particles are highlighted with red arrows.

7.3.1.5 Shotgun

Figure 43 shows a number of still frames taken from the fast video footage of a S/S Gorosabel shotgun being discharged. Apart from the below images there was not really any important additional information gained from this recording. No individual particles of propellant powder were observed emanated from the barrel end of the weapon, and due to the length of the barrel contact between residues and the shooter (at least during and immediately following discharge) seems to be a lot less likely than with side arms such as revolvers and pistols.

Figure 43: still frames taken from fast video footage of a discharge Gorosabel s/s shotgun (wider framing). Settings of the fast video equipment were; frame rate 10000 fps, exposure time 100usec.

The findings of these preliminary tests showed that the potential exists for partially burnt and potentially unburned propellant materials to come in contact with the environment in front of a firearm discharge. Therefore, an investigation into the extraction of OGSR from materials impacted by GSR materials was deemed to be appropriate.

7.3.2 The effects of temperature on SPME extraction efficiency

Figure 44 contains data from a swatch of a lab coat that was shot by a round of Winchester .410 ammunition that was extracted at 40°C, 60°C and 80°C. These results clearly showed that 80°C was the most appropriate of the three temperatures tested, with greater abundances of all the compounds of interest being extracted. 80°C was, therefore, selected as the extraction temperature for all other extracts carried out.

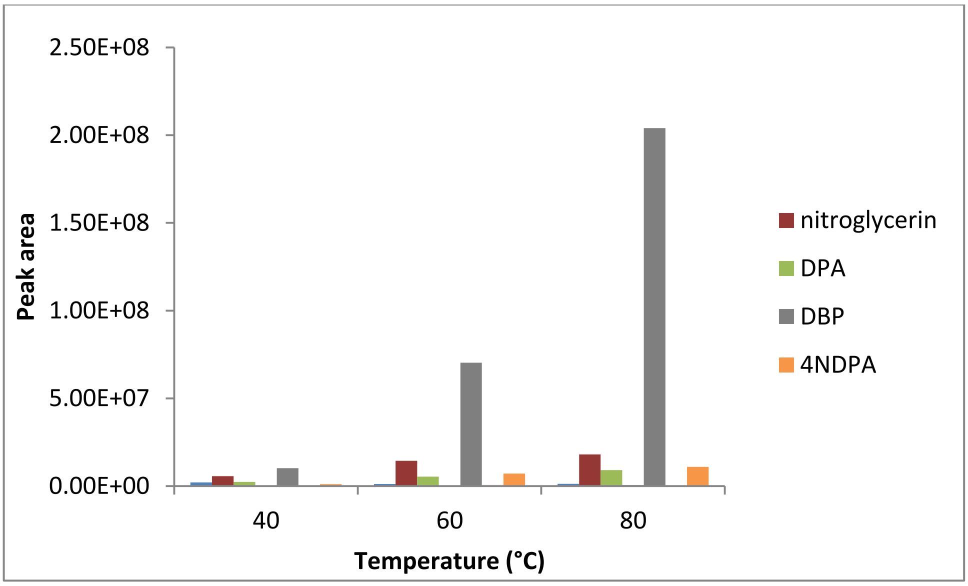


Figure 44: Extraction temperature tests for lab coat swatch shot by Winchester .410 ammunition, carried out at 40, 60 and 80 °C.

7.3.3 Fabric blanks

Extracts from blank swatches of the fabrics showed a small peak for the Grey jumper (Figure 45) and fleece material occurring at the same retention time as DBP. This peak was also identified by the NIST database as DBP.

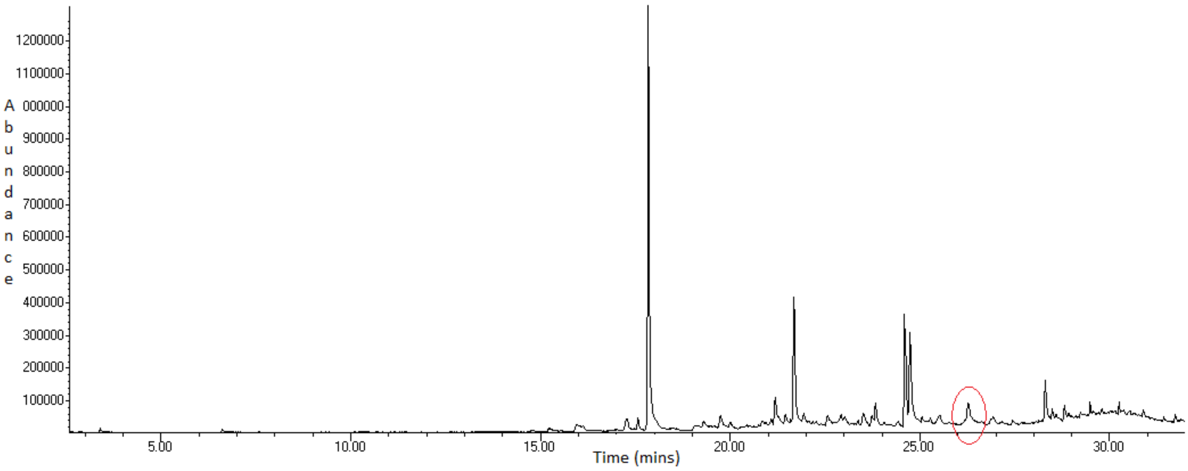
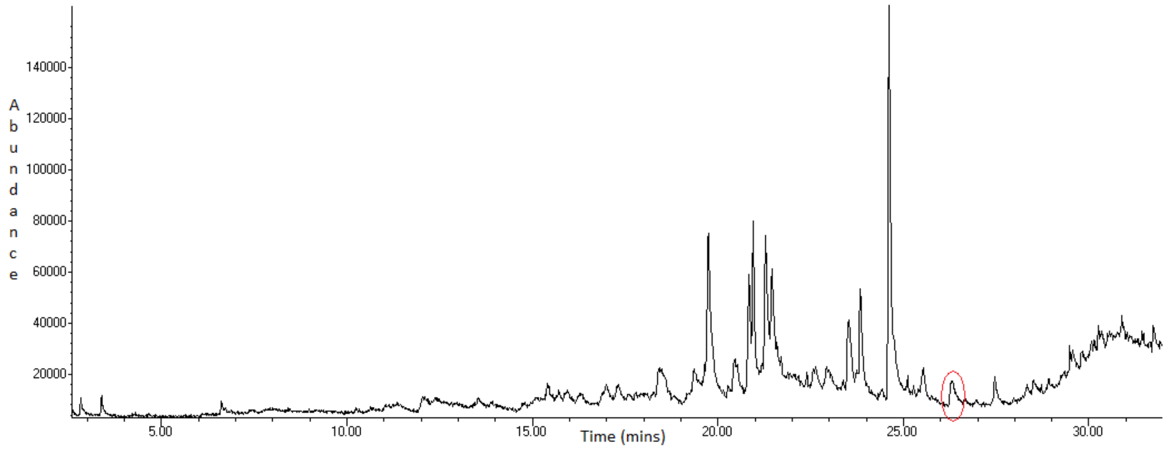


Figure 45: Blank extract from grey jumper. DBP peak circled in red.

These results show that the analysis of a control sample is necessary before the relevance of the presence of any compound which might be related to OGSR can be properly assessed. However, in the extracts from shot fabric samples the peaks for DBP were of higher abundances than the control samples. This is represented for the fleece material in Figure 46. In this case the abundance of DBP is an order of magnitude greater in the shot sample than in the control blank.

The T-shirt, brown jumper and lab coat blank extracts did not contain any of the compounds seen in the ammunitions analysed in this investigation.

a)



b)

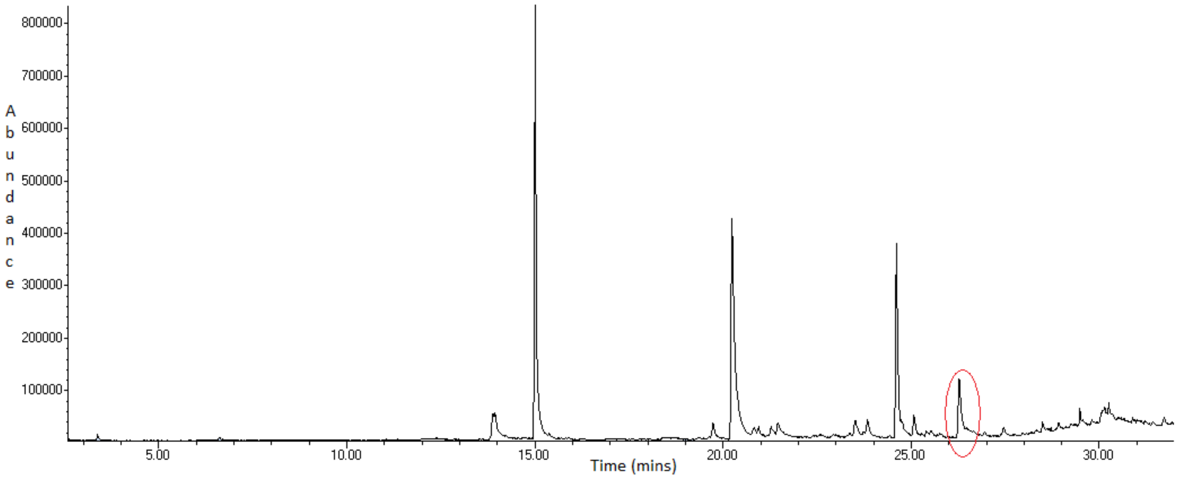


Figure 46: Blank fleece extract (a)) showing DBP peak circled in red, and extract of fleece fabric shot by a single round of Winchester 9mm ammunition (b)). Elevated abundance of DBP (again circled in red) seen in the shot sample.

7.3.4 Retention of OGSR by various fabric types

Figure 47 contains graphical representations of both total ion count and SIM data for extractions taken from the 5 different fabric types tested. Data is presented in the figures in the form of Log_{10} the original abundance figures. This has been done so that the presence of all the compounds extracted can be easily seen. It can be seen from these figures that the use of SIM in the GC-MS methodology has allowed many more compounds to be detected than if TIC data had been used solely.

The fleece fabric was seen to retain the greatest levels of OGSR. Due to the structure of fleece materials this might be expected, with a deeper pile for residue particles to become lodged in. The lab coat was seen to be the second best at retaining residues. The fabric that was shown to perform the worst was the grey jumper, retaining the least number of compounds in two of the three ammunition tests (and joint bottom for the other ammunitions).

1) L and B .357Mag

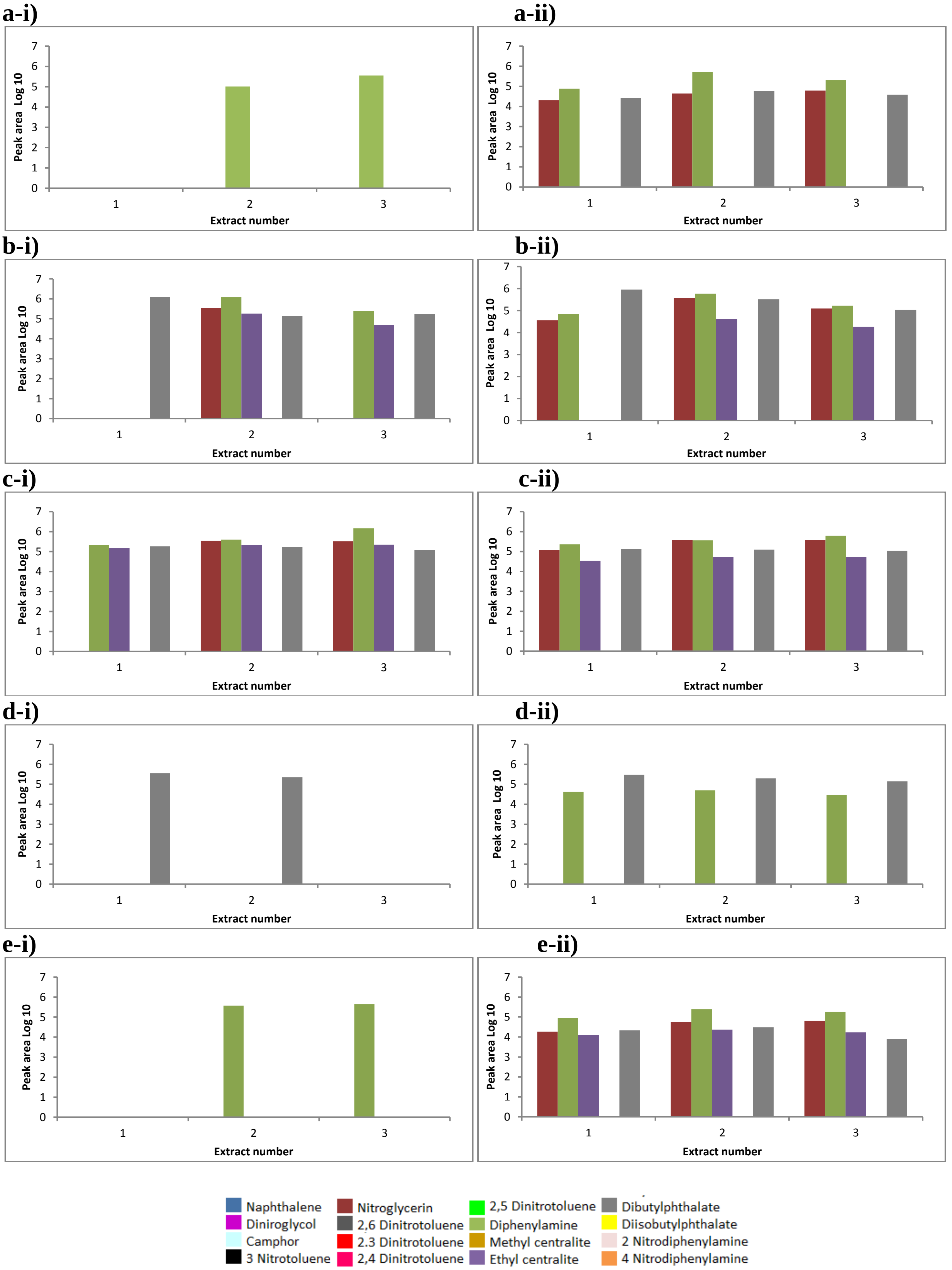


Figure 47: Fabric extract results: a-i) T-shirt TIC, a-ii) T-shirt SIM, b-i) Lab coat TIC, b-ii) Lab coat SIM, c-i) Fleece TIC, c-ii) Fleece SIM, d-i) Grey jumper TIC, d-ii) Grey jumper SIM, e-i) Brown jumper TIC, e-ii) Brown jumper SIM.

2) Winchester 9mm

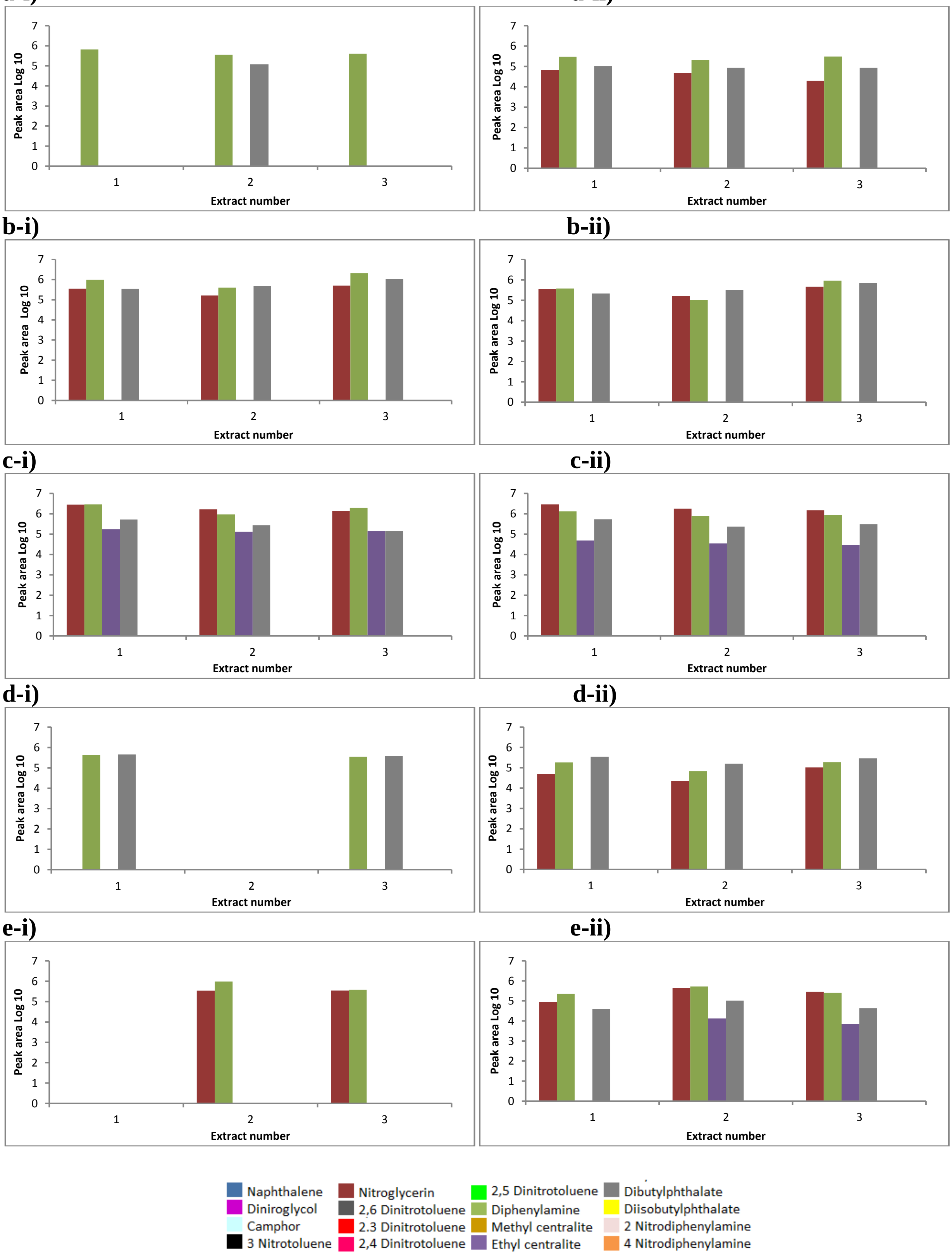

a-i) a-ii) b-i) b-ii) c-i) c-ii) d-i) d-ii) e-i) e-ii)

Figure 47 continued: Fabric extract results: a-i) T-shirt TIC, a-ii) T-shirt SIM, b-i) Lab coat TIC, b-ii) Lab coat SIM, c-i) Fleece TIC, c-ii) Fleece SIM, d-i) Grey jumper TIC, d-ii) Grey jumper SIM, e-i) Brown jumper TIC, e-ii) Brown jumper SIM.

3) Samson 9mm

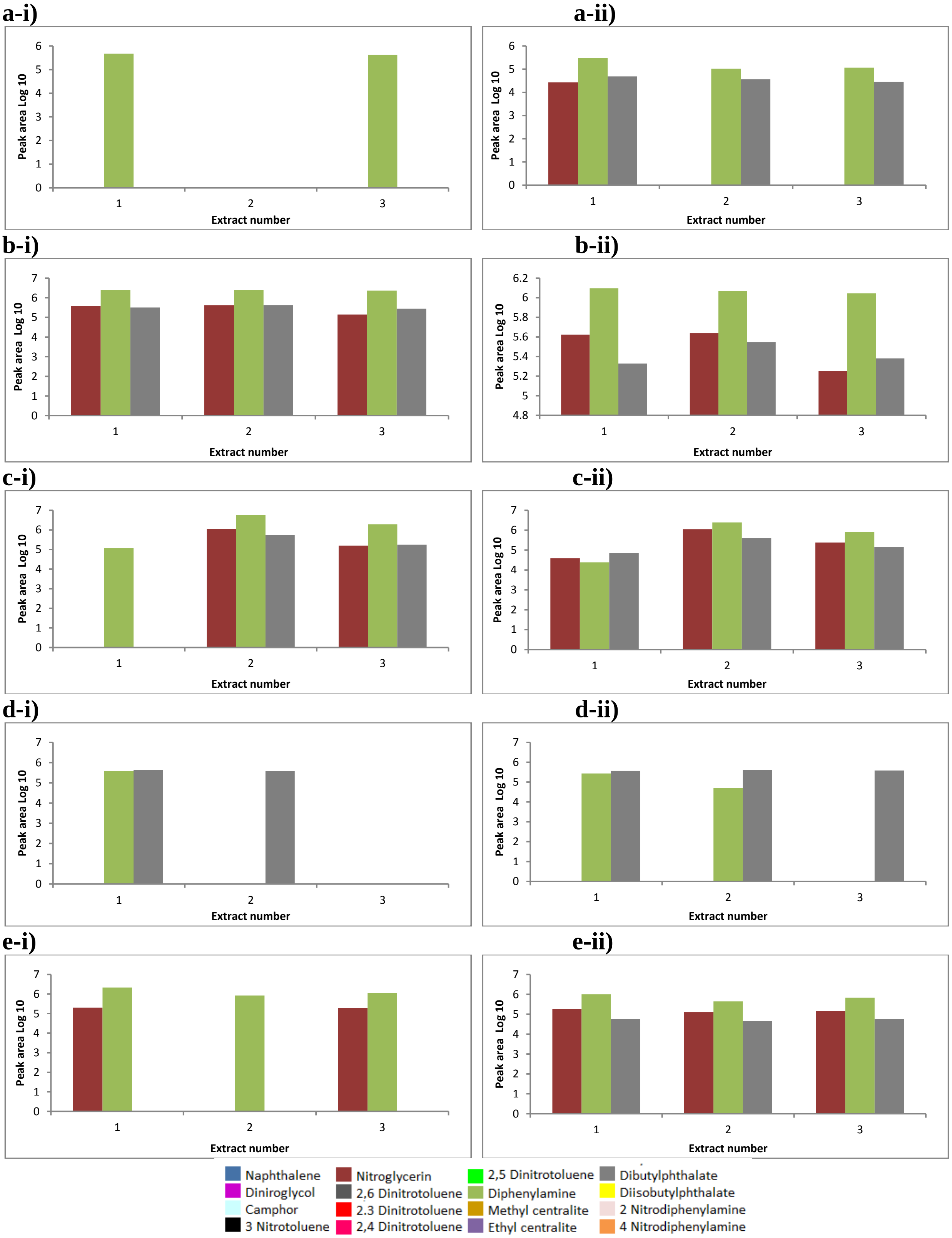


Figure 47 continued: Fabric extract results: a-i) T-shirt TIC, a-ii) T-shirt SIM, b-i) Lab coat TIC, b-ii) Lab coat SIM, c-i) Fleece TIC, c-ii) Fleece SIM, d-i) Grey jumper TIC, d-ii) Grey jumper SIM, e-i) Brown jumper TIC, e-ii) Brown jumper SIM.

For each of the shot fabrics a piece of A4 paper was placed behind the swatch. This was intended to prevent cross contamination from the bullet capturing wall. However, these pieces of paper also served as records of the amounts of residue travelling through each of the different fabric types. Figure 48 contains images taken of pieces of paper placed behind each of the fabric types. It can be seen that both the fleece and lab coat fabrics did not visibly allow any residue to pass though them, therefore, retaining more OGSR within the fabric itself. The T-shirt, brown jumper and grey jumper fabrics all allowed residues to pass through them and impact on the paper. It is, therefore, hypothesised that this was a cause for the poorer extractions seen with these fabrics. If a person was shot at close range while wearing these fabric types it is, therefore, likely that these residues would be found on the skin and may, therefore, be collected for analysis.

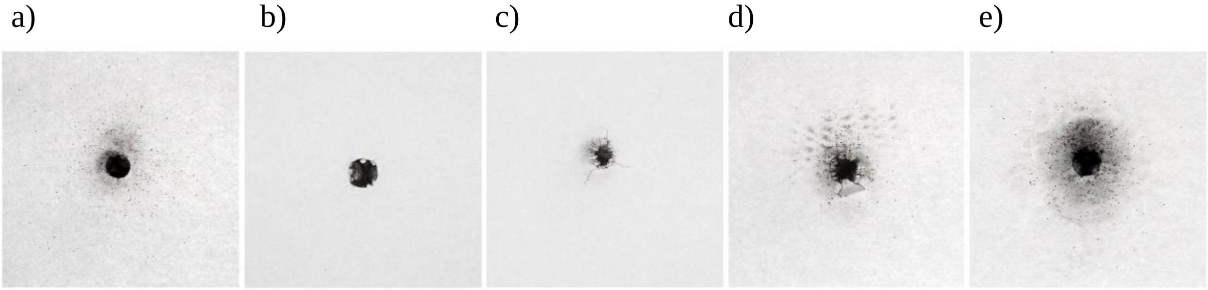


Figure 48: Images of paper placed behind each fabric type during discharge. a) T-shirt, b) Lab coat, c) fleece, d) brown jumper, e) grey jumper.

Based on these results and the blank fabric extract data it was decided to use the lab coat material for further research. Even though the fleece material performed better it was determined that the lab coat material would be a better standard for further tests as its blank extracts did not contain DBP.

7.3.5 Comparing fabric extracts to unburned propellant powders

It was possible to link some of the extracted residues from the fabric samples to one of the 9 ammunitions tested. Examples of this are the Vostok .22LR ammunition which was the only propellant to contain methyl centralite and the Eley .410 which contained diisobutylphthalate. The presence of these compounds in the extracted fabrics made it possible to isolate these ammunitions as the only sources of the residues.

In terms of linking the fabric extracts back to unburned propellants by matching all compounds present, this was only possible for some of the revolver rounds, the Magtech .357mag and the Winchester .38spl. For these ammunitions all of the compounds extracted from the unburned propellants were seen in the fabric extracts (using SIM).

The revolver ammunitions contained compounds that are very common and were found in other propellants analysed for this study (NG and DBP found in Vostok .22LR, Winchester .410, Nato 7.62x51, Privi 7.62 x 51 and Geco .38spl and NG and EC found in Remington .22LR, Votok .22LR, Eley .410, Winchester .410 and Nato 7.62x51). Therefore, the presence of these compounds alone would not make it possible to link the residues on the fabric to specific propellants with certainty. However, with other information for any given case these results may be of use. For example, if there were two suspects in a shooting case and one suspect's firearm had Winchester .38spl ammunition and the other Magtech .357mag ammunition the results from these fabric extracts would make it possible to differentiate which one of these firearms discharged the shot.

With regards to the Geco .38spl ammunition, for which no compounds of interest were found in the fabric extracts, the composition of the propellant itself might offer an explanation. The colour of the propellant, a greyish green (Figure 49) would suggest the presence of nitroglycerin (Meng and Caddy 1997). This is usually found in the centre of propellants with a burn rate adulterants coating around it. If it is the case with this ammunition that there is no coating present it may lead to faster burn rates and, therefore, the combustion of more propellant material. However, the propellant was shown to contain gelatinisers (DBP and EC), intended to slow burning rates. The weight of the propellants in the cartridges were very similar to those of the Winchester .38 special (averages for Geco = 0.2437g and Winchester 0.2765g) and, therefore, is not likely to be a factor.

Figure 49: Macroscopic image of Geco .38spl unburned powder. 30 x magnification.

Perhaps one of the most useful elements of the fabric extracts in respect to unburned propellants is the finding of NG. As this compound's presence is indicative of double (or potentially triple) based powders, if it is found in an extract it will suggest that the originator propellant was not single based (not containing NG). This is shown in the extracts of the Winchester .38 spl, the Winchester .410 and the Nato 7.62x51ammunitions. However, the lack on NG in an extract cannot be taken as definitive evidence of a single base powder originator. This was seen in the Remington .22LR, in which the propellant contained NG, but the compound was not seen in the fabric extracts.

7.3.6 Comparing fabric extracts to spent cartridge cases

Figure 50 contains peak area data for compounds extracted from unburned propellants, spent cartridges and shot fabric samples and Table 33 contains a simplified version of these results.

Five of the ammunitions tested showed a good level of similarity between spent cartridges and fabric extracts. For the Vostok .22LR, Magtech .357mag and the Winchester .38spl

(Figure 51) the same compounds extracted from each of cartridge cases were found in the corresponding fabric extracts. This was also the case for one of the sets of Eley .410 and Remington .22LR extractions. For the other ammunitions none (Geco .38spl and Privi 7.62x51) or some of the compounds seen in the spent cartridges where extracted from fabrics.

1). Remington .22LR

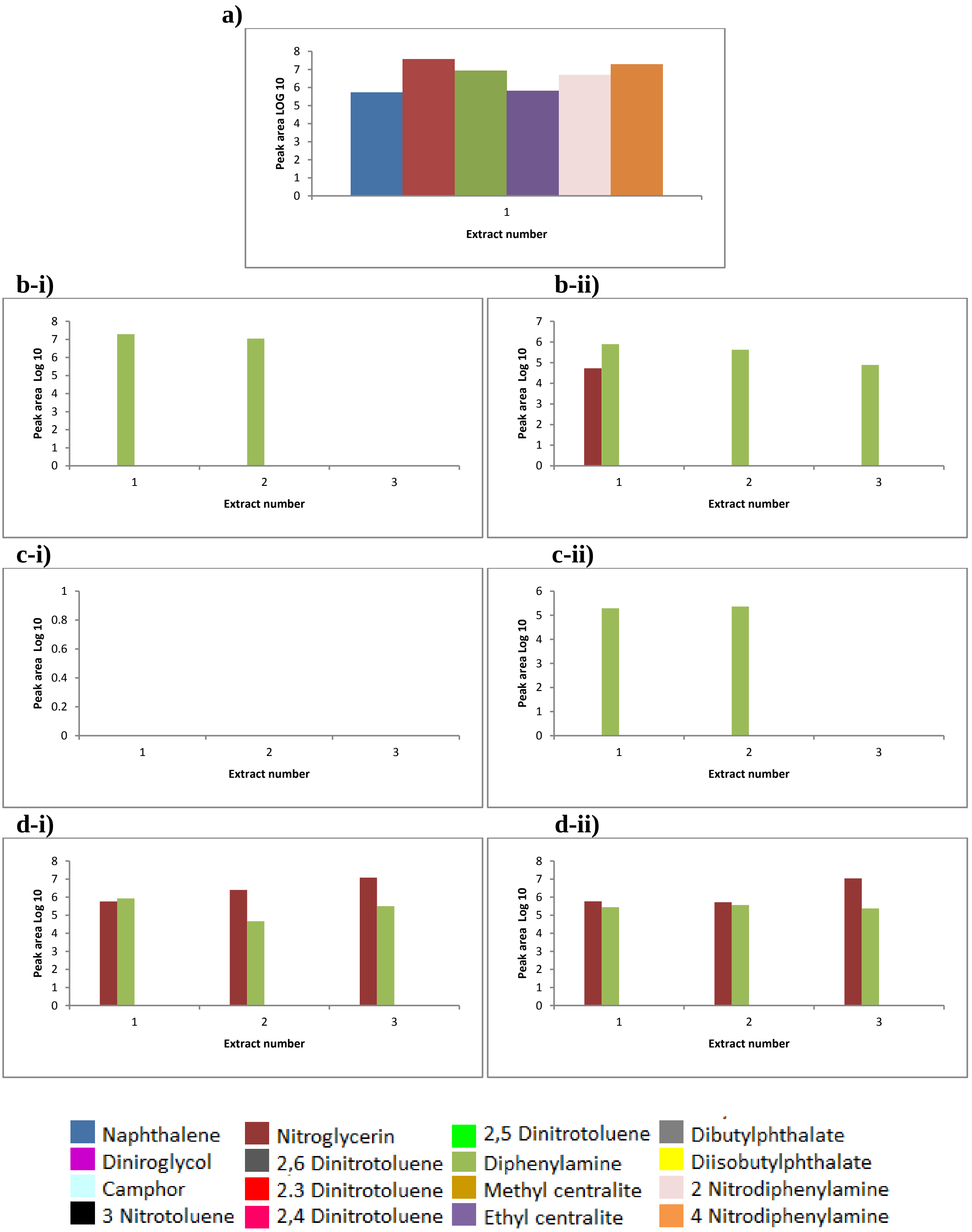


Figure 50: Extracts from; a.) unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i) are TIC results while those dentoted ii). are SIM results.

2). Vostok .22LR

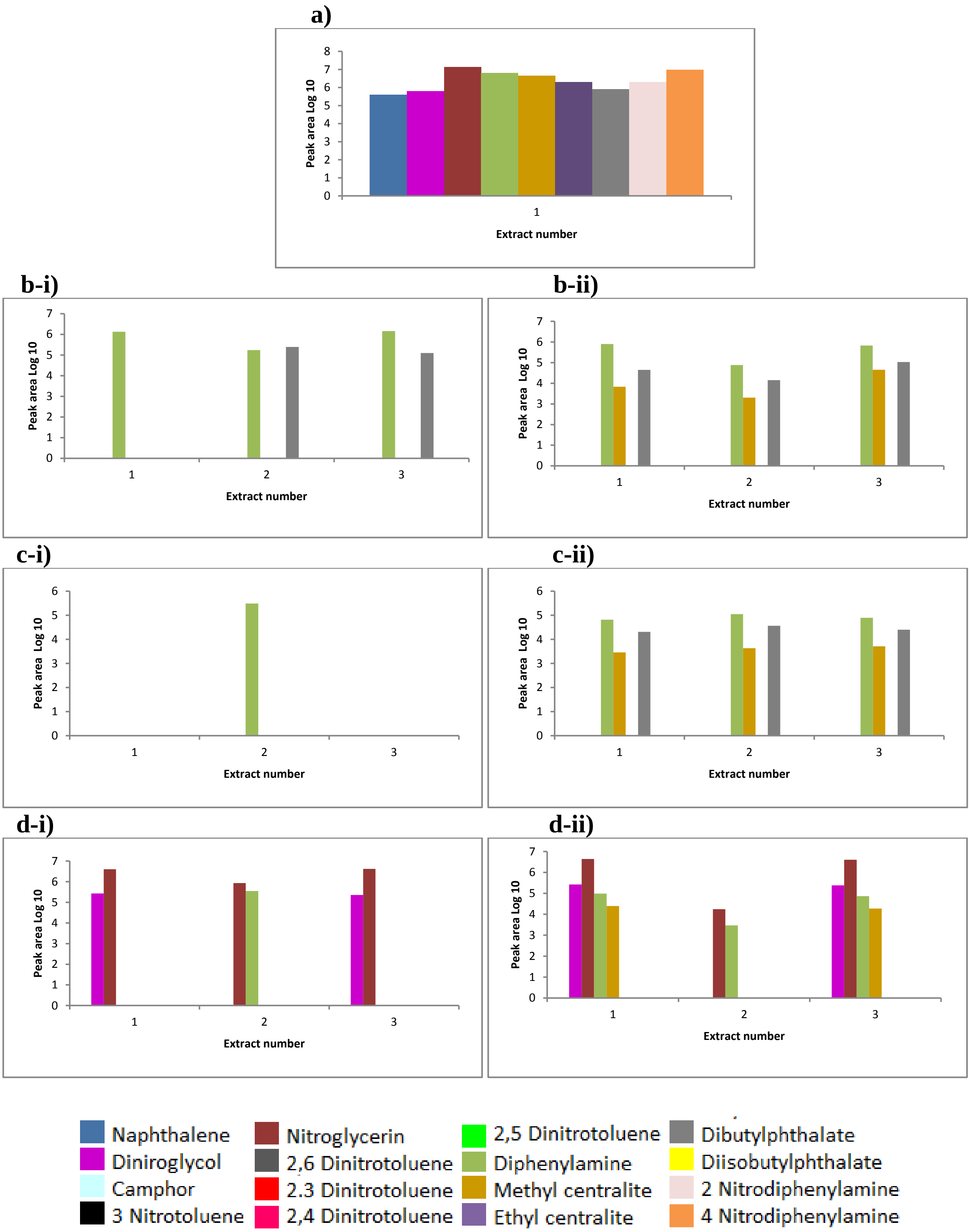


Figure 50 continued: Extracts from; a). unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i.) are TIC results while those dentoted ii). are SIM results.

3) Magtech .357Mag

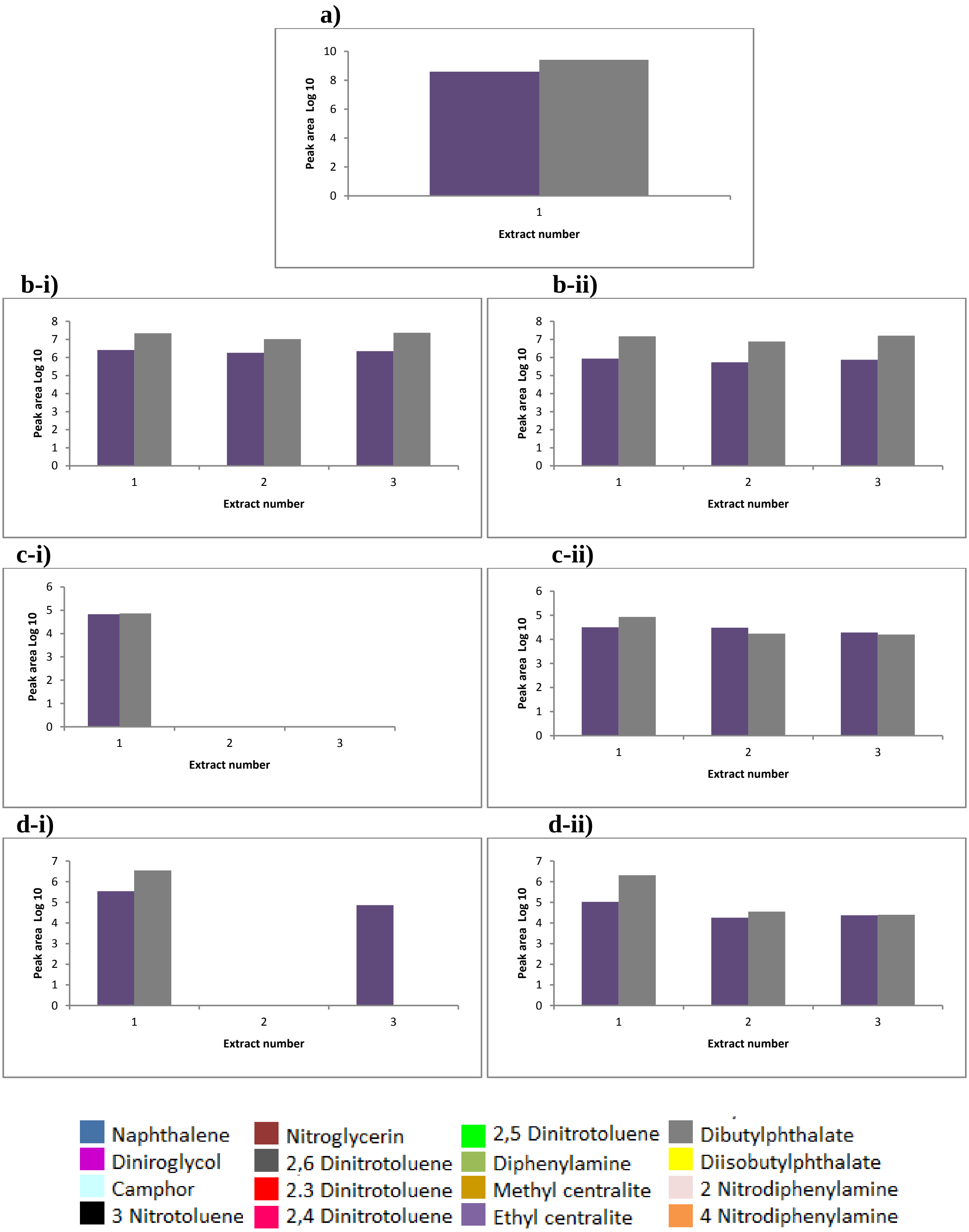


Figure 50 continued: Extracts from; a). unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

4). Geco 38.spl

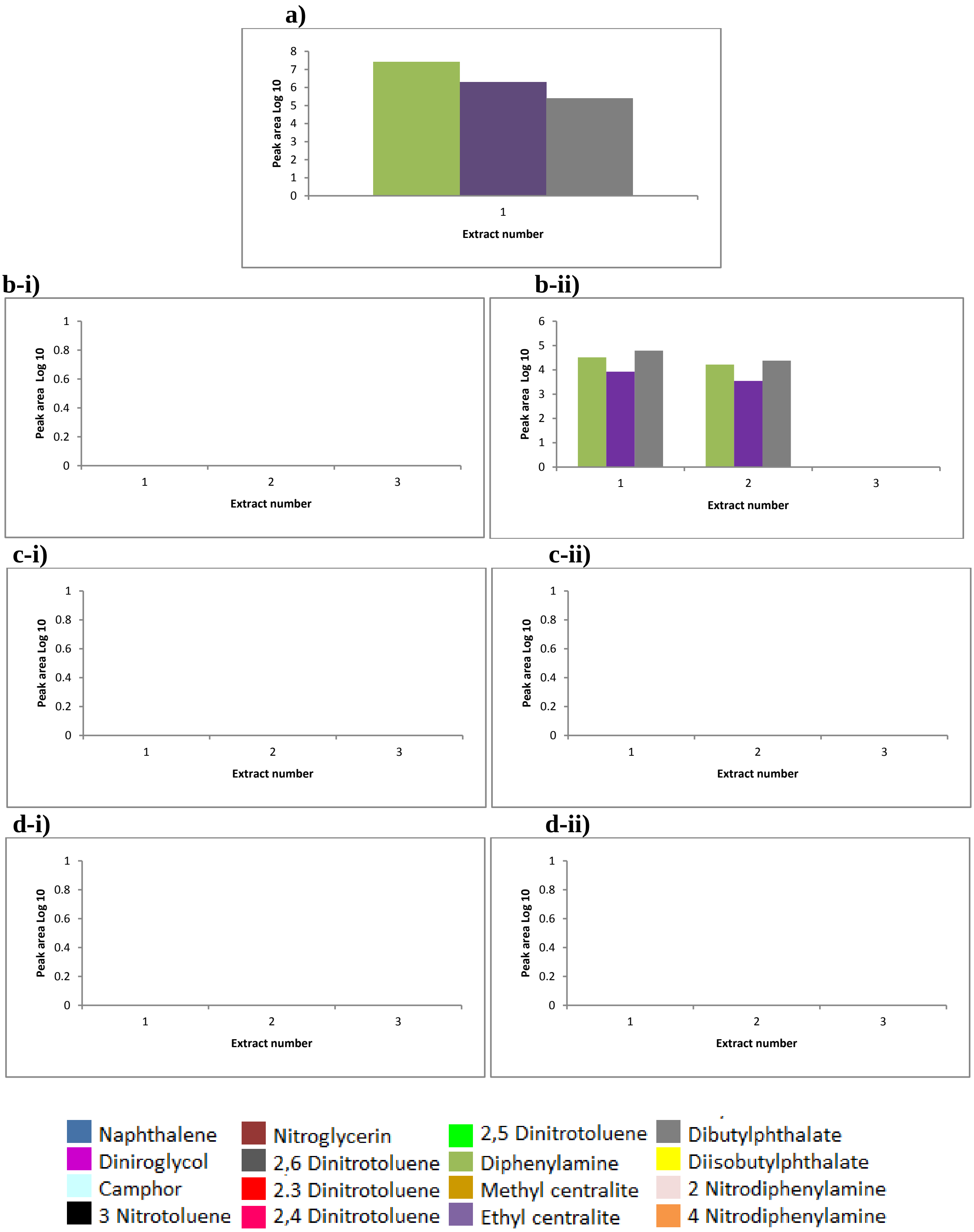


Figure 50 continued: Extracts from; a). unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

5). Winchester .38spl

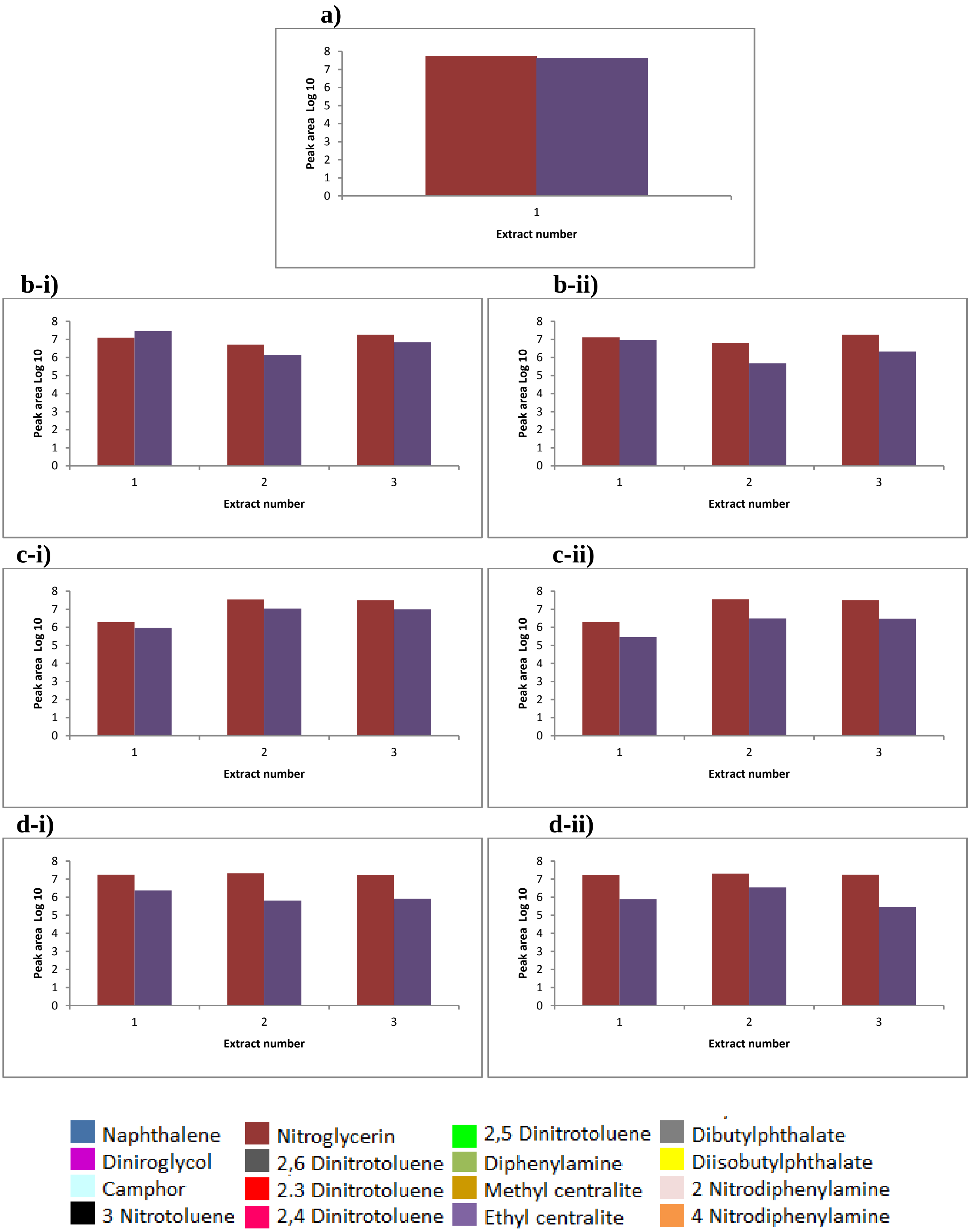


Figure 50 continued: Extracts from; a.) unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

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6). Eley .410

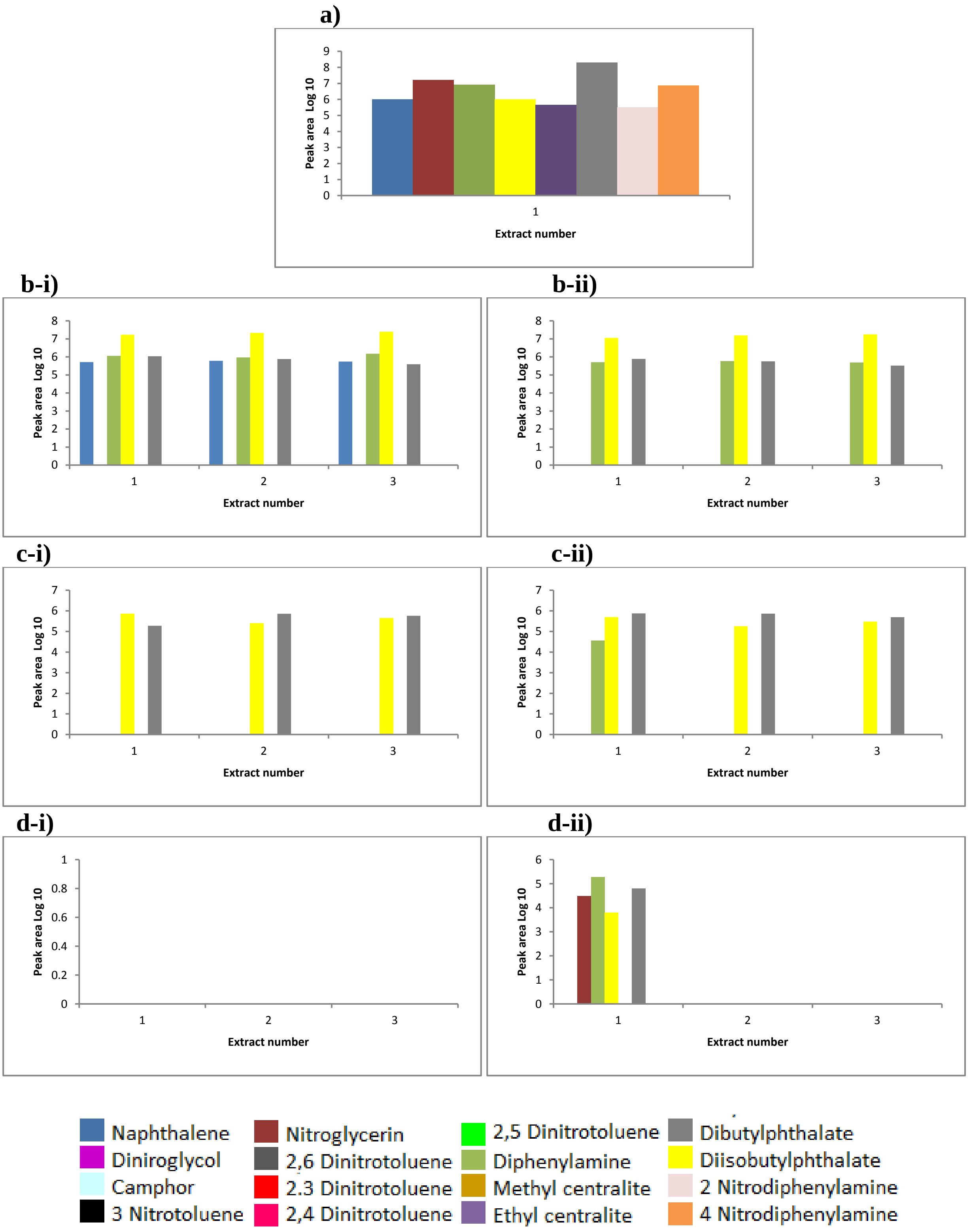

Figure 50 continued: Extracts from; a). unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

7). Winchester .410

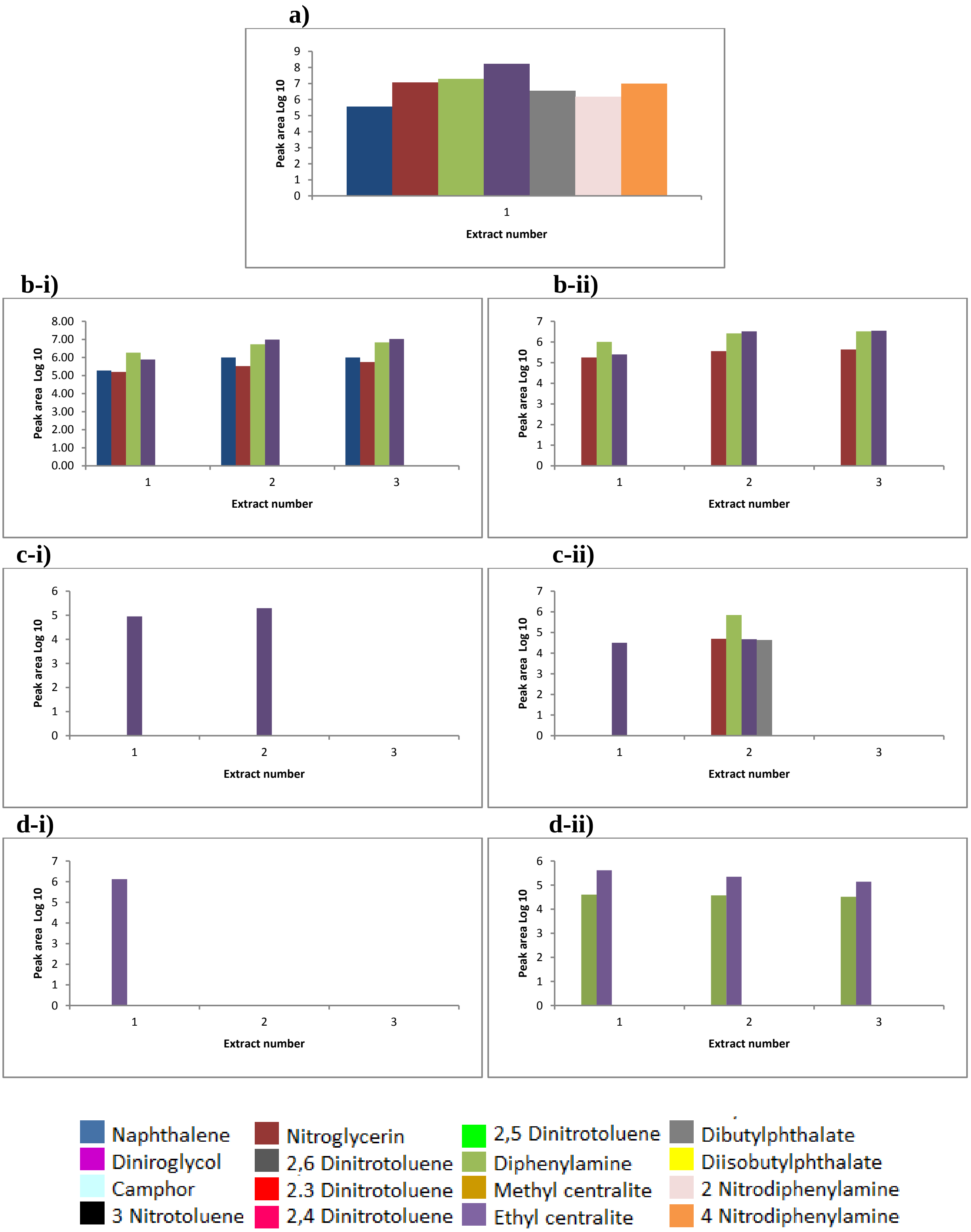

Figure 50 continued: Extracts from; a) unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

8). NATO 7.62x51

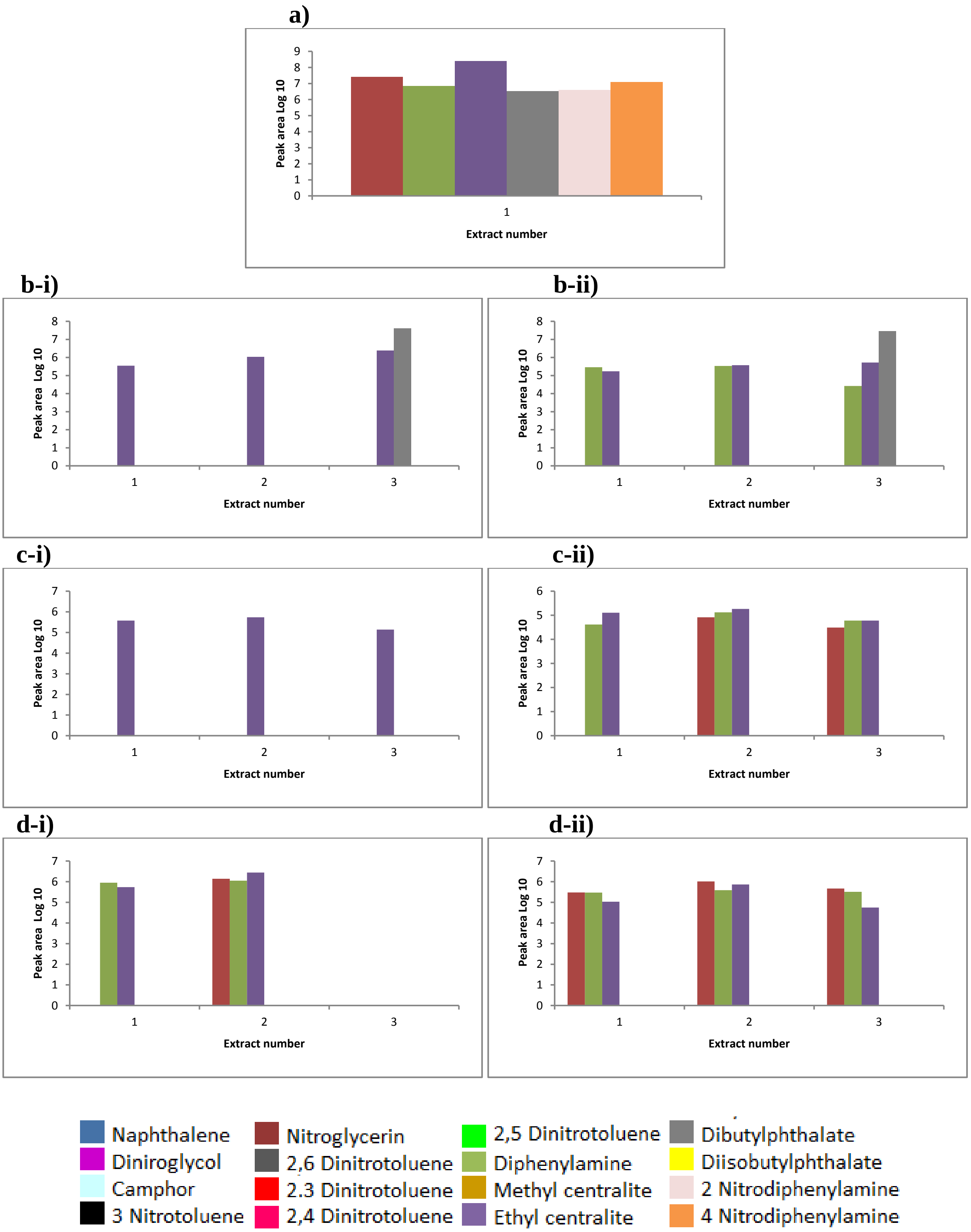

Figure 50 continued: Extracts from; a) unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

9). Privi Partizan 7.62x51

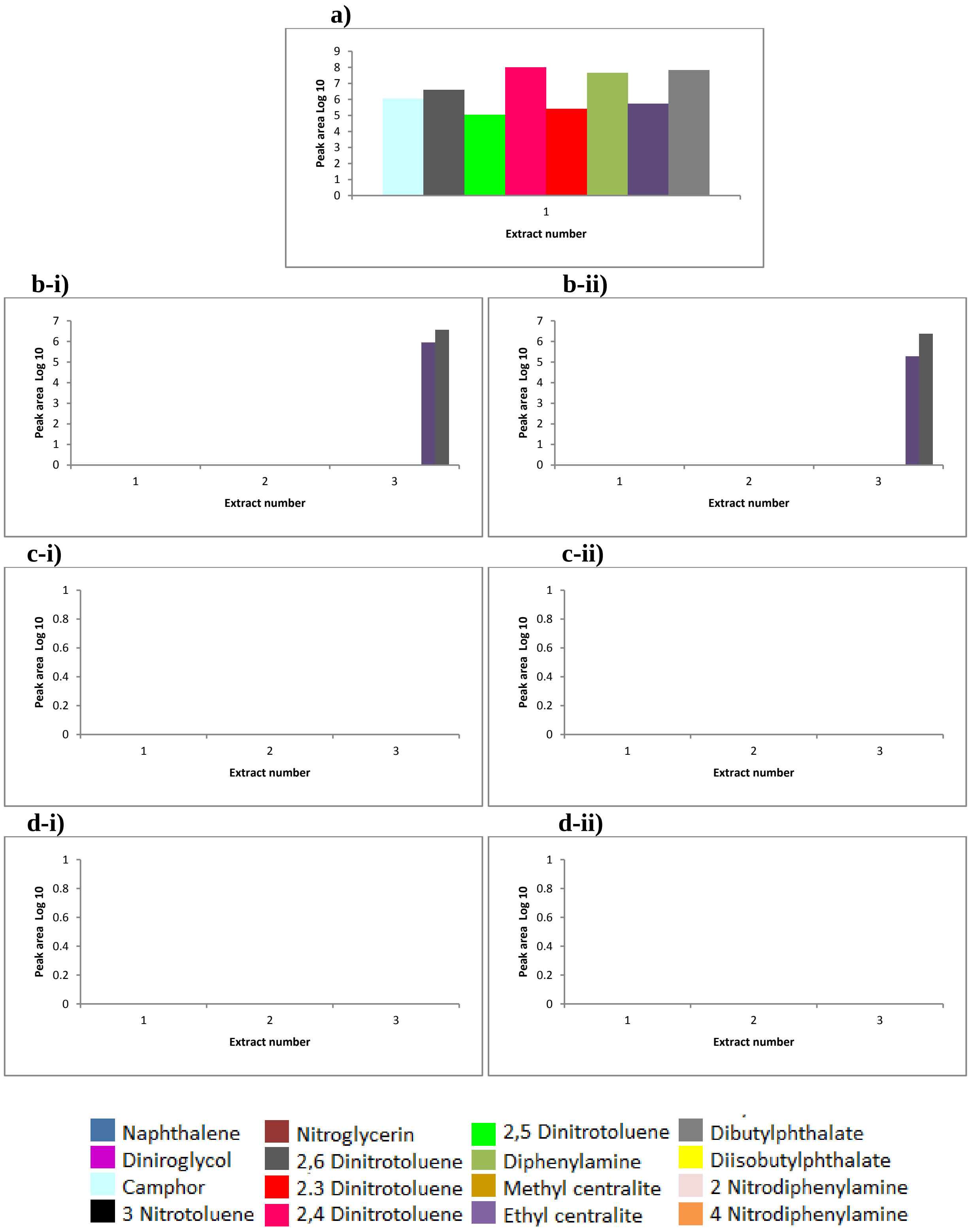

Figure 50 continued: Extracts from; a) unburned propellants, and OGSR extracts from; b). spent cartridges, c). lab coat fabric extracts and d). materials collected by fabric scraping. Graphs denoted with i). are TIC results while those dentoted ii). are SIM results.

Table 33: Summary of compounds detected in unburned propellant powders, spent cartridge cases and fabric extracts

AMMUNITION	SAMPLE TYPE	NAPH	DNG	CAMPH	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22	**Unburned powder**	✓				✓					✓		✓			✓	✓
	Case	✗				✓					✓		✗			✗	✗
	Fabric	✗				✗					✓		✗			✗	✗
VOSTOK 22	**Unburned powder**	✓	✓			✓					✓	✓	✓	✓		✓	✓
	Case	✗	✗			✗					✓	✓	✗	✓		✗	✗
	fabric	✗	✗			✗					✓	✓	✗	✓		✗	✗
MAGTECH 357 MAG	**Unburned powder**												✓	✓			
	Case												✓	✓			
	Fabric												✓	✓			
GECO 38SPL	**Unburned powder**										✓		✓	✓			
	Case										✗		✗	✗			
	Fabric										✗		✗	✗			
WIN 38 SPL	**Unburned powder**					✓							✓				
	Case					✓							✓				
	Fabric					✓							✓				
ELEY 410	**Unburned powder**	✓				✓					✓		✓	✓	✓	✓	✓
	Case	✓									✓		✓	✓	✓	✗	✗
	Fabric	✗									✓		✗	✓	✓	✗	✗
WIN 410	**Unburned powder**	✓				✓					✓		✓	✓		✓	✓
	Case	✓				✓					✓		✓	✗			
	Fabric	✗				✓					✓		✓	✓			
NATO 7.62X51	**Unburned powder**					✓					✓		✓	✓		✓	✓
	Case					✗					✓		✓	✓		✗	✗
	Fabric					✓					✓		✓	✗		✗	✗
Privi 7.62x51	**Unburned powder**			✓			✓	✓	✓	✓	✓		✓	✓			
	Case			✗			✗	✗	✗	✗	✗		✗	✗			
	Fabric			✗			✗	✗	✗	✗	✗		✗	✗			

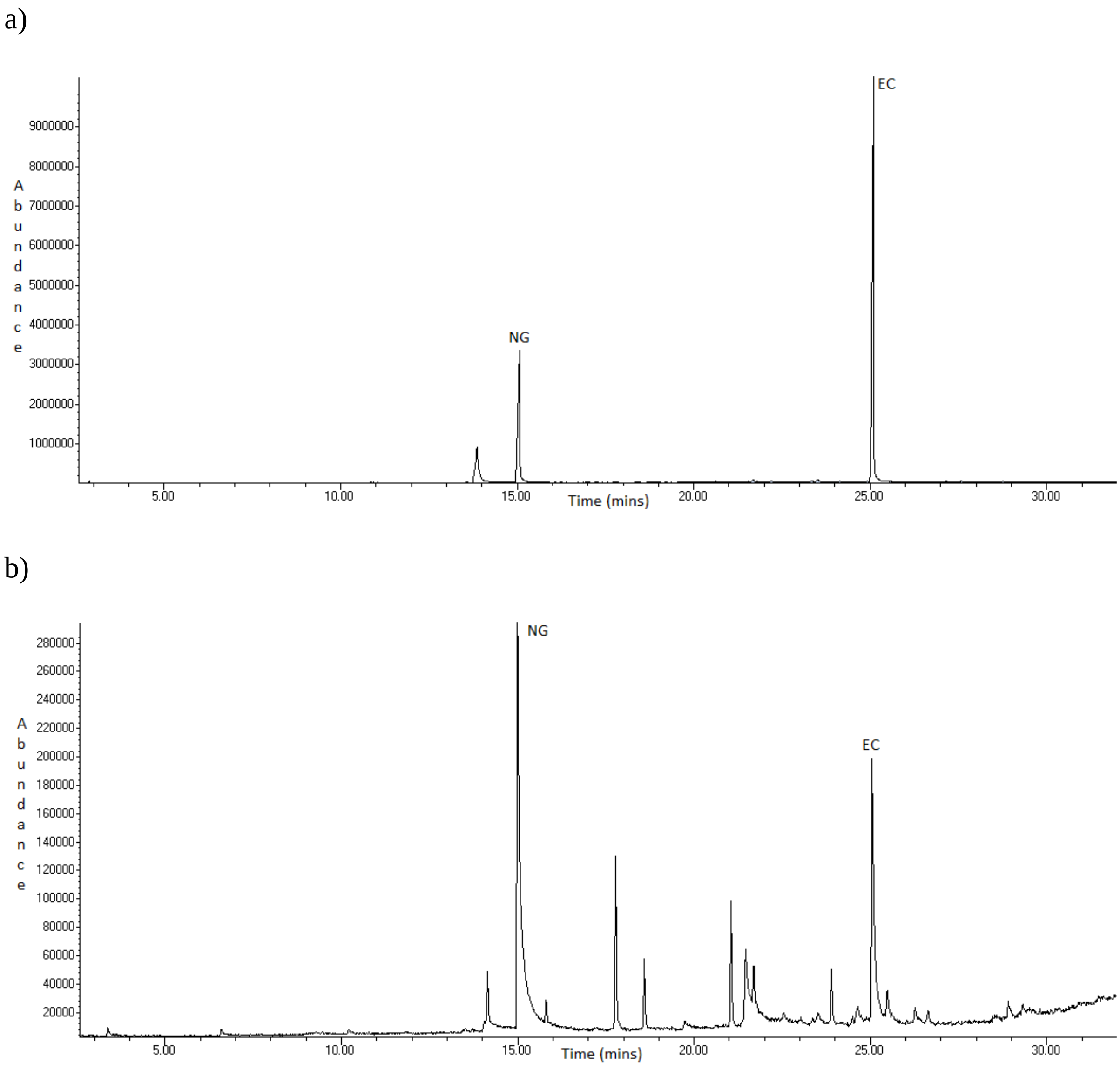

Figure 51: Chromatograms (TIC) from extracts taken from; a) Winchester .38spl spent cartridge, b) fabric shot by the same round of Winchester .38spl ammunition.

The abundance ratios of the compounds extracted from fabrics were never the same as those seen in the cartridge cases, this is visually represented in figures 50 and 51. Therefore, it is only the presence or absence of the compounds of interest that is useful in this context. This project has been concerned wholly with qualitative analysis. Although quantitative analysis is possible with SPME it is more complex and requires any sample to have reached a state of equilibrium (Wercinski, 1999), something that was not determined for each of the sample types analysed in this work. A natural progression of this work would be to investigate quantitative analysis and the viability of its application to this area.

Table 34 contains information on the max pressures experienced in various cartridge cases types. This shows that .357mag rounds have max pressures much greater than the .410 shot gun. Therefore, it is unlikely that the pressures alone lead to the levels of degradation in each ammunition type. Instead it is likely to be a combination of factors; the pressure in the firearm barrel, the design of the propellant (morphology and compositional), the shape of the cartridge case, the amount of powder loading into the ammunition and the length of the barrel.

Table 34: Maximum pressure figures for ammunitions (saami.org)

Ammunition type	Max Pressure (psi)
.410	135
.38spl	170
.357mag	350
9mm	350
.22LR	240
7.62x51	520

As with comparing fabric extracts to unburned propellant samples only a relatively small number of ammunition types have been analysed for this piece of research. A much larger population of ammunitions must be analysed before the true worth of these findings can be properly contextualised. It has become clear from this study that it is important to carry out multiple test fires (in this study 3) in order to assess the value of a match or non-match between case and fabric or fabric and propellant. The variability documented between firings means that relying on a result from one set of tests may be unsound.

7.3.7 Extracts from materials scraped from garments

The SPME results of extracts carried out on materials scraped from the same fabric samples (Figure 50) discussed above showed some interesting and unexpected findings. For the Magtech .357mag, Geco .38spl, Winchester .38spl (Figure 52), Nato 7.62x51 (2 of the 3 extracts) and Privi 7.62x51 the same compounds as where extracted from the original shot fabrics were found. In the case of the Remington .22LR, Vostok .22LR and Eley .410, additional compounds not seen in the fabric extracts were observed. With scraped Remington .22LR samples NG, which was seen in one of the case extracts and in the unburned propellant was observed in all three scraped material samples, as well as DPA which was seen in the fabric extracts. With Vostok .22LR scraped fabric extracts, DNG and NG where seen in 2 of the scraping extracts. These compounds again were not seen in the fabric extracts and also not in the case extracts, but were in the unburned powders. In one of the Eley .410 scrapings NG was seen, which was not in the fabric or case extracts (but was in the propellant).

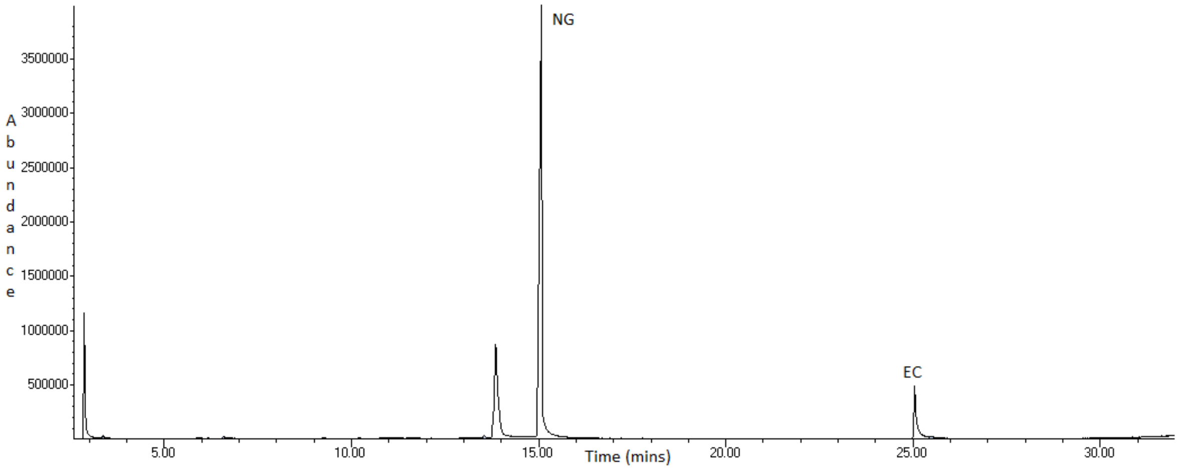

Figure 52: example of an extract from materials scraped from a fabric sample shot by a round of Winchester .38spl ammunition.

Scraping extracts did not contain all of the compounds observed in fabric extracts for Winchester .410 and Vostok .22LR sample.

These results show that additional, useful information may be gained by carrying out such extracts as these. The fact that different compounds were seen in fabric and scraping sample extracts and that in some cases neither extraction method contained all of the compounds observed in both extracts combined suggests that the application of both extraction methods might be useful in providing a fuller picture of the compounds present in the originating propellants.

7.3.8 Relative distribution figures for extractions

Table 35 contains relative distribution figures for extracts from shot fabric samples. It can be seen from these figures that the compounds extracted between different fabric samples are not reproducible. These results tally with the conclusions drawn from relative distribution figures calculated for cartridge case extractions (section 6.3.3 (page 137)). All but DBP in the Vostok .22LR ammunitions had relative distribution figures higher than those for unburned propellant powder extracts.

These results again suggest that quantitative analysis might not be that applicable. From the research carried out during this project it would appear that it is the presence or absence of compounds which is the most useful in being able to link residues from fabrics back to spent cartridges and unburned powders.

Table 35: Relative distribution calculations for extracts from lab coat fabric samples and unburned propellant powders.

Ammo	sample	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22	propellant	123.64	/	/	/	13.11	/	/	/	/	44.44	/	/	/	/	/	30.20
	fabric	-	/	/	/	-	/	/	/	/	162.88	/	-	/	/	-	-
VOSTOK 22	propellant	42.82	/	/	/	50.77	/	/	/	/	8.48	20.30	210.09	81.04	/	18.03	9.83
	fabric	-	-	/	/	-	/	/	/	/	54.92	54.47	-	58.71	/	-	-
MAG 357 MAG	propellant	/	/	/	/	/	/	/	/	/	/	/	17.82	12.75	/	/	/
	fabric	/	/	/	/	/	/	/	/	/	/	/	45.53	175.83	/	/	/
GECO 38SPL	propellant	/	/	/	/	/	/	/	/	/	17.78		15.75	47.31	/	/	/
	fabric	/	/	/	/	/	/	/	/	/	-	/	-	-	/	/	/
WIN 38 SPL	propellant	/	/	/	/	18.22	/	/	/	/	/	/	3.78	/	/	/	/
	fabric	/	/	/	/	145.26	/	/	/	/	/	/	137.48	/	/	/	/
ELEY 410	propellant	47.11	/	/	/	13.43	/	/	/	/	15.88	/	22.72	11.12	27.10	/	144.35
	fabric	-	/	/	/	-	/	/	/	/	300.00	/	-	39.30	98.16	-	-
WIN 410	propellant	28.86	/	/	/	10.37	/	/	/	/	10.71	/	2.27	31.90	/	27.09	24.44
	fabric	-	/	/	/	300.00	/	/	/	/	300.00	/	179.07	300.00	-	-	-
NATO 762X51	propellant	/	/	/	/	25.63	/	/	/	/	27.52	/	7.83	2.94	/	14.90	11.198
	fabric	/	/	/	/	218.35	/	/	/	/	116.40	/	100.17	-	/	-	-
PRIVI 762X51	propellant	/	/	/	/	/	/	/	/	/	/	/	17.16	7.24	/	/	/
	fabric	/	/	/	/	/	/	/	/	/	/	/	-	-	/	/	/

7.4 Conclusions

The results presented in this section have shown the potential worth of applying nylon bags to the collection and analysis of shot fabrics. For the Magtech .357mag and the Winchester .38spl ammunitions all the compounds present in the original unburned propellants were extracted from shot fabric samples. In other fabric extracts the compounds extracted were shown to match those from spent cartridge extracts, as was the case for the Magtech .357mag, Winchester .38spl, Remington .22LR (1 extract), Vostok .22LR and Eley .410 (1 extract). For other ammunitions within the analysed ammunition population it was possible to link fabric extracts to ammunitions by the presence of single indicative compounds. This was so with Vostok .22LR (MC) and Eley .410 (DIBP) ammunitions.

Extracts carried out on scrapings from fabrics were also shown to be of worth, providing additional compositional information that might be useful in determining the originating propellant powder. In Remington .22LR samples, NG, which was seen in one of the case extracts and in the propellant, was observed in all three scraped material samples, as well as DPA which was seen in the fabric extracts. With Vostok .22LR extracts, DNG and NG where seen in 2 of the scraping extracts. These compounds again were not seen in the fabric extracts and also not in the case extracts, but were in the unburned powders. In one of the Eley .410 scrapings NG was seen, which was not in the fabric or case extracts but again was present in the unburned powders.

7.5 Future work

This study has concentrated on a relatively small number of ammunition types, and before the true value of the methodologies developed can be fully understood an investigation into a much larger population is required.

This area of investigation has yielded some interesting results. It has also raised further questions which would be worthy of future investigation. With regards to fabric samples, it would be of value to carry out further investigation into a larger range of fabrics made from different materials. It would also be very important to investigate extracts from worn/used garments; especially those from persons working in environs which may have elevated levels of the compounds of interest, for example firework handlers and those working with explosives.

This work has focussed on extracts from fabrics which have been shot at close range (20cm), it would be necessary to investigate a range of distances in order to assess the worth of the developed methodology at greater shooting distances.

It is suspected that many of the particles that interact with the fabrics were either forced through the bullet hole, or bounced off the sample. It would, therefore, be of interest to apply a forensic vacuum collection methodology to the environs surrounding shot fabric samples in order to try and collect more propellant materials for analysis.

The focus of this study was to assess the potential of linking extracts from shot fabrics to spent cartridges and unburned propellant materials based on the compounds present in the unburned propellants. Some preliminary data has been collected showing that the analysis of products of combustion may well yield more useful information and is a possible area of future work.

As the most valuable results were attained from extracts from handgun ammunitions it would be of interest be look specifically at a larger range of calibres and firearm types for this type of firearm.

From conversations with UK based firearms experts it has become clear that shootings involving the use of converted blank firing ammunitions are relatively common in the UK. It would be of interest to carry out an investigation into the OGSR produced by these blank firing ammunitions.

7.6 Summary

This project has investigated a number of areas related the analysis of ballistic materials. Initially appropriate GC/MS and SPME extraction methodologies were developed. These methods were then shown to be suitable for the extraction and analysis of unburned propellant powder samples from 16 different ammunitions. An investigation into the analysis of such a large number of unburned powers (using SPME and GC/MS) has not been found in the previously published literature. It was shown that all of the powders could be differentiate from one another by reference to the abundances of the compounds extracted.

The developed SPME and GC/MS methodologies were then applied to the analysis of spent cartridge cases. The comparisons of spent cartridge extracts to unburned powders showed that it would not be possible to link extracts from cases to powders in most cases. The data collected may, however, be useful as a discriminatory technique.

The application of nylon evidence bags to the collection and extraction of OGSR from shot fabric samples was then investigated. Results showed that for 4 of the ammunitions tested could be linked back to the originator ammunition by comparison of the compounds present in the extracts. Five ammunitions could also be linked to the residues in spent cartridge cases. The application of nylon evidence bags for OGSR analysis is novel and has not previously been reported in the literature.

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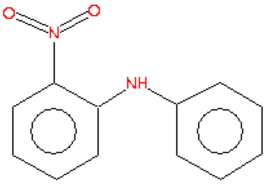
9 Appendix I: Compounds of interest structural information



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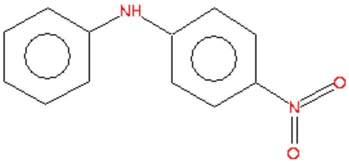

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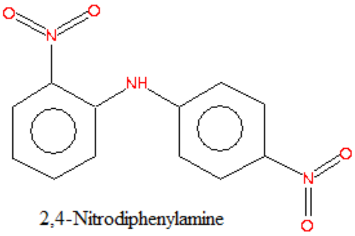

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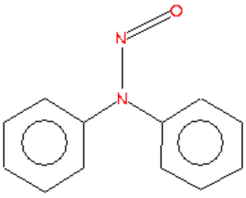
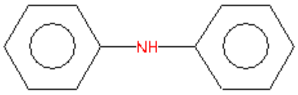
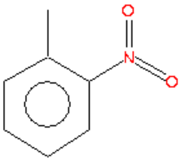


N-Nitrosodiphenylamine



Diphenylmine



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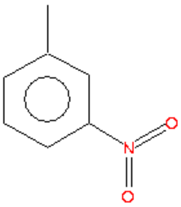

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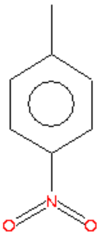

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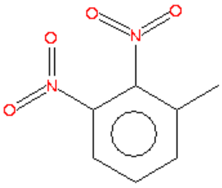
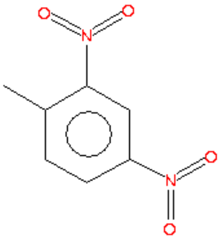


2,3-Dinitrotoluene



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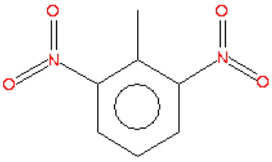

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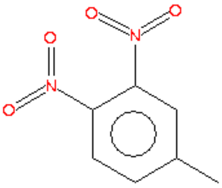
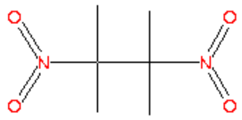
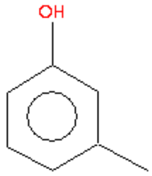


3,4-Dinitrotoluene

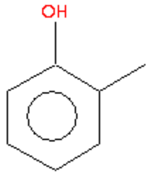
Figure 53:Structures of compounds of interest



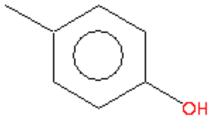
2,3-Dimethyl-2,3-Dinitrobutane



M-Cresol



O-Cresol



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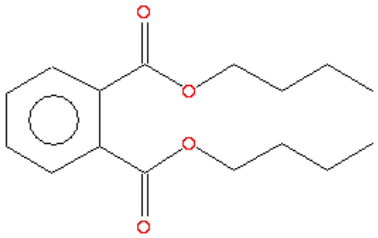
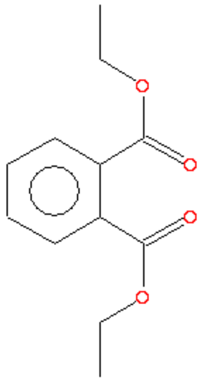


Dibutyl Phthalate



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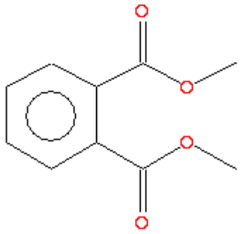

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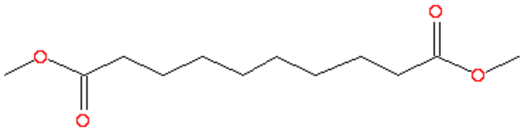
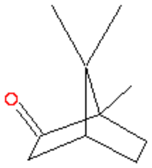
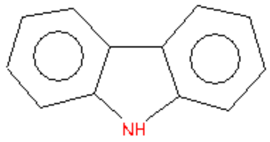


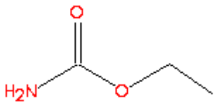
Dimethyl Sebacate



Camphor

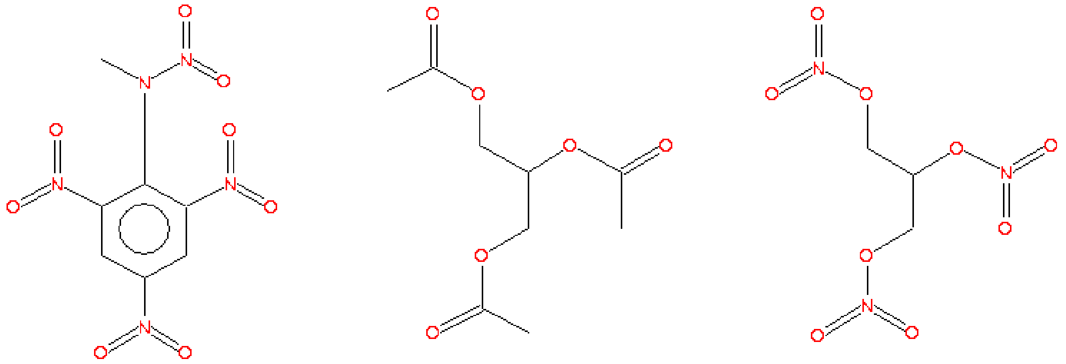


Carbazole



Urethane

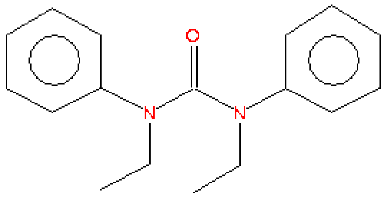
Figure 53 continued: Structures of compounds of interest



Tetryl

Triacetin

Nitroglycerin



Ethyl centralite

Figure 53 continued: Structures of compounds of interest

10. Appendix II: Raw data from section 4

Table 36: Raw date from various fibre type extracts of Magtech 9mm ammunition

Fiber type	Run number	Compound	Peak area
100um PDMS	1	NG	210210467
		EC	10566536
	2	NG	98084211
		EC	4508942
	3	NG	57380891
		EC	7313127
5030umPDMSCARDVB	1	NG	202066167
		EC	2509866
	2	NG	230959168
		EC	3532263
	3	NG	257729478
		EC	3178606
65umPDMSDVB	1	NG	279667730
		EC	53926890
	2	NG	300234772
		EC	49102905
	3	NG	375235638
		EC	47904831
75umCARPDMS	1	3 NT	250981
		NG	66967751
		DPA	3326893
		EC	17931026
	2	3 NT	/
		NG	137759837
		DPA	2937584
		EC	31690101
	3	3 NT	/
		NG	58685048
		DPA	/
		EC	4299739
7umPDMS	1	NG	80890128
		DPA	323389
		EC	5719992
	2	NG	36309876
		DPA	210789
		EC	5213410
	3	NG	78546591
		DPA	/
		EC	6230370

Table 36 continued: Raw date from various fibre type extracts of Magtech 9mm ammunition

Fibre type	**Run number**	**Compound**	**Peak area**
30umPDMS	1	NG	68962876
		EC	7516558
	2	NG	66141954
		EC	6887564
	3	NG	69353622
		EC	12500042
85umPA	1	NG	77651236
		EC	8401333
	2	NG	57897870
		EC	4651288
	3	NG	46478324
		EC	5042175

Table 37: Raw date from various fibre type extracts of Magtech 5.56mm ammunition

Fibre type	Run number	Compound	Peak area
100um PDMS	1	NG	13119906
		DPA	18119236
		DBP	11630425
		4 NDPA	2757964
	2	NG	14545435
		DPA	16747971
		DBP	6309787
		4 NDPA	2990679
	3	NG	14214570
		DPA	17686946
		DBP	6532812
		4 NDPA	2690210
5030umPDMSCARDVB	1	NG	36677479
		DPA	21649809
		DBP	3108765
	2	NG	31771270
		DPA	8966900
		DBP	2705731
	3	NG	31789823
		DPA	10531306
		DBP	2259433
65umPDMSDVB	1	NG	71695295
		DPA	42584265
		DBP	2983697
		4 NDPA	1339897
	2	NG	58305825
		DPA	25269241
		DBP	6243618
		4 NDPA	610533
	3	NG	69035929
		DPA	27953993
		DBP	11453013
		4 NDPA	2940824

Table 37 continued: Raw date from various fibre type extracts of Magtech 5.56mm ammunition

Fiber type	Run number	Compound	Peak area
75umCARPDMS	1	NG	1686654
		DPA	6837901
		DBP	1559529
	2	NG	2221078
		DPA	7509863
		DBP	2050647
	3	NG	2479995
		DPA	8937368
		DBP	2276446
7umPDMS	1	NG	481227
		DPA	1214293
		DBP	3107907
	2	NG	240197
		DPA	783991
		DBP	2079428
	3	NG	367757
		DPA	731446
		DBP	2322049
30umPDMS	1	NG	4327876
		DPA	11813882
		DBP	8569210
	2	NG	3289388
		DPA	7387895
		DBP	10599611
	3	NG	8564415
		DPA	11530273
		DBP	3754676
85um PA	1	NG	25944671
		DPA	59768493
		DBP	8347983
	2	NG	19224297
		DPA	49129056
		DBP	6871796
	3	NG	14905878
		DPA	37310614
		DBP	13007699

Table 38: Raw date from various fibre type extracts of Federal 7.62x51 ammunition

Fibre type	**Run number**	**Compound**	**Peak area**
100um PDMS	1	NG	7396093
		DPA	15998322
		DBP	10137928
		4 NDPA	455259
	2	NG	7753418
		DPA	18042092
		DBP	7238053
		4 NDPA	495127
	3	NG	9345376
		DPA	18190924
		DBP	8737149
		4 NDPA	717101
5030umPDMSCARDVB	1	NG	21464168
		DPA	36661580
		DBP	9695299
		4 NDPA	/
	2	NG	27668707
		DPA	38419831
		DBP	9013777
		4 NDPA	/
	3	NG	29263180
		DPA	41197459
		DBP	9459867
		4 NDPA	/
65umPDMSDVB	1	NG	35262881
		DPA	53528514
		DBP	18408161
		4 NDPA	/
	2	NG	33823868
		DPA	47115986
		DBP	9683270
		4 NDPA	/
	3	NG	34215332
		DPA	46818417
		DBP	9187477
		4 NDPA	/

Table 38 continued: Raw date from various fibre type extracts of Federal 7.62x51 ammunition

Fibre type	Run number	Compound	Peak area
85umCARPDMS	1	NG	1356327
		DPA	24901198
		DBP	6377720
		4 NDPA	/
	2	4 NDPA	1073961
		DPA	27792192
		DBP	6705231
		4 NDPA	/
	3	NG	661637
		DPA	28900855
		DBP	5575457
		4 NDPA	/
7umPDMS	1	DPA	4441985
		DBP	3879249
		NG	/
		4 NDPA	/
	2	DPA	4425578
		DBP	6008582
		NG	/
		4 NDPA	/
	3	DPA	3101287
		DBP	3616603
		NG	/
		4 NDPA	/
30umPDMS	1	NG	1136942
		DPA	12532066
		DBP	7788771
		4 NDPA	/
	2	NG	2019089
		DPA	15099410
		DBP	6035786
		4 NDPA	/
	3	NG	2741645
		DPA	19889849
		DBP	10960162
		4 NDPA	/

Table 38 continued: Raw date from various fibre type extracts of Federal 7.62x51 ammunition

Fibre type	Run number	Compound	Peak area
85um PA	1	NG	17527264
		DPA	69531089
		DBP	14844929
		4 NDPA	/
	2	NG	10210447
		DPA	52582124
		DBP	11241513
		4 NDPA	2889519
	3	NG	22125368
		DPA	60332072
		DBP	11921733
		4 NDPA	261481

Table 39: Raw date from various fibre type extracts of Lapua 7.62x51 ammunition

Fibre type	Run number	Compound	Peak area
100um PDMS	1	DPA	22633039
		EC	10853513
	2	DPA	16608474
		EC	11535891
	3	DPA	19071320
		EC	11896771
5030umPDMSCARDVB	1	DPA	7573762
		EC	6421128
	2	DPA	6698615
		EC	5935253
	3	DPA	7515118
		EC	5884330
65umPDMSDVB	1	DPA	8495649
		EC	5703314
	2	DPA	10459728
		EC	5914100
	3	DPA	8359449
		EC	4512446
85umCARPDMS	1	DPA	6773443
		EC	8194988
	2	DPA	7763435
		EC	8656731
	3	DPA	6554853
		EC	7833022
7umPDMS	1	DPA	1316941
		EC	4473196
	2	DPA	1631475
		EC	7282646
	3	DPA	854135
		EC	5328340
30umPDMS	1	DPA	6866883
		EC	6677618
	2	DPA	11521612
		EC	10787679
	3	DPA	7572055
		EC	9461040
85um PA	1	DPA	12204140
		EC	7808894
	2	DPA	11383191
		EC	7428141
	3	DPA	14900804
		EC	10419865

11 Appendix III: Raw data from section 5

Table 40: Raw data from SPME extracts of unburned propellant powders

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22	593322	0	0	0	36829211	0	0	0	0	8553552	0	652436	0	0	5378412	19503763
REM 22	75957	0	0	0	41768013	0	0	0	0	9424934	0	579527	0	0	4233783	17540948
REM 22	598384	0	0	0	36727880	0	0	0	0	5889518	0	561655	0	0	4505208	14332558
mean	422554	0	0	0	38441701	0	0	0	0	7956001	0	597873	0	0	4705801	17125756
range (+/-)	261214	/	/	/	2469401	/	/	/	/	1767708	/	45391	/	/	572315	2585603
VOSTOK 22	319626	518628	0	0	9527460	0	0	0	0	6569592	4233195	4877947	638570	0	2137727	9286631
VOSTOK 22	491073	706223	0	0	16659646	0	0	0	0	6876615	4104222	723851	1241038	0	1832820	9656230
VOSTOK 22	390355	662304	0	0	15954128	0	0	0	0	6317727	5007011	561678	577366	0	2203941	10242740
mean	400351	629052	0	0	14047078	0	0	0	0	6587978	4448143	2054492	818991	0	2058163	9728534
range (+/-)	85724	/	/	/	3566093	/	/	/	/	279444	451395	2158135	331836	/	185561	478055
L&B 357MAG	0	0	0	0	14736592	0	0	0	0	2778411	0	2458738	295651	0	0	2112198
L&B 357MAG	0	0	0	0	16607469	0	0	0	0	3174828	0	2399664	103574	0	0	2145796
L&B 357MAG	0	0	0	0	15531240	0	0	0	0	2321257	0	2245163	203860	0	0	2227124
mean	0	0	0	0	15625100	0	0	0	0	2758165	0	2367855	201028	0	0	2161706
range (+/-)	/	/	/	/	935439	/	/	/	/	426786	/	106788	96039	/	/	57463
MAG 357 MAG	0	0	0	0	0	0	0	0	0	0	0	342401184	2408247045	0	0	0
MAG 357 MAG	0	0	0	0	0	0	0	0	0	0	0	409798155	2732785359	0	0	0
MAG 357 MAG	0	0	0	0	0	0	0	0	0	0	0	382209961	2497647168	0	0	0
mean	0	0	0	0	0	0	0	0	0	0	0	378136433	2546226524	0	0	0
range (+/-)	/	/	/	/	/	/	/	/	/	/	/	33698486	162269157	/	/	/
GECO 38SPL	0	0	0	0	0	0	0	0	0	28338494	0	2253346	232191	0	0	0
GECO 38SPL	0	0	0	0	0	0	0	0	0	28636453	0	1928792	317687	0	0	0
GECO 38SPL	0	0	0	0	0	0	0	0	0	23564940	0	1998170	199506	0	0	0
mean	0	0	0	0	0	0	0	0	0	26846629	0	2060103	249795	0	0	0
range (+/-)		/	/	/		/	/	/	/	2535757	/	162277	59091	/	/	/
WIN 38 SPL	0	0	0	0	51524438	0	0	0	0	0	0	44481237	0	0	0	0
WIN 38 SPL	0	0	0	0	62098131	0	0	0	0	0	0	44418002	0	0	0	0
WIN 38 SPL	0	0	0	0	60453722	0	0	0	0	0	0	46118709	0	0	0	0
mean	0	0	0	0	58025430	0	0	0	0	0	0	45005983	0	0	0	0
range (+/-)	/	/	/	/	5286847	/	/	/	/	/	/	850354	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
ELEY 410	1284234	0	0	0	18063360	0	0	0	0	9107063	0	531707	204011412	877517	212295	10938024
ELEY 410	801505	0	0	0	15800517	0	0	0	0	8184025	0	442926	196547281	1011826	580442	383728
ELEY 410	988566	0	0	0	16672361	0	0	0	0	7779995	0	425663	182404281	1152261	198307	10613525
mean	1024768	0	0	0	16845413	0	0	0	0	8357028	0	466765	194320991	1013868	330348	7311759
range (+/-)	241365	/	/	/	1131422	/	/	/	/	663534	/	53022	10803566	137372	184074	5277148
WIN 410	303232	0	0	0	10657127	0	0	0	0	18263689	0	168272869	2968707	0	1555916	8463873
WIN 410	408022	0	0	0	11812788	0	0	0	0	18292339	0	166158058	4100787	0	1757408	10880166
WIN 410	377937	0	0	0	11843408	0	0	0	0	20293582	0	169979870	3578040	0	1337459	10311358
mean	363064	0	0	0	11437774	0	0	0	0	18949870	0	168136932	3549178	0	1550261	9885132
range (+/-)	52395	/	/	/	593141	/	/	/	/	1000622	/	1910906	566040	/	209975	923743
MAG 556CBC	0	0	0	0	71695295	0	0	0	0	42584265	0	0	2983697	0	0	1339897
MAG 556CBC	0	0	0	0	58305825	0	0	0	0	25269241	0	0	6243618	0	0	610533
MAG 556CBC	0	0	0	0	69035929	0	0	0	0	27953993	0	0	11453013	0	0	2940824
mean	0	0	0	0	66345683	0	0	0	0	31935833	0	0	6893443	0	0	1630418
range (+/-)	/	/	/	/	6694735	/	/	/	/	7315136	/	/	4234658	/	/	1165146
PRIVI 762X39	0	0	4543229	0	0	0	0	0	0	2758358	0	266908	0	0	0	0
PRIVI 762X39	0	0	5115702	0	0	0	0	0	0	3249046	0	377996	0	0	0	0
PRIVI 762X39	0	0	8323793	0	0	0	0	0	0	3782504	0	437948	0	0	0	0
mean	0	0	5994241	0	0	0	0	0	0	3263303	0	360951	0	0	0	0
range (+/-)	/	/	1890282	/	/	/	/	/	/	512073	/	85520	/	/	/	/
FED 762X51	0	0	0	0	35262881	0	0	0	0	53528514	0	0	18408161	0	0	0
FED 762X51	0	0	0	0	33823868	0	0	0	0	47115986	0	0	9683270	0	0	0
FED 762X51	0	0	0	0	34215332	0	0	0	0	46818417	0	0	9187477	0	0	0
mean	0	0	0	0	34434027	0	0	0	0	49154306	0	0	12426303	0	0	0
range (+/-)	/	/	/	/		/	/	/	/		/	/		/	/	/
LAPUA 762X51	0	0	0	0	0	0	0	0	0	53528514	0	18408161	0	0	0	0
LAPUA 762X51	0	0	0	0	0	0	0	0	0	47115986	0	9683270	0	0	0	0
LAPUA 762X51	0	0	0	0	0	0	0	0	0	46818417	0	9187477	0	0	0	0
mean	0	0	0	0	0	0	0	0	0	49154306	0	12426303	0	0	0	0
range (+/-)	/	/	/	/	/	/	/	/	/	3355049	/	4362446	/	/	/	/
NATO 762X51	0	0	0	0	23758908	0	0	0	0	7084583	0	264758652	3399626	0	3669645	11144758
NATO 762X51	0	0	0	0	30593738	0	0	0	0	7994733	0	259231091	3372911	0	3866298	12491356
NATO 762X51	0	0	0	0	25638552	0	0	0	0	6055630	0	244688354	3473347	0	4255620	12438804
mean	0	0	0	0	26663733	0	0	0	0	7044982	0	256226032	3415295	0	3930521	12024973
range (+/-)	/	/	/	/	3417415	/	/	/	/	969552	/	10035149	50218	/	292988	673299

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
PRIVI 762X51	0	0	1163977	0	0	3988267	194430	107427877	118200	47644227	0	522830	65242789	0	0	0
PRIVI 762X51	0	0	1210561	0	0	4003496	329137	103903131	114049	47024569	0	597723	70152784	0	0	0
PRIVI 762X51	0	0	1025599	0	0	4057271	264461	100278084	100122	44963908	0	504742	68148566	0	0	0
mean	0	0	1133379	0	0	4016345	262676	103869697	110790	46544235	0	541765	67848046	0	0	0
range (+/-)	/	/	92481	/	/	34502	32338	3574897	59100	1340160	/	46491	2454998	/	/	/
MAG 9MM	0	0	0	366805	159313883	0	0	0	0	0	0	1958629	0	0	0	0
MAG 9MM	0	0	0	239743	213243047	0	0	0	0	0	0	4210035	0	0	0	0
MAG 9MM	0	0	0	424162	196503875	0	0	0	0	0	0	5100231	0	0	0	0
mean	0	0	0	343570	189686935	0	0	0	0	0	0	3756298	0	0	0	0
range (+/-)		/	/	92210	26964582	/	/	/	/	/	/	1570801	/	/	/	/
WIN 9MM	0	0	0	0	16325909	0	0	0	0	1853458	0	178491	295651	0	0	1170923
WIN 9MM	0	0	0	0	23338792	0	0	0	0	1790682	0	99716	103574	0	64668	2034035
WIN 9MM	0	0	0	0	24888000	0	0	0	0	1383019	0	213871	203860	0	292770	2157974
mean	0	0	0	0	21517567	0	0	0	0	1675720	0	164026	201028	0	119146	1787644
range (+/-)	/	/	/	/	4281046	/	/	/	/	235220	/	57078	96039	/	146385	493526

12 Appendix IV: Raw data from section 6

Table 41: Raw data from spent cartridge case extracts

Ammo	NAPH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22	0	/	/	/	0	/	/	/	/	19697751	/	0	/	/	0	0
REM 22	0	/	/	/	0	/	/	/	/	11200657	/	0	/	/	0	0
REM 22	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22	0	/	/	/	0	/	/	/	/	8079311	/	0	/	/	0	0
REM 22	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
mean	/	/	/	/	/	/	/	/	/	7795544	/	/	/	/	/	/
range	/	/	/	/	/	/	/	/	/	19697751	/	/	/	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	252.6796	/	/	/	/	/	/
VOSTOK 22	0	0	/	/	0	/	/	/	/	1356389	0	0	0	0	0	0
VOSTOK 22	0	0	/	/	0	/	/	/	/	172922	0	0	246226	0	0	0
VOSTOK 22	0	0	/	/	0	/	/	/	/	1450175	0	0	126167	0	0	0
VOSTOK 22	0	0	/	/	0	/	/	/	/	0	0	0	0	0	0	0
VOSTOK 22	0	0	/	/	0	/	/	/	/	11511852	0	0	150952	0	0	0
mean	/	/	/	/	/	/	/	/	/	2898268	/	/	104669	/	/	/
range	/	/	/	/	/	/	/	/	/	11511852	/	/	246226	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	397.1977	/	/	235.2425	/	/	/
L&B 357MAG	/	/	/	/	0	/	/	/	/	0	/	0	/	/	/	0
L&B 357MAG	/	/	/	/	88200	/	/	/	/	525917	/	0	/	/	/	0
L&B 357MAG	/	/	/	/	310446	/	/	/	/	897727	/	0	/	/	/	0
mean	/	/	/	/	132882	/	/	/	/	474548	/	/	/	/	/	/
range	/	/	/	/	310446	/	/	/	/	897727	/	/	/	/	/	/
relative distriubtion	/	/	/	/	233.6253	/	/	/	/	189.1752	/	/	/	/	/	/

Ammo	NAPH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	2595963	22155150	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	1818320	10515965	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	2270867	23511870	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	3187359	27258273	/	/	/
MAG 357 MAG	/	/	/	/	/	/	/	/	/	/	/	1117589	10648742	/	/	/
mean	/	/	/	/	/	/	/	/	/	/	/	2198020	18818000	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	2069770	16742308	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	94.16522	88.96965	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
mean	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
WIN 38 SPL	/	/	/	/	12521009	/	/	/	/	/	/	29284900	/	/	/	/
WIN 38 SPL	/	/	/	/	5121382	/	/	/	/	/	/	1407546	/	/	/	/
WIN 38 SPL	/	/	/	/	18303332	/	/	/	/	/	/	7038936	/	/	/	/
WIN 38 SPL	/	/	/	/	9124084	/	/	/	/	/	/	4409668	/	/	/	/
WIN 38 SPL	/	/	/	/	24874688	/	/	/	/	/	/	10896220	/	/	/	/
mean	/	/	/	/	13988899	/	/	/	/	/	/	10607454	/	/	/	/
range	/	/	/	/	19753306	/	/	/	/	/	/	27877354	/	/	/	/
relative distriubtion	/	/	/	/	141.207	/	/	/	/	/	/	262.8091	/	/	/	/

Ammo	NAPH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
ELEY 410	0	/	/	/	0	/	/	/	/	1141362	0	0	1083971	17121940	0	0
ELEY 410	0	/	/	/	0	/	/	/	/	942004	0	0	757898	21641146	0	0
ELEY 410	0	/	/	/	0	/	/	/	/	1500879	0	0	394048	25241507	0	0
ELEY 410	0	/	/	/	0	/	/	/	/	1890222	0	0	2893307	22827978	0	0
ELEY 410	0	/	/	/	0	/	/	/	/	2192824	0	0	2611674	20187710	0	0
mean	/	/	/	/	/	/	/	/		1533458	/	/	1548180	21404056	/	/
range	/	/	/	/	/	/	/	/		1250820	/	/	2499259	8119567	/	/
relative distriubtion	/	/	/	/	/	/	/	/		81.56857	/	/	161.4321	37.93471	/	/
WIN 410	191036	/	/	/	158251	/	/	/	/	1845665	/	771749	0	/	0	0
WIN 410	1000548	/	/	/	332522	/	/	/	/	5382097	/	9750748	0	/	0	0
WIN 410	997184	/	/	/	557131	/	/	/	/	6833199	/	10566388	0	/	0	0
WIN 410	922696	/	/	/	256832	/	/	/	/	5965422	/	9722315	0	/	0	0
WIN 410	1318049	/	/	/	383585	/	/	/	/	1125674	/	562057	0	/	0	0
mean	885902.6	/	/	/	337664.2	/	/	/	/	4230411		6274651	/	/	/	/
range	1127013	/	/	/	398880	/	/	/	/	5707525		10004331	/	/	/	/
relative distriubtion	127.2164	/	/	/	118.1292	/	/	/	/	134.9165		159.4404	/	/	/	/
MAG 556CBC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	0
MAG 556CBC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	0
MAG 556CBC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	0
mean	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
PRIVI 762X39	/	/	873812	/	/	/	/	/	/	/	0	0	/	/	/	/
PRIVI 762X39	/	/	1323380	/	/	/	/	/	/	/	0	14372	/	/	/	/
PRIVI 762X39	/	/	3237029	/	/	/	/	/	/	/	0	96804	/	/	/	/
PRIVI 762X39	/	/	4325905	/	/	/	/	/	/	/	0	109461	/	/	/	/
PRIVI 762X39	/	/	4506974	/	/	/	/	/	/	/	563121	245848	/	/	/	/
PRIVI 762X39	/	/	3304339	/	/	/	/	/	/	/	0	86322	/	/	/	/
mean	/	/	2928573	/	/	/	/	/	/	/	93853.5	92134.5	/	/	/	/
range	/	/	3633162	/	/	/	/	/	/	/	563121	245848	/	/	/	/
relative distriubtion	/	/	124.0591	/	/	/	/	/	/	/	600	266.836	/	/	/	/

Ammo	NAPH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
FED 762X51	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
FED 762X51	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
FED 762X51	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
mean	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	0	/	0	/	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	0	/	0	/	/	/	/
LAPUA 762X51	/	/	/	/	/	/	/	/	/	0	/	0	/	/	/	/
mean	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
NATO 762X51	/	/	/	/	0	/	/	/	/	0	/	351193	0	/	0	0
NATO 762X51	/	/	/	/	0	/	/	/	/	0	/	1087189	0	/	0	0
NATO 762X51	/	/	/	/	0	/	/	/	/	0	/	2441578	40434786	/	0	0
NATO 762X51	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
NATO 762X51	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
mean	/	/	/	/	/	/	/	/	/	/	/	775992	8086957	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/			/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	269.3823	500	/	/	/
PRIVI 762X51	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51	/	/	0	/	/	0	0	0	0	0	/	893748	3612937	/	/	/
PRIVI 762X51	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51	/	/	0	/	/	0	0	0	0	0	/	1282855	75715600	/	/	/
mean	/	/	/	/	/	/	/	/	/	/	/	435320.6	15865707	/	/	/
range	/	/	/	/	/	/	/	/	/	/	/	1282855	75715600	/	/	/
relative distriubtion	/	/	/	/	/	/	/	/	/	/	/	294.692	477.228	/	/	/

Ammo	NAPH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
MAG 9MM	/	/	/	/	4296482	/	/	/	/	/	/	297872	0	/	/	/
MAG 9MM	/	/	/	/	6125774	/	/	/	/	/	/	445018	0	/	/	/
MAG 9MM	/	/	/	/	1605243	/	/	/	/	/	/	92806	0	/	/	/
MAG 9MM	/	/	/	/	2324993	/	/	/	/	/	/	160863	0	/	/	/
MAG 9MM	/	/	/	/	2014794	/	/	/	/	/	/	1488157	0	/	/	/
mean	/	/	/	/	3273457	/	/	/	/	/	/	496943.2	/	/	/	/
range	/	/	/	/	4520531	/	/	/	/	/	/	1395351	/	/	/	/
relative distriubtion	/	/	/	/	138.0965	/	/	/	/	/	/	280.7868	/	/	/	/
WIN 9MM	/	/	/	/	528751	/	/	/	/	857206	/	0	0	/	0	0
WIN 9MM	/	/	/	/	45843	/	/	/	/	790689	/	0	0	/	0	0
WIN 9MM	/	/	/	/	30869	/	/	/	/	444530	/	0	0	/	0	0
mean	/	/	/	/	201821	0	0	0	0	697475	/	/	/	/	/	/
range	/	/	/	/	497882	/	/	/	/	412676	/	/	/	/	/	/
relative distriubtion	/	/	/	/	246.6948	/	/	/	/	59.16714	/	/	/	/	/	/

13 Appendix V: Raw data from section 7

Table 42: Raw fabric extract data (peak heights)

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
L and B .357mag	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	20820	/	/	/	/	76037	/	0	27339	/	/	0
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	103275	/	0	0	/	/	0
		SIM	/	/	/	/	43872	/	/	/	/	510956	/	0	58296	/	/	0
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	358190	/	0	0	/	/	0
		SIM	/	/	/	/	61990	/	/	/	/	204563	/	0	38299	/	/	0
	Lab coat 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	1229426	/	/	0
		SIM	/	/	/	/	36252	/	/	/	/	69861	/	0	905378	/	/	0
	Lab coat 2	TIC	/	/	/	/	333347	/	/	/	/	1215891	/	181600	138687	/	/	0
		SIM	/	/	/	/	372095	/	/	/	/	578511	/	41604	325622	/	/	0
	Lab coat 3	TIC	/	/	/	/	0	/	/	/	/	241666	/	48769	173562	/	/	0
		SIM	/	/	/	/	123794	/	/	/	/	165073	/	18263	108324	/	/	0
	Fleece 1	TIC	/	/	/	/	0	/	/	/	/	212576	/	147952	181890	/	/	0
		SIM	/	/	/	/	119236	/	/	/	/	231986	/	34232	137331	/	/	0
	Fleece 2	TIC	/	/	/	/	343293	/	/	/	/	395005	/	210601	167142	/	/	0
		SIM	/	/	/	/	380855	/	/	/	/	367588	/	52135	123268	/	/	0
	Fleece 3	TIC	/	/	/	/	326439	/	/	/	/	1465849	/	220754	120029	/	/	0
		SIM	/	/	/	/	376976	/	/	/	/	615062	/	53191	106663	/	/	0
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	361178	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	41537	/	0	298745	/	/	0
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	0	223519	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	50380	/	0	198948	/	/	0
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	29198	/	0	142139	/	/	0
	Brown Jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	18433	/	/	/	/	89044	/	12555	21446	/	/	0
	Brown Jumper 2	TIC	/	/	/	/	0	/	/	/	/	371820	/	0	0	/	/	0

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
		SIM	/	/	/	/	57426	/	/	/	/	246311	/	23186	30805	/	/	0
	Brown Jumper 3	TIC	/	/	/	/	0	/	/	/	/	445477	/	0	0	/	/	0
		SIM	/	/	/	/	64229	/	/	/	/	180683	/	17263	7926	/	/	0
Winchester 9mm	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	657347	/	0	0	/	0	0
		SIM	/	/	/	/	65618	/	/	/	/	301612	/	0	103596	/	0	0
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	361329	/	0	116917	/	0	0
		SIM	/	/	/	/	46263	/	/	/	/	207592	/	0	86280	/	0	0
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	401572	/	0	0	/	0	0
		SIM	/	/	/	/	19826	/	/	/	/	307393	/	0	85558	/	0	0
	Lab coat 1	TIC	/	/	/	/	350715	/	/	/	/	973717	/	0	348598	/	0	0
		SIM	/	/	/	/	358010	/	/	/	/	375555	/	0	214741	/	0	0
	Lab coat 2	TIC	/	/	/	/	164320	/	/	/	/	400225	/	0	488205	/	0	0
		SIM	/	/	/	/	160971	/	/	/	/	100636	/	0	322458	/	0	0
	Lab coat 3	TIC	/	/	/	/	502655	/	/	/	/	2116276	/	0	1078616	/	0	0
		SIM	/	/	/	/	462651	/	/	/	/	915335	/	0	696935	/	0	0
	Fleece 1	TIC	/	/	/	/	2796310	/	/	/	/	2909767	/	174959	525258	/	0	0
		SIM	/	/	/	/	2903356	/	/	/	/	1314062	/	48476	528010	/	0	0
	Fleece 2	TIC	/	/	/	/	1648291	/	/	/	/	925117	/	131687	272426	/	0	0
		SIM	/	/	/	/	1776710	/	/	/	/	764969	/	34967	234615	/	0	0
	Fleece 3	TIC	/	/	/	/	1392474	/	/	/	/	1952172	/	141945	141945	/	0	0
		SIM	/	/	/	/	1479142	/	/	/	/	860007	/	28806	303947	/	0	0
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	437470	/	/	450965	/	0	0
		SIM	/	/	/	/	48760	/	/	/	/	182744	/	/	349895	/	0	0
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	0	0
		SIM	/	/	/	/	22517	/	/	/	/	68833	/	/	159241	/	0	0
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	350899	/	/	371118	/	0	0
		SIM	/	/	/	/	105115	/	/	/	/	188794	/	/	292820	/	0	0
	Brown Jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
		SIM	/	/	/	/	89499	/	/	/	/	223252	/	0	40487	/	0	0
	Brown Jumper 2	TIC	/	/	/	/	344711	/	/	/	/	963381	/	0	0	/	0	0
		SIM	/	/	/	/	451122	/	/	/	/	528273	/	13215	104113	/	0	0
	Brown Jumper 3	TIC	/	/	/	/	349346	/	/	/	/	385137	/	0	0	/	0	0
		SIM	/	/	/	/	287426	/	/	/	/	254037	/	7114	42907	/	0	0
Samson 9mm	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	472371	/	/	0	/	/	/
		SIM	/	/	/	/	26293	/	/	/	/	310209	/	/	49069	/	/	/
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	103756	/	/	36246	/	/	/
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	426980	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	115700	/	/	28023	/	/	/
	Lab coat 1	TIC	/	/	/	/	377485	/	/	/	/	2479437	/	/	319262	/	/	/
		SIM	/	/	/	/	420672	/	/	/	/	1249875	/	/	213110	/	/	/
	Lab coat 2	TIC	/	/	/	/	415621	/	/	/	/	2483632	/	/	422158	/	/	/
		SIM	/	/	/	/	434994	/	/	/	/	1167533	/	/	351303	/	/	/
	Lab coat 3	TIC	/	/	/	/	139887	/	/	/	/	2322183	/	/	276283	/	/	/
		SIM	/	/	/	/	177955	/	/	/	/	1109807	/	/	240482	/	/	/
	Fleece 1	TIC	/	/	/	/	0	/	/	/	/	119283	/	/	0	/	/	/
		SIM	/	/	/	/	38502	/	/	/	/	24321	/	/	71658	/	/	/
	Fleece 2	TIC	/	/	/	/	1126056	/	/	/	/	5624523	/	/	539119	/	/	/
		SIM	/	/	/	/	1122662	/	/	/	/	2463361	/	/	403590	/	/	/
	Fleece 3	TIC	/	/	/	/	159031	/	/	/	/	1946552	/	/	175158	/	/	/
		SIM	/	/	/	/	241877	/	/	/	/	823490	/	/	140397	/	/	/
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	376806	/	/	436427	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	270837	/	/	368889	/	/	/
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	/	371651	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	49654	/	/	408573	/	/	/
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	0	/	/	380034	/	/	/

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
	Brown Jumper 1	TIC	/	/	/	/	200732	/	/	/	/	2136606	/	/	0	/	/	/
		SIM	/	/	/	/	184084	/	/	/	/	997225	/	/	57309	/	/	/
	Brown Jumper 2	TIC	/	/	/	/	200732	/	/	/	/	2136606	/	/	0	/	/	/
		SIM	/	/	/	/	184084	/	/	/	/	997225	/	/	57309	/	/	/
	Brown Jumper 3	TIC	/	/	/	/	0	/	/	/	/	833104	/	/	0	/	/	/
		SIM	/	/	/	/	129082	/	/	/	/	442875	/	/	45100	/	/	/
	Brown Jumper 3	TIC	/	/	/	/	191356	/	/	/	/	1127708	/	/	0	/	/	/
		SIM	/	/	/	/	145677	/	/	/	/	678976	/	/	56889	/	/	/

Table 43: Raw fabric extract data (peak heights)LOG10

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
L and B .357mag	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	4.3184807	/	/	/	/	4.881025	/	0	4.4367826	/	/	0
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	5.0139952	/	0	0	/	/	0
		SIM	/	/	/	/	4.6421874	/	/	/	/	5.7083835	/	0	4.7656388	/	/	0
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	5.5541135	/	0	0	/	/	0
		SIM	/	/	/	/	4.7923216	/	/	/	/	5.3108271	/	0	4.5831874	/	/	0
	Lab coat 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	6.0897024	/	/	0
		SIM	/	/	/	/	4.559332	/	/	/	/	4.8442348	/	0	5.9568299	/	/	0
	Lab coat 2	TIC	/	/	/	/	5.5228966	/	/	/	/	6.0848946	/	5.259116	5.1420358	/	/	0
		SIM	/	/	/	/	5.5706538	/	/	/	/	5.7623116	/	4.619135	5.5127137	/	/	0
	Lab coat 3	TIC	/	/	/	/	0	/	/	/	/	5.3832156	/	4.688144	5.2394546	/	/	0
		SIM	/	/	/	/	5.0926996	/	/	/	/	5.217676	/	4.261572	5.0347247	/	/	0
	Fleece 1	TIC	/	/	/	/	0	/	/	/	/	5.3275142	/	5.170121	5.2598088	/	/	0
		SIM	/	/	/	/	5.0764074	/	/	/	/	5.3654618	/	4.534432	5.1377686	/	/	0
	Fleece 2	TIC	/	/	/	/	5.5356649	/	/	/	/	5.5966026	/	5.32346	5.2230856	/	/	0
		SIM	/	/	/	/	5.5807597	/	/	/	/	5.5653613	/	4.717129	5.0908503	/	/	0
	Fleece 3	TIC	/	/	/	/	5.513802	/	/	/	/	6.1660892	/	5.343909	5.0792862	/	/	0
		SIM	/	/	/	/	5.5763137	/	/	/	/	5.7889189	/	4.725838	5.0280138	/	/	0
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	5.5577213	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	4.6184351	/	0	5.4753006	/	/	0
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	0	5.3493144	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	4.7022582	/	0	5.2987396	/	/	0
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	0	/	/	/	/	4.4653531	/	0	5.1527133	/	/	0
	Brown Jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	/	0
		SIM	/	/	/	/	4.265596	/	/	/	/	4.9496047	/	4.098817	4.3313463	/	/	0
	Brown Jumper 2	TIC	/	/	/	/	0	/	/	/	/	5.5703327	/	0	0	/	/	0

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
		SIM	/	/	/	/	4.7591086	/	/	/	/	5.3914838	/	4.365226	4.4886212	/	/	0
	Brown Jumper 3	TIC	/	/	/	/	0	/	/	/	/	5.6488253	/	0	0	/	/	0
		SIM	/	/	/	/	4.8077312	/	/	/	/	5.2569173	/	4.237116	3.8990541	/	/	0
Winchester 9mm	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	5.8177947	/	0	0	/	0	0
		SIM	/	/	/	/	4.817023	/	/	/	/	5.4794486	/	0	5.015343	/	0	0
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	5.5579028	/	0	5.0678777	/	0	0
		SIM	/	/	/	/	4.6652338	/	/	/	/	5.3172106	/	0	4.9359101	/	0	0
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	5.6037634	/	0	0	/	0	0
		SIM	/	/	/	/	4.2972351	/	/	/	/	5.487694	/	0	4.9322606	/	0	0
	Lab coat 1	TIC	/	/	/	/	5.4829293	/	/	/	/	5.8661089	/	0	5.4489597	/	0	0
		SIM	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
	Lab coat 2	TIC	/	/	/	/	4.9563365	/	/	/	/	5.4637706	/	0	5.6541245	/	0	0
		SIM	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
	Lab coat 3	TIC	/	/	/	/	5.6812304	/	/	/	/	6.3044031	/	0	6.0023359	/	0	0
		SIM	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
	Fleece 1	TIC	/	/	/	/	6.4465853	/	/	/	/	6.4638582	/	5.242936	5.7203727	/	0	0
		SIM	/	/	/	/	6.4629003	/	/	/	/	6.1186159	/	4.685527	5.7226421	/	0	0
	Fleece 2	TIC	/	/	/	/	6.2170339	/	/	/	/	5.9661967	/	5.119543	5.4352486	/	0	0
		SIM	/	/	/	/	6.2496165	/	/	/	/	5.8836438	/	4.543658	5.3703558	/	0	0
	Fleece 3	TIC	/	/	/	/	6.1437871	/	/	/	/	6.2905181	/	5.15212	5.1521201	/	0	0
		SIM	/	/	/	/	6.1700099	/	/	/	/	5.934502	/	4.459483	5.4827979	/	0	0
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	5.6409483	/	0	5.6541428	/	0	0
		SIM	/	/	/	/	4.6880637	/	/	/	/	5.2618431	/	0	5.5439377	/	0	0
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
		SIM	/	/	/	/	4.3525105	/	/	/	/	4.8377967	/	0	5.2020549	/	0	0
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	5.5451821	/	0	5.569512	/	0	0
		SIM	/	/	/	/	5.0216647	/	/	/	/	5.2759882	/	0	5.4666007	/	0	0
	Brown Jumper 1	TIC	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
		SIM	/	/	/	/	4.9518182	/	/	/	/	5.3487954	/	0	4.6073156	/	0	0
	Brown Jumper 2	TIC	/	/	/	/	5.5374551	/	/	/	/	5.9837981	/	0	0	/	0	0
		SIM	/	/	/	/	5.654294	/	/	/	/	5.7228584	/	4.121067	5.017505	/	0	0
	Brown Jumper 3	TIC	/	/	/	/	5.5432558	/	/	/	/	5.5856152	/	0	0	/	0	0
		SIM	/	/	/	/	5.4585261	/	/	/	/	5.404897	/	3.852114	4.6325282	/	0	0
			/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
Samson 9mm	T shirt 1	TIC	/	/	/	/	0	/	/	/	/	5.6742832	/	/	0	/	/	/
		SIM	/	/	/	/	4.4198401	/	/	/	/	5.4916544	/	/	4.6908072	/	/	/
	T shirt 2	TIC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	5.0160132	/	/	4.5592601	/	/	/
	T shirt 3	TIC	/	/	/	/	0	/	/	/	/	5.6304075	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	5.0633334	/	/	4.4475146	/	/	/
	Lab coat 1	TIC	/	/	/	/	5.5768997	/	/	/	/	6.3943531	/	/	5.5041472	/	/	/
		SIM	/	/	/	/	5.6239436	/	/	/	/	6.0968666	/	/	5.3286038	/	/	/
	Lab coat 2	TIC	/	/	/	/	5.6186975	/	/	/	/	6.3950872	/	/	5.625475	/	/	/
		SIM	/	/	/	/	5.6384833	/	/	/	/	6.0672692	/	/	5.5456819	/	/	/
	Lab coat 3	TIC	/	/	/	/	5.1457774	/	/	/	/	6.3658964	/	/	5.4413542	/	/	/
		SIM	/	/	/	/	5.2503102	/	/	/	/	6.0452475	/	/	5.3810826	/	/	/
	Fleece 1	TIC	/	/	/	/	0	/	/	/	/	5.0765786	/	/	0	/	/	/
		SIM	/	/	/	/	4.5854833	/	/	/	/	4.3859814	/	/	4.8552647	/	/	/
	Fleece 2	TIC	/	/	/	/	6.05156	/	/	/	/	6.7500857	/	/	5.7316846	/	/	/
		SIM	/	/	/	/	6.050249	/	/	/	/	6.3915281	/	/	5.6059404	/	/	/
	Fleece 3	TIC	/	/	/	/	5.2014818	/	/	/	/	6.289266	/	/	5.24343	/	/	/
		SIM	/	/	/	/	5.3835946	/	/	/	/	5.9156583	/	/	5.1473578	/	/	/
	Grey jumper 1	TIC	/	/	/	/	0	/	/	/	/	5.5761178	/	/	5.6399116	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	5.432708	/	/	5.5668957	/	/	/
	Grey jumper 2	TIC	/	/	/	/	0	/	/	/	/	0	/	/	5.5701353	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	4.6959542	/	/	5.6112697	/	/	/

Ammo	fabric type	MS mode (TIC/SIM)	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
	Grey jumper 3	TIC	/	/	/	/	0	/	/	/	/	0	/	/	0	/	/	/
		SIM	/	/	/	/	0	/	/	/	/	0	/	/	5.5798225	/	/	/
	Brown Jumper 1	TIC	/	/	/	/	5.3026166	/	/	/	/	6.3297244	/	/	0	/	/	/
		SIM	/	/	/	/	5.265016	/	/	/	/	5.9987932	/	/	4.7582228	/	/	/
	Brown Jumper 2	TIC	/	/	/	/	0	/	/	/	/	5.9206992	/	/	0	/	/	/
		SIM	/	/	/	/	5.1108657	/	/	/	/	5.6462812	/	/	4.6541765	/	/	/
	Brown Jumper 3	TIC	/	/	/	/	5.2818421	/	/	/	/	6.0521967	/	/	0	/	/	/
		SIM	/	/	/	/	5.163391	/	/	/	/	5.8318544	/	/	4.7550283	/	/	/

Table 44: Cartridge case extract data (peak heights).

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	0	/	/	/	/	19697751	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	52521	/	/	/	/	784675	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	0	/	/	/	/	11200657	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	0	/	/	/	/	422823	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	0	/	/	/	/	77257	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	0	/	/	0	/	/	/	/	1356389	0	0	0	/	0	0
VOSTOK 22 SIM1	0	0	/	/	0	/	/	/	/	796679	6797	0	44839	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	0	/	/	/	/	172922	0	0	246226	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	0	/	/	/	/	76952	2007	0	14125	/	0	0
VOSTOK 22 TIC 3	0	0	/	/	0	/	/	/	/	1450175	0	0	126167	/	0	0
VOSTOK 22 SIM 3	0	0			0	/	/	/	/	674374	45407	0	108032	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	2595963	22155150	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	872985	15036176	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	1818320	10515965	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	546540	7695605	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	2270867	23511870	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	750496	16174078	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
WIN 38 SPL TIC 1	/	/	/	/	12521009	/	/	/	/	/	/	29284900	/	/	/	/
WIN 38 SPL SIM 1	/	/	/	/	13041225	/	/	/	/	/	/	9555613	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	5121382	/	/	/	/	/	/	1407546	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL SIM 2	/	/	/	/	6487303	/	/	/	/	/	/	475909	/	/	/	/
WIN 38 SPL TIC 3	/	/	/	/	18303332	/	/	/	/	/	/	7038936	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	17718556	/	/	/	/	/	/	1410101	/	/	/	/
ELEY 410 TIC 1	517840	/	/	/	0	/	/	/	/	1141362	/	0	1083971	17121940	0	0
ELEY 410 SIM 1	0	/	/	/	0	/	/	/	/	509677	/	0	772559	11322659	0	0
ELEY 410 TIC 2	609029	/	/	/	0	/	/	/	/	942004	/	0	757898	21641146	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	591859	/	0	572321	15610339	0	0
ELEY 410 TIC 3	556489	/	/	/	0	/	/	/	/	1500879	/	0	394048	25241507	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	494219	/	0	331259	17879630	0	
WIN 410 TIC 1	191036	/	/	/	158251	/	/	/	/	1845665	/	771749	0	/	0	0
WIN 410 SIM 1	0	/	/	/	179496	/	/	/	/	1017991	/	251295	0	/	0	0
WIN 410 TIC 2	1000548	/	/	/	332522	/	/	/	/	5382097	/	9750748	0	/	0	0
WIN 410 SIM 2	0	/	/	/	362367	/	/	/	/	2617177	/	3296840	0	/	0	0
WIN 410 TIC 3	997184	/	/	/	557131	/	/	/	/	6833199	/	10566388	0	/	0	0
WIN 410 SIM 3	/	/	/	/	437441	/	/	/	/	3285846	/	3539312	0	/	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	0	/	351193	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	0	/	/	/	/	288587	/	172748	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	0	/	/	/	/	0	/	1087189	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	0	/	/	/	/	338193	/	374841	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	2441578	40434786	/	0	0
NATO 762X51 SIM 3	/	/	/	/	0	/	/	/	/	26686	/	527753	29500290	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Table 45: Cartridge case extract data (peak heights) LOG 10

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	0	/	/	/	/	7.2944166	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	4.720333	/	/	/	/	5.8946898	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	0	/	/	/	/	7.0492435	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	0	/	/	/	/	5.6261586	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	0	/	/	/	/	4.8879378	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	0	/	/	0	/	/	/	/	6.1323843	0	0	0	/	0	0
VOSTOK 22 SIM1	0	0	/	/	0	/	/	/	/	5.9012834	3.8323173	0	4.6516559	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	0	/	/	/	/	5.2378502	0	0	5.3913339	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	0	/	/	/	/	4.8862199	3.3025474	0	4.1499885	/	0	0
VOSTOK 22 TIC 3	0	0	/	/	0	/	/	/	/	6.1614204	0	0	5.1009458	/	0	0
VOSTOK 22 SIM 3	0	0			0	/	/	/	/	5.8289008	4.6571228	0	5.0335524	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	6.4142985	7.3454747	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	5.9410068	7.1771374	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	6.2596703	7.0218491	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	5.737622	6.8862428	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	6.3561917	7.3712872	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	5.8753484	7.2088195	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
WIN 38 SPL TIC 1	/	/	/	/	7.0976393	/	/	/	/	/	/	7.4666437	/	/	/	/
WIN 38 SPL SIM 1	/	/	/	/	7.1153184	/	/	/	/	/	/	6.9802586	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	6.7093872	/	/	/	/	/	/	6.1484626	/	/	/	/
WIN 38 SPL SIM 2	/	/	/	/	6.8120642	/	/	/	/	/	/	5.6775239	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL TIC 3	/	/	/	/	7.2625302	/	/	/	/	/	/	6.847507	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	7.2484283	/	/	/	/	/	/	6.1492502	/	/	/	/
ELEY 410 TIC 1	5.7141956	/	/	/	0	/	/	/	/	6.0574234	/	0	6.0350177	7.233553	0	0
ELEY 410 SIM 1	0	/	/	/	0	/	/	/	/	5.707295	/	0	5.8879317	7.0539484	0	0
ELEY 410 TIC 2	5.784638	/	/	/	0	/	/	/	/	5.9740527	/	0	5.8796108	7.3352803	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	5.7722183	/	0	5.7576397	7.1934123	0	0
ELEY 410 TIC 3	5.7454566	/	/	/	0	/	/	/	/	6.1763457	/	0	5.5955491	7.4021153	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	5.6939194	/	0	5.5201677	7.2523585	0	
WIN 410 TIC 1	5.2811152	/	/	/	5.1993465	/	/	/	/	6.2661529	/	5.8874761	0	/	0	0
WIN 410 SIM 1	0	/	/	/	5.2540548	/	/	/	/	6.0077439	/	5.4001838	0	/	0	0
WIN 410 TIC 2	6.0002379	/	/	/	5.5218204	/	/	/	/	6.7309515	/	6.9890379	0	/	0	0
WIN 410 SIM 2	0	/	/	/	5.5591486	/	/	/	/	6.4178331	/	6.5180979	0	/	0	0
WIN 410 TIC 3	5.9987753	/	/	/	5.7459573	/	/	/	/	6.8346241	/	7.0239266	0	/	0	0
WIN 410 SIM 3	/	/	/	/	5.6409195	/	/	/	/	6.5166472	/	6.5489188	0	/	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	0	/	5.5455459	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	0	/	/	/	/	5.4602768	/	5.237413	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	0	/	/	/	/	0	/	6.036305	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	0	/	/	/	/	5.5291646	/	5.5738471	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	6.3876706	7.6067551	/	0	0
NATO 762X51 SIM 3	/	/	/	/	0	/	/	/	/	4.4262835	/	5.7224307	7.4698263	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Table 46: Raw data Lab coat fabric extracts (peak areas)

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	0	/	/	/	/	195116	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	0	/	/	/	/	231757	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	0	/	/	0	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM1	0	0	/	/	0	/	/	/	/	65460	2891	0	20463	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	0	/	/	/	/	311717		0	0	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	0	/	/	/	/	112468	4315	0	36519	/	0	0
VOSTOK 22 TIC 3	0	0	/	/	0	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM 3	0	0	/	/	0	/	/	/	/	78861	5131	0	25064	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	67940	73134	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	31583	85621	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	30490	17328	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	19241	15939	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
WIN 38 SPL TIC 1	/	/	/	/	1995912	/	/	/	/	/	/	958110	/	/	/	/
WIN 38 SPL SIM 1	/	/	/	/	2017827	/	/	/	/	/	/	290205	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	35199688	/	/	/	/	/	/	10949585	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL SIM 2	/	/	/	/	35516688	/	/	/	/	/	/	3129307	/	/	/	/
WIN 38 SPL TIC 3	/	/	/	/	31378340	/	/	/	/	/	/	9895725	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	32163391	/	/	/	/	/	/	3031035	/	/	/	/
ELEY 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	189918	747237	0	0
ELEY 410 SIM 1	0	/	/	/	0	/	/	/	/	35484	/	0	757542	502594	0	0
ELEY 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	728045	247892	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	0	/	0	735997	180585	0	0
ELEY 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	575492	446279	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	496818	300912	0	0
WIN 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	90052	0	0	0	0
WIN 410 SIM 1	0	/	/	/	0	/	/	/	/	0	/	31799	0	0	0	0
WIN 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	196836	0	0	0	0
WIN 410 SIM 2	0	/	/	/	48325	/	/	/	/	707005	/	47088	43319	0	0	0
WIN 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	0	/	379794	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	0	/	/	/	/	41337	/	127232	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	0	/	/	/	/	0	/	545086	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	82636	/	/	/	/	131990	/	185089	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	138132	0	/	0	0
NATO 762X51 SIM 3	/	/	/	/	30903	/	/	/	/	60322	/	60581	0	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Table 47: Raw data lab coat extracts LOG 10

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	0	/	/	/	/	5.29029	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	0	/	/	/	/	5.36503	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	0	/	/	0	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM1	0	0	/	/	0	/	/	/	/	4.81598	3.46105	0	4.31097	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	0	/	/	/	/	5.49376		0	0	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	0	/	/	/	/	5.05103	3.63498	0	4.56252	/	0	0
VOSTOK 22 TIC 3	0	0	/	/	0	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM 3	0	0	/	/	0	/	/	/	/	4.89686	3.7102	0	4.39905	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	4.83213	4.86412	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	4.49945	4.93258	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	4.48416	4.23875	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	4.28423	4.20246	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL TIC 1	/	/	/	/	6.30014	/	/	/	/	/	/	5.98142	/	/	/	/
WIN 38 SPL SIM 1	/	/	/	/	6.30488	/	/	/	/	/	/	5.4627	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	7.54654	/	/	/	/	/	/	7.0394	/	/	/	/
WIN 38 SPL SIM 2	/	/	/	/	7.55043	/	/	/	/	/	/	6.49545	/	/	/	/
WIN 38 SPL TIC 3	/	/	/	/	7.49663	/	/	/	/	/	/	6.99545	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	7.50736	/	/	/	/	/	/	6.48159	/	/	/	/
ELEY 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	5.27857	5.87346	0	0
ELEY 410 SIM 1	0	/	/	/	0	/	/	/	/	4.55003	/	0	5.87941	5.70122	0	0
ELEY 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	5.86216	5.39426	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	0	/	0	5.86688	5.25668	0	0
ELEY 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	5.76004	5.64961	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	5.6962	5.47844	0	0
WIN 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	4.95449	0	0	0	0
WIN 410 SIM 1	0	/	/	/	0	/	/	/	/	0	/	4.50241	0	0	0	0
WIN 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	5.2941	0	0	0	0
WIN 410 SIM 2	0	/	/	/	4.68417	/	/	/	/	5.84942	/	4.67291	4.63668	0	0	0
WIN 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	0	/	5.57955	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	0	/	/	/	/	4.61634	/	5.1046	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	0	/	/	/	/	0	/	5.73647	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	4.91717	/	/	/	/	5.12054	/	5.26738	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	5.14029	0	/	0	0
NATO 762X51 SIM 3	/	/	/	/	4.49	/	/	/	/	4.78048	/	4.78234	0	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Table 48: Raw data fabric scrapings

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	576400	/	/	/	/	859930	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	587601	/	/	/	/	281763	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	2534756	/	/	/	/	46957	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	530217	/	/	/	/	371288	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	12018939	/	/	/	/	316521	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	10930702	/	/	/	/	238840	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	270330	/	/	4020889	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM1	0	267690	/	/	4380816	/	/	/	/	98090	24694	0	0	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	855387	/	/	/	/	345029		0	0	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	17478	/	/	/	/	2936	0	0	0	/	0	0
VOSTOK 22 TIC 3	0	227393	/	/	4206722	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM 3	0	241942	/	/	4037173	/	/	/	/	74134	18914	0	0	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	344990	3409571	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	106470	2069336	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	18078	35392	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	73201	0	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	23766	25064	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
WIN 38 SPL TIC 1	/	/	/	/	17525532	/	/	/	/	/	/	2352955	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL SIM 1	/	/	/	/	17178524	/	/	/	/	/	/	772444	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	20973740	/	/	/	/	/	/	654644	/	/	/	/
WIN 38 SPL SIM 2	/	/	/	/	20331855	/	/	/	/	/	/	3483401	/	/	/	/
WIN 38 SPL TIC 3	/	/	/	/	17359249	/	/	/	/	/	/	812497	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	17532199	/	/	/	/	/	/	283751	/	/	/	/
ELEY 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 1	0	/	/	/	31064	/	/	/	/	186775	/	0	63568	6147	0	0
ELEY 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 TIC 1	0	/	/	/	0	/	/	/	/	1296656	/	0	0	0	0	0
WIN 410 SIM 1	0	/	/	/	40242	/	/	/	/	414561	/	0	0	0	0	0
WIN 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 2	0	/	/	/	37510	/	/	/	/	222275	/	0	0	0	0	0
WIN 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 3	0	/	/	/	32761	/	/	/	/	139598	/	0	0	0	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	889372	/	547362	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	301338	/	/	/	/	299041	/	107646	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	1362835	/	/	/	/	1124375	/	2773123	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	1033737	/	/	/	/	390841	/	730608	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
NATO 762X51 SIM 3	/	/	/	/	465971	/	/	/	/	325282	/	56049	0	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

Table 49: Raw data fabric scrapings Log 10

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
REM 22 TIC 1	0	/	/	/	5.76072	/	/	/	/	5.93446	/	0	/	/	0	0
REM 22 SIM 1	0	/	/	/	5.76908	/	/	/	/	5.44988	/	0	/	/	0	0
REM 22 TIC 2	0	/	/	/	6.40394	/	/	/	/	4.6717	/	0	/	/	0	0
REM 22 SIM 2	0	/	/	/	5.72445	/	/	/	/	5.56971	/	0	/	/	0	0
REM 22 TIC 3	0	/	/	/	7.07987	/	/	/	/	5.5004	/	0	/	/	0	0
REM 22 SIM 3	0	/	/	/	7.03865	/	/	/	/	5.37811	/	0	/	/	0	0
VOSTOK 22 TIC 1	0	5.43189	/	/	6.60432	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM1	0	5.42763	/	/	6.64156	/	/	/	/	4.99162	4.39259	0	0	/	0	0
VOSTOK 22 TIC 2	0	0	/	/	5.93216	/	/	/	/	5.53786	0	0	0	/	0	0
VOSTOK 22 SIM 2	0	0	/	/	4.24249	/	/	/	/	3.46776	0	0	0	/	0	0
VOSTOK 22 TIC 3	0	5.35678	/	/	6.62394	/	/	/	/	0	0	0	0	/	0	0
VOSTOK 22 SIM 3	0	5.38371	/	/	6.60608	/	/	/	/	4.87002	4.27678	0	0	/	0	0
MAG 357 MAG TIC 1	/	/	/	/	/	/	/	/	/	/	/	5.53781	6.5327	/	/	/
MAG 357 MAG SIM1	/	/	/	/	/	/	/	/	/	/	/	5.02723	6.31583	/	/	/
MAG 357 MAG TIC 2	/	/	/	/	/	/	/	/	/	/	/	0	0	/	/	/
MAG 357 MAG SIM2	/	/	/	/	/	/	/	/	/	/	/	4.25715	0	/	/	/
MAG 357 MAG TIC 3	/	/	/	/	/	/	/	/	/	/	/	4.86452	0	/	/	/
MAG 357 MAG SIM 3	/	/	/	/	/	/	/	/	/	/	/	4.37596	4.39905	/	/	/
GECO 38SPL TIC 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 1	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 2	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL TIC 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
GECO 38SPL SIM 3	/	/	/	/	/	/	/	/	/	0	/	0	0	/	/	/
WIN 38 SPL TIC 1	/	/	/	/	7.24367	/	/	/	/	/	/	6.37161	/	/	/	/

Ammo	NAPHTH	DNG	CAMPHOR	3NT	NG	26DNT	23DNT	24DNT	25DNT	DPA	MC	EC	DBP	DIBP	2NDPA	4NDPA
WIN 38 SPL SIM 1	/	/	/	/	7.23499	/	/	/	/	/	/	5.88787	/	/	/	/
WIN 38 SPL TIC 2	/	/	/	/	7.32168	/	/	/	/	/	/	5.81601	/	/	/	/
WIN 38 SPL SIM 2	/	/	/	/	7.30818	/	/	/	/	/	/	6.542	/	/	/	/
WIN 38 SPL TIC 3	/	/	/	/	7.23953	/	/	/	/	/	/	5.90982	/	/	/	/
WIN 38 SPL SIM 3	/	/	/	/	7.24384	/	/	/	/	/	/	5.45294	/	/	/	/
ELEY 410 TIC 1	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 1	0	/	/	/	4.49226	/	/	/	/	5.27132	/	0	4.80324	3.78866	0	0
ELEY 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
ELEY 410 SIM 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 TIC 1	0	/	/	/	0	/	/	/	/	6.11282	/	0	0	0	0	0
WIN 410 SIM 1	0	/	/	/	4.60468	/	/	/	/	5.61759	/	0	0	0	0	0
WIN 410 TIC 2	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 2	0	/	/	/	4.57415	/	/	/	/	5.34689	/	0	0	0	0	0
WIN 410 TIC 3	0	/	/	/	0	/	/	/	/	0	/	0	0	0	0	0
WIN 410 SIM 3	0	/	/	/	4.51536	/	/	/	/	5.14488	/	0	0	0	0	0
NATO 762X51 TIC 1	/	/	/	/	0	/	/	/	/	5.94908	/	5.73827	0	/	0	0
NATO 762X51 SIM 1	/	/	/	/	5.47905	/	/	/	/	5.47573	/	5.032	0	/	0	0
NATO 762X51 TIC 2	/	/	/	/	6.13444	/	/	/	/	6.05091	/	6.44297	0	/	0	0
NATO 762X51SIM 2	/	/	/	/	6.01441	/	/	/	/	5.592	/	5.86368	0	/	0	0
NATO 762X51 TIC 3	/	/	/	/	0	/	/	/	/	0	/	0	0	/	0	0
NATO 762X51 SIM 3	/	/	/	/	5.66836	/	/	/	/	5.51226	/	4.74857	0	/	0	0
PRIVI 762X51 TIC 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 1	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 2	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 TIC 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/
PRIVI 762X51 SIM 3	/	/	0	/	/	0	0	0	0	0	/	0	0	/	/	/

14 Appendix VI: Published articles

JOURNAL OF FORENSIC SCIENCES

J Forensic Sci, July 2010, Vol. 55, No. 4
doi: 10.1111/j.1556-4029.2010.01370.x
Available online at: interscience.wiley.com

PAPER

CRIMINALISTICS

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Analysis of Gunshot Residue and Associated Materials—A Review

ABSTRACT: A comprehensive review of the scientific literature on gunshot residue (GSR) is presented. Aspects of both inorganic and organic GSR are discussed, from formation and distribution, to sample collection, preparation, and analysis using a variety of techniques. The interpretation of GSR results is also considered including issues surrounding the contamination, distribution, and transfer of GSR. Potential problems with ulterior sources of GSR like particles have been reported in the literature. For example, particles from environmental and occupational sources have been highlighted as exhibiting similar chemical and morphological characteristics to GSR. These findings are put into context with regard to interpreting samples. A move toward a "case by case" approach is argued to be more preferable to a "formal" classification system where possible. The analysis of both inorganic and organic compositions of residue samples as well as morphological considerations is considered to be a more ideal approach to GSR analysis, whereever practicable.

KEYWORDS: forensic science, ballistics, gunshot residue, cartridge discharge residue, firearm discharge residue, scanning electron microscopy, gas chromatography, liquid chromatography, environmental sources

Between 2006/2007 there were 9650 reported incidents involving firearms in England and Wales (excluding air rifles), 566 of which involved serious or fatal injuries. Firearms were discharged in 40% of these reported incidents. Despite a drop in the number of incidents involving firearms in the last 3 years, the general trend appears to show a rise in their numbers (Fig. 1). A variety of firearm types were used in reported incidents and these are summarized in Fig. 2 (1). Despite firearm offenses accounting for only 0.2% of the total crime volume in England and Wales (2006/07) (1), the gravity of their nature means that they must not be overlooked and it must be seen as paramount that forensic evidence involved in such cases is as reliable and accurate as practicable.

Mejia (2) raised a number of questions about the methods currently used for the analysis of gunshot residues (GSR): Which methods of analysis are most effective? How can false negative or positive results be best minimized? Is it actually possible to state with certainty that a person has discharged a firearm?

Ronald Singer, former president of the American Academy of Forensic Sciences thinks not, stating "None of what we do can establish if anybody discharged a firearm" (2).

Aleksandar (3) comments "In my 10 years of very intense practice… I still haven't met the method on the basis of which with absolute reliability, as a court expert working on identification activities of eventual shooters, I could confirm that the suspect 100% fired from the firearm on that occasion."

High profile cases in the U.K. such as the Jill Dando murder trial (4) have brought the evidential value of GSR analysis further into question. Therefore, a review of techniques used for the analysis of GSR and their effectiveness is valuable, relevant and timely. This review covers the formation and distribution of GSR, the collection, preparation, and analysis of GSR samples, and discusses factors that may affect the interpretation of any given GSR sample.

What is Gunshot Residue?

Gunshot residue, which may also be known as cartridge discharge residue (CDR) or firearms discharge residue are particles produced during the discharge of a firearm. When a cartridge/round is fired in a firearm, combustion products from both the primer and the propellant will be released at the same time (5).

Gunshot residues are composed of unburned and partially burnt propellant powder, particles from the ammunition primer, smoke, grease, lubricants, and metals from the cartridge as well as the weapon itself (6,7). Organic compounds mainly originate from propellant and firearm lubricants, taking the form of unburned and partially burned gunpowder particles, some products of their

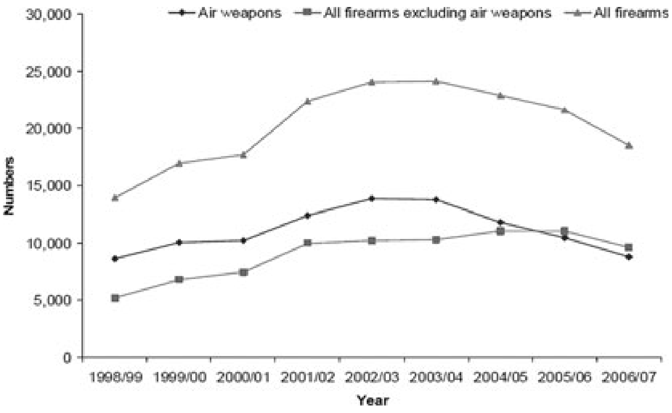

FIG. 1—*Government statistics for the number of reported incidences involving firearms in England and Wales 2006/2007 (1).*

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Received 19 Jan. 2009; and in revised form 13 May 2009; accepted 31 May 2009.

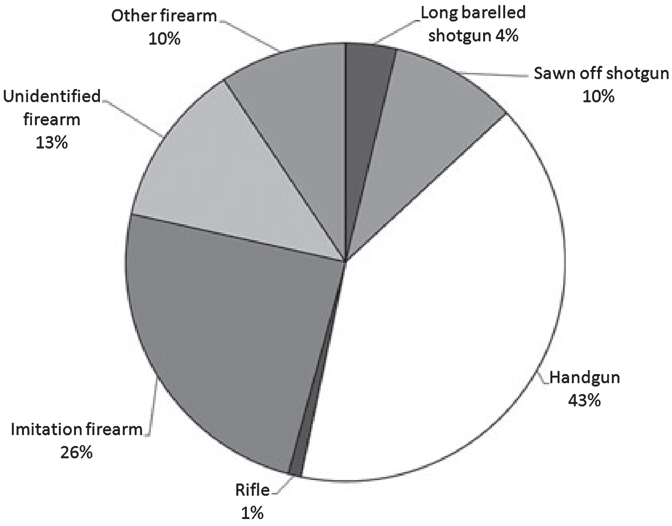

FIG. 2—*Government statistics of the types of firearms used in reported incidents in England and Wales 2006/2007 (1).*

transformation, and hydrocarbons. Inorganic residues such as nitrates, nitrites, and metallic particles originate from the primer and propellant as well as the cartridge case, the projectile jacket or its core and from the weapon barrel itself (8). These combustion materials from the primer, propellant, and other sources escape from weapon openings and vaporized materials solidify into particulates. These particulates are usually of sizes ranging from 0.5 μm to 10 μm (diameter) (5), although sizes of up to 100 μm have been reported (9).

Organic Compounds Present in GSR

Organic compounds are predominantly found in the propellant powder and the primer mixture, but can also originate from every part of the ammunition used (10). Table 1 contains a list of organic compounds that may contribute to the composition of organic GSR (OGSR).

The original propellant type used in firearms was black powder. The first recorded European recipe for black powder was produced by Roger Bacon in 1250 (5). Black powder is typically composed of 75% potassium nitrate (saltpeter), 15% sulfur, and 10% charcoal (fuel) (10,11). Today black powder is hardly ever used as a firearm propellant; however, it may still be encountered, usually linked to persons involved in military re-enactments.

Smokeless powders have long since replaced black powder as the main propellant used in firearms. Single base powders are based around nitrocellulose (NC) as an explosive, while double base powders contain both NC and nitroglycerine (NG), with NG increasing the energy potential of a powder. In triple base powders, a portion of NC and NG is replaced by nitroguanidine (10).

All smokeless powders, in addition to explosive ingredients, contain a number of additives, including stabilizers, plasticizers, flash inhibitors, coolants, moderants, surface lubricants, and anti-wear additives. A particular propellant powder will contain one or more of these additives depending on its intended use (10,12–18).

Inorganic Compounds Present in GSR

Inorganic components predominantly derive from primer mixtures. The particular type of primer used in a cartridge will generate materials of interest because of variations in formulation compositions from manufacturer to manufacturer. The history of primer formulation development can be found elsewhere (5). The first example of a "modern" primer formulation was produced in 1921, containing lead styphnate, barium nitrate, and antimony trisulfate (5).

TABLE 1—*Organic compounds that may contribute to gunshot residue (10–14,21,90,93,94,117,127,142).*

Compound	Source of Compound
2,4,6-Trinitrotoluene (TNT)	Propellant powder/primer mix
2,4-Dinitrodiphenylamine (2,4-DPA)	Propellant powder
2,3-Dinitrotoluene (2,3-DNT)	Propellant powder
2,4-Dinitrotoluene (2,4-DNT)	Propellant powder
2,6-Dinitrotoluene (2,6-DNT)	Propellant powder
2-Nitrodiphenylamine (2-NDPA)	Propellant powder
4-Nitrodiphenylamine (4-NDPA)	Propellant powder
Akaridte II (AKII)	Propellant powder
Butyl phthalate	Propellant powder
Butylcentralite (*N,N*-Dibutylcarbanilide)	Propellant powder
Camphor	Propellant powder
Carbanilide	Propellant powder
Carbazole	Propellant powder
Charcoal (major carbon)	Black powder
Cresol	Propellant powder
Dextrin	Primer mix
Diazodinitrophenol	Primer mix
Diazonitrophenol	Primer mix
Dibutyl phthalate	Propellant powder
Diethyl phthalate	Propellant powder
Dimethyl phthalate	Propellant powder
Dimethylsebacate	Propellant powder
Dinitrocresol	Propellant powder
Diphenylamine (DPA)	Propellant powder
Ethyl centralite (*N,N*-Diethylcarbanilide)	Propellant powder
Ethyl phthalate	Propellant powder
Ethylene glycol dinitrate	Propellant powder
Gum Arabic	Primer mix
Gum tragacanth	Primer mix
Karaya gum	Primer mix
Methyl cellulose	Propellant powder
Methyl centralite (*N,N*-Dimethylcarbanilide)	Propellant powder
Methyl phthalate	Propellant powder
Nitrocellulose (NC)	Propellant powder/primer mix
Nitroglycerine (NG)	Propellant powder/primer mix
Nitroguanidine	Propellant powder
Nitrotoluene	Propellant powder
N-nitrosodiphenylamine (N-NDPA)	Propellant powder
Pentaerythritol tetranitrate (PETN)	Propellant powder/primer mix
Picric acid	Propellant powder
RDX (Cyclonite)	Propellant powder
Resorcinol	Propellant powder
Rubber cement	Primer mix
Sodium Alginate	Primer mix
Starch	Propellant powder
Tetracene	Propellant powder/primer mix
Tetryl	Propellant powder/primer mix
Triacetin	Propellant powder

This list is not exhaustive. Some of the substances present may now be obsolete from production but are included as obsolete ammunition may still be in circulation.

The most recent major development in primer manufacture has been the introduction of numerous types of lead (Pb) and heavy metal-free primers. These primer types have been produced in response to increased concerns over health problems relating to airborne pollution and exposure to high levels of heavy metals, such as those found in "modern" primer mixtures (19). There is currently a large number of manufacturers' producing completely lead-free ammunition (20), while others produce cartridges with lead-free primers but not lead-free bullets. The compounds used in lead-free primers differ from manufacturer to manufacturer (19).

Further inorganic constituents may originate from the cartridge case, primer cup, bullet (including jacket), and the barrel of the firearm (21). Table 2 contains a list of inorganic compounds that may contribute to the composition of inorganic GSR.

The Formation of Inorganic GSR Particles

Gunshot residue particles form during the discharge of a firearm. As the firing pin strikes the primer cap, the primer mixture is ignited, creating an environment of rapid temperature and pressure increases within the cartridge. This increase in temperature melts the primer mixture and within a few milliseconds the vaporization points of lead (Pb), barium (Ba), and antimony (Sb) are exceeded (Pb 1620/C, Ba 1140/C, Sb 1380/C). The effects of supersaturation cause vaporized particles to condense back onto the liquefied primer surface as droplets. There has been evidence to suggest that inorganic GSR particles of materials originating solely from the primer (primer GSR) are formed even before the propellant is ignited (22).

TABLE 2—*Inorganic compounds that may contribute to gunshot residue (5,11,12,21,60,116,117,127,143).*

Compound	Source of Compound
Aluminum	Primer/case
Aluminum sulfide	Primer mix
Antimony	Case/bullet
Antimony sulfide	Primer mix
Antimony sulfite	Primer mix
Antimony trisulfide	Primer mix
Arsenic	Case
Barium nitrate	Primer mix/propellant powder
Barium peroxide	Primer mix
Bismuth	Case
Boron	Primer mix
Brass	Case
Bronze	Bullet
Calcium carbonate	Propellant powder
Calcium silicide	Primer mix
Chromium	Bullet
Copper	Bullet jacket/primer cup/case
Copper thiocyanate	Primer mix
Cupro-nickel	Bullet jacket
Gold	Primer mix
Ground glass	Primer mix
Iron	Rust inside barrel, bullet
Lead	Bullet
Lead azide	Primer mix
Lead dioxide	Primer mix
Lead nitrate	Primer mix
Lead peroxide	Primer mix
Lead stifnate (styphnate)	Primer mix
Lead thiocyanate	Primer mix
Magnesium	Primer mix
Mercury	Primer mix
Mercury fulminate	Primer mix
Nickel	Case
Nitrate	Black powder
Phosphorus	Case
Potassium chlorate	Primer mix
Potassium nitrate	Propellant powder/primer mix
Prussian blue	Primer mix
Red brass	Bullet jacket
Silicon	Primer mix
Sodium nitrate	Primer mix
Sodium sulphate	Propellant powder
Steel	Bullet core/case
Strontium nitrate	Primer mix
Sulphur	Primer mix/black powder
Tin	Primer mix
Titanium	Primer mix/Lead free primer mix
Tungsten	Bullet
Yellow brass	Bullet jacket/case
Zinc	Primer cup
Zinc peroxide	Primer mix
Zirconium	Primer mix

This list is not exhaustive. Some of the substances present may now be obsolete from production but are included as obsolete ammunition may still be in circulation.

As the primer mix ignites the propellant powder, a second rapid increase in pressure and temperature occurs and the bullet is expelled from the firearm barrel. During this process, the particles involved are subjected to extreme temperature and pressure followed by rapid cooling. Particles form as liquid droplets, which subsequently solidify (22).

Wolten and Nesbitt (23) suggested that GSR particles formed from inorganic substances can be divided into two categories, "primer particles" and "bullet particles." Primer particles were shown to contain oxides, sulfides and salts in which the anion contained oxygen (oxysalts), such as barium meta-antimonate and basic lead sulfate (lanarkite). It was reported that primer ingredients are initially compounds and therefore cannot be expected to be reduced to elements in the oxidizing environment of the primer ignition. Elemental particles should therefore originate from bullet materials (23).

Basu (22) further divided inorganic GSR particles originating from the primer (with a lead styphnate, barium nitrate and antimony trisulfate mixture) into three categories (Table 3), each formed differently, depending on how they interact during firearm discharge. Categories II and III are larger sized particles that are thought to travel slower through the propellant ignition front and are therefore subjected to a second, greater increase in pressure and temperature. This causes these particles to pass through various metastable states because of boiling, fragmenting, or etching until a stable shape is again reached (22).

Burnett (24) suggested an alternative reason for the formation of irregular inorganic GSR particles (Basu's category II type), reporting the observation of particles still being molten upon impact onto target materials. Particles were observed to be splattered or flattened on target impact causing sometimes drastic modification of spherical form. This occurred especially at muzzle to target distances between 20 and 30 cm (although observed between 10–70 cm). Larger particles (>2 μm diameter) that came into contact with a target within 40 cm of the muzzle were often molten on impact (9 mm semi-automatic pistol). At distances >50 cm, it was shown that particles may shatter or adhere to the target surface (24).

GSR Collection Techniques

The areas from which GSR may be collected are wide ranging. Skin, vehicles (seats and seat backs, doors, windows, dashboards, headliners, interiors, and exteriors), the surroundings of an incident, doors, windows, body parts, clothing, and any surfaces in the immediate vicinity of a firearm discharge may all be sample targets (9). There are numerous techniques that can be used for GSR sample collection and selecting the most appropriate one is important in ensuring maximum collection efficiency.

Tape Lifts

Tape lifts are the most commonly used procedure for the collection of inorganic residues from skin surfaces (7). It has also been applied to sample collection from hair (25) and other mediums (26,27).

TABLE 3—*Inorganic primer residue particle types proposed by Basu (22).*

Particle Category	Mechanisms of Formation
I	Most commonly found type on the hands of a person who has previously discharged a firearm. Small spheroid particles that may have small nodules/bulges upon their surfaces. Nodules are usually of single elemental composition, which may originate from the primer or bullet and may be nonspecific (not Pb, Ba, or Sb). Believed nodules are captured by the main particle mass when a degree of cooling has occurred and the particle is solidifying. The main body of these particles contains a uniform and concurrent mixture of Pb, Ba, and Sb. Sizes range from 2 μm to 10 μm in diameter. Generally solid with no space in the core. Particles likely homogeneous due to thermal agitation and Brownian motion. Particles are formed prior to the ignition of the propellant mix and because of their smaller size travel through the propellant ignition detonation front much faster than larger particles leaving unaffected. Represented 68% of the total gunshot residue on a firer's hands
II	Twenty five percent of all particles found. Inhomogeneous and have a discontinuous distribution of Pb, Ba, and Sb. Heterogeneity produced by a final irregular distribution of lead, barium, and antimony which may reflect the way in which the particle grows. Particles often have air central cavities, which suggest they have been subjected to some form of disturbance during formation, which may explain elemental distribution
III	The least commonly found. They consist of a Pb crust, which surround a homogeneous core of Ba and Sb. It is believed that the Ba and Sb core is in the process of solidifying when it captures Pb vapours from burnt residues and the etched bullet (caused by barrel rifling as the bullet travels down the barrel). The Pb coating may also take on a peeled orange appearance in certain conditions

Wrobel (27) compared the efficiency of a number of different adhesives for the collection of inorganic GSR particles. Fifteen assorted adhesives were investigated, with a variety of criteria being used to assess the suitability of each adhesive. Eight double-sided tapes, three adhesive tabs, two adhesive liquids, a glue stick, and a carbon conductive cement were all tested. Out of all the adhesives tested Sellotape 404 double-sided tape was the medium chosen as the best performer.

Shaffer and Yi (26) compared tape/sticky lifts to swabs (isopropanol as solvent) for the collection of inorganic GSR for scanning electron microscope (SEM) analysis. Results showed that tape lifting was much more effective than swabbing. The average lifting efficiency for tape was 389 particles in total, with 126 being classified as "unique" (the classification of particles is discussed in a later section). The average for swabbing was 60 particles in total with only three particles classified as "unique."

DeGaetano (28) compared three techniques developed for the sampling and analysis of inorganic GSR by SEM with energy dispersive X-ray detection (EDX); tape lift (3 M brand adhesive), glue lift (29), and a centrifugal concentration technique (30). The number of particles of inorganic GSR found on the collection surface in 1 h was used as an indicator of the lift efficiency of each medium. Of the three techniques, tape lifts were reported to be the most effective, being cheap, having good collection efficiency, and performing well in the SEM. A shelf life of at least 6 weeks was reported and samples were shown to be able to withstand being in the high temperatures that may be expected in a crime scene vehicle, for at least 12 h without being effected. However, a number of problems were reported with tape lifts including the large surface area to be searched (dependent on tape size), the requirement to carbon coat samples prior to analysis (something which can now be avoided by using carbon-coated adhesives), and the collection of debris that may mask particles. The sample concentration technique tested, which theoretically should reduce the search area (by repeated centrifugal concentration through high density liquid), was shown to produce highly variable results and be less efficient than tape lifting.

Zeichner (31) also found concentration techniques problematic, concluding that the build-up of debris on filter surfaces was to such a degree that direct observation of a tape or glue lift was preferable.

Wallace and Keely (32) reported a successful concentration technique. Samples were suspended in nonpolar solvent as particles and subjected to a two-stage filtration process firstly removing extraneous materials and secondly retaining small particles including any inorganic GSR. Particles from sizes 0.5 to 2 μm were captured on the second filter. Recovery levels as high as 90% for Pb and 91% for barium were shown. However, as GSR particles may be as large as 100 μm in diameter (9), potentially helpful particles may be lost using this method. This must be seen as a drawback to this particular concentration technique.

Zeichner (33) reported a technique for extracting OGSR from tape stubs following SEM-EDX analysis. Extraction with an aqueous (0.1% w/v sodium azide)/ethanol mix (80/20) at 80°C for 15 min, followed by further extraction with methylene chloride and concentration by evaporation was shown to be the optimal procedure for gas chromatography with thermal energy analysis (GC–TEA) and ion mobility spectrometry (IMS). However, tests on single base powder showed variable results, with recovery levels for NG and DNT ranging from 30% to 90%.

Plasma ashing of tape samples has been reported to be successful for reducing organic material (skin cells, etc.) that may be present on the surface of a tape lift, making GSR particles easier to analyze (34). However, Varetto (35) argued that a combination of contamination by the electron beam of the SEM and oxygen plasma ashing was required to destroy the cells of the skin epidermis, leaving only thin filaments. Plasma ashing alone was reported to be ineffective.

Zeichner (36) reported that in fact skin debris posed little threat to impeding the analysis of inorganic GSR particles using SEM. Particles completely covered in skin cells that could not be detected by the secondary electron image were detected without problem by the backscatter electron image and EDX detector. Although morphological information could not be gained, Zeichner argued that the American Society for the Testing of Materials (ASTM) considered morphology a secondary criterion for GSR identification. This must though be seen as problematic, as particles from ulterior environmental sources have been shown to have elemental compositions that may be easily mistaken for GSR (37–39); in such situations it is the morphological information that is of key importance in correctly determining a particle's origin.

Collecting samples from clothing using tape lifts may also create problems with fibers and other debris. This detritus is likely to be nonconductive and may hold charge during SEM analysis. Carbon/gold coating of the sample may therefore be required which involves extra time and expense (40).

The collection of inorganic GSR particles from hair has been reported as important because of the longevity of particle retention when compared to hands (41). Tape lifts have been reported to be unsuitable for GSR collection from hair (41). However, Zeichner (25) reported that tape lifting was an acceptable method for use on hair (both curly and straight) and no significant difference between tape stubs and more complicated hair comb swab and solvent damp cloth were observed. Maximum collection efficiency was reported at 200–300 dabs (60–120 dabs for hands).

Vacuum Lifts

Vacuuming is used primarily for the collection of GSR from clothing. Speers et al. (42) reported the successful application of a vacuum collection technique for both organic and inorganic residues from items of clothing. Residues were collected from clothes following only one firearm discharge. More organic then inorganic residues were seen. Solid phase extraction (SPE) was used to clean up and concentrate samples in order to maximize the high performance liquid chromatography-pendent mercury drop electrode (HPLC–PMDE) and gas chromatography–mass spectrometry (GC–MS) systems being used. Recovery levels from the vacuum filters used were in the region of 57–78% depending on the compound of interest. Debris and garment fibers present on the filter were reported as a possible cause of reduced extraction efficiency.

Zeichner et al. (43) investigated the vacuum collection of OGSR with two different types of vacuum filter, fiber glass and Teflon. Four solvents (acetone, methylene chloride, ethyl acetate, and chloroform) were also tested for their ability to extract residue collected on the filters. No significant differences between the solvents in their extraction efficiency of the propellant components were found. Collection levels were highly variable, with between 30–100% yields for the same solvent. Methylene chloride was chosen because of the advantage of not dissolving/extracting NC (which is not volatile enough to be analyzed by GC-MS [44]). Teflon filters were shown to have greater collection efficiency. The use of tape lifts on clothing for the collection of inorganic GSR, followed by vacuum lifting to collect organic residues was shown to be an effective technique (43).

Andrasko and Pettersson (45) reported the use of a double filtration vacuum system. A prefilter with a pore size of 20 μm allowed the separation of residue particles from debris and fibers. Residues were collected on the second filter (0.8 μm), and concentrated onto a tape stub for SEM analysis. As with previously discussed concentration methods, the range of filters used in this study could potentially lead to the loss of inorganic GSR particles larger than 20 μm.

Mastruko (40) reported that vacuum lifts from clothing collect particles from the surface of the material but also the depth of the clothing. This was determined to be problematic as it increased the difficulty of interpreting sample analysis, as particles from other shoots (for example a hunter or sports shooter) may be present. In this respect, tape lifting is advantageous as it only lifts particles settled on the surface of a material. However, Andrasko and Petterson (45) reported that tape lifting was not very suitable for the collection of GSR from clothing as the loss of tape stickiness restricted the area that could be sampled and also fibers and other unwanted particles were transferred to the tape making analysis using SEM more difficult.

Swabbing

Twibell et al. (46) assessed the efficiency of eight solvents for the collection of NG from hands followed by GC analysis. Solvent efficiency was determined based on the amount of NG removed from the hands, the amount of interfering material removed from the hands, and the stability of NG within the solvent. Aqueous solvents showed the best recoveries, when thin layer chromatography was used for partial purification. However, NG was degraded by micro-organisms that grew in the solutions. Ethanol was determined to have performed best, with the most complete, stable, and consistent recovery.

Organic solvents are commonly used for the collection of explosive residues as such residues are readily dissolved in them. However, this causes the problem that many other compounds are also dissolved causing interference issues. Thompson (47) reported that this matrix of interfering compounds may be removed by using water as an extraction agent and adding an additional step, SPE. Water extraction followed by SPE was reported to be an effective process for treating organic explosive residues on cotton swabs for subsequent analysis by liquid chromatography (LC) or GC–MS and fast GC-TEA. When compared to a solvent extraction (acetone) and direct injection method, the water/SPE was shown to be just as effective at recovering organic explosives. Water/SPE also gave much greater selectivity in most cases.

Lloyd and King (48) reported a method by which swabs used to collect explosives and firearm residues were extracted and cleaned up by SPE in the containers issued for the return of samples to the laboratory. Recovery over the range 63–75% was reported. Inorganic GSR particulates also remained on the swab after organic compounds had been extracted and could be subsequently recovered for characterization by SEM by sonication in an organic solvent followed by membrane filtration of the extract. This method was reported to reduce the possible problems of sample loss because of transfer and minimize the chances of cross contamination.

Reardon and MacCrehan (49) compared supercritical fluid extraction (SFE) and ultrasonic solvent extractions (USE) in order to determine whether a reliable quantitative extraction technique for smokeless powders could be achieved. SFE was shown to be unsuitable for quantitative extraction of double base powders, although it has been shown as successful with regard to single base powders. Even after optimization of the extraction process, yields of below 90% with smokeless powder standards were recorded. NG was also shown to readily react with stabilizers under the conditions of SFE. 2-butanol:methanol (1:3) was reported as the most efficient solvent for USE. The most desirable extraction time was determined to be 15 min (handgun powders). For ball type rifle powders, 75 min extractions were recommended. No significant differences between temperature of 0°C and 50°C were reported and therefore 25°C was selected.

Glue Lifts

Glue lifts have been applied to the collection of GSR from hands (29,50). Basu and Ferriss (29) reported that glue lifting was a very usable technique for the collection of GSR from the surface of hands. When compared to tape lifts, glue lifts required less dabs on the skin surface and collected less debris because of the glue being less tacky than tape lifts. This increased the speed of SEM analysis. The glue also contained no elements of high atomic numbers that could potentially interfere with the GSR particle analysis with a SEM.

In contradiction, DeGaetano et al. (28) reported glue lifts to be an ineffective lifting medium. However, a different type of glue lifting planchet was used to that of Basu and Ferriss (29), which could potentially have led to the different results.

Nasal Collection

Schwartz et al. (51) reported the development of a technique for the collection of airborne inorganic GSR particles from human nasal mucus. Samples were collected on a 5 × 5 piece of substrate by normal nose blowing. SEM-EDX was used for sample analysis. Inorganic GSR particles were recorded at times >48-h post firing. This collection method must be seen as promising in terms of determining whether a person has been in the vicinity of a firearm discharge. However, it may not be of value in trying to determine whether a person actually discharged a firearm, as airborne GSR particles have been shown to take relatively long periods of time to settle (52).

Collection of GSR from Hair

Smoke plumes exiting the breach of a weapon during discharge frequently extend posterior to the face and head (53), with potentially useful GSR being deposited in the hair. A number of methods for the collection of GSR from hair have been reported including a swab and comb method and tape lifting (25,54).

MacCrehan et al. (53) used a fine toothed comb to collect residue samples from head hair. Nearly intact grains of incompletely burned propellant powder residues approaching mm diameters were recovered from handgun firings. Particles smaller than the gaps in the teeth of the comb were also recovered with this method. Difficulties with curly hair were reported because of the fine teeth of the comb. Twenty positive results from 23 tests were reported for human hair wig tests. Tests on shooters show NG positive results for all three different shooters tested. NG and ethyl centralite (EC) were found on the collections from rifles and revolvers. When compounds from unfired powders, exemplar residues (taken from the inside of a cartridge) and residues collected from the hair were compared, it was reported that there was an amount of variation between the unburned powder and hair combed residue but that the exemplar and the combed residue were in good agreement. It was concluded that although EC was detected in some of the residue samples there was not an effective enough extraction for it to be reliably detected using capillary electrophoresis (CE). It was also concluded that a more effective protocol for hair residue collection and analysis would be required to enable reliable detection of stabilizers such as EC that are present in OGSR.

GSR Analysis

Color/Spot Testing

Color/spot tests are most commonly used for the estimation of firing distances (9). However, they can also be used as a rapid test for the presence of GSR and the determination of bullet holes/entrance wounds (55). Such tests have been in use since 1933, when the dermal nitrate or paraffin test was introduced (7,10). Table 4 contains a list of some of the most common color/spot tests used for GSR detection.

The main problem that arises from using spot/color tests is their presumptive nature. However, despite this they are still used in case work in some countries (e.g., Brazil) for determining the presence of GSR (19).

Inorganic GSR Analysis

Neutron Activation Analysis—Neutron activation analysis (NAA) has been used as a bulk analysis method for various elements, which can be found in inorganic GSR. Ba and Sb are the two main elements identified using this method (56–59). However, Cu and Au (60), Ag, Ni, and Co (61) have also been analyzed. Capannesi and Sedda (61) used NAA to examine the trace elements present in lead core, jacketed bullet fragments. With this method, as many as 13 trace elements could be analyzed. As the elements present in bullets can become part of inorganic GSR, this NAA method could theoretically be used for GSR analysis. NAA has also been used for the determination of firing distances (62) and the determination of GSR on the hands of shooters (57,59,60,62,63).

The levels of compounds in samples are usually compared to hand blanks in order to determine if elevated levels of the compounds of interest are present. Ruch et al. (58) reported average levels on hands of nonfirearm firers (130 samples) of Ba and Sb to be 0.05–0.10 μg and 0.01–0.03 μg, respectively. A smaller study (14 samples) by Pillay et al. (60) reported Ba and Sb levels at 0.061 μg and 0.036 μg and Cu and Au levels as 1.085 μg and 0.020 μg. Kilty (63) determined the average Sb and Ba as 0.01 μg and 0.32 μg respectively, although daily fluctuations in concentration levels, especially with Ba were reported.

A number of problems have been reported with NAA; the technique cannot be applied to Pb analysis, samples must be irradiated, which requires a nuclear reactor as a neutron source, trained personnel are required to carry out the analysis procedure (7), and it is also an expensive and time consuming technique (9).

TABLE 4—*Color/spot tests that have been applied to GSR (7,9,10,55,113,114,127,143–148).*

Test Name	Compounds Detected	Additional Notes
Dermal nitrate/ paraffin test	Nitro groups	False positive results may be found by reaction with compounds present in tobacco, leguminous plants, fertilizers, pharmaceuticals, fingernail polish, urine, and as a result of striking a match, tires, and outer garments, solid rocket fuels, pesticides and dyes, pharmaceuticals, veterinary medicines, and the storage preservation of apples. Chlorates, dichromates, iodates, bromates, permanganates, and higher metal oxides may all cause reactions that may lead to false positives. Aleksandar tested 250 persons that had not handled firearms using the dermal-nitrate test. 117 of them produced positive results (46.8%)
Walker test/Griess test	Nitrites	Tests specific for nitrites but not for GSR
Modified Griess test	Nitrites	Test specific for nitrites but not for GSR
Harrison and Gillroy test	Pb, Ba, and Sb	Reported as much more successful than the dermal nitrate test as it produced much fewer numbers false positive results. Test specific for Pb, Ba, and Sb but not GSR
Alizarin red S (ARS)	Ca and other metal ions, including Pb and Ba present in primer residues	None specific and will stain many heavy metal ions including Fe, Ba, Sr, Be, Cd, La, Pb, and U
Sodium rhodizonate test	Pb	Test specific for Pb but not GSR
Marshal and Tewari test	Nitrites	Test specific for nitrites but not GSR
Lunge	NC	Test specific for NC but not GSR
Zincon reagent	Zn and Ti	Applied to Pb free ammunition. Will also react with copper. Test not specific to GSR

GSR, gunshot residue.

Atomic Absorption Spectrometry

Conventional atomic absorption spectrometry (AAS) has been reported sensitive enough for the detection of Pb in GSR samples, but inadequate for Ba and Sb. However, the introduction of electro thermal atomizers (carbon rod, tantalum, and graphite tube furnace) made flameless AAS suitable for the analysis of Ba and Sb in GSR samples (7). Samples are most commonly collected using cotton-tipped swabs and 5% nitric acid (64,65).

Flameless AAS has been reported as a successful technique for the analysis of inorganic GSR as it is both readily available and cost effective (66). It has an advantage over NAA, having excellent sensitivity for Ba and Sb and can be used to detect other elements of interest including Pb (67).

AAS has been applied to the determination of shooting distances, based on concentration patterns of Pb around bullet holes, (68) and the detection of GSR on collection swabs taken from hands by the determination of antimony and barium concentrations (67).

Ravreby (69) reported the use of flame and flameless AAS for the analysis of residues collected from bullet holes. Elements originating from the bullet, case, primer and firearms were analyzed (Cu, Zn, Pb, Sb, Ni, Fe, Ba, K, Sr [from the paint on the bullet tips of tracer rounds] and tin). The results provided a means for identifying the type of ammunition used.

Reed et al. (70) applied AAS to the analysis of GSR on the hands of 112 suicide cases. With threshold levels set at 0.2 μg for Sb and 0.3 μg for Ba positive results were found in 38% of cases. The most important factor in obtaining good results was reported to be the condition of the hands being sampled. Dry clean hand sampled at the scene or protected by paper bags during transport provided the most GSR consistent results. Time delays, weapon characteristic, and body location were all secondary considerations.

Cooper et al. (64) used flameless AAS for the analysis of Sb and Ba levels on the hands of persons in close proximity to firearm discharges, using porcine skin as a substitute. Threshold levels were set at 0.05 μg/mL for Sb and 0.50 μg/mL for Ba. In most cases, levels of Sb and Ba were only slightly elevated at a distance of 1 foot from discharge.

Koons (65) discussed a number of problems associated with AAS. Incomplete extraction of Sb from collection swabs was shown to be an issue; even with an optimized method only 60–70% was extracted, compared to a nearly complete extraction of Pb and Ba. Further problems arising from the extraction process included variable absorbance-time profiles for Sb and the enhancement of Ba absorbance caused by various matrix constituents. Heavily soiled swabs that potentially prevented effective extractions were also reported as problematic. Ashing methods have been proposed to overcome this problem; however, Koons also reported good recoveries from soiled swabs using a 10% nitric acid sample digestion method (65).

The worth of AAS in term of GSR analysis was further brought into question by Aleksandar (3), who criticized the method on the basis of the large number of false negative results it has been shown to produce (about 40%).

Inductively Coupled Plasma

Inductively coupled plasma (ICP) is a bulk analysis technique that is usually used to analyze trace amounts of Pb, Ba, and Sb in primer residues (9).

Koons (71) reported the use of ICP with atomic emissions spectroscopy (AES) for the analysis of Ba levels in swabs. The method was determined more successful than the previously used AAS because of the lack of interference from common swab constituents, a wide linear dynamic range, and good precision and accuracy (limits of detection for barium, defined as three times the baseline noise level were determined to be 0.002 μg/mL for AAS and 0.0008 μg/mL for ICP-AES. Relative standard deviations of multiple measurements of the same solution having a barium concentration of 0.05 μg/mL were reported as 5% to 10% for AAS and less than 1% with ICP-AES).

Koons (72) also reported the use of ICP-MS for the analysis of residues originating from primers. This method was chosen because of superior detection limits in comparison with ICP-AES and graphite furnace-AAS (GFAAS) (0.052, 0.020, and 0.14 ng/mL for Sb, Ba, and Pb, respectively) and faster analysis times than GFAAS. The use of MS allowed the detection of several isotopes for each of the elements of interest (Pb, Ba, Sb). ICP-MS was reported as potentially useful in several areas; the determination of levels of additional elements which may be associated with the handling of a firearm or ammunition component, or elements which may be present in specific ammunitions, such as strontium in some nontoxic primers, cobalt in Nyclad™ bullets, or copper, nickel, or zinc in jacketed bullets. ICP-MS also provided the possibility of some sourcing of primer derived Pb by isotope distribution (72).

Steffen et al. (73) reported the use of ICP-MS in conjunction with SEM-EDX. Following SEM analysis, GSR particles on the adhesive stub were dissolved using 2% v/v HNO_3 in nanopure water. Pb isotope ratios were determined for eight lead-based primer ammunitions. Ratio comparisons were shown to be promising and some of the lead-based primers could be distinguished from one another. However, such a method was not recommended for everyday case work, being both destructive and time consuming.

Zeichner (74) investigated lead isotope ratios in inorganic GSR using multiple-collector ICP-MS (MC-ICP-MS). Lead isotope levels were reported as potentially useful in specific types of scenarios, for example in a shoot out situation where several firearms and ammunition are discharged. It was reported to be possible to link a bullet hole to the firearm that discharged the bullet. However, problems were reported with "lead memory." Even after thorough cleaning of a firearm, some amounts of Pb from previous firings remained and contributed to the residues of following discharges. This memory was reported to lower the levels of association between residues collected from the firearm barrel and residues from the fired ammunition (bullet and case).

Sarkis (75) employed sector field, high-resolution-ICP-MS (SF-HR-ICP-MS) to determine the levels of Pb, Ba, and Sb in residue samples, allowing identification of these elements at concentrations as low as 1 ng/mL. Ternary graphs were used to better visualize the results and allow direct comparisons between the relative percentages of the three compounds of interest in different samples. Such graphs were reported to provide strong evidence concerning the origins of sample components on hands (GSR or environmental).

Scanning Electron Microscopy

Scanning electron microscope equipped with an X-ray detector (wavelength dispersion, or energy dispersion [EDX]) is the most commonly used method of analyzing inorganic GSR. Information on the principles of SEM and the development of this technique for inorganic GSR analysis are presented elsewhere and will therefore not be included here (7).

The advantage that SEM and X-ray detection has over bulk analysis techniques is the ability to analyze individual particles of inorganic GSR both morphologically and chemically. Bulk elemental techniques are problematic as the total sample levels of specific compounds (usually Pb, Ba, and Sb) must be above predetermined thresholds for a positive result to be concluded. Therefore, because of the small levels of GSR that are often encountered in case work, many cases involving such analysis techniques are determined inconclusive. A further problem with bulk analysis lies with the fact that the elements being analyzed are not exclusively found in GSR and therefore elevated levels of such compounds on the hand of a suspect must not be taken as conclusive evidence that they have discharged a firearm (76).

Aleksandar (3) comments that the ability of SEM-EDX to morphologically and chemically analyze samples makes it possible to determine that particles could have only originated from the discharge of a firearm and no other way. Despite this SEM-EDX cannot determine whether a person discharged a weapon on any given occasion.

Brozek-Mucha (8) used SEM-EDX to examine the differences between inorganic airborne and cartridge case residues. Both similarities and differences were observed in the two residue types. It was reported that the composition of a residue is influenced by two main factors:

- The direction of movement of the expanding products of burning propellant at the stage of internal ballistics.
- The kind of materials that were applied to construct the gun and ammunition.

Lebiedzik and Johnson (77) reported the use of specific morphological and elemental indicators within inorganic GSR particles to differentiate between the firearm used to discharge a round, the case and bullet material of the ammunition and ultimately differentiate one type of ammunition from another. Twenty-one elements, within 60 types of ammunition were assessed by individual particle analysis using SEM, with automated image analysis and X-ray micro analysis. In ideal conditions, it was reported possible to differentiate between residues produced by firearms with barrels made of stainless steel, carbon steel, and titanium. Ammunition caliber could be estimated and information on the materials used for the bullet and case of a cartridge could be determined.

Brozek-Mucha and Jankowicz (78) compared the residues collected from the hands of six different shooters using six different lead-based ammunition types. Purely visual inspections of the results allowed differentiation between three ammunition types. Statistical comparison approaches to the results were also evaluated. The Wilcoxon rank sum method was shown to be unsuitable for such an application. T-Kendall rank correlation coefficients and the R Spearman methods proved suitable for the evaluation of mutual relationships among frequencies of occurrence of certain chemical classes of primer residue. One ammunition type could be distinguished from the others and two other ammunition types could be differentiated from one another. It was concluded that further research would be required in order to determine the most suitable statistical analysis method for such applications.

Steffen et al. (73) reported the use of chemometric classification of inorganic GSR. Residues from eight lead-based and seven lead-free primer ammunitions were analyzed. Regularized discriminant analysis presented the ability to enter unknown samples into a distribution model consisting of various classes. Differentiation of lead-based primers was achieved and successful classification rates varied from 51–86%, with a misclassification risk of 9%. Problems in classification occurred because of the very similar qualitative compositions of lead-based primers, which were inorganically consistent. Therefore, only the semi-qualitative information gained from the EDX could be used for classification purposes. Lead-free primers proved much easier to classify as both qualitative and quantitative differences could be used for classification. The risk of misclassification was determined to be as low as 2.4%, with particles being correctly assigned 90–100% of the time.

Miyauchi et al. (79) used SEM-EDX to analyze smokeless powders from 20 different ammunition types. Cur, Si, K, S, Al, Ca, Fe, Cl, Ba, and Zn were all found. It was suggested that propellant powders may contribute to inorganic residues to a greater degree than was previously thought.

Collins et al. (80) reported the analysis of glass fragments in inorganic GSR in .22 caliber ammunitions. Particles containing glass fragments were found on the hands of shooters, with sizes varying from 2–100 μm. Particles were described as having morphologies indicative of the fusion of Pb and Ba compounds with glass of varying viscosities. Such particles were reported to provide a further area of interest which may allow discrimination between inorganic GSR and environment sources of GSR like particles. Only break linings were determined to be a potential source of similar particles.

One of the biggest drawbacks to SEM analysis was the tedious and time-consuming task of manual particle searching within samples. The introduction of automated GSR search programs has eliminated such a problem, reducing the total search time for a sample, freeing the SEM operator to do other tasks and reducing the number of potential human error sources (81).

Germani (82) investigated the effects of changing SEM-EDX variables on search results, in an attempt to compile a set of standard settings for the analysis of inorganic GSR particles. It was reported that no one set of standard operating procedures could be determined, as the required search parameters between different samples are likely to be variable. For example, a sample collected from a suspected shooter a number of hours after firearm discharge is likely to contain smaller sized particles than a sample collected immediately and a search program would need to be tailored accordingly.

Zeichner and Levin (54) reported the success rates in case work of inorganic GSR analysis using SEM-EDX on samples from hands, hair, and clothing over a period of 6 years. The overall success rate for finding GSR was reported at about 10%, which was determined to increase the probative value of positive results, as it diminished the danger of accidental sample contamination leading to positives. In 39% of positive cases, only one particle of inorganic GSR was discovered.

The analysis of the inorganic GSR can provide a great deal of information. However, in some cases where inorganic residues are not present in a sample, or are only present in relatively low levels, OGSR components may be used. Even when inorganic residues are present at large enough levels to be useful, the analysis of OGSR may provide complementary and additional information that may strengthen the probative value of a sample (10) and potentially provide additional means of differentiating between GSR and environmentally sourced residues.

Organic Analysis Methods

The analysis of OGSR up until the year 1997 has been reviewed in detail previously (10). Therefore work up until 1997 will be briefly covered, while more attention will be directed toward work published after this point. Techniques covered previously where no additional noteworthy articles were found during the compilation of this review are not included.

Gas Chromatography

Gas chromatography coupled with a number of different detectors has been applied to OGSR analysis, including flame ionization, TEA, electron capture, and MS. TEA has been most commonly used for OGSR analysis.

Andrasko et al. (83) reported the use of GC–TEA and GC–MS for the detection of various constituents and degradation products from smokeless powders in the barrels of firearms after test shootings. GC–TEA was employed for the analysis of samples and GC–MS was used to identify some of the compounds of interest.

Zeichner (43) assessed the value of GC–TEA and GC–MS alongside IMS for the analysis of OGSR. GC–TEA showed a good level of sensitivity for the compounds of interest. Limits of detection were: 0.2 ng for NG, 0.05 ng for 2,4 DNT and 0.05 ng for 2,6 DNT. The considerably lower sensitivity of GC–TEA for NG compared to DNT was reported as being because of thermal decomposition of the NG in the GC column, creating a nonlinearity of the NG peak height as a function of concentration, in particular when approaching the limit of detection. An increase in column length (15–30 m) yielded two peaks for NG, a second smaller peak being determined as 1,2-GDN, a thermal decomposition product of NG. This decomposition was reported as a drawback to sensitivity. However, the presence of two peaks increased the probability of identifying NG using GC–TEA. Two GC–MS systems were used to analyze standard mixtures, details of which can be found elsewhere (43). Neither of these systems was optimized for explosive analysis; however, limits of detection for the compounds of interest were reported at several nanograms. Not one case work example which was found positive for NG by GC–TEA could be confirmed by GC–MS. It was therefore reported that GC–MS was not sensitive enough for the majority of real life cases. IMS was shown as a good complementary technique for GC–TEA for the detection OGSR.

Kirkbride et al. (84) reported the use of GC–MS for the detection of explosive compounds, many of which may be found in firearm ammunition. As reported by Zeichner (43) the limits of detection for many of the compounds were several nanograms (NG 10 ng, TNT 10 ng, RDX 10 ng, Pentaerythritol tetranitrate [PETN] 0.5 ng).

A potentially useful method for the combined analysis of inorganic and organic GSR by SEM-EDX, and GC–TEA and IMS has been reported (33). Samples were collected onto aluminum stubs and inorganic analysis carried out by SEM-EDX. Samples were then extracted from the stub with a water/ethanol mixture (80/20) at 80°C with sonication for 15 min, followed by further extraction with methylene chloride and concentrated by evaporation for analysis of OGSR by GC–TEA and IMS (33).

Gas chromatography techniques suffer from the inability to analyze NC, as it is not sufficiently volatile. Its introduction (as a major component) to a GC column may also accelerate the deterioration of the column's performance (43). Nitrate esters which are frequently found in GSR are also incompatible with the usual condition of GC systems because of their thermal instability. Such compounds will decompose on improperly prepared columns. PETN has been reported to suffer particularly from this (10). It has also been reported that GC is unsuitable for the analysis of stabilizers such as N-nitrosodiphenyleamine because the temperatures involved in such systems may cause denitrosation to diphenylamine (DPA) (10,16).

High Performance Liquid Chromatography

HPLC has been applied to OGSR analysis with various types of detector. NG, 2,4-DNT, and DPA have been analyzed with electrochemical detection (85). Lloyd (86) applied amperometric detection at a mercury drop electrode, and coulometric detection at porous carbon electrodes to the analysis of NG and DPA and size exclusion chromatography/PMDE for NC.

Speers et al. (42) reported the use of HPLC–PMDE and GC–MS in the analysis of organic propellant powder residues combined with SEM-EDX for the analysis of inorganic residues. HPLC–PMDE was used to detect NG and 2,4-DNT (GC–MS for DPA, EC,MC). The analysis of residues for organic components was shown to yield more positive results than inorganic analysis. The combined analysis of both kinds of residue was reported to produce the most useful/powerful results. HPLC–PMDE and GC–TEA have also been used in conjunction with one another (87).

Laza et al. (14) reported the use of LC–MS/MS for the quantitative analysis of common propellant powder stabilizers in OGSR. Residues were collected from the hands of shooters with cotton swabs (ethanol, water 75/25% v/v). An SPE technique was used for the concentration and purification of the samples. DPA, N-nitrosodiphenylamine (N-NDPA), 4-nitrodiphenylemaine (4-NDPA), 2-nitrodiphenylemaine (2-NDPA), Akardite II (AKII), Methylcentralite (MC), and EC were all resolved from standard mixtures using multiple reaction monitoring, allowing the presence of precursor ions in the samples to be determined and therefore the identification of the corresponding target compounds. The limits of detection were reported to be 0.29, 0.27, 0.34, and 0.21 nmol/L for DPA, N-NO-DPA, 4-NO2- DPA, and 2-NO2-DPA, respectively. EC as well as MC had a limit of detection of 0.07 nmol/L and a limit of detection of 1.3 nmol/L was determined for AK II. Converted into the equivalent amount of target compounds injected onto the column, the limits of detection were of 5, 6, 20, 27, 32, 34, and 115 μg injected onto the column for EC, MC, 2-NDPA, N-NDPA, 4-NDPA, DPA, and AK II, respectively. The method was determined to be very sensitive for the centralites (EC and MC) and poor AKII results were linked to problems with recovery levels during SPE. The analysis of samples collected from the hands of shooters confirmed that the method was suitable for routine analysis of OGSR. However, it was reported that further investigation into the longevity of OGSR components on the hands of shooters was required before the true value of such a technique could be truly determined.

Xu et al. (88) developed a combination of three HPLC–atomic pressure ionization (API)–MS systems for the analysis of 21 nitroaromatics, nitramines, and nitric esters, some of which may be found in firearm ammunition. Limits of detection for most compounds were reported to be between 0.012 and 1.2 ng. The method was also determined to be superior to a previously developed HPLC-thermospray ionization–MS, allowing a greater screening range and an increase in selectivity by a factor of ten. The HPLC–API–MS method was reported as specific, stable, and reproducible.

Mathis and McCord (89) reported the application of a reverse-phase LC–electospray ionization–MS for the comparison of organic additives in several smokeless powders. The method was determined useful in the analysis of compositional variations in smokeless powders.

Cascio et al. (90) compared HPLC and micellar electrokinetic capillary chromatography (MEKC) for their ability to analyze OGSR. Results indicated that both reverse phase HPLC and MEKC with UV detectors were capable of resolving standard mixtures of organic components of smokeless powders. Statistical analysis using the Spearman's rank correlation test showed the separate patterns from the two systems were highly correlated. Because of the broader range of analytes detected, better suitability for diode array detection, and lower operation costs MEKC, diode array UV detection looked particularly interesting as a screening technique.

Capillary Electrophoresis

CE is an important analytical technique, which can provide rapid, high-resolution separations of complex mixtures. Although electrically neutral compounds such as those found in OGSR cannot be separated by conventional CE, micellar electrokinetic capillary electrophoresis (MECE) permits the separation of such substances (10).

Reardon et al. (91) reported the use of CE for the analysis of NG, DPA and N-NDPA and EC in seven reloading propellant powders (one single base and six double base). Both bulk samples and single particles were analyzed. Compositional variations between particles were shown to be significant in some cases. Because of potential blending in finished propellant powders, it was reported that individual particles may not be sufficient in representing the sample bulk. The ratio of propellant/total amount of stabilizer (p/s) was shown to be a more robust way of linking residues to powders. In five of six of the double base powders, the p/s ratio of ten particles taken from the bulk was in agreement with the p/s of the bulk. Forty-nine of 60 particles analyzed gave reliable comparisons to bulk samples. It was also reported that the combination of quantitative and qualitative information with details of particle size, shape, and color could help associate unknown powders or OGSR with a known sample.

MacCrehan et al. (92) also used the propellant to stabilizer ratio in order to associate handgun fired OGSR with unfired propellant powders. Of seven powders analyzed, four could be easily differentiated. However, when visual examinations of particle morphologies were combined with the results of the P/S ratios all seven of the powders could be reliably differentiated. It was reported that a much larger sample of ammunitions would however need to be evaluated before such observations could be considered as generally acceptable.

Northorp (93,94) assessed the application of MECE to case work. SEM and MECE were used together to provide information on both inorganic and organic substances present within propellant powders and residue samples. Samples were collected on adhesive stubs and analyzed using SEM before being extracted with methanol for MECE analysis. The limits of detection for 13 characteristic organic gunpowder components (2,3-DNT, 2,4-DNT, 2,6-DNT, 3,4-DNT, 2-NDPA, 4-NDPA, Dibutylphthalate, Diethylphthalate, DPA, EC, MC, NG, N-NDPA) ranged from 0.9–3.8 pg for standard solutions. One hundred commercial propellant powders were analyzed in order to create a reference library. It was concluded that the detection of characteristic organic gunpowder components was a strong indication of OGSR with little or no likelihood that they resulted from environmental exposure. MECE found detectable residues on all ammunition types examined except for .22 caliber. Levels of OGSR were also shown to vary between firings carried out under the same conditions, leading to the conclusion that residue deposition mechanisms and collection efficiency significantly affected the outcome of OGSR analysis. In case work both inorganic and organic compounds were identified on some samples collected from the hands of suspect shooters and the clothing of victims. MECE was concluded to be a potentially valuable tool in the examination of OGSR.

CE has also been applied to the analysis of inorganic GSR. Hopper and McCord (95) reported the use of capillary zone electrophoresis for the analysis of inorganic ion profiles from smokeless powders. Seven smokeless powders were analyzed in both unburned and burnt states. Results demonstrated that ionic profiles could be used for characterizing smokeless powders.

Romolo et al. (96) reported the worth of CE for the detection of nitrate and nitrite ions in GSR. The used method proved simpler, cheaper, and faster than the traditional approaches to GSR analysis based on AAS, AES, ICP-MS, or SEM. Hair and skin samples from a victim shot in the head were also successfully analyzed for the presence of nitrite and nitrate. This preliminary study indicated that CE offered a sound potential for forensic GSR investigation as a screening technique prior to more expensive and time-consuming analytical methods. It was also reported that CE could be useful in the detection of residues produced by lead-free ammunition, where the evidential value of analytical results obtained with SEM can be poor (96).

Morales and Vazquez (6) developed a CE method for the simultaneous detection of both inorganic and organic substances in GSR, with 11 organic and 10 inorganic compounds being analyzed. The method did suffer from poor detection limits for some compounds, including Ba and Sb. A preconcentration method did however allow OGSR to be detected. It was concluded that two separate runs for inorganic and organic residues might be a better option, or alternatively the analysis of inorganic compounds with CE and organic compound with another technique, for example GC.

Other Techniques That Have Been Applied to GSR Analysis

Tong et al. (97) reported the use of a tandem MS/MS method for the quantitative analysis of DPA and its nitrated derivatives in smokeless gunpowders. Detection limits for DPA, N-NDPA, and 4-NDPA were 1.0, 0.5, 2.5 ng/mL, respectively. The method was determined highly selective and sensitive.

Meng and Caddy (98) reported the use of a fluorescence method for the detection of EC in GSR. The limit of detection for EC in spiked swabs and standard solutions was 5 ng and 1 ng, respectively. Three of six test firings were determined to contain EC. One of these swabs was collected 180 min following firearm discharge.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF–SIMS) has been applied to both organic and inorganic GSR analysis. Cumbaros et al. (99) reported TOF–SIMS analysis as a useful method of detecting inorganic residues. The technique was determined to have a number of advantages over SEM–EDX including lower detection limits, the elimination of signal overlaps, the ability to analyze both organic and inorganic compounds, near surface depth profiling allowing elemental distribution to be monitored as a function of depth and elemental and compound mapping from raw data. However, it was reported that because of a lack of high-resolution imaging capabilities, such as those provided by SEM back scatter electron detection, SEM-EDX should still be considered the method of choice for routine detection and counting of potential GSR particles.

Mahoney et al. (100) applied TOF–SIMS to the analysis of both organic (such as EC, dibutyl phthalate, and NC) and inorganic substances (such as potassium nitrate, potassium perchlorate, and sulfur) in smokeless and black powders (and black powder substitutes). However, because of the high-vacuum conditions inside the instrument the technique was reported to be unsuitable for more volatile components such as NG.

X-ray microfluorescence has been reported as an applicable method for the analysis of inorganic GSR (101–103). However, despite several advantages over SEM-EDX being reported (larger potential scanning area [20 × 20 cm] and direct visualization of target materials e.g., fabrics), the inability to analyze particles smaller than 10 μm led to the conclusion by Flynn (101) that X-ray microfluorescence could not replace SEM-EDX as the method of choice for inorganic residue analysis. Berendes (103) reported that although X-ray microfluorescence could not replace other commonly used techniques in GSR investigation it does offer a good supplement, especially with nontoxic primer residues.

Niewohner and Wenz (104) applied focused ion beam systems to GSR investigation. It was reported that scanning ion microscopy allowed particles to be cross sectioned, revealing interior morphologies that could be used for the identification of ammunition manufactures. Some particles were shown to be solid throughout, in which case such cross sectional information was not useful. However, where morphological details were present, different ammunition types produced characteristics that could be used to differentiate between them. However, the study only investigated four types of ammunition, and although each of these ammunitions did produce unique interior morphologies an investigation of a much larger number of ammunition types would be required to confirm the true worth of such analysis.

Pun and Gallusser (105) reported the worth of macroscopic observations of the morphological characteristics of propellant powders, investigating 181 cartridges of different calibers. The color and shape of the powder grains were shown to be an effective way of linking partially burnt powders from discharged rounds back to unburned samples. On these observations alone, a number of potential ammunitions matches for any residue sample could be determined. The correct source ammunition was always within those selected as possibilities for any given sample. However, a quantity of particles was required for accurate analysis of both color and shape. In real situations, factors such as weapon type, spatial distribution of GSR and problems with contamination arising from previously discharged cartridges were all reported as potential hindrances to the successful application of such observations.

Environmental Sources of GSR-Like Particles and Their Influence on GSR Classification and Analysis

Environmental Sources of Inorganic GSR-Like Particles

The possibility that there could be other sources of GSR-like particles is very important. If it were found that any other process or activity could produce particles with indistinguishable morphological and/or compositional characteristics to those of GSR then the weight of such particles as forensic evidence would be greatly reduced.

The analysis of GSR with bulk analysis techniques such as NAA or AAS does not take into account the morphology of individual particles being analyzed and therefore the possibility of false positive results is much greater. The three elements most commonly analyzed using these techniques are Pb, Ba, and Sb, which may be picked up from a number of environmental sources. Pb particles can be found in the emissions of leaded petrol, plumbing materials, battery plates, solder, glass, and paints. Sb is found in several alloys, often with Pb, and its oxides are used as a fire retardant in cotton and polyester blend fibers. Ba is found in paint, car grease, and barium sulfate from paper (7).

The application of SEM and X-ray detectors allows the morphology and elemental composition of individual particles to be determined. Wolten et al. (21) produced a list of particle types that were considered unique (characteristic) and consistent to inorganic GSR particles based on particle composition (Table 5), size, and morphology. In the majority of cases, 70–100% of particles analyzed were spheroid, with smooth or fuzzy surfaces, scaly or covered with smaller spheres. The remaining (rarely above 30% depending on ammunition) particles had irregular morphologies. The vast majority of particles had diameters less than 5 μm.

TABLE 5—*Classification of inorganic gunshot residue particles (21).*

Unique	Characteristic
Pb,Sb,Ba	Pb,Sb
Ba,Ca,Si with trace S	Pb,Ba
Sb,Ba	Pb
	Ba if S is absent or only trace levels

The aforementioned particles may also contain the following Si, Ca, Al, Cu, Fe, S, P (rare), Zn (only if Cu>Zn), Ni (rare and only with Cu and Zn), K Cl and Sn (in obsolete ammunition).

A number of studies have since been published that have investigated whether or not inorganic GSR particles of such compositions are indeed unique to firearm discharge.

Wolten et al. (106) carried out SEM-EDX analysis on samples taken from the hands of people working in areas that were considered to be possible sources of GSR-like particles. Areas with the most potential for producing GSR-like particles were described as critical occupations. These were made up of industrial and commercial operations involving metals or compounds of Pb, Ba, and Sb. Sectors that involved melting and/or vaporization of such elements were of particular interest. An overview of their results is presented in Table 6. The possibility of particles being created in some of the areas investigated that were of similar morphological and compositional structures to inorganic GSR was observed. It was reported that such particles would be classified as indicative of GSR using the "formal" classification system presented in the Aerospace report (21). Such particles were seen in residue samples collected from stud guns. It was concluded that individual particles should be considered within the context of all other particles within the sample in which they are found if the potential for misinterpretation was to be minimized. The occupation of the person from which a sample is taken was also considered as potentially relevant to the interpretation of samples (106). None of the samples analyzed contained particles of Pb, Ba and Sb or Ba and Sb, which were still considered to be unique to GSR (21). The results of this study showed the possibility that particles from other sources could be confused with GSR. This must be seen as an important finding, especially if a sample being analyzed has only a small number of particles present.

Wallace and McQuillan (107) carried out a more detailed study of particles produced by stud guns, analyzing (SEM-EDX) the primer and residue compositions of six types of stud gun ammunition. All of the particles found were between 1–12 μm in diameter and both spherical and irregular morphologies were observed. Morphologies were consistent with vaporizing or melting of the compounds involved. No crystalline structures were seen in any of the collected particles (which would indicate the particles would have been created in an environment not consistent with those involved in a firearm discharge [21]). It was concluded that the physical characteristics of the samples analyzed were indistinguishable from GSR. The results from Wallace and McQuillan (107), together with their past experience led to a conclusion that the original classification system for inorganic GSR particles (Table 5) should be modified to take into account particles generated from cartridge operated tools (Table 7). This classification system was stated to be only applicable to brass cased, Pb, Ba and Sb primed and Pb, Ba primed ammunition types. A simplified version of this system was adopted in the ASTM standard guide for inorganic GSR analysis by SEM/EDX (108,109).

Wallace and McQuillan (107) also suggested that the term GSR should be reworked in relation to the classification system, suggesting the term "primer residues" should be adopted as this would

TABLE 6—*Results of investigations into environmental sources of inorganic GSR-like particles (106).*

Vocation/Activity	Findings
Stud guns	Two particles consistent with GSR particles were found in samples from one brand of stud gun cartridge (Remington); these were small spheroid particles containing Ba, Pb, Zn, and Cu. It was only the abundance of larger non-GSR-like particles that led to sample being determined as not GSR. Thirteen particles consistent with GSR were found in samples collected from Omark brand cartridges. A typical composition of these particles was Cu and Zn (3:1) with Pb, Fe, and Ba (major) and Si, K, Cu, Ca, and Zn (minor). Again it was only the abundance of non-GSR-like particles that meant samples were not determined to be GSR
Cap guns	No GSR-like particles were found in these samples. Sb was seen but there was no Pb or Ba present. Both crystalline (Sb, S [major] Cl and P [minor]) and spheroid (Cl, Ca and P and Ca, P, Zn and K [major] Sb, Cl and S [minor]) morphologies seen
Blanks	No GSR particles found with two blank types Winchester 0.22 with black powder and Winchester Western 0.38 with smokeless powder
Lead smelting	Pb and Sb particles were found in samples, 50% were spheroid and 50% irregular (determined not consistent with GSR). None of the samples were determined to be GSR
Car brake mechanics	Two particles consistent with GSR (Pb and barium with other element associated with GSR). The first contained Fe, Cu, S, Si, Ba, and Pb. The second, Pb, Fe, Cu, Si, Ba, and Cl. The elemental proportions were however determined not to be that of GSR and the particles were dismissed
Pb acid battery assemblers	Particles consistent with GSR were found. These included the following 1. Pb and Sb. 2. Pb, Sb, Fe, Si, Zn. 3. Pb, Ca, Ba, Fe, and Zn. 4. Pb, Fe, and Ba. 5. Pb, Cu, Si, and Zn. 6. Pb, Ca, Ba, Fe, and Zn. However by taking into account all particles present, samples were discounted as GSR. The size distribution of particles was also deemed inconsistent with GSR samples
Car mechanics, exhaust fitters, and environmental lead.	Nothing relating to GSR particles was found

GSR, gunshot residue.

incorporate all percussion-activated charges based on Pb, Ba, Sb compounds, therefore including cartridge-based tools.

In addition to this proposed change, Wallace and McQuillan (107) also suggested a number of other considerations that should be taken into account when analyzing inorganic GSR. Spent cartridges, they argued may be used for chemical composition comparisons but not for morphological checks, as particles found inside cartridge cases will be different from those ejected from the firearm. The analysis of inorganic GSR by comparing samples collected from hands or other sources to cartridge cases/ammunition is a move away from a "formal" approach in which samples are interpreted following the rules of a formal general interpretation system, to a "case by case" or "specific" approach (an approach concluded as the most appropriate for GSR analysis wherever possible by Romolo and Margot [7]). Further more, individual particles within a sample should be considered in relation to all the others that are present. The fewer the number of particles that are present in a sample the more difficult it is to discriminate between tool and GSRs (107).

TABLE 7—*Inorganic gunshot residue classification system proposed by Wallace and McQuillan (107).*

Unique	Indicative*
Pb, Sb, Ba	Ba, Ca, Si[†]
Sb, Ba	Pb, Sb
	Pb, Ba
	Sb (with or without S)
	Ba[†]
	Pb
	Pb, Sb, and Ba absent[‡,§]

*Indicative particles listed in order of decreasing significance.

[†] S absent or acceptable as trace only when Ba present at a major level.

[‡] Any of the above may also include some or all of the following: Al, Ca, S, Si at major, minor or trace levels; Cl, Cu, Fe, K, Zn (only if Cu also present and Zn:Cu < 1) at minor or trace level; Mg, Na, P at trace levels only.

[§] Particles containing no Pb, Sb, or Ba may be considered indicative if they are composed entirely of the elements in [‡] above and are accompanied by other types of indicative particles.

Zeichner and Levin (110) agreed with Wallace and McQuillan (107) that GSR-like particles could be found in residues from cartridge-operated tools.

Garofano et al. (111) followed on and expanded upon the work of Wolten et al. (106), investigating the same vocations/activities that were flagged as potential sources of GSR-like particles. One hundred and seventy-five samples from the hands of persons undertaking these activities of interest were analyzed using SEM-EDX. Their results corroborated those of Wolten et al. (106) and confirmed that particles of Pb, Ba, and Sb were unique to inorganic GSR (although they were found in samples collected from stud gun operators). However, Garofano et al. (111) found particles of Sb and Ba in samples relating to car repair and maintenance activities. Even taking into account the morphology of these particles there were some that were hard to distinguish from genuine inorganic GSR Sb, Ba particles. It was therefore suggested that Ba, Sb particles (with iron present) no longer be classed as unique to inorganic GSR (21,106,107) and instead be seen as characteristic (unless found with Pb, Ba and Sb particles in which case they would still be seen as unique). Ba and Sb particles in the absence of Fe should be seen as borderline particles. Garofano et al. (111) also concluded that both the elemental and the morphological compositions of the particles being analyzed are important if a correct interpretation of a particle's source is to be achieved.

Mosher et al. (37) investigated the possibility of fireworks and pyrotechnic devices producing particles that resembled inorganic GSR. Residues from pyrotechnic devices only available to professional display organizers as well as those available to the general public were analyzed with SEM-EDX. Results showed that it was possible to find firework residue particles that could be mistaken for inorganic GSR. Samples collected from the hands of the professional firework display organizers contained some Sb and Ba particles that were morphologically (at least externally) similar to inorganic GSR particles (spheroid, noncrystalline, and between 0.5–5 μm in diameter). Such particles could be classified as unique to

GSR using the original guidelines (21). Other Sb and Ba particles, with irregular morphologies and much larger in size (up to 40 μm) were also present. These particles, although not considered typical of GSR could still be classified as such under the original formal classification system (21).

The analysis of the fireworks available to the general public showed that all of the unburned powders contained both Pb and Ba, with two also containing Sb. Residue samples indicated that the fireworks without antimony could produce Pb and Ba particles (seven were found), which had been reported in inorganic GSR produced from some .22 caliber rim fire primer units (10). Residues from one of the firework types that also contained antimony had particles that consisted of Pb, Ba, and Sb, an elemental composition classified as unique to GSR (21). Many of these particles were irregular and shaped between 10 and 35 μm in size and containing other elements. These other elements and the morphology of the particles would, it was determined, allow a trained GSR examiner to differentiate such particles as coming from some form of pyrotechnic device. However, a few particles contained Mg, which had been reported as being present in some inorganic GSR particles (11). Therefore, a potential for such particles to be wrongly identified as GSR has been shown to exist. There was also two Pb, Ba, and Sb particles found that did not contain Mg, which had the potential to be mistaken for GSR.

Torre et al. (38) carried out an investigation into car brake linings and their potential for producing inorganic GSR-like particles. It was argued that Sb, Ba particles should not be considered unique (as suggested by Wallace and McQuillan [107]) as they can be found readily in urban areas rich in metallic particulates such as those exposed to road traffic. Brake linings appeared to be an obvious source of GSR-like particles, as many contain lead sulfide, antimony sulfide, and barium sulfate in different combinations and while breaking disks can reach temperatures in excess of 600°C, reaching up to 1500°C in friction spots on the surface, similar temperature to those that occur during a firearm discharge (38). The results of tests on 40 different types of brake discs showed that it was possible to obtain Pb, Ba, and Sb particles from the wear of brake linings. Such particles were subdivided by Torre et al. into two groups, "clean" and "unclean." "Unclean" particles contained the three elements of interest, but with other elements or concentrations of elements that were inconsistent with inorganic GSR. "Clean" particles were described as those collected from car front brakes and new brake linings composed of Ba, Sb or Pb, Sb, Ba, which were of a similar size to inorganic GSR with elements and elemental concentrations that were consistent with inorganic GSR. Such particles as these were found mainly in new break linings, while those collected from car front breaks often had iron present within them at major levels. Results were in agreement with other recent publications in that Sb, Ba particles could not be considered "unique" to GSR (111); further more, the observation of "clean" Pb, Ba, Sb particles also suggested that such particles could not be considered "unique" to GSR. The only two compositions that were not found were: "clean" Ba, Sb particles with no sulfur, or sulfur at trace levels and "clean" Pb, Sb, Ba particles with Ba and/or Sb levels higher than lead. These particle types could still in theory be considered "unique"; however, it was suggested that the "unique" classification be dropped altogether in favor of the "more prudent" "consistent" categorization. It was reported that in order to discriminate between primer discharge residue and environmental particles, analysis of particle morphology must be re-evaluated (38,111). Particles identical to primer discharge residue in elemental composition may be found, but never of a typical shape. The only reliable particle would be of the "ideal" morphology, spherical or globular, with a surface either perfectly smooth, pitted with craters, or coated with rounded and smooth nodules, but never, even in part dusty or rough (38). Torre et al. (38) agreed with Wallace and McQuillan (107) suggesting that the term GSR should be dropped and replaced by either "primer discharge residue" or "residues of the detonation of a mixture of Pb, Ba, and Sb compounds." Finally, it was concluded that if ammunition that was recovered from a suspect/scene is not available for comparison with residue samples then any conclusions should be drawn with extreme caution (38).

Cardinetti et al. (39) used X-ray mapping techniques to analyze a number of nonfirearm sources of possible inorganic GSR-like particles. Break lining samples from 42 different makes and models of car were taken. Hand (palm and back) samples from car electricians, motor mechanics, and pyrotechnic and firework operators were also collected. A number of different genuine firearm cartridge residues were also analyzed to re-evaluate compositions and morphologies that may be encountered. Results confirmed that it was possible to find particles containing Pb, Sb and Ba and Sb, Ba in nonfirearm-related samples. Two particles containing Pb, Sb, Ba were found in samples collected from car brake linings, along with 214 Sb, Ba particles. Each of the samples collected from the hands of workers contained Sb, Ba particles. The analysis of residue from within cartridge cases showed that it was also possible to find irregular particles in GSR samples, which could in theory lead to false negative results for actual inorganic GSR. It was reported that X-ray mapping techniques, which can analyze the internal elemental structures of particles, could reduce the probability of mistakes in inorganic GSR analysis occurring, because true GSR particles and those from other environmental sources have very different internal element distributions. Inorganic GSR particles showed homogenous elemental distribution, whereas environmental particles, which had been created under much lower temperatures and pressures, showed a layered structure of individual elemental plaques (39).

The findings of Cardinetti et al. (39) are interesting; however, there are two areas which may be problematic. Firstly, tested residues were taken from inside cartridge cases, which although valid in some respects (chemical comparisons) may not accurately represent the particles that may leave a firearm during a discharge (107). Secondly, it is stated that by looking at the internal structures of particles, it is possible to differentiate GSR from environmental particles by analysis of internal elemental distributions. However, work carried out by Basu (22) showed that a number of different internal structures may be found among GSR particles, including ones in which elements are layered. Therefore, it may not be possible to accurately determine the source of a particle using this method.

Environmental Sources of Organic Compounds Found Within Organic GSR

If the analysis of the organic compounds present in GSR is to improve the evidential value of GSR analysis, it must be determined to what extent these compounds of interest could come from other sources.

Lloyd (112) listed a variety of environmental sources of the stabilizer compound DPA; the surface of apples, tires, and outer garments were all shown to be possible sources. Solid rocket fuels, pesticides, dyes, pharmaceuticals, and veterinary medicines are also formulations known to contain DPA (113).

Direct swabbing of the skins of apples, pears, bananas, and citrus fruit have been reported to produce chromatogram peaks at the same retention time (HPLC) as DPA (114). Grapefruit, oranges, and pears have also been reported to produce peaks at the same retention time as EC. Items of clothing, shoe polish, and many rubber products all produced interfering peaks (114). Leggett and Lott therefore commented that HPLC analysis of organic compounds is not an infallible method of determining the presence of OGSR in any given sample (114).

Inorganic GSR from Ammunitions with Lead Free/Nontoxic Primers

Another aspect of residue analysis that must be taken into account is ammunition types that do not have primers that contain Pb, Ba, and Sb compounds. A number of studies into GSR produced by lead-free/nontoxic ammunitions have been published and their findings are summarized in Table 8.

Gunaratnam (12) analyzed the inorganic residue particles formed by Sintox lead-free ammunition (cal .375 Magnum) with SEM-EDX. Characteristic particles were reported to contain Zn and Ti, with spheroid morphologies. Morphology was determined as the only way of truly discriminating such particles from environmental sources (irregular particles could not be used). However, a much smaller number of spheroid particles were found in residue samples than in those collected from cartridges with Pb, Sb, and Ba based primers. Ti and Zn are found in paint pigments but never as major elements and never with inorganic GSR characteristic spherical morphologies. However, scenarios involving burning paint and the particles formed have not been fully investigated (12).

Harris (115) analyzed GSR from CCI Blazer lead-free ammunition using SEM-EDX. The only significant metallic element found in the residue particles was Sr. Particles were mostly 0.5–10 μm (some up to 35 μm) and spherical, as would be expected from Pb,Ba,Sb primers. Traces of Ba were seen in some residues, even though not stated by the manufacturer as being included; however, natural deposits of Sr are often found in association with Ba. It was reported that Sr particles with spherical morphologies could result from exposure to flares and fireworks, limiting the evidential value of such particles.

Oommen and Pierce (116) analyzed a number of lead-free ammunition types with SEM-EDX, reporting different elemental compositions for each (Table 8). Similarities were observed between Federal Ballisticlean™ and sparkler pyrolysis residues, although it was determined that a trained analyst should not have problems differentiating them. K, Ca, Mg, and Na salt, present in some of the residues are soluble in water and therefore would be expected to be dissolved by human sweat. These elements would not be expected to persist on shooters' hands for as long as those elements that are not water soluble.

Martiny et al. (19) characterized the inorganic GSR elements present in Magtech Cleanrange® ammunition (SEM-EDX). Two varieties of 9 mm Luger, .40S&W, .380 Auto and .38 special types were analyzed. None of the residue particles analyzed could be considered unique to GSR using the ASTM formal classification system (109). Cleanrange® produced predominantly irregular-shaped particles, which would also be considered atypical using formal classification. The elements present in residues for Cleanrange® may also be found in association with automobile components, lubricants, and combustibles. For this reason, it was reported that elemental compositions of primer resides from Cleanrange® products cannot be used to confirm firearm discharge. The use of alternative analysis techniques, for example organic residue analysis, was reported to be a potential means of improving the evidential value of residues from such ammunitions.

Lead-free and nontoxic ammunitions are problematic when it comes to determining whether residues originated from firearm discharge or environment sources using a "formal approach" (7). Therefore, a "case by case" assessment procedure would be more appropriate for such cases as these (7,111,117). Additional research into possible environmental sources of particles like those produced by lead-free and nontoxic ammunitions is also required before the evidential value of such particles can be truly determined (116).

The Effects of Changing Ammunition Types on the Composition of GSR

The effects of changing ammunition types in any given firearm have been shown to produce inorganic particles of exceptional compositions. Such particles may differ greatly from the "classic" criteria for the identification of inorganic GSR (using a "formal" identification approach) (118). Even the thorough cleaning of a firearm has been shown not to remove all traces of previous residues and lead to a kind of memory effect within the firearm barrel (74,115). Therefore, a "case by case" basis for analysis should be adopted where possible if the potential misinterpretation of the evidence is to be minimized.

TABLE 8—*Elemental compositions of residues from various lead-free/nontoxic ammunitions (12,19,116,117).*

Ammunition	Primer Composition	Residue Particles
Sintox (0.375 Mag)	Diazodinitrophenol (DDNP), tetracene, zinc peroxide, titanium metal powder, nitrocellulose	Zn–Ti Zn–Pb Ti–Zn–Pb–Ba
CCI Blazer® Lead free (0.38 SPL+P)	Tetracene, DDNP, smokeless powder, strontium nitrate	Sr Sr–Ba
Winchester Winclean™ (9 mm and .45ACP)	Copper and zinc (primer cup), DDNP, potassium nitrate, boron, nitrocellulose (MSDS contents)	Cu–Zn K–Al–Si–Na Al–Na,Ca or Mg
Remington/UMC LeadLess™ (9 mm and 0.45ACP)	Copper and zinc (primer cup), DDNP, barium, tetracene (MSDS contents)	Cu–Zn Al–Si–K (trace Na) Al–Si–K (Na or Ca)
Federal Ballisticlean™ (9 mm and 0.45ACP)	Copper and zinc (primer cup), tetracene, barium nitrate, aluminum, nitrocellulose, nitroglycerine	Cu–Sn Al,Si,Ba,K (Na)
Speer lawman Cleanfire™(9 mm and 0.45ACP)	Copper, Zinc, nickel, DDNP, tetracene, strontium nitrate, nitrocellulose, nitroglycerine	Cu Cu-Zn Sr–Al/Si or Cl
Cleanrange 1st generation (9 mm Luger)	DDNP, tetracene, nitrocellulose, strontium nitrate, gum tragacanth (patent claim)	Sr (plume) Sr–Na–K–Fe (hand residue)
Cleanrange 2nd generation (9 mm Luger, 0.40S&W, 0.380 AUTO and 0.38SPL)	DDNP, tetracene, nitrocellulose, potassium nitrate, aluminum powder, ground glass, gum tragacanth (patent claim)	Al,Si,Ca (plume) Al–K–Si–Ca-Fe (S in 0.38 SPL) (hand residue)

Lebiedzik and Johnson (77) reported that in cases where a variety of ammunition types are fired by one firearm, descriptive indicators (21 elements) may be difficult to interpret because of the combined influence of ammunitions (77).

Torre (20) collected samples of lead-free and nontoxic GSR by swabbing the insides of spent cartridges; these were compared to samples collected from hands and targets. Variable pressure SEM-EDX was used for analysis. Results showed that previous shots of lead-based ammunition within a given firearm could influence the composition of residues produced from subsequently discharged lead-free rounds. Because of the poor evidential value of the results obtained from solely using this technique on lead-free and nontoxic GSR, it was recommended that further analysis techniques should be employed to gain as detailed a picture of composition of any given GSR sample as possible.

MacCrehan et al. (119) reported that compositional analysis of residues from firearms in which ammunition types had been changed showed only trace amounts of organic compounds (from propellant powder) from previous firings in the first shot and none in subsequent shots.

Distribution and Transfer of GSR Following a Firearm Discharge

Once a firearm has been discharged, it is essential to understand the distribution of GSR in relation to the shooter and their surroundings, not only in terms of sample collection but also minimization of contamination/secondary transfer within samples which could potentially lead to an inaccurate conclusion as to whether a subject has been involved in handling or discharging firearms. An understanding of these processes may also aid in the accurate interpretation of analysis results (7).

Schwoeble and Exline (9) investigated the evolution of residue plumes from a number of different weapon types (pistols, revolvers, rifles, and shotguns), using high-speed photography. A great amount of variation in plume evolution patterns between firearms was described (Table 9). Blow back or drift of residue plumes toward the chest, shoulder, face, and hair was observed. Cartridge ejection was shown to be a factor in the dispersion of GSR (contradictory to Wolten et al. [21]). Ejection plumes were then shown to spread out in all directions and therefore be subject to the influences of any air turbulence in the vicinity of discharge (9).

Schwoeble and Exline (9) also investigated inorganic GSR particle fall out. Rates were shown to vary widely, based upon the physical characteristics (size, shape, and particle density) of particles.

Carreras et al. (120) also used fast photography to examine the ejection of residues from the muzzle end of a 9 mm parabellum, a 9 mm short gun, a .38 revolver, and a 7.62 carbine rifle. Residues leaving a firearms muzzle were divided into three categories: Primary—residues leaving the barrel prior to the projectile, secondary—residues leaving the barrel at the same time as the projectile, and tertiary—residues leaving the barrel after the projectile. This process will affect the amount of residue available for collection dependent on muzzle to target distance. At close ranges, the gunpowder combustion residues reach the target and cause soiling. The characteristics and the amount of GSR on a target are dependent on the distance of the shot. Contact wound shots may yield little or no external GSR as the residues are forced into the bullet hole (120).

TABLE 9—*Characteristic residue distribution plume patterns by firearm type (9).*

Firearm	Residue Distribution
Smaller caliber semi-automatic weapons (high/forward cartridge ejection)	Sometimes plumes concentrations to the front of the fingers, but in most cases the plumes tend to follow in the direction of the ejected cartridge
Larger caliber revolvers	Widespread plumes
Larger caliber semi-automatic pistols	Smaller more compact plumes (compared to larger revolvers)
Shotguns and rifles	Consistent area of plume concentration in the crook of the support arm

Basu et al. (50) investigated the evolution of inorganic GSR from the rear of firearms, described as “trigger blast.” It was demonstrated that deposits of residue on the hands of shooters came almost exclusively from GSR emanating from the rear of the firearm (as suggested by Wolten et al. [21]) and not the muzzle (overlap of muzzle and trigger residues was observed in unclean firearms). This was shown to occur in both open and closed breach weapons. Residues on hands were deposited by blasting because of firearm discharge and not from the deposition of airborne particles. These results were in agreement with Schlesinger (121) who reported that wind velocity has no effect on the deposition of residue particles on the hands of a shooter. Therefore, for a nonfiring individual to have residue present on their hands, they would have to be in very close proximity to a weapon discharge. It was also hypothesized that deposits of GSR that have been found on forward facing portions of shooters’ bodies could also be deposited by the firearm discharge blast and not the fallout of airborne particulates (50).

Fojtasek et al. (122) investigated the distribution of GSR particles surrounding a pistol shooter. Experiments carried out in a closed environment showed that “unique” (Pb, Sn, Ba, Si, Ca and Pb, Sn, Sb, Ba [123]) inorganic GSR particles could be found at distances up to 10 m from the shooter. The maximum quantity of residue particles were found at 45° to the right in front of the shooter (several 1000 particles were found in this area); however, several hundred particles were also found in front of the shooter and to their right. In an open environment, distribution patterns were the same, but particle concentrations were 10 times lower in magnitude. This demonstrates a significant influence of climatic conditions on the amount of residue that might be available for collection. There were no particles found after a distance of 6 m (122). There was no indication of any observable differences in the distribution of particles with different sizes as a function of distance. The majority of the particles were less than 3 μm in diameter.

Gerard et al. (124) reported that GSR can travel much further than suggested by Fojtasek et al. (122), detecting inorganic GSR at distances up to 18 m. These particles were reported to have been carried such distances in association with the projectile. It was also demonstrated that inorganic GSR could spread outward laterally from the firearm to at least a distance of 3 m.

Work carried out by Bergman et al. (125) demonstrated that inorganic GSR particles can be consistently found on the bottom of discharged bullets, including those which have been severely deformed on impact or undergone other severe conditions. Many of these particles were shown to have a strong adhesion to the bullet, even after 20 min in an ultrasonic bath, only “loose” particles were removed. The high temperatures and pressures in the firearm on discharge appeared to cause particles to fuse to the base of the bullet. Such particles may prove very useful in determining which weapon a specific bullet was discharged from during an incident involving multiple shooters, especially if said bullet is greatly deformed, rendering visual comparisons to test firings difficult/impossible (125).

Fojtasek and Kmjec (52) carried out an investigation of inorganic GSR deposition rates. A 9-mm and a 7.65-mm pistol and a .38 special revolver were tested. Results showed that each weapon type had a different time period of maximum deposition. Time periods were dependent on the firearm and the caliber of the ammunition used. With a pistol discharge, the possibility of airborne contamination was reported to exist within ca. 8 min after discharge. With a revolver, the time could be as long as 10 min after discharge. The relationship between particle size and deposition time was also investigated. As would be expected (126) larger particles (6–10 μm) were deposited first, followed by those with smaller diameters (1–5 μm). Different firearms and ammunitions produced varying levels of "unique" particles in different size ranges (the 9 mm produced most "unique" particles in the 1–5 μm range, while the 7.65 were in the range of 6–10 μm).

Andrasko and Pettersson (45) investigated the possibilities of nonfiring persons, present in locations where a firearm discharge had occurred being contaminated with inorganic GSR. A summary of the results from the experiments can be seen in Table 10. Contamination was shown to be possible when a person walked through the particle cloud of a firearm discharge and not just as a consequence of staying close to a shooter. This conclusion is particularly important when considering the evidential value of any given GSR sample.

The papers mentioned earlier present evidence to suggest that there is a real possibility that contamination of persons in or entering a room/location where a firearm has been discharged could occur.

Shooter Activities Post Firearm Discharge and Effects on GSR Loss

It is of importance to understand the potential longevity of GSR particles on hands, other skin, clothing, and other materials from which samples may be collected. Not only is this information useful when determining whether a sample should be taken (in cases where the subject is suspected of discharging a firearm days, weeks or months prior to apprehension), but also in interpreting the results of any given sample analysis.

Gunshot residue deposits on a person are continuously lost as a result of normal activities and as a consequence of this it is very difficult to generalize a time period during which GSR may be retained (10).

Inorganic GSR retention on the hands of shooters has been shown to vary greatly following normal activities. Maximum recovery times ranging from 1–48 h have been reported for particles on shooters' hands (40,59,63,123,127–133). Rapid decreases in particle numbers have been shown to occur within 1–3 h post discharge (63,128,131,133). The rapid loss of inorganic GSR particles from hands is a great disadvantage in terms of collection, but on the other hand increases its value if found, as this indicates a very short time frame between firearm discharge and sample collection (40).

Specific everyday actions have been shown to radically affect the amount of inorganic GSR on shooters' hands. Kilty (63) investigated the effects of various activities on inorganic GSR levels on hands using bulk analysis, antimony, and barium. Washing hands with soap and water then drying on a paper towel effectively removed all traces of inorganic GSR. Rinsing hands for 3 sec under low-pressure water removed substantial amounts of residue, as did wiping hands on clothing (63), bringing levels close or equal to those levels found on the hands of nonshooters (133). Rubbing the hands together transferred residue from one hand to the other and placing hands in pockets removed residues (63); however, residues could be subsequently detected within the pocket (133).

Lloyd (86) reported that NG could be detected up to 7 h post firing on a shooter's hands, face, and throat, whereas it could be detected on clothes worn without restrictions for up to 5 h only. Douse (134) reported contradictory results showing a 0.5-h detection limit for NG on skin. Northrop (94) reported that recoverable organic GSRs may not persist on skin for more than 1 h.

The longevity of GSR on clothing has been reported to be generally much greater than on skin. Particles have been found days or even weeks after firearm discharge (40). Jane et al. (135) reported that clothing removed and stored post firing as opposed to clothing that was continually worn retained organic residues (NG, NC, and DPA) for a much longer period of time (residue found on the stored cloths the following day, the worn garments retained residue for up to 6 h). Residues deposited on a cotton sheet placed 1 m in front of a revolver that discharged five rounds remained detectable for up to 2 months, if the sheet was undisturbed. These experiments suggest that the loss of GSR is caused by physical activity rather than compound degradation (135). Further evidence for this theory was provided by Douse (134), who reported that inorganic GSR particles may be found on the hands of suicides for up to 48 h and potentially longer, a much greater time period than would normally be expected on a shooter's hands. Inorganic GSR particles have even been recovered from the garments of a badly decomposed man who was discovered after being outside for 2 months, further strengthening the case for physical activity being the major cause of particle loss from a subject.

Zeicher and Levin (54) reported the detection of inorganic GSR in samples collected from hair up to 24 h post discharge, if the hair was not washed. However, this time was seen to be greatly reduced in case work, where inorganic GSR was reported to persist on hands and hair for about the same period of time (hands 2.7 h and hair 3.3 h). However, other factors such as shootings occurring outside and wind affecting the deposition rate of GSR in hair were suggested as potential reasons for this (54).

Machine washing or brushing of clothing has been reported to decrease considerably the amount and the density of inorganic GSR remaining on clothing (136).

TABLE 10—*Contamination experiments and particles found (45).*

Experiment	Particles Found
Walking into a contaminated area. Subject walked in a shooting room in which no shooting had occurred that day. The floor was cleaned every second day	Two particles observed in lower part of the coat
Clothing hung in a shooting gallery: coat hung 2 m behind shooter who fired over 300 rounds (0.22)	Hundreds of gunshot residue and bullet particles observed
Clothing present in the same room as a shooter. Two persons (A 1 m to right and B 4 m behind) in a room with a shooter. Four 357 magnum shots fired. Subjects then walked across area in front of the shooter while leaving the room	A: 6 particles found B: 8 particles found

Studies into Contamination Relating to the Arrest and Transfer of Suspects

Gialamas et al. (137) investigated the levels of GSR that were present on the hands of firearm carrying U.S. police officers at the end of their shifts. Of the 43 officers that were tested, only 3 of them had any "unique" particles on their hands, about 7% of the total. None of the officers were found to have more than one unique particle present on their hands. There were no GSR particles found on 25 of the officers in the study (about 58%). Gialamas et al. (137) commented that although the potential for secondary transfer contamination was present, the low empirical numbers of GSR particles found on these nonshooting officers suggest the potential for this occurrence was relatively low. However, it must be taken into account that GSR particles are lost from the surface of the hands relatively rapidly (depending on activities undertaken); therefore, taking samples at the end of shift may not be the most representative method of assessing transfer potential.

Pettersson (138) showed that around 25% of samples collected from a selection of Swedish police vehicles contained six or more inorganic GSR particles. Samples collected from crime scene investigators also showed positive results in 25% of cases. One sample had as many as 16 inorganic GSR particles (none had handled a firearm for at least 12 h previous to being sampled).

Berk et al. (139) also looked at the possibility of secondary transfer within the police. Two hundred and one samples were collected from law enforcement vehicles and detention facilities in order to assess the probability of inorganic GSR present in these locations being transferred to those persons in detention. Both "unique" and "consistent" inorganic GSR particles were recorded. Of the 201 samples, 173 had no unique particles, while the other 23 contained 56 (two tactical vehicles, 34 table type surfaces, 20 restraining bars). A second collection of samples suggested that there was no accumulation of particles over time. A blank study of persons reputed to have had no primary contact with firearms also presented one case of a "unique" particle being found. Berk et al. (139) stated that although the possibility of unique GSR particles being transferred did exist the low number of unique particles observed suggested the potential for secondary transfer was relatively low.

Berk et al. (139), Pettersson (138), and Gialamas et al. (137) have shown that the potential for secondary GSR transfer does exist within the police. Berk et al. (139) and Gialamas et al. (137) both also commented that the potential for this occurring was relatively low. However, the possibility of even one particle of GSR being transferred to a person who is to be tested for GSR must be seen as important, as such a small quantity of GSR has been used in court as evidence of a person discharging a firearm (4). A survey in 1990 by DeGaetano et al. (140) showed that 41% of laboratories (two surveys of 200 US labs, 1st 51.0% response, 2nd 71.5% response) considered one "unique" particle to be conclusive evidence of GSR. Technically, the presence of one "unique" particle (SEM-EDX) does confirm the presence of GSR; however, it is the opinion of the expert as to the particle's significance that is of paramount importance (140). Another survey of 50 labs in 1996 by Singer et al. (141) showed only one lab considered finding one particle of GSR enough to indicate a person had discharged or been in the vicinity of the discharge of a firearm (one indicated two particles were sufficient and all other stated that their criteria were under review or that interpretation was dependent on the particle type found). Even though it would seem that there has been a general move away from one particle being seen as much of a significant indicator, the existence of a secondary transfer potential of one particle must still be seen as relevant to the interpretation of analysis results. However, the level of significance such a particle holds as a piece of evidence is in the hands of the expert witness and it is an expert's interpretation of any given sample that is of primary importance.

Summary

A review of various aspects of GSR has highlighted a number of areas worthy of consideration. The use of a "formal" classification system has been shown to be problematic. The introduction of numerous lead-free and nontoxic ammunitions as well as ammunitions that do not produce "characteristic" or "indicative" residues, combined with the potential for the misinterpretation of particles from environmental sources means that such an approach must be applied with great care. Particles produced by firearms through which numerous different ammunition types have been discharged may also produce particles that do not fit into a "formal" system.

The adoption of a "case by case" approach to GSR analysis must be seen as preferable. This is in agreement with Romolo et al. (7). The comparison of samples collected from a victim, suspect, or crime scene to firearms, bullets, or cartridge cases has been shown to be an effective approach within a "case by case" framework. The application of statistical evaluation and the construction and utilization of databases have also been shown to be promising approaches to the evaluation of results.

The analysis of both inorganic and organic residues has been shown as a promising method of gaining as much information about any given sample as possible. A combination of these techniques with microscopic or even macroscopic analysis of particle/grain morphologies would be even more favorable. Therefore, this must be seen as the most ideal approach to sample analysis. Having as much information as possible must be seen to increase the probability of the accurate interpretation of results and also increase the evidential value of any given sample.

With regard to the analysis of trace elements/compounds within both organic and inorganic residues, the development of increasingly sensitive and selective analytical techniques has increased the analyst's ability to gain a truer picture of the composition of such residues. With a large number of potential substances that may be present in ammunition, further research into the applicability of such analytical techniques to the analysis of GSR is required.

The interpretation of the results of any sample analysis by an expert witness is incredibly important. A further study into the guidelines which are applied to the interpretation of GSR by independent laboratories/experts would be incredibly valuable in terms of assessing the levels of consistency within the field.

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Journal of Chromatography A, 1217 (2010) 7183–7188

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

The evaluation of solid phase micro-extraction fibre types for the analysis of organic components in unburned propellant powders

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ARTICLE INFO

Article history:
Received 1 June 2010
Received in revised form 23 August 2010
Accepted 3 September 2010
Available online 15 September 2010

Keywords:
Solid phase micro-extraction (SPME)
Organic gun shot residue (OGSR)
Propellant powder
Forensic science
Firearms

ABSTRACT

This work describes the evaluation of various solid phase micro-extraction (SPME) fibre types for the detection of compounds originating from particles of unburned propellant powders. These compounds may also be found in association with organic gunshot residues (OGSR). Seven SPME fibres were assessed based on their ability to extract the compounds of interest (diphenylamine (DPA), 4-nitrodiphenylamine (4-NDPA), ethyl centralite (EC), nitroglycerin (NG) and dibutyl phthalate (DBP)) from four ammunition types across three calibres (9 mm, 5.56 mm and 7.62 mm). Extracts were analysed by gas chromatography/mass spectrometry (GC/MS). Results indicated that the 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) was the most suitable fibre type for the extraction of these compounds across the ammunition types tested. Optimal extraction time parameters were also assessed with a 35-min period determined to be suitable. A number of previously unreported considerations for extracting propellant powders and potentially OGSR related materials are discussed.

1. Introduction

The chemical analysis of gunshot residue can be divided into two areas; inorganic and organic. Inorganic analysis has been much more widely investigated and applied to case work. Scanning electron microscopy (SEM) combined with wavelength dispersion (WDX) or energy dispersion (EDX) X-ray analysis is the method of choice for such inorganic analyses. These techniques have the advantage of being able to provide both chemical and morphological information from a sample [1].

The analysis of the inorganic GSR by SEM can provide a great deal of information, however in recent years a number of papers have been published highlighting some potential problems with this methodology. Particles of chemical compositions and morphologies similar to or potentially indistinguishable from inorganic GSR particles have been reported, originating from fireworks [2], stud guns [3–5], and vehicle brake linings [6,7]. In some cases where inorganic residues are not present in a sample, or are only present in relatively low levels, organic gunshot residue (OGSR) components may potentially prove useful. Even when inorganic residues are present at larger levels, the analysis of OGSR may provide complementary additional information that may strengthen the probative value of a sample [8] and potentially provide an additional means of differentiating between GSR and environmentally sourced residues. However OGSR identification and characterisation methods are rarely used in laboratories at the present time [8].

Solid phase micro-extraction (SPME) has been commercially available since 1993 [9]. The technique is a variation of solid phase extraction (SPE), allowing the collection of trace and ultra-trace levels of analytes from liquid, gaseous or solid samples (via headspace) by concentrating them onto a fused-silica optical fibre coated with a layer of polymeric substances such as polydimethylsiloxane (PDMS). These coatings range in thickness between 5 and 100 μm. Coatings are attached to a supporting injection device that resembles a microsyringe. Extraction is an equilibrium process, affected by temperature, analyte, sample component concentration and the volume/thickness of the polymeric coating. A major advantage of SPME is that no solvents are required to carry out extractions; this is both economically and environmentally advantageous [10]. SPME has been applied to a number of areas within the forensic arena including fire arson investigation [11], explosives [12] and ballistic materials [13–19].

The SPME work carried out to date on ballistic materials has generally focussed on "time since discharge" back calculations based on the loss of compounds from spent cartridge cases or firearm barrels over time. These authors have applied a number of different SPME fibre types, chosen using a variety of selection criteria [18–20].

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doi:10.1016/j.chroma.2010.09.012

Furton et al. [12] investigated the suitability of 6 different SPME fibre types for the recovery of explosives and ignitable liquid residues from forensic specimens. It was determined that the 65 μm polydimethylsiloxane/divinylbenzene gave the highest overall recoveries. 65 μm polydimethylsiloxane/divinylbenzene fibres were also determined to be the most suitable for recovery of nitro-aromatics by Jonsson et al. [21], while Calderara et al. [22] reported the 65 μm polydimethylsiloxane/divinylbenzene fibres to be the most appropriate for the recovery of organic explosives (some of which may be found in ammunition). However to date a comprehensive study of a large number of SPME fibre types for their ability to recover compounds present in ammunition propellant powders, and therefore potentially in OGSR, has not been published. Seven SPME fibre types have been assessed in an attempt to determine a universally applicable fibre, by assessing which type best extracted compounds present in unburned propellant (smokeless) powders.

Propellant powders contain a variety of compounds, all of which are intended to fulfil specific requirements within the powder mixture, for example as stabilisers, plasticisers and deterrents. Stabilisers (diphenylamine and ethyl centralite) are intended to increase shelf life, by removal of nitric acid formed by decomposition of the nitrated energetic. Plasticisers (nitroglycerin ethyl centralite and dibutyl phthalate) reduce the hygroscopicity of powders and deterrents (ethyl centralite and dibutyl phthalate) are used to coat powder particles in order to reduce initial burn rates and lower burn temperatures [23]. The compounds included above are common within smokeless powders, lists of other compounds that have been reported to be contained in powders maybe found elsewhere [1].

2. Materials and methods

2.1. Solvents and standards

Diethyl phthalate, carbazol, monomethyl phthalate, triacetin, resorcinol, 3,4-dinitrotoluene, 3-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,3-dinitrotoluene, diphenylamine, N-nitrosodiphenylamine, 4-nitrodiphenylamine, 2-nitrodiphenylamine, nitroguanidine, *m*-cresol, *o*-cresol, *p*-cresol, dimethyl phthalate, dibutyl phthalate, 2-nitrotoluene, 4-nitrotoluene, dimethyl sebacate, 2,4-dinitrodiphenylamine, urethane, camphor, 2,3-dimethyl-2,3-dinitro butane, 2,4-dinitrotoluene were sourced from Sigma–Aldrich (St. Louis, MO, USA). Tetryl, RDX, nitroglycerin, and ethyl centralite were purchased from LGC Standards (Middlesex, UK). Working standard mixtures were prepared in analytical grade methanol purchased from Fisher Scientific (Fair Lawn, NJ).

2.2. Solid phase micro-extraction

Seven SPME fibre types; 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 7 μm polydimethylsiloxane (PDMS), 30 μm polydimethylsiloxane (PMDS), 100 μm polydimethylsiloxane (PDMS), 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and 85 μm polyacrylate (PA) were purchased from Supelco (Bellefonte, PA, USA). Fibres were conditioned prior to use as recommended by the manufacturer. Table 1 shows the characteristics of the fibres being assessed.

2.3. Propellant powders

Propellant powders from four ammunition types (9 mm Magtech, 5.56 mm Magtech, 7.62 mm Lapua and 7.62 mm Federal) were supplied by Nottinghamshire Police. Cartridges had their bullets pulled and the propellant powders were collected into 8 mL headspace vials for analysis.

2.4. Solvent extraction of unburned propellant powders

100 mg of unburned propellant powder from three cartridges from each of the ammunition types were extracted with 2 mL of methanol, samples were placed in an ultrasonic bath for 1 h. None of the powders were completely dissolved; the 9 mm Magtech ammunition left a fine powder on the bottom of the tube, while the other three ammunitions remained as small white pellets. Samples were then placed in a centrifuge for 15 min at 13,000 rpm, the supernatant was removed and filtered through a 0.22 μm PTFE filter before being injected into the GC/MS.

2.5. SPME extraction of 100 mg samples of unburned propellant powders

100 mg of each of the 4 ammunition types were extracted three times by each of the 7 fibre types. Extractions were carried out in an oven at 40 °C, a temperature high enough to volatilise the compounds of interest in to the headspace of the sample vial. Nitroglycerin is also known do begin to decompose at temperatures above 50 °C and this was not desired [26]. Extracts were carried out for 35 min and the fibres introduced to the injection port of the GC/MS immediately following extraction.

Following each injection fibres were conditioned for 20 min in the GC injection linear at 250 °C in order to ensure no carryover of the compounds of interest occurred. Blank fibre runs were carried out between every extraction in order to show that the fibres were clean before each powder extraction.

2.6. The extraction of single particles of unburned propellant powder

The fibre determined to be the most suitable was then used to extract single particles of unburned propellant powder from the 4 ammunition types. In order to determine the most suitable extraction time for single particles of unburned powder 1 particle from each ammunition type was extracted for time periods of 5, 15, 25, 35, 45 and 55 min. Peak areas for extracted compounds were recorded.

Table 1
SPME fibres and their characteristics and applications. NP: non-polar, P: polar and BP: bipolar [24,25].

Fibre coating type	Coating stability	Property	Polarity	Recommended analyte type
PDMS 100 μm	Non bonded	Absorbant	NP	Volatiles (MW 60–275)
PDMS 30 μm	Non bonded	Absorbant	NP	Non-polar volatiles (MW 80–500)
PDMS 7 μm	Bonded	Absorbant	NP	Non-polar high MW (MW 125–600)
Polyacrylate 85 μm	Crosslinked	Absorbant	P	Polar semi-volatiles (MW 80–300)
DVB/CAR/PDMS 50/30 μm	Highly crosslinked	*Adsorbant*	BP	Trace compound analysis (MW 40–275)
PDMS/DVB 65 μm	Highly crosslinked	*Adsorbant*	BP	Volatiles, amines, nitro-aromatics (50–300)
CAR/PDMS 85 μm	Highly crosslinked	*Adsorbant*	BP	Gases, low molecular weight (MW 30–225)

2.7. GC/MS equipment and conditions

The GC was an Agilent Technologies 6890N and the MS was an Agilent 5975MS. A J&W Scientific HP5-MS (30 m × 0.25 mm × 0.25 μm) was used. Run conditions were as follows; thermal desorption of the SPME fibres was carried out using an injector temperature of 250 °C with splitless injection. A SPME/direct inlet linear was purchased from Sigma–Aldrich in order to minimise band broadening. The initial oven temperature was 50 °C, rising to 200 °C by 6 °C/min, at 27 min the temperature was raised by 20 °C/min until 300 °C at 32 min. The total run time was 32 min. The carrier gas was Helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England).

3. Results and discussion

3.1. Analysis of standards

The developed method allowed the identification of 27 of the standard compounds (Fig. 1). *m*- and *p*-cresol were shown to co-elute but could be identified by use of mass spectral data. *N*-Nitrosodiphenylamine degraded in the injector port of the GC into DPA and was therefore seen in the DPA peak. This method was developed to allow the analysis of a much broader range of ammunitions than those used in this investigation. It should therefore be applicable to ammunitions containing any of the 27 compounds separated.

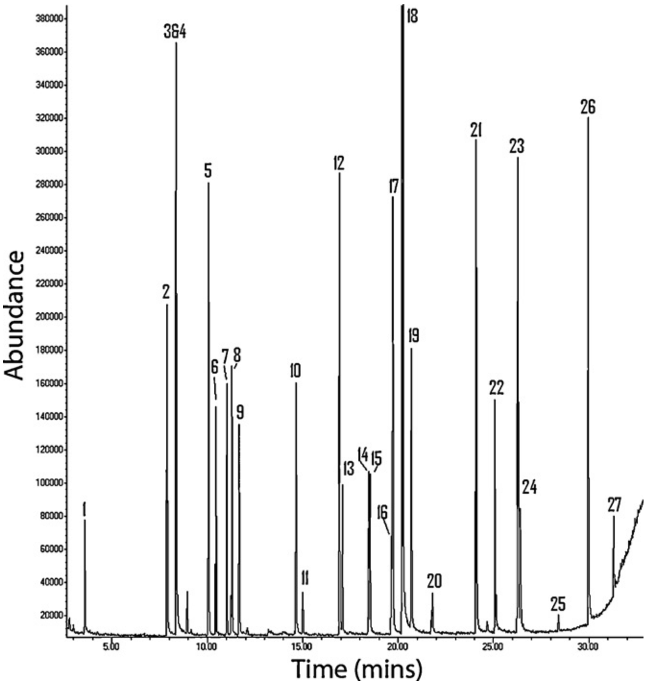

Fig. 1. Chromatogram of standard compound mixture: 1. urethane, 2. *o*-cresol, 3 and 4. *m*-cresol and *p*-cresol, 5. camphor, 6. 2-nitrotoluene, 7. 2,3-dimethyl-2,3-dinitrobutane, 8. 3-nitrotoluene, 9. 4-nitrotoluene, 10. triacetin, 11. nitroglycerin, 12. dimethyl sebacate, 13. 2,6-dinitrotoluene, 14. 2,3-dinitrotoluene, 15. 2,4-dinitrotoluene, 16. 3,4-dinitrotoluene, 17. diethylphthalate, 18. diphenylamine (including *n*-NDPA), 19. dimethylsebacate, 20. 2,4,6-trinitrotoluene, 21. carbazole, 22. ethyl centralite, 23. dibutylphthalate, 24. 2-nitrodiphenylamine, 25. tetryl, 26. 4-nitrodiphenylamine, 27. 2,4-dinitrodiphenylamine.

3.2. The comparison of solvent and SPME extractions of unburned propellant powder samples

Comparisons of solvent and SPME extracts from the same types of ammunition showed high levels of similarity. All of the compounds of interest extracted using solvents were extracted by the SPME fibre. Fig. 2 shows chromatograms from solvent and SPME extracts of 100 mg of unburned Magtech 5.56 mm calibre ammunition. In the SPME extraction of ammunitions containing DPA, 4-NDPA was also sometimes seen. The decomposition pathways of DPA in ammunition powders have been previously documented, with 4-NDPA being a degradation product of this process [27]. The fact that 4-NDPA was not seen in the solvent extractions is likely to be because there was no pre-concentration performed on the samples.

Due to the selective nature of SPME fibres relative abundances of extracted compounds varied from solvent to SPME methodologies, but as it was qualitative and not quantitative analysis that was the basis of this study these differences were determined to not be detrimental to the application of SPME extraction.

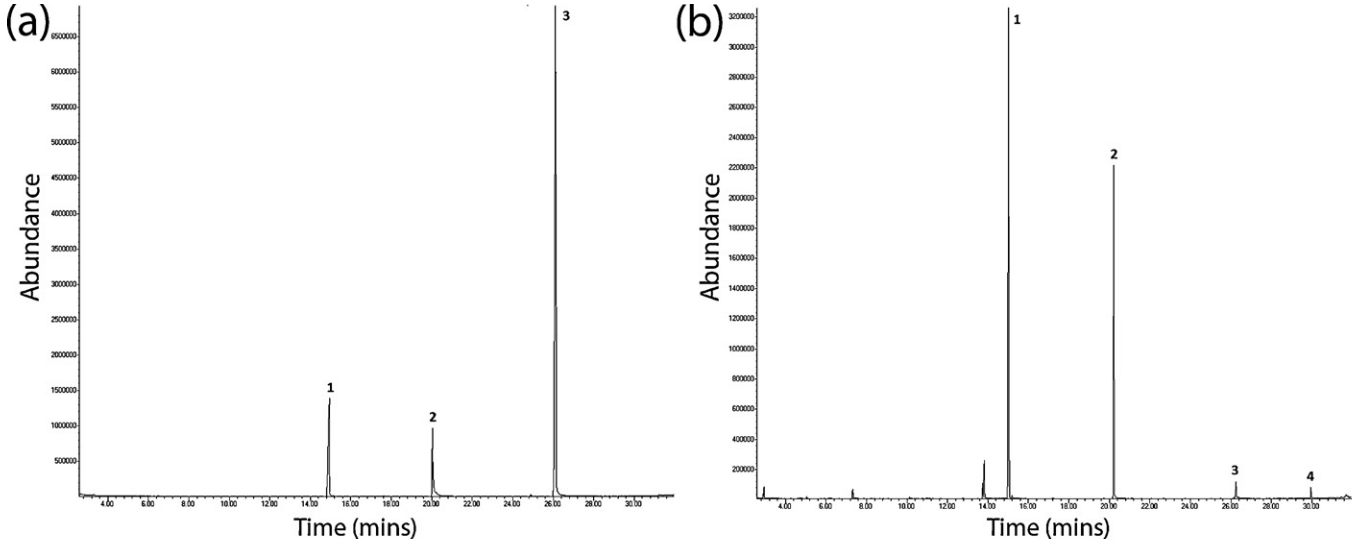

Fig. 2. Chromatograms from extractions of 100 mg samples of Magtech 5.56 mm propellant powders: (a) solvent extraction, (b) SPME extraction (1. nitroglycerin, 2. diphenylamine, 3. dibutyl phthalate, 4. 4-nitrodiphenylamine).

3.3. The use of unburned powder samples

The use of unburned propellant powders to determine the most suitable SPME fibre type for potentially extracting compounds associated with OGSR was chosen for a number of reasons. Although it might have been preferable to use OGSR samples, the loss of materials from such samples over time has been reported to occur [17,18]. Therefore, using such samples for the selection of the most suitable fibre type would most likely yield irreproducible results. This would obviously be bias to the fibres used to carry out the initial extractions on any sample, with the compounds present for extraction diminishing with time. The amount of variability of the compounds of interest between different samples was also not known and therefore carrying out extractions across different sample was determined to be unsuitable. Secondly the use of a blown down standard mixture was decided against due to the varying amounts of each compound which are found in real samples. The levels of NG in one ammunition are unlikely to be the same in another. Furton et al. [12] reported that lower molecular weight hydrocarbons reach optimal relative recoveries much earlier than molecules of higher molecular weights. It can therefore be extrapolated that with ammunitions having variable amounts of compounds of varying molecular weights the extraction profiles are likely to be different compared to homogenous standard mixtures of compounds all at the same concentration. It was also not known whether the structures (rod, ball, flake, etc.) of different propellant powders would also affect compound recoveries, something which could not be taken into account using blown down standards. It has been reported that when a firearm is discharged both unburned and partially burned powder granules are propelled from the barrel along with the projectile [8]. Therefore it is reasonable to say that using unburned powders can justified as these unburned and partially burned residue particles will have structures identical to or similar to the non fired unburned particles. Further Newton and Booker reported that there was no difference between the chemical compositions of partially burned powders, residues taken from the barrels of fired weapons and unburned propellant powders (40 powders tested) [28].

3.4. Comparison of SPME fibre types

Fig. 3(a)–(d) shows the mean peak areas of compounds extracted from the four unburned propellant powders used to determine the suitability of the 7 SPME fibre types tested. It was determined that overall the most suitable fibre type for the extract of the compounds present in the unburned powders was the 65 μm PDMS/DVB type. This was based on the comparisons of the average peak areas of the compounds recovered and the relative stand deviations calculated for each fibre type. The 65 μm PDMS/DVB fibre extracted the greatest amount of NG in all powder samples. For the other compounds extracted 65 μm PDMS/DVB provided either the highest extraction amount or extracted levels very close to the leading fibre type.

Average relative standard deviations were calculated for each fibre type by taking the means of all relative standard deviations from each of the compounds extracted by each fibre. This allowed the fibres that performed the best over the entire range of compounds to be determined. The 65 μm PDMS/DVB was shown to have the third lowest relative standard deviation (Table 2). However there was only a 3% difference between the lowest average relative standard deviation and that of 65 μm PDMS/DVB. Neither 85 μm CAR/PDMS or the 100 μm PDMS fibre types performed as well as the 65 μm PDMS/DVB in terms of extracting the compounds of interest. As it was qualitative rather than quantitative information that was more important in this study the relative standard deviation figures were determined to not be as significant as the extraction yield data. Therefore it was concluded that the most suitable fibre type was 65 μm PDMS/DVB.

Table 2
Average relative standard deviation figures for the 7 fibre SPME fibre types.

Fibre	Average relative standard deviation
7 μm PDMS	26.6
30 μm PDMS	28.9
50/30 μm DVB/CAR/PDMS	47.2
65 μm PDMS/DVB	20.9
85 μm carboxen/PDMS	17.9
85 μm PA	36.0
100 μm PDMS	18.1

It was shown that despite 65 μm PDMS/DVB being the most appropriate fibre overall it was not always the best performer for every compound in every propellant powder. The extraction of powders using SPME is a complex process and some unexpected occurrences were observed. For example the same compound found in different propellant powders was not always extracted in the highest abundances by the same fibre. For example DPA was recovered in three of the ammunitions, with 65 μm PDMS/DVB extracting the greatest amounts in the Magtech 5.56 mm ammunition, while 100 μm PDMS performed best with the Lapua 7.62 mm ammunition, with 85 μm PA extracting the greatest levels in the Federal 7.62 mm powders. It is therefore suggested that the structural composition of different ammunitions and the ratios of compounds present may both influence the extraction process. For example the use of deterrents and other coatings such as graphite on particle surfaces may affect the levels of some compounds entering the headspace. Reference to the relative abundances of extracted compounds from the four ammunition types (Fig. 3) show variations, suggesting the partition coefficient values are different in the extraction systems for each powder analysed [28]. It has also been reported that higher concentrations of a competitive interface compound can dislodge other analytes from fibres [9]. A combination of these factors may explain this variation in which different fibres perform best for any given compound between different propellant powder samples.

The ammunitions that were used in this investigation only contained a limited number of compounds, however the inherent characteristics of the 65 μm PDMS/DVB fibre, for example its bipolar character and suitability for extracting volatiles, amines and nitro aromatics [25] suggest that it should be the most suitable fibre across most other ammunition types. Research by Furton et al. [12] into SPME extractions of explosives concluded that 65 μm PDMS/DVB was the most suitable overall for a number of additional compounds that may also be found in firearm ammunitions including nitrotoluenes, dinitrotoluenes and trinitrotoluene. Further work is being undertaken assessing this fibre type with a larger number of ammunitions and OGSR samples.

3.5. Evaluating the effects of extraction time on single particles of propellant powders

In OGSR samples there will obviously be variable amounts of the compounds of interest and depending on these amounts, the volume of headspace from which compounds of interest will be extracted and the volume of the sample being analysed, the optimum extraction time will vary. Although it would be impossible to account for all the potential variability from sample to sample, extracting from one particle of propellant powder was an attempt to mimic lower amounts of sample that might be found in relation to OGSR. As stated previously both unburned and partially burnt propellant powder particles may be found in association with firearm discharges [8]. Pun and Gallusser [30] showed that

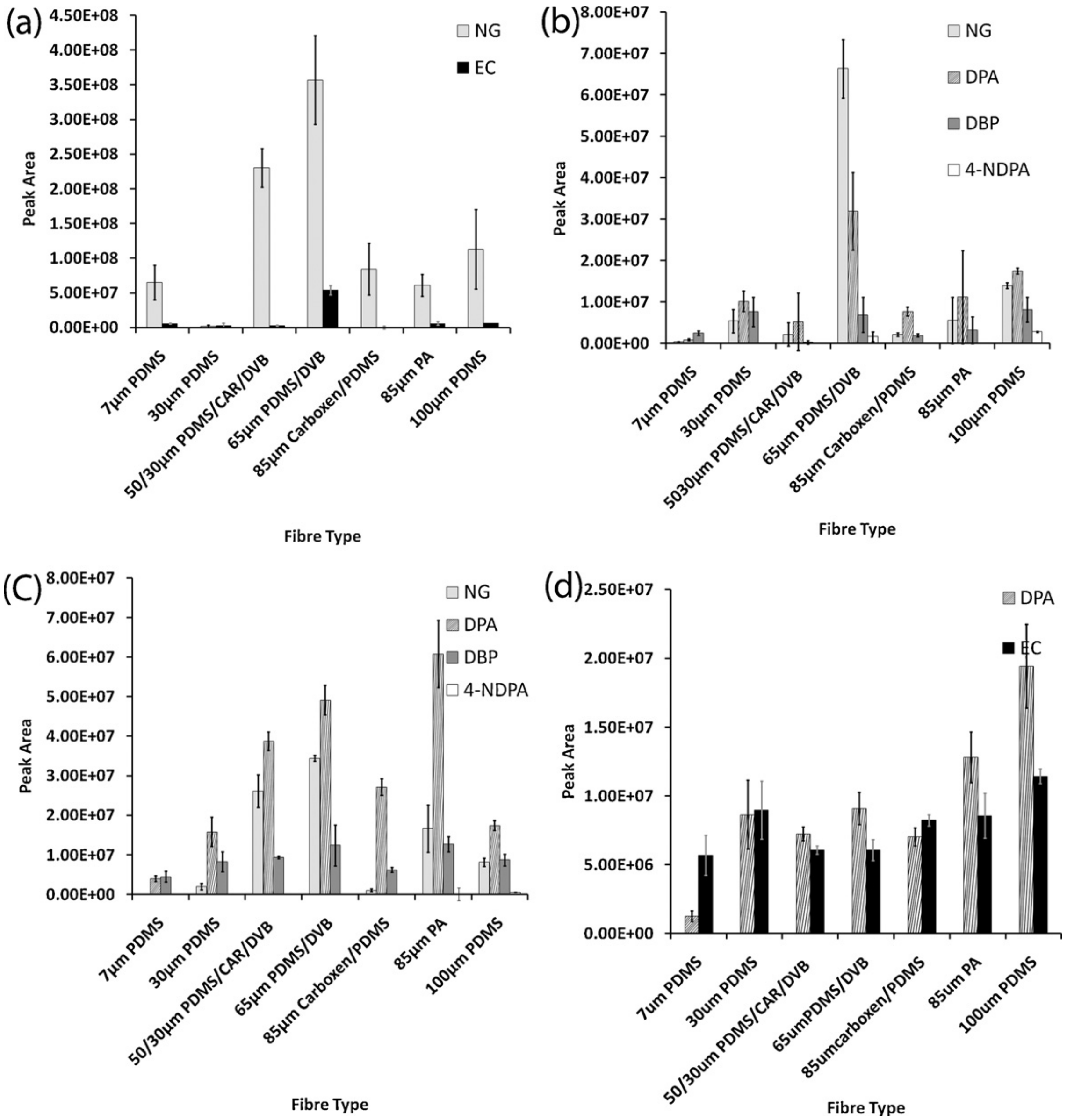

Fig. 3. Average peak areas for compounds extracted from 4 ammunition types by the 7 SPME fibre types: (a) Magtech 9 mm, (b) Magtech 5.56 mm, (c) Federal 7.62 mm, (d) Lapua 7.62 mm.

partially burnt powder particles can be found in various stages of decomposition exiting the firearm barrel following discharge. The SPME extraction of partially burned particles has been shown to be possible by Burleson et al. [19].

Results for single particles extracted across the range of times (5–55 min) showed a great level of variation between individual particles from the same ammunition type and between different ammunition types.

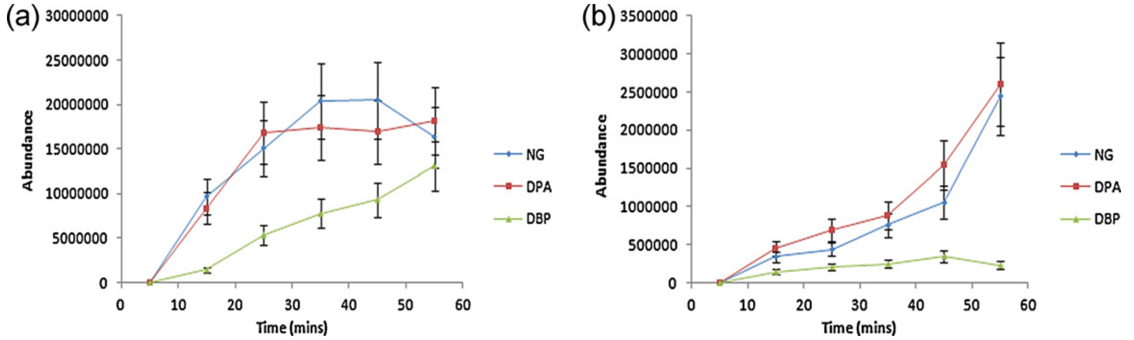

Fig. 4. Extractions of two different single particles of Magtech 5.56 mm ammunition collected from the same cartridge.

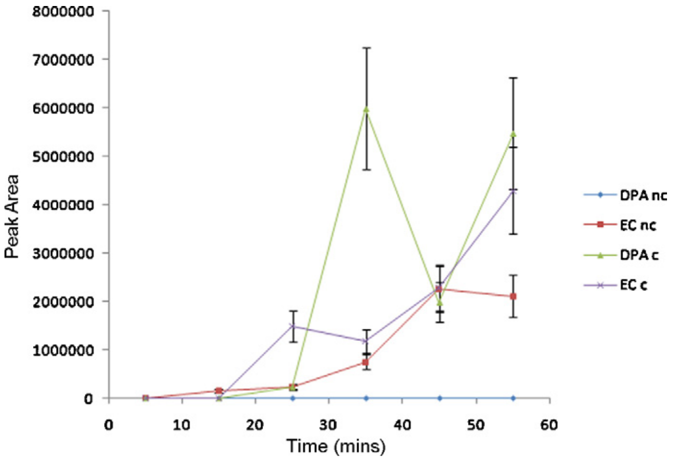

Fig. 5. Lapua 7.62 mm single particle extracts from cut (c) and non-cut (nc) particles.

Extractions of compounds from the same ammunition type but different individual particles showed the potential for orders of magnitude differences in extraction abundances to occur. For example two sets of extractions of 9 mm Magtech ammunition carried out consecutively on two separate particles from the same cartridge yielded abundance levels for 35 min extractions of 8,417,107 and 380,380 for NG. This suggests that on a particle to particle basis extraction efficiency may be highly variable.

The optimum extraction time for particles was also shown to vary from particle to particle within the same ammunition type. Fig. 4 shows the extractions of two different particles of the same Magtech 5.56 mm ammunition taken from the same cartridge. It can be seen that in the first set of particle extractions the levels of both NG and DPA reach an equilibrium within the extraction system at 35 min (and in the case of NG begin to drop after 45 min) and this would therefore be determined as the optimum extraction time. However in the second set of extractions the levels of DPA and NG extracted continue to increase with time up to the last extraction of 55 min suggesting this would be a more suitable time for this particle. Work is ongoing in this area.

Extractions from single particles of Magtech 9 mm and 5.56 mm ammunition types proved successful. It was determined that despite variation between particles an extraction time of 35 min was suitable. Providing good extraction and having a time similar to that of the GC/MS analysis (32 min), something stated as preferable by Wercinski [29].

Extractions from single particles of the two 7.62 mm ammunition types proved to be less effective than those of the smaller calibre ammunition types. With Lapua 7.62 mm no DPA was extracted from the individual particles, even after 55 min extractions. This compound was known to be present in this ammunition type by reference to the extracts from 100 mg samples. When this particle was subsequently cut in half, DPA was detected in extraction of 25 min and above. These findings are illustrated in Fig. 5. By exposing the inner core of the powder particle and increasing the surface area, extraction efficiency was shown to increase. However extracts from single particles of Federal 7.62 mm ammunition exhibited none of the compounds which were previously determined to be present in the ammunition (by analysis of 100 mg of the propellant powder), even at the maximum tested extraction time of 55 min. Cutting these particles into pieces had no effect and still no compounds of interest were extracted. These finding would suggest that the shape of a particle, together with the internal and external morphologies and compositions may affect the success of SPME extractions.

These results show that the specific type of ammunition being analysed can have an effect on SPME extractions. No one extraction time was shown to be universally optimal for all ammunition types, or even between individual particles of the same ammunition. However, with the exception of the Federal 7.62 mm ammunition, an extraction time of 35 min was determined to be suitable, yielding peaks for all of the OGSR compounds determined to be present in the ammunitions in this study.

4. Conclusions

The most suitable SPME fibre for the extraction of the compounds found in relation to unburned propellant powders and therefore potentially OGSR was determined to be the 65 μm PDMS/DVB fibre type, performing well across all of the compounds present in the ammunition investigated.

Results from extraction optimization work have shown that no one extraction time was universally optimal for all compounds being extracted. However a 35 min extraction time was determined to be suitable, allowing detection of the compounds of interest. Issues experienced with extracting compounds from the 7.62 mm ammunition types suggest that the shape of a particle, its internal and external morphologies and compositions may influence the effectiveness of SPME extractions.

Further work will be to apply these methodologies to the extraction of OGSR compounds from various media and forensic evidence types. The results of this study may also be useful to those investigating improvised explosive devises (IEDs) in which smokeless propellant powders have been used [31].

Acknowledgements

The authors would like to thank Nottinghamshire Police for the preparation of samples, and Nottingham Trent University for research funding through the VC Bursary Scheme.

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