FORENSIC PROFILING OF GUNSHOT RESIDUES (GSR) FROM SPENT CARTRIDGES BY SOLID PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY (SPME-GC-MS)

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by

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LIST OF SYMBOLS

%	Percentage
%RSD	Percentage of relative standard deviation
$\bar{x}$	Mean
°C	Degree Celsius
°C/min	Degree Celsius per minute
µ	micro
cm	centimeter
eV	Electron volt
min	Minute
mL	milliliter
mL/min	Milliliter per minute
mm	Millimeter
pH	hydrogen ion concentration in water
rpm	Revolutions per minute
s	Standard deviation
µg/mL	Microgram per milliliter
µm	micrometer

LIST OF ABBREVIATIONS

2,3-DNT	2,3-dinitrotoluene
2,5-DNT	2,5-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
2-NDPA	2-nitrodiphenylamine
2-NT	2-nitrotoluene
3,4-DNT	3,4-dinitrotoluene
3-NT	3-nitrotoluene
4-NDPA	4-nitrodiphenylamine
4-NT	4-nitrotoluene
AAS	Atomic absorption spectroscopy
ARX	Advance rotation extreme
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectrometry
Ba	Barium
$Ba(NO_3)_2$	Barium nitrate
BHT	Butylated hydroxytoluene
C_2H_5	Ethyl group
C_4H_9	Butyl group
C_6H_5	Phenyl group
$C_6HN_3O_8Pb$	Lead styphnate
CAR/PDMS	Carboxen/polydimethylsiloxane
CE	Capillary electrophoresis
CH	Methine
CNT	Carbon nanotube
CO	Carbon monoxide
COOH	Acidic group
CV	Coefficient of variation
CW/DVB	Carbowax/Divinylbenzene
CW/TPR	Carbowax/templated resin
DBP	Dibutyl phthalate
DNT	Dinitrotoluene

DOA	dioctyl-adipate
DOP	dioctyl-phthalate
DPA	Diphenylamine
DVB/CAR/PDMS	Divinylbenzene/Carboxen/polydimethylsiloxane
EC	Ethyl centralite
FMJ	Full metal jacket
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography-mass spectrometry
GSR	Gunshot residue
H	Hydrogen
HEX	Hexagon
HPLC	High-performance liquid chromatography
HPLC-UV	High-Performance Liquid Chromatography-Ultraviolet
HSSE	Headspace sorptive extraction
HS-SPME	headspace solid phase microextraction
ICP-OES	Inductively coupled plasma optical emission spectrometry
IGSR	Inorganic gunshot residue
IR	Infrared spectroscopy
JDP	Jacketed deform projectile
JHP	Jacketed hollow point
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry
LIBS	Laser induced breakdown spectroscopy
LRN	Lead round nose
m/z	Mass-to-charge ratio
M^+	Molecular ion peak
MC	Methyl centralite
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
MTBE	Methyl-t-butyl ether
N	Nitrogen
NAA	Neutron activation analysis
NC	Nitrocellulose

NG	Nitroglycerine
NGu	Nitroguanidine
NIST	National Institute of Standards and Technology
O	Oxygen
OGSR	Organic gunshot residue
OH	Hydroxy group
PA	Polyacrylate
PAC	Powdered activated carbon
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PDMS	Polydimethylsiloxane
PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PEG	Polyethylene glycol
PTFE	Polytetrafluoroethylene
PULAPOL	Police Training Centre Kuala Lumpur
PVC	Polyvinylchloride
RSD	Relative standard deviation
S/N	Signal-to-noise ratio
Sb	Antimony
Sb_2S_3	Antimony trisulfide
SD	Standard deviation
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray
SLA-ICPMS	Scanning laser ablation-inductively coupled plasma-mass spectrometry
SPME	Solid phase microextraction
SPME-GC-MS	Ssolid phase microextraction-gas chromatography-mass spectrometry
TAC	Tributyl acetylcitrate
TLC	Thin-layer chromatography
TNT	Trinitrotoluene
TOF	Time of flight analysers
VOCs	Volatile organic compounds
XRF	X-ray fluorescence

LIST OF EQUATIONS

PEMPROFILAN FORENSIK BAGI SISA TEMBAKAN (GSR) DARI KELONGSONG PELURU TERTEMBAK DENGAN MIKRO-PENGEKSTRAKAN FASA PEPEJAL-KROMATOGRAFI GAS-SPEKTROMETRI JISIM (SPME-GC-MS)

ABSTRAK

Sisa tembakan (GSR) yang dihasilkan daripada pelbagai amunisi selepas penembakan menggunakan senjata api yang sama boleh berbeza berdasarkan kandungan yang digunakan untuk membuat serbuk perejang. Disebabkan pengenalan amunisi tak toksik, pengesanan konvensional plumbum, barium dan antimoni telah dilaporkan kekangannya untuk penentuan secara sah bagi GSR. Dalam kes sedemikian, profil organik bagi GSR boleh bertindak sebagai bahan bukti sokongan untuk membuktikan aktiviti penembakan atau untuk membezakan amunisi. Objektif kajian ini adalah untuk memprofil GSR organik daripada kelongsong peluru tertembak dengan mikro-pengekstrakan fasa pepejal-kromatografi gas-spektrometri jisim (SPME-GC-MS) untuk perbandingan forensik. Dalam kajian ini, sebelas kelongsong peluru tertembak telah dikenakan kepada SPME-GC-MS dan tanda-tanda atribusi kimia dalam setiap profil telah dikenal pasti. Seterusnya, profil organik GSR dalam pelbagai jenis peluru telah dibandingkan, dan akhirnya, satu metodologi saringan untuk pengkelasan profil GSR telah dicadangkan. Analisis SPME-GC-MS yang dilakukan ke atas kelongsong peluru telah mengesan lima sebatian utama, termasuk difenilamina (DPA), dibutil ftalat (DBP), etil sentralit (EC), tributil asetilsitrat (TAC), dan butil sitrat yang mempunyai fungsi penting dalam serbuk perejang. Analisis perbandingan profil organik GSR antara pelbagai jenis amunisi telah mengungkapkan pilihan penggunaan pelapik dan plastik yang berbeza. Berdasarkan cadangan metodologi saringan yang menggunakan kehadiran OGSR yang dikesan untuk mengelaskan dan membezakan sampel, lima kategori yang berlainan telah terbentuk. Dengan mengaplikasikan metodology saringan tersebut, sampel-sampel yang tidak diketahui boleh dikaitkan dengan jenis yang berkemungkinan atau dibezakan berdasarkan sumber yang spesifik. Kesimpulannya, kajian ini telah berjaya memprofil GSR organik daripada kelongsong peluru dan metodologi saring tersebut boleh bertindak sebagai alat yang berguna untuk mengelaskan dan membezakan sampel GSR. Hal ini dapat membantu penyiasatan forensik dalam kes jenayah melibatkan senjata api.

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ABSTRACT

Gunshot residues (GSR) produced from different ammunitions upon firing using the same firearm could be varied according to the compositional ingredients used to make the propellant powder. Due to the introduction of non-toxic ammunition, the conventional detection of lead, barium and antimony has also reported obstacles for the confirmative determination of GSR. In such cases, the organic profiles of GSR could serve as the supporting evidence to prove a firing activity and to differentiate the ammunitions. The objective of this study was to profile the organic GSR from spent cartridges by solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) for forensic comparison. In this study, eleven spent cartridges were subjected to SPME-GC-MS and the chemical attribution signatures in each profile were identified. Subsequently, the organic GSR profiles across various ammunition types were compared, and lastly, a screening methodology for classification of GSR profiles was proposed. The SPME-GC-MS analysis carried on the spent cartridges had detected five key compounds, including diphenylamine (DPA), dibutyl phthalate (DBP), ethyl centralite (EC), tributyl acetylcitrate (TAC), and butyl citrate, that possessed important role in propellant powders. Comparative analysis of OGSR profiles across different ammunition types revealed the choice of stabilisers and plasticisers used were found to be varied. Based on the proposed screening methodology that employing the presence of detected OGSR compound to categorise and differentiate samples, five distinct categories were formed. By applying such screening methodology, unknown samples could be associated with potential ammunition types or distinguished based on the specific sources. To conclude, the study had successfully profile the organic GSR from spent cartridges, and the screening method could serve as a useful tool for classifying and distinguishing GSR samples, assisting forensic investigation in criminal cases involving firearm.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Gunshot residue (GSR) is the trace evidence that assists forensic experts in resolving cases involving firearms. It can be found on the skin, hair, body parts, clothing of the shooter, and the immediate surroundings of the incident (Kabir et al., 2012). Such residue may also be transferred through contact with items like fired weapons, spent cartridge cases, or contaminated surfaces. From the forensic science perspective, the existence of GSR on a sample may provide additional evidence supporting that a surface could have been involved being near a firearm discharge, having a connection to firearms, or recently touching a contaminated surface (Pitts & Bonnar, 2023).

GSR comprises two primary constituents, specifically organic GSR (OGSR) and inorganic GSR (IGSR), originating from distinct elements of ammunition. OGSR compounds likely stem from the firearm's propellant and lubricant, whereas IGSR particulates may result from various sources such as the propellant, primer, bullet, and cartridge casing (Feeney et al., 2021). A detailed examination of the organic component, which includes substances like diphenylamine (DPA), nitrocellulose (NC), nitroglycerine (NG), and ethyl centralite (EC), can provide valuable insights in criminal investigations (Shrivastava et al., 2021).

Introduction of heavy-metal free ammunition has led to the need to screen for OGSR. Currently, analytical efforts are divided into the analyses of IGSR and OGSR. In fact, the determination of IGSR continues to the be gold standard for the confirmation of GSR particles. However, the analysis of OGSR could serve to support the IGSR profiles where they might not be conclusive enough for confirmation especially due to the shift of primer composition in the ammunition. In this context, gas chromatography coupled with mass spectrometry (GC-MS) has shown promising results for OSGR determination. Its availability of instrumentation and ability to analyse wide range of OGSR relevant analytes further supports its potential in this field (Charles et al., 2020; Rockwood et al., 2018). Its application could offer fair delivery of justice, providing valuable insights in firearm-related cases. It was also noted that traditional methods of GSR detection, particularly utilising liquid-liquid extraction and/or dissolution of recovered sample into solution form, have encountered challenges related to the speed of sample preparation step and analysis, and adaptability to new types of ammunition (Trejos et al., 2022).

In Malaysia, there have been reported cases of violent crimes involving firearms. A study on the demographic data on the incidence of firearm-related deaths from 2006 to 2016 was also reported in which the data was collected retrospectively from four government hospitals in Klang Valley with a total of 204 firearm-related cases deaths throughout the 11 years (Adawiyah et al., 2018). Moreover, according to statistics provided by Royal Malaysia Police (2021), cases involving firearm has increased from 182 to 227 from 2019 to 2020. The significant increase in firearm-related cases even with a strict legal control over firearms within the country has alarmed the forensic community.

1.2 Problem statement

In recent times, firearm manufacturers have unveiled new types of ammunition often labelled as 'eco-friendly,' 'non-toxic,' 'heavy-metal-free,' or 'lead-free.' These innovative ammunitions employ various chemical compounds or materials to propel projectiles, aiming to achieve comparable performance to traditional ammunition while simultaneously mitigating the risk of exposure to hazardous heavy metals like lead (Pb), barium (Ba), and antimony (Sb) for both the shooter and the environment (Feeney et al., 2021). Its emergence has required firearm examiners to characterise and interpret the output from their analyses, whether a shooting was caused by a specific firearm and/or a suspect has involved in a shooting. Note that these ammunitions do not contain the three key elements for definite determination of a shooting (Feeney et al., 2021). Therefore, the organic profiles upon a shooting could provide details whether a shooting was made.

Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis on evidence with suspected GSR was the routine protocol during forensic investigations. However, it may not yield sufficient data to determine the specific type of ammunition used in a firing case, especially with those lead-free ammunition. With that, the determination of OGSR could become particularly helpful in criminal cases whenever lead-free ammunition is discharged. By examining both inorganic and organic profiles, the characterisation of the fired ammunition could be more convincing and subsequently improve its identification (Black et al., 2021). Organic profiles are not the main concern by firearm examiner during routine examination on caseworks. As they can serve to support a shooting event, the organic profiles of various ammunitions, especially between conventional and lead-free ammunitions, were lacking and not practiced in real case scenarios. Establishment of chemical attribution signatures originated from propellant powders, as proposed in this study, can aid in determining a specific type of ammunition, or in excluding an ammunition from others, subsequently assisting in forensic investigation.

1.3 Objectives of the study

1.3.1 General objective

The general objective of this study was to profile the organic GSR from spent cartridges by solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) for forensic comparison.

1.3.2 Specific objectives

To achieve the general objective of the study, the specific objectives of this study are as follows:

i. To determine the chemical attribution signatures in the organic GSR recovered from varying spent cartridges.
ii. To compare the organic GSR profiles among varying ammunitions.
iii. To propose a screening methodology for the classification of various ammunitions.

1.4 Significance of study

GSR is a crucial trace evidence in firearms-related incidents, providing valuable information for forensic investigators. Such information could aid in various aspects of crime scene reconstruction, ranging from identifying the shooter to bullet identification from gunshot wounds (Shrivastava et al., 2021). Furthermore, the significance of this study lies in its potential contributions to firearm-related crime-solving, as the successful implementation of this research could establish a valuable database for future investigations.

In recent years, there has been a growing interest in analysing organic compounds in GSR. Research trends are now focused on developing a complementary examination based on organic residue, which could offer the advantages of broadening the range of target traces that can be detected. Through an established method for the analysis of OGSR, compounds that make up a significant percentage of the propellant could be detected after discharge compared to those present in trace amounts. Apart from that, the compounds unique to propellant manufacture and have no potential alternative sources could also ensure a higher level of confidence in their association with GSR (Gassner et al., 2019).

This research study will assist the identification of OGSR profiles from different types of ammunition recovered at crime scenes. Chemical attribution signatures originated from propellant powders holds great potential in forensic science to compare among ammunitions, especially from those which illegally manufactured. The proposed screening methodology could also be utilised to determine or exclude specific ammunitions, aiding the forensic investigation of firearm-related cases.

CHAPTER 2

LITERATURE REVIEW

2.1 Gunshot residue analysis in forensic science

Forensic investigators aim to establish connections between suspects and specific shooting incidents through the examination of ballistic evidence retrieved from the crime scene. The process involved a thorough examination of fired projectiles or cartridge cases, with a focus on identifying unique microscopic striations that could be linked to a specific firearm. This form of toolmark analysis required the involvement of a skilled examiner, which introduced the potential for subjectivity and variations between different examiners (Brigida et al., 2023).

Challenges of shot-to-shot variation and shared subclass characteristics pose difficulties for ballistics examiners. For instance, consecutively fired bullets from the same firearm often exhibit observable differences under the comparison microscope. Therefore, examiners could not definitively conclude that a specific bullet or cartridge case could have come from a particular firearm to the exclusion of all other possible sources (Morgan, 2023).

When delivering forensic evidence related to firearms and ammunition to a forensic laboratory, ballistics experts often play a crucial role in determining the firing distance, bullet type, calibre, and the specific firearm from which had made a firing. This process typically involves comparing test-fired projectiles directly with the questioned projectiles to establish their linkages. The examination is most effective when the projectile remains intact and not deformed, and it was successfully recovered from the crime scene or victims' bodies (Waghmare et al., 2019).

In such investigative process, the class characteristics were related to the firearm's model, while subclass characteristics corresponded to a group of firearms of the same model sharing a common manufacturing history, such as barrels produced consecutively. Moreover, examiners use available case information to further narrow down the number of firearms considered for comparison. This could involve restricting the set to firearms associated with the specific case, those linked to related crimes (Morgan, 2023). If a suspected firearm was found, the test-fired samples could be compared with the questioned samples to investigate if they were shot from the same firearm, contributing to individual characteristics. While toolmark examination remained a significant practice, it was important to acknowledge that obtaining a bullet or cartridge in optimal condition for comparison may not be always feasible, especially given the potential for deformation. As such, chemical analysis could have offered additional insights.

Due to the restrictions associated with toolmark examinations, alternative approaches were explored for reconstructing shooting incidents such as the tracking of firer and determination of the source of ammunition. The advancement in analytical methods have the potential to enhance the values of GSR. GSR was comprised of remnants generated during the discharge of a firearm, encompassing minute metallic constituents originating from the discharged firearm, spent cartridge cases, projectiles, and chemical elements derived from the ammunition's propellant and primer. Particles stemming from the primer and metallic components were denoted as IGSR, while particles emanating from the propellant were commonly referred to as OGSR. OGSR predominantly included nitrate ester explosive materials such as NC or NG. Following the discharge of a firearm, GSR particles dispersed throughout the crime scene, often landing on the shooter's body or clothing. Consequently, the detection of GSR on a suspect's person could potentially establish a connection to the crime (Katz & Halámek, 2016).

During forensic investigation, the primary and standardized method for GSR analysis is the Scanning electron microscopy-energy dispersive X-ray (SEM-EDX), which is highly effective in detecting heavy metals including lead (Pb), barium (Ba), and antimony (Sb). The distinctive presence of these metals in spherical particles ranging in size from 0.5 to 10 µm shows the characteristic feature of GSR. These three constituents are contributed by the ignition of a primer cap, exhibiting unique characteristics that are specific to IGSR and are rarely encountered together in the general population or environment (Pyl et al., 2023).

As reported in the study by Ritchie et al. (2020), sampling of potential GSR particle could be achieved through various methods, such as swabbing or tape-lifting, to collect gunshot residue particles. The gathered samples were then subjected to examination using SEM-EDX. The SEM enables the high-resolution imaging of GSR particles, while the EDX provides information about their elemental composition. Through SEM-EDX analysis, the elemental composition of the IGSR particles could be determined. By analysing the X-ray signals emitted by the particles, the presence and relative abundance of different elements could be identified and confirmed the identity of GSR particles.

SEM-EDX stands out as the widely acknowledged and definitive technique for IGSR detection. Its superiority is rooted in its capabilities for imaging, particle enumeration, and individual particle elemental analysis, even for GSR particles as small as 0.5 µm. The accessibility of SEM-EDX within forensic laboratories, coupled with its versatility in scrutinizing trace evidence, solidify its status as the gold standard for IGSR identification. Nevertheless, when dealing with contemporary ammunition, particularly lead-free GSR, relying solely on SEM-EDX can pose certain challenges. Lead-free ammunition can produce IGSR particles devoid of heavy elements like Pb, Ba, and Sb.

Additionally, some formulations may yield IGSR particles containing only low atomic number elements, such as potassium, making definitive determinations challenging. These low atomic particles are less conspicuous in backscatter imaging and, therefore, can be challenging to distinguish from other background materials during automated examinations (Menking-Hoggatt et al., 2021).

Another limitation of SEM-EDX analysis for GSR is that the particles identified in IGSR could potentially originate from a variety of environmental and occupational sources. Examples include brake linings, fireworks, paints, and occupations involving cartridge operation. These sources have been known to produce particles resembling IGSR, introducing the possibility of false positives in some scenarios. Consequently, it is essential to consider the comprehensive informational content of GSR as forensic trace evidence, rather than relying solely on target elements analysed via SEM-EDX. In certain cases, it may be necessary to analyse both IGSR and OGSR, as they can offer valuable insights into addressing the challenges associated with false positive and false negative results (Taudte et al., 2014).

2.1.1 Ammunition

Ammunition, often referred to as cartridges, was composed of essential components, including a priming system, gunpowder, a projectile (bullet), and a cartridge case housing all these elements (Monturo, 2019). Conversely, shotgun ammunition, distinct from conventional cartridges, typically contained multiple spherical lead balls fully enclosed within the cartridge case. These shotgun cartridges were commonly constructed from plastic material with a metal base. In contrast, cartridges designed for rifled firearms were frequently fabricated from brass, with the bullet's base fitted into the cartridge case's neck. Figure 2.1 illustrates the cross-sectional view of the pinfire cartridge (Wallace, 2018).

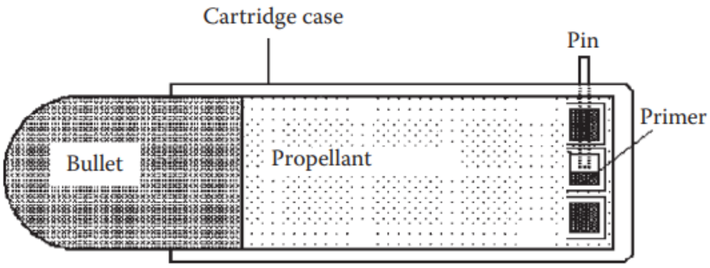

Figure 2.1 Cross-sectional view of the pinfire cartridge.

Source: (Wallace, 2018).

In most ammunitions, the projectile is made up of a metal core or slug covered with brass jacket, usually consisting of 70% copper and 30% zinc. In contrast, unjacketed lead bullet is frequently lubricated with some form of wax or grease. Other than the two common types of projectiles, other materials such as steel, coated with either zinc, brass, gilding metal, copper, lacquer or blackened; copper; nickel-plated brass; cupronickel (approximately 80% copper and 20% nickel); gilding metal (approximately 90% copper and 10% zinc); aluminium, and Teflon-coated aluminium and plastic are also encountered in the ammunition markets (Wallace, 2018)

Propellant for small arms can be primarily differentiated into two categories which are single-base nitrocellulose (NC) and double-base NC with nitroglycerine (NG). It was said that the double base propellant powder burns more rapidly than the single-base type. In the various ammunition, the weight and granulation of propellant powder varies depending on specific requirements for velocity and distance. The propellant is assembled loosely within the cartridge case (Wallace, 2018).

Primer is important in initiating the firing process. It consists of a cup made of brass or gilding metal. A primer composition pellet, a paper disc, and a brass anvil are found in the cup. Primer composition will be compressed between the cup and the anvil when it was struck by the firing pin, causing it to explode. The vent in the anvil allows the flame to pass through and subsequently ignites the propellant (Monturo, 2019).

Modern ammunition employed two distinct priming systems: centrefire primers and rimfire primers. Centrefire primers were comprised of separate components positioned at the rear of the cartridge within the primer pocket area. These primers contained a shock-sensitive explosive that initiated or detonated upon being crushed between the rear of the primer cup and its internal anvil, a result of the impact from the firing pin or striker (Monturo, 2019). On the other hand, rimfire primers featured the priming compound distributed along the entire rim at the base of the cartridge case. When the firing pin or striker was released, it crushed the rim, igniting the priming compound, which in turn initiated the ignition of the gunpowder. Presently, modern rimfire cartridges were typically limited to .22 calibre ammunitions in terms of size (Monturo, 2019).

The cartridge case is typically made of drawn brass or steel. It plays a crucial role in assembling the other components, including the primer, propelling charge, and bullet, into a single unit. Additionally, it serves as a mean of expanding and sealing the chamber when the cartridge is fired, preventing the escape of gases to the rear. To maintain the waterproofing property of an ammunition and to keep the propellant dry, the primer is sealed within the primer seat, and the projectile is sealed within the neck of the cartridge case using a thin film of lacquer or varnish during manufacturing. An extractor groove appeared on the head of cartridge case allows for its easy removal from the weapon's chamber after a firing activity (Wallace, 2018).

2.1.2 Classification of ammunition

Various types of ammunition are available in the markets. These ammunitions can be categorised, usually by their projectiles, based on their weight, diameter, length, number of plain or knurled cannelures, type (such as full jacketed or hollow point), colour (copper, lead, brass, silver), and core type (hard or soft core). This classification system allows for a wide range of projectile types to exist, each designed for specific purposes and applications. In modern ammunition, the projectiles typically have a thin metal covering known as a jacket, where the composition and design of jacket could be varied depending on the intended purpose of the ammunition. Figure 2.2 provides visual examples of the four common appearances of the projectiles in various ammunitions (Jenzen-Jones & Schroeder, 2018).

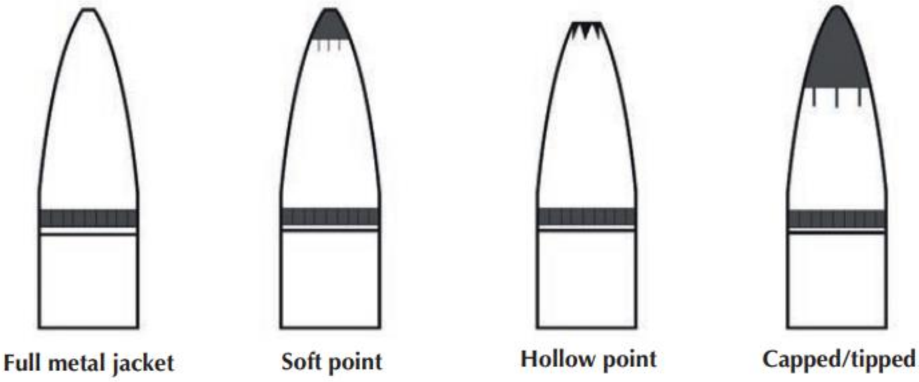

Figure 2.2 Common configurations of projectiles.

Source: (Jenzen-Jones & Schroeder, 2018).

The most common bullet type encountered in ammunition was the full metal jacket (FMJ). This design incorporated a lead alloy core enveloped by a metal jacket, typically crafted from copper, although brass or copper jackets were also employed. To enhance the durability of lead in all-lead bullets or bullet compositions, various alloys were incorporated, often including antimony. The primary objective of the metal jacket was to minimize fouling within the barrel grooves. Lead was relatively soft in comparison to copper; therefore, if bullets were exclusively made from lead, the heat generated during gunpowder combustion and the friction from the bullet's movement would have resulted in barrel fouling and reduced accuracy. Consequently, FMJ ammunition was predominantly favoured for target shooting, as it effectively mitigated fouling issues, contributing to improved shooting precision (Monturo, 2019).

Apart from the two conventional types of ammunition, a hydraulic displacement can be generated through the transferring of energy to the target via a unique fluted design in the advance rotation extreme (ARX) projectile (Malik et al., 2022). Unlike expanding bullets, it does not rely on the expansion upon impact. Instead, it is made of injection-moulded polymer-copper matrix to provide adequate toughness for an all-purpose defence round (Inceptor Ammunition, 2018a; Mahoney’s Outfitters, 2023). This non-expanding bullet is preferred and suitable for various firearms including the large-frame handguns and carbines (Inceptor Ammunition, 2018b). As ARX bullet is crafted with advanced materials and precision engineering, it can achieve remarkable levels of pinpoint accuracy and extreme terminal performance (Inceptor Ammunition, 2018c).

Jacketed deform projectile (JDP) is a type of projectile that incorporates a jacket or casing surrounding is core. The jacket undergoes controlled deformation, which is either expanding or fragmentation in a controlled manner upon impact. Such deformation allows the transfer of energy to happen and creates larger wound channel on the target. JDP ammunition has impressive performance on both soft and hard targets, such as glass and tyres. It is specifically designed to prevent over-penetration and minimise collateral damage. Commonly, JDP is widely applied for hunting, selfdefence, and law enforcement applications, where their terminal ballistics and stopping power are the critical considerations (Deese, 2021; Lord, 1997; RUAG AmmoTec, 2023).

A jacketed hollow point (JHP) type ammunition is specifically designed to rapidly expand when strikes on a target, further enhances the effectiveness of projectile, and reduces the risk of over-penetration. The projectile's nose is coated with harder metal, preventing lead exposure in firearm, and reducing environmental impact. Additionally, the performance of JHP ammunition in automatic pistols and rifles can also be augmented with the presence of coating and ensuring the reliability of its (Carter, 2023).

Hexagon ammunitions are engineered with precision and accuracy in mind, which featuring a hollow point of approximately 2 mm achieved through bending of bullet tip and obtaining a distinctive golden section (Ardovini, 2015). However, the expansion properties are not primary consideration even though the hexagon bullet are modelled after the hollow-point design (GECO, 2023). Extensive testing has been conducted for this ammunition to ensure high accuracy and precision which making it ideal for competitive shooting purpose (Schmidt, 2014).

In contrast, a full lead bullet is lack of any jacket or coating on it. It is prone to deform easily and can cause damage over a large tissue area when it strikes on the target (Ashok, 2006). Specifically, lead round nose (LRN) ammunition is exposed lead projectiles without protective jacket on it. Due to lack of jacket, they are more susceptible to deformation as compared to jacketed bullets, where this also will reduce their accuracy (Malik et al., 2022).

In short, there are different types of ammunition, sharing the same calibre, that can be fired from the same firearm. These different ammunition types have varying impacts on the target due to their distinct composition and design. To ensure their effective performance, the propellant composition of each ammunition type may differ, thus requiring a thorough examination of their profiles. Understanding and analysing these characteristics are crucial for their proper functioning of each type of ammunition when used with the firearm.

2.1.3 Propellant

Small arms ammunition propellants were described as explosive materials engineered to produce controlled, high-temperature gases at specified rates(Kumar & Dixit, 2019). Ideally, an optimal propellant should have been a single, solid, environmentally friendly compound with excellent stability, ease of storage, and ignition, all while maintaining a compact mass. Furthermore, the ideal propellant would have left no smoke or solid residues, undergoing complete conversion into gas during combustion. Propellant powder inherently provided its own oxygen source for combustion within enclosed spaces, facilitating rapid, non-detonating burns (Wallace, 2018).

In practice, a propellant need to fulfil certain general requirements. It should be easily and quickly manufactured and at a reasonable cost, as well as using ingredients readily available during wartime, such as the military propellants (Wallace, 2018). Loading of the propellant must also be simple and safe, without any hygroscopic substances and free from combustion products that can be hard to remove or harmful to the firearm or cartridge case (Virginio et al., 2023). It must deliver consistent performance under varying storage and climate conditions, and not deteriorate with age. Such characteristics are crucial and particularly critical for military that need reservation for long periods. Apart from that, the propellant must not ignite when exposed to the high heat inside a firearm's chamber for an extended period, including the primer composition (Tırak et al., 2019).

The energy-to-weight-to-volume ratio and the rate at which energy was delivered by propellant powder had to align with the specific demands of the firing system, considering factors such as available space within the cartridge case and gun barrel, bullet mass, pressure criteria, and the desired bullet velocity. Consequently, there existed a wide array of propellant powders tailored to cater to the varied ballistic needs of different firearms and ammunition types (Wallace, 2018).

Burning rate of a propellant powder is of utmost importance, as it directly affects the performance and safety of the firearm and ammunition. If the propellant releases hot gases too quickly, it may lead to detonation, resulting in the destruction of firearm and introducing potential injury to the shooter. On the other hand, if it burns too slowly, it becomes inefficient, leading to a lack of sufficient velocity for the bullet. Thus, controlling the burning rate is achieved through various factors, including the size and geometrical design of individual granules that make up the propellant powder. These granules also referred to as grains or kernels, can vary greatly in size and complexity. Additionally, the burning rate might also be influenced by applying surface coatings, known as moderants such as phthalates, centralites, and natural resins, to the propellant granules (Davis-Foster, 2018). Process of delivering propellant gases at a predetermined rate involves carefully selecting a propellant composition of required burning rate at the firearm's operating pressure. Propellant granules are designed to offer the necessary burning surface, ensuring the desired mass rate of gas evolution, and achieving the required time/-pressure relationship (Wallace, 2018).

In the historical context, black powder served as a prevalent propellant for small arms ammunition until the advent of smokeless powders between 1870 and 1890

(Bergman, 2022). Black powder consisted of a mechanical blend of charcoal, potassium nitrate (saltpetre), and sulphur, typically in proportions of 15:75:10, respectively. Charcoal functioned as the primary fuel, saltpetre provided the essential oxygen for combustion within confined spaces, while sulphur acted as a binding agent that not only bound the mixture but also contributed as a secondary fuel source. The burn rate of black powder was influenced by the size of its granules (Ritchie et al., 2021; You, 2020).

It was worth noting that black powder retained its application in specialized domains such as baton guns, punt guns, cable guns, signal flares, and among enthusiasts of black powder firearms. However, its utilization significantly declined due to several prominent drawbacks. One significant disadvantage was the substantial residue that remained post-combustion. This residue was prone to attracting atmospheric moisture, which could lead to the corrosion of firearms. Additionally, black powder often led to heavy fouling, potentially impeding the smooth operation of firearm mechanisms. Furthermore, it produced a substantial amount of smoke upon combustion, potentially obstructing the shooter's line of sight for subsequent shots and revealing their firing position (Wallace, 2018).

When black powder underwent combustion, the initial ignited portion triggered a chemical reaction, resulting in the generation of hot gases. These gases expanded in all directions, raising the adjacent material to its ignition temperature, causing it to ignite and perpetuating the process. As this combustion transpired within the confined space of the cartridge case, pressure experienced a rapid surge, and heat could not escape from the compartment. Consequently, this led to an exceedingly swift combustion process and an escalation in pressure (Wallace, 2018). As the pressure built up and propelled the projectile into the gun barrel, the projectile initiated its movement just before the chamber pressure reached its zenith. Subsequently, the pressure inside the chamber rapidly declined upon the departure of the projectile from the cartridge. The projectile continued its journey down the bore and eventually exited the muzzle. Throughout this sequence, the projectile underwent deceleration and eventually halted upon impact with a target (Rozumov, 2017).

Burning of black powder results in the production of dense white smoke containing tiny particles suspended temporarily by the hot combustion gases. These distinctive characteristics of black powder make it less favourable for general small arms ammunition usage in comparison to modern smokeless powders (Wallace, 2018).

A modern substitute for black powder is known as "Pyrodex," which offers significant advantages in terms of safety during transport, storage, and use, as well as cleaner burning characteristics as compared to conventional black powder (Lundgaard, 2022). Pyrodex consists of smaller amounts of charcoal and sulphur compared to the conventional black powder. Additionally, it includes potassium nitrate and other ingredients like benzoate, nitrate, chlorate, and perchlorate. Sodium benzoate is commonly including as a burn rate modifier, while potassium nitrate and potassium perchlorate were often employed as oxidizers in the formulation. The presence of chlorate could be attributed to the degradation of perchlorate, a phenomenon frequently observed in perchlorate-based black powder substitutes (Gallidabino et al., 2019).

Gun propellants are categorized into three groups based on their composition. Single base propellants primarily consisted of NC, which served as an energetic polymeric binder. The incorporation of NG, a highly energetic and sensitive plasticiser, into NC used to result in the creation of a double base propellant, known for its high energy and heat generation (Rozumov, 2017). The proportion of NG in double-base propellants can vary widely, ranging from as low as 5% to as high as 44% (Wallace, 2018). To adapt double-base propellants for use in large-calibre firearms and extend the lifespan of barrels, nitroguanidine (NGu) is introduced to lower the flame temperature. This combination of NC, NG, and NGu has led to the development of triple-base propellants, which have been reported to exhibit intermediate energy levels and flame temperatures between single and double-base propellants (Rozumov, 2017).

In the context of stabilisers, DPA is commonly used, especially in single-base powders. However, it has been observed that DPA may not be as effective at stabilizing double-base propellants because it can hydrolyse NG. For double-base and triple-base propellants, 2-nitrodiphenylamine (2-NDPA) is often used as a more suitable stabiliser. Another stabiliser frequently employed is ethyl centralite (EC), although methyl centralite (MC) is sometimes found in ammunition formulations as well. EC is typically present in double-base propellants, and resorcinol is another stabiliser used in specific formulations (González-Méndez & Mayhew, 2019; Kotter & Kellar, 2022; Wallace, 2018).

To achieve specific performance characteristics, various other chemicals are added to the formulation. Fuel-type plasticisers such as phthalates, polyester adipate, or urethane are introduced to enhance the physical properties and processing of the propellant. It's important to note that plasticisers are additives that provide strength and flexibility to the propellant granules (Yang et al., 2021). Plasticisers function by inserting themselves between the polymer chains, disrupting the weak Van der Waals forces and hydrogen bonding interactions that hold these chains together. This process causes the material to swell, resulting in increased void volumes between the polymer chains. Consequently, the plasticized material becomes more flexible and easier to process (Rozumov, 2017).

The inclusion of an energetic plasticiser is critical to prevent the fracture of propellant grains during the ballistic cycle. It enhances the grain modulus, making them more resistant to stress and strain-induced fractures. If the grains were to fracture, the sudden increase in available surface area for deflagration could lead to a rapid rise in pressure inside the firearm, which would have detrimental ballistic effects and could potentially result in catastrophic firearm failure (Rozumov, 2017).

Muzzle flash suppressors, also known as flash reducers, incorporate substances like dinitrotoluene (DNT) to diminish the heat of explosion and muzzle flash (Botelho et al., 2015). NGu is another flash suppressor that operates by producing nitrogen, thereby diluting the combustible muzzle gases. Potassium nitrate and potassium sulphate also serve as flash suppressors, but they have the disadvantage of potentially generating smoke during firing (Wallace, 2018). Additionally, NGu functions as an effective stabiliser and is compatible with various other energetic materials, including nitrate esters, ammonium perchlorate, and hydrazinium nitroformate. This compatibility is attributed to the mild basicity of NGu and its capacity to form strong hydrogen bonds, which stabilize other covalent or ionic compounds. Propellants containing NGu have relatively low combustion and explosion temperatures, resulting in minimal muzzle flash and reduced erosion. Its incorporation in propellants enhances their stability and performance, making it a valuable component in various ammunition formulations (Koch, 2021).

Stabilisers like DPA, 2-NDPA, DNT, N-methyl-p-nitroaniline, centralites, or acardites (e.g., N,N-diphenylurea) are important additives in gun propellants. Stabilisers play a crucial role in gun propellants by reacting with the nitrogen oxides produced during the decomposition process. This reaction neutralises the nitrogen oxides, effectively preventing further decomposition and inhibiting the formation of harmful decomposition products. As a result, stabilisers could prevent the aging of propellants and improve their shelf life by eliminating the formation of harmful decomposition products that can lead to instability. Their presence ensured the long-term chemical stability and reliability of the propellants, contributing to the overall performance and safety of ammunition (Elbasuney et al., 2018).

Stabilisers are essential because NC tends to decompose over time, leading to the production of dinitrogen tetroxide. Such decomposition product may act as an auto catalyst, accelerating the decomposition process. Therefore, the stabilisers serve as the scavengers of dinitrogen tetroxide, thereby extending the shelf life of propellant powder, and finally the ammunition. Stabilisers are typically added in the range of 0.5% to 2.0%. One common stabiliser used is DPA or its nitro derivatives (Wallace, 2018).

Other than that, gun propellants contain additives that are essential to provide specific required properties. These additives can be classified based on their functions, as summarised in Table 2.1 (Ahkhavan, 2022).

Table 2.1 Additives used in gun propellants (Ahkhavan, 2022).

Function	**Additive**	**Action**
Stabiliser	Carbamite (diphenyl diethyl urea), methyl centralite (diphenyl dimethyl urea), chalk and diphenylamine	Increase shelf life of propellant
Plasticiser	Dibutyl phthalate, carbamite and methyl centralite	Gelation of nitrocellulose
Coolant	Dibutyl phthalate, carbamite, methyl centralite and dinitrotoluene	Reduce the flame temperature
Surface moderant	Dibutyl phthalate, carbamite, methyl centralite and dinitrotoluene	Reduce burning rate of the grain surface
Surface lubricant	Graphite	Improve flow characteristics
Flash inhibitor	Potassium sulphate, potassium nitrate, potassium aluminium fluoride and sodium cryolite	Reduce muzzle flash
Decoppering agent	Lead or tin foil, compounds containing lead or tin	Remove deposits of copper left by the driving band
Anti-wear	Titanium dioxide and talc	Reduce erosion of gun barrel

Propellant-activated devices have a wide range of applications beyond their use in firearms ammunition. They find utility in various contexts, such as powering turbines, driving pistons, facilitating ejections in jet planes, cutting bolts and wires, controlling rocket vanes, serving as heat sources in specialized operations, operating pumps in missiles, clearing obstructed drill bits underground, initiating aircraft engines, and ejecting stores from aircraft. These devices are generally effective in power systems where precise and controlled high-force applications are required within relatively short time frames (Wallace, 2018).

2.2 Gunshot residue (GSR)

During the process of firearm discharging, projectile is discharge from the firearm along with various substances emitted from the muzzle and other potential openings within the firearm itself. The firing process in a firearm is commonly initiated by striking the firing pin on the base of a cartridge case containing the primer cup. A sequence of firing events is as shown in Figure 2.3 (Bell, 2022). This impact causes an explosion that converts the materials within the primer cup into liquid and gas phases. As this material cools down, particles are formed, including primer, propellant residues, and the metallic components from the projectile and cartridge case. The primary source of GSR is originated from the primer compound, in which additional materials to be contributed by the cartridge case, the firearm itself, and any residue from previous firings present in the firearm (Stamouli et al., 2021).

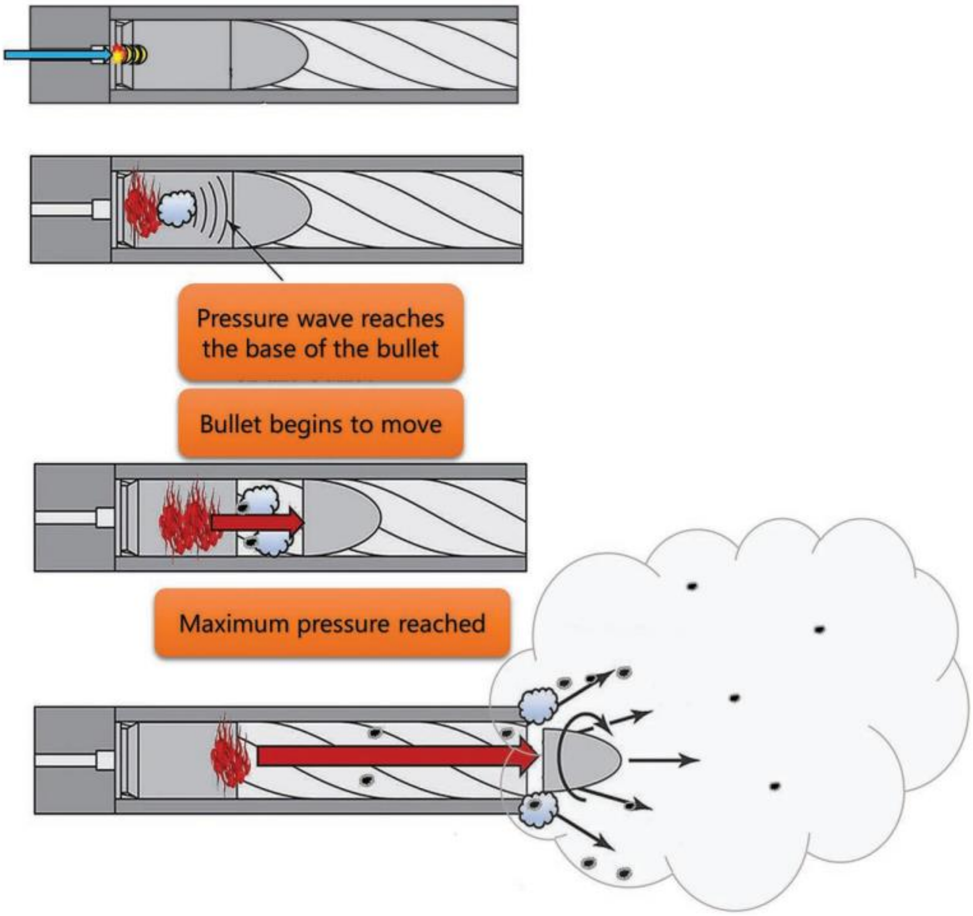

Figure 2.3 Conditions in which GSR is formed.

Source: (Bell, 2022).

GSR holds great potential to identify an individual who is involved in firearm-related cases, particularly when such evidence is recovered from his/her body surfaces (Black et al., 2021). As described in previous section, GSR consists of mixtures of both organic and inorganic compounds. Today, forensic investigators are mainly focused on the identification of IGSR based on their morphology and elemental composition. However, due to the advancements in ammunition formulation and complexities associated with GSR transference such as secondary and tertiary transfer, more comprehensive examinations and necessitate alternative analytical technique are required for definite confirmation and determination (Feeney et al., 2021).

2.2.1 Component of GSR

There are two classifications of GSR, namely the organic and inorganic GSR, respectively. Majority of organic constituents in GSR could be come from propellant and lubricant materials, while the inorganic constituents originated from the primer, propellant, cartridge case, core of the bullet jacket, and the ammunition barrel. The lubricant and propellant that literally explode to force projectile out of barrel of firearm contributes to the formation of OGSR. This included the complex hydrocarbons NG and DPA originates (Feeney et al., 2021; Grabenauer et al., 2023; Shrivastava et al., 2021).

2.2.2 Inorganic gunshot residue

IGSR comprises residues composed of metals, metal salts, or metal oxides that originate from various components such as the primer, cartridge case, projectile, or firearm. These residues consist of substances like nitrates, nitriles, and metallic particles, and they can be found in the primer, propellant, cartridge case, projectile jacket, core, and weapon barrel. Through examination, the diameter of GSR particles typically falls within the range of 0.5 µ to 10 µ (Aggrawal, 2015; Bell, 2022).

IGSR comprises metallic particles formed through the vaporisation and subsequent condensation of inorganic elements, primarily present in the primer mixture of firearms ammunition. Indicators for IGSR often include lead (Pb), barium (Ba), and antimony (Sb). These elements are sourced from compounds within the primer, namely lead styphnate ($C_6HN_3O_8Pb$), which serves as the shock-sensitive primary explosive, barium nitrate ($Ba(NO_3)_2$) functioning as the oxidizer, and antimony trisulfide (Sb_2S_3) acting as the fuel. Additionally, the primer mixture may contain other elements such as