CRANFIELD UNIVERSITY

NEVEEN ABDEL-KARIM

THE CHARACTERISATION AND PROVENANCE OF AMMUNITION COMPONENTS

CRANFIELD FORENSIC INSTITUTE

Security and Defence

MSC BY RESEARCH

Academic Year: 2015 - 2017

Supervisor: Dr James P. Shackel

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ABSTRACT

The objective was to create a comprehensive data set of analytical results relating to the physical construction and chemical composition of ammunition components; to be used to determine the provenance of ammunition. The study focusses on 7.62 x 39 mm ammunition due to its ubiquitous nature in crime and conflict zones around the world.

Ammunition identification and classification currently relies heavily on the information provided on cartridge case headstamps and packaging. In the absence of this information, there is no definitive method to ascertain the potential origin of ammunition. The aim of this study was to examine the physical and chemical composition of ammunition components from different origins in an attempt to establish if the construction and elemental composition of these components could be used to differentiate between sources of ammunition.

Initially, various physical and chemical techniques were employed to analyse samples of ammunition from known sources. Currently, there are 24 known countries and 42 known manufacturers who produced 7.62 x 39 mm ammunition (Ness and William, 2011). This study aimed to analyse a representative sample of 7.62 x 39 mm ammunition to determine if differentiation between the manufacturers is feasible. A further temporal study was explored to establish if differences in the materials and manufacturing techniques occurred in a single manufacturing plant over a period of time.

A detailed analysis of ammunition components generated information pertaining to differences particular to each manufacturer’s ammunition. It is reported that there are sufficient distinguishing features between the 7.62 x 39 mm ammunition analysed, and can be said with a degree of certainty that a particular round of 7.62 x 39 mm ammunition could have originated from a particular manufacturer.

This research was conducted with the ambition of creating a publication to be used by professionals and academics in relation to identification of ammunition origin. Working with Cranfield University to contribute to work conducted by national and international organisations it is presented as a database set; to be used as a reference where standard forensic techniques currently provide no information of the provenance ammunition origin. Promising results provide avenues for further research to be continued temporally or even into other calibres – ultimately comprising of a resource that is invaluable to many.

Keywords:

7.62 x 39 mm, manufacturer, M43 projectile, projectile, cartridge case

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
AAS	Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
Ag	Silver
ANOVA	One-Way Analysis of Variance
As	Arsenic
Ba	Barium
BATFE	Bureau of Alcohol, Tobacco, Firearms and Explosives
Bi	Bismuth
CBLA	Compositional Bullet Lead Analysis
Cd	Cadmium
CDR	Cartridge Discharge Residue
CT	Computed Tomography
Cu	Copper
DB	Double-based
EAC	Elemental Analysis Comparison
FBI	Federal Bureau of Investigation
FDR	Firearm Discharge Residue
Fe	Iron

GFAAS	Gas Furnace Atomic Absorption Spectroscopy
GSR	Gunshot Residue
Hv	Vickers Hardness
ICP	Indcutive-Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IGSR	Inorganic Gunshot Residue
Kg	Kilogram
NAA	Neutron Activation Analysis
Nb	Niobium
NC	Nitro-cellulose
NG	Nitro-glycerine
Ni	Nickel
NISAT	Norweigan Initiative on Small Arms Transfers
NRC	National Research Council
O	Oxyen
OGSR	Organic Gunshot Residue
Pb	Lead
ppm	parts per million

S	Sulphur
Sb	Antimony
SB	Single-based
SEM	Scanning Electron Microscope
Si	Silicon
Sn	Tin
U.K.	United Kingdom
U.S.	United States
UN	United Nations
XRF	X-Ray Fluorescence

1 Chapter 1: INTRODUCTION

Ammunition is often overlooked in its complexity. Containing several components, each serves a specific purpose and is manufactured with great precision. The intricacy of ammunition and its development has been studied extensively with many attempts to characterise different parts. 7.62 x 39 mm ammunition - associated with the infamous AK type assault rifles - is abundantly present. Initially designed by the Soviet military, this ammunition is now manufactured globally and traded commercially. There are published variations between manufacturers [1]; differences in mass, elements, propellants etc. which have been noted individually, however no study of this size has ever been conducted to combine the comparison of these characteristics. The popularity of Avtomat Kalashnikova (AK) model rifles is reflected in the prominence of 7.62 x 39 mm ammunition - making it the ideal calibre for this study.

The Small Arms Survey (SAS) and Conflict Armament Research (CAR) have highlighted the scale of this issue. Recent publications (2014 & 2015) calculated that 46% of ammunition found across seven studies was of this particular calibre; demonstrating its widespread and ubiquitous distribution. Some studies report the presence of ammunition that lacks a headstamp or any packaging. Similar cases reiterate the implications; though the origin cannot present the flow of illicit ammunition, it identifies points of diversion. In the absence of this, there are new challenges for Non-Government Organizations (NGOs) to overcome when trying to determine patterns of illicit trade.

Around 535,000 people die every year due to armed conflict, gang disputes, and domestic violence; primarily using firearms and ammunition that have been obtained illegally [2]. Determining the origin of illicit products is the first step in mitigating its trade. The current method of identification relies heavily on headstamps (described below) and packaging. This places limitations in identification on ammunition examiners when these are not available. This research is designed to overcome these issues by utilising established analytical techniques (discussed below) to develop a method that can identify the origin of the ammunition; improving the prospects of mitigating illicit trade and potentially reducing related fatalities. The long term results would be improved social, cultural and economic stability.

Traditionally, scientists utilise information stamped into the bottom of ammunition casings – known as a headstamp. This information implicitly details the manufacturer, but may be purposefully omitted in order to conceal these details, especially in warfare. In the absence of a headstamp, there is currently no standardised method for determining the origin of ammunition. In some instances, educated assumptions are made based on similarities between ammunition from known and unknown sources. Research using new techniques, (such as inductively-coupled plasma discussed in **Section 2.2.1.1**), have been explored, however the equipment involved is expensive and involves a highly skilled operator for detailed analysis. Therefore, it is not feasible for most forensic or government organisations to use such techniques. The increasing frequency of ammunition devoid of a headstamp prevents the current forensic methods from being used. Successfully differentiating between ammunition based on its chemical and physical composition targets the current obstacles faced by researchers.

This project is designed to employ established analytical techniques to develop a low cost and efficient method to differentiate between ammunition (both the casing and the projectile) from different sources. Analysis of ammunition involves conventional methods for different components: microscopy is used for analysis of physical markings; a scanning electron microscope is used for the examination of gunshot residue (the substance released upon discharging a firearm). Elemental analysis of the metals used can be conducted using X-ray fluorescence, whilst microindentation hardness testing may reveal variations in manufacturing methods. Combining these techniques will facilitate the development of a method that will hold up to scrutiny and provide definitive results for interpretation.

Utilising well established techniques is cost effective, efficient and requires no change in facilities/training. Conducting this research will produce a data set that will assist in identification of ammunition origin in the absence of a headstamp. Ammunition is often overlooked when it comes to global security. The Arms Trade Treaty (2013) is the first political agreement to implicitly include ammunition, which was previously omitted. Disrupting the supply of ammunition has the potential to immediately disengage those involved in armed conflict. This research is targeted at assisting military, police, security services and NGOs in their task of mitigating the illicit trade of ammunition, in order to improve social, economical and political stability.

The null hypothesis for this research is that there are no significant differences between the physical and chemical composition of ammunition components. Conversely, the hypothesis is that such differences are significant. Such differences would allow for characterisation of ammunition and the potential for determining provenance.

2 Chapter 2: AMMUNITION

2.1 History of Ammunition

For this paper, ‘ammunition’ will be used to describe the combination of the following components: the projectile, the cartridge case, the propellant and the primer. Ammunition is essential for use of firearms which are designed to convert the chemical energy stored in ammunition propellant, into kinetic energy. This conversion causes the ‘firing’ of the projectile down the barrel of the firearm at high velocity [3].

The history of ammunition began in China between 1200 and 1300 years ago; the Chinese developed and utilised gunpowder (also known as black powder) in their fireworks. Approximately 700 years ago that Western countries adopted gunpowder and originally utilised it for cannons in Europe. Black powder was later developed for propellant in muzzle loading firearms, however, it possessed undesirable characteristics that prevented it from being safely stored; being susceptible to moisture and having a low combustion rate. Furthermore, the excessive residue produced, caused fouling of the weapon barrel [4], [5].

Further advancements during the 1860’s and 1870’s facilitated the employment of smokeless powders and toward the end of the 19th Century, a nitrocellulose-based smokeless powder was developed. These were more powerful than black powders and caused less barrel fouling. Additionally, they were safer to transport and store [6]. Variations of such powders are found within the self-contained rounds of ammunition that are now ubiquitous. It is the ignition and expansion of these gases that causes the projectile to be fired down the barrel, while the cartridge case expands. Ammunition as we know it today is a result of 760 years worth of technical development resulting, from *muzzle loading* to *breech loading* rounds of ammunition [3], [7].

Industrially produced until late in the 19th century, muzzle loading rounds of ammunition were widely available for purchase. Often referred to in literature as “Antique” ammunition, the operator was required to individually weigh out the black powder, insert wadding and load the projectile into the muzzle end of the firearm. Muzzle loading ammunition is named as such based on how it is utilised with the main differences between it and breech loading ammunition (discussed in **Section 2.2**) being the absence of a primer and cartridge case. There were many endeavours to make this process more efficient with attempts at containing the elements continuing until approximately 1850 when the ammunition became ‘self-contained’ [7]. Muzzle loading ammunition typically consists of a non-metallic cartridge (such as paper/percha), containing a pre-determined quantity of black powder and a projectile. Production of paper cartridges is low cost. Conversely, they must be handled delicately and afford almost no defence against moisture – this can in turn affect the performance of the ammunition. The projectile is a spherical ball composed of lead [3].

It is arguable that muzzle loading ammunition would be obsolete were it not for nostalgic shooters who (in some instances) still use black powder. There has been an increased level of interest recently which has influenced manufacture’s to produce ammunition that mimics the older designs for use with replica firearms [7].

The development of the ‘self-contained’ round of ammunition was a stepping stone to develop new methods of reloading. Being able to reload the firearm at a portion closer to the operator was safer and more effective, thus firearms were developed to open using various mechanisms and breech loading ammunition was industrialised.

2.2 Ammunition Components

Also referred to as “modern” ammunition, the components are all contained within the cartridge case. For most mass produced rounds of ammunition, they are ‘fired’ when the pin from a firearm strikes the primer. This material ignites and consequentially ignites the propellant within the cartridge case. The expansion of these gases causes enough pressure to expel the projectile down the barrel of the firearm, simultaneously creating a seal to prevent gasses escaping back into the firearm chamber. **Figure 2.1** shows this process for a centrefire round of ammunition (varying types are discussed later in **Section 2.2.2**).

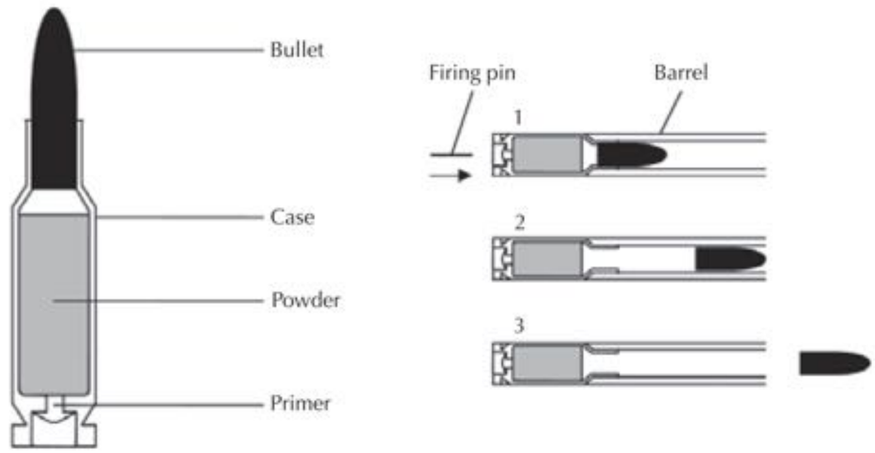

Figure 2.1 Components and operation of a round of centrefire ammunition [8].

Manufacturers will set the engineering standards for ammunition based on their purpose [3]. For commercial and military purposes, the majority of ammunition is breech loading with the calibre relating to the maximum diameter of the bullet and the overall length of the case (e.g. 7.62 x 39 mm represents a diameter of 7.62 mm with a case length of 39 mm). It is worth noting that ammunition is referred to using both metric and imperial measurements and the two are used interchangeably. The focus of this research is small arms ammunition – defined by the United Nations as rounds with a calibre below 12.7 mm [8].

2.2.1 Projectile

The term “bullet” is often used interchangeably to describe a part of/all of each round of ammunition – describing the projectile (as in **Figure 2.1** above), or the collection of components (i.e. the projectile, cartridge case, propellant powder and primer). This paper will use the term “projectile” to avoid such confusion. This is the component of the ammunition that is expelled down the barrel of a firearm and discharged. Desirable characteristics require projectiles to have a high degree of accuracy and retain the majority of its weight (in order to achieve reliable penetration) [7].

The historic development of projectiles is discussed in ammunition literature and will not be covered here [4], [9], [10], [11]. Only conventional ‘modern’ projectiles and variations will be described. Typically, the projectile is elongated, almost cylindrical in shape, with a ‘coned’ end. Although there are differences between projectiles they generally have the following components: metplat, tip, ogive, body, cannelure, groove, core, heel, base, shown in **Figure 2.2** [3].

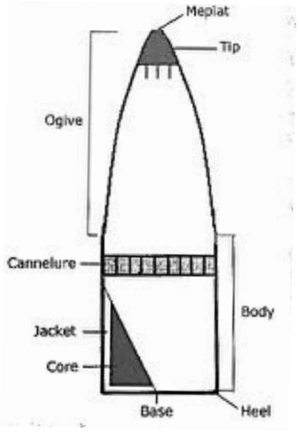

Figure 2.2 Projectile features [1].

Projectiles may be *monolithic*, meaning that they are composed of a single piece. This is most commonly lead or a lead alloy and antimony is typically used as it improves the strength of lead. Lead is an appropriate metal due to its properties; it is relatively soft, dense and malleable. Attempts to link projectile lead to a common ‘source’ have been investigated and are discussed in **Section 2.2.1.1**.

Projectiles are most commonly made by *casting* or *swaging* [3]. Casting involves heating the metal to its molten form and pouring it into a mould or cast. Once cooled, the cast (which is typically hinged) is opened and the projectile removed with any defects being cut/filed away. Swaging occurs in the absence of heat and is known as a cold forming process. The required mass is measured from an extruded wire and positioned within a die made of a harder material with one end ‘open’ so that pressure can be applied. This is done using a metal punch and the pressure encourages the the material within the die to take the shape of the cavity. Excess metal is squeezed out of bleed holes. Several steps may be present to add features and defects are removed as above. This type of projectile often has a lubricated surface in lieu of a *jacket* [3].

As firearms developed, so too did projectiles. Improved bolt strength and increased pressures of nitrocelluslose based powders required the projectile to evolve to withstand the increasing forces [7]. Most commercial and military projectiles are lead coated with a layer of a harder metal (usually *gilding metal* – a brass alloy of 90 to 95% copper and 5 to 10% zinc) referred to as a *jacket* [7]. This alloy is known to posses a desirable low work-hardening rate. In some cases, the projectile may have a steel jacket which has been coated in copper or has a lacquer present to help prevent oxidisation (rust).

The manufacture of jackets usually involves 'punching' a circular piece of metal from a sheet (similar to the mechanism used by a paper hole-puncher). The alloy is unlikely to be soft enough to cold work it and must be annealed (heated) before it is placed into a series of dies that ultimately form the jacket shape (**Figure 2.3**). The jacket thickness is normally regulated by the manufacturer, with the lead portion being inserted or otherwise assembled [12].

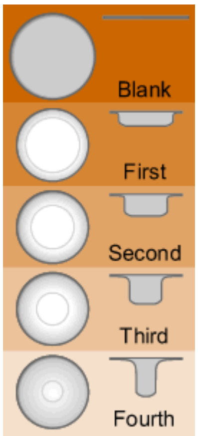

Figure 2.3 Draw operation and expanded projectile [12].

The use of a jacket can prevent deformation of the lead core and aid in penetration. Jackets have been thought to decrease the level of friction between the projectile and the barrel of the firearm and also prevent *fouling* [7]. In a forensic context, the jacket of the projectile is frequently useful in determining the type of firearm that it has been discharged from. Spiralled grooves cut into the bore of the firearm barrel are designed to give the projectile gyroscopic stability during flight. The *grooves* are the lower areas in the barrel and will result in higher areas on the surface of the bullet due to minimal contact. The lower areas on the surface of the bullet are caused by *lands* in the barrel which are protrusions. Analysing the number, width and twist direction of the lands and grooves of the barrel rifling may assist in identifying the type of firearm used [13], [14].

Variation is present between the projectile jackets. Whilst manufacturers dictate the name of their products, these can generally be divided into the following three groups: *Full Metal Jacket* (FMJ), which can be misleading to those not familiar with projectiles; although the term suggests that this type of projectile would be completely covered, there is a part of the base which indeed remains uncovered with a small amount of lead exposed. *Total Metal Jacket* (TMJ) is in actuality a completely covered projectile with no lead exposed. Finally, *Semi-Jacketed* (SJ) projectiles have the tip of the lead exposed and this is relevant to the functionality; encouraging the projectile to 'mushroom' upon impact as the end expands and changes shape. Once a projectile has come into contact with the target it is likely to deform, altering so greatly in shape that identification of the ammunition relies heavily on the jacket. This variation in projectile morphology and behaviour is pivotal when considering wound ballistics: i.e. the creation of permanent/temporary cavities [15].

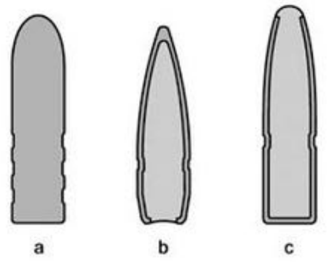

Figure 2.4 Cross sections of various types of bullet. **a.** Solid lead. **b.** Full metal jacket **c.** Semi-jacketed [16].

Another component that may survive the impact is a *core*; a cylindrical component within the lead of a projectile. Steel or tungsten is often present in military rounds displacing some of the lead used. These harder metals are linked to the function of the projectile – such as in armour piercing ammunition –

and may also be present alongside the aforementioned jacket. Steel is also commercially preferential due to its lower price [17]. The core may vary physically (with regards to the dimensions and mass) or it may vary elementally; often composed of mild steel, the specifications for this material have high tolerances as shown in **Table 2.1**.

Table 2.1 A table showing the ASTM grade designations and chemical compositions (weight percent, (wt.%)) of carbon steel bars [18].

GRADE DESIGNATION	**CHEMICAL COMPOSITION LIMITS (WT.%)**			
	Carbon	**Manganese**	**Phosphorus, max**	**Sulphur, max**
1010	0.08 – 0.13	0.30 – 0.60	0.40	0.05
1011	0.08 – 0.13	0.60 – 0.90	0.40	0.05
1012	0.10 – 0.15	0.30 – 0.60	0.40	0.05
1013	0.11 – 0.16	0.50 – 0.80	0.40	0.05
1015	0.13 – 0.18	0.30 – 0.60	0.40	0.05
1016	0.13 – 0.18	0.60 – 0.90	0.40	0.05
1017	0.15 – 0.20	0.30 – 0.60	0.40	0.05
1018	0.15 – 0.20	0.60 – 0.90	0.40	0.05
1019	0.15 – 0.20	0.70 – 1.00	0.40	0.05

A steel core may also have different microstructural properties dependent upon the cold-working of the material. It must be respected that metallurgy is a study in itself and cannot be covered in detail here. Ferrous materials in particular can be studied in great detail and their microstructures will reveal manufacturing processes. The importance of this becomes apparent when reminded that a projectile is likely to deform/fragment when fired and the physical aspects (dimensions) may be difficult to examine. The softer materials (lead and gilding metal) are likely to be significantly damaged and the examination of elemental and metallurgical properties may provide invaluable information in establishing links to the manufacturer [18].

Not all projectiles will have a core present. An additional disparity may be the presence of an 'air pocket' as shown in **Figure 2.5**.

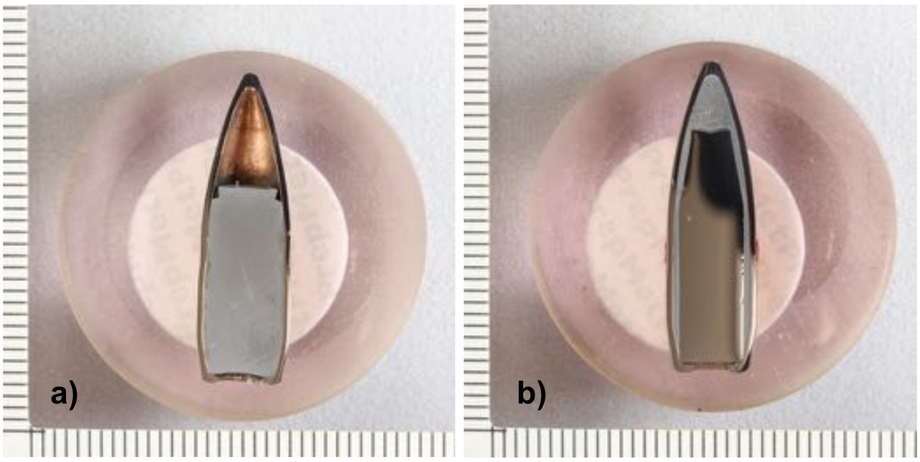

Figure 2.5 Photographs of sectioned and polished projectiles a) with a lead core and an 'air pocket' present, and b) with a steel core and no 'air pocket' present..

This air pocket has been known to have an impact in wound ballistics. This research will not focus on the area of wound ballistics, however, it is worth noting that adaptations have been made to induce *yawing* at an earlier stage; causing the projectile to change projection upon impact and impart more energy into the target.

Further variations of projectiles may be seen in the *ogive, body, core, heel and base* shapes and are covered extensively elsewhere [3].

2.2.1.1 Projectile Lead

Often when discharged projectiles are recovered, they are too significantly deformed or fragmented for visual comparison. Furthermore, the firearm from which they were discharged may not be available or functioning for comparison. Projectile lead has been analysed in an attempt to link projectiles to a common 'source' and make associations between samples from crime scenes and suspects. This protocol was developed by the United States Federal Bureau of

Investigation (FBI) with Dr Vincent Guinn as the “practice’s pioneer” [19]. Referred to by the FBI as compositional bullet lead analysis (CBLA) this paper will utilise the more commonly employed acronym EAC (elemental analysis comparison) [20], [21]. CBLA was established on the premise of three assumptions:

1. A projectile or projectile fragment is compositionally representative of the ‘source’ from which it originates.
2. The molten source from which the projectile originated is homogenous in its composition.
3. Each molten source of lead has an elementally unique composition [19] [22].

In order to address these suppositions the importance of metallurgical and manufacturing processes should be considered; some literature suggests that this did not occur during the development of CBLA techniques [21]. A basic overview of the manufacturing process is described below.

Lead’s ability to be recycled effectively [23] means that the majority of lead used comes from recycled or secondary refiners, whose main source is spent-lead acid batteries. The quality control standards are dictated by the requirements of the battery community and not the production of ammunition, which utilises less than 5% of refined lead annually. Trace elements must be below a maximum level, typically: arsenic – 0.10%, tin – 0.15%, copper – 0.10%. (bismuth, and silver are also present) but exact values are not required [21], [22]. Antimony, arsenic and tin are initially removed, then bismuth is removed in a separate process. The removal of silver is generally only conducted during primary lead refining [21]. Antimony may be added as an alloying element however the range depends on the ammunition manufacturer; Randich et al. quotes “0.6 – 0.8%” and “0.6 – 1.1%” for two manufcaturers, demonstrating varying ranges [21].

In the United States, ammunition manufacturers will obtain lead from refiners. This may be as a cylindrical billet that requires no further preparation before being extruded into lead wire although these are more expensive. In most cases, lead is supplied in the form of cast ingots (also known as pigs) that weigh 30 – 60 kg, provided in batches of 20,000 – 100,000 kg. Continuous oxidation and stratification causes inconsistency within ingots, thus discrediting the certainty of homogeneity. Furthermore, the phenomenon of segregation causes ingots to solidify from the outside first (as this is cooler), with the core being the last area to solidify [21], [22]. Peele et al., addressed concerns over the “variability [of the elemental mix] within a production run” in 1991 [24]. Another study by Koons and Grant showed that even during a pour elemental concentrations can vary greatly, with a 60% decrease in the amount of tin occurring over 30 minutes [25].

The billets are then extruded through dies to form wires, which are then cut (into slugs) with the length and diameter to fit the intended calibre. Once pressed into shape these slugs are randomly deposited into bins. Some manufacturers box ammunition immediately whilst others will be stored until ordered; they will then be unsystematically selected and boxed. These arbitrary methods can lead to mixing at many stages during manufacture and negate claims of batch uniqueness [20], [26], [19].

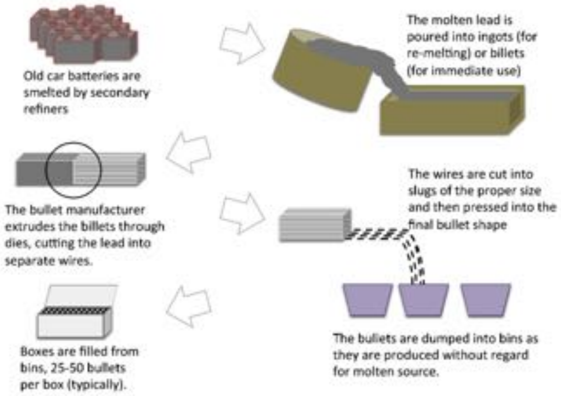

Figure 2.6 Bullet manufacturing process [22].

Various elemental techniques have been employed to determine if it is possible to distinguish between elements present in projectile lead, and consequentially, to link projectiles to a common ‘source’. EAC has been explored for over 40 years using a number of analytical techniques, outlined below.

Atomic absorption spectrometry (AAS), allowed for low detection limits, however, it only allowed for analysis of a few elements and proved time-consuming. Atomic spectrometry provides scientists with the ability to identify and quantify elements. This technique involves the use of a flame, furnace or plasma to disturb the composition of a sample – information regarding the concentrations can then be obtained [27] by the resulting absoption/emmision. The most commonly used form of atomic spectrometry used is AAS [28], [29]. A portion of the light source is absorbed by atoms, rather than reaching the detector. Another variation is the atomic emission spectroscopy (AES), whereby the detection is dependant on the emission (energy lost) by atoms in an excited state. This excitation is thermally conducted as the dissolved sample is sprayed into the flame. The lights emissions are measured by their intensity and the lines produced are used to determine the elements within the sample [27]. Blacklock et al., utilised this technique to analyse shotgun pellets (in response to relevant crime in the UK) and reported that not only could "chemical analysis for the elements antimony, arsenic, bismuth and copper [can] distinguish between shot-gun pellets from different manufacturers", but also between batches. They concluded that analysis of the aforementioned elements would add value to evidence, however, identification could not be made based solely on lead pellets [30]. Following this, Kramer claimed that using indium as an internal standard provided more precise and accurate results [31]. Both methods detect the radiation (whether absorbed or emitted) at a specific wavelength and can determine concentrations at parts per million (ppm) [27].

Guinn and Lukens utilised neutron activation analysis (NAA) to identify and quantify (ppm) the radioactive elements in each sample, and this was initially the technique utilised for CBLA analysis by the FBI [19], [32]. NAA relies on the theory that irradiation and decay produce qualitative and quantitative data on all elements present within samples; exploiting the specific energies emitted from the atoms' nuclei. Whilst eight elements were reported in projectile lead (antimony, silver, copper, magnesium, chlorine, sodium, manganese, and aluminium), Guinn emphasised that antimony was the most important trace element, followed by silver and noted the persistent presence of copper. This resulted in analysis of these three elements with the aim of proving two hypotheses:

1) *That it possible to accurately measure the amounts of antimony, silver, and copper in a given sample of bullet material*.

2) *That bullets of different calibres, from different manufacturers, from different manufacturing lots, and from different individual bullets within a given lot or box have distinctive and unique amounts of antimony, silver and copper.*

Whilst Guinn and Lukens claimed that they had made progress toward ‘bullets of common origin [having] the same composition, and bullets of different origins [having] different composition” their conclusions reported that the pattern of trace elements present in various bullet leads proved not to be distinctive for individual brands, lots or bullets. Despite having identified antimony as the most important trace element, problems arose where manufacturers had the same levels of this element present. In some instances, other elements (copper and lead) allowed for differentiation, however, this was not always possible. Guinn and Lukens concluded that there was a “28% chance that whole bullets with the same antimony level may have a different origin" – an arguably high percentage [32].

Guinn et al. also explored the importance of antimony, copper, and arsenic, however, the aforementioned issues were still present and less than 50% of projectiles could be categorised. The authors concluded that “a significant difference in concentration of any one of the three elements between two bullet specimens indicates that they came from different lots, but that matching concentrations of all three elements does not indicate that two bullets came from the same lot” [33]. Whilst NAA has the advantage of low detection limits, only a few elements can be analysed. Additionally, it requires access to a detector. Regardless of claims that characterisation of a source could not be made based on three or four elements, these claims (and more) were still made in the courtroom.

Advancements in analytical techniques saw the use of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (later known as inductively coupled plasma-optical emission spectroscopy (ICP-OES)) employed for EAC of projectile lead. This resolved some of the issues with the inadequate sensitivity of AES, the flame traditionally used has been replaced by the use of an inductively coupled flame (ICP), it also allowed for analysis of more elements when discriminating between samples. Achieved by ionising a flowing gas (e.g. Argon) in a magnetic field, comparatively more elements can be analysed owing to the range of temperatures that can be attained – up to 10,000 K. This technique also allows for sensitive measurements of concentrations at ppb instead of ppm [27]. ICP-OES has been utilised where ammunition is too impaired to conduct physical analysis in order to attempt to associate it to a source. One disadvantage of ICP-OES is that it is a destructive technique, requiring acid digestion of approximately 60 milligrams of each sample of bullet lead. This trace elemental analysis involves dissolving sample in nitric acid and analysing for the following elements: Sb, Sn, Cd, As, Cu, Bi and Ag. Presence of these (in combination) may allow determination of sources of projectiles [27], [29]. Tobin summarises key finding within literature that refute the above claims:

- Tin was not always present.
- Bismuth and silver are poor discriminants based on narrow, yet consistent ranges (an observation that has been testified to by CBLA experts).

Tobin concludes when the exclusion of these elements – in conjunction with cadmium’s rarity – results in analysis of three elements and is reflective of earlier uses of NAA for EAC. As such, this technique is open to the same criticism that three or four elements cannot be used to characterise a ‘source’ [19].

Inductively coupled plasma mass spectrometry (ICP-MS) has been utilised to explore EAC. This method involves atomising the sample and converting them to a stream of ions [27]. The ions are typically positive with a single charge and are divided based on their mass-to-charge (*m/z*) ratio. The separation is characteristic of mass-spectrometry which involves the use of a magnetic field to distinguish between ions based on their mass. This method is used to conduct analysis of atoms, molecules and molecular fragments and may be qualitative or quantitative [27], [34]. This technique is more sensitive that AAS and ICP-OES however, results can be erratic due to suppression of signals [34], [35]. Rectifying this issue increases the amount of time required for preparation and lowers the precision and accuracy of the element measurements [35]. Keto explored EAC using ICP-MS and concluded that the analysis of eight elements could provide information on the "rarity" of "commonality" of compositions, however, lead analysis "does not generate individualising information" [36].

Randich et al. addresses the three assumptions mentioned at the start of this section and highlights uncertainty relating bullet lead based on compositional analysis [21]. The first two premises for CBLA combined to present a paradigm where bullet fragments were representative of the molten source of lead, and that these ingots or billets of lead were homogenous. With an understanding of the manufacturing process these assumptions seem questionable and have been disputed by studies describing metallurgical principles and phenomena [19], [20], [22]. The FBI required three, 60 mg samples of lead and had been criticised for believing this to have been a representative sample. Koons references the manufacture of approximately nine billion bullets annually from between "85 and 118 million pounds of lead" [22]. Tobin speculates that as many as "1.53 billion samples with different compositions" could be contained within one 100 ton lot of lead. His research concluded that a single lot could vary from the beginning to the end of the pour in terms of the content of antimony (12%), copper (142%), tin (1,871%), or arsenic (31%), thus contradicting the assumption of homogeneity [19]. The National Research Council (NRC) advised in its review that "if a source is not homogeneous, no bullet can be representative of the source" [20], thus it is inconceivable that 60 mg sample could have been representative of the 'source'.

Randich results show that lead 'sources' from 12 years apart that were not "analytically indistinguishable", disputing the final conjecture of CBLA that lead ‘sources’ have a unique composition [21]. Known as ‘repeats’, Tobin discusses how this is attributable to the strict specifications for battery lead (which is recycled for projectile lead) [19], [22]. Gianelli comments that the significance of CBLA would be improved if fewer bullets had the same elemental composition [37]. The NRC provides a comprehensive review of CBLA and refers to additional issues including “the definition of a source of lead, the distribution of bullets and loaded ammunition, and the validity of specific statements made in court by expert witnesses” [20].

Despite a lack of supporting evidence in scientific literature, testimony was given in criminal cases involving the FBI advising that ammunition has come from “the same box” or was manufactured “about the same day”, some claims have even concluded that ammunition could have been made at “exactly the same time”[1]. Used exclusively by the FBI in over 2,500 cases, CBLA was discontinued in 2005 following a report by the Committee on Scientific Assessment of Bullet Lead Elemental Composition Comparison and National Research Council [20]. Concerns were raised about the presentation of results. Whilst CBLA could prove useful in determining whether two bullets could had come from the same compositionally indistinguishable volume of lead, it did not have the “unique specificity” of other forensic techniques and that the limitations should be communicated. Whilst the FBI still supports the scientific foundation of CBLA , it cited that the significance of a “match” could not be explained by manufacturers nor scientists; something that should have been assessed when the technique had been rejected by other USA forensic laboratories, due to unreliability. For these reasons, as well as practical limitations, CBLA was not considered for this research.

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[1] State of Florida vs. Michael Mordenti, Hillsborough County Case #90-3870, 1990.
State of New Jersey vs. Michael Scott Behn, 164 N.J 561, 753 A.2d 1153 (N.J. 19 May, 2000) (Table No. C-1022 Sept Term 1999, 49, 201.
State of Colorado vs. Timothy John Kennedy, Trial Court395CR4541, App.#97CA2006.

2.2.2 Cartridge Case

The purpose of the cartridge case is to safely contain and protect component parts – especially during transit and use (loading). Furthermore, cartridge cases must withstand the heat and pressure applied as a result of the propellant ignition and gasses released.

Generally, there are three types of cartridge cases that are widely accepted; *rimfire*, *centrefire* and *shotshell* [3]. This paper will not discuss shotshell cartridges and will focus primarily on centrefire cartridges, however, to understand and appreciate their benefits, it is important to understand the functionality of rimfire cartridge cases.

Rimfire cartridge cases owe their name to the configuration of the head of the case where the primer is situated. This primer is in an inactive state and the process of insertion is inexact [3]. The cartridge cases are usually cylindrical (although they can also be necked) with projectiles typically crimped so as to aid the ignition. Although they are often used due to their low cost and reliability, rimfire cartridge cases are known to have fundamental flaws in design including a weak case; this sets boundaries with regards to the level of pressure that can be withstood in the breech. These lower pressures translate into restricted ballistic performance [3].

In centrefire cartridge cases, the primer is located in the centre of the case head, going forward this type of cartridge case will be exclusively discussed and referred to simply as a ‘cartridge case’. **Figure 2.7** illustrates the various parts of a typical cartridge case and **Figure 2.8** displays three commonly observed alternative shapes. *Bottlenecked* cases have a reduced diameter at the mouth of the cases where the projectile is secured. The rest of the case has a wider diameter with the shoulder angle being dependent upon the difference in size between the mouth and the body. This shape permits an increased of volume for smaller diameter projectiles that cannot be achieved with *straight cased* cartridges. A *tapered case* has a gradual reduction in diameter along the body of the case. Many bottle neck cases are also tapered [38].

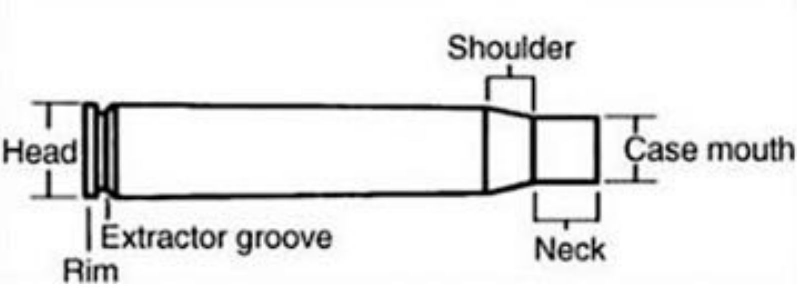


Figure 2.7 Cartridge case parts [38].

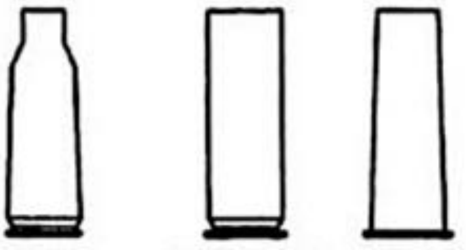
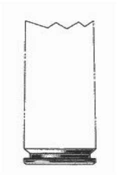


Figure 2.8 Cartridge case types (from left to right): bottlenecked, straight, tapered [38].

One pivotal advancement with regards to the size of cartridge cases concerned the development of nitrocellulose based propellants; utilising the increased power of the propellants allowed for a decrease in the diameter of the cartridge cases [3]. Longer cases are able to contain more powder where higher velocities are required. The head of the cartridge also contains the lesser known "web of the case" [3] not shown in **Figure 2.7** as it exists internally. This is a solid portion of brass (or steel) between the base of the cartridge case and the primer pocket. There are five universally accepted formations of cartridge case heads shown in **Table 2.2** below:

Table 2.2 Cartridge case formations [39].

Name	Image	Defined By
Rimmed		The diameter of the rim **extends beyond** that of the body of the cartridge case. There is a **small undercut** present on the head.
Rimless		The diameter of the rim **corresponds to** that of the body of the cartridge case. There is a **profound extractor groove** present on the head.
Semi-rimmed		The diameter of the rim **extends beyond** that of the body of the cartridge case. There is a **profound extractor groove** present on the head.
Rebated		The diameter of the rim **is less than** that of the body of the cartridge case. There is a **profound extractor groove** present on the head.
Belted		The diameter of the rim **corresponds to** that of the body of the cartridge case. There is a **belt of greater diameter** and an **extractor groove** present on the body.

The names of some of the above may be misleading and it is worth noting that all cartridges cases have rims of varying diameters.

The majority of cartridge cases are manufactured from brass comprised of 70% copper and 30% zinc with elemental impurities (Pb, Sn, Fe, O, etc.) kept to less that 0.5% [39], [40]. “70/30 brass” is known to have the most desirable properties; it is available globally, resistant to rust, and possesses good ductility and strength (much more so than pure copper) as shown in **Figure 2.9** below [3], [38], [40].

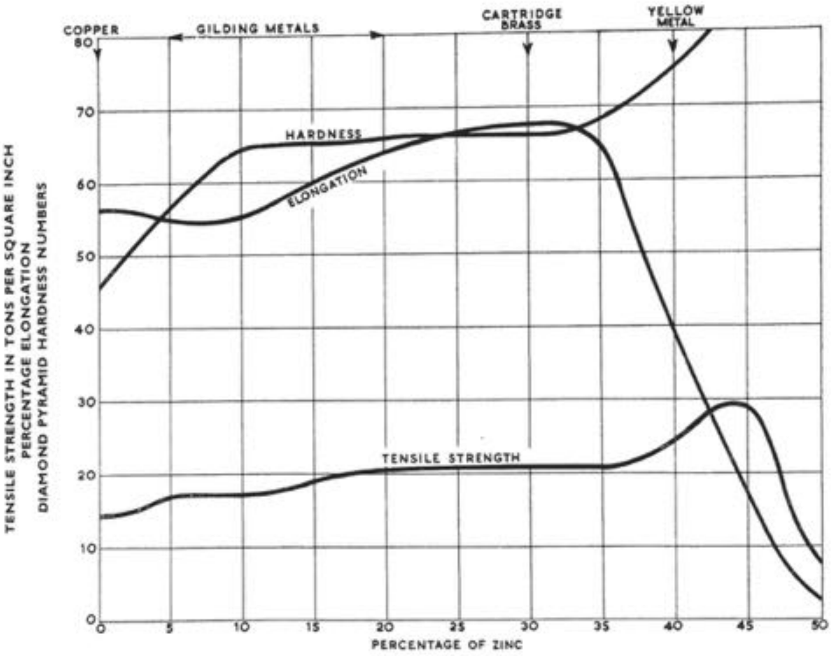


Figure 2.9 Mechanical properties of annealed copper-zinc alloys [41].

These properties make 70/30 brass ideal for the cold deep drawing involved in cartridge case manufacture. A *disc* is initially punched from a sheet and then pressed by a ram into a die, forming a cup (*cupping*) [17]. The cup is driven through a die and elongated – this drawing is done in stages with the brass being intermittently annealed (heated and softened) to remove stress. The cup will also be upturned and supported by a bolster in order to perform *indenting* (for the primer cap), *heading* (pushing the sides of the case head outwards to create a rim) and in some instances *tapering* [17]. Although production varies with each manufacture, the main stages are shown in **Figure 2.10**.

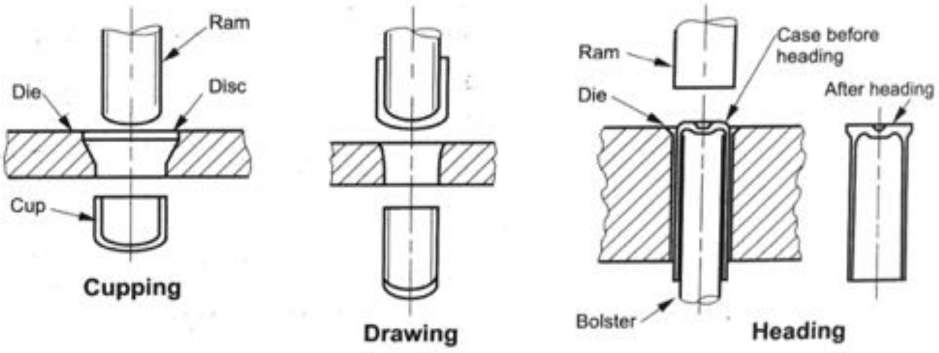


Figure 2.10 Main stages of cartridge case manufacture [17].

These forming operations have an impact on the metallurgical properties of cartridge cases. Residual stress (especially in bottle necked cases) requires high-temperature annealing in order to prevent issues such as cracking; this involves heating to its critical temperature and allowing it to cool slowly (in water). The most common method of annealing is by using a gas flame, however, induction flames have also been employed by ammunition manufacturers. Detailed methods have remained unpublished due to their commercially sensitive nature, however patents assigned to ammunition companies have been published [42]–[46]. In addition to this, some companies advertise the use of induction annealing, claiming it allows them to “control the temperature applied to each casing” [47] and “gives brass the consistency requirements required for increased reloading opportunities” [48].

Flame annealing causes discolouration to the area (shown in **Figure 2.11**), although for cosmetic reasons, this may be polished until no longer visible [28].

Figure 2.11 A round of ammunition showing discolouration of the cartridge cases where flame annealing has occurred (the neck and shoulder area) [12].

Heating of the neck and shoulder area causes an increase in the grain size and cooling then sets the microstructure, thus, larger grains will be present at the mouth of the cartridge case with a decrease in grain size at the base. This property is imperative to the cartridge case function and correlates to the hardness gradient along the cartridge case wall.

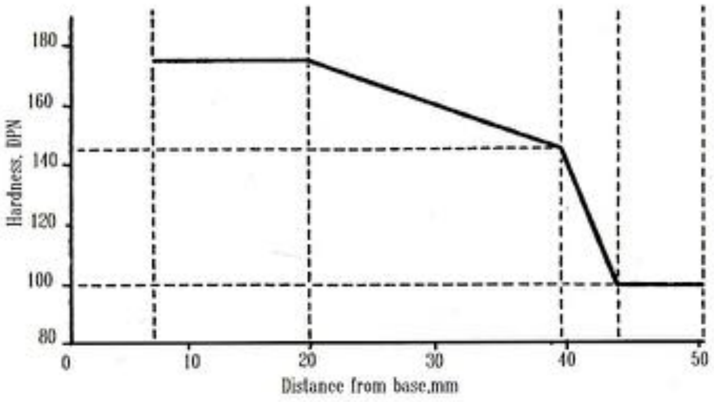


Figure 2.12 Typical hardness profile of cartridge case [6].

This hardness profile is representative of the variable metallurgical properties required by different parts of the cartridge case during firing and *obturation*. This is the name given to the expansion (and slight retraction) of the cartridge case during firing and prevents the high pressure gases from escaping through the breech [38]. The base of the case must be harder in order to withstand the forces of the breech, extraction and ejection. The body of the case requires both strength and flexibility in order to deform both plastically (creating a seal) and elastically ('closing' enough to be extracted). The mouth of the case is the softest portion in order to allow crimping of the projectile without the risk of cracking [17].

Steel cartridge casings were successfully forged by Germany using similar techniques during World War and used by both Germany and Russia during World War Two. They are still made for military use by Russia, China and several ex-Warsaw Pact countries [38]. As mentioned, steel offers an attractive alternative to brass in terms of its low cost to purchase, however, it presents its own issues, one being that it is vulnerable to corrosion/rust. To help combat this issue, steel cases are usually coated with either another metal (i.e. copper) or an appropriate lacquer [17]. The ductility of steel is also less than that of brass and the clearance within the firearm chamber must be reduced to compensate for this [6]. Although mild steel is mentioned as the material used, specifications are not often quoted. 'Mild steels' (also known as 'carbon steels') are a type of steel in which carbon is the primary alloying element; the level of carbon is recorded as weight percent ((wt.%)) and will affect the mechanical properties. Mild steel has a maximum of 1.65% manganese, 0.6% silicon or 0.6% copper. Wallace reports one composition as: “carbon 0.08% to 0.12%, copper 0.25%, manganese 0.6%, phosphorus 0.035%, sulfur [sulphur] 0.03%, and silicon 0.12%” [40].

Attempts have been undertaken to manufacture cartridge cases out of other materials. Aluminium, zinc, and plastic have all been experimented with however, none have been manufactured on the same scale as brass/steel cartridge cases.

The head of a cartridge case is typically indented or ‘stamped’ with information pertaining to its manufacture. Known as a *headstamp,* information displayed usually denotes a combination of the following: the calibre, manufacturer details, year of production. This information may be coded or clandestine headstamps may be encountered – where a fake head stamp has been applied or this information has been omitted completely [49], [50]. Additionally, the head will contain the *primer* cap although this will be discussed in **Section 2.2.4**.

The body of the cartridge case will contain the *propellant*.

2.2.3 Propellant

As mentioned in **Section 2.1** propellants were developed into nitrocellulose based, smokeless powders. Due to their function in accelerating the projectile down the firearm barrel, propellants have been referred to as “the limiting weapon system characteristic related to the ballistic output” [51]. When combustion occurs, this solid substance must quickly convert into a large volume of gas. As a result of its confinements within the chamber of the firearm, there is a intensified build up of heat and pressure that would not occur were the propellant unrestricted [38].

The materials used for propellants are complex and specifically selected in order to be fit for purpose. They must also meet economical demands of availability, cost, and be relatively safe and simple to manufacture – particularly in times of war. The chemical properties of propellants pose significant threat if they do not behave expectedly; there is an inherent need for consistency of performance, stability when stored, and to be completely converted into gas (that is not visible). Further demands on the product require it to rapidly burn, yet not detonate [40].

Propellants tend to be split into black or smokeless powders [52]. It has been identified that smokeless, nitrocellulose (NC) based powders that were introduced between 1870 and 1890 have largely replaced black powders in small arms ammunition and will therefore be the focus of this section [40].

The type of propellant can be further divided into two categories: single-based (SB) and double-based (DB). SB propellants contain NC as the only oxidiser and energy source, whilst DB propellants occur where NC is dissolved into nitro-glycerine (NG). NG propellants combust at higher temperatures, produce larger volumes of gas and increased energy levels. These characteristics can however, lead to increased barrel wear rates. A third category of triple-based propellants exists, however, as it is unlikely to be found in small arms ammunition, it will not be discussed here [40]. As these powders combust almost completely into gas they can provide much higher pressures than previously achieved by black powder, or similar pressures using less powder [6], [16], [38], [40].

Modern propellants also contain other necessary components. These are covered elsewhere in great detail [53], [54] but will be briefly explored here: Stabilisers are utilised in order to mitigate the decomposition of nitrocellulose and increase shelf life. Plasticisers improve the strength and flexibility of the grains whilst binders are added in order to maintain such shapes. Other additives, including those designed to reduce wear and muzzle flash may also be present. Wallace notes that some additives may also be utilised in order to prevent copper build up in the barrel of the firearm [5], [40]. Furthermore, some of these additions may be used to chemically ‘moderate’ the burn rate [38].

One important factor that must be considered is the geometric configuration of propellants as this will predominantly determine the *burn rate*. The burn rate must correspond to the barrel length of the firearm that the ammunition is to be used in conjunction with. Shapes will dictate whether the burn rate is *regressive, neutral, or progressive*. **Figure 2.13** below illustrates some commonly encountered propellant grain shapes.

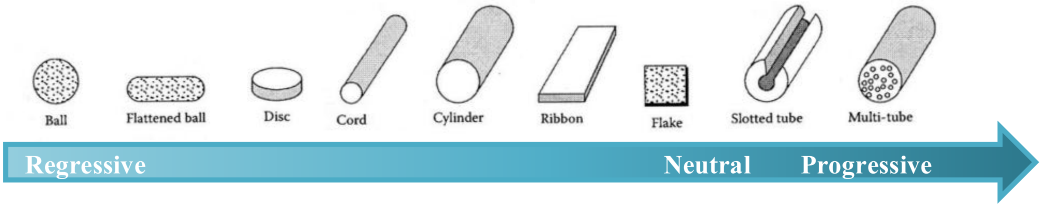


Figure 2.13 Propellant shapes on a scale of burning rates (adapted from [40]).

As defined by Piobert's Law, when propellant is burnt the external layer (or surface) of each grain is consumed [55]. When the propellant grains surface area decreases in size whilst burning this is classified as a regressive burn rate. Slightly more complex is the neutral burn rate of grains such as 'slotted tube'. Here the outer surface area decreases whilst the inner surface area increases - the two opposing reactions 'cancelling each other out'. Progressive burning occurs in grains with multiple perforations where the surface area increases. These will provide different time/pressure curves when considering internal ballistics with grains that have a larger surface area resulting in a faster release of gasses [55].

2.2.4 Primer

A primer is an "ignition system" [3] contained within a metal *cap* (also referred as a cup) which initiates the 'firing' of the projectile. This reaction is offset by the impact of the firing pin compressing the primer cap and igniting the explosive compound. This is the source of ignition for the propellant [3].

As mentioned in **Section 2.2.2**, primers for rimfire cartridge cases are located within the rim. The functionality of primers remains the same regardless of location. For rimfire cartridge cases, the firing pin compresses the rim against the rear of the barrel. For centrefire cartridge cases, this is located at the centre of the head of the cartridge case and an *anvil* is struck by the firing pin –

causing a spark [38]. Centrefire cartridge cases may have a *Boxer* primer cap or a *Berdan* primer cap as shown in **Figure 2.14**.

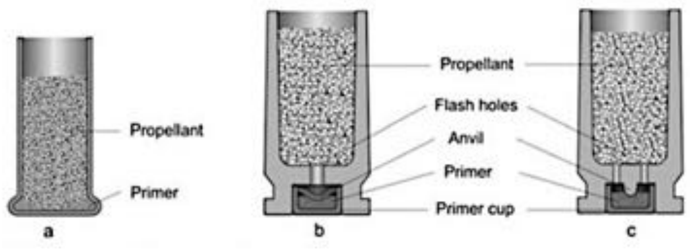


Figure 2.14 Types of primer: **a.** Rimfire, **b.** Boxer, **c.** Berdan [16].

Boxer primer caps consists of a dedicated compartment positioned centrally at the head of the cartridge case, with the presence of a sole flash hole. Within the compartment is the explosive primer compound, covered by a paper foil and a lacquer sealer [3]. The primer cap may be *sensitised* or *desensitised*: The former is used to described a primer where the anvil portion makes contact with the sealer, paper foil and priming compound. Conversely, desensitised primer caps see a small gap between the anvil and the aforementioned components (sealer, paper foil and priming compound) [3]. Due to their many constituents, boxer primer caps require more skill to manufacture, resulting in an increased cost. Reduced sensitivity (until seated in the cartridge case), a separated anvil and the relative ease with which they can be reloaded, are all factors that contribute to the popularity of this type of primer cap; particularly within sporting and military ammunition [3], [38].

The formation of Berdan primer caps differs primarily in that the anvil is not integrated into the primer compartment and is instead, part of the cartridge case. There is still the presence of an explosive primer compound, covered by a paper foil cover and lacquer sealer, however, the anvil is instead held within the cartridge case. Its central position causes the flash holes to be aligned with on opposing sides – resulting in two flash holes. Although Berdan primer caps are simpler to manufacturer (thus involving lower costs), the cartridge cases that contain such primers are actually challenging and costly to make. Predominantly used in military ammunition, reloading this type of primer cap is complicated and unpopular – particularly by hand [3], [38].

The material for primer caps is typically cartridge case brass although copper alloys have also been noted. Wallace quotes two compositions:

1. 95% - 98% copper, 5% - 2% zinc, 0.05% (max) lead, 0.1% arsenic, 0.002% bismuth, 0.01% antimony, less than trace of any other impurity.
2. 72% - 74% copper, 28% - 26% zinc, 0.1% (max) total impurities, 0.1% lead, 0.05% iron.

Additional materials such as copper, nickel-plated copper/brass, cupronickel and zinc-coated steel have also been observed in primer caps. Bussard advises that even though the compartment is formed out of brass, the anvil may be brass or steel [3], [40].

Due to the materials held within (see below) some care must be taken to preserve the primer cap. Varnishing may occur prior to loading and again as a sealant. The annulus may also be sealed to protect against moisture [40].

The primer material is composed of volatile chemicals that explode when impacted by the firing pin/hammer and the resulting flame will ignite the propellant within the cartridge case. The ignition of both the primer and the propellant mixtures will occur within a few ten thousandths of a second and will form part of the *gunshot residue* described in **Section 2.2.5**. The inorganic components of the primer will be vaporised by the resulting heat before re-condensing into droplets [54].

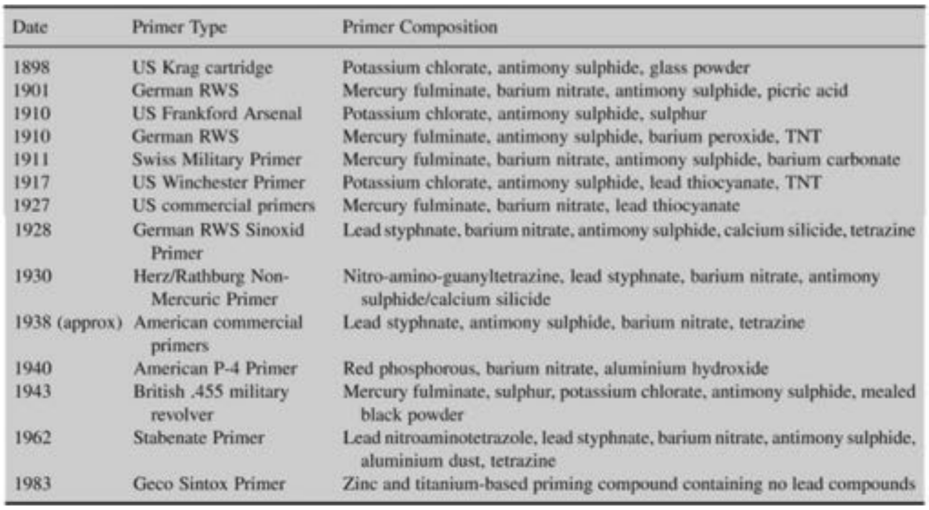
In order to achieve a mixture that will undergo rapid exothermic decomposition whilst remaining cost efficient, reasonably safe and readily available, a combination of chemical compounds must be employed. Priming compositions for small arms ammunition will typically consist of several chemicals (detailed below). As well as one/several *detonating* agents (explosives), *oxidising* agents will aid in production of a flame while *fuels* increase the temperature and duration of the flame. *Frictionators* (such as ground glass) are appropriately abrasive and can assist in the initial ignition of the explosive. *Sensitizers*, and *binding* agents may also be present – the latter of which prevents the compounds from separating. Due to the reluctance of manufacturers to release information on their products, there is a small amount of disjointed information on primer compositions within the literature available [38], [40].

It is widely accepted that the development of priming material originated around 1806 with Rev. Alexander Forsythe who used mercury fulminate [3]. Characteristics that made this material favourable include its prevailing ignition potential and the availability of the raw materials required for its manufacture. The fact that mercury fulminate is sensitive to impact is essential, however its unpredictable nature and tendency to explode without provocation, encouraged the development of primers. Furthermore, metallic cartridge cases were introduced (around 1850) and these mercuric primers caused brittleness in brass cartridge cases, resulting in high pressure gas leaks from the breech and firing failures. Additionally, this made these cases unsuitable for reloading. Hobbs resolved this in 1869 by varnishing the brass primer caps and cartridge cases; preventing contact between brass and mercury fulminate [3], [38], [40].

Forsythe also attempted to mix potassium chlorate, sulphur and charcoal in order to increase stability [3]. Dreyse used a combination of potassium chlorate and antimony sulphide in 1828. Antimony sulphide is a solid fuel with the purpose of prolonging the burning time of the primer. Potassium chlorate remains insensitive throughout wet manufacturing and the product was more stable than mercury fulminate at high temperatures. Unfortunately, the combustion of potassium chlorate produces potassium chloride; a compound which proved to be incredibly corrosive to the bore of the firearm. Development continued with the US military adopting a mercury fulminate potassium chlorate mixture in 1873. The later addition of mercury fulminate to the above materials did not help to resolve these issues [3], [38], [40].

The above mixture of mercury fulminate and corrosive potassium chlorate is known as a *mercuric and corrosive* primer type. With the known issues of this primer type, a German company used mercury fulminate and antimony sulphide but replaced potassium chlorate with barium nitrate making this primer *mercuric and noncorrosive*. The Swiss had also experimented replacing potassium chlorate with barium peroxide and small amounts of barium carbonate. America followed suit utilising a combination of mercury fulminate with barium nitrate and lead thiocyanate [3], [38], [40].

In order to try and produce *nonmercuric and noncorrosive*, Sinoxyd primers, a replacement for mercury fulminate was needed. The first realistic replacement was lead styphnate (lead trinitroresorcinate), however, there were high risks involved in the preparation of this compound. Wallace provides a more detailed history of the development of primers and some known compositions which would be too lengthy to include here [40]. Heard's table (**Figure 2.15**) below demonstrates how primer development can assist in understanding the diverse compositions present.



Date	Primer Type	Primer Composition
1898	US Krag cartridge	Potassium chlorate, antimony sulphide, glass powder
1901	German RWS	Mercury fulminate, barium nitrate, antimony sulphide, picric acid
1910	US Frankford Arsenal	Potassium chlorate, antimony sulphide, sulphur
1910	German RWS	Mercury fulminate, antimony sulphide, barium peroxide, TNT
1911	Swiss Military Primer	Mercury fulminate, barium nitrate, antimony sulphide, barium carbonate
1917	US Winchester Primer	Potassium chlorate, antimony sulphide, lead thiocyanate, TNT
1927	US commercial primers	Mercury fulminate, barium nitrate, lead thiocyanate
1928	German RWS Sinoxid Primer	Lead styphnate, barium nitrate, antimony sulphide, calcium silicide, tetrazine
1930	Herz/Rathburg Non-Mercuric Primer	Nitro-amino-guanyltetrazine, lead styphnate, barium nitrate, antimony sulphide/calcium silicide
1938 (approx)	American commercial primers	Lead styphnate, antimony sulphide, barium nitrate, tetrazine
1940	American P-4 Primer	Red phosphorous, barium nitrate, aluminium hydroxide
1943	British .455 military revolver	Mercury fulminate, sulphur, potassium chlorate, antimony sulphide, mealed black powder
1962	Stabenate Primer	Lead nitroaminotetrazole, lead styphnate, barium nitrate, antimony sulphide, aluminium dust, tetrazine
1983	Geco Sintox Primer	Zinc and titanium-based priming compound containing no lead compounds

Figure 2.15 Timeline of primer development with examples of primer variation (adapted from [38]).

The six modern primer types identified by Wallace based on their compositions are detailed in **Table 2.3** below:

Table 2.3 Primer categories and example compositions [41].

Category	Example Composition
Mercuric and corrosive.	• Mercury fulminate • Potassium chlorate • Antimony sulphide
Mercuric and noncorrosive.	• Mercury fulminate • Barium peroxide • Antimony sulphide • Barium carbonate • Powdered glass
Nonmercuric and corrosive.	• Gum Arabic (acacia gum) • Phosphorus sulphide • Magnesium carbonate • Calcium carbonate • Potassium chlorate
Nonmercuric and noncorrosive (Sinoxyd).	• Lead styphnate • Barium nitrate • Antimony sulphide • Aluminuim
Lead free (Sintox).	• 2-Diazo-4,6-dinitrophenol (Diazole) • Tetrazine • Zinc peroxide • Titanium
Miscellaneous/other	

There are several resources that can assist in identifying compounds in primer mixtures [3], [38], [40]. This becomes imperative when considering that these compounds will (in some form) be present as a component of gunshot residue.

2.2.5 Gunshot Residue (GSR)

When depressing the trigger of a loaded firearm, the interactions between the firing pin, primer, and propellants, eject the projectile down the barrel of the firearm. During this discharge, there is a release of particles, the majority of which originate from the ammunition; from the primer, propellant powder and metals from the projectile. A minimal amount of this residue may be a result of the firearm - in the form of lubricants, greases and metals. The gases produced during this interaction are initially subject to high temperatures and pressures and exit via openings present (mostly the muzzle). As the gasses cool and condense, they are deposited onto nearby persons and surfaces [27], [56]. This fusion is most commonly referred to as gunshot residue (GSR) although varying literature may refer to is as firearm discharge residue (FDR) [38] or cartridge discharge residue (CDR) [54]. GSR is discussed in detail in **Appendix K**.

A number of techniques have been utilised in the analysis of inorganic GSR. Bulk analysis methods include neutron activation analysis (NAA) [57], and atomic absorption spectroscopy (AAS) [28], [57]. NAA allowed for detection of Ba and Sb. AAS could initially only detect Pb successfully and was not sensitive enough to detect certain elements (Ba and Sb). This has been improved by utilising “electro thermal atomizers” [57], for example, the use of gas furnace atomic absorption spectroscopy (GFAAS) has demonstrated effectiveness in determining concentrations of the order of $\mu g\ ml^{-1}$ for these elements [27]. Inductively-coupled plasma mass spectrometry (ICP-MS) has also been employed for bulk analysis with a focus on detecting Pb, Ba and Sb in primer residues [58], [59].

The most widely accepted analytical technique for analysis of inorganic components of GSR is conducted using a scanning electron microscope (SEM) coupled with wavelength or energy dispersive X-rays (WDX/EDX). Introduced by the Aerospace Corporation in 1974 [60] this technique has since become globally accepted for GSR analysis. It allows for elemental and morphological characterisation of particles and is non-destructive [61]. This technique and its applications are further discussed in **Section 3.2.2**.

2.3 7.62 x 39 mm Ammunition

2.3.1 History

The 7.62 x 39 mm round of ammunition is the product of Soviet development that began in 1943. It can be argued that the design began with Vladimir Grigoryevich Federov (VG). An officer, engineer and weapons designer, his persistence for a new round of ammunition can be linked to the creation of the 7.62 x 39 mm cartridge [49].

It is reported that the Soviets were interested in a lower calibre and reduced-power alternative to the 7.62 x 54 mm round of ammunition. Prior to World War One, Federov designed a rimless 6.5 x 57 mm cartridge. This was however, discarded and substituted with the 6.5 mm SR Japanese Arisaka cartridge. Due to higher priorities, the start of the war saw developments cease until 1943 when the Soviet OKB-44 (Experimental Design Bureau) began designing new ammunition. They assembled 8 models and tested these before adopting this ammunition in December 1943 [49].Initially, the cartridge case length was 41mm and has been referenced as the 7.62 x 41mm. The corresponding projectile was 22.8mm in length with a solid lead core and no boat tail. Report's cite a small quantity were produced and circulated from 1944 [49].

It is noted repeatedly in the literature that there is striking similarity between the 7.62 x 39 mm and the 7.9 x 33 mm Kurz Cartridge developed by the Germans in 1942. Russian records however, do not allude to the aforementioned ammunition and accredit the design of the 7.62 x 39 mm to N.M Yelizarov and B.V Semin [49], [62].

The 7.62 x 39 mm was termed the Model 1943 (or M.1943) – presumably to reflect the year of design. The Russians opted to keep the diameter but change the length of the cartridge case in efforts to reduce the range to what they believed was more optimal; 600 – 800 metres. The ammunition was adapted until it was finally accepted in 1948 – which is also the present edition. Sometimes known as the M43, this version has a reduced length of the cartridge case (to 39 mm), increased length of the projectile (to 26.5 mm) and the inclusion of a steel core [49].

2.3.2 Overview

The M.1943 7.62 x 39 mm cartridge cases may be constucted from brass, however, they are predominantly manufactured from steel; either lacquered (typically grey, green or brown) or coated in brass/gilding-metal clad-steel. This is to help prevent oxidisation (rust) occuring [49]. The cartridge case has a tapered body, is necked and rimless, with the cartridge case mouth being slightly coned in order to secure the projectile as shown in **Figure 2.16**.

Although it is colloquially known as the 'standard ball bullet PS', the military designation is actually 57-N-231 and the projectile contains a mild steel core, surrounded by a lead sheath, with a jacket of gilding-metal clad-steel [63]. It is commonly boattailed in shape with flattened ends, and the presence of a single cannelure [49]. These characteristics are known to vary in accordance with purpose (**Section 2.3.3**), or due to differences manufacturer specifications (**Section 2.3.4**). Typical dimension for the Model 1943, Soviet Type PS, 7.62 x 39 mm ammunition are shown in **Table 2.4**.

Table 2.4 Specifications for the Model 1943, Soviet Type PS, 7.62 x 39 mm Adapted from Labbett [29] with varying values from Jane's Ammunition Handbook represented using an asterisk * [63].

MEASUREMENT	**FIGURES**	
	Metric	**Imperial**
CARTRIDGE CASE LENGTH	38.61 (mm) _*38.35 (mm)_	1.52 (inches) *1.51 (inches)
RIM DIAMETER	11.30 (mm)	0.44 (inches)
HEAD DIAMETER	11.25 (mm)	0.44 (inches)
PROJECTILE WEIGHT	7.97 (grams) _*7.75 - 8.05 (grams)_	123 (grains) *119.60 – 124.23 (grains)
MUZZLE ENERGY	205 (m/kg)	1480 (ft/lbs)
OBSERVED VELOCITY	710 (m/s) _*710 – 725 (m/s)_	2330 (ft/sec) *2330 – 2378 (ft/sec)
OVERALL AMMUNITION LENGTH	55.54 (mm) _*56.11 (mm)_	2.19 (inches) *2.20 (inches)
PRIMER CAP DIAMETER	5.25 (mm)	0.21 (inches)
PRIMED EMPTY CASE WEIGHT – STEEL	6.48 – 7 (grams)	100 – 108 (grains)
PRIMED EMPTY CASE WEIGHT – BRASS	7.51 – 7.77 (grams)	116 – 120 (grains)
PROPELLANT WEIGHT	1.52 – 1.65 (grams) _*1.60 (grams)_	23.46 – 25.46 (grains) *24.69 (grains)
PROJECTILE LENGTH	26.5 (mm)	1.04 (inches)
PROJECTILE DIAMETER	7.94 (mm) _*7.82 (mm)_	0.31 (inches) *0.31 (inches)

Ammunition manufactured in countries under communist influence (i.e USSR nations or Warsaw Pact Allies) have been known to possess neck seals. The variance in colour is not known to be representative of any particular characteristics, and it would appear that the primary purpose of these is to act as a sealant against damp. The cartridges primarily display a centrefire berdan primer system – the primer typically being corrosive - with the following cap composition:

Mercury Fulmitate: 25.0%

Potassium Chlorate: 37.0%

Antimony Sulphide: 38.0%

The original propellant for most communist countries is usually graphited tubular nitrocellulose [49]. When examined, the appearance of the propellant is similar with the following approximate composition:

Nitrocellulose plus graphite: 96.0%
Diphenylamine: 1.0%
Camphor: 1.2%
Volatile Matter: 1.8%

Figure 2.16 7.62 mm Soviet Cartridge [63]

2.3.3 Technical Variation

Commercial and military ammunition often display markings such as headstamps and colour codes that allow the operator to discern certain features. These include but are not limited to whether the projectile is: ball, practice, armour piercing, incendiary, tracer, or blank [62]. Ammunition is designed to be used in a vast number of different circumstances and must be adapted accordingly. A selection of different 7.62 x 39 mm rounds of ammunition have been chosen for discussion below. Whilst the list is not extensive, it gives an overview of how dissimilarities exist.

Amour Piercing Incendiary (API) ammunition is common amongst all communist countries. The Soviet Type BZ is recognised in most countries by the presence of a black tip over a red band. This marking is not reflected in China where since 1967, the API has simply been marked with a black projectile tip. While the overall ammunition length and projectile diameter remain unchanged (at 55.5 mm and 7.9 mm respectively), the length of the projectile is slightly longer at 27.5 mm. This disparity may be the result of the addition of incendiary composition at the base of the projectile. The Type BZ also has a two-piece jacket which may contribute minimally to the length of the projectile [49].

Incendiary Tracer ammunition is used primarily for examination. Designated as the Soviet Type Z, the projectile is comprised of a two-piece envelope with a flat base. The rear portion is composed of gilding-metal clad-steel and the tip of gilding-metal whilst the nose is flat, containing a mild steel core and a small amount of incendiary composition. A lead sheath is present around the mild steel core. China has customised their incendiary tracer ammunition by opting for a gilding-metal clad-steel, single- piece envelope with a more fragile tip. The nomenclature for both variations remains the same, as do the dimensions with a projectile length of 27.6 mm, diameter of 7.9 mm and weight of 6.67 grams [49].

Proof ammunition is ammunition which has been pressure loaded. Identified by by markings on the cartridge case headstamp, these are “loaded to higher maximum average pressures for greater velocity” [3]. It has been noted that the previous territories of Czechoslovakia, Poland, Romania and the USSR mutually manufactured a proof cartridge with the following dimensions: projectile length 28.5 mm, projectile diameter 7.9 mm and projectile weight 9.14 grams. The overall cartridge length is greater than the Type PS at 61.27 mm. Former Yugoslavia also manufactured two different types of proof cartridges; both of these were known to possess boxer primers. For one, the pressure given was over 20% over that of normal service. The second was designed to give 30% pressure over that of normal service. The propellant for both was comprised of nitrocellulose flakes weighing 1.33 grams and 1.36 grams respectively [49].

Jane's also reports manufacture of "tracer, incendiary, API, and heavy-bullet subsonic rounds" as well as an armour piercing round featuring "a bullet core machined from special high-carbon steel" developed in the late 1990's [63]. Walker also reports the manufacture of a 7.62 x 39 mm ammunition in the late 1970's by Tula (factory 539), where the projectile (designation "7n6 type") is claimed to have a "hardened steel core" [62].

2.3.4 Manufacturer Variation

Manufactured in vast quantities and varied locations, the 7.62 x 39 mm round has become somewhat omnipresent. Whilst they may vary in order to meet specific purposes – mentioned above – with such uncompromising standards, these rounds of ammunition are usually constant in weight and dimensions, irrespective of the country of manufacture. There are however, some notable differences and these can be attributed to socio-economic factors and differences in availability of resources and manufacturing procedures.

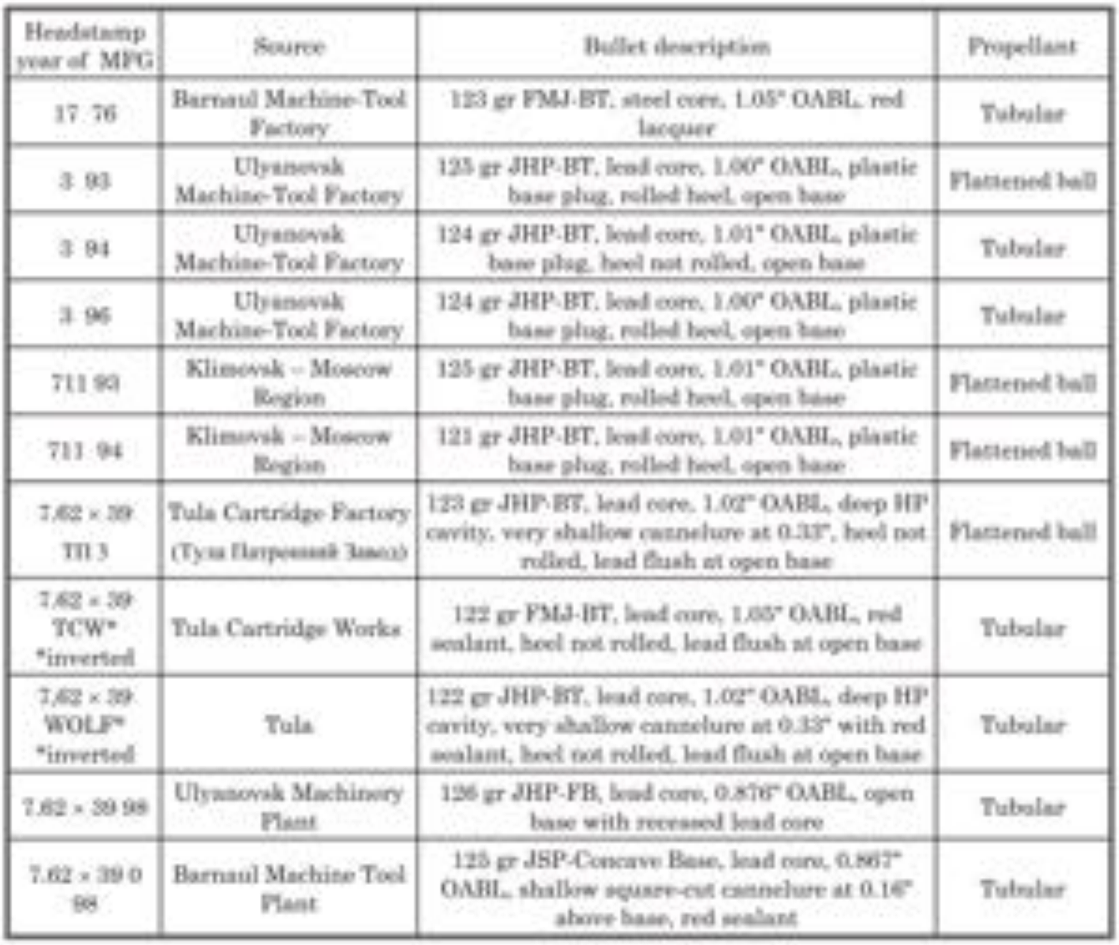
Neck seals are present in some ammunition manufactured in communist countries. The variance of colour is not known to be representative of any particular characteristics, and it would appear that the primary purpose of these is to act as a sealant against moisture. A known exception to this is with Chinese ammunition where the a green primer is related to the purpose [49].

Primers are mostly consistent in diameter and type (5.25 mm and Berdan) there is a slight discrepancy in some of the Cuban-manufactured ammunition – where the diameter of the primer is slightly smaller [49]. In addition, 7.62 x 39 mm (former) Yugoslavian ammunition intended for export has exhibited a boxer primer’s [49].

The primer annulus colour is generally irrelevant to its purpose and serves as a sealant. These are predominantly red, although purple and black annuli have also been observed. It is unusual to encounter green annuli except in regard to tracer ammunition – where the whole primer may have been lacquered. This has been observed in some Chinese ammunition, perhaps to compliment the green bullet tips found on tracer projectiles [49]. Other countries where the entire primer has been lacquered are Czech (black), Romania (red) and China (red or pale yellow) [49].

Propellant variations have been noted in Czech Republic and Bulgarian ammunition; in contrast to the ‘standard’ tubular nitrocellulose used, a ball powder propellant has been observed in M.43 ball and tracer ammunition [49].

Walker provides comprehensive information of the manufacturing processes for selected nations which covers over 70 states and would be too long to re-iterate here [62]. Haag details some contemporary Russian 7.62 x 39 mm projectiles **Figure 2.17** simultaneously bringing to attention the scope of variation present by 2001 [64].



Headstamp year of MFG	Source	Bullet description	Propellant
17 76	Barnaul Machine-Tool Factory	123 gr FMJ-BT, steel core, 1.05" OABL, red lacquer	Tubular
3 93	Ulyanovsk Machine-Tool Factory	125 gr JHP-BT, lead core, 1.00" OABL, plastic base plug, rolled heel, open base	Flattened ball
3 94	Ulyanovsk Machine-Tool Factory	124 gr JHP-BT, lead core, 1.01" OABL, plastic base plug, heel not rolled, open base	Tubular
3 96	Ulyanovsk Machine-Tool Factory	124 gr JHP-BT, lead core, 1.00" OABL, plastic base plug, rolled heel, open base	Tubular
711 93	Klimovsk – Moscow Region	125 gr JHP-BT, lead core, 1.01" OABL, plastic base plug, rolled heel, open base	Flattened ball
711 94	Klimovsk – Moscow Region	121 gr JHP-BT, lead core, 1.01" OABL, plastic base plug, rolled heel, open base	Flattened ball
7.62 × 39 ТП 3	Tula Cartridge Factory (Тула Патронный Завод)	123 gr JHP-BT, lead core, 1.02" OABL, deep HP cavity, very shallow cannelure at 0.33", heel not rolled, lead flush at open base	Flattened ball
7.62 × 39 TCW* *inverted	Tula Cartridge Works	122 gr FMJ-BT, lead core, 1.05" OABL, red sealant, heel not rolled, lead flush at open base	Tubular
7.62 × 39 WOLF* *inverted	Tula	122 gr JHP-BT, lead core, 1.02" OABL, deep HP cavity, very shallow cannelure at 0.33" with red sealant, heel not rolled, lead flush at open base	Tubular
7.62 × 39 98	Ulyanovsk Machinery Plant	126 gr JHP-FB, lead core, 0.876" OABL, open base with recessed lead core	Tubular
7.62 × 39 0 98	Barnaul Machine Tool Plant	125 gr JSP-Concave Base, lead core, 0.867" OABL, shallow square-cut cannelure at 0.16" above base, red sealant	Tubular

Figure 2.17 Contemporary Russian 7.62 x 39 mm projectiles [69].

Previously, 7.62 x 39 mm ammunition was traded between America and China who supplied ammunition up until 1994. The Bureau of Alcohol, Tobacco, Firearms and Explosives (BATFE) banned such imports, classifying the rounds as “armour piercing” and proceeded to apply a comprehensive ban on Chinese ammunition [62]. In relation to this, Russian replaced the steel cores with lead, however, the higher density of lead resulted in an increased mass of the projectile. Russian manufacturers realised this issue and released a new design of projectile during the 1990s. This projectile contained “translucent polyethylene plastic and has been reported as “uniquely Russian” indicating its significance for differentiation [64]. Another variation of this calibre possessed a lead core with a cavity present. This resolved the previous mass issues and is shown in **Figure 2.18.** The alternative designs available are seemingly in response to import requirements.

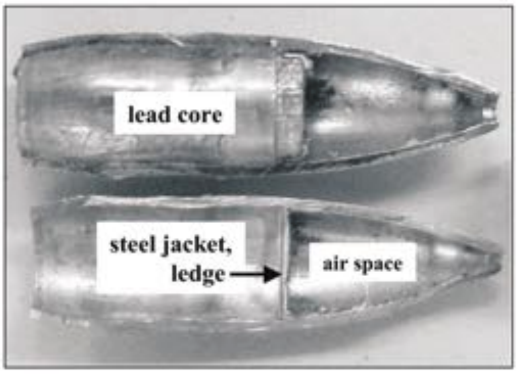


Figure 2.18 Sectioned projectile with lead core and cavity ("air space") present [64].

When referring to 7.62 x 39 mm ammunition it is typically the Soviet Type PS that is being discussed, the production of which is still common amongst former Warsaw Pact countries. The use of phosphate steel for the jacket of some Czech Republic Type PS ammunition has been noted. Furthermore, there are three ball alternatives which deviate from this design [49].

The first is the PRC ball Type 56. This is a former Yugoslavian product that diverges with the potential intention of trade. The jacket is still made of gilding-metal, however the shape of the projectile differs; it is flat-based. The most noteable difference is the lead core – and the absence of a steel core – which is odd considering the cost of lead is known to be higher [49]. The slightly smaller size can be attributed to lead's density being higher than that of steel, thus in order to maintain a weight of 7.97 grams and the projectile length has been shortened from 26.5 mm to 23.6 mm and the diameter reduced from 7.9 mm to 7.85 mm.

Former Yugoslavia also developed the M.67 during the 1960's; lighter than the Type PS, the projectile has no jacket and is constructed of sintered iron. The weight of the projectile is key to its ballistic performance and the dimensions have again been altered to try and reduce any negative impacts a change in weight may have; the projectile diameter remains at 7.9 mm but the length increases from 26.5 mm to 28 mm. The projectile is slightly lighter than the Type PS at 7.68 grams (as opposed to 7.97 grams) [49].

Another known variation is the Type US Heavy. The projectile here has a flat-base shape with a black tip upon a green band. Its internal structure comprises of a lead core towards the rear, and a hardened steel core contained within the ogive portion, towards the tip. Known to be used with a silenced rifle, it can be inferred that the structure of this projectile indicates it may be used to pierce body amour. Significantly longer at 33.3 mm and weighing 4.6 grams more than the Type PS ammunition (12.57 grams) the discrepencies here do not affect the overall ammunition length which remains at 55.5 mm [49].

Albanian factory K.M. Polican identifies the 7.62×39 mm that it produces as the M54 – as opposed to the Soviet M43 designation. Regenstreif claims that “a contract was signed at the beginning of the 1980s between the Albanian Government and the French firm MANURHIN” and can be recognised by the crude nature of the headstamps present [62]. During the Cold War, Albania was a major repository for ammunition originating from the Soviet Union and China, in addition to domestically produced munitions. Albania has been the site of a number of accidents involving munitions stockpiles, and great investment has been made to reduce the amount of stockpiled munitions stored in the country. The state-operated arsenal, K.M. Polican, has produced 7.62×39 mm cartridges, among others. K.M. Polican identifies the 7.62×39 mm as the M54, as opposed to the Soviet M43 designation. The arsenal uses the number 3 to identify itself on the casing head stamp. The code 3 is marked at the 6 o’clock position, with the last two digits of the date at the 12 o’clock position. Albanian ammunition dating to at least as early as the mid-1980s used brass cartridge casings [65], [66], [67].

Headstamp practices are discussed in more detail below.

2.3.4.1 Headstamps

A headstamp is the term given to markings on the base of a cartridge case (see **Figure 2.19**). There is no global standard for the information that must be included, nor the ‘style’ in which the markings are placed. As a result the location of markings may vary as shown in **Figure 2.20**. Generally, ammunition reveals the following:

- Manufacturer (this may be coded or abbreviated)
- Calibre (imperial or metric)
- Date (typically the last one or two digits of the year of production)
- Symbols (either to specify technical variation or conceal the manufacturer) [62].

This information is featured as alphanumerical characters, symbols, or a combination of both. The headstamp should not be accepted as an explicit and unconditional indication of the source of manufacturer as will be discussed throughout **Section 2.4** [68].

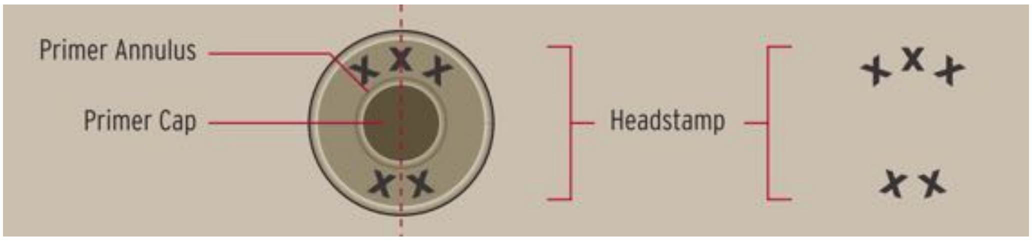


Figure 2.19 Diagram showing one formation of headstamp markings [68].

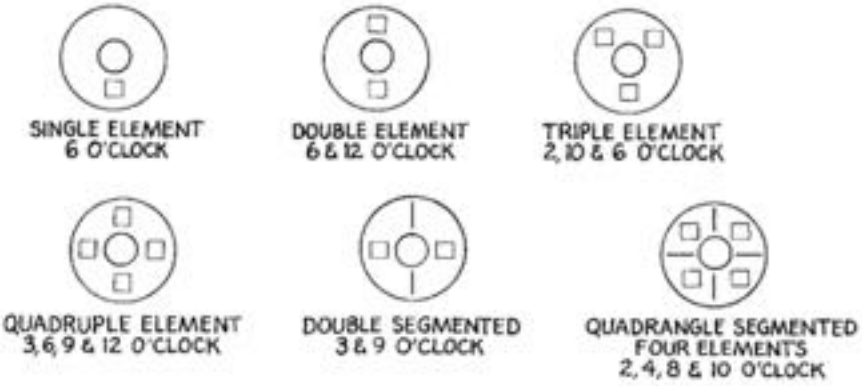


Figure 2.20 Diagram showing alternative location of headstamp markings [7].

This information is featured as alphanumerical characters, symbols, or a combination of both. The headstamp should not be accepted as an explicit and unconditional indication of the source of manufacturer as will be discussed throughout **Section 2.4** [68].

One area of interest regarding headstamps is in determining provenance. Where headstamps are absent this creates issues in monitoring transfers [69]. Clandestine headstamps have been a source of interest for intelligence purposes and may be partially or completely omitted. Manufacturers may also mark ammunition with headstamps know to belong to another manufacturer in an attempt to prevent accountability [49], [50], [62].

In the absence of a headstamp, some attempts have been made to identify unknown rounds of ammunition using physical measurements of the projectiles or cartridge case dimensions. These results however, these are comparative in nature and cannot provide truly definitive results. There is growing interest to improve markings on ammunition in order to assist in identifying trade patterns are increase market transparency. Some suggestions include mechanical engraving/scribing and laser engraving, both of which provide high quality markings. These techniques are not without limitation and have been met by economical concerns from ammunition manufacturers as the market is reactive to small price increases [68], [70].

2.4 Ubiquity of Ammunition

In 1974, the Soviet military developed the 5.45 x 39 mm cartridge to be used in combination with new AK variants chambered for this round – such as the AK-74[63] – however, its utilisation does not compare to that of its predecessor.

Despite being created over 70 years ago 7.62 x 39 mm ammunition remains extensively used globally. The first firearms designed to chamber this cartridge were the SL Siminov self-loading rifles reportedly used in 1944. Due to notable defects, 1945 saw the introduction of the more familiar SKS 45 Siminov self-loading carbine. Two years later, in 1947 the *Avtomat Kalashnikova* (AK) was developed and accepted in 1949. The 7.62 x 39 mm round of ammunition, in combination with the aforementioned rifle was embraced by not only former Warsaw Pact countries but also by many other countries. The M.1943 displays appealing characteristics for use; with favourable recoil energy and muzzle velocity. It has reasonable accuracy when fired as a single shot. Alternatively, if combat requires a larger ‘spread’ then this ammunition can be burst fired to cover a larger area [49].

Most notorious for its use with AK variants (such as the AK-47 and AKM), of which there are a substantial number currently in circulation [63]. As well as these older variants, recently designed firearms such as the AK-103 and AK-104 have been have been developed for use with 7.62 x 39 mm – an indication that it is likely to remain in production and use for the foreseeable future [63].

There are many lesser known firearms that are chambered to the 7.62 x 39 mm ammunition further demonstrating its ubiquity. Some of these have been summarised below in **Table 2.5**.

Table 2.5 Firearms chambered to 7.62 x 39 mm ammunition [1], [70].

Country	**Make/Model**
China	• Type 56 carbine • Type 56 and 56-1 rifles • Type 68 rifle • Type 75 and Type 81 light machine guns
Finland	• Colt Model 6830 lightweight rifle • M60, M62, M76 and M90 rifles • M78 heavy-barrel rifle • M62 machine gun
Hungary	• AMD-65 rifle
North Korea	• Type 68 rifle
Poland	• PMK, PMK- DGN and PMKM rifles
Russian Federation	• AK, AKS, AKM, AKMS, AK-103, AK-104 and SKS rifles • RPD and RPK machine guns
Serbia	• Ruger Mini-Thirty rifle • M59/66A1, M70B1 and M70AB2 rifles • M72 and M72AB1 machine guns

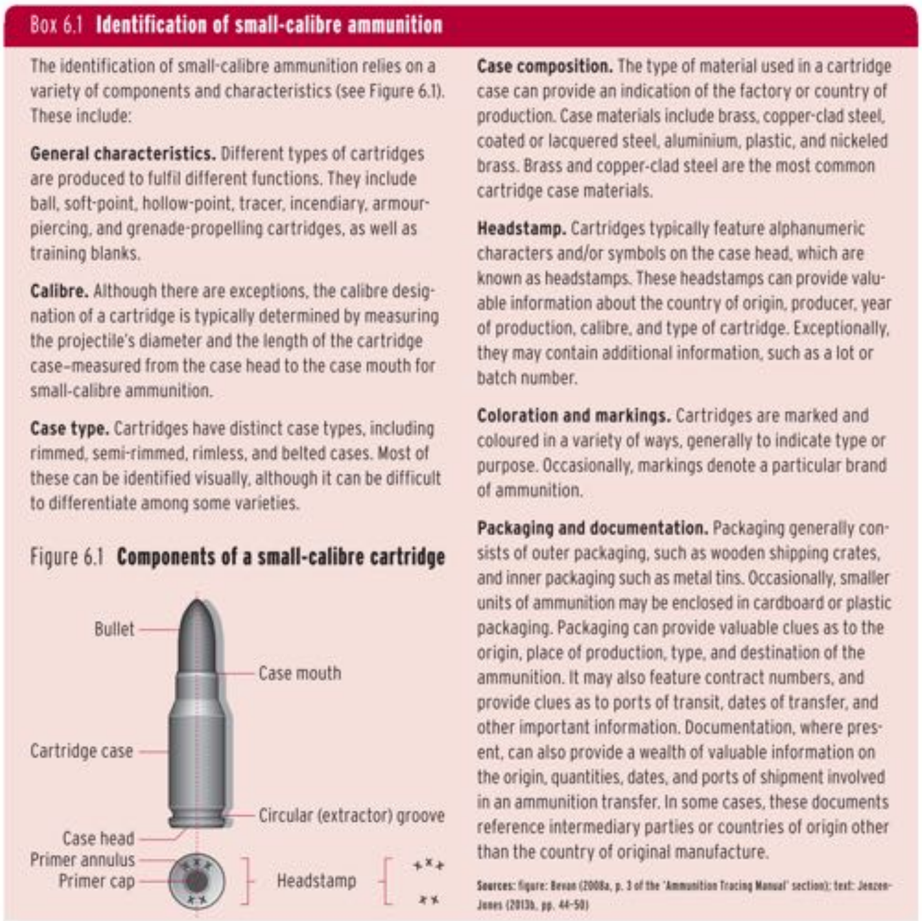
The popularity of Soviet weapons such as the AK pattern rifles increase the likelihood of encountering 7.62 x 39 mm ammunition globally with numerous countries manufacturing and importing this calibre. It is imperative to understand that the information supplied by the headstamp is not absolute; headstamp markings denote the earliest feasible date for cartridge assembly. In some instances, the assembly may occur at a later date, with ammunition components produced in different locations at different times [71], [72]. Although the above must be considered, the information found on the headstamp is commonly accepted as evidence of the production facility and date of manufacture [69]. In order to try to document information regarding production, many researchers photograph markings (including headstamps) and packaging present. With varying agendas and sample sizes available, there is currently no standardised method of reporting. However, toolkits have been developed in order to try and improve precision [68], [71].

Recent studies enforce the claims of 7.62 x 39 mm ammunition ubiquity with it being found in various countries – particularly in conflict zones [13-18], [78]. The Small Arms Survey recently reviewed a combination of studies conducted in seven countries/territories; it found that ammunition examined came from plants in 39 countries. Facilities were predominantly located in China and the former Soviet Union (37%), and over 75% of the samples were of Ex-Warsaw Pact calibres. Amalgamation of the results shows that 258 out of 560 samples were of 7.62 x 39 mm ammunition (46%) [71]. This was the most common calibre present across all case studies, produced not only in China and the Russian Federation but also in Sudan, Iran, Algeria, Egypt, Israel, Syria, Turkey, Uganda, and Zimbabwe [71].

The studies were conducted during varying periods, between 2010 and 2014. Almost all of the samples found ammunition manufactured between 1946 and 2012, signifying the extensive lifespan of small-calibre ammunition. 54% of the ammunition samples were identified as manufactured prior to 1990, indicating the potential for several transfers to occur between many parties, with various uses (including use conflict). Ammunition produced during the Cold War was observed in Somaliland, Côte d'Ivoire and Libya [71].

In Côte d'Ivoire, the diversity of 7.62 x 39 mm ammunition was clearly illustrated with production being from 13 different states over the period of 60 years [72]. Additionally ammunition from Bangladesh was observed, and two further samples - one with markings present but unknown (suspected to be China), the other with no headstamp markings ("possibly Sudanese") [72].

The Small Arms Survey of 2014 summarises the typical components of small calibre cartridges and how analysing various components and characteristics can assist with identification as shown in **Figure 2.21** below.



Box 6.1 **Identification of small-calibre ammunition**

The identification of small-calibre ammunition relies on a variety of components and characteristics (see Figure 6.1). These include:

General characteristics. Different types of cartridges are produced to fulfil different functions. They include ball, soft-point, hollow-point, tracer, incendiary, armour-piercing, and grenade-propelling cartridges, as well as training blanks.

Calibre. Although there are exceptions, the calibre designation of a cartridge is typically determined by measuring the projectile's diameter and the length of the cartridge case–measured from the case head to the case mouth for small-calibre ammunition.

Case type. Cartridges have distinct case types, including rimmed, semi-rimmed, rimless, and belted cases. Most of these can be identified visually, although it can be difficult to differentiate among some varieties.

Figure 6.1 **Components of a small-calibre cartridge**

Case composition. The type of material used in a cartridge case can provide an indication of the factory or country of production. Case materials include brass, copper-clad steel, coated or lacquered steel, aluminium, plastic, and nickeled brass. Brass and copper-clad steel are the most common cartridge case materials.

Headstamp. Cartridges typically feature alphanumeric characters and/or symbols on the case head, which are known as headstamps. These headstamps can provide valuable information about the country of origin, producer, year of production, calibre, and type of cartridge. Exceptionally, they may contain additional information, such as a lot or batch number.

Coloration and markings. Cartridges are marked and coloured in a variety of ways, generally to indicate type or purpose. Occasionally, markings denote a particular brand of ammunition.

Packaging and documentation. Packaging generally consists of outer packaging, such as wooden shipping crates, and inner packaging such as metal tins. Occasionally, smaller units of ammunition may be enclosed in cardboard or plastic packaging. Packaging can provide valuable clues as to the origin, place of production, type, and destination of the ammunition. It may also feature contract numbers, and provide clues as to ports of transit, dates of transfer, and other important information. Documentation, where present, can also provide a wealth of valuable information on the origin, quantities, dates, and ports of shipment involved in an ammunition transfer. In some cases, these documents reference intermediary parties or countries of origin other than the country of original manufacture.

Sources: figure: Bevan (2008a, p. 3 of the 'Ammunition Tracing Manual' section); text: Jenzen-Jones (2013b, pp. 44–50)

Figure 2.21 Identification of Small-Calibre Ammunition [71].

Throughout the studies Iranian and Sudanese ammunition was also widely observed (in four and five out of the seven case studies, respectively). In contrast ammunition produced by Syrian facilities was only found in Syria [16], [18]. Some of the Sudanese ammunition found had been produced relatively recently. 29 of the samples found displayed headstamp information to indicate their production dates were between 2010 and 2012 [71]. Of these, almost half (48%) were 7.62 x 39 mm samples, and 57% of these with Sudanese.

In Côte d'Ivoire eight types of 7.62 x 39 mm ammunition were documented as Sudanese, produced between 2001 and 2011. Unmarked ammunition of this calibre was also recorded – with the potential to be of Sudanese origin. This case study discusses the similarity in characteristics known to be indicators of Sudanese production; with "unevenly applied yellow neck sealant and red primer sealant" [72], [79]. This study raises an additional consideration regarding ammunition without headstamp information; the presence of marked and unmarked cartridge cases packaged together implies that certain cartridges *appear* to be unmarked due to inconsistencies in the depth and legibility, rather than details being purposefully omitted [72].

Traditionally a calibre associated with the Russian Federation, Soviet Union and Ex-Warsaw Pact countries, these studies demonstrate a shift in the market. This shift is not only prevalent in African and Middle-Eastern countries. Production has been noted by United States based manufacturer Hornady who began producing this calibre in 2010 indicating an increase in popularity of this calibre in America [62].

The analysis of ammunition trade and transfers has been progressively integrated into arms monitoring processes [78], however, discrepancies in reported values indicate that not all states confirm to these practices [80], [81]. Ammunition in conflict areas is 'traditionally' expected to be sourced from 'former colonial powers or Eastern Bloc states' [72]. Recently, the evidence of a globalised, international ammunition market has been supported by the presence of recently manufactured ammunition from territories such as Sudan and Iran [72]. Additionally, countries who originally sourced Western-standard ammunition, have been known to expand their ammunition stockpile to include

Eastern-Bloc standard calibres; with claims that it is cheaper to obtain these in comparison to their western counterparts [72].

A mutiny of soldiers in Côte d'Ivoire in September 2002, closely followed by the emergence of the Forces Nouvelles rebel movement, are recognised as a significant factors in the increased demand of ammunition by the government. They proceeded to procure a variety of ammunition in "large quantities" which were produced in the former Soviet Union in the 1950s [72]. Countries who have previously experienced armed conflict may wish to replenish ammunition stockpiles once their circumstances begin to stabilise. This is likely to lead to further variation of ammunition supplies for a particular state [72]. In some instances, research by UN Groups of Experts combined with information displayed on the original packaging can identify the legitimate recipient of ammunition. One such case is the 7.62 x 39 mm and 7.62 x 54R mm ammunition made by the Prvi Partizan factory (Serbia), believed to correspond to voluntarily submitted export statistics (USD 580,000) from Serbia and Montenegro to Côte d'Ivoire [72].

2.4.1 Illicit Trade Flow

The complexity of the illicit flow of small arms and small arms ammunition should not be undermined. Studying the supply chain has allowed us to understand the multiple channels that exist and contribute to the proliferation of the aforementioned – particularly in developing countries.

Initially the source of the ammunition must be established. The interdependent nature between small arms and ammunition (there is a mutual reliance between the two), allows us to apply the following theories to both. An important consideration is that the presence of ammunition in a particular country or territory does not implicitly denote that the manufacturing country is responsible [72]; the ammunition may have been traded legally, then diverted illicitly. Bearing this in mind, knowledge of the manufacturer may help to determine legitimate trade and the point of diversion [72].

Understanding the stockpiles from which illicit small arms and ammunition are sourced is essential. These stockpiles are usually legitimate government resources, acquired through trade. Referred to as the “white market” these function in accordance with national and international laws and are considered legal. However, the data on trade within these markets is not subject to complete transparency and is of varied quality; there are regular discrepancies between national import and export statistics provided by officials [66], [80]. The ‘Norweigan Initiative on Small Arms Transfers’ (NISAT) website has an interactive resource known as the Mapping Arms Database (MAD) [81] that “features over 35,000 records of the exports and imports of small arms and ammunition from more than 262 states and territories between 1992 and 2012.” In addition, the extensive database provided by NISAT reflects differences in the reported imports and exports between nations.

NISAT is also in possession of information on the “black market”. This refers to dealings which occur in the absence of government approval, and sometimes violate national and international laws [66]. Illicit trade, by its very definition, describes arms and ammunition from prohibited sources – often not through conventional ‘purchase’. Obtained and utilised unlawfully, these are usually in the possession of non-state armed actors; because these factions operate outside of government control, they present a threat to social and economic stability. The governments of most states possess sole authority of lethal force, and non-state armed groups can use small arms to contest these, alternatively, criminals may exploit them to take control of areas. Whist it cannot be assumed that those representing national governments will not abuse small arms, it can be observed that distribution of illicit small arms and ammunition contribute to both injury, and mortality rates [66].

It is believed that mercenaries and militias may conduct attacks in an attempt to disrupt current governments. One illustration of this was by Liberian/Ivorian parties in Côte d’Ivoire in June 2012, where an attack allowed them to obtain 1,000 rounds of 7.62 x 39 mm, also resulting in the death of seven UN peacekeepers [72], [79], [82]. 7.62 x 39 mm ammunition is regularly found to be illicitly diverted: The UN Group of Experts determined that Romanian produced 7.62 x 39 mm ammunition found in the possession of the Forces Nouvelles in Côte d'Ivoire, was indeed intended for Burkina Faso [83]. Additionally, the evacuation of the UN camp in 2006 saw approximately 1,000 Bangladesh produced rounds of the same calibre stolen, only to be observed later, in the possession of "uniformed arms men" [72].

2.4.2 Disrupting Illicit Trade

Reports such as "Identifying Sources" clearly express their interest in trying to "disrupt and dismantle" flows of ammunition in an attempt to "contribute to regional security and stability" [72]. Documenting the types of ammunition present is a foundation and allows for the identification of newly introduced ammunition. This may indicate that actors involved are no longer sourcing ammunition from Ivorian stockpiles and now have the means (financial and otherwise) to access regional and global markets [72]. By documenting and reporting ammunition in areas of conflict, or post-conflict, researchers are hoping to assist governments in monitoring the security of state-controlled stockpiles. Maintaining the profiles of ammunition can assist in detecting diversions and help to develop a better understanding on the illicit circulation of ammunition, allowing parties involved to intervene more effectively [72].

Often non-state actors will repackage ammunition in an attempt to conceal the source. This may be in polyethylene bags [72], hessian sacks, or unmarked boxes [72]. The types of cartridges present are typically homogenous; indicating that the ammunition was transferred directly from the original packaging, possibly to conceal the source [72]. More heterogeneous ammunition may also be observed in the absence of packaging and stored in " buckets and boxes" [72].

Efforts to disrupt the illicit flow of ammunition will not always be successful; in 2004 the UN Security Council enforced an arms embargo on Côte d'Ivoire. However, evidence implies that this prevented neither the government nor rebellion groups from receiving ammunition [84]. Specifically, 7.62 x 39 mm ammunition (manufactured subsequently to the above date) was documented with the remaining cartridges from 2005, 2007, in 2008, and Sudanese cartridges from 2009, 2010, in and 2011. Cartridges produced in Czechoslovakia, Hungary, and Poland from 1970-2000 were also documented. However, these were not recorded in the government stockpiles prior to the 2004 embargo [72].

The argument to support disrupting the illicit flow of ammunition is perhaps more significant than that of firearms. Whilst firearms can be retained for years (sometimes decades) of use, ammunition can only be used once and requires frequent replenishment. Disrupting the supply of ammunition has the potential to to immediately disengage those involved in armed conflict.

3 Chapter 3: ANALYTICAL TECHNIQUES

A variety of analytical techniques were employed with the purpose of examining the physical and chemical differences between ammunition from different origins. These were, X-ray Fluorescence (XRF), SEM-EDX (Scanning Electron Microscope – Energy-dispersive X-ray Spectroscopy), and H_v (Vickers Hardness) micro indentation testing. This chapter describes the techniques and discusses their current uses within ammunition research. The employment, and limitations, of these techniques and the associated data are discussed below.

3.1 X-ray Fluorescence (XRF)

This method allows the examination of the elemental composition of materials [85], [86], [87]. XRF exploits the unique energy levels of electron transfers between outer and inner shells of atoms. The X-ray tube emits high-energy photons and the sample is positioned to receive these. If sufficient energy is radiated, the atom may absorb the radiation and transfer it to the innermost electron, leaving unoccupied spaces on the inner shells as electrons are expelled. Atoms with vacancies on inner shells are considered unstable and electrons will relocate from outer to inner shells. The resulting X-ray shows the disparity between the binding energies of the atomic shells with each element displaying unique characteristics representative of the energy level sets [27].

Wavelength Dispersive X-ray Fluorescence (WDXRF) is one of the standard methods of XRF and determines the wavelength energy of samples, however, it is inferior to Energy Dispersive X-ray Fluorescence (EDXRF) in that it requires relatively large sample sizes and expensive equipment [27]. EDXRF measures the energy of the fluorescent radiation using less complicated equipment, thus being less costly. In addition, the development of portable equipment (using radioisotope sources in place of X-ray tubes) that can rapidly analyse samples in situ means that this is preferential for use within a forensic context as it helps mitigate the risk of contamination [27]. Micro-XRF is utilised where there is a very small surface area of a sample and provides detailed information such as the distribution of elements within a sample [27].

XRF has been used to analyse the elemental composition of GSR, examining for K, Fe, Cu, Ba and Pb [27], [86], [88]. Micro-XRF can also be utilised to produce a spectrum or information regarding the distribution of GSR – known as a ‘distribution map’ [27], [88]. Additional analysis has utilised XRF to determine the “placement and distribution of GSR particles” This method has the advantage of being non destructive however, it can not be utilised for individual particle identification [89], [57], [90].

Spectrum interference may cause problems when trying to interpret the spectrum produced. Several phenomena may occur and are only covered briefly here. Scattered X-rays or ‘scattering’, occurs when primary X-rays are dispersed (‘scattered’) by atoms in the sample. These X-rays subsequently reach the detector and are the result of both *continuous* and *characteristic* X-rays. Continuous X-rays are more colloquially known as ‘background noise’. This is particularly problematic with organic materials or elements that have a low atomic number. An increase in the intensity of continuous X-rays is the result of increased detection of scattering and is prevalent when measuring samples composed of lighter elements. Characteristic X-rays relate to peaks known as *Rayleigh Scattering*; these represent the energy of the X-ray tube target metal. At a lower energy position there will be a broader peak known as *Compton Scattering*. *Escape* and *Sum* peaks relate to small peaks detected at positions relative to the energy of the characteristic X-ray of the main element. Escape peaks exist 1.74keV (for Si detectors) below the energy position and are the result of some of the energy being absorbed by the detector. Sum peaks occur when two X-rays reach the detector at the same time and will have twice the energy of peaks for elements in abundance [91].

XRF is more sensitive to higher atomic weight elements than SEM/EDX, however, the two techniques are supplementary rather than interchangeable. The use of an X-ray beam means that samples do not need to be coated, and the exposure to higher excitation makes the identification of heavy elements easier.

3.2 Microscopic Techniques

3.2.1 Optical Microscopy

Optical microscopy allows the study of properties that cannot be otherwise observed. Valuable in many disciplines of forensic sciences, the magnification occurs through utilisation of lenses, initiating refraction [92], [93]. Within forensic laboratories these may be compound microscopes, stereomicroscopes, polarising microscopes and/or fluorescence microscopes [27]. Light microscopes comprise of a light source, a condenser and two lenses (optical and ocular). The condenser accumulates light from the source, directing it to the sample. The image produced is magnified by the ocular lens and these magnifications can reach up to x1300 [27].

For ammunition analysis, a comparison microscope is the most appropriate choice as it allows the simultaneous assessment of more than one object. Comprised of two compound microscopes beside each other to give a single field of view, this may be used to assist in determining the origin of markings. For example, two projectiles can be placed into the adjustable holders and observed beneath the lenses. The items can be moved and rotated individually until a particularly distinguishing marking is observed. It may be possible to align this with corresponding striations in the adjacent sample and determine the similarities/differences present [27].

3.2.2 Scanning Electron Microscope Energy Dispersive X-Ray (SEM-EDX)

This chemical technique uses the application of an electron beam to produce sample images that are magnified [27], [94]. SEM relies on an electron gun producing an electron beam which is focused into a vacuum and through electromagnetic lenses. Termed *rastering*, the beam moves back and forth over the chosen area. The entire process relies upon the electrons from the beam interacting with those from the sample and becoming displaced. These are then identified, magnified and displayed [27].

Many signals can be produced from beam-sample interactions. The sample is analysed under vacuum to ensure that there is no interference with the electrons as they travel towards the sample, and then toward the detector [95]. There are two imaging modes that are commonly used in SEM: *Backscatter Detection* and *Secondary Electron Imaging*. For Backscatter Detection, the electrons from the beam reach the sample and partially orbit it, before being forced away by the momentum. This indicates *heavy* elements with a dense nucleus. As the elements being analysed in inorganic GSR are metals, this may be a good indicator and these would be expected to appear as bright images. Secondary Electron Imaging occurs when electrons from the beam displace electrons in the sample. Electrons will move within the sample in order to reinstate stability; this is useful for imaging the surface of the sample and assists with determining morphology. These electron interactions cause the movement of electrons between shells (from outer shells to inner shells) emitting X-rays that are characteristic to the sample elements [91], [95].

The preparation process is crucial in order to obtain high quality, reproducible results. The sample is retained on an adhesive tape which is fixed to a metallic disc (stub) [8]. For the analysis of GSR it is preferable to use a carbon based adhesive (aluminium is also available) as this is unlikely to interfere with X-Ray lines of interest. Furthermore, if a sample is nonconductive, the surface must be coated with a conductive layer to prevent secondary electrons generating superfluous levels of positive charge as this will result in a blurred image [27]; this can be mitigating by using the SEM in variable pressure mode. The samples may also be placed onto a conductive block; this prevents a negative charge from building on the surface which could otherwise result in the electrons being repelled and the phenomena of *charging* from occurring. Charging will otherwise generate images with blurred lines [95].

The expected morphology of GSR is spheroidal. This is due to the particles of being heated during discharge, before cooling rapidly as they reach the cooler external temperatures. The molten vapour results in droplets that cool prior to being affected by gravity (preventing 'teardrop' shapes) [95].

SEM is often used in combination with EDX for elemental analysis in order to determine the configuration of different sections of a sample. The EDX detector is typically set at about 10 mm from the sample [95]. Examining ratios of lead-barium-antimony allows the detection of GSR particles [27] and application of this method is widely accepted and considered the primary method of analysis for this component [6], [96], [89], [90], [57].

EDX can also be used to identify additional elements that may be present, however, these do not necessarily signify the presence of GSR and may be connected to other sources [27], [57]. The SEM is capable of producing electron micrographs and the results can be translated into EDX spectrum. Many attempts have been made to characterise and differentiate between sources of inorganic GSR. Brozek-Mucha compared residues and found that visual inspection showed variances between three ammunition types, however, further research was required for statistical analysis to be appropriately conducted [97]. A comprehensive study by Lebiedzik and Johnson allowed for differentiation between the firearm used, the cartridge case, and the projectile. They analysed 60 different types of ammunition for 21 elements and reported the ability to estimate calibres and materials used [98].

The combination of SEM-EDX can provide information about the size, morphology and chemical composition particles within a sample. This is done on individual particles rather than an analysis on the entire sample as one entity. This capability is advantageous to many fields of forensics with the technique being regularly used to analyse paint [99], [91], [100], fibres [101], [102], [103], glass [96], [104], [105], [106], [107], and document samples [27], [108].

The resulting concentrations of elements are generally categorised into three groups: major, minor, and trace. The aforementioned terms relate to peak height, rather than concentration. Wallace explains that the “strongest peak height should be “on scale” and background levels must be allowed for. The peak heights depend on sample surface irregularities and matrix effects and there is a further complication with overlapping peaks” [40].

3.3 Hardness Testing

The concept of hardness is relative to the context in which is is used. It is generally accepted that a harder material will mark or scratch a softer material. *Shaw* suggested that ‘hardness’ may be defined by the resistance of ‘x’ to an action (e.g. cutting or penetration) [109]. Related to the plastic stress of a material, it is a valuable technique when studying the lattice’s resistance to local deformation [110], [111]. Plastic stress describes changes in the material that are non-reversible – i.e. if a paper-clip is bent out of shape, it will not revert to its original shape once released. This is not a comprehensive definition of hardness and does not account for the various characteristics of a material which may be encompassed by this feature. *Ashby*’s definition is widely accepted describing hardness as “a measure of the resistance to permanent deformation or damage” – advising that the hardness is related to the ability to resist structural breakdown [112]. This differs from *Stillwell*’s earlier description that is is the materials resistance against lattice destruction [113]. Although there are various ways in which this property is defined, it is referred to one of the most significant mechanical properties of materials [114], [115], [116], and is accepted as a suitable measure of strength and plastic properties [117].

It is commonly acknowledged that hardness testing involves both elastic and plastic deformation, however, it cannot be determined using a single physical property. Measurements are carried out in order to provide classification of materials. Conducted with relative ease, *Mott* describes it as a non-destructive technique that allows for determination of material suitability, homogeneity and effectiveness of heat treatment [111].

The most common technique used to determine the hardness value is indentation. For static hardness testing a consistent load is applied by means of a ball, diamond or cone and the subsequent area/depth of the indentation is used to calculate the hardness [111]. One recognised method is *Vickers Hardness* testing covered extensively by ASTM E92-16 [118]. Considering the size of small arms ammunition, microindentation testing is a more appropriate method (although the theory for both methods is identical). There are some particular points should be highlighted regarding how testing is conducted:

- The plane of the surface being testing should be perpendicular to the axis of the indenter.
- Inhomogeneity may exist within a material and several areas should be tested then an average calculated.
- Temperature should be controlled as much as possible (close to 23±3°C) and kept within the limits of 10 to 35°C.
- Measurements should be at least 2.5 x the distance of the diagonal length as shown in **Figure 3.1.** Where dV is the diagonal length.

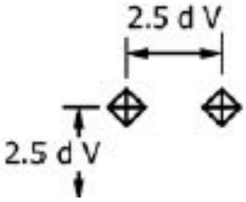


Figure 3.1 Minimum recommended spacing for Vickers indentations [118].

- (FCC) metals (copper, nickel, silver and gold) are more radically affected by work hardening than (BCC) metals (ferritic steels) therefore the distance between indents is more important to prevent indents in areas that have already been subject to deformation [117].

4 Chapter 4: AIMS AND CONSIDERATIONS

The overall aim of this thesis was to investigate whether there are statistically significant variations in 7.62 x 39 mm ammunition that allow for differentiation of ammunition components from different manufacturers. This thesis will use the term provenance in relation to the manufacturers (and year/batch), whilst acknowledging 'source' as the source for materials (i.e. steel, brass, primer mixture). The manufacturers will be assumed to have produced all of their own components, rather than purchasing components and assembling them. In particular, the manufacturing/production techniques are of interest, as these are likely to be representative of historical context.

A wide range of physical and analytical techniques were employed and the results amalgamated. In order to provide further insight into the processes involved in ammunition manufacture, it was necessary to appreciate the complexities of the materials used in each component. This study utilised industry standard accepted practices, from several disciplines in order to develop methods of analysis. The individual thesis objectives are as follows:

1. Investigate physical and chemical characteristics of ammunition components to determine if there are statistically significant differences between components from different manufacturers.
2. Characterise differences and create a Bayesian Network model that allows for inputted variables to be selected.
3. Determine which components and techniques are most valuable and how these can assist with mitigating the illicit trade of ammunition.

The choice of calibre and its ubiquity (discussed in **Section 2.4**) demonstrate the scope of application for this research. Whilst there is value for identification of 7.62 x 39 mm within the U.K [119], the literature demonstrates the regularity with which this calibre is encountered in conflict zones globally (see **Section 2.4**). This is likely due to historic events that preceded and followed the Second World War. The formation of the Union of Soviet Socialist Republics (USSR) – aka the Soviet Union – in 1922 was arguably in response to the formation of

NATO. It included both Russia and Ukraine as well as 13 other ‘core nations’. These nations were considered allies, with supposedly equal input into economics and politics, however, Russia was notably assertive in its communist ideologies. This characteristically dominant style of governing continued through to the formation of the Warsaw Pact in 1955. More formally known as ‘The Warsaw Treaty Organization’, this agreement was between the USSR and several communist run countries. These included: Albania (until 1968), Poland, former Czechoslovakia, Bulgaria, Romania and Hungary. Manufacturers in Albania and former Czechoslovakia were for nationalised in 1945 with many others following suit in the early 1950’s – in line with USSR ideologies. Considering that the majority of manufacturers selected for this study are historically associated with the USSR and/or the Warsaw Pact, many manufacturers were state owned for a significant period of time. 7.62 x 39 mm ammunition was produced on a mass scale using materials and marking practices (headstamp and lacquer) that were aligned with those by the USSR. From 1989, the communist parties in the majority of these countries collapsed. Both the USSR and the Warsaw Pact formally existed for another couple of years until dissolved in 1991 [62], [120].

Once these entities disbanded, ammunition manufacturers were privatised and began to align with the requirements of global markets. Ammunition was exported in large quantities and this is reflected in the abundance 7.62 x 39 mm ammunition being found in various countries – particularly in conflict zones [13-18], [78]. As this originates from manufacturers predominantly in China and the former Soviet Union (37%) [71], identifying unique characteristics from these manufacturers may assist in determining if unmarked ammunition has been traded. Over half of ammunition samples in conflict zones were manufactured prior to 1990, indicating the potential for several transfers to occur between many parties [71]. Whilst knowledge of the manufacturer does not identify the path of trade, it may help to determine legitimate trade and the point of diversion [72]. Both historic and current affairs demonstrate how being able to provenance ammunition in the absence of a headstamp could provide valuable assistance in preventing illicit trade.

5 Chapter 5: MATERIALS AND METHODS

This chapter details the materials and methods utilised throughout this project. This research was designed to establish whether there is significant variation in physical and chemical properties for 7.62 x 39 mm ammunition produced by different manufacturers/countries. The provenance of the ammunition has been defined as the manufacturer and every effort has been made to ensure that the headstamp information is accurate (matching the FOLIO information for Defence Academy, Shrivenham, UK). The reliability of provenance by headstamp has been addressed in **Section 2.3.4.1**, however, this information will be assumed to be accurate, in order to allow for comparisons to be made between results. Ammunition was considered from known manufacturers and examined using widely accepted analytical techniques; namely, SEM-EDX, XRF and H_v. This ensured that the analysis conducted by forensic/NGOs could be replicated without the requirement for additional resources. For each of the methods employed, the number of samples and the number of repeats varies; however, the lowest frequency was not less than 3. This was due to the availability of samples as well as limitations imposed by the equipment used. The techniques used for analysis are outlined in **Table 5.8**, **Section 5.6**. The data collected from each technique is diverse, and in some instances, complimentary.

5.1 Sample Components

Samples were obtained from the ammunition stores at the Defence Academy, Shrivenham, UK, however, some components for certain manufacturers were not available for analysis. This was a result of improper labelling when samples had been stored, and rather than risk the validity of this project's results, these components were omitted. The list below outlines the different components and for which manufacturers they were omitted (explained in **Table 5.1.** below):

- Steel Core: Serbia (PPU/1994), Serbia (PPU/1985), South Africa (13/88), Bosnia (NK/1983)
- Cartridge Case: Serbia (PPU/1994), Bulgaria (10/99a)

- Primer Cap: Serbia (PPU/1994), Bulgaria (10/99a)
- Primer Residue: Serbia (PPU/1994), Bulgaria (10/99a), Poland (21/91), Albania (11/89/3), China (61/64)

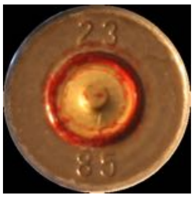
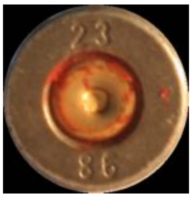
5.2 Sample Details/ Observations/ Physical Characteristics

The information on the headstamps was utilised to categorise the samples and each was assigned an alphabetical letter during the project. This allowed for a simple labelling system and effectively mitigated some cognitive bias.

The weight, dimensions, materials and composition of the ammunition components were recorded, as well as the headstamp information. The headstamps and relevant information are detailed below in **Table 5.1.**

Table 5.1 Details of ammunition samples.

Production Facility and Country	Year	Headstamp	Photograph	Sample
Sellier & Bellot JSC Vlašim **Czechoslovakia** [121], [73].	1983	bxn/83		B
Prvi Partizan **Serbia and Montenegro** [122], [73], [65].	1994	PPU/1994		E
Arsenal JSCo., Kazanlak **Bulgaria** [73], [65], [74].	1999	10/99		F

Prvi Partizan **Serbia and Montenegro** [122], [73], [65].	1985	PPU/1985		G
Femaru-Fegyver-es Gepgyar Reszvenytarsasag **Hungary** [62], , [73], [76]**,** [123].	1985	23/85		H
Femaru-Fegyver-es Gepgyar Reszvenytarsasag **Hungary** [62], , [73], [76]**,** [123].	1986	23/86		I
Lugansk Cartridge Works, Lugansk **Ukraine** [65].	1967	270/67		J
Pretoria Metal Pressings, Pretoria **South Africa** [124].	1988	13/88		K
Arsenal JSCo., Kazanlak **Bulgaria** [73], [65], [74].	1999	10/99		L
“Societatea Comercială Uzina Mecanică SADU - S.A." of Bumbesti-Jiu, Gorj county.[2] **Romania** [125], [126], [76].	1994	324/94		M

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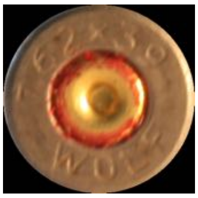
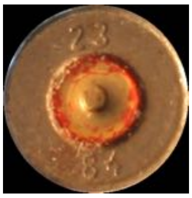
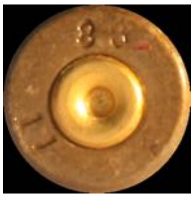
[2] Romania used an alternate code system from the late 1980’s until 2006 when they switched to “SADU”. Codes related to the last digit of the year: e.g. 321, 322, 323, 324,325 [146].

Igman, Konjic **Bosnia & Herzegovina (Yugoslavia)** [65].	1983	NK/1983		N
Ulyanovsk Machinery Plant or Tula Cartridge Works **Russia** [76].	Unknown	7.62 x 39/ WOLF		O
Femaru-Fegyver-es Gepgyar Reszvenytarsasag **Hungary** [62], , [73], [76], [123].	1984	23/84		P
Bakony Fém és Elektromos Készülék Mûvek/ Zaklady Metalowe MESKO, Skarzysko-Kamienna **Poland** [127].	1991	21/91		Q
K.M. Poliçan, Poliçan **Albania** [65].	1989	11/89/3		R
State Factory 61 **China** [76].	1964	61/64		S
Tula Cartridge Works **Russia** [73].	1976	539/76		T

5.2.1 Photographing Samples

Photography is important in providing an accurate representation of the sample being analysed. It also helps to provide objectivity where descriptions may vary between individuals (for example when colours are described).

All photographs were taken with a scale present using a Canon EOS100 digital camera and 18-55 mm f/3.5-5.6 IS STM Zoom Lens. A Patterson Photographic, BENBO1 stand/ camera mount was utilised for most of the photographs in addition to PIXAPRO LED 170 lamps. The lens used varied depending on the requirements; for pictures of the inside of the base of the cartridge cases a MACRO: Canon MacroLens EF-S60mm f/2.8 Macro USM Lens was utilised.

The settings utilised are detailed below in **Table 5.2**.

Table 5.2 Camera settings utilised.

Item	**Setting**	**Explanation/Content**
Aspect Ratio	Lens at 34 mm	Ensures a 1:1 ratio.
ISO	200 *(100)	The camera's level of sensitivity to available light.
Shutter Speed	1/3 (seconds)	The amount of time the shutter is open to expose light into the camera sensor.
Aperture	f16 *(f13)	A hole within a lens, through which light travels into the camera body. Also responsible for the depth of field.
Timer*	2 Seconds	Prevent blur from manual photography.

*For photographs of the cartridge case bases the camera was controlled remotely using CANON EOS UTILITY 2: Version 2.14.10 (2.14.10.2).

5.3 Sample Preparation

The ammunition was disassembled using a Rock Chuck Bullet Swage (RCBS) Reloading Press shown in **Figure 5.1**. The entire round of ammunition is loaded with the cartridge case base being seated. The round is then lifted using the lever, the projectile secured, and the lever is pulled to move the cartridge case downward; separating it from the projectile. The separated components were then measured, photographed and packaged separately into labelled bags: projectiles, cartridge cases, and propellants were all prepared this way as shown in **Figure 5.2** to **Figure 5.5**.

Figure 5.1 RCBS Loading press set up with pulled cartridge case seated.

Figure 5.2 Complete Round of Ammunition.

Figure 5.3 Projectile.

Figure 5.4 Cartridge Case.

Figure 5.5 Propellant in plastic boat.

For each manufacturer (or batch where there were two present from the same manufacturer and year), five rounds of ammunition were prepared in this way and the dimensions and characteristics recorded. This number of samples allow for some statistical analysis (both parametric and nonparametric) whilst still being achievable within the time limitations of this project.

5.3.1 Primer Residue

The primer residues were obtained by discharging the primed cartridge cases from which the projectile and propellant had been removed. This was done using a standard AK 47 barrel fitted to a Number 3 Proof Housing. The cartridge cases were weighed before and after the primers were discharged in order to estimate the primer material weight. Once the primers were discharged the cartridge cases were then individually sealed and bagged and the transported to the SEM lab.

In Cranfield University's SEM lab, a small wooden stick was utilised to scrape the insides of the cartridge cases and pour the primer residue onto a sheet of high quality (less fibrous) paper as shown below in **Figure 5.6**. The papers were then stubbed using a 12.5mm (122.7mm^2) diameter carbon stub (AGAR) on a no groove, 3.2 x 8mm aluminium pin. Gloves, the wooden implements and the sheets of paper were changed between each sample in an effort to mitigate the risk of cross-contamination. For the same reason, the adhesive cover of each SEM stub was only removed immediately prior to stubbing the primer contents [90]. Samples were then stored in AGAR SEM stub holder boxes, in a dedicated SEM lab at Cranfield University, until analysis. Whilst this method may have included traces of propellant, it mitigated and risks regarding health and safety. It was considered to attempt to extract 'live' primers and then detonate these in a controlled environment, however, the explosive material can prove dangerous even in small quantities. The method used proved suitable for the required analysis and time constrainst of the project.

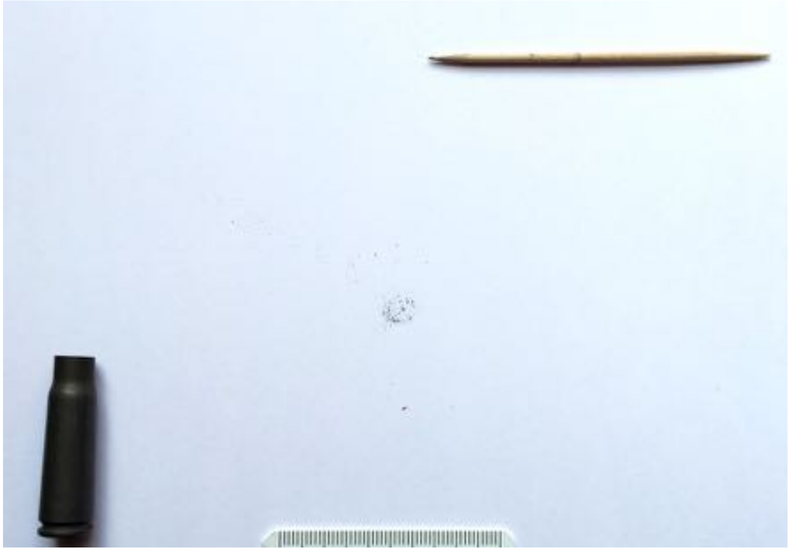


Figure 5.6 Discharged cartridge case, wooden stick and primer residue on high quality paper.

5.3.2 Sectioning Cartridge Cases: Lengthways

7.62 x 39 mm cartridge cases are notoriously tapered, as such, it was not possible to simply saw these lengthways using conventional methods. A bespoke cartridge case holder was manufactured by Technical Services at Cranfield University. This was constructed of mild-steel (EN3) and designed so that the cases could be placed inside, secured using small bolts, placed into a holder, then sawn as shown below This technique allowed for examination of both halves of the cartridge case.

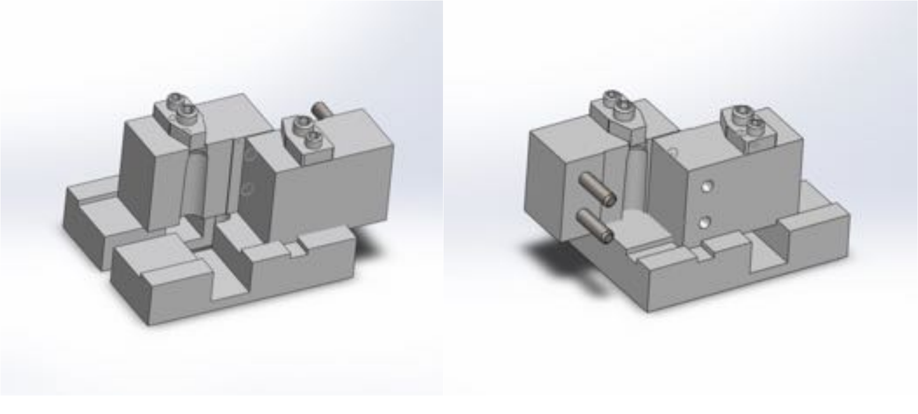


Figure 5.7 Bespoke cutter for 7.62 x 39 mm cartridge cases.

Two cartridge cases from each manufacturer were sectioned in this way – providing four halves per manufacturer and eight ‘sides’ that could be tested for hardness gradients. (see **Figure 5.8**). The primer caps were simultaneously sectioned and later analysed using XRF analysis as described in **Section 5.4.1**. Every attempt was made to ensure that the cases were lined up similarly (with one flash-hold either side), however, this could not be guaranteed and it must be noted that the two halves may not be identical/exactly equal. The weights of each half were recorded.

Figure 5.8 Sectioned cartridge case: lengthways showing four sides available for hardness testing.

5.3.3 Sectioning Cartridge Cases: Bases

For the remaining three cartridge cases from each manufacturer, the base of the cartridge case was removed. As the dimensions had been measured previously (**Section 5.3**) it was possible to calculate the depth of the base: This was done by subtracting the ‘inside’ length from the ‘total cartridge case length’. The average results for each manufacturer were below 5 mm. After discussions with Technical Services at Cranfield University, it was agreed that the bases would all be cut at 5mm. This was done using a high speed steel turning tool with a soluble oil lubricant with the sectioned case shown in **Figure 5.9**.

Figure 5.9 Sectioned cartridge case: base removed to analyse web of case.

The samples were then rinsed in water and dried to prevent oxidisation and photographed using a macro lens as shown in

Figure 5.10**.**

Figure 5.10 Inside of cartridge case showing bolster marks and flash holes.

The above images were then utilised to measure characteristics as detailed in **Section 5.5.1**.

5.3.4 Mounting Samples:

5.3.4.1 Projectiles

ASTM E3 – 11 Standard Guide for Preparation of Metallographic Specimens was consulted when determining preparation methods to utilise. In order to conduct analysis, the projectiles needed to be sectioned and remain flat. For metallographic samples, this is usually done using a castable mount: a two component (resin and hardener) castable plastic, prepared at room temperature, that does not require heat or pressure to cure [128]. METPREP Ltd. UK (KLEER-SET TYPE FF (REF 11 10 81)) Polyester Casting Resin was chosen in combination with the corresponding hardener (KLEER-SET (REF 11 10 89)). Whilst non-conductive, the ability to cold-mount several samples at once helped to relieve some of the time limitations. Additionally, polyester resins are transparent and allowed for the half-way point of each sample to be determined. Alternative resins had the advantage of being conductive, however, they also required heat and pressure to mount samples – this would have introduced a risk of distorting the sample.

The projectile was secured to the base of a 40 mm diameter sample holder before securing the upper part of the sample holder. As many of the analytical techniques required samples to be at the same height, the same amount of resin (15g per sample) was used whilst mounting each sample in an attempt to mitigate future issues. The polyester cure time is listed as 30 – 60 minutes, although it is recommended to leave them at least 8 hours to ensure that there the material temperature has cooled prior to grinding and polishing [128]. Once set, the samples were removed from the sample holders: there was a meniscus present on the side which the label had been placed. This is due to the adhesion of the resin to the sample holder and must be manually ground until the surface is flat.

5.3.4.2 Cartridge Cases

As the cartridge cases were sectioned prior to mounting them, they did not require double-sided tape to secure them to the base of the sample holders. The process for mounting these was almost identical to the process for mounting the projectiles in **Section 5.3.4.1** (above) with a few variations:

- 50 mm diameter sample holders must be used as the cases are longer than the projectiles.
- 30g of resin was used per sample.

The samples took the same length of time to set and required manual removal of the meniscus that was present.

5.3.5 Grinding Samples

5.3.5.1 Projectiles

Sectioning the projectiles required them to be ground using progressively finer grades of Silicone Carbide (SiC) grinding papers as described in ASTM E3 – 11 [128]. The grinding papers used were 200mm in diameter, STRUERS ApS, Denmark QC07090200, Silicone Carbide grinding paper for wet grinding of materials (30-800H_v) in the following coarseness (descending coarseness):

- SiC-Paper, grit 220. Code: PAPER. 40400007
- SiC-Paper, grit 320. Code: PAPER. 40400008
- SiC-Paper, grit 500. Code: PAPER. 40400009
- SiC-Paper, grit 800. Code: PAPER. 40400010
- SiC-Paper, grit 1000. Code: VARUS. 40400072
- SiC-Paper, grit 1200. Code: PAPER. 40400073.

The sample widths were measured at the tip, middle and base of each mounted projectile prior to grinding in order to calculate how much needed to be removed. Planar grinding (grit 240 and coarser) is recognised as a method to remove considerable amounts of the sample material [128]. The aim was to achieve projectiles sectioned in half (or as close to half as possible). These widths were checked and the width measured at regular intervals to ensure that less than 50 per cent of the width had been ground away. Fine grinding was utilised to remove any damage that planar grinding may have caused to the sample [128].

A STRUERS ApS, Denmark, ROTOPOL-21 was used in combination with a STRUERS ApS, Denmark, ROTOFORCE-4 (automated sample holder). The bespoke sample holder allowed for six samples to be processed simultaneously and is considered advantageous as it allows for consistency of quality [128].

This was placed into the rotary wheel and the samples were ground using the parameters shown in **Table 5.3**.

Table 5.3 Parameters used for grinding of mounted samples.

Option	**Setting**
Direction	Rotates the sample and grinding paper in the same direction.
Force	25 newtons.
Time	3.5 minutes.
Lubricant	Water (also used to wash away grinding debris and to act as a coolant).
Rotations per Minute	150.

Once removed, the mounted and sectioned projectiles were cleaned thoroughly in water and dried immediately to prevent oxidisation (rust) from occurring. They were then wrapped in tissue and placed into appropriately labelled sample bags. The tissue helped to prevent both scratching and sweating of the samples.

5.3.5.2 Cartridge Cases

Again, this process was similar between to that of the projectiles in **Section 5.3.5.1**, however, as the cartridge cases had been sectioned prior to mounting, this was labour intensive. The cartridge cases were ground using the following papers (all 200 mm diameter):

- SiC-Paper, grit 500. Code: PAPER. 40400009
- SiC-Paper, grit 800. Code: PAPER. 40400010
- SiC-Paper, grit 1000. Code: VARUS. 40400072
- SiC-Paper, grit 1200. Code: PAPER. 40400073.

The parameters shown in **Table 5.3** in **Section 5.3.5.1** (shown above) were also used. Providing that the resin did not prevent the metal of the case being visible under a microscope then the cartridge cases could be polished.

5.3.6 Polishing Samples

Once the projectiles and cartridge cases were mounted and sectioned (and vice versa), they required polishing in order to remove any scratches. As before, this was done in line with ASTM E3 – 11. The process of polishing is similar to that of grinding, however a loose abrasive (≤6μm) is utilised [128]. This was done using the same apparatus as the grinding process (STRUERS ApS, Denmark ROTOPOL-21 was used in combination with a STRUERS ApS, Denmark ROTOFORCE-4) but using a separate rotor and polishing cloths. For brass jacketed projectiles with lead cores, and brass cartridge cases, a 200 mm diameter STRUERS ApS, Denmark, MD/DP-Mol polishing disc was used. For steel jacketed/steel core projectiles, and steel cartridge cases, a 200 mm diameter STRUERS ApS, Denmark, MD/DP-Dur polishing disc was used.

The parameters used varied slightly and are shown in **Table 5.4** below:

Table 5.4 Parameters used for polishing of mounted samples.

Option	**Setting**
Direction	Rotates the sample and grinding paper in the same direction.
Force	30 newtons.
Time	4 minutes.
Lubricant	METPREP Ltd. UK 3μm diamond spray (applied every 2 minutes).
Rotations per Minute (RPM)	150.

Specimens were again cleaned thoroughly in water and dried immediately to prevent oxidisation (rust) from occurring. They were then wrapped in tissue and placed into appropriately labelled sample bags until further examination.

5.3.7 Etching of Microstructure

For selected projectiles where a steel core was present, samples were polished using a 1μm diamond spray, cleaned thoroughly and then dried using hot air (to prevent staining). They were then etched chemically using 2% nitric acid in ethanol by means of ‘swab-etching’, i.e. swabbing them with cotton wool soaked in the aforementioned. This then revealed the composition of the grains, known as the microstructure [17]. ASTM E3 – 11 recognises that “microstructures have a strong influence on the properties and successful application of metals and alloys. Determination and control of microstructure requires the use of metallographic examination” [128]. Examination was conducted using a light optical microscope, the images saved and analysed as described in **Section 5.5.3.**

5.4 Analytical Techniques

The analytical techniques employed for this research were chosen based on their acceptability and accessibility. This section describes the parameters/instrumental set up, any additional sample preparation and data analysis for each technique. The information obtained from each technique is summarised at the end of this chapter in **Table 5.8.** For each sample, measurements were taken in various locations.

5.4.1 XRF Analysis

X-ray fluorescence analysis for projectiles, steel cores, cartridge cases, and primer caps was carried out using a Seiko SEA6000VX High Sensitivity Fluorescent X-ray Analyser, SIINT, Japan. This machine possessed a rhodium X-ray tube and a silicone detector. The software used in conjunction was X-ray Station (Version 1.5). Mounted samples could be secured onto a polyester stand and loaded into the instrument in groups. A spirit level was used to check that samples were flat, however, the equipment is able to compensate for height differences of 30mm or less (also correcting effects of changing distances on the detector) [129].

In addition to an annual external calibration and service, Dr J. Rock of Cranfield University performed weekly internal calibration of the equipment. Analysis of standards was undertaken to understand the accuracy achievable by the machine. Three reference standards were used for this analysis, one steel and two brass:

- EURONORM-ZRM-193-1 (Steel)
- 31X MNB5R (Brass – Manganese Brass)
- 31X CZ114A (Brass – Leaded Brass)

Details of the reference standards can be found in **Appendix J**.

The reference standards were then utilised to create analysis condition files for automated sequential measurements, otherwise known as 'mapping'. Mapping of the samples varied for each component and are shown in **Figure 5.11** for the projectile jackets, **Figure 5.12** for the projectile steel cores.

For the projectile jackets, five points were analysed in a clock-wise direction, shown in **Figure 5.11**.

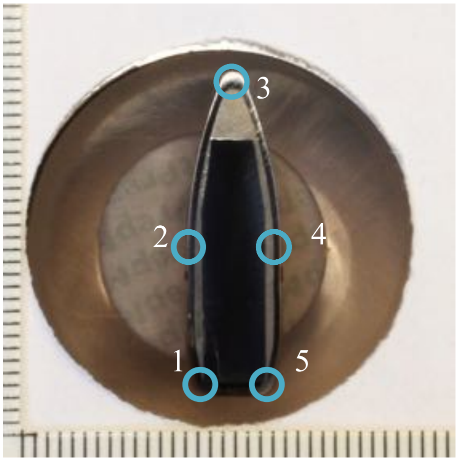


Figure 5.11 Sectioned projectile showing five points in the jacket for XRF analysis.

For the projectiles where a steel core was present, this was analysed in three areas, shown in **Figure 5.12**.

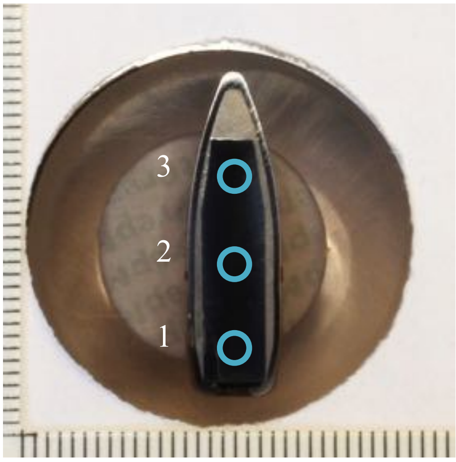


Figure 5.12 Sectioned projectile showing three points on the core for XRF analysis.

For the cartridge cases, two areas were analysed at the base. This is where there is the most material available for analysis and therefore a larger collimator size was used on the areas shown in **Figure 5.13**.

Figure 5.13 Sectioned cartridge case showing two points for XRF analysis.

The primer caps were also analysed in two points. Care was taken to ensure that this was done on the edge that had been sectioned in an attempt to prevent analysing material that may have been present in the primer mixture. These are shown in **Figure 5.14**.

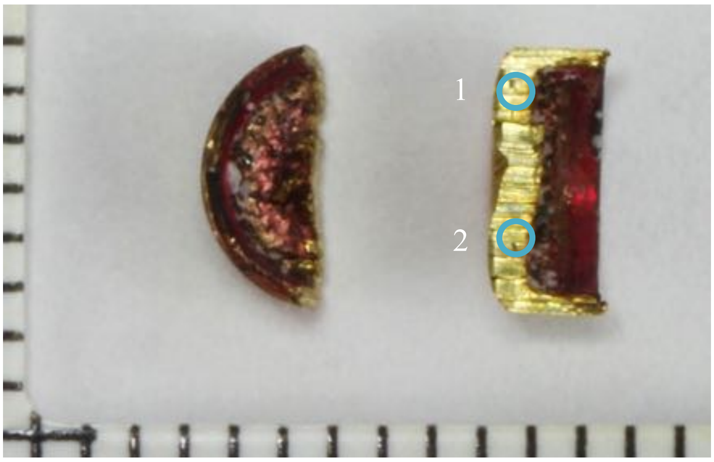


Figure 5.14 Sectioned primer caps showing two points for XRF analysis.

The measurement conditions used to analyse the sample components are detailed below in **Table 5.5**.

Table 5.5 Parameters used for XRF analysis of samples.

Parameter	**For Steel**		**For Brass**	
	Condition 1	Condition 2	Condition 1	Condition 2
X-ray Tube	Rhodium	Rhodium	Rhodium	Rhodium
Tube Voltage (KV)	15	50	15	50
Analysis Time (Seconds)	300*	300*	300*	300*
Tube Current (μA)	1000	1000	1000	1000
Analysis Environment	Air	Air	Helium Purge	Air
Peaking Time (μs)	1.0	1.0	1.0	1.0
Filter	For Cr	For Pb	No Filter	For PbMap
Collimator Size for Jacket (mm)	0.2 x 0.2	0.2 x 0.2	0.2 x 0.2	0.2 x 0.2
Collimator Size for Core (mm)	0.5 x 0.5	0.5 x 0.5	N/A	N/A
Collimator Size for Cartridge Case (mm)	0.5 x 0.5	0.5 x 0.5	0.5 x 0.5	0.5 x 0.5
Collimator Size for Primer Caps (mm)	0.2 x 0.2	0.2 x 0.2	0.2 x 0.2	0.2 x 0.2

* Reference Standards run for 500 seconds.

The spectra were saved and the quantified results exported to Microsoft Excel and compared in **Section 6.1**.

5.4.2 SEM and SEM-EDX

5.4.2.1 Projectile Jacket Imaging

The majority of the projectiles were M43 type (steel core, boat-tailed) and of these, all but one of the jackets were composed of steel (confirmed with XRF **Section 5.4.1**).

The external copper plating of the steel jacket is visible to the naked eye. In order to obtain accurate measurements of the width of this plating, a Hitachi SU3500 Scanning Electron Microscope, Hitachi, Ltd, UK, was utilised with the "Scanning Electron Microscope" software (version 2.1) installed. The samples were placed – in the same orientation - onto a 127mm diameter sample mount. As these samples were cold mounted into a non-conductive resin, they required a section of conductive copper tape (Scotch Brand) to run from an exposed piece of the projectile jacket to the sample mount (holder). This prevents charging which would have been detrimental to the image received (discussed in **Section 3.2.2**). The tape was attached to the sample at the tip/nose of the projectile, shown in **Figure 5.15**, as this portion of the sample would not be analysed using the SEM.

Figure 5.15 Sectioned projectiles secured to 127mm mount with conductive copper tape to prevent charging.

The samples were all marked at 2 mm intervals from the base. The analysis of the jacket was conducted at between 4 and 10 mm from the base of the projectile, as shown in **Figure 5.16**. The software was used to ensure that the samples were correctly orientated and moved only along the x-axis to the jacket of the projectile.

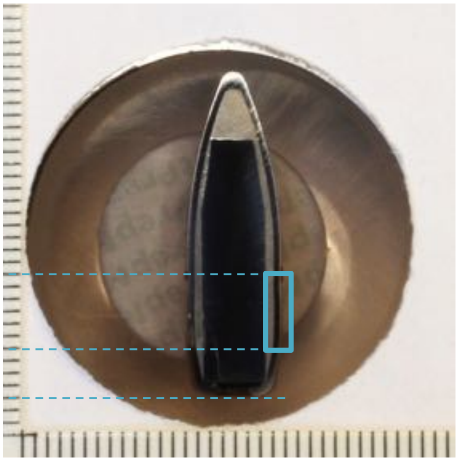


Figure 5.16 Sectioned projectile showing area selected for SEM imaging.

The analysis conditions were set to VP – SEM (Variable pressure vacuum mode). This means that the chamber is back filled with a gas in order to allow imaging with little or no charging of the sample.

All samples were analysed at x150 magnification with contrast at 55 (±10) and brightness at -7 (±5). These were adjusted by manual operation in order to obtain an image that allowed for differentiation between the plating edges and the steel portion of the projectile jacket. Each image was then analysed as described in **Section 5.5.2**.

The beam conditions were set as described in **Table 5.6.**

Table 5.6 Parameters used for SEM analysis of projectile jackets.

Option	Setting
Accelerating Voltage	15kV
Spot Intensity	50
Magnification	x150
Condition	Variable Pressure-SEM
Vacuum Pressure	30Pa
Detector	BSE
Working Distance (WD)	5mm (Variable)

5.4.2.2 Primer Residue Analysis

The carbon stubs that contained primer residue from **Section 5.3.1** were analysed using a Hitachi SU3500 Scanning Electron Microscope, Hitachi, Ltd, UK, and Texture & Elemental Analytical Microscopy (TEAM) EDX software (Version V4.4). The stubs were then placed into a 6 stub in a clockwise manner as shown in **Figure 5.17** with a small marking next to the first sample so that they could be correctly identified and labelled once they were placed into the SEM chamber.

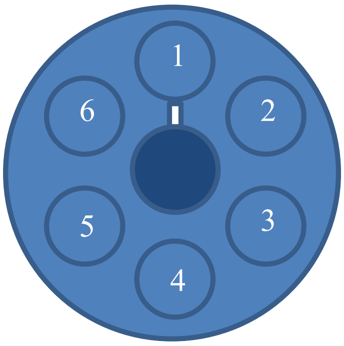


Figure 5.17 Drawing showing positioning of SEM stubs in holder.

The analysis parameters are shown in **Table 5.7**:

Table 5.7 Parameters used for SEM-EDX analysis of primer residue.

Option	Setting
Accelerating Voltage	25kV
Spot Intensity:	70
Working Distance (WD):	10.0mm
Magnification	x35
Condition	High Vac - SEM
Signal	BSE
Time	30 seconds

The length of time required to analyse an entire SEM stub is prohibitively time-consuming, especially in the absence of automated software. In casework, primer particles are randomly collected it is understood that there is a low chance of clustering and therefore it is acceptable to analyse a portion of the stub surface using appropriate protocols [90]. As the stubs were not speculative samples and instead reference sample collected from discharged primers, it was expected that they would be loaded with primer residue. Wolten et al. conclude that “examination of 5 percent of the total area is a safe procedure for estimating the total number of particles within a factor, of two, and that 10 percent can be expected to provide reliable statistics on the distribution of the particles among the various size and composition classes” [60].

In line with ASTM standards [90], an area of approximately 39 mm^2 was analysed at a central point of each stub with the magnification at a low setting (approx. x35). As the primer was discharged from a mounted barrel and in the absence of propellant, the expected number of gunshot residue particles was not the focus of this analytical technique, rather the elemental analysis of the particles present. An area with 30 points of various contrast were selected for elemental analysis in order to obtain a spectrum. Each spectrum was collected for 30 live seconds using an octane plus detector. The results are included in **Appendix D**.

The TEAM Software has a built in “Element ID’ and the ability to have automatically identified elements based on their respective energies, however, the auto-peak ID is not entirely accurate. It was necessary to manually re-analyse the spectra analysis to ensure that the correct peaks were identified. As many elements had similar energies, it is not that the software was making unreasonable identifications, but rather, that the possibility of identifying certain elements in primer compositions was unlikely.

5.4.3 Microindentation Hardness Testing

Hardness testing was conducted on sectioned projectiles that had a steel core present to give an average hardness value. Testing was also undertaken along the wall of the sectioned cartridge cases (both steel and brass) to provide a hardness profile as shown in **Section 6.3.2**. This was done in line with ASTM Standard E384 – 16.

All testing was conducted using an INDENTEC Hardness Testing Machine, model HWDM-7, with a load of 300 gf. The machine was zeroed and calibrated using an AHITI 700H_v force block prior to each period of use. The equipment was designed to load for three seconds, indent for 10 seconds and unload for three seconds. This resulted in a pyramidal mark which was measured vertically for its width (**Figure 5.18**) to give D1 (dimension one) and horizontally (**Figure 5.19**) to give D2 (dimension 2). The internal software then calculated the Vickers Hardness value and Rockell Hardness Value and reported these for each indent.

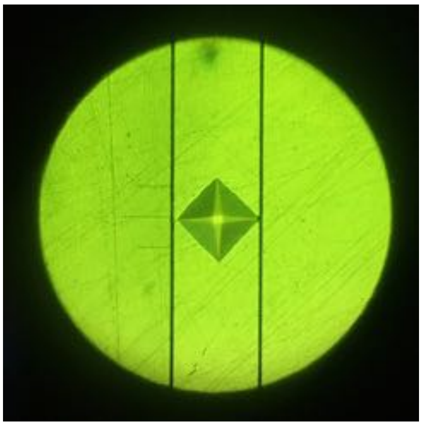


Figure 5.18 Pyramidal indentation mark with vertical measurement lines to give D1.

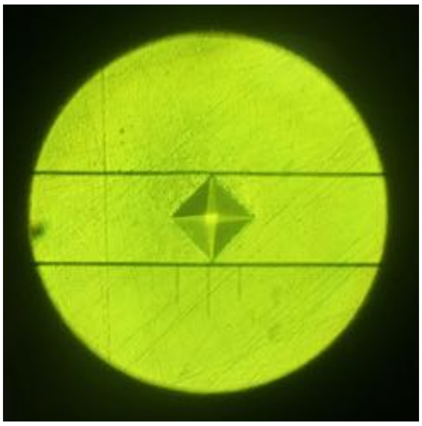


Figure 5.19 Pyramidal indentation mark with horizontal measurement lines to give D2.

For the sectioned projectiles, hardness testing was conducted at five points in 2mm intervals from the base of the core as shown below in **Figure 5.20**. The section of the core closest to the tip of the projectile was slightly truncated and avoided as it is expected that this portion will have undergone some cold working during the swaging process; resulting in a higher H_v result. Unfortunately, time limitations prevented the testing of this hypothesis.

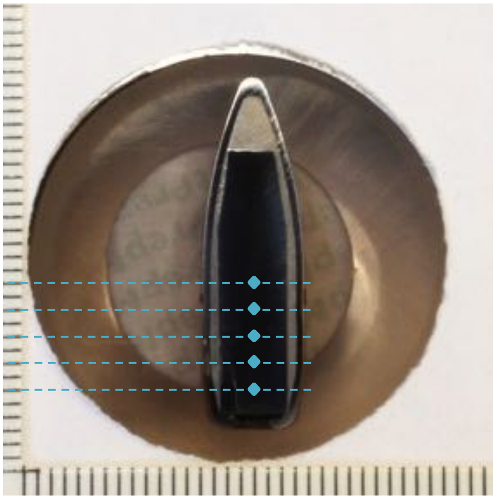


Figure 5.20 Sectioned projectile showing five points at 2mm intervals selected for hardness testing.

The manufacturing process for cartridge cases requires heating and cooling (annealing) to achieve desirable properties, as discussed in **Section 2.2.2**. Variations in the hardness gradients could indicate whether there are variations in the manufacturing processes used by different manufacturers. In order to examine where along the sectioned cartridge case this increase in hardness occurred, testing was initially conducted at 2mm intervals along the cartridge case wall. Where a sharp increase between two points was observed, this area was then examined more closely (at 0.5mm intervals) in order to attempt to accurately determine where the increase occurred. The process for each sectioned case was the same and started at the mouth of the cartridge case. The INDENTEC Hardness Testing Machine, model HWDM-7, was used to move the cartridge cases accurately and examine the case wall. It is worth noting that the number of indentations varied per manufacturer in line with the area covered by increased hardness. **Figure 5.21** shows a sectioned cartridge case prepared for indentation with the general pattern shown by diamond 'indent' shapes.

Figure 5.21 Sectioned cartridge case showing general pattern for hardness testing.

5.5 Image Analysis

Image analysis was conducted using ImageJ version 1.50i. This software was created by National Institutes of Health, USA and is in the public domain [130].

5.5.1 Cartridge Case Bases

Cartridge cases were sectioned as described in **Section 5.3.3** and ImageJ was utilised to measure characteristics marks:

1. Outer diameter.
2. Inner diameter.
3. Bolster mark diameter.
4. Flash hole diameter (x2).
5. Distance between flash holes.
6. Diameter of bolster mark between flash holes.

The numbers above correspond to the labels in **Figure 5.22**.

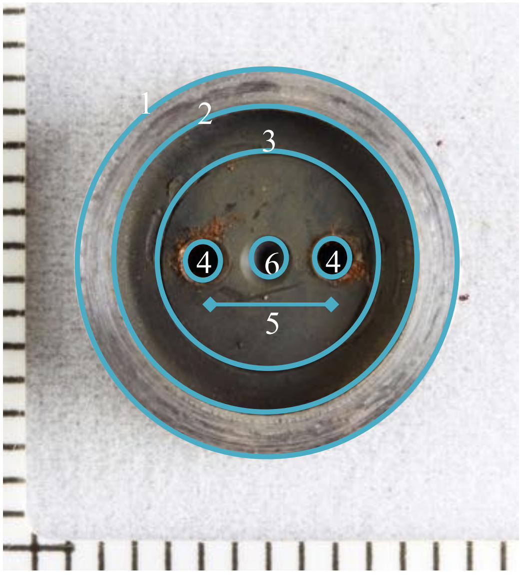


Figure 5.22 Inside of cartridge case showing labelled bolster marks and flash holes.

As the central point of each flash hole could not be definitively identified, it would be difficult and time consuming to ensure that a 'line' measurement taken was truly representative of the diameter. ImageJ allows measurement of circular shapes and provides the area. Determining the area was much more accurate and this method allowed for the radius to be calculated using the following equation:

$$r = \sqrt{\left(\frac{A}{\pi}\right)} \tag{5-1}$$

Where:

- r = radius
- A = area

Multiplying the radius by two provides the diameter as shown in the equation below:

$$d = r \times 2 \tag{5-2}$$

Where:

- d = diameter
- r = radius

The diameters were then recorded and where applicable, compared.

The distance between flash holes was calculated by utilising the x,y coordinates at the centre of each flash hole . This information can be set to record as one of the measurements in ImageJ.

$$\mathcal{D} = \sqrt{((x_1 - x_2)^2 + (y_1 - y_2)^2)} \tag{5-3}$$

Where:

- $\mathcal{D}$ = distance between the centre of the two flash holes
- x_1 = x coordinate of flash hole 1 (on left hand side of image)
- y_1 = y coordinate of flash hole 1 (on left hand side of image)
- x_2 = x coordinate of flash hole 2 (on right hand side of image)
- y_2 = y coordinate of flash hole 2 (on right hand side of image)

These results where also recorded and are reported in **Section 6.3.3**

5.5.2 Projectile Jackets

SEM images of the projectile jackets were obtained as outlined in **Section 5.4.2.1**. These were then analysed using ImageJ software. Prior to calibration, a same horizontal grid was applied to each image at 0.13 inches which created 10 lines shown in **Figure 5.23**. The scale in each image was utilised to to calibrate individual images; this provided an average of each component width and ensured that the points of measurement on each projectile were consistent, and therefore, comparable.

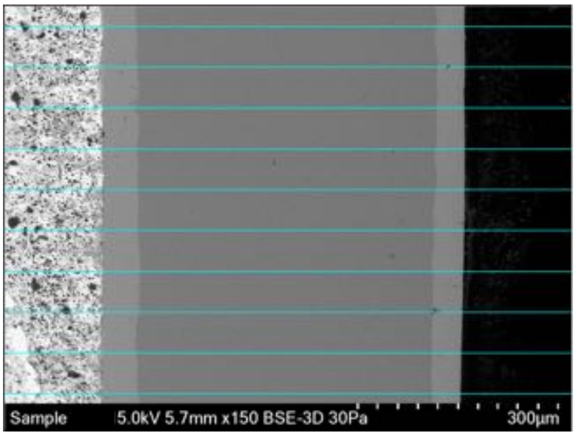


Figure 5.23 SEM image of projectile jacket showing grid overlay and scale bar used for calibration.

Three components of the jacket were measured and one was calculated using the aforementioned. The total jacket width and width of the copper plating on both sides (inner and outer) were measured manually. The total width of both sets of plating was then subtracted from the total jacket width to give the remaining steel jacket width. The different components are shown below in **Figure 5.24**.

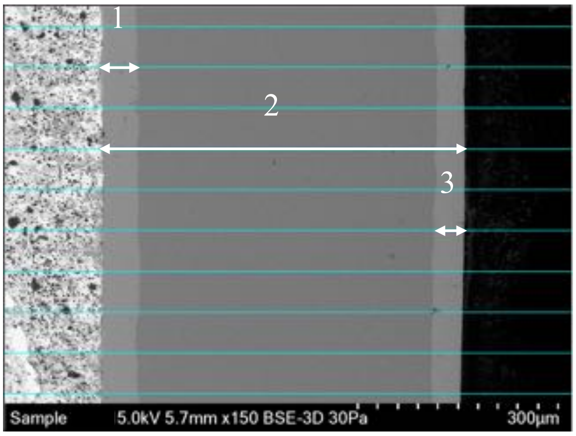


Figure 5.24 SEM image of projectile jacket showing widths of 1) inner copper plating, 2) total jacket, and 3) outer copper plating.

These measurements were then recorded (see **Section 6.1.2**), the average per sample taken, and where applicable, this characteristic was compared.

5.5.3 Microstructure of Cores

For projectiles where a steel core was present, a selection of these were etched as described in **Section 5.3.7**. Images were taken using a light microscope.

These images were used to estimate the percentages of ferrite (light, iron areas) and pearlite (dark, carbon areas). Images were converted from colour images (**Figure 5.25**) to binary images as shown in **Figure 5.26**, with the threshold being manually selected. The white and black areas were then measured (pixels) and used to estimate the amount of ferrite and pearlite as a percentage of the overall image area (pixels).

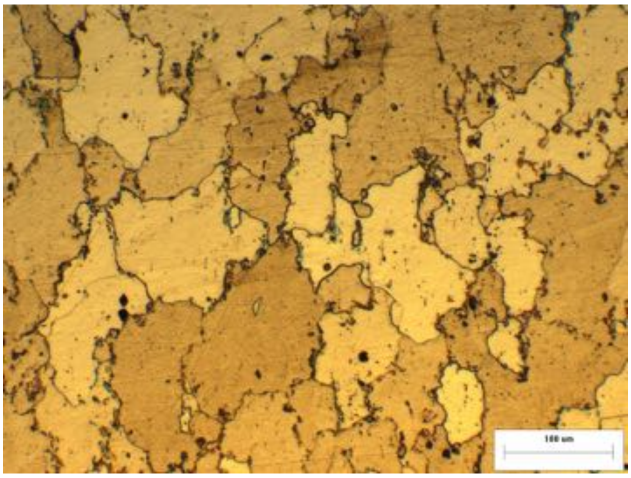


Figure 5.25 Colour image of etched microstructure of steel core.

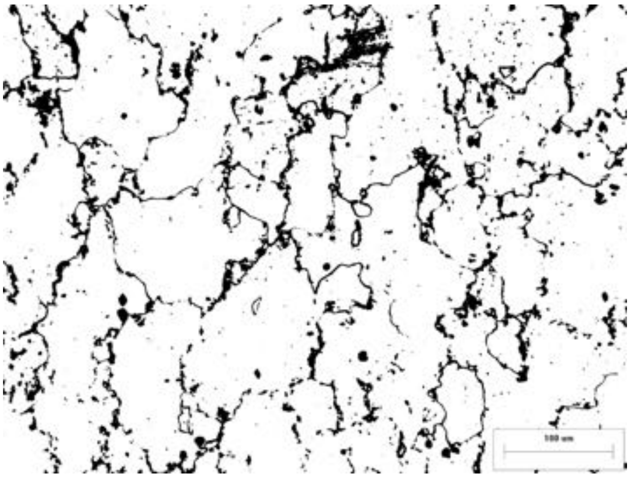


Figure 5.26 Binary image of etched microstructure of steel core.

It is worth mentioning that small dots observed across the samples are the likely result of either the diamond paste particles embedded during preparation, or impurities from the ingot [17].

5.6 Summary of Techniques

A summary which outlines what each technique measures, the information acquired from these techniques for this research and the limitations associated with each technique can be found in **Table 5.8**.

Analytical Techniques	Components	Measures	Used in this research	Limitations
XRF	Projectile Jacket Projectile Core Cartridge Case Primer Cap	Elemental analysis of materials	Quantification of elements present in metal specimens.	May not be suitable for analysis of light elements. E.g. silicone.
SEM/ SEM-EDX	Projectile Jacket Primer Residue	Composition dimensions Elemental analysis of inorganic materials	Measurement of jacket components. Identification of primer composition type.	Time consuming and relies heavily on sample preparation.
H_v	Projectile Core Cartridge Case	Hardness of materials	Average hardness value. Hardness profile.	Inhomogeneity may cause extreme values.
Image Analysis	Projectile Jacket Projectile Core Cartridge Case	Measurement of dimensions	Accurate measurement of component widths. Analysis of microstructure composition. Dimensions and distances of flash holes.	Operator subjectivity when conducting measurements and determining thresholds.

Table 5.8 Summary of techniques utilised.

5.7 Analysis of Results

5.7.1 Statistical Analysis

Statistical analysis was conducted using IBM SPSS Statistic (Version 24). Both parametric and nonparametric tests were utilised. Parametric tests work on some general assumptions that are summarised here:

1. Level of measurement: measurements must be on a continuous scale.
2. Random sampling: although not always the case in research, the sample should be randomly selected.
3. Independence of observations: this addresses bias and is considered serious.
4. Normal distribution: if sample sizes are over 30 then violation of this assumption is unlikely to cause major problems.
5. Homogeneity of variance: this refers to the variability of the scores within each group being similar. Providing that the groups are of similar size, analysis of variance is "reasonably robust to violations of this assumption" [131].

Further information on the assumptions and how to check for violations is covered in detail by Tabachnick [132].

One-way analysis of variance (ANOVA) allows for comparison of mean scores of two or more groups, on a continuous variable; this was ideal for this study. The impact of single independent variable (manufacturer) on dependent variables is assessed. ANOVA tests report whether groups are significantly different but require post-hoc analysis to determine which groups vary.

The *Bonferroni* test is a post-hoc technique that allows for exploration of the differences between each sample set whilst adjusting to prevent inflated results. This adjustment assists in setting a more stringent significance level by dividing the chosen significance/alpha level (0.05) by the number of comparisons that are intended. The resulting value is then utilised as the new significance value. For example, if four comparisons are intended at a significance level of 0.05, then 0.05 would be divided by four to give 0.0125. This new value is required in order for a significance level of 0.05 to be calculated. Furthermore, this will provide some protection against Type 1 errors (false positives) that may occur as a result of several comparisons being made [132].

The above test is only valid where homogeneity of variance is not violated. In order to test for this assumption, Levene's test was used. If $p<0.05$ then this indicates that this assumption has been violated. Similarly, in order to test for normality, the Shapiro-Wilk test was utilised. Where $p < 0.05$, the assumption of normality has been violated.

The *Games-Howell* test is a post-hoc technique that allows for exploration of the differences between each sample set but does not assume equal variances and can be utilised where the assumption of homogeneity has been violated.

The requirements for nonparametric tests are less stringent and assumptions are not made regarding the distribution. It is necessary for samples to be random, independent observations; the data for each round of ammunition can only be counted once and not be present in more than one group [131]. Two nonparametric tests were utilised.

The *Kruskall-Wallis* test allows for analysis of several groups (inter-batch analysis) and works by converting results into ranks and then comparing the mean ranks. The comparison of means removes the issue of distribution and allows this test to function as a nonparametric version of one-way between group analysis of variance providing that the results are continuous.

The *Mann-Whitney U* test functions similarly to parametric t-testing, however, like the Kruskall-Wallis test, medians are compared instead of means. Only two groups can be compared (one categorical and one continuous).

One major disadvantage of nonparametric tests is that they are less sensitive and may fail to detect (inter-batch) differences that are present. Where possible, enough data should be collected in order to conduct parametric testing [131].

SPSS provides values that can be interpreted to determine if there are significant differences. Where “Sig.” is less than or equal to 0.05 then significant differences can be reported. Where results for ANOVA or Kruskall-Wallis tests are less than or equal to 0.05 additional testing (Bonferroni/Mann-Whitney U) can identify where these significant differences are present.

5.7.2 GeNIe

Characterisation of properties to identify a common source has been described as “the ultimate goal of a forensic examination” [133]. Bayes’ theorem and likelihood ratios (LR) are increasingly used to assess the value of corresponding characteristics for evidence. Described in detail by Inman and Rudin [133] and Aitken and Taroni [134], the theorem actually disputes true individualisation in forensic science and suggests that the relationship between materials can never be absolutely certain. Attempts are made to establish strong relationships by assessing the evidence from two perspectives, or two hypotheses:

1. The unknown sample originate from the same source as the reference sample.
2. The unknown sample originates from another source.

Before the likelihood of a match can be examined, contextual information is needed; allowing the examiner to understand intra-batch variation (i.e. ammunition from the same manufacturer) and inter-batch variation (i.e. ammunition from different manufacturers).

The results obtained were analysed using GeNIe Academic (Version 2.1.1104.0), licensed by BayesFusion, LLC. This software is a graphical user interface (GUI) to SMILE (Structural Modeling, Inference, and Learning Engine) and was developed at the Decision Systems Laboratory, School of Information Sciences, University of Pittsburgh.

Time limitations resulted in only the data for the projectiles being input into a model. In order to utilise the results obtained, they first had to be formatted specifically into a .csv file, with each column responding to a variable (e.g. jacket material) and each row specifying the result for that sample (e.g.

brass/steel). For samples where the data was continuous, it had first to be discretised; this was done at the operator’s discretion, based on averages and standard deviations.

GeNIe required the input of data for each individual projectile as a separate sample with the variable “Type” being used to group ammunition from the same manufacturer/year/batch. As the data from each analytical technique was only available for four out of five projectiles, samples with missing observations (the 5th round for each sample set) were removed; resulting in 68 cases. This was to improve classification accuracy and ensure a fair reflection of the Bayesian network's performance – i.e. when those variables would be expected to be available in a real case. All of the continuous variables required discretisation which was conducted based on prior knowledge of the projectiles in combination with descriptive statistics (e.g. mean, median, standard deviations).

GeNIe has the ability to ‘learn’ the information in this type of data file and use it to build a Bayesian network. Two types of networks were utilised in this study: Naïve Bayesian networks, and Augmented Naïve Bayesian networks. The theory behind Bayesian networks is covered extensively within the literature and will not be the focus of this study. Prior understanding of such networks is not necessary for operation of this software, however, it is required to understand the significance of the results.

Figure 5.27 to **Figure 5.30** below demonstrate the user interface for the results obtained from analysis of the projectiles. They are reflective of an augmented naïve Bayesian network based on the information in file 4 (five projectiles of each type). At the centre of **Figure 5.27** is the “Type” (in yellow, ammunition ‘origin’), surrounded by the characteristics (in blue). The characteristics included in the initial file were minimal (10 selected), of which “VNose_ND” (Nose diameter) provided no discrimination. When no characteristics are selected, there is an equal chance of the ammunition being from each “Type” (6%):

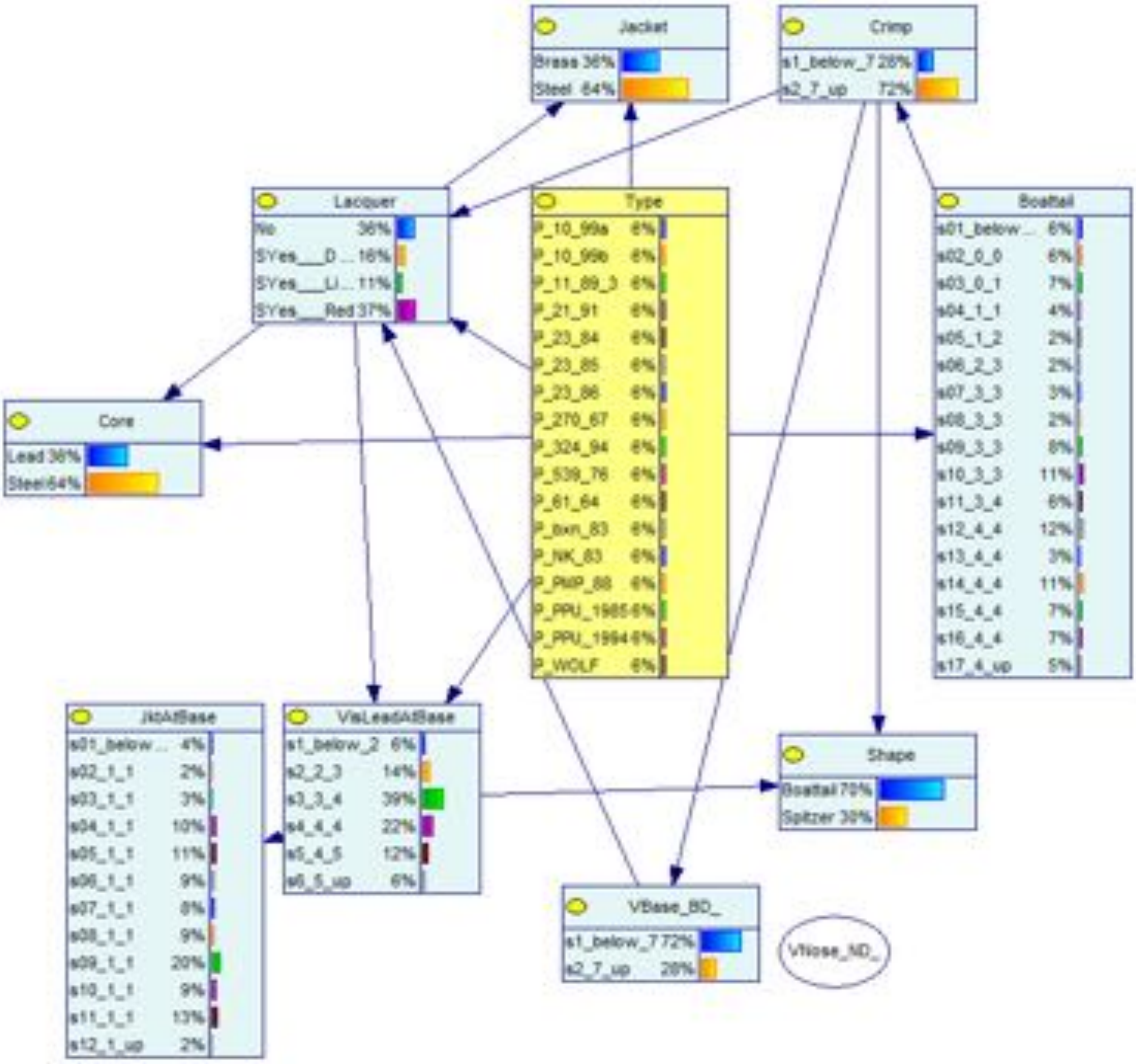


Figure 5.27 GeNIe model: augmented naïve Bayesian network for projectile "Types" and 10 characteristics.

*VNose_ND_ did not assist in discrimination.

Brass was then selected as the jacket material. With the updated beliefs of the network **Figure 5.28** now reflects the likelihood of a brass jacketed projectile being from each “Type” of ammunition.

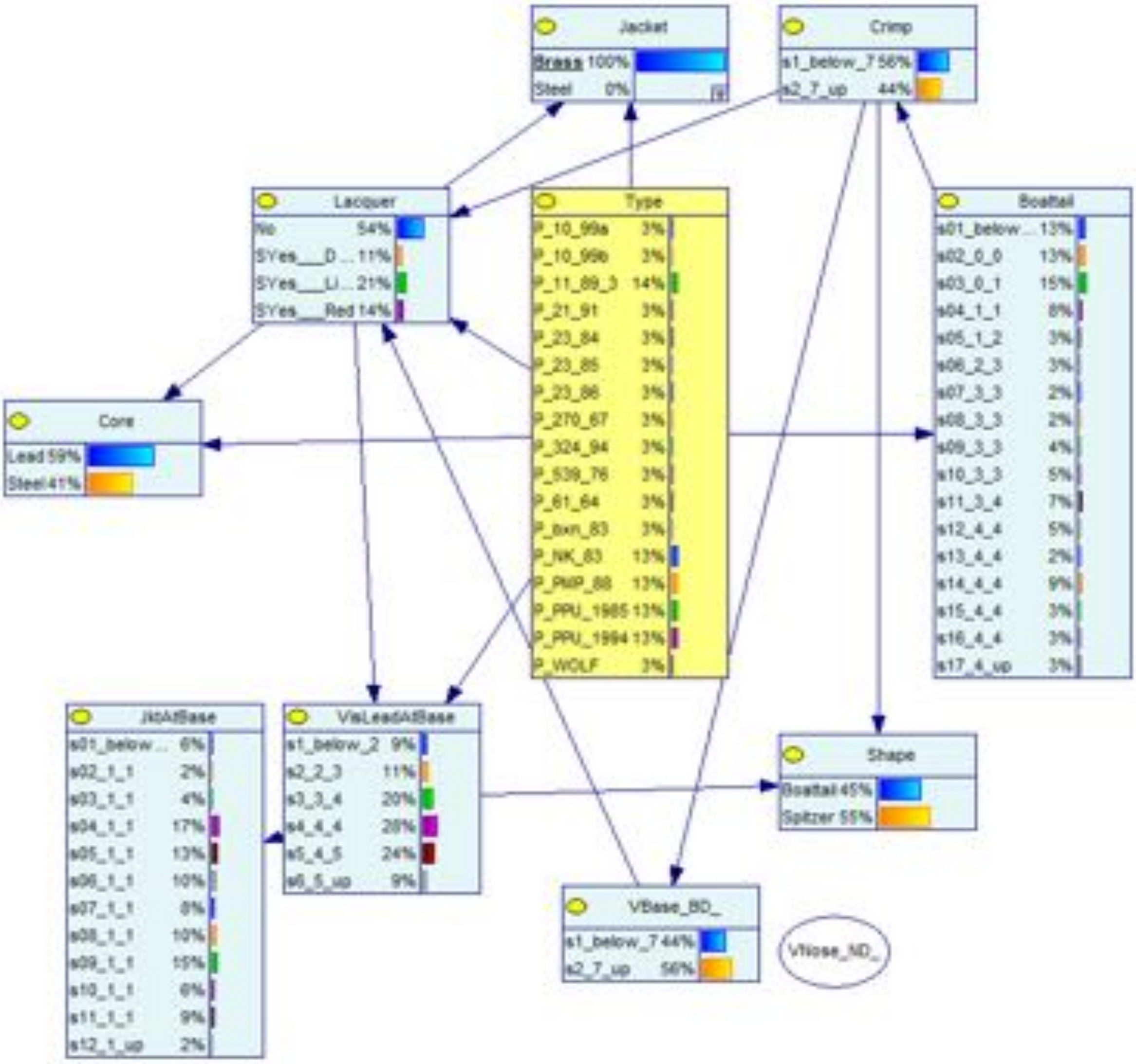


Figure 5.28 GeNIe model: augmented naïve Bayesian network for projectile "Types" and with the "Brass" selected as the "Jacket" material.

*VNose_ND_ did not assist in discrimination.

The core material was then set to steel and the beliefs updated and shown below in **Figure 5.29**. These unusual characteristics have purposefully been chosen for demonstration purposes, however, the model now shows a noticeable choice in “Type” – namely “P_11_89_3”.

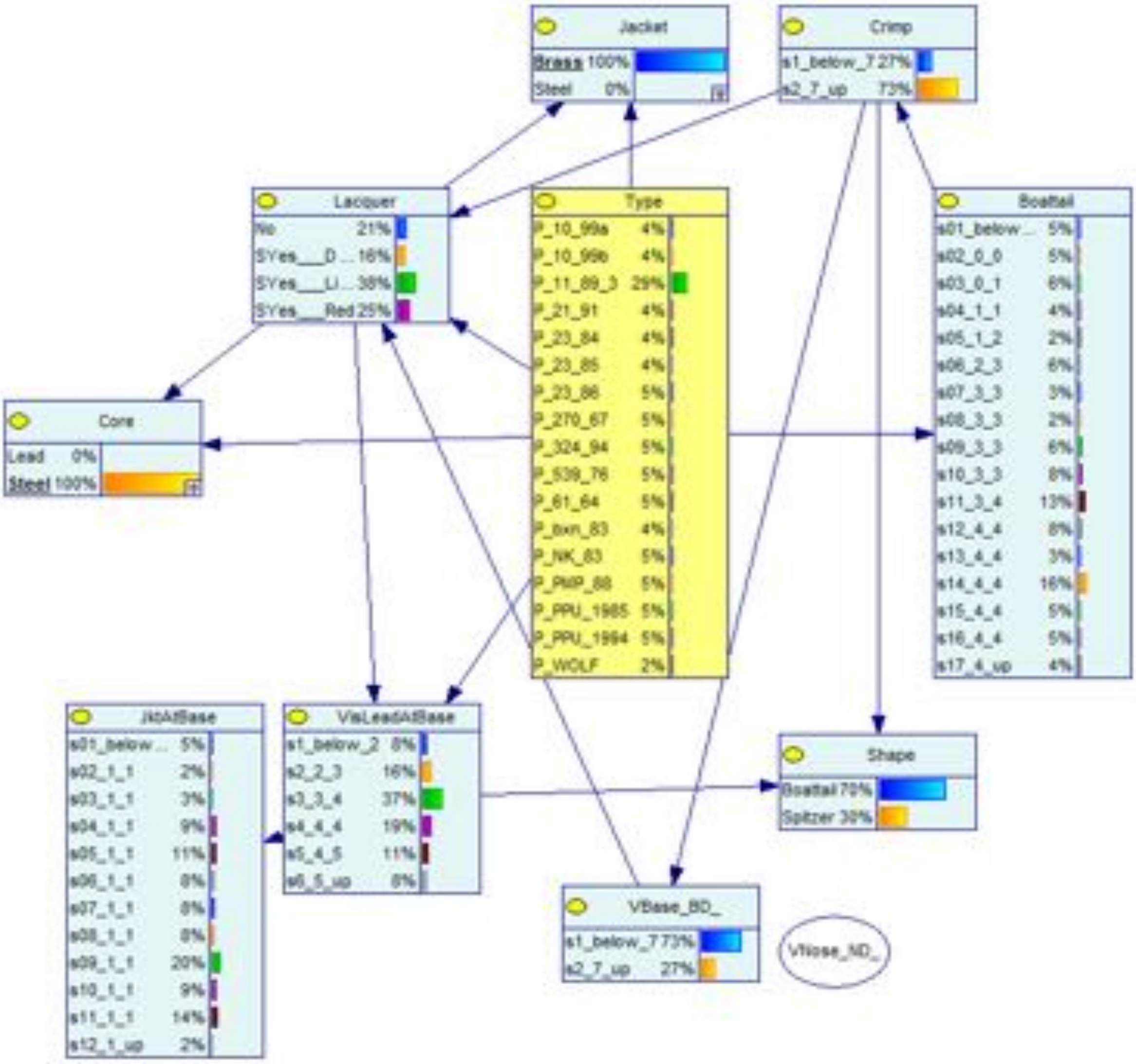


Figure 5.29 GeNIe model: augmented naïve Bayesian network for projectile "Types" and with the "Steel" selected as the "Core" material**.**

*VNose_ND_ did not assist in discrimination.

The inclusion of a few more characteristics ("Shape", Boattail" and "Lacquer") provides a significantly higher likelihood shown in **Figure 5.30** at 92%. GeNIe software also considers the sample size being used (for this data, five of each projectile were available) and the likelihood ratios quoted take into that alternative results may be seen in future samples. The software will learn how much/little tolerance to account for based on the sample size.

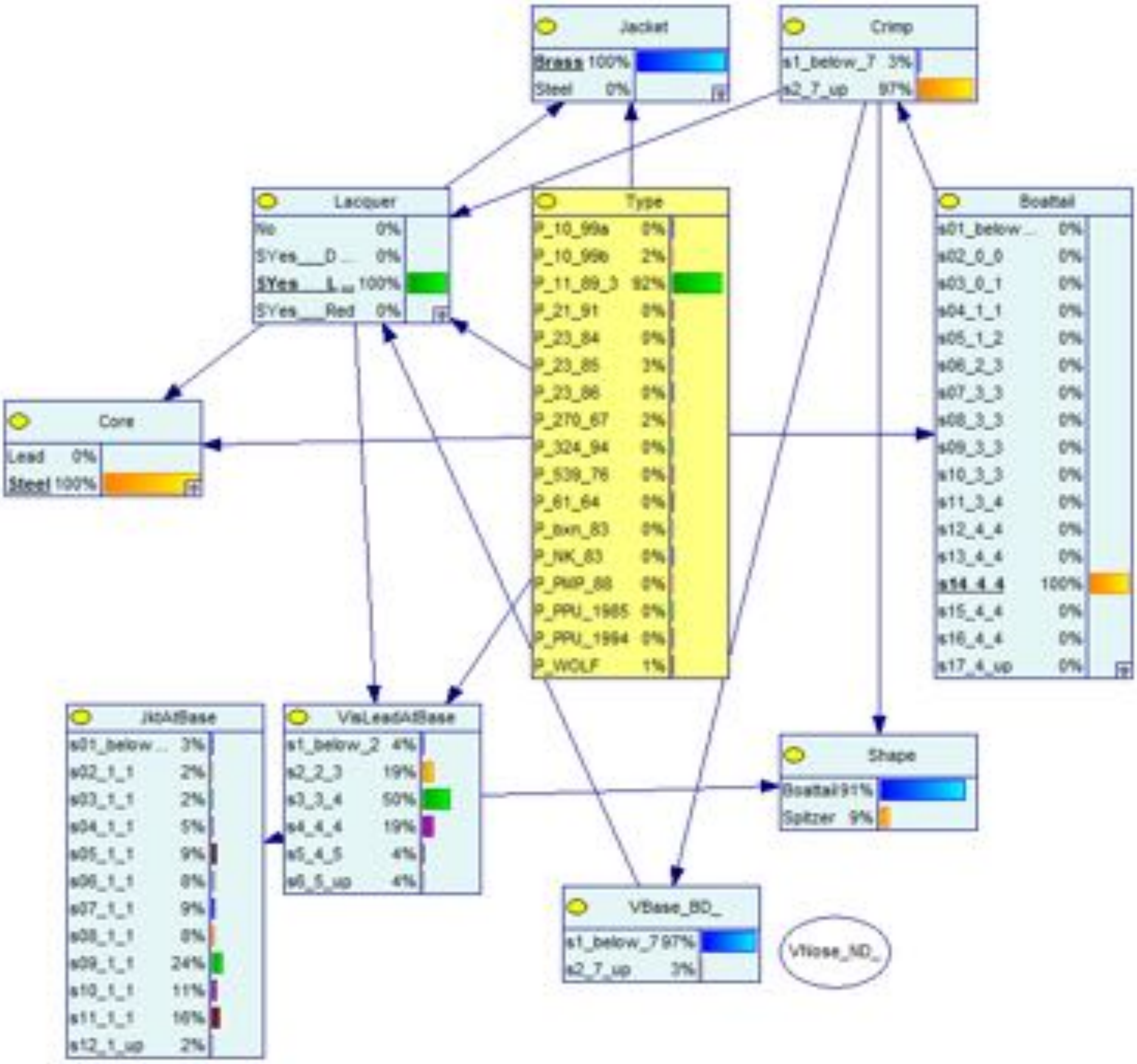


Figure 5.30 GeNIe model: augmented naïve Bayesian network for projectile "Types" and with "Shape", "Boattail" and "Lacquer" options selected.

*VNose_ND_ did not assist in discrimination.

6 Chapter 6: RESULTS AND DISCUSSION

This chapter reports the results of the thesis and discusses them (an electronic appendix for each of the sections has been provided on a CD submitted in conjunction with this thesis). The data below is comparative in nature and aims to establish a) whether there are differences between ammunition produced by different countries/manufacturers, and b) whether these differences are within the expected variance observed between batches/years, or if they are statistically significant enough to be utilised in differentiating the manufacturer.

There a several limitations to consider throughout this research. This research assumes that the information of the headstamps is to be trusted implicitly and used to identify the manufacturer. As discussed in **Section 2.3.4.1**, the reliability of such an assumption can be called into question as a result of dubious practices. Furthermore, this research considers manufacturers to have produced all component parts, however, it is possible that components (such as cartridge cases) are provided to several manufacturers, who then assemble rounds of ammunition. The final assumption complicates matters further: Even if the first two assumptions prove to be correct, it is assumed that manufacturers use different 'sources' for raw materials (unlike the process described for projectile lead in **Section 2.2.1.1**). In keeping with the cartridge case example, this would mean that a supplier for mild steel (for cartridge cases), supplies only one ammunition manufacturer. Violation of this assumption could potentially preventing any compositional differences from being present. If even one of these scenarios is challenged, there would have be a fundamental impact on the interpretation of the results. As the legitimacy of such assumptions was not the subject of this research, the results were interpreted on the basis that all of the assumptions were confirmed.

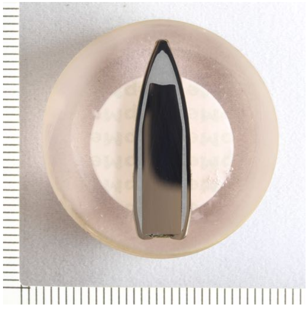
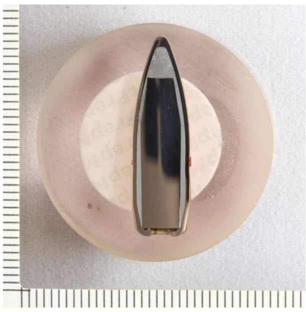
The results will be presented in subsections relating to the components analysed and the techniques utilise. Initially, qualitative analysis of components will be reported (e.g. materials based on colours). Although potentially subjective, they are not to be overlooked and will be presented in order to ensure that the data provided can be used as one comprehensive resource. Next, the results for the analysis of the projectiles will be presented, including the chemical analysis of the elements present (XRF), the hardness results for projectiles where a steel core was present and where applicable measurements of the thickness of jacket components (SEM). The primer residue was examined using SEM-EDX in order to identify inorganic components present in primer residue whilst elemental analysis (XRF) was conducted on the primer caps. For the cartridge cases, microindentation hardness results will be provided as well as elemental analysis results (XRF). Additionally, the web of the case was examined visually. The findings from the above techniques allowed for observation of physical and chemical characteristics – results that were fundamental to determining whether ammunition from selected origins could be differentiated.

Throughout the chapter statistical analysis will highlight whether or not there are significant differences between characteristics. If present, an attempt will be made to determine where these variations are present (i.e. between which sample sets). Data associated with different characteristics of ammunition projectiles was then applied to develop Bayesian networks that can be used to determine the likelihood of ammunition being from different origins based on nominal and ratio results (that have been discretised).

6.1 Projectiles

The projectiles were photographed before and after being sectioned, in order to allow for examination of colour, shape (Type 56/ M43) and materials. The photographs are shown below in **Table 6.1**.

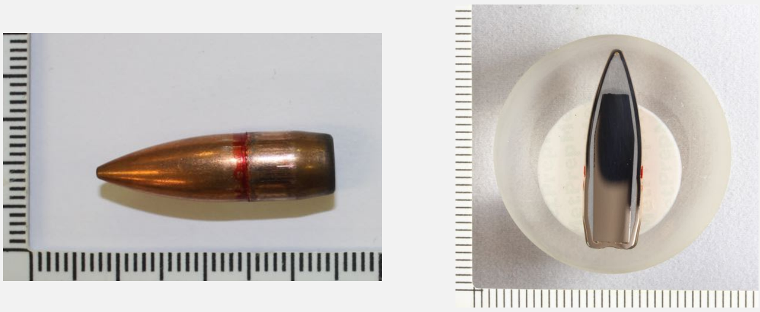
Table 6.1 Photographs of projectiles before and after sectioning.

Manufacturer	**Photographs**	
	Projectile	Projectile (Sectioned)
Czech (bxn/83)		
Serbia (PPU/85) Serbia (PPU/94)		
Bulgaria (10/99a) Bulgaria (10/99b)		

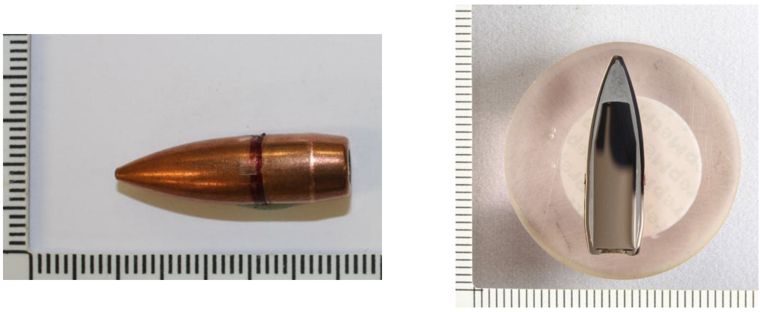
Hungary (23/84)

Hungary (23/85)

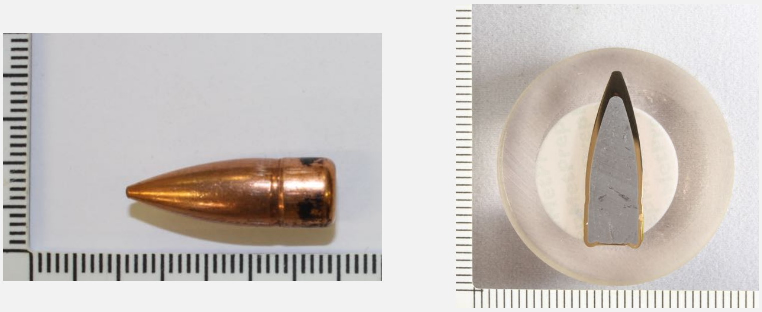
Hungary (23/86)



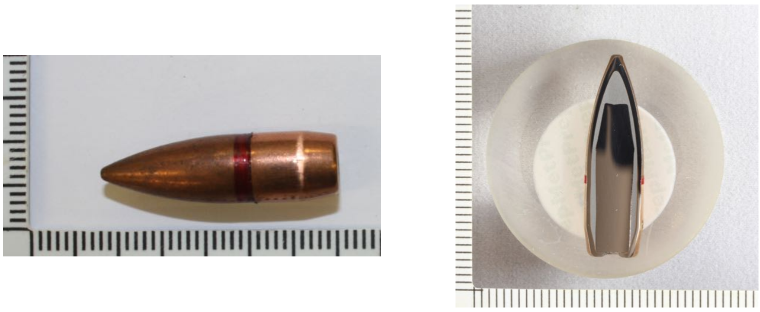
Ukraine (270/67)



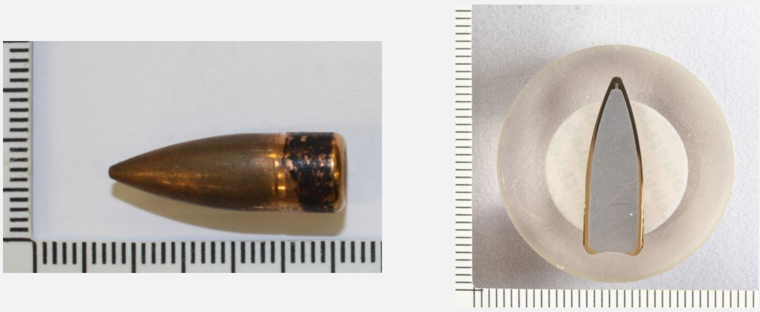
South Africa (13/88)



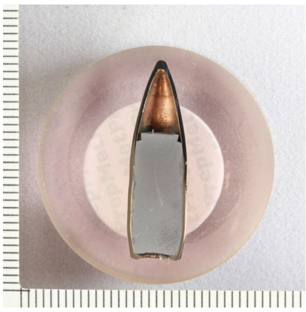
Romania (324/94)



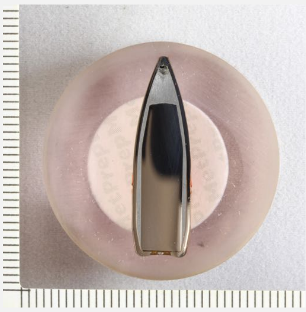
Bosnia (IK/83)



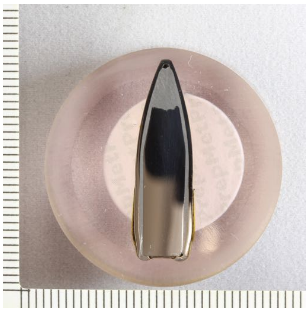
Russia (WOLF)



Poland (21/91)

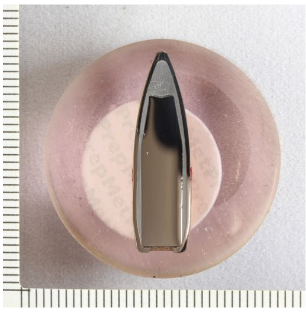


Albania (11/89/3)



China (61/64)

Russia (539/76)



It was possible to group projectiles based initially on their shape (M43 or Type 56), whether there was lacquer present, and for Albania (11/89/3), on the variation in colour. **Figure 6.1** shows some examples of such adaptation.

Figure 6.1 Photographs of projectiles from a) Albania (11/89/3), b) Russia (539/76) and c) South Africa (13/88), showing variation in jacket colour, lacquer, and shape.

Four sample sets demonstrated the Type 56 shape projectile shown above in **Figure 6.1 (c)**. These are listed below:

- Serbia (PPU/94)
- Serbia (PPU/85)
- South Africa (13/88)
- Bosnia (IK/83)

The remaining 13 of the projectiles exhibited an M43 type shape. Whilst none of the Type 56 projectiles displayed a red lacquer of (varying shades), most of the M43 shaped projectiles did. Only Czech (bxn/83), Poland (21/91) and Russia (WOLF) had no lacquer present on the projectiles – this was just one of the ways that the commercial ammunition from Russia (WOLF) varied from the military ammunition from Russia (539/76).

Once sectioned, it was possible to predict the material of the projectile jacket based on visual inspection of the colour as shown in **Figure 6.2**.

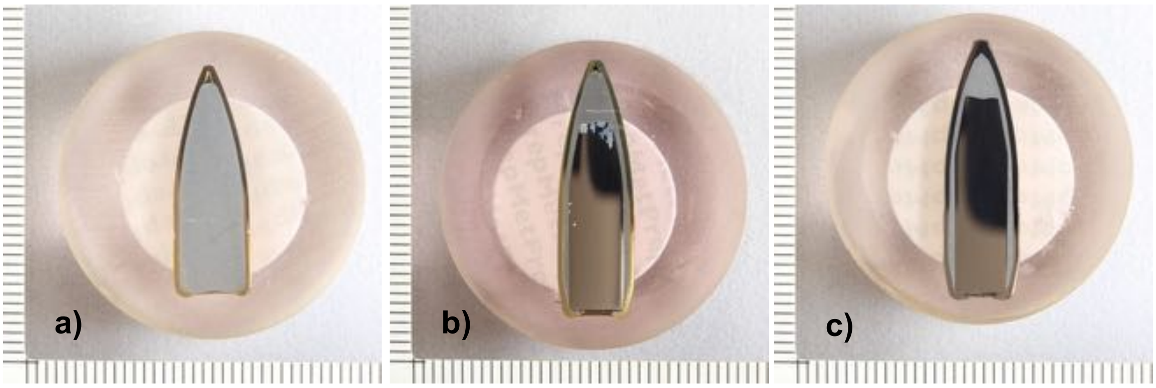


Figure 6.2 Photographs of sectioned and polished projectiles from a) Serbia (PPU/94), b) Albania (11/89/3), and c) Russia (539/76), showing variation in jacket material.

The brass jacketed projectile included all of the Type 56 projectile manufacturers as well as Albania (11/89/3). Furthermore, this projectile was the only one with a brass jacket and a steel core. These unique characteristics meant that out of the manufacturers selected for this study, Albania (11/89/3) could be identified without any further analysis.

The aforementioned core material could be classified as lead, or steel with a lead sheath as shown in **Figure 6.3**.

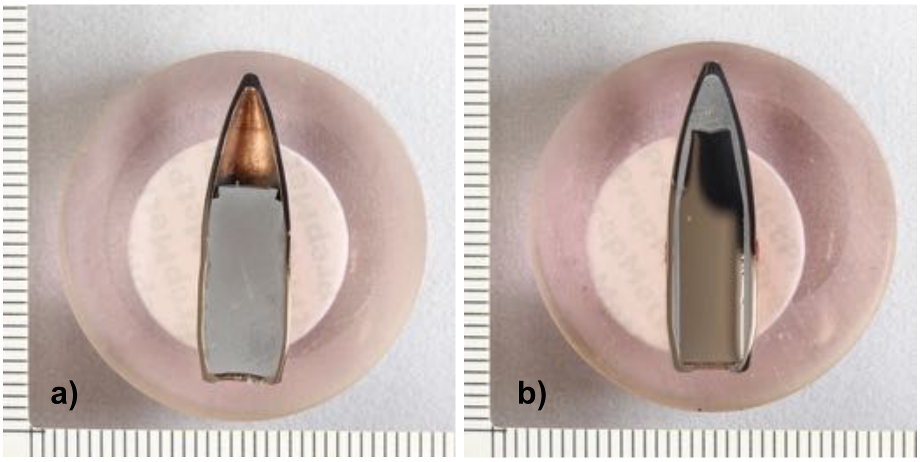


Figure 6.3 Photographs of sectioned and polished projectiles from a) Russia (WOLF), and b) Russia (539/76), showing the presence of an ‘air pocket’ and variation in core material.

For the steel jacketed projectiles, all but one exhibited a steel core. The only steel jacket projectile that had a lead core was the commercial ammunition: Russia (WOLF) – further distinguishing it from its military counterpart. Moreover, these projectiles displayed and ‘air pocket’ as can be seen in **Figure 6.3**. This is due to the difference in density between lead and steel (lead is denser) therefore requiring a reduction in the amount of material. These unique characteristics allowed sectioned projectiles from Russia (WOLF) to be identified without any further analysis.

6.1.1 X-Ray Fluorescence analysis of Materials

Compositional analysis was conducted using XRF. As expected, projectile jackets were composed of copper plated/lacquered mild steel, or a gilding metal brass with the results shown below in **Table 6.2**. As with any industry, manufacturers must consider the costs involved especially with large volumes of ammunition being manufactured. It was expected to note the presence of other elements (considered impurities), as the cost of achieving high purity is expensive compared to the advantages. Other elements that were observed in projectile brass jackets include; Sn, Pb, Fe, Al, Cr, Co, Mn, Si, P, Ag, Ni and Bi.

Table 6.2 Summary of the material used for projectile jackets.

Material	Manufacturers
Brass	Serbia (PPU/94), Serbia (PPU/85), South Africa (13/88), Bosnia (IK/83), Albania (11/89/3)
Steel	Czech (bxn/83), Bulgaria (10/99a) , Bulgaria (10/99b) Hungary (23/84), Hungary (23/85) , Hungary (23/86), Ukraine (270/67), Romania (324/94), Poland (21/91), China (61/64), Russia (WOLF), Russia (539/76)

The average percentage weights for the elements present in all components are are detailed in **Appendix A.**

For the brass projectile jackets three out of four displayed the archetypal composition of gilding metal discussed in **Section 2.2.1**. A gilding metal is used with a composition that typically contains 85 or 90 per cent copper and 15 or 10 per cent zinc [41]. **Figure 6.5** displays a notable difference observed in the results for the Albanian (11/83/3) sample; percentage weights were approximately 80% copper and 20% zinc. Whilst still within the ranges for gilding metal (80 to 95% copper and 20 – 5% zinc), this composition more closely represents cartridge case brass (70% copper and 30% zinc). It is unclear why the manufacturer has chosen to deviate from other compositions as zinc is an expensive element to add and provides no increase in hardness, only ductility [41]. This may be in an attempt to increase the life-span of the dies used during manufacture. The golden colour of this projectile is visually different to the jacket of the projectiles from Serbia, South Africa and Bosnia (shown in **Figure 6.4**), and the XRF analysis of elements provides confirmation as to why there are physical differences present.

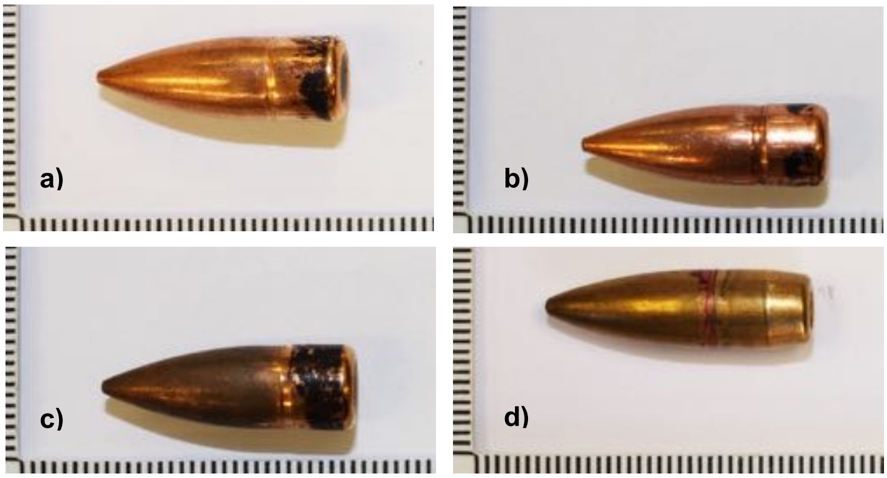


Figure 6.4 Photographs of projectiles displaying visual differences in colour from a) Serbia, b) South Africa, c) Bosnia and, d) Albania.

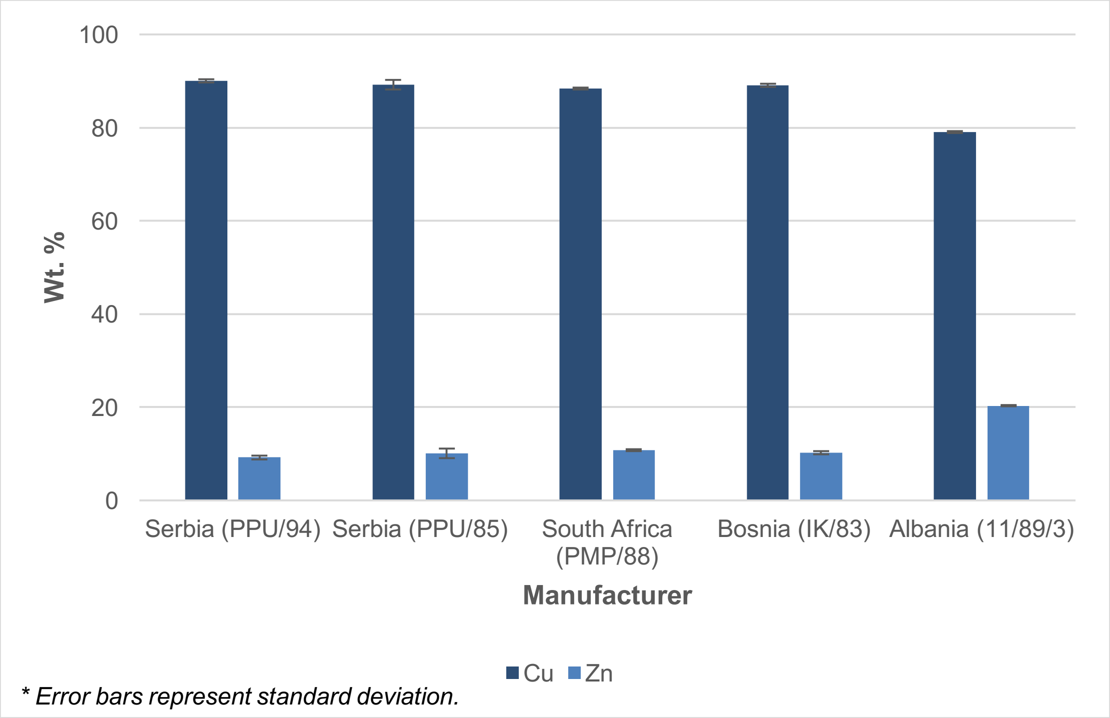
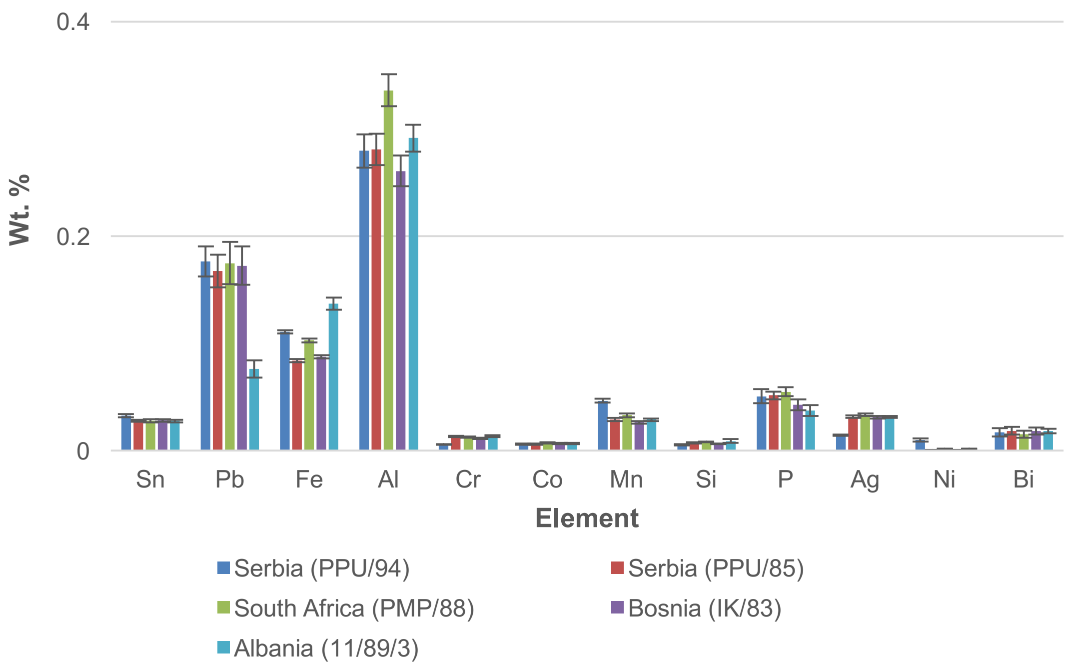


Figure 6.5 Chart showing the quantification (weight percent, (wt.%)) of Cu and Zn present within projectile brass jackets.

There was a statistically significant difference between groups as determined by one-way ANOVA: for Cu (F(4,15) = 231.856, p = 0.000) whilst for Zn (F(4,15) = 230.713, p = 0.000).

For the additional elements present in the projectile brass jackets, the results can be seen in **Figure 6.6**.



** Error bars represent standard deviation.*

Figure 6.6 Chart to show additional elements (weight percent, (wt.%)) present in projectile brass jackets.

Figure 6.6 is a visual representation of the (wt.%) of elements. There was a statistically significant difference between groups for most of the elements (not for P, Bi and Co) as determined by one-way ANOVA:

- Sn (F(4,15) = 5.058, p = 0.009)
- Pb (F(4,15) = 88.074, p = 0.000)
- Fe (F(4,15) = 74.731, p = 0.000)
- Al (F(4,15) = 4.540, p = 0.013)
- Cr (F(4,15) = 38.819, p = 0.000)
- Mn (F(4,15) = 14.673, p = 0.000)
- Si (F(4,15) = 3.84, p = 0.024)
- Ag (F(4,15) = 45.787, p = 0.000)
- Ni (F(4,15) = 8.366, p = 0.001)

The statistical results are shown in **Appendix H**.

For elements where the (wt.%) showed significant differences between groups the Bonferroni post-hoc test was utilised (see **Section 5.7.1** for reasons why this more stringent test was selected). Between manufacturer Bonferroni comparisons revealed statistically significant differences (where p<0.05) in several elements – the most noticeable of which are discussed below.

Serbia (PPU/94) and Albania (11/89/3) showed the most statistically significant differences from other manufacturers of brass jacketed projectiles. For Serbia (PPU/94) there were differences (where p<0.05) for the elements: Sn, Cr, Mn, Ag, and Ni. The disparity between this composition and Serbia (PPU/85) supports the considerations that manufacturers will modify their source/manufacturing processes over time and could potentially assist in differentiation temporally (as discussed in **Section 8**). Albania (11/89/3) showed differences (where p<0.05) from all other manufacturers for the elements: Cu, Zn, Pb, and Fe. Most of the elements analysed demonstrated that there is potential to use the results in order to determine if the (wt.%) of elements is statistically significantly different for brass jacketed projectiles from different manufacturers/temporally.

As previously mentioned, the analysis of P, Bi and Co was not beneficial. Additionally, the examination of Al (wt.%) only showed two statistically significant differences between manufacture: between South Africa (13/88) – and Serbia (PPU/94) and Bosnia (IK/83). For Serbia (PPU/85) there were fewer differences compositionally and these were mostly between Serbia (PPU/94) and Albania (11/89/3) – which are highlighted above. The only other statistically significant difference for Serbia (PPU/85) was for Iron and this was with South Africa (13/88).

The presence of lead in copper alloys is related to lower wear rates and ease of machinability – both of which can limit production rates [135]. Variations in the (wt.%) of Pb and Fe present could be attributed to the preparation process; the Albania (11/89/3) projectile contains a steel core as opposed to being composed of lead. Possible contamination could have occurred during the grinding/polishing processes.

The analysis was conducted using the Bonferroni post-hoc test which assumes equal variances (i.e. homogeneity of variance). Levene’s test was utilised to confirm this and found that this assumption was violated for: Cu, Zn, Sn, Al, Si, and Ni. Accordingly, the results achieved were checked using the Games-Howell post-hoc test which does not assume equal variances. There was no change in the results produced.

In order to ensure that the assumption of normality was not violated, the results were grouped per manufacturer, and the (wt.%) per element examined. This was done by using the Shapiro-Wilk Test which is more appropriate for small sample sizes (below 50 samples) and produced numerical means of assessing normality. For the majority of the results $p > 0.05$ – indicating that the data did not significantly deviate from a normal distribution – i.e. the data had normal distribution. This was confirmed graphically by examining Q-Q Plot diagrams.

For Serbia (PPU/94) the numerical results showed that $p<0.05$ for Co, Mn and Ni, however, a known disadvantage of statistical tests is not being sensitive enough at low sample sizes. Visual inspection of Q-Q Plot diagrams for all three elements showed data points were close to the diagonal line – indicating that the data was normally distributed. Similarly, for Bosnia (IK/83) the numerical value for Pb was $p<0.05$, however, examining the Q-Q Plot diagram confirmed normally distributed data points. On the other hand, for Albania (11/89/3) $p<0.05$ for Fe and this was confirmed by the non-linear distribution of points on the Q-Q Plot diagram. As the assumption of normality was violated for this element with this manufacture; this implies that the mean for Fe (wt.%) for Albania (11/89/3) was not accurately representative of the data collected – potentially due to large differences in individual values. The results used for differentiation should be approached with caution and would benefit from an increased sample size.

For the steel jackets and cores, the majority of variances fell within usual tolerances for mild steels (see **Section 2.2.2**) and were most likely due to variations in the materials supplied. Alloying steels with various elements can produce favourable and unfavourable characteristics, however to remove them completely is prohibitively expensive. ASTM provides approximations on the range and maximum of weight percentages that should be present shown in **Table 6.3**.

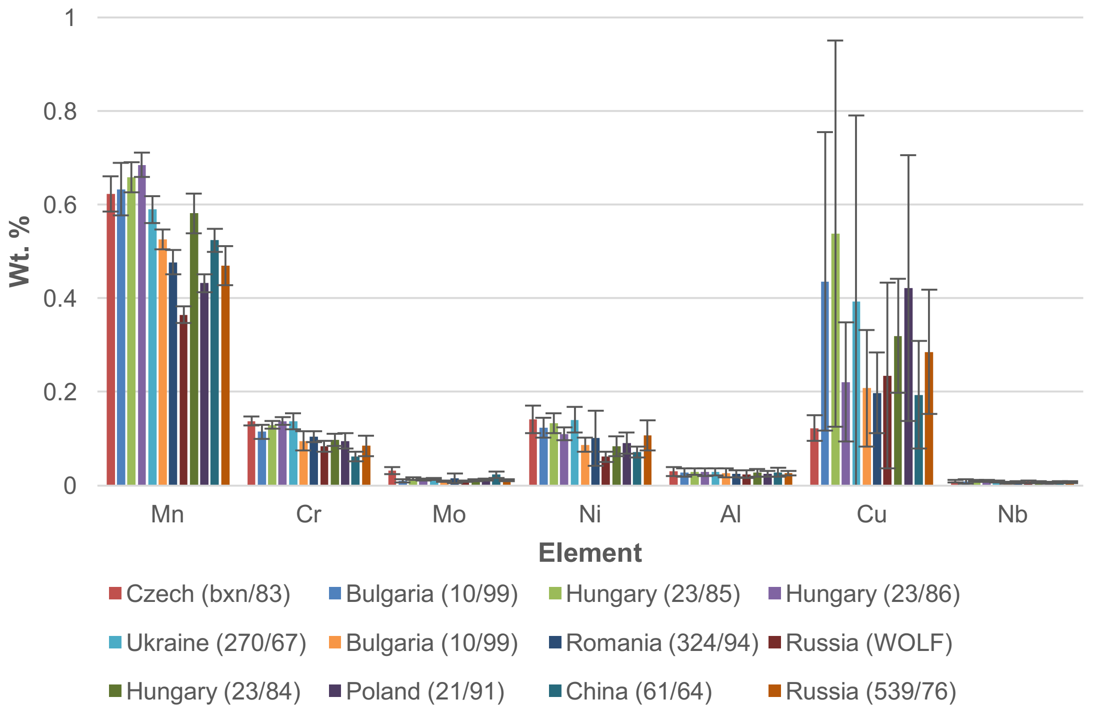
Table 6.3 A table showing the ASTM grade designations and chemical compositions (weight percent, (wt.%)) of carbon steel bars [18].

GRADE DESIGNATION	CHEMICAL COMPOSITION LIMITS (WT.%)			
	Carbon	Manganese	Phosphorus, max	Sulphur, max
1010	0.08 – 0.13	0.30 – 0.60	0.40	0.05
1011	0.08 – 0.13	0.60 – 0.90	0.40	0.05
1012	0.10 – 0.15	0.30 – 0.60	0.40	0.05
1013	0.11 – 0.16	0.50 – 0.80	0.40	0.05
1015	0.13 – 0.18	0.30 – 0.60	0.40	0.05
1016	0.13 – 0.18	0.60 – 0.90	0.40	0.05
1017	0.15 – 0.20	0.30 – 0.60	0.40	0.05
1018	0.15 – 0.20	0.60 – 0.90	0.40	0.05
1019	0.15 – 0.20	0.70 – 1.00	0.40	0.05

Other elements are not general reported in standards. On occasion, silicon ranges/limits are reported at 0.1 – 0.3%. Copper additions are acknowledged but ranges not reported in 10xx series steels [136]. For alloy steel bars, low amounts of certain elements are considered as incidental and may be present to the following maximum amounts: copper, 0.35 %; nickel, 0.25 %; chromium, 0.20 % and molybdenum, 0.06 % [18].

The silicon values observed (in steel samples) using the XRF were higher that those reported above (in **Table 6.3**) and showed considerable variability within the results. It is known that XRF analysis of lighter elements can provide dubious reported values, and the use of a helium purge when obtaining these results has since been proven to report inconsistent results [137]. This is supported by the observation of unusually abnormal average values (0.4 – 0.9 (wt.%)), large standard deviations (both intra-sample set and inter-sample set), and high levels of uncertainty being reported. Silicon at over .02% in steels is known to have a negative effect – causing graphitisation of carbides [138]. Taking these factors into consideration, the silicon results have been omitted as they could not be reliably statistically analysed.

The average percentage weights for steel projectile jackets showed some discrepancies between origin – however, these were mostly within the expected tolerances for mild steel. It is logical to expect that each manufacturer has tolerances within the acceptable levels of impurities. Providing that the materials meet the required characteristics to perform as desired, the cost of further processing in an attempt to remove these, outweighs the benefits.



** Error bars represent standard deviation.*

Figure 6.7 Chart showing quantities of additional elements (weight percent, (wt.%)) present within projectile steel jackets.

Figure 6.7 is a visual representation of the (wt.%) of elements. There was a statistically significant difference between groups for all of the elements analysed as determined by one-way ANOVA:

- Mn (F(11,36) = 49.63, p = 0.000)
- Cr (F(11,36) = 12.697, p = 0.000)
- Mo (F(11,36) =9.834, p = 0.000)
- Ni (F(11,36) = 5.706, p = 0.000)
- Al (F(11,36) = 2.168, p = 0.040)
- Cu (F(11,36) = 5.589, p = 0.000)
- Nb (F(11,36) = 7.821, p = 0.000)
- Fe (F(11,36) = 9.394, p = 0.000)

The results are shown in **Appendix H**.

For elements where the (wt.%) showed significant differences between groups the Bonferroni post-hoc test was utilised (see **Section 5.7.1** for reasons why this more stringent test was selected). Between manufacturer Bonferroni comparisons revealed statistically significant differences (where $p<0.05$) in several elements and these are summarised in **Table 6.4**.

Table 6.4 Summary of Bonferroni post-hoc results where $p < 0.05$**.**

MANUFACTURER

	Czech (bxn/83)	Bulgaria (10/99a)	Hungary (23/85)	Hungary (23/86)	Ukraine (270/67)	Bulgaria (10/99b)	Romania (324/94)	Russia (WOLF)	Hungary (23/84)	Poland (21/91)	China (61/64)
Bulgaria (10/99a)	Mo, Cu										
Hungary (23/85)	Mo, Cu										
Hungary (23/86)	Mo		Cu								
Ukraine (270/67)	Mo			Mn							
Bulgaria (10/99b)	Mn, Cr, Mo, Ni	Mn	Mn, Cu, Ni, Fe	Mn, Cr, Ni	Cr						
Romania (324/94)	Mn, Mo	Mn	Mn, Cu, Ni, Fe	Mn, Ni	Mn						
Russia (WOLF)	Mn, Cr, Mo, Ni	Mn, Ni, Fe	Mn, Cr, Ni, Cu, Fe	Mn, Cr, Fe	Mn, Cr, Ni, Fe	Mn	Mn				
Hungary (23/84)	Cr, Mo		Mn, Ni	Mn, Cr, Ni	Cr		Mn	Mn			
Poland (21/91)	Mn, Cr, Mo, Cu, Ni	Mn, Fe	Mn, Ni, Fe	Mn, Cr, Ni	Mn, Cr	Mn			Mn		
China (61/64)	Mn, Cr, Ni, Fe	Mn, Cr, Mo, Fe	Mn, Cr, Ni, Cu, Ni, Fe	Mn, Cr, Ni, Fe	Cr, Ni, Fe	Mo	Cr	Mn, Mo	Mo, Fe	Mn	
Russia (539/76)	Mn, Cr, Mo	Mn, Fe	Mn, Cr, Ni, Fe	Mn, Cr, Ni	Mn, Cr, Fe			Mn	Mn		Mo

The most beneficial elements analysed proved to be Mn, Cr, Fe, Mo and Nb. These elements showed statistically significant differences ($p < 0.05$) for 62%, 35%, 26%, 23% and 21% of comparisons between manufacturers. The variation in (wt.%) of these elements (sometimes in combination) provides a strong foundation for the use of XRF for distinguishing between 7.62 x 39 mm ammunition from different manufacturer. In contrast, the analysis of Al showed no statistically significant differences ($p < 0.05$). Whilst this would not be enough to refute the benefits of conducting elemental analysis, it does highlight the need to consider which elements should be examined. For Cu and Ni statistically significant differences ($p < 0.05$) were observed for 12% and 11% of manufacturers (respectively). Many of the elements analysed demonstrated that there is potential to use the results in order to determine if the (wt.%) of elements is statistically significantly different for steel jacketed projectiles from different manufacturers/temporally. This implies that there is some value in examining the (wt.%) of these elements, however, this would need to be further explored as discussed in **Section 8**.

The results for Mo are of particular interest. This element showed statistically significant differences ($p < 0.05$) for almost all of the comparisons with Czech (bxn/83) – bar China (61/64). The potential for this element to be used to uniquely identify the manufacturer is evident – however, as the results produced are comparative in nature, this would require more detailed analysis in order to establish the (wt.%) tolerances and combinations unique to the steel projectile jackets for Czech (bxn/83). An additional concern arises where the normality of these results was examined using the Shapiro-Wilk test and this assumption was violated for the Mo content in Czech (bxn/83) with $p=0.018$. This indicates that the data significantly deviated from a normal distribution and was further explored by visually examining Q-Q Plot diagrams as shown in **Figure 6.8**.

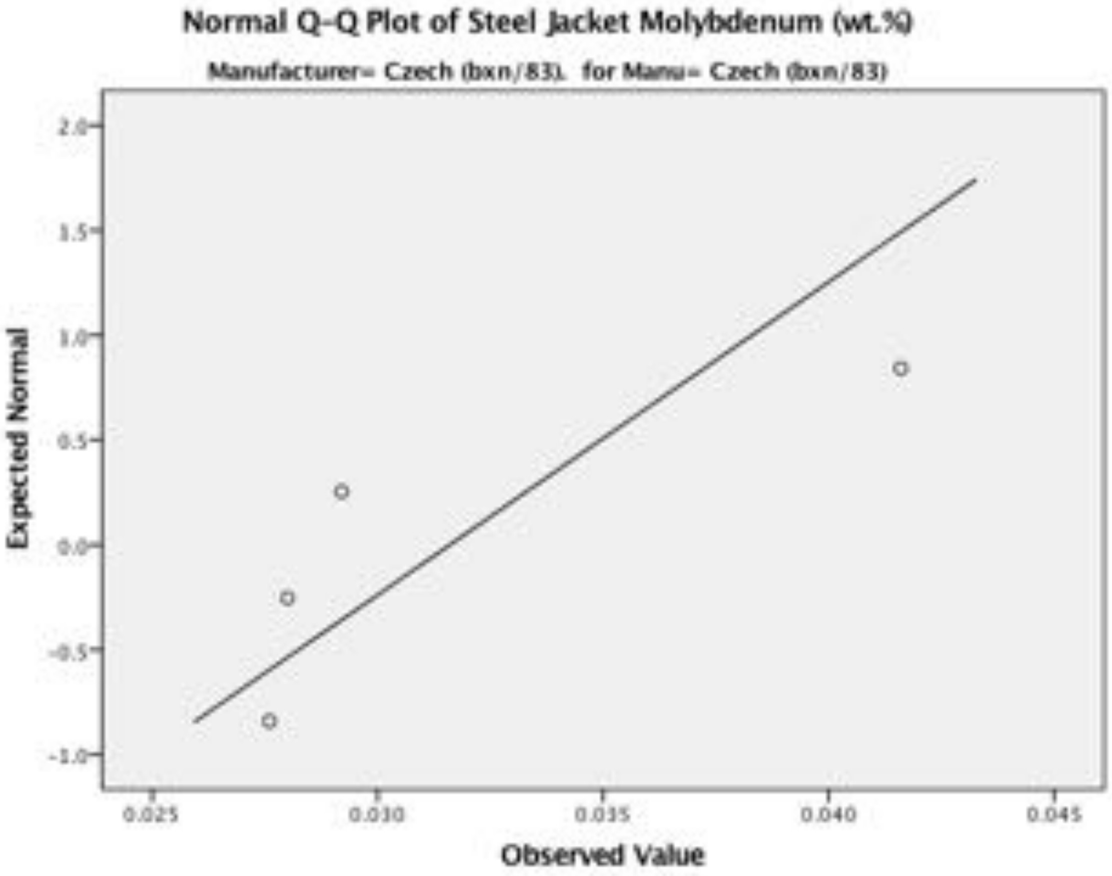


Figure 6.8 Q-Q Plot Diagram for Expected vs Observed Values of Mo (wt.%) present in Steel Jacket Projectiles from Czech (bxn/83).

The assumption of normality was also violated for the Mo content (wt.%) for Russia (WOLF), Romania (324/94) and China (61/64). Further investigation using Q-Q Plot diagrams negated concerns as in these three instances as the data points did not significantly deviate from the diagonal line representing normal distribution. Similar occurrences arose for Ni content ((wt.%)) for Bulgaria (10/99b) and Romania (324/94) and Mn content ((wt.%)) for Poland (21/91), China (61/64), and Russia (539/76) were represented by similar Q-Q Plot diagrams to that shown in **Figure 6.8**. As the assumption of normality was violated for these elements with these manufacturers, the results used for differentiation should be approached with caution and would benefit from an increased sample size.

The analysis was conducted using the Bonferroni post-hoc test which assumes equal variances (i.e. homogeneity of variance). Levene's test was utilised to confirm this and found that this assumption was violated for: Cr, Mo, Ni and Cu.. Accordingly, the results were checked using the Games-Howell post-hoc test which does not assume equal variances. There was no change in the results produced.

The manganese values in **Figure 6.7** are all within tolerances for 10xx grade steels, however, some variation is present. Manganese improves the hardenability of a steel and prevents a brittle film from forming due to ferrous sulphide. Excessive ***WHAT ARE EXCESSIVE??** values can however, encourage undesirable temper-brittleness and levels of grain coarsening; the effect of which can be countered by adding molybdenum and nickel, respectively [138].It may be possible to utilise the (wt.%) of manganese to distinguish between manufacturers, however, the statistical significance of the differences needs to be assessed.

The addition of copper may be useful in preventing segregation of phosphorous rich and pearlite-free regions; causes of weakness and brittleness [138]. The copper values also vary, with some quantities going beyond the maximum accepted amount of 0.35%. The sporadic values reported in **Figure 6.7** may have been influenced by a) the preparation process (grinding and polishing), and b) the fact that XRF will penetrate layers and may be accounting for the copper coating. Thus, caution should be utilised when interpreting the results as copper may not be reliable for use in differentiation. This may be reconsidered if an alternative sectioning technique is adopted and is discussed in **Section 8**.

6.1.2 Scanning Electron Microscope analysis of jacket components.

SEM analysis was conducted in two capacities: The first utilised the high powered magnification to measure the width of different components of the steel projectile jackets. Steel jackets were photographed and the component widths measured (where present). This was conducted for sample sets with steel jackets (11 in total), the results are presented in **Appendix C.**

Comparisons were made between the total and steel portion of the projectile jacket, as well as the inner and outer plating shown in

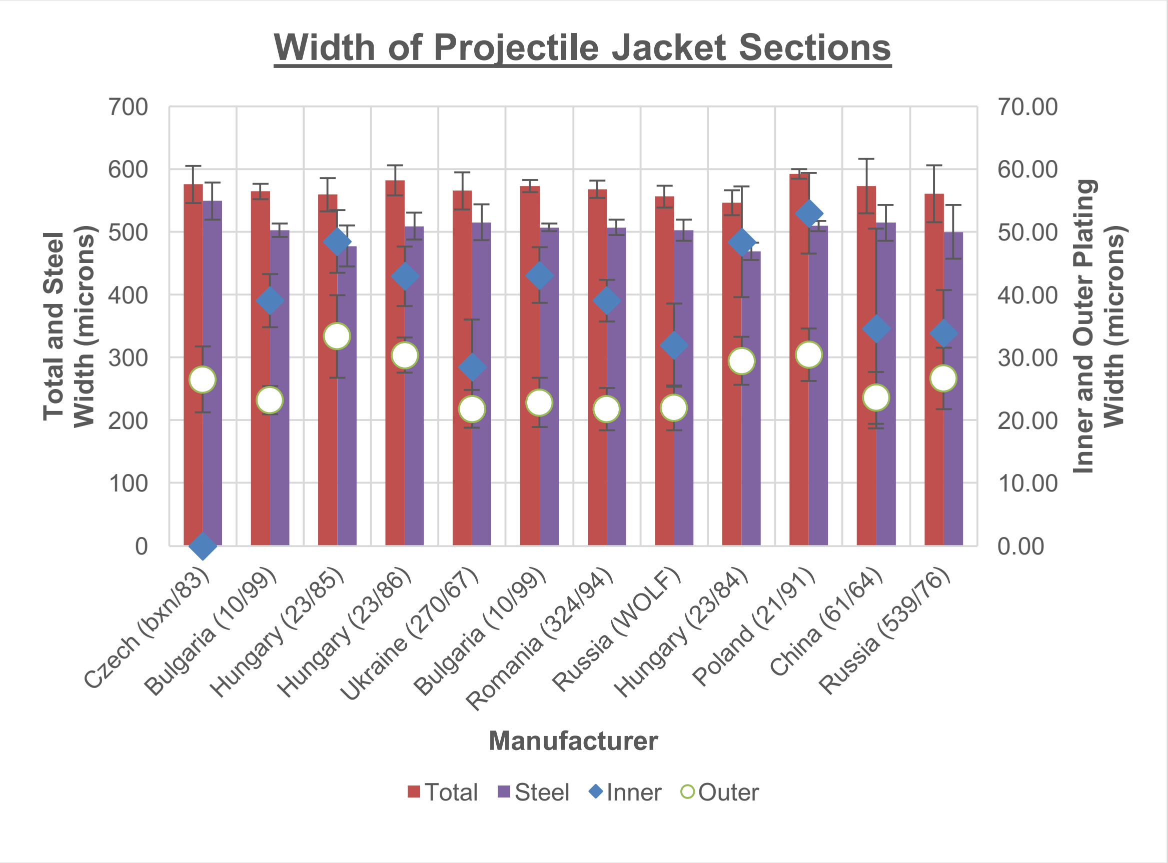
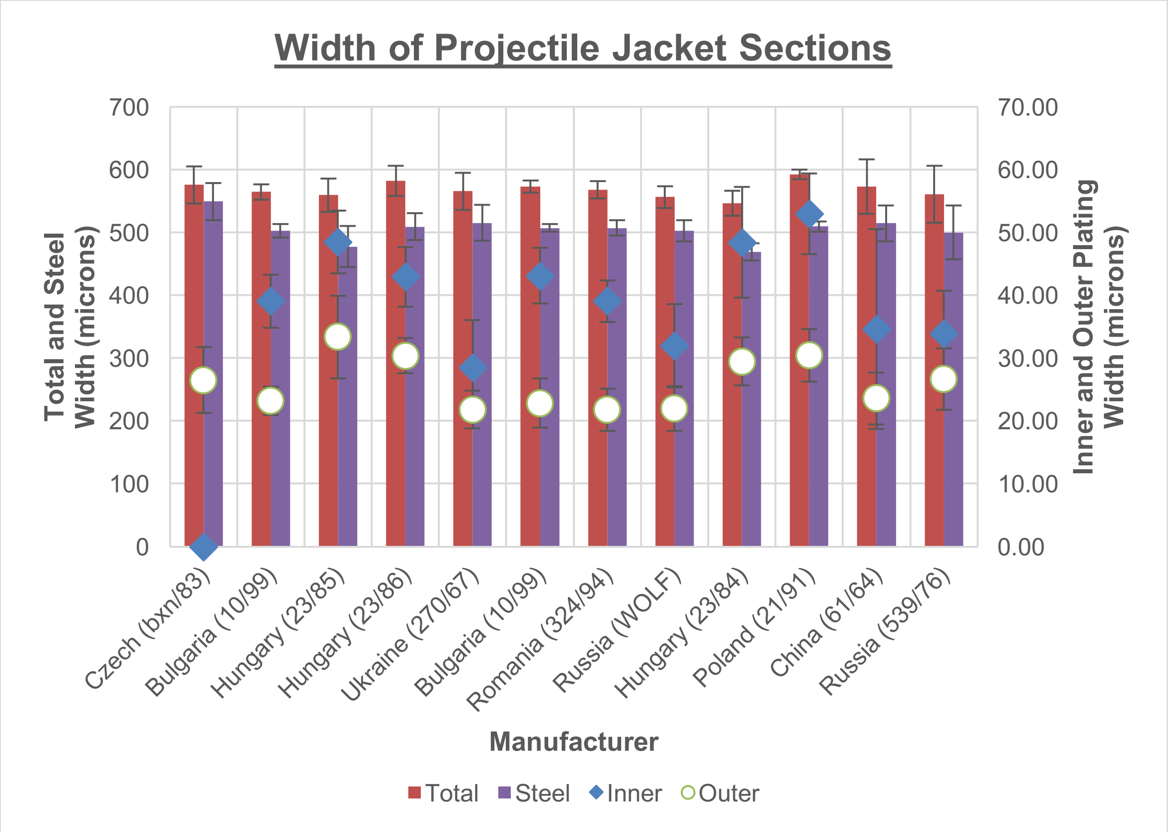


Figure 6.9.



** Error bars represent standard deviation.*

Figure 6.9 Chart showing the total, steel, inner and outer widths (microns) for projectile steel jackets.

DESCRIPTIVE STATISTICS

JACKET COMPONENT	N	Range	Minimum	Maximum	Mean		Std. Deviation	Variance	Skewness		Kurtosis	
	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic	Statistic	Statistic	Std. Error	Statistic	Std. Error
Jacket Total	48	123.48	518.23	641.71	568.1876	4.10708	28.45469	809.670	.510	.343	.316	.674
Jacket Steel	48	152.37	445.02	597.39	505.2844	4.34158	30.07936	904.768	.482	.343	1.079	.674
Jacket Outer Plating	48	24.66	18.76	43.42	25.9896	.74283	5.14649	26.486	.964	.343	1.280	.674
Jacket Inner Plating	48	61.17	.00	61.17	36.9118	2.12506	14.72286	216.763	-1.072	.343	1.329	.674
Valid N (listwise)	48											

Table 6.5 Descriptive statistics for jacket width data (μm).

There were several z scores noted as above 3.29 – indicating statistical ‘outliers’ that were over 3 standard deviations away from the mean of the data. The unexpected negative value for inner plating may be the result of the Czech (bxn/83) samples; observation of the Histogram (**Figure 6.10**) for this data supports this suggestion. Accordingly, the results for inner plating widths for Czech (bxn/83) was excluded during data analysis.

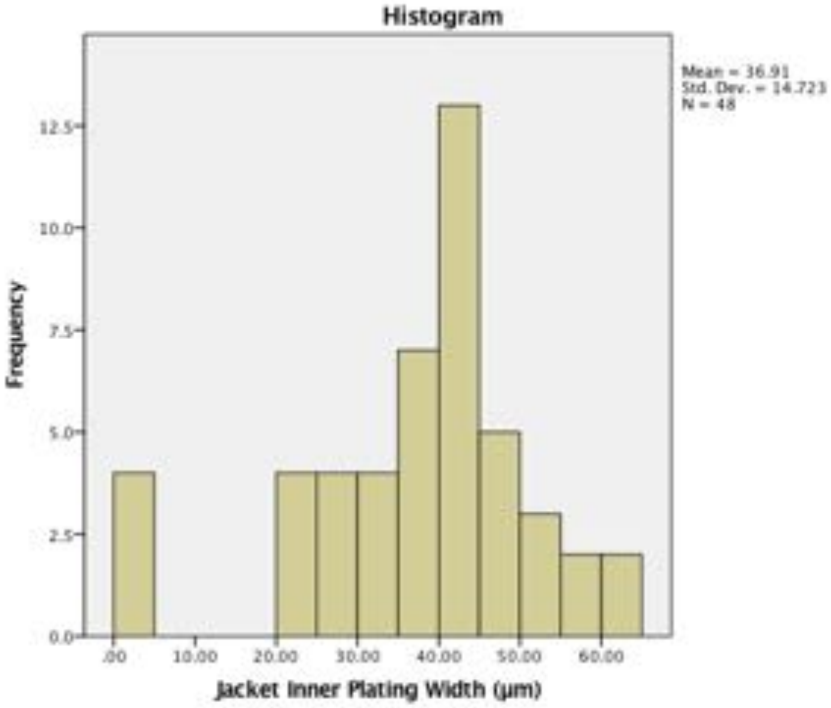
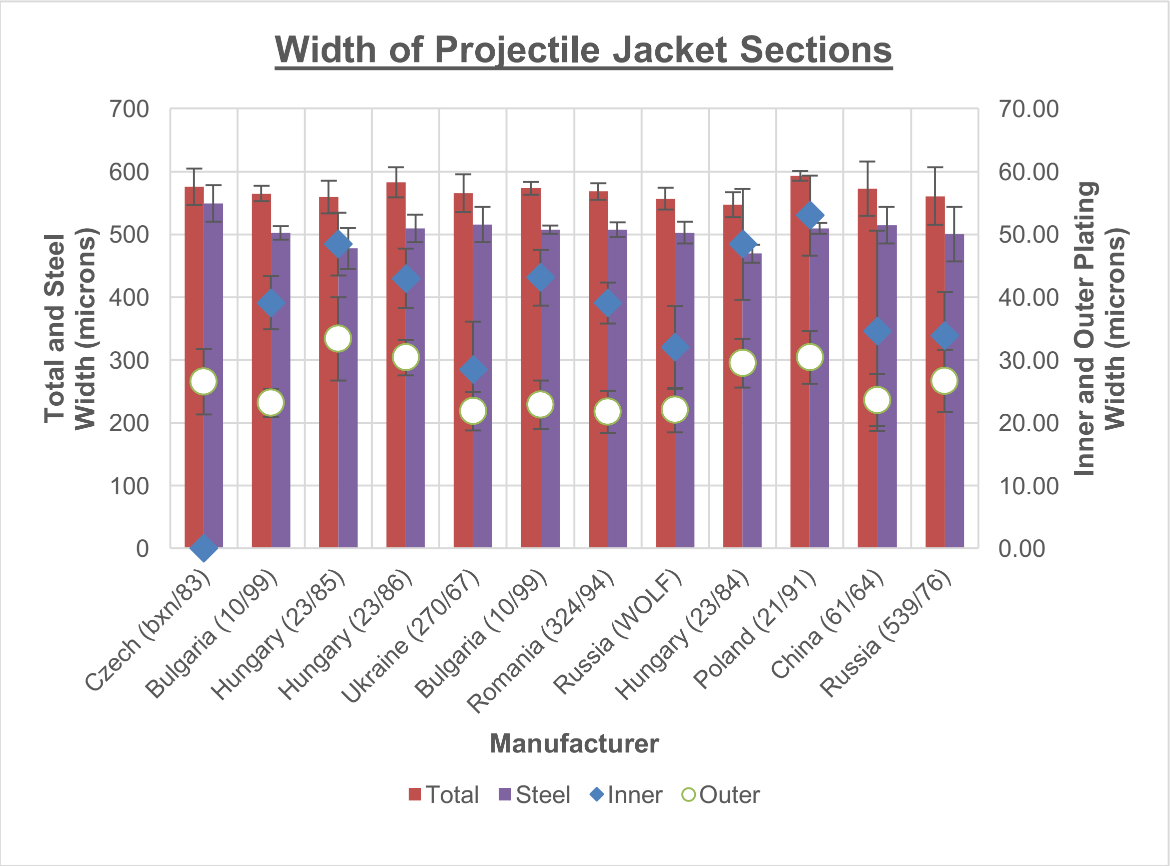


Figure 6.10 Histogram showing distribution frequency for jacket inner plating (µm).



In order to determine if the differences observed in **Figure** 6.9 were statistically significantly different, an ANOVA test was conducted on the widths of the jacket components. The results showed manufacturer difference in respects to the steel portion as well as the outer and inner plating widths. They can be reported as follows:

- Steel: (F (11, 47) = 2.21, MSE = 705.55, p = 0.037)
- Outer: (F (11,47) = 4.56, MSE = 14.45, p = 0.000)
- Inner: (F (10,43) = 4.199, MSE = 56.577, p = 0.001).

This indicated that whilst the total width of the projectile jacket is unlikely to vary, the proportions of each section do. Homogeneity of variance was not violated for steel and outer widths and between manufacturer Bonferroni comparisons revealed significant differences between manufacturers. For the inner plating width, the homogeneity of variance was violated (p = 0.009) and therefore the post-hoc analysis was conducted using the Games-Howell test.

Czech (bxn/83) was the only sample set where no inner copper plating was present. This could be indicative of a variation in the manufacturing process. The entire projectile being plated after being composed rather than the steel being plated prior to the jacket being formed. It could also suggest that the steel was only plated on one 'side'. This stark variation is unique to Czech (bxn/83) and allows for unique identification of this manufacturer when analysing the plating widths for steel jacket projectiles. Additional variations between manufacturers for the inner plating showed that the width for Poland (21/91) was statistically significantly different from that for Ukraine (270/67) and Russia (WOLF).

Examination of the steel portion of the jacket further supported the ability to differentiate between Czech (bxn/83) and Hungary (23/84) and Hungary (23/85) with statistically significant different widths ($p < 0.05$). Interestingly, this variation was not present between Czech (bxn/83) and Hungary (23/86) and could imply that the manufacturing processes or quality control requirements have fluctuated.

For the outer plating component, Hungary (23/85) showed statistically significant differences ($p < 0.05$) with the following: Bulgaria (10/99a), Bulgaria (10/99b), Ukraine (270/67), Romania (324/94) and Russia (WOLF). It is unclear why the outer plating width for Hungary (23/85) diverges as such whilst the values for Hungary (23/84) and Hungary (23/86) do not.

In order to ensure that the assumption of normality was not violated, the results were grouped per manufacturer, and the width of each portion of the jackets was examined. This was done by using the Shapiro-Wilk Test which is more appropriate for small sample sizes (below 50 samples) and produced numerical means of assessing normality. For the majority of the results $p > 0.05$ – indicating that the data did not significantly deviate from a normal distribution. For the inner plating, the assumption of normality was violated for Ukraine (260/70) and China (61/64) with p values of 0.038 and 0.021 (respectively). This was confirmed graphically by examining Q-Q Plot diagrams show in **Figure 6.11** and **Figure 6.12.**

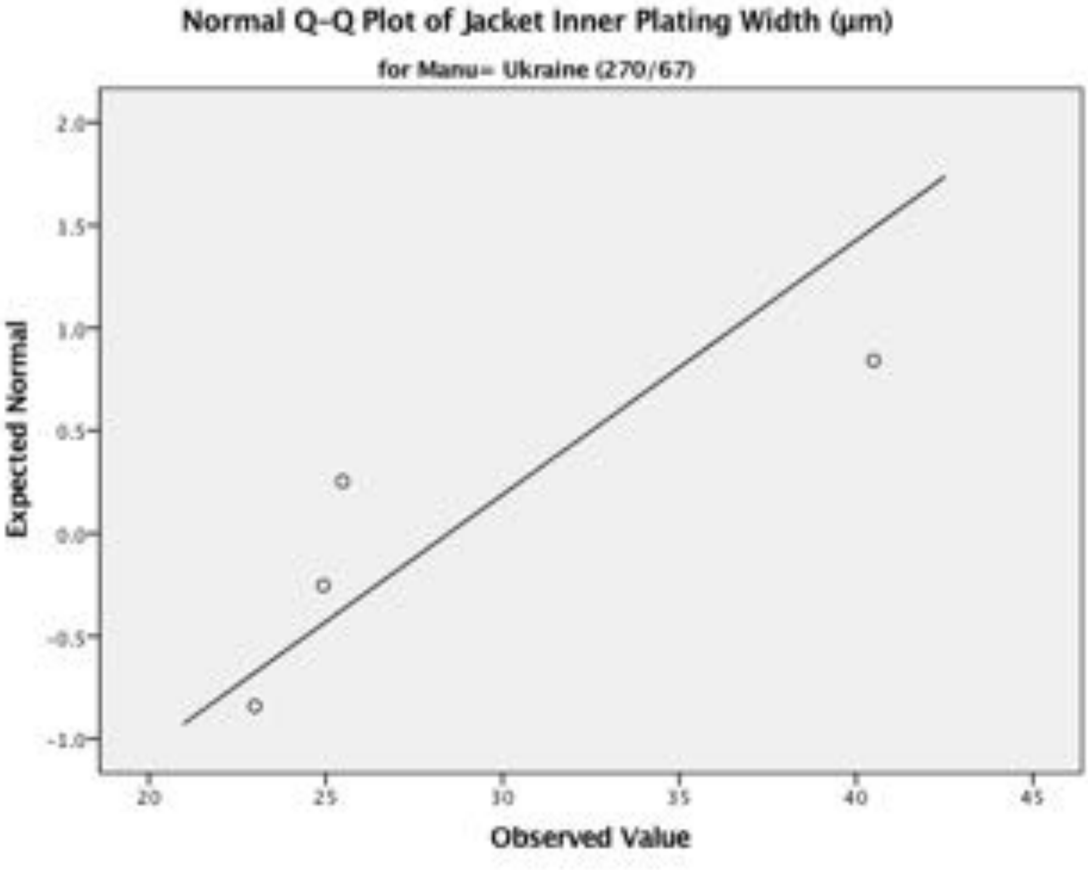


Figure 6.11 Q-Q Plot Diagram for Expected vs Observed Values of Jacket Inner Plating Width (µm) present in Steel Jacket Projectiles from Ukraine (260/70).

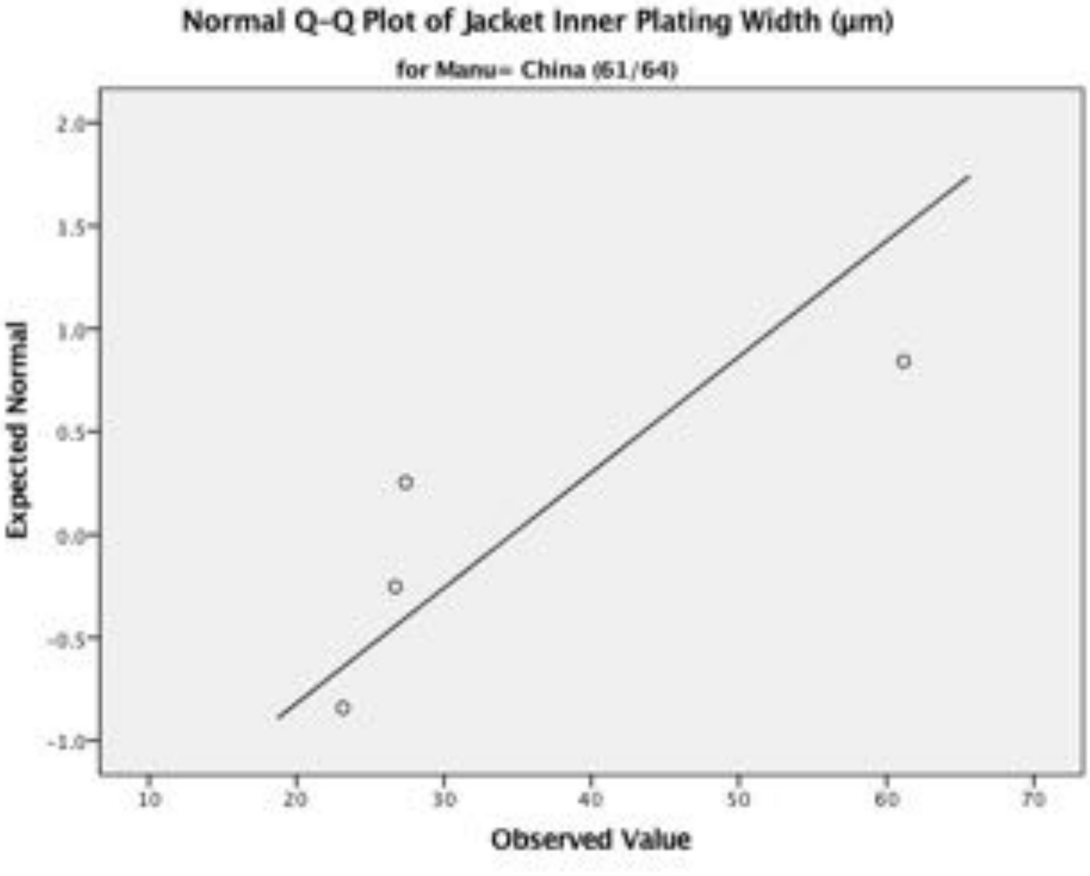


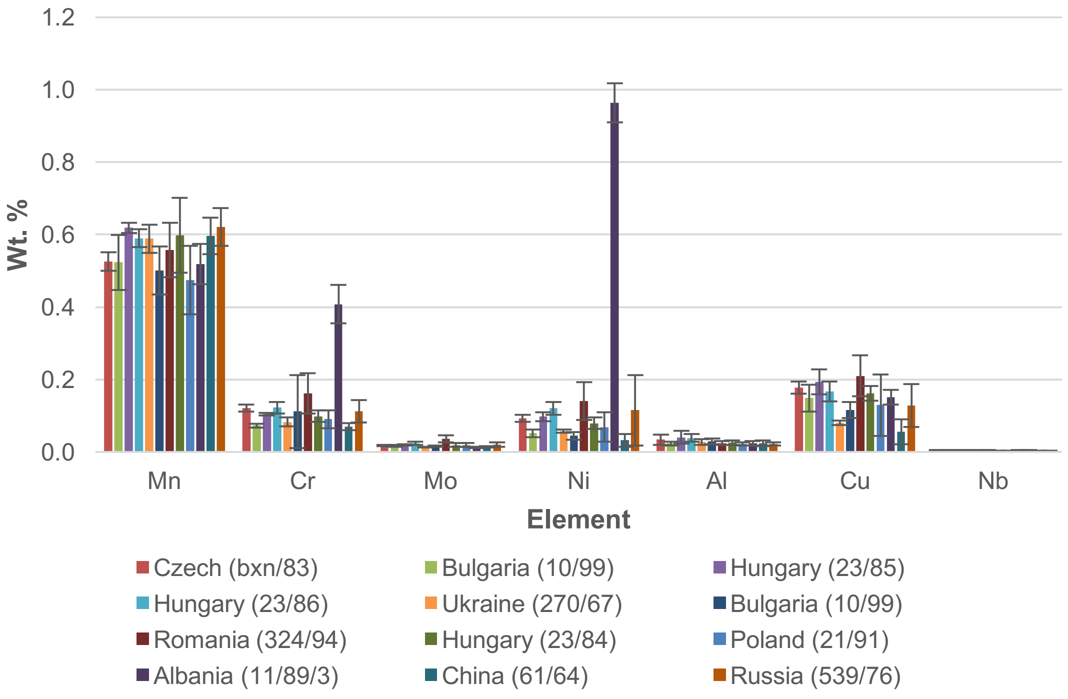
Figure 6.12 Q-Q Plot Diagram for Expected vs Observed Values of Jacket Inner Plating Width (µm) present in Steel Jacket Projectiles from China (61/64).

From the analysis conducted it can be inferred that there is value in analysing the widths of the steel jacket components. Whilst the overall width was not suitable for differentiation, there were statistically significant variations within other components – although typically only for one or two manufacturers. As this process is somewhat time-consuming, it must be considered as to whether the benefit of the results outweigh the energy input into obtaining them. Automation of the measurements would greatly reduce the time involved and is discussed in **Section 8**.

6.2 Projectile (Steel Core)

6.2.1 X-Ray Fluorescence Analysis of Materials

Where present, the steel cores were also analysed to determine their composition. The averages have been calculated from analysis of four samples, at three points for each with the results shown in **Figure 6.13**.



** Error bars represent standard deviation.*

Figure 6.13 Chart showing quantities of additional elements (weight percent, (wt.%)) present within projectile steel cores.

Figure 6.13 is a visual representation of the (wt.%) of elements present. There was a statistically significant difference between groups for all of the elements analysed as determined by one-way ANOVA:

- Mn (F(11,36) = 4.222, p = 0.000)
- Cr (F(11,36) = 38.365, p = 0.000)
- Mo (F(11,36) =9.58, p = 0.000)
- Ni (F(11,36) = 178.121, p = 0.000)
- Al (F(11,36) = 4.301, p = 0.000)

- Cu (F(11,36) = 4.801, p = 0.000)
- Nb (F(11,36) = 10.503, p = 0.000)
- Fe (F(11,36) = 13.812, p = 0.000)

The results are shown in **Appendix H**.

For elements where the (wt.%) showed significant differences between groups the Bonferroni post-hoc test was utilised (see **Section 5.7.1** for reasons why this more stringent test was selected). Between manufacturer Bonferroni comparisons revealed statistically significant differences (where $p < 0.05$) in several elements and these are discussed below. The Bonferroni post-hoc test which assumes equal variances (i.e. homogeneity of variance). Levene's test was utilised to confirm this and found that this assumption was violated for: Mn, Cr, Mo, Ni, Cu and Nb. Accordingly, the results were checked using the Games-Howell post-hoc test which does not assume equal variances. The ANOVA results (as reported above) remained unchanged, however, there was some variation in the comparison of statistically significant differences present.

The most beneficial element analysed proved to Nb. This precipitate is commonly observed in steels and associated with grain refinement – leading to substantial enhancements in strength [139]. Nb allowed for observation of 29 statistically significant differences ($p < 0.05$). The most noticeable of these were between Bulgaria (10/99a), Hungary (23/86) and Ukraine (270/60). These three manufacturers all showed statistically significant differences ($p < 0.05$) with the same seven manufacturers: Bulgaria (10.99b), Romania (324/94), Hungary (23/84), Poland (21/91), Albania (11/89/3), China (61/64) and Russia (539/76). When compared with the results from the Games-Howell post-hoc test, there were 12 fewer statistically significant differences ($p < 0.05$) reported. There were no longer statistically significant differences present between Bulgaria (10/99a), Hungary (23/86) and Ukraine (270/60), and Poland (21/91), Albania (11/89/3), China (61/64). There was variation ($p < 0.05$) observed between Hungary (23/85) and five manufacturers, using the Bonferroni post-hoc test that was also not present using the Games-Howell test. Conversely, using the Bonferroni post-hoc test, Czech (bxn/83) showed statistically significant differences with only three manufacturers: Romania (324/94), Hungary (23/84), and Russia (539/76). When analysed using the Games-Howell test, two additional manufacturers showed statistically significant variation in Nb ((wt.%)) with Czech (bxn/83) with $p < 0.05$ for Bulgaria (10/99b), and China (61/64). The most noticeable variation in analysis between the two post-hoc test results was that the statistically significant differences present between Hungary (23/85) and five other manufacturers all showed no statistically significant differences ($p < 0.05$). These were for Bulgaria (10.99b), Romania (324/94), Hungary (23/84), China (61/64) and Russia (539/76). These results have the implication of separating the manufacturers into two ‘groups’ based on their Nb content and indicate that the value of analysing Nb content (wt.%) can be appreciated regardless of the post-hoc test used to compare ANOVA results.

Also beneficial for analysis were Cr, Ni, Fe and Mo with 14, 12, 12 and 11 statistically significant differences observed (respectively) using the Bonferroni post-hoc test. For Cr, Ni and Fe 11 out of the 12 variations were between Albania (11/89/3) and every other manufacturer – allowing this particular manufacturer to be uniquely identified by comparing the levels (wt.%) of these elements. The results from the Games-Howell post-hoc test were very similar with only one variations: the content (wt.%) of Fe not being statistically significantly different ($p <0.05$) between Albania (11/89/3) and Bulgaria (10/99b), where $p = 0.09$. Using the Bonferroni test, these same three elements also displayed statistically significant differences between Romania (324/94) and China (61/64) and for Cr, differences were also observed with Bulgaria (10/99a) and Ukraine (270/67). When analysed using the Games-Howell post-hoc test, additional statistically significant differences were observed and are summarised below:

- Bulgaria (10/99a) – Czech (bxn/83), and Hungary (23/85) for both Cr and Ni.
- Bulgaria (10/99b) – Czech (bxn/83), Hungary (23/84), Hungary (23/85), and Hungary (23/86) for Ni.
- China (61/64) – Czech (bxn/83) for both Cr and Ni.

- Ukraine (270/67) – and Czech (bxn/83), Hungary (23/84), Hungary (23/85), and Hungary (23/86) for Ni.

The value of analysing the wt.% of these elements is supported in cases where the manufacturer is suspected or to theorise about the possible manufacturers, however, if comparing completely unknown samples the chances of identification drop from 18% to 1% (or 21% to 4%).

The results for Mo from the Bonferroni test conflict drastically with those from the results from the Games-Howell post-hoc test: with the former, Mo has the potential to uniquely identify projectiles from Romania (324/94) based on the statistically significantly different p values for this element ((wt.%)). In contrast, the latter shows no statistically significantly different results ($p < 0.05$) and could not be used to identify Romania. Moreover, there are statistically significantly ($p < 0.05$) different levels ((wt.%)) of Mo between Czech (bxn/83) and Albania (11/89/3) and Ukraine (270/67). Allowing for further differentiation of Czech (bxn/83).

Hungary (23/85) showed statistically significant differences ($p < 0.05$) in Al content ((wt.%)) with Bulgaria (10/99a), Poland (21/91), Albania (11/89/3), China (61/64), and Russia (539/76). Interestingly, Hungary (23/86) also showed variation with Poland (21/91) and Russia (539/76), however, Hungary (23/84) did not. This may be another indication that there are variances between projectiles from the same manufacturer but difference years. These results were obtained using the Boneferroni post-hoc test as the ANOVA results for Al did not violate Levene’s test of homogeneity of variance.

Cu showed similar levels of comparison and could add value to identifying projectiles from China (61/64) which showed statistically significant differences in (wt.%) with Czech (bxn/83), Hungary (23/84), Hungary (23/85), Hungary (23/86) and Romania (324/94). There were also statistically significant differences between Ukraine (270/67) and Hungary (23/85) and Romania (324/94). When analysed using the Games-Howell post-hoc test there was also a statistically significant difference ($p < 0.05$) between Albania (11/89/3) and China (61/64) and Ukraine (270/67). These results indicate the possibility for utilising the difference in (wt.%) to differentiate between several manufacturers; namely China (61/64), Ukraine (270/67) and Romania (324/94).

Mn conducted using the Bonferroni post-hoc test only displayed statistically significant variation ($p < 0.05$) between Poland (21/91) and Hungary (23/85) and Russia (539/76) – creating reservations about the value of analysing this element in future research. As homogeneity of variance was violated for Mo, the results we re-examined using the Games-Howell test. These results conflicted with those above and the p values for the above comparisons were all above 0.05. Furthermore, there were new statistically significant differences observed between:

- Bulgaria (10/99b) –China (61/64), Hungary (23/85) and Russia (539/76)
- Hungary (23/85) – Czech (bxn/83) and Romania (324/94).

The results above imply that there is value in examining the (wt.%) of various elements, however, this would need to be further explored as discussed in **Section 8**.

The results separated by manufacturer and the normality was examined using the Shapiro-Wilk test. This assumption was violated for several of the manufcaturers/elements, however, upon investigation of extreme values, most were less than three standard deviations from the mean. Nonetheless, values where $p < 0.05$, indicated that the data significantly deviated from a normal distribution and was further explored by visually examining Q-Q Plot diagrams similar to the ones shown in **Figure 6.14** and **Figure 6.15**.

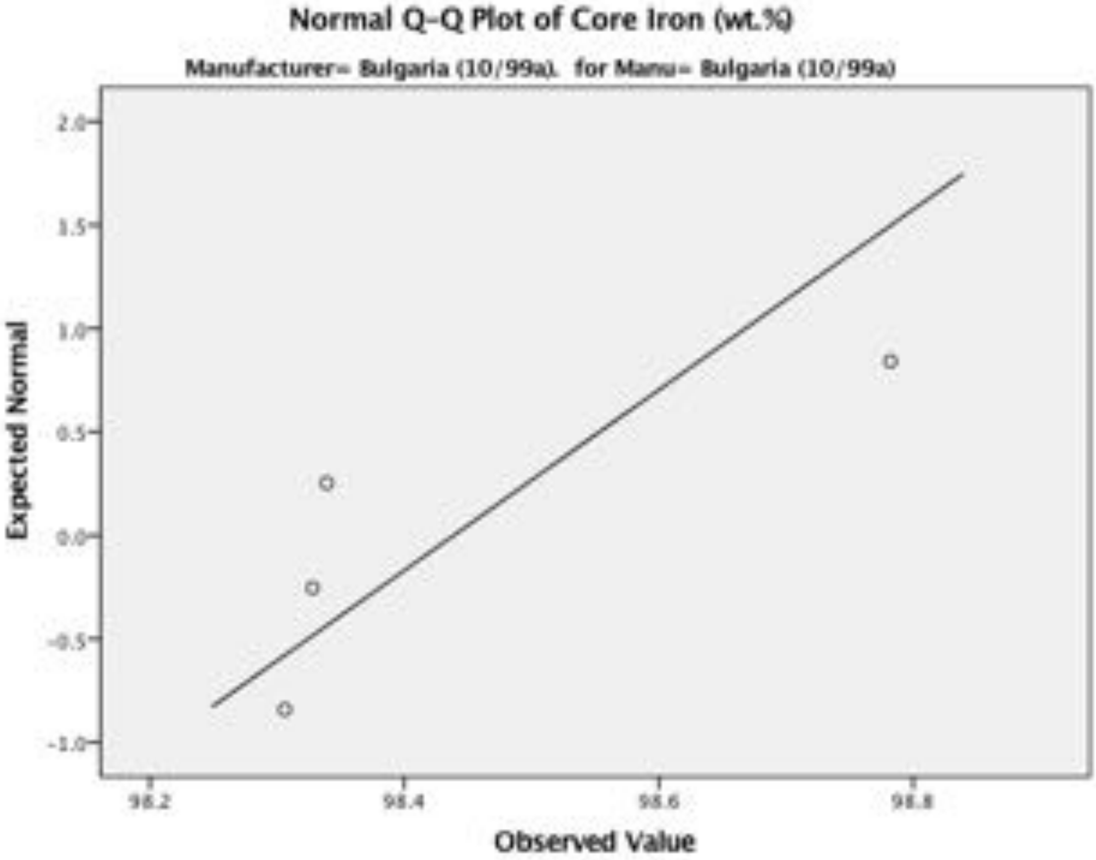


Figure 6.14 Q-Q Plot Diagram for Expected vs Observed Values of Fe (wt.%) present in Steel Cored Projectiles from Bulgaria (10/99a).

The assumption of normality was also violated for the Mn content (wt.%) for Hungary (23/85), Ukraine (270/67), and Poland (21/91). These were all similar shaped Q-Q Plot Diagrams to that in **Figure 6.14**.The assumption of normality for Nb (wt.%) was violated for Hungary (23/86), Poland (21/91) Albania (11/89/3) and China (61/64). The shape of these Q-Q Plot Diagrams more closely followed that shown in **Figure 6.15**.

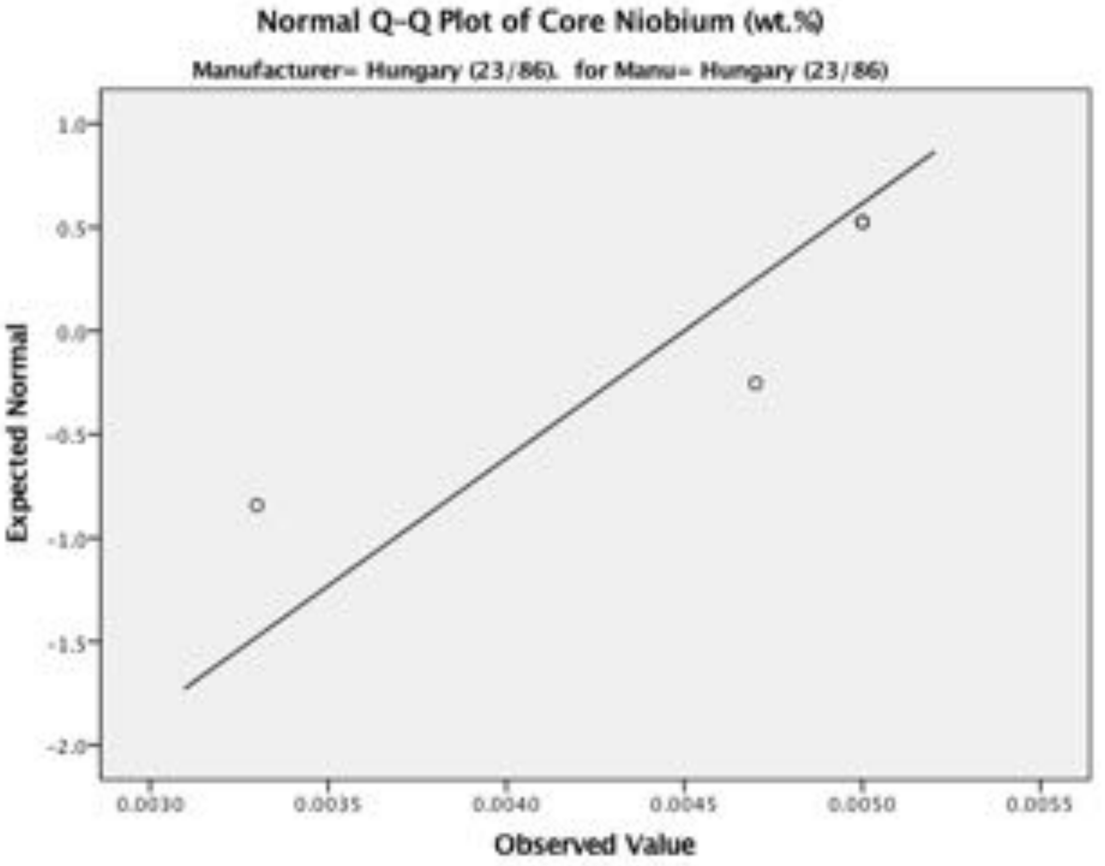


Figure 6.15 Q-Q Plot Diagram for Expected vs Observed Values of Nb (wt.%) present in Steel Cored Projectiles from Hungary (23/86).

The Q-Q Plot diagrams demonstrate that the data points did not vastly deviate from the diagonal line representing normal distribution. Similar occurences arose for:

- Bulgaria (10/99b) – Cr and Ni.
- Poland (21/91) – Cr and Mo.
- Albania (11/89/3) – Ni.
- China (61/64) – Mo and Cu.

As the assumption of normality was violated for these elements with these manufacturers, the results used for differentiation should be approached with caution and would benefit from an increased sample size.

The manganese values in **Figure 6.7** are all within tolerances for 10xx grade steels, however, some variation is present. Manganese improves the hardenability of a steel and prevents a brittle film from forming due to ferrous sulphide. Excessive values can however, encourage undesirable temper-brittleness and levels of grain coarsening; the effect of which can be countered by adding molybdenum and nickel, respectively [138].It may be possible to utilise the (wt.%) of manganese to distinguish between manufacturers, however, the statistical significance of the differences needs to be assessed.

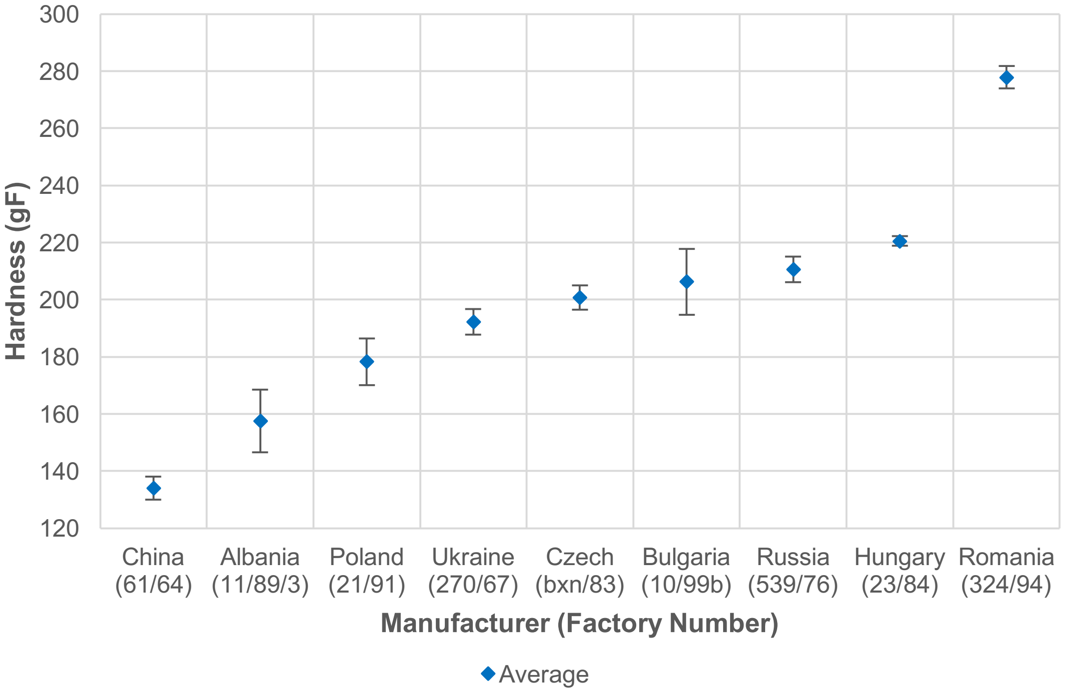
The results for the steel cores showed variances in composition once again for the Albanian (11/83/3) manufacturer. Here, high levels of chromium and nickel were observed. The combination of these two alloying elements in ‘appropriate proportions’ are known to produce the highest quality structural steel, and this composition more closely matches that of an alloy steel [18], [138].

The addition of copper may be useful in preventing segregation of phosphorous rich and pearlite-free regions; causes of weakness and brittleness [138]. The copper values also vary, with some quantities going beyond the maximum accepted amount of 0.35%. The sporadic values reported in **Figure 6.7** may have been influenced by a) the preparation process (grinding and polishing), and b) the fact that XRF will penetrate layers and may be accounting for the copper coating. Thus, caution should be utilised when interpreting the results as copper may not be reliable for use in differentiation. This may be reconsidered if an alternative sectioning technique is adopted and is discussed in **Section 8**.

6.2.1 Hardness Testing

For projectiles where a steel core was present (typically M43 type), microindentation hardness testing was conducted. These tests reveal disparities commonly present within most materials, therefore it is advised that multiple indents are made and an average and standard deviation calculated in order to obtain a value representative of the bulk hardness [140]. Four samples were selected per manufacturer with five locations sampled per projectile core. The results are available in **Appendix E**.

The hardness values for different manufacturers were compared with the results listed shown in **Figure 6.16**:



** Error bars represent standard deviation.*

Figure 6.16 Chart showing average Vickers hardness value (gF) for the steel cores present in projectiles from different manufacturers.

Some of the variations in hardness (gF) can be observed visually in **Figure 6.16.** In order to determine whether these are significantly different an ANOVA test was conducted on the hardness values (gF) additional elements present (shown in **Table 6.6** below) and where $p<0.05$ cells are highlighted.

CORE HARDNESS (H_V) **ANOVA RESULTS**

	Sum of Squares	df	Mean Square	F	Sig.
BETWEEN GROUPS	58617.429	11	5328.857	67.153	**0.000**
WITHIN GROUPS	2856.74	36	79.354		
TOTAL	61474.17	47			

Table 6.6 ANOVA test for hardness values.

It can be observed that all of the core hardness values showed significant differences between groups. Levenes test for homogeneity gave a p value of 0.003 – indicating that this assumption had been violated. Accordingly, the Games-Howell post-hoc test was utilised. **Table 6.7** summarises the p values for individually compared sets. Where $p<0.05$ cells cells are highlighted.

	MANUFACTURER										
	Czech (bxn/83)	Bulgaria (10/99a)	Hungary (23/85)	Hungary (23/86)	Ukraine (270/67)	Bulgaria (10/99b)	Romania (324/94)	Hungary (23/84)	Poland (21/91)	Albania (11/89/3)	China (61/64)
Bulgaria (10/99a)	0.996										
Hungary (23/85)	0	0.633									
Hungary (23/86)	0	0.6	1								
Ukraine (270/67)	0.174	0.641	0.002	0.002							
Bulgaria (10/99b)	1	1	0.578	0.552	0.93						
Romania (324/94)	0	0.011	0	0	0	0.016					
Hungary (23/84)	0.001	0.56	0.992	1	0.005	0.521	0				
Poland (21/91)	0.371	0.303	0.135	0.132	0.622	0.428	0.017	0.129			
Albania (11/89/3)	0.014	0.017	0.004	0.004	0.019	0.051	0.001	0.006	0.992		
China (61/64)	0	0.011	0	0	0	0.022	0	0	0.343	0.093	
Russia (539/76)	0.102	0.999	0.141	0.115	0.012	0.972	0	0.103	0.211	0.004	0

Table 6.7 Comparison of p values for hardness values using the Games-Howell post-hoc test.

The statistically significant differences observed above have the potential to suggest that the manufacturers from Bulgaria (10/99), Hungary (23) and Russia (539/76) are supplied by the same source however, this theory is not confirmed by the elemental analysis in **Section 6.2.1**. Time constraints prevented the analysis of the microstructure of the steel cores in projectiles from these manufacturers although this is a potential avenue for further exploration. It could be suggested that similar manufacturing techniques (i.e wire drawing), and the effects of cold working a mild carbon steel in this way, resulted in similar hardness values (gF).

As discussed in **Section 6.1** previous composition analysis using XRF showed significantly higher levels of Ni and Cr content for Albania (11/89/3). The presence of these elements lead to the expectation of higher H_v values, however, Albania (11/89/3) showed the second to lowest average values. The observation of varied hardness values independent of elemental variation indicated that this was due to physical processes and that further investigation was required. Four samples were selected with varying H_v values: China, (61/64), Albania (11/89/3), Czech, (bxn/83), and Romania, (324/94). The sectioned core was polished and etched chemically using 2% nitric acid in ethanol. This then revealed the composition of the grains, known as the microstructure [17]. The samples were observed using an optical microscope with the images shown below:

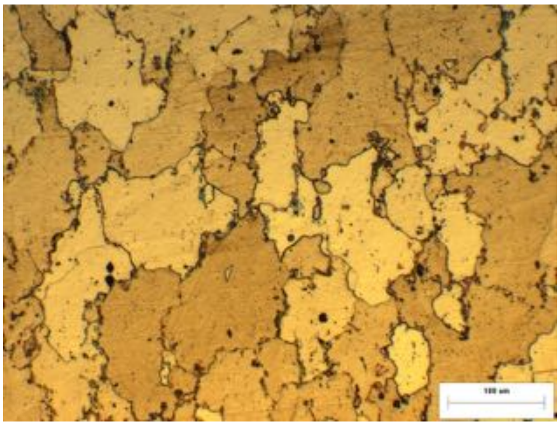


Figure 6.17 Microstructure of steel core at 100 x magnification for China (61/64).

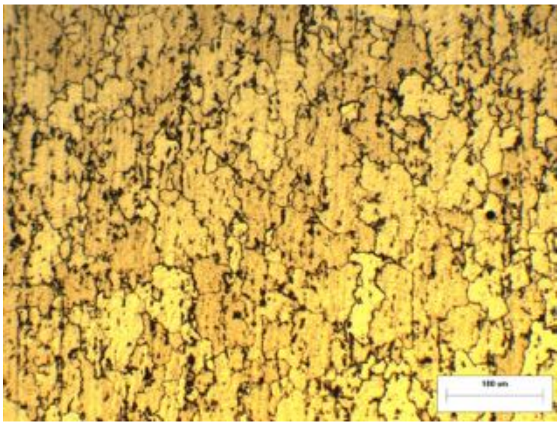


Figure 6.18 Microstructure of steel core at 100 x magnification for Albania (11/89/3).

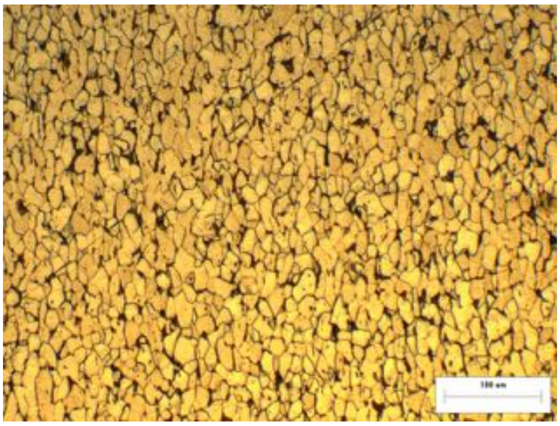


Figure 6.19 Microstructure of steel core at 100 x magnification for Czech (bxn).

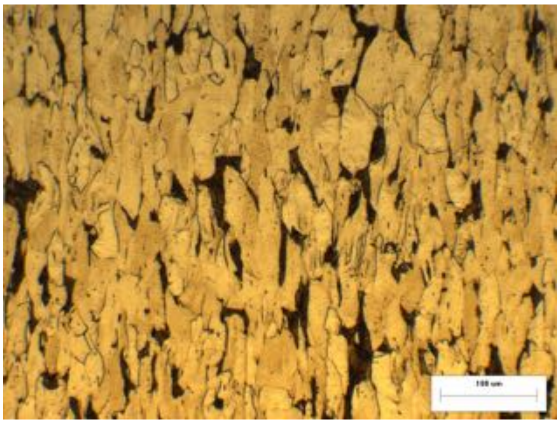


Figure 6.20 Microstructure of steel core at 100 x magnification for Romania (324/94).

Differences in the microstructure were clearly visible in regard to the size, directionality and how equi-axed the grains were, as well as the amount of each grain type present. The formation of ferrite and pearlite is the result of slow air cooling from around 850˚C to form light, ductile iron (known as ferrite) and dark, hard areas of carbon containing, iron carbide plates. The hardness of these two grain types in 90H_v and 250H_v, respectively [17]. Doig describes a *mild carbon steel* with a “75/25 ferrite/pearlite mix” to have a “bulk hardness of about 130H_v”. ImagJ was used to calculate approximate the ratio ferrite/pearlite and the results are shown in **Table 6.8** below.

Table 6.8 Estimated percentages (%) of ferrite/pearlite.

Manufacturer	Hardness (H_v)	Ferrite (%)	Pearlite (%)
China (61/64)	134.09	89	11
Albania (11/89/3)	157.56	77	23
Czech (bxn/83)	200.72	77	23
Romania (324/94)	277.88	78	22

The above figures are only estimations, however they support the observation of a higher bulk hardness at 180H_v that *medium carbon steel* possesses [17]. It is worth mentioning that small dots observed across the samples are the likely result of either the diamond paste particles embedded during preparation, or impurities from the ingot [17].

China (61/64) displayed a 1:1.3 equi-axed grain structure with a little directionality. This was indicative of being partially cold worked. The size of the grain structure was larger than those observed in Albania (11/89/3), and Czech (bxn/83). A larger grain size is indicative of lower yield strength and lower ductility [17]. With Albania (11/89/3) and Czech (bxn/83) having similar ferrite/pearlite ratios, the difference in H_v value was likely the result of the variation in average grain size.

Romania (324/94) displayed a distinctly higher H_v value. This sample had a relatively large grain size, and the microstructure is comparable to those displaying 0.2% C. On the assumption that it was air cooled before it was hardened, the directionality (1:4.3) is indicative of work hardening; caused by dislocations in the crystalline structure [17]. This was likely to have occurred during the manufacturing process as the original billet/bar was drawn through a die. Although it is probable that the process is similar between manufacturers, any number of factors could be the cause of this variation. These possibilities are further discussed in **Section 8**.

An additional observation was the inconsistency within samples. Although not present in all samples this was obvious in the deviation of results for Albania (11/89/3), Poland (21) and Bulgaria (10). The results for all manufacturers are detailed below:

In order to explore whether these high deviations were the result of outliers intra batch variation was analysed and has been presented for the three samples with the highest standard deviations: Albania (11/89/3), Poland (21/91) and Bulgaria (10/99a).

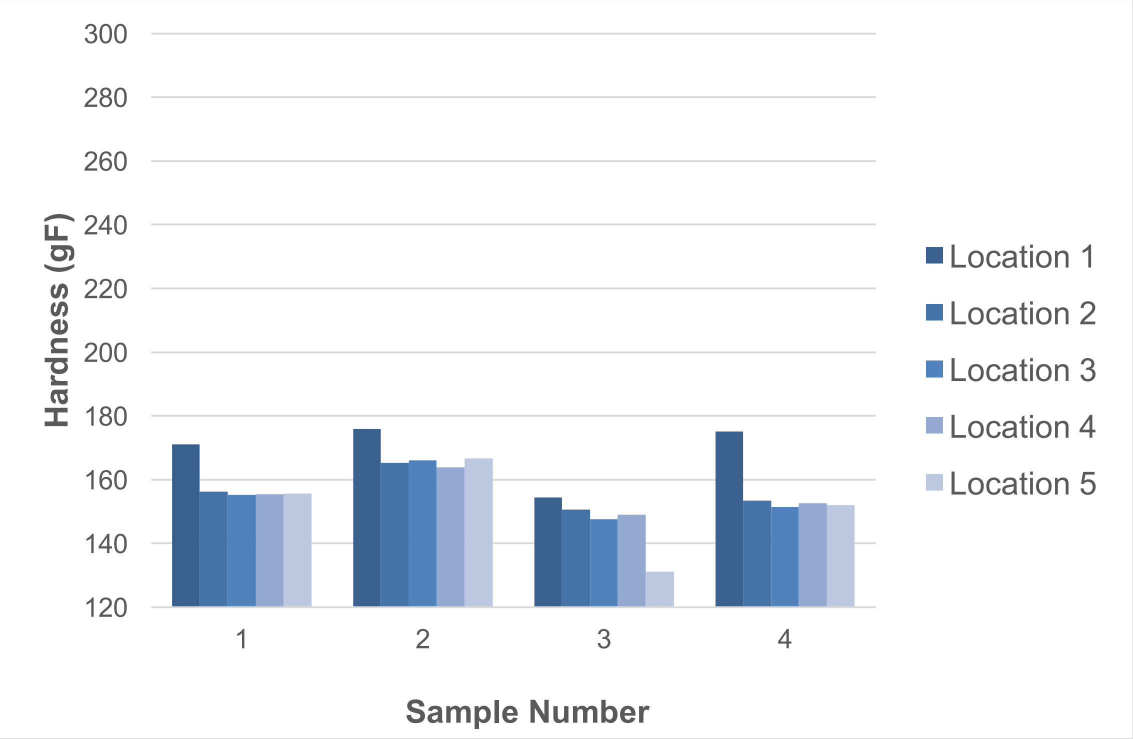


Figure 6.21 Chart showing average Vickers hardness value for the steel cores from the same manufacturer: Albania (11/89/3).

Albanian (11) steel core values present the most interesting variation. There are slightly lower hardness values for sample 3, however, these are not particularly noteworthy in comparison to the obvious variation between Location 1 and the other Locations (2,3,4, and 5). Location 1 for all samples has a higher hardness value. This was the Location closest to the base of the projectile and may be indicative of the manufacturing process involving an element of cold working. **Figure 6.21** is a visual representation of the hardness (gF) of the differences locations for the different samples. There was no statistically significant difference between Locations for the hardness (gF) as determined by one-way ANOVA:

- Location (F(4,15) = 2.001, p = 0.146)

In addition to the aforementioned variation, the values for sample 3 are consistently lower than those for 1, 2, 4. This variation within the batch could be indicative of intra-batch variation as a result of quality control standards.

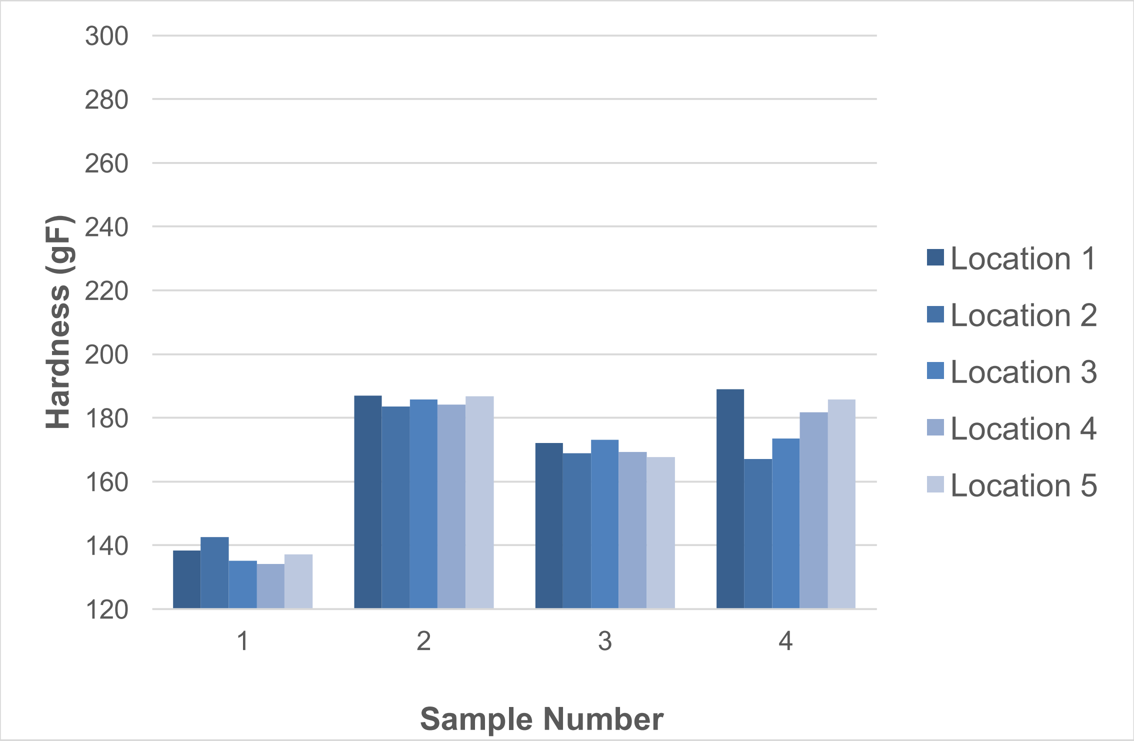


Figure 6.22 Chart showing average Vickers hardness value for the steel cores from the same manufacturer: Poland (21/91).

The average microindentation hardness values for the Polish (21/91) samples are relatively consistent apart from those for 1 which are noticeably lower. If sample 1 were to be discounted, then the standard deviation would be reduced by over 50% from 19.54 to 8.21. In this particular instance the standard deviation is still relatively high and the reason for this undetermined. **Figure 6.22** is a visual representation of the hardness (gF) of the difference Samples for the manufacturer Poland (21/91). The differences between the hardness (gF) were determined by one-way ANOVA:

- Sample (F(3,16) = 92.131, p = 0.000)

As the results violated the assumption of homogeneity, multiple comparisons were conducted using the Games-Howell post-hoc test. This revealed statistically significant differences ($p < 0.05$) between Sample 1 and every other sample. The results also determined statistically significant differences (p = 0.000) between Sample 2 and Sample 3. The variation may again be the result of the quality control standards of this manufacture, however this information is difficult to verify, thus this reasoning is only observational. This inconsistency could be further explored by analysing the grain structure of these steel cores – a task that was not achievable within the time-frame of this research.

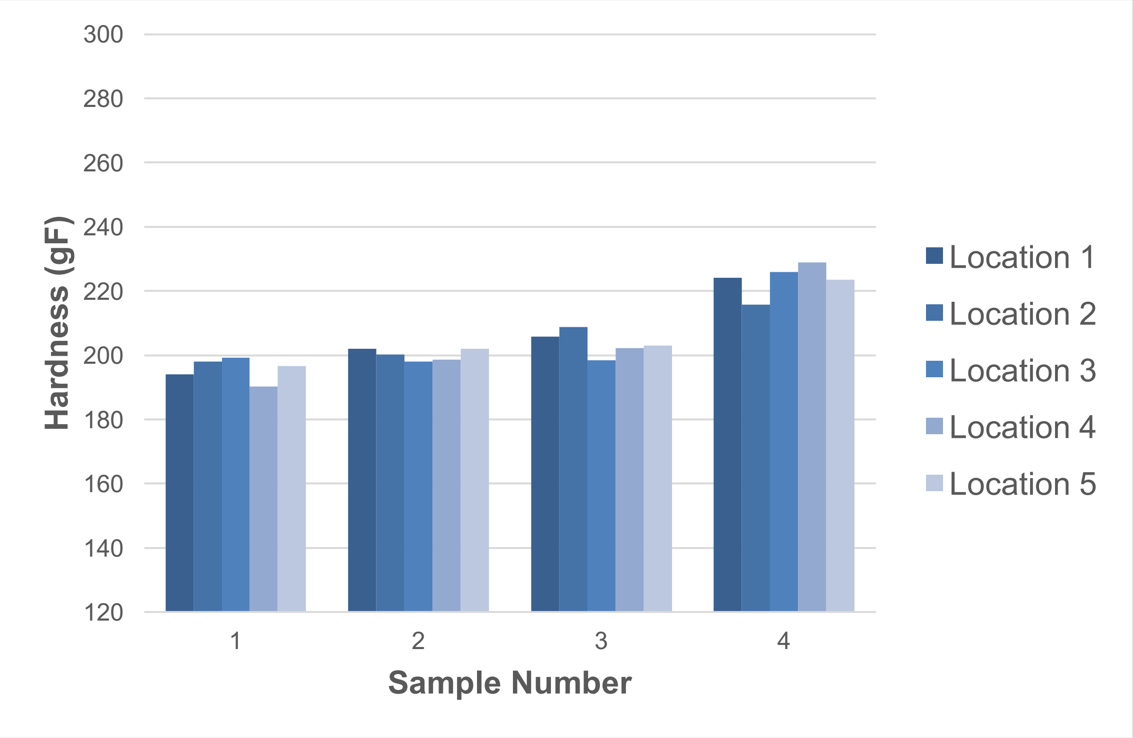


Figure 6.23 Chart showing average Vickers hardness value for the steel cores from the same manufacturer: Bulgaria (10/99a).

For Bulgaria (10/99a) the variation in samples is subtler and a slight increase (of $20H_v$) is noted in Sample 4. This difference is not overly obvious, however the impact on the results is a recognisable increase in standard deviation. **Figure 6.39** is a visual representation of the hardness (gF) of the difference Samples for the manufacturer Bulgaria (10/99a). The differences between the hardness (gF) were determined by one-way ANOVA:

- Sample ($F(3,16) = 55.424$, $p = 0.000$)

As the results did not violate the assumption of homogeneity, multiple comparisons were conducted using the Bonferroni post-hoc test. This revealed statistically significant differences ($p < 0.05$) between Sample 4 and every other sample. The results also determined no other statistically significant variation between Samples 1, 2, and 3.

Further investigation revealed that this deviation was present in additional batches of ammunition from Bulgaria (10/99b). **Table 6.9** shows the comparative standard deviations for ammunition from the same manufacture and the same year, but from different batches.

Table 6.9 Average Vickers hardness value for the steel cores present in projectiles from two different batches, in the same year, from the same manufacturer in Bulgaria (10/99a) and Bulgaria (10/99b).

Manufacturer	**Hardness Value (gF)**	**Standard Deviation**
Bulgaria (10/99a)	206.27	11.58
Bulgaria (10/99b)	201.76	13.49

Table 6.9 in combination with the ANOVA results suggests that whilst there is low deviation between batches from the same year, there is significant intra-batch variation within that year. This could also be inferred as the result of less stringent quality control standards in regard to ammunition manufacture and differences in tolerances.

One of the factors that was somewhat explored was the temporal variation in ammunition variation. For Hungary (23) ammunition was analysed from three consecutive years (1984, 1985 and 1986). The results are recorded below.

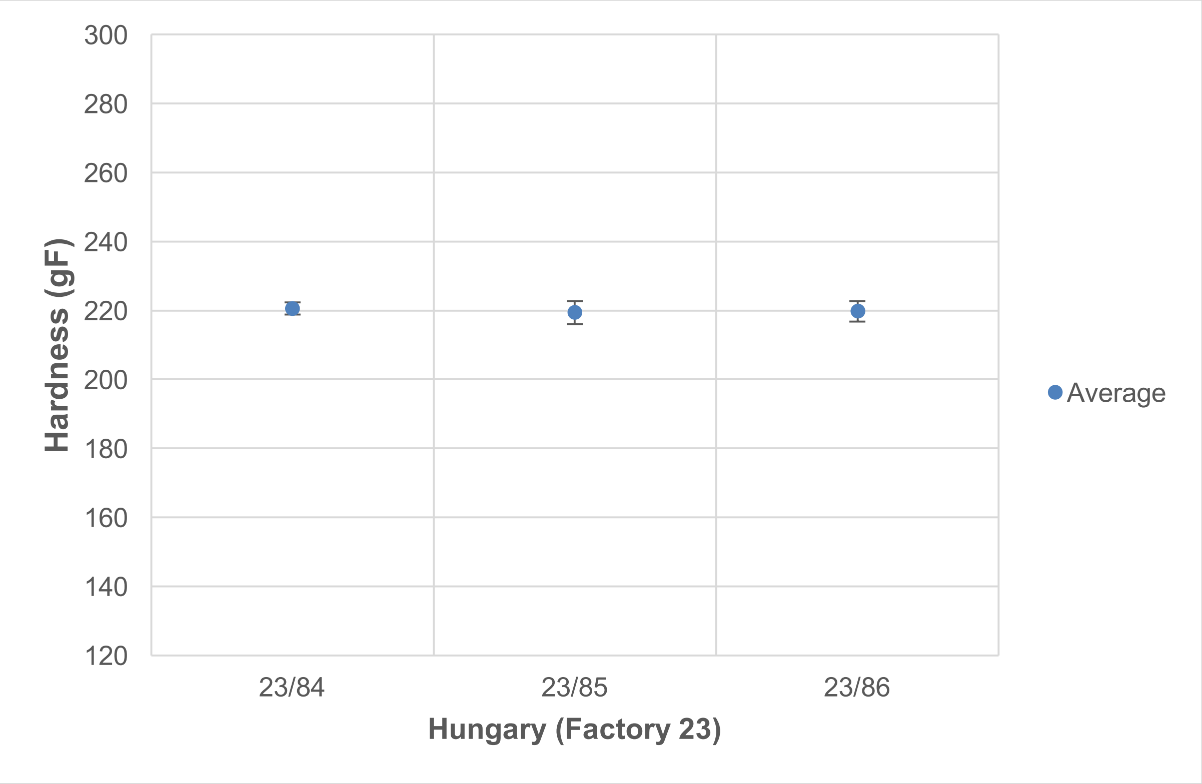


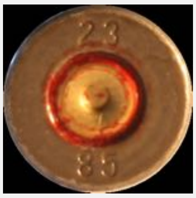
Figure 6.24 Chart showing average Vickers hardness value for the steel cores present in projectiles from the same manufacturer in Hungary (23) over three consecutive years (1984, 1985, 1986).

Figure 6.24 infers that the microindentaion hardness values of various projectiles from the same manufacturer, spanning consecutive years in unlikely to fluctuate significantly. The limitations of this study must be recognised in terms of the sample size and that only three years are examined in this study. Studying the ammunition from one manufacturer temporally is discussed in **Section 8**.

6.3 Cartridge Cases

The cartridge cases and headstamps were photographed before and after being sectioned, in order to allow for examination of colour of materials and primer lacquers (on the annuli). The photographs are shown below in **Table 6.10**.

Table 6.10 Photographs of cartridge cases and headstamps.

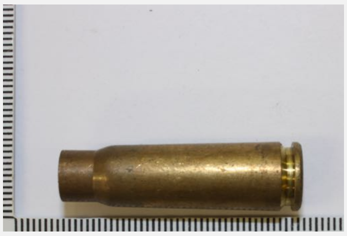
Manufacturer	**Photograph**	
	Cartridge Case	Headstamp
Czech (bxn/83)		
Bulgaria (10/99b)		
Serbia (PPU/85)		
Hungary (23/84) Hungary (23/85) Hungary (23/86)		

Ukraine (270/67)

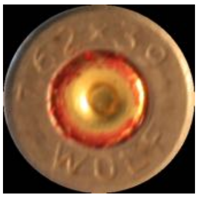
South Africa (13/88)

Romania (324/94

Bosnia (IK/83)

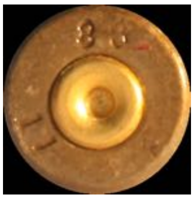


Russia (WOLF)



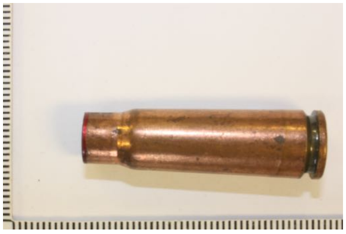
Poland (21/91)

Albania (11/89/3)



China (61/64)

Russia (539/76)



The material used for the cartridge cases examined was either brass, or steel (including plated steel). This material could be determined using a magnet (for steel cartridge cases) and the following cartridge cases were found to be brass:

- Serbia (PPU/85)
- South Africa (13/88)
- Bosnia (IK/83)

Upon examination of the lacquer around the primer annuli, it was noted that South Africa (13/88) showed a green lacquer – a feature that not present in any of the other cartridge cases examined in this study. Serbia (PPU/85) and Bosnia (IK/83) both displayed a red lacquer around the primer annulus.

The red lacquer was also prevalent for most of the steel cartridge cases examined. For the majority of samples, there was a ‘ring’ of lacquer around the primer annuli, however, there were two noticeable variations: Lacquer appeared to be absent on the primer annulus for Czech (bxn/83), whilst the entire primer annulus for Romania (324/94) was coated in lacquer. Photographs of the cartridge case base are shown below in **Figure 6.25**.

Figure 6.25 Photographs of primer annuli and lacquer from (left to right) Hungary (23/85), Czech (bxn/83) and Romania (324/94), showing variation (and absence) in lacquer.

Variations in the colour of the steel cartridge cases were also observed. These can be seen in **Table 6.10** and grouped into four colours:

- Grey: Czech (bxn/83) and Russia (WOLF)
- Greenish brown: Hungary (all), Ukraine (270/67), Bulgaria (10/99), Poland (21/91)
- Olive green: Romania (324/94), Albania (11/89/3)
- Copper Plated: China (61/64) and Russia (539/76)

These variations in colour reflect similar colours defined by Walker [62] and the use of steel in production of cartridge cases is often associated with the USSR and Warsaw Pact countries.

6.3.1 X-Ray Fluorescence analysis of Materials

XRF analysis was also conducted for the cartridge cases to determine their composition. As expected, they were composed of copper plated/lacquered mild steel, or a cartridge case brass (70% Cu, 30% Zn) with the results shown below in **Table 6.11**. Once again, the present of additional elements (considered impurities), was expected. Other elements that were observed in brass cartridge cases include; Sn, Pb, Fe, Al, Cr, Co, Mn, Si, P, Ag, Ni and Bi.

Table 6.11 Summary of the material used for cartridge cases.

Material	**Manufacturers**
Brass	Serbia (PPU/85), South Africa (13/88), Bosnia (IK/83),
Steel	Czech (bxn/83), Bulgaria (10/99b) Hungary (23/84), Hungary (23/85) , Hungary (23/86), Ukraine (270/67), Romania (324/94), Poland (21/91), Albania (11/89/3), China (61/64), Russia (WOLF), Russia (539/76),

The average percentage weights for the elements present in all components are are detailed in **Appendix D.**

6.3.1.1 Brass

The brass cartridge cases were also analysed and their composition observed. **Figure 6.26** shows the percentages of copper and zinc present whilst **Figure 6.27** provides quantification for additional elements.

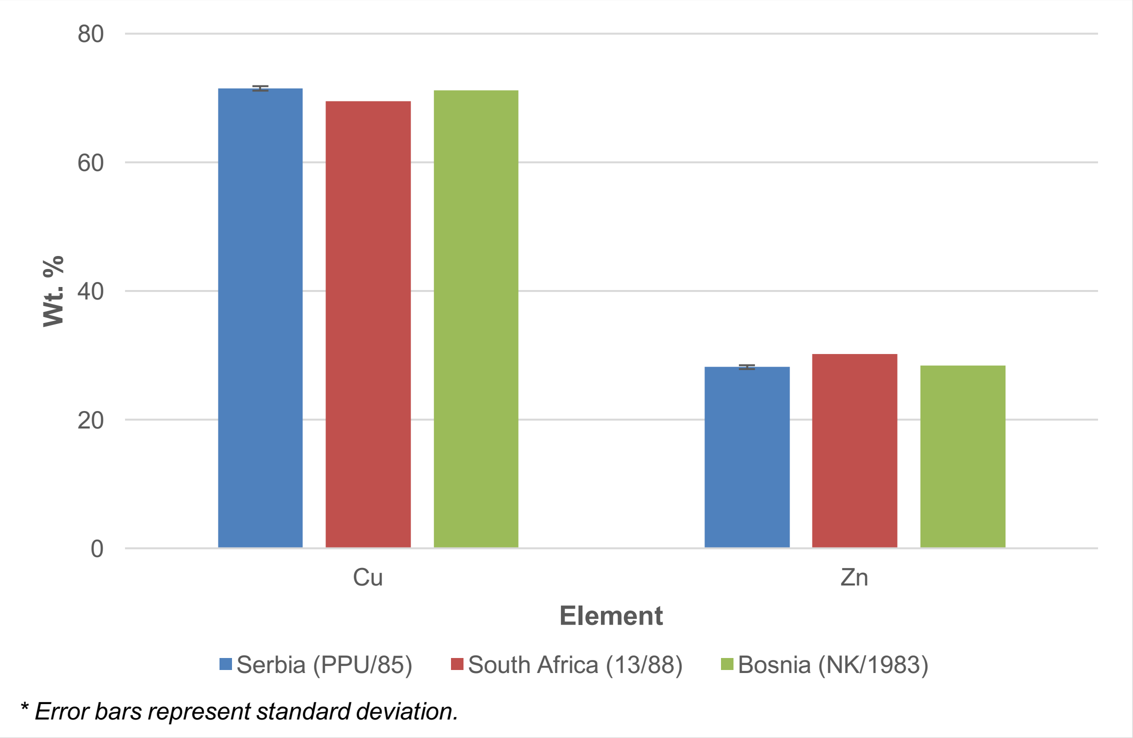
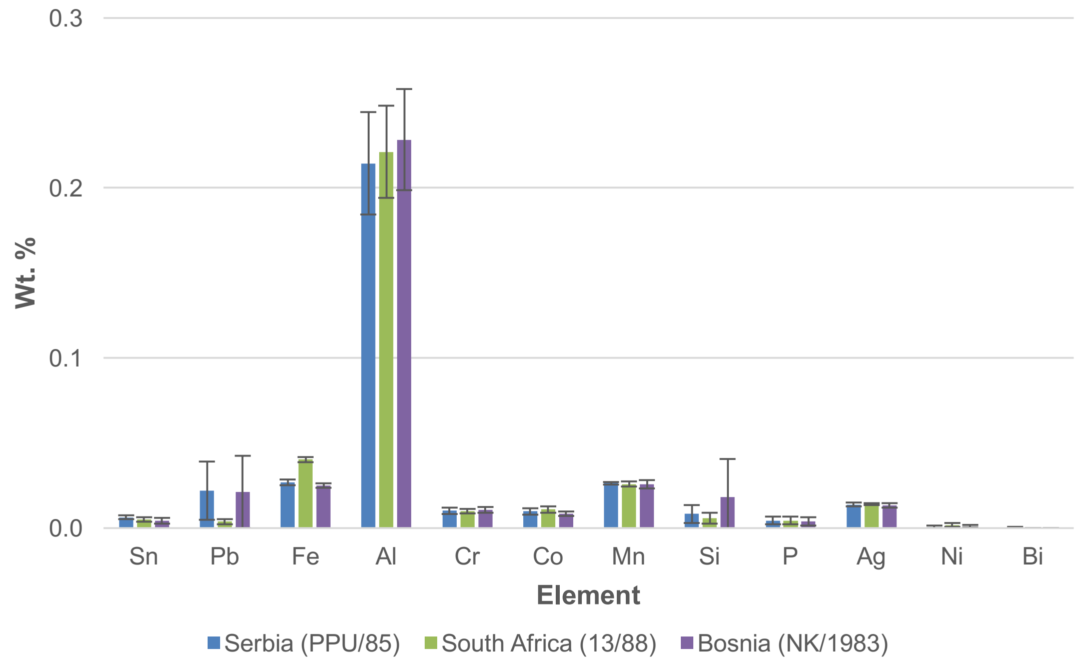


Figure 6.26 Chart showing the quantification (weight percent, (wt.%)) of Cu and Zn present within brass cartridge cases.

Brass that is composed of 70 per cent copper and 30 per cent zinc is known globally as cartridge case brass. When pure, this alloy amalgamates the desirable qualities of strength and ductility which is ideal for deep drawing and cold-pressing [71], [138]. It also has good general resistance to corrosion [17]. With this in mind, it was unlikely that differences in the composition of the brass cartridge cases analysed would be observed. Whilst minor variation in composition was present, these were relatively low. This suggests that there are high levels of quality control present in regard to the cartridge case manufacture with low tolerance levels for impurities; this relates to the functionality required by cartridge cases during obturation, extraction and ejection.



** Error bars represent standard deviation.*

Figure 6.27 Chart showing additional elements (weight percent, (wt.%)) present in brass cartridge cases.

The low levels of bismuth observed above are expected as both bismuth and iron are known to have embrittling effects on brass [138]. The levels of iron and lead were very low (wt.%), however the variation could have been significant enough to differentiate the origin. All of the elements present were analysed statistically.

Again, only two cartridge cases from each sample set were analysed. To determine if these variations in wt.% are significantly different a Kruskall-Wallis test was conducted. The results are shown in **Table 6.12** and where p<0.05 cells are highlighted.

Table 6.12 Kruskall-Wallis test of elements present in brass cartridge cases.

Test Statistics[a,b]	**Element ((wt.%))**													
	Tin	Lead	Zinc	Iron	Aluminium	Chromium	Cobalt	Manganese	Silicon	Phosphorus	Silver	Copper	Nickel	Bismuth
Chi-Square	5.000	1.176	3.714	4.571	.286	.583	3.712	1.250	3.529	.227	2.000	3.714	4.333	.000
df	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Asymp. Sig.	.082	.555	.156	.102	.867	.747	.156	.535	.171	.893	.368	.156	.115	1.000

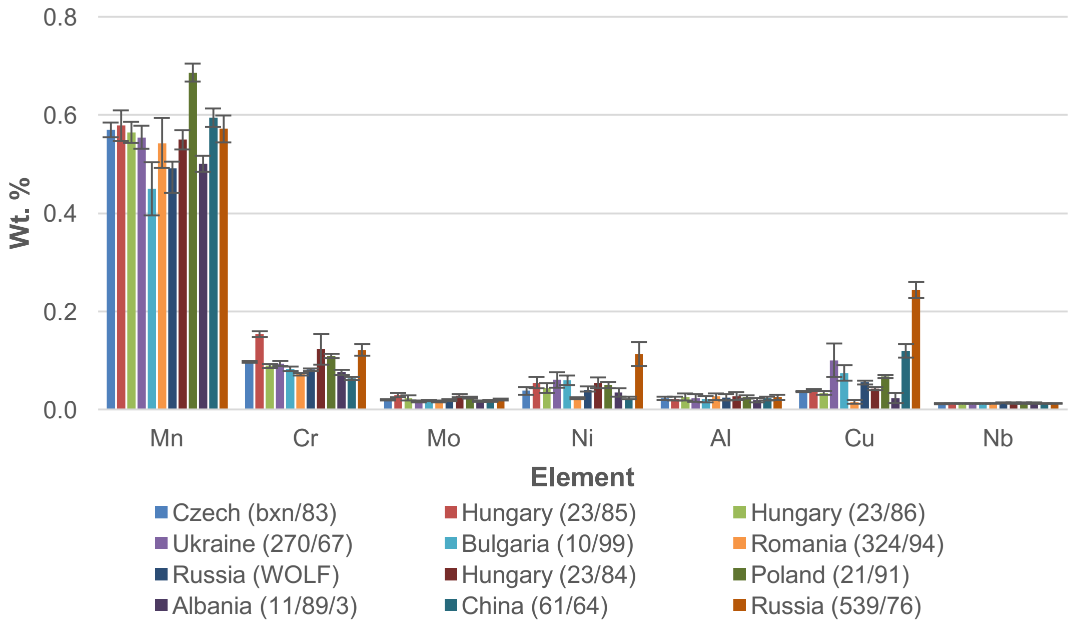
a. Kruskal Wallis Test

b. Grouping Variable: Manufacturer

For none of the elements analysed, $p < 0.05$. The significance value for tin is not highlighted but is approaching the required significance level and may be worth exploring. The sample size should be considered when reporting that there are no statistically significant differences in the composition ((wt.%)) of brass cartridge cases from different manufacturers. This result is based on two cartridge cases from each manufacturer and a more substantial number of samples should be analysed. Nonetheless, considering that the tolerances must remain low in order for cartridge case brass to withstand the manufacturing and firing processes, this result was somewhat expected.

6.3.1.2 Steel

Cartridge cases manufactured using steel, are inherently cheaper to manufacture at approximately 10 per cent of the cost of 70/30 brass, however, they are prone to corrosion [17]. Analysis of the steel cartridge cases for differentiation showed some disparities (**Figure 6.28**).



** Error bars represent standard deviation.*

Figure 6.28 Chart showing quantities of additional elements (weight percent, (wt.%)) present within steel cartridge cases.

Some variations are again observed here noticeably, manganese, chromium, nickel and copper. Some of the reasons for such additions have been discussed above along with their specific effects on the structure or properties of steel. It is also worth noting that aluminium is present in all of the steel components analysed; both aluminium and chromium improve the corrosion resistance of steel [138].

The data in **Figure 6.28** represents the average of eight areas being analysed, however, the fact that these originated from only two cases should not be misrepresented. As only two cartridge cases from each sample were analysed in this way (the other three had the base of the case removed) it is not possible to conduct parametric testing as a normal distribution cannot be assumed – thus disallowing the use of the parametric ANOVA test – as the assumption of normality cannot be supposed. The Shapiro-Wilk Test for Normality can only be conducted where the number of samples is greater than two (n>2). The Kruskall-Wallis test is a nonparametric alternative to one-way between-groups analysis of variance and allows for the comparison of three or more groups. The data here does not violate the assumptions for nonparametric tests discussed in **Section 5.7.1.** To determine if these variations in wt.% are significantly different a Kruskall-Wallis test was conducted (**Table 6.13**) and where p<0.05 cells are highlighted.

Table 6.13 Kruskall-Wallis test of additional elements present in steel cartridge cases.

Test Statistics[a,b]	**ELEMENTS ((wt.%))**							
	Manganese	Chromium	Molybdenum	Nickel	Aluminium	Copper	Niobium	Iron
Chi-Square	18.115	21.629	20.095	21.060	7.667	22.383	.000	12.922
df	11	11	11	11	11	11	11	11
Asymp. Sig.	.079	**.027**	**.044**	**.033**	.743	**.022**	1.000	.298

a. Kruskal Wallis Test

b. Grouping Variable: Manufacturer

The significance levels for chromium, molybdenum, nickel and iron were all below 0.05 indicating a 95% confidence level. These elements can be reported as significantly different statistically, however, this should be done with caution. This proposed difference should be further investigated by examining additional samples. The significance value for manganese was not highlighted but was approaching the required significance level of 0.05 and may also benefit from analysis of additional samples.

In order to identify which groups were statistically significant from one another, Mann-Whitney U tests were to be conducted between pairs of groups. To mitigate Type 1 errors, the Bonferroni correction was be applied to the alpha values as previously discussed (see **Section 5.7.1**). There were 12 sample sets with steel cartridge cases, thus, the alpha level of 0.05 had to be divided by 66 (the number of tests intended) to give a value of 0.001 (rounded up from 0.00075).

The results from the Mann-Whitney U tests provided no values where where $p < 0.05$ **nor** for the correct alpha level ($p < 0.001$). It has been noted that nonparametric tests tend to be "less sensitive" and may "fail to detect differences between groups that actually exist" [131]. Conducting an ANOVA test with Bonferroni post-hoc analysis would potentially prove more powerful, however, due to the sample size (n = 2) too many assumptions would be violated for this to produce reliable data.

The absence of statistically significant variation between individual manufacturers could be reflective of the requirements in functionality; cartridge cases must perform in a specific way – with the ability to undergo obturation, then be extracted from the firearm. The similar compositions observed for these manufacturers would support this theory with statistically significant differences being unexpected. Drastic modifications to the elements present are known to alter the behaviours of mild steels and could increase the risk of malfunctions – both with ammunition and firearms.

The cartridge cases from China (61/64) and Russia (539/76) showed some variation in elemental composition despite being very similar visually as shown in **Figure 6.29.**

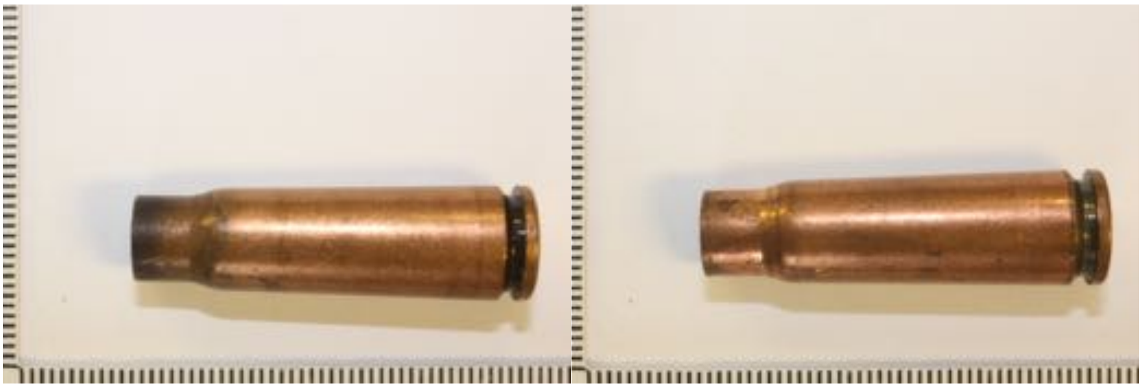


Figure 6.29 Photographs of cartridge cases from China (left) and Russia (right) showing similar colouring.

Whilst both manufacturers employed a copper plated steel, Russia (539/76) shows higher levels in copper, nickel and chromium. An increase in the the sample size may have allow for more sensitive parametric testing (ANOVA). This has the potential to show statistically significant differences in the (wt.%) of these elements, regardless of the lack of visual differences. Alternative techniques, that would not penetrate through several layers, may also be considered that and are discussed in **Section 8**.

6.3.2 Hardness Testing

Hardness testing was also conducted along the length of sectioned cartridge cases to provide a ‘profile’. As expected, cartridge cases were ‘softer’ at the mouth of the case and harder at the base. The requirement for this was discussed in **Section 2.2.2**. The gradient of the increase in hardness and the distance from the mouth where the hardness increased were both of interest. As expected, the brass cartridge cases were softer than those made of mild steel and these results have been presented separately in **Figure 6.30** with the results for the steel cartridge cases in **Figure 6.31**.

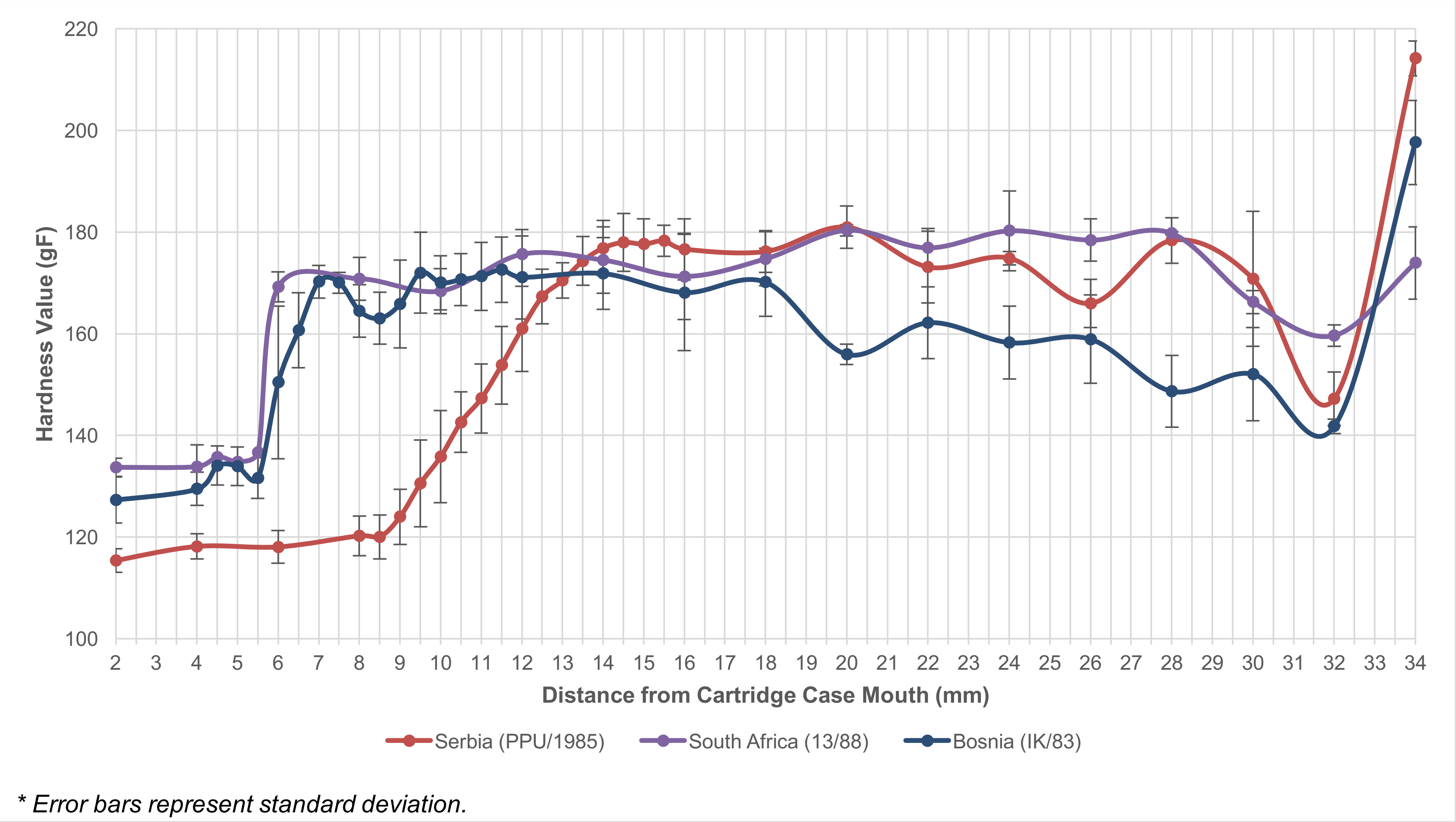


Figure 6.30 Chart showing the hardness profile for brass cartridge cases.

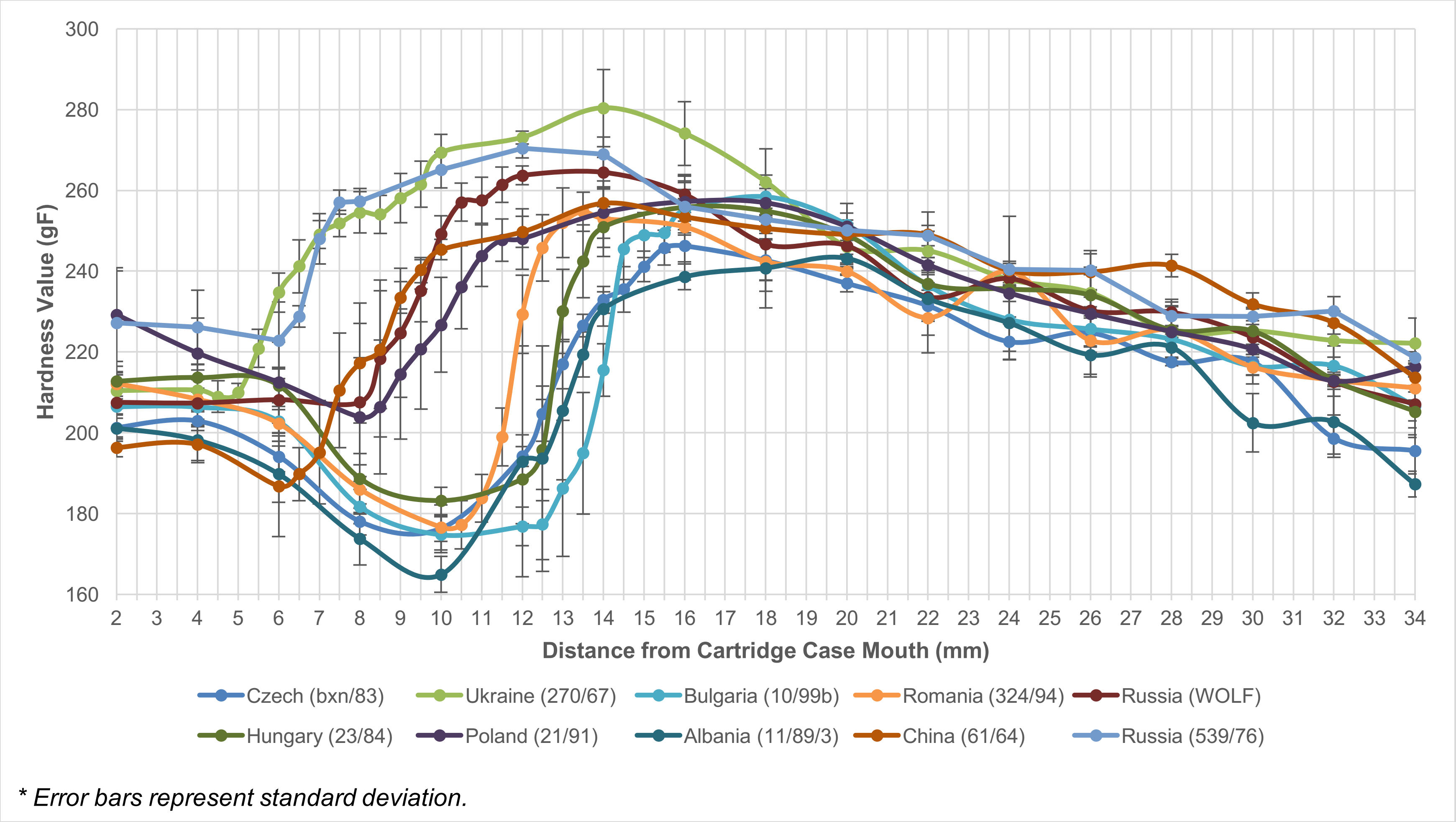


Figure 6.31 Chart showing the hardness profile for steel cartridge cases

For brass cartridge cases shown in **Figure 6.30** Serbia (PPU/85) shows a less drastic incline than the other two samples. The fact that the increase in hardness is gradual and over a larger surface area may suggest that the annealing technique for this sample was not as localised as discussed in **Section 2.2.2** [47]. For example, Serbia (PPU/85) cartridge cases may have been flame annealed rather than induction heating. There was a statistically significant difference between manufacturers of brass cartridge cases at 6mm, 8mm, and 10mm from the cartridge case mouth, as determined by one-way ANOVA:

- 6mm (F2,5) = 67.891, p = 0.003)
- 8mm (F2,5) = 233.363, p = 0.001)
- 10mm (F2,5) = 17.515, p = 0.022)

For manufacturers where the hardness (gF) showed significant differences between groups, a post-hoc test was utilised. Levene's test shows that the assumption of homogeneity was violated. Accordingly, the results were analysed using the Games-Howell post-hoc test which does not assume equal variances. There were statistically significant differences ($p < 0.05$) present in the hardness value (gF) between Serbia (PPU/85) and South Africa (13/88) (at 6mm and 8mm) and between Serbia (PPU/85) and Bosnia (IK/83) (at 8mm). These differences in combination with the lack of statistically significant differences in hardness (gF) between South Africa (13/88) and Bosnia (IK/83) could indicate that these manufacturers may be obtaining their cartridge cases/cartridge case materials from the same source.

Figure 6.31 demonstrated how the hardness values for steel cartridge cases follow a similar pattern to one another. The gradient of the increase in hardness is relatively similar, however this increase begins in different places. Three 'groups' can be observed in **Figure 6.32** and are listed below separated depending on whether the incline begins at 6mm, 8mm or 10mm from the cartridge case mouth:

- **Group 1** – 6mm: Ukraine (270/67), Russia (539/76)
- **Group 2** – 8mm: China (61/64), Russia (WOLF), Poland (21/91)
- **Group 3** – 10mm: Czech (bxn/83), Romania (324/94), Hungary (23/84), Albania (11/89/3), Bulgaria (10/99b)

Although manufacturing processes cannot be determined, this technique may prove useful in determining manufacturer. There was a statistically significant difference between the above groups for steel cartridge cases as determined by one-way ANOVA:

- 6mm (F9,19) = 10.870, p = 0.000)
- 8mm (F9,19) = 15.243, p = 0.000)
- 10mm (F9,19) = 141.390, p = 0.000)

At 6mm there were statistically significant differences ($p < 0.05$) between the hardness values (gF) for Ukraine (270/67) and Bulgaria (10/99b), and between Ukraine (270/67) and Hungary (23/84). This variation between a manufacturer in **Group 1** and two manufacturers in **Group 2** was (to some extent) expected. More unpredictable was the statistically significant (p = 0.041) difference between Bulgaria (10/99b) and Hungary (23/84) – which were both manufacturers from **Group 2** whose incline began at 10mm.

Russia (539/76) in **Group** 1 showed the most statistically significant variation; displaying disparities with every manufacturer in **Group 2** at 8mm. The manufacturers and p values are listed below:

- Czech (bxn/83), p = 0.038
- Bulgaria (10/99b), p = 0.006
- Romania (324/94), p = 0.014
- Hungary (23/84), p = 0.039
- Albania (11/89/3), p = 0.16

This manufacturer has the potential to be distinguished from most other manufacturers based on the hardness (gF) profile of the cartridge case. Statistically significant differences ($p < 0.05$) were also present between the hardness values (gF) for Ukraine (270/67) compared to Bulgaria (10/99b) and Albania (11/89/3), and between Czech (bxn/83) and Hungary (23/84).

When looking at the hardness values (gF) for 10 mm from the case mouth, most of the manufacturers showed statistically significant differences ($p <0.05$) from four or five other manufacturers. It was only Poland (21/91) that showed no statistically significant differences ($p <0.05$) in hardness values (gF) from any other manufacturer and for this manufacturer it would not be possible to differentiate at 6mm, 8mm or 10mm. For Bulgaria (10/99b) there were fewer variations of statistical significance ($p < 0.05$), and these were with Ukraine (270/67), and both Russia (WOLF) and Russia (539/76). Considering the placement of Lugansk Cartridge Works (in Eastern Ukraine), and that the date imprinted on the cartridge cases is 1967 (before Ukraine’s independence in 1991), it is unsurprising that there are similar variations between these manufacturers. Moreover, Ukraine (270/67), Russia (WOLF) and Russia (539/76) have no statistically significant variation from each other - nor China (61/64) – and this observation was supported by historical timelines [120]. The aforementioned four manufacturers also showed statistically significantly disparities ($p < 0.05$) in hardness values (gF) from all of the other manufacturers – bar Poland (21/91).

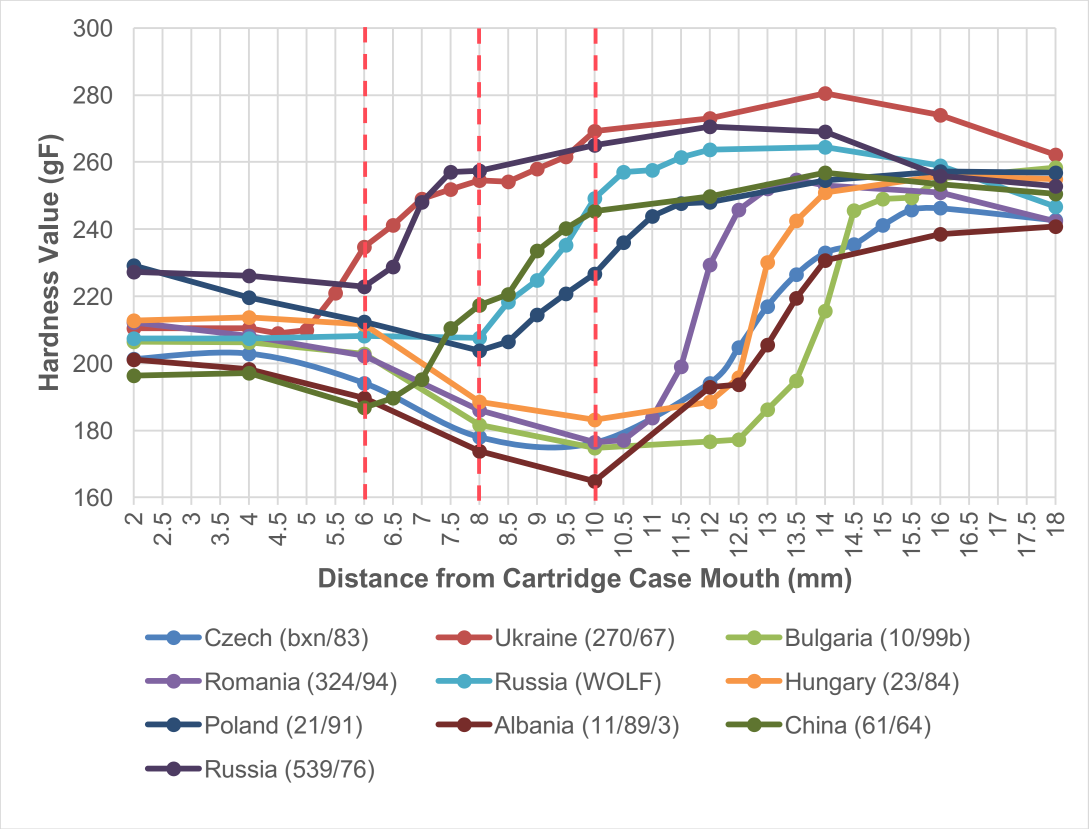


Figure 6.32 Chart showing the hardness profile for steel cartridge cases with points of increase marked.

To continue the temporal exploration of Hungarian (23) ammunition. The hardness profiles for these cartridge cases were plotted and can be compared in **Figure 6.33** below. These hardness profiles follow extremely similar patterns and again show that production techniques are unlikely to vary annually.

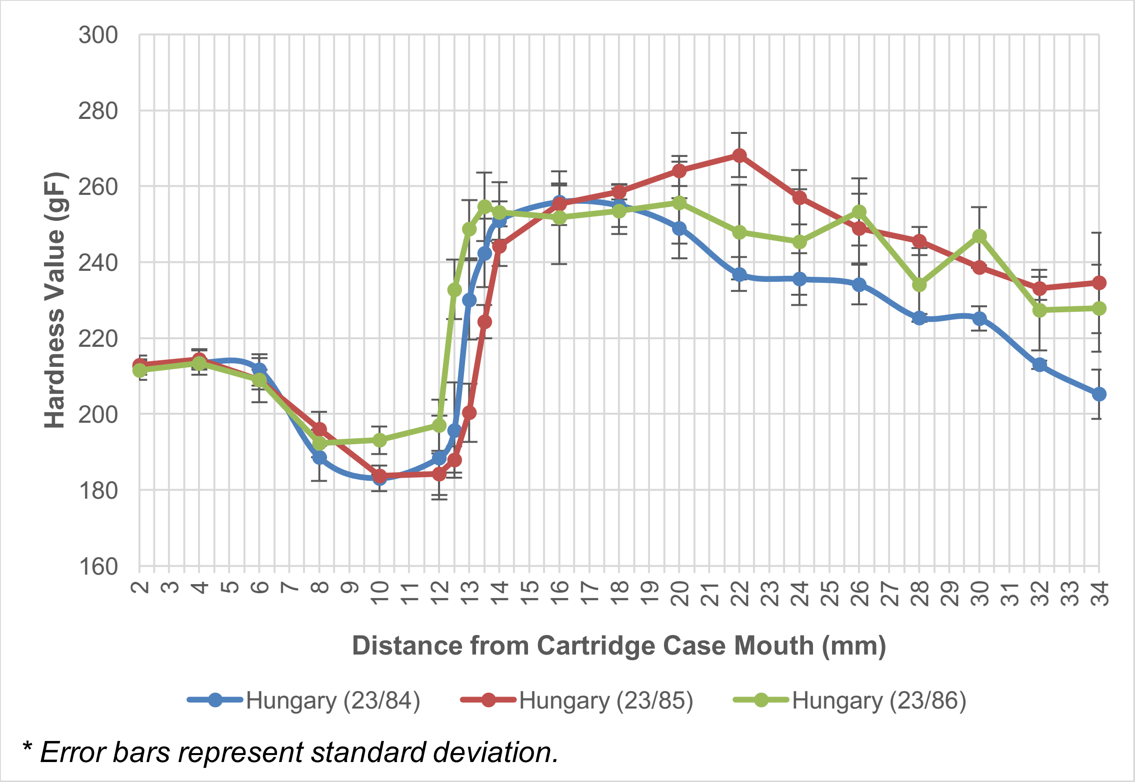


Figure 6.33 Chart showing the hardness profile for steel cartridge cases from Hungary (23) over three consecutive years.

6.3.3 Web of Case

The web of case was analysed in two capacities: two determine the distance between flash holes, and to calculate the diameter of a bolster mark if present. The results are available in **Appendix G** and displayed in **Figure 6.34** and **Figure 6.35**.

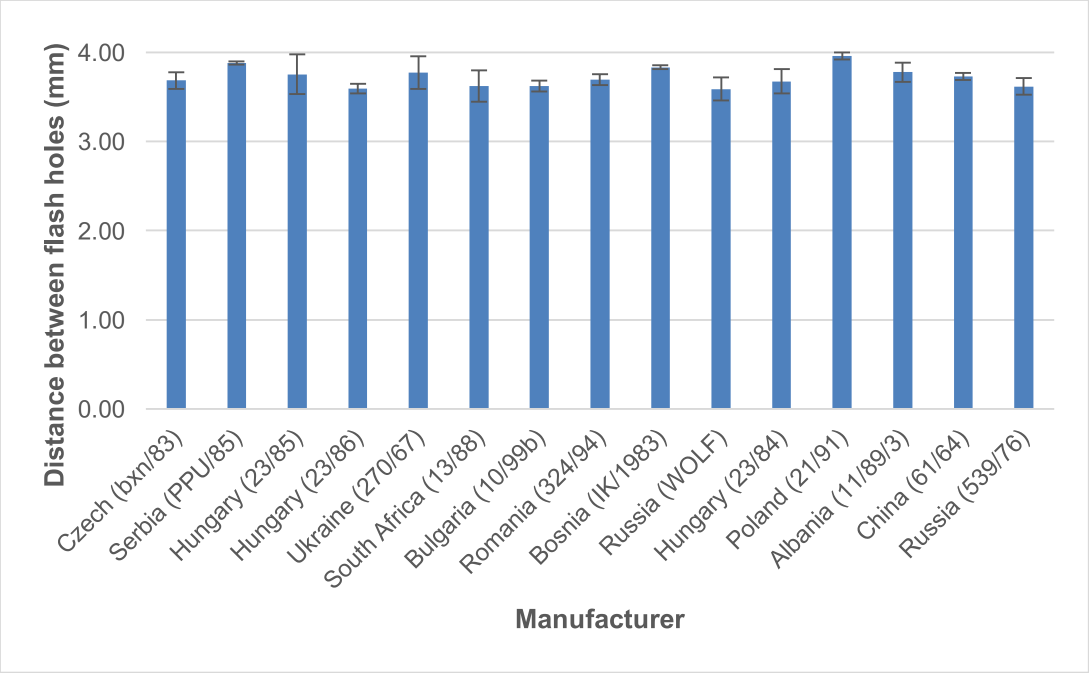


Figure 6.34 Chart displaying distances between flash holes (mm).

As two holes were present this confirms that Berdan primers are prevalent in 7.62 x 39 mm ammunition and may not be particularly useful in terms of discrimination between manufacturers. **Figure 6.34** is a visual representation of the distance between flash holes (mm). There was a statistically significant difference between some of the manufacturers as determined by one-way ANOVA:

- Distance ($F(14,44) = 2.854$, $p = 0.008$)

The results are shown in **Appendix H**.

In order to identify which manufactures showed statistically significant differences in the distance between the flash holes (mm), the Games-Howell post-hoc test was utilised (Levenes test showed that this data violated the assumption of homogeneity with p = 0.004). Between manufacturer Games-Howell comparisons revealed a few statistically significant differences (where p < 0.05) in the distance between flash holes (mm) – which are discussed below.

Poland (21/91) showed the most statistically significant differences (p < 0.05) and these were with Hungary (23/86), Bulgaria (10/99b) China (61/64). Hungary (23/86) also showed statistically significant differences with Serbia (PPU/85). This method of examination was relatively labour intensive and time consuming – it is questionable as to whether the results are proportionately beneficial as few statistically significant comparisons can be made.

The similarities in the distance between flash holes may be indicative of the manufacturing processes being similar. Another suggestion could be that this is the optimum distance between the flash holes for this calibre in order for firing to function correctly (allowing the primer to ignite the propellant correctly). The results used for differentiation should be approached with caution and would benefit from an increased sample size.

In order to ensure that the assumption of normality was not violated, the results were grouped per manufacturer, and the diameter between the flash holes (mm) examined. This was done by using the Shapiro-Wilk Test which is more appropriate for small sample sizes (below 50 samples) and produced numerical means of assessing normality. For the majority of the results p > 0.05 – indicating that the data did not significantly deviate from a normal distribution – i.e. the data had normal distribution. This was confirmed graphically by examining Q-Q Plot diagrams. Hungary (23/85) was the only group that violated the assumption of normality with a p value of 0.007 for the Shapiro-Wilk test.

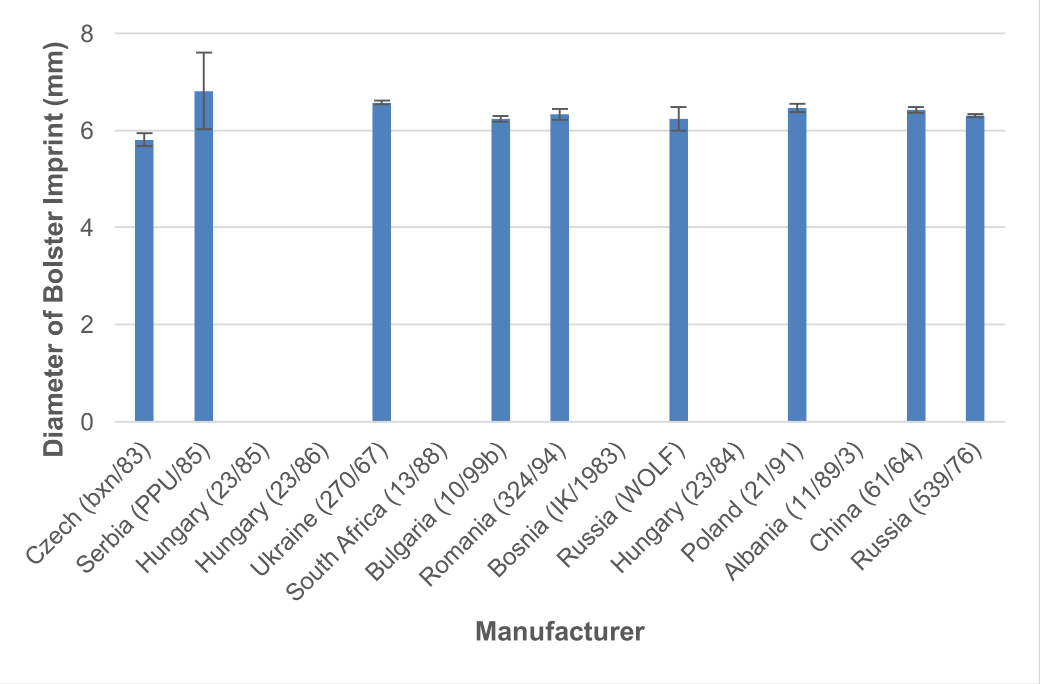


Figure 6.35 Chart displaying diameters of bolster mark (mm).

Bolster marks appeared to be of similar sizes (mm) when present. **Figure 6.35** is a visual representation of the diameter of bolster mark (mm). The cartridge cases of manufacturers where there was no bolster mark present were omitted and one-way ANOVA was used to determine if there was a statistically significant difference between manufacturers:

- Diameter (F(8,26) = 2.781, p = 0.034)

The results are shown in **Appendix H.**

In order to identify which manufactures showed statistically significant differences in the diameter of the bolster mark (mm), the Games-Howell post-hoc test was utilised (Levene's test showed that this data violated the assumption of homogeneity with p = 0.000). Between manufacturer Games-Howell comparisons revealed a few statistically significant differences (where p < 0.05) in the diameter of the bolster mark (mm) – which are discussed below.

Czech (bxn/83) and Ukraine (270/67) showed three statistically significant differences (p < 0.05) each. For Czech (bxn/83), these were with Ukraine

(270/67), Poland (21/91) and China (61/64). Ukraine also showed statistically significant variation ($p < 0.05$) with Bulgaria (10/99b) and Russia (539/76).

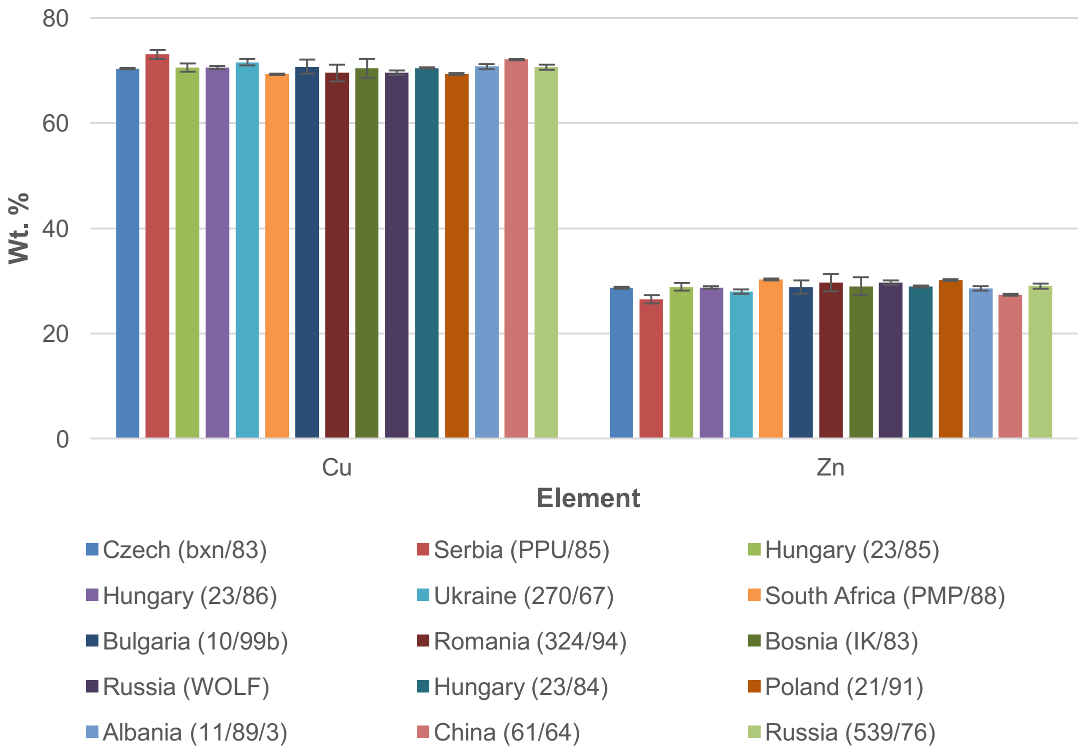
The similarities in the diameter of the bolster marks are indicative of similar production techniques and considering the history of the countries in which the manufacturers are based this is to be expected. It is therefore surprising that there are statistically significant ($p < 0.05$) difference present. One clear differentiation is the absence of a bolster mark which can be used to exclude potential manufacturers. The results used for differentiation should be approached with caution and would benefit from an increased sample size.

In order to ensure that the assumption of normality was not violated, the results were grouped per manufacturer, and the diameter of the bolster (mm) examined. This was done by using the Shapiro-Wilk Test which is more appropriate for small sample sizes (below 50 samples) and produced numerical means of assessing normality. For all of the results $p > 0.05$ – indicating that the data did not significantly deviate from a normal distribution – i.e. the data had normal distribution. This was confirmed graphically by examining Q-Q Plot diagrams.

6.4 Primer

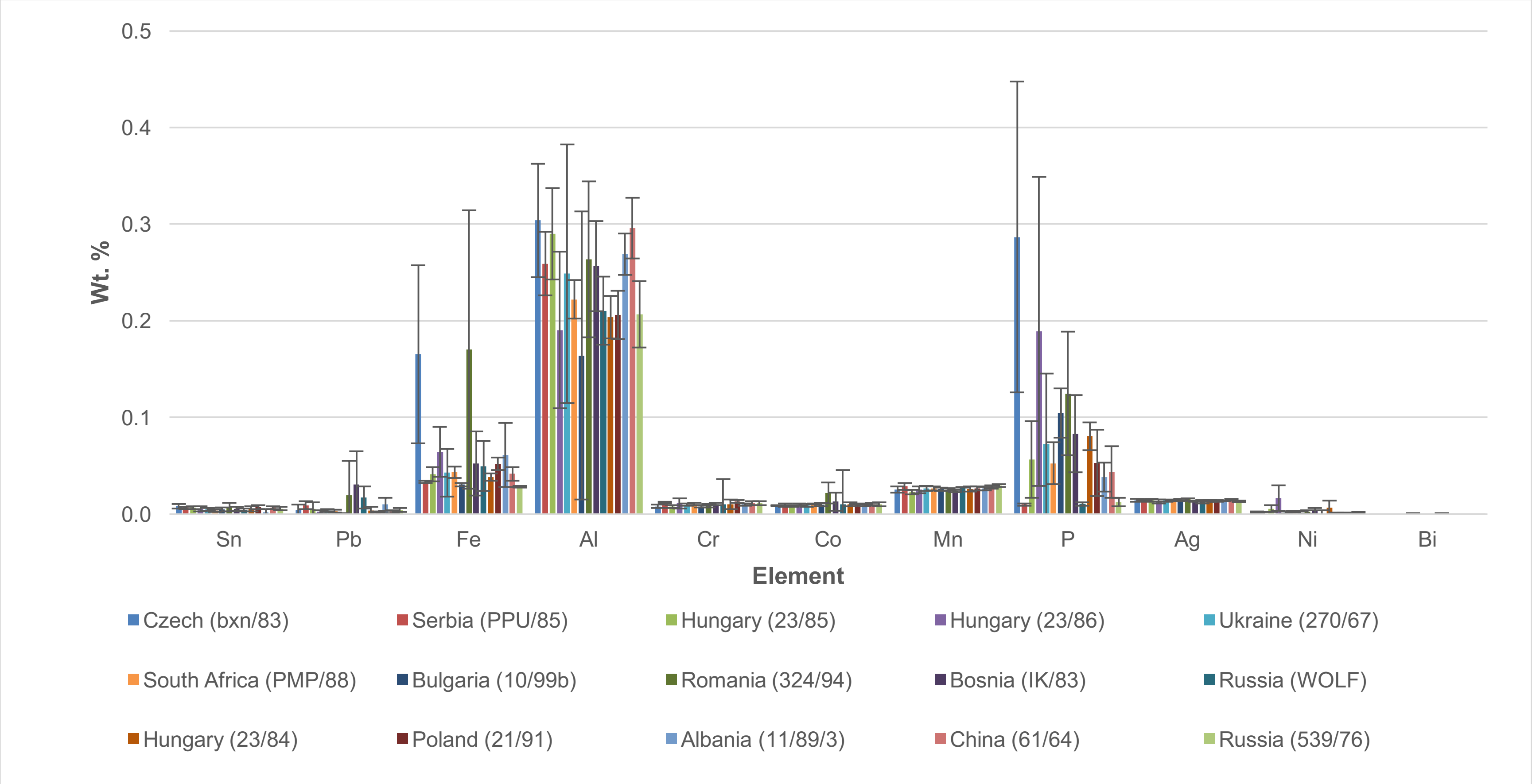
6.4.1 Primer Caps – X-Ray Fluorescence analysis of Materials

The primer caps for the cartridge cases that were sectioned length ways were also analysed for their elemental composition. The results are shown in **Figure 6.36** and **Figure 6.37.**



** Error bars represent standard deviation.*

Figure 6.36 Chart showing the quantification copper and zinc (weight percent, (wt.%)) present in brass primer caps.



** Error bars represent standard deviation.*

Figure 6.37 Chart showing additional elements (weight percent, (wt.%)) present in primer caps.

As with the cartridge cases, low levels ((wt.%)) of bismuth are expected as a result of its embrittling effects on brass [138]. The levels of iron, aluminium and phosphorus (wt.%) appeared to be higher from observation of **Figure 6.37**. Again, only two primer caps from each sample set were analysed. To determine if these variations in wt.% were significantly different a Kruskall-Wallis test was conducted. The results are shown in **Table 6.14** and where p < 0.05 cells are highlighted.

Table 6.14 Kruskall-Wallis test of elements present in brass primer **caps.**

Test Statistics[a,b]	**ELEMENT (WT.%)**													
	Tin	Lead	Zinc	Iron	Aluminium	Chromium	Cobalt	Manganese	Silicon	Phosphorus	Silver	Copper	Nickel	Bismuth
Chi-Square	17.347	18.544	20.929	21.935	20.013	16.653	14.477	19.992	22.852	25.040	16.083	21.252	25.090	14.000
df	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Asymp. Sig.	.238	.183	.103	.080	.130	.275	.415	.130	.063	.034	.308	.095	.034	.450

a. Kruskal Wallis Test

b. Grouping Variable: Manufacturer

The significance levels for phosphorus and nickel are below 0.05 indicating that these elements ((wt.%)) can be reported as significantly different between manufacturers. The sample size should be considered when reporting that there are statistically significant differences in the composition ((wt.%)) of brass primer caps from different manufacturers. This result is based on two primer caps from each manufacturer and a more substantial number of samples should be analysed.

In order to identify which groups were statistically significant from one another, Mann-Whitney U tests were to be conducted between pairs of groups. To mitigate Type 1 errors, the Bonferroni correction was be applied to the alpha values as previously discussed (see **Section 5.7.1**). There were 15 sample sets with brass primer caps, thus, the alpha level of 0.05 had to be divided by 105 (the number of tests intended) to give a value of 0.0004 (truncated from 0.000435).

The results from the Mann-Whitney U tests provided no values where where $p < 0.05$ **nor** for the correct alpha level ($p < 0.0004$). It has been noted that nonparametric tests tend to be "less sensitive" and may "fail to detect differences between groups that actually exist" [131]. Conducting an ANOVA test with Bonferroni post-hoc analysis would potentially prove more powerful, however, due to the sample size ($n = 2$) too many assumptions would be violated for this to produce reliable data.

6.4.2 Primer Residue – Scanning Electron Microscope Analysis

SEM-EDX was utilised to explore possible primer composition based on elements observed. Spectra produced for each point were manually evaluated for probable elements present, based on known primer compositions. A typical EDX spectra is shown below in **Figure 6.38.** Some elements share energy peaks present and therefore conflicting elements must be considered. For the primer residues analysed, the main concern was the overlap of sulphur (Kα and Kβ) peaks with lead (Mα) peaks as discussed by Schwoeble [58]. The data produced allowed for qualitative analysis of elements present. Although the software uses an intelligent method of automatic identification, operator knowledge was required to manually confirm the results.

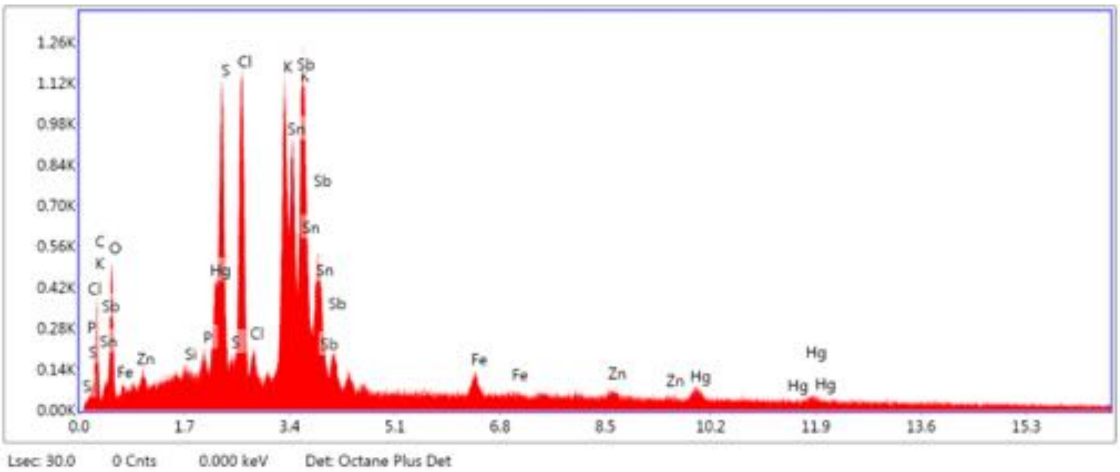


Figure 6.38 A typical SEM-EDX spectra showing Energy (keV) on the x-axis and Counts (in thousands) on the y-axis.

Wallace describes categorisation for major, minor and trace components [40]. This is generally accepted practice for analysis of gunshot residue particles, however, time constraints prevented analysis from running for over 30 seconds. This resulted in spectra with prevalent background ‘noise’. Therefore, elements were identified as present or absent and then recorded as a percentage of elements present overall. A threshold was set for a minimum of 1% and organic elements C and O were omitted. The remaining elements were then plotted and are shown in **Figure 6.5**. The percentages can be seen in **APPENDIX D.**

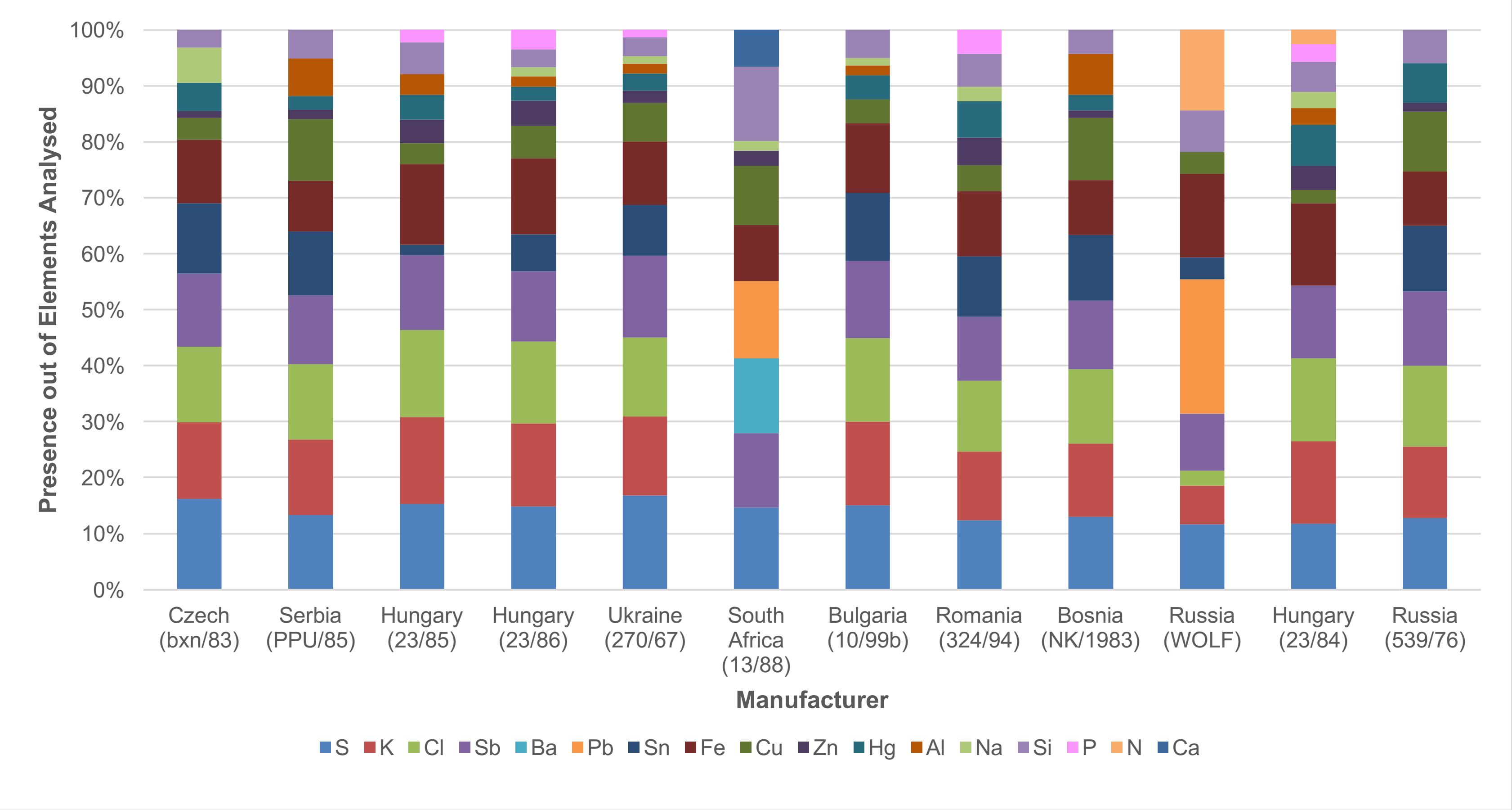


Figure 6.39 A chart displaying elements observed as a percentage of the total elements observed per manufacturer.

*More than one element may have been observed per particle analysed.

Serbia (PPU/85) showed the following composition (elements listed in descending order): K, Cl, S, Sb, Sn, Cu, Fe, Al, Si, Hg, Zn. These were consistent with most of the elements reported by Wallace although he also reported Ca being present as the ‘final’ element on this list. An additional variation was also the order in which Wallace presents the elements [40]. This composition indicated the presence of mercury fulminate, antimony sulphide, and potassium chlorate and was consistent with a mercuric and corrosive primer. The occurrence of tin supported the observed presence of mercury within discharged particles; meaning it was possible that a tinfoil disc was used to seal the primer cap in mercury fulminate primers to mitigate corrosion [40], [141].

Many other sample sets contained similar compositions: Czech (bxn/83), Hungary (23/85), Hungary (23/86), Ukraine (270/67), Bulgaria (10/99) Romania (324/94), Bosnia (IK/83), Hungary (23/84), Russia (539/76). The ‘percentage’ of particles that these elements were observed in is similar for the aforementioned and suggested similar primer compositions for which the composition is summarised by Wallace as “Sb/Hg” – and was most commonly observed for this calibre [40]. This supported his statement regarding “mercury fulminate/potassium chlorate-based primer compositions” being manufactured by some Eastern Bloc countries [40]. Conversely it could also have implied that the primers were outsourced were merely assembled by the manufacturers.

In contrast, the sample set South Africa (13/88) showed a composition of (elements listed in descending order): S, Pb, Ba, Sb, Si, Cu, Fe, Ca, Zn. The presence of Pb and Ba, in conjunction with the absence of K and Cl indicated that the potassium chlorate was replaced by barium nitrate to create a nonmercuric and and noncorrosive primer [40]. The fact that both the cartridge case and the primer cap were composed of brass in conjunction with the noncorrosive primer negated the risk of corrosion whilst simultaneously explaining the absence of tin (from a tin seal). This ‘Pb/Sb/Ba” primer type was commonly observed by Wallace [40]. Higher levels of Si and Ca were also observed in these primers and suggests the presence calcium silicide (which acts as a fuel and frictionator) [54], [89], [142].

The commercial Russian ammunition (WOLF) varied from the majority of the other sample sets (Sb/Hg), including the Russian military ammunition (539/76). The composition contained the following (elements listed in descending order): Pb, Fe, N, S, Sb, Si, K, Sn, Cu, Cl. This was a corrosive and nonmecuric primer and consistent with Wallace's "Pb/Sb" category. Lead styphnate was used as a substitute for mercury fulminate. The observed levels of K and Cl were also comparatively lower. Conversely, N was observed more regularly, this implies that the oxidisers used were a combination of potassium chlorate and lead nitrate [40]. The variation between Russia (539/76) and Russia (WOLF) indicated that the latter was produced at a later date as contemporary production had diverged from using mercuric corrosive compounds [62].

There are some elements whose purpose within primer residue is relatively well known. Where aluminium was observed, this may have been the result of its presence as a fuel or a frictionator. Sodium alginate is a binder and rationalises why sodium was present in some of the sample sets. Other metals that were observed were magnesium and zirconium and these are known as fuels when present as powdered metals [40].

Copper was also present and was likely due to the primer caps being manufacturer from brass **(Section 6.4).** For sample sets where the cartridge case was also made of brass, the copper levels were noticeably higher: Serbia (PPU/85), South Africa (13/88), Bosnia (IK/83). Interestingly, Russia (539/76) also presented higher level of copper despite the cartridge cases being steel. Wolten reports that one possible explanation for this is the presence of copper thiocyanate. Wallace elaborates on this, reporting it at 4.70% [40], [60]. Another possible explanation is the use of copper ammonium nitrate. This was initially introduced in an attempt to create a nonmercuric noncorrosive priming composition and designed to replace mercury fulminate % [40].

Whilst similar in all other aspects, Hungary (23/84) varied from Hungary (23/85) and Hungary (23/86) in that the particles analysed showed no Sn. This may have been indicative of a change in manufacturing practices: with the addition of a tin foil cap to primers after 1984. Similarities were also present between Serbia (PPU/85) and Bosnia (IK/83). These similarities could signify the history of both countries with the year of manufacture for both sample sets being prior to the Dayton Peace Accords of 1994 – before Yugoslavia had divided into six independent states [62].

Whilst high levels of mercury were observed during analysis of the primer composition, these results would be unlikely to reflect the results from analysis of GSR by forensic practitioners. Conversely, GSR particles containing mercury have been seldom encountered during casework [141], [119]. Elemental mercury is reported as one product in the decomposition of mercury fulminate [141] and its volatility is often referred to as one reason for its scarcity. With a relatively boiling point 357°C, it is believed that when mercury is subjected to the heat and pressure of discharging ammunition it vaporises. The result is fewer mercury containing GSR particles being observed in samples taken from casework [40], [141]. This must be recognised by practitioners when interpreting GSR case results.

Furthermore, mercury fulminate is known to deteriorate over a long period of time. The most recently manufactured ammunition examined was produced 27 years ago (1999) and the levels of mercury observed are likely to have been impacted by the decomposition of the mercury fulminate. Additionally, Wallace reports that “amalgamation with zinc in the primer cup and/cartridge case” can result in lower levels of mercury [119]. If SEM-EDX in unable to detect mercury particles, then the absence of Pb or Pb and Ba may be indicative of a mercuric primer.

Table 6.15 separates manufacturers into three groups based on the possible primer compositions inferred from elements present during SEM-EDX analysis.

Table 6.15 Major constituents present in primer elements and example compositions.

MANUFACTURER	ELEMENTS								EXAMPLE COMPOSITION
	Sb	Ba	Pb	Sn	Hg	S	K	Cl	
CZECH (BXN/83)	✓			✓	✓	✓	✓	✓	Mercury fulminate. Potassium chlorate. Antimony sulphide.
SERBIA (PPU/85)	✓			✓	✓	✓	✓	✓	
HUNGARY (23/84)	✓				✓	✓	✓	✓	
HUNGARY (23/85)	✓			✓	✓	✓	✓	✓	
HUNGARY (23/86)	✓			✓	✓	✓	✓	✓	
UKRAINE (270/67)	✓			✓	✓	✓	✓	✓	
BULGARIA (10/99)	✓			✓	✓	✓	✓	✓	
ROMANIA (324/94)	✓			✓	✓	✓	✓	✓	
BOSNIA (IK/83)	✓			✓	✓	✓	✓	✓	
RUSSIA (539/76)	✓			✓	✓	✓	✓	✓	
SOUTH AFRICA (13/88)	✓	✓	✓			✓			Lead styphnate. Barium nitrate. Antimony sulphide. Aluminium.
RUSSIA (WOLF)	✓		✓	✓		✓	✓	✓	Phosphorus sulphide. Magnesium and calcium carbonate. Potassium chlorate.

6.5 GeNIe

Data from the output files described in **Section 5.7.2** was validated using the "Leave one out test". This compared each sample with every other sample apart from itself, thus, the data which 'one' was compared against was calculated without its inclusion. The purpose of this was to protect against inflated results whereby a sample would be 'matched' with itself and included in the results. Due to time constraints, the creation of a Naïve Bayesian Network was only possible for the projectiles examined. The variables that were inputted and a description of the input is shown in **Table 6.16**.

Table 6.16 Variables and described input for Naïve Bayesian Network for projectiles.

VARIABLE	INPUT
Core material	Lead/steel
Steel core elements	Elements (wt.%)
Jacket Material	Brass/steel
Brass jacket elements	Elements (wt.%)
Steel jacket elements	Elements (wt.%)
Lacquer	Colour/no
Hardness of the steel core (if present)	Hardness value (gF)
Location of the crimp	Measured using callipers (mm)
Steel jacket component widths	Total, steel, inner and outer plating (µm)
Visible jacket/lead at base	Measured using callipers (mm)
Nose/base diameter	Measured using callipers (mm)

The output included an accuracy list with percentages, and a confusion matrix which showed where the model was not able to differentiate between different sample sets. The most successful output models included all projectile variables as shown in **Figure 6.40**. The model was able to correctly identify 60 out of 68 projectiles based on the information by utilising Naïve Bayesian networks. In model 6B, two sample sets from the same year and manufacturer but separate batches were shown as one sample: Bulgaria (10/99). These were separated into their respective batches in model 6C: Bulgaria (10/99a and 10/99b). The results are detailed in

Table 6.17**.**

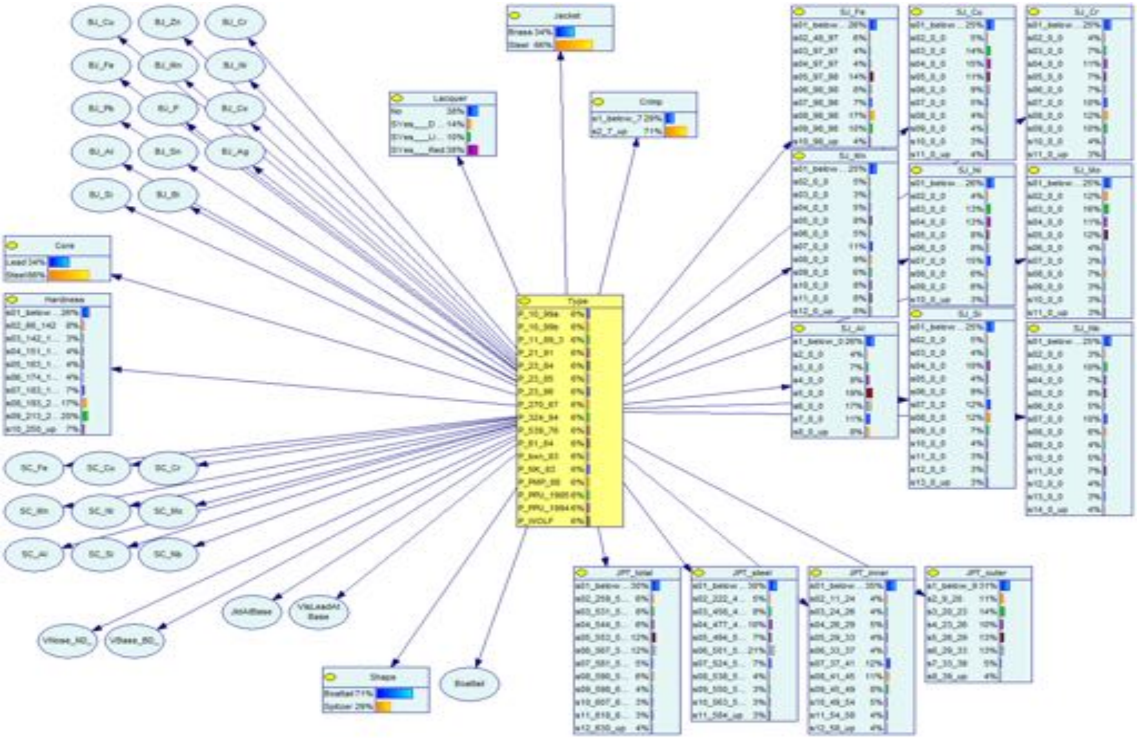


Figure 6.40 Naïve Bayesian Network for projectiles including all inputted variables.

Table 6.17 Percentage (%) of projectiles matched to the correct manufacturer.

MODEL 6B			MODEL 6C		
MANUFACTURER (‘TYPE’)	**CORRECT MATCHES**	**CORRECT MATCHES (%)**	**MANUFACTURER (‘TYPE’)**	**CORRECT MATCHES**	**CORRECT MATCHES (%)**
Bulgaria (10/99)	$\frac{7}{8}$	87.5	Bulgaria (10/99a)	$\frac{3}{4}$	75
			Bulgaria (10/99b)	$\frac{3}{4}$	75
Albania	$\frac{4}{4}$	100	Albania (11/89/3)	$\frac{4}{4}$	100
Poland (21/91)	$\frac{4}{4}$	100	Poland (21/91)	$\frac{4}{4}$	100
Hungary (23/84)	$\frac{3}{4}$	75	Hungary (23/84)	$\frac{3}{4}$	75
Hungary (23/85)	$\frac{3}{4}$	75	Hungary (23/85)	$\frac{3}{4}$	75
Hungary (23/86)	$\frac{4}{4}$	100	Hungary (23/86)	$\frac{4}{4}$	100
Ukraine (270/67)	$\frac{3}{4}$	75	Ukraine (270/67)	$\frac{4}{4}$	100
Romania (324/94)	$\frac{4}{4}$	100	Romania (324/94)	$\frac{4}{4}$	100
Russia (539/76)	$\frac{3}{4}$	75	Russia (539/76)	$\frac{3}{4}$	75
China (61/64)	$\frac{4}{4}$	100	China (61/64)	$\frac{4}{4}$	100
Czech (bxn83	$\frac{4}{4}$	100	Czech (bxn83	$\frac{4}{4}$	100
Bosnia (IK/83)	$\frac{3}{4}$	75	Bosnia (IK/83)	$\frac{3}{4}$	75
South Africa (13/88)	$\frac{4}{4}$	100	South Africa (13/88)	$\frac{4}{4}$	100
Serbia (PPU/85)	$\frac{2}{4}$	50	Serbia (PPU/85)	$\frac{2}{4}$	50
Serbia (PPU/94)	$\frac{4}{4}$	100	Serbia (PPU/94)	$\frac{4}{4}$	100
Russia (WOLF)	$\frac{4}{4}$	100	Russia (WOLF)	$\frac{4}{4}$	100
OVERALL	$\frac{60}{68}$	**88.24**	**OVERALL**	$\frac{60}{68}$	**88.24**

Both networks showed the ability to differentiate “Type” (Manufacturer) at 88.24%. In model 6C where sample sets from Bulgaria (10/99) were separated into their respective batches (10/99a and 10/99b), discrimination occurred between different manufacturers to model 6B. This was identified using the confusion matrices for each model (included in **Appendix G**). For model 6C, incorrectly differentiated samples will be discussed in detail, with the variations in model 6B only addressed briefly.

For 6C, one sample from Bulgaria (10/99b) was incorrectly identified as being from Bulgaria (10/99a), showing that the model was not able to correctly distinguish between batches in every instance, however, 75% of the samples being correctly identified is impressive considering the small sample size. One sample from Bulgaria (10/99a) was identified as being of Hungarian origin 23/84 as opposed to Bulgarian and the same is true of one of the Hungarian 23/84 samples being misidentified as Bulgarian (10/99a). When considering the similarity of projectile design and construction materials (M43 type, steel jacket etc.), this confusion can be appreciated. Furthermore, both Hungary and Bulgaria were under Soviet influence from around 1947 until the 1991 and 1989 (respectively), and the manufacturers were state owned during this period [62]. Despite the headstamp for Bulgaria indicating that the ammunition was manufactured after in 1999 (after the fall of the Soviet Union in 1991), it is unlikely that manufacturing processes would have changed drastically as limited by established production techniques.

For Hungary (23/85), the network was able to correctly identify the manufacturer but could not correctly distinguish the year for all samples. Interestingly, for Hungary (23/86), all four were correctly identified – this signifies subtle differentiation between sample sets from the same manufacture but different years. In order to confirm this, more samples would be required over a longer period of time.

This theory is reinforced by the network’s ability to distinguish between sample sets Serbia (PPU/85 and PPU/94). For Serbia (PPU/94), the network was able to correctly identify the manufacturer (“Type”) for all four. In contrast, for Serbia (PPU/85), the network misidentified two samples; one with Bosnia (IK/83) and one with South Africa (13/88). Both were brass jacketed projectiles of similar composition. As there were few distinguishing features elementally between the brass jackets, the confusion is not surprising. Historically, pre-1990 both Serbia (PPU) and Bosnia (NK) were part of Yugoslavia, whilst these manufacturers previously employed Soviet marking practices, they diverged to use Roman or Cryllic characters to indicate the manufacturer [62]. Similarities in marking practices is potentially indicative of similarities in manufacturing practices – as supported by the findings of this research.

For model 6B, the network was more successful in discriminating Bulgarian ammunition as one sample set (of eight projectiles – shown as Bulgaria (10/99)), however, it was less successful at distinguishing between samples from Ukraine (270/67). Both models 6B and 6C were relatively successful for identification of manufacturers based on the physical and chemical analysis of the projectiles used in this research. With an 88.24% success rate of identification based on the inputted variables for four projectiles, this model shows good potential for use in differentiation between manufacturers. Limitations must be recognised and the sample size is the most prominent one: Ideally, this research should be continued with an increase sample size that will allow for determination of whether the samples examined were representative of ammunition from the selected manufacturer and year. This is discussed further in **Section 8**.

7 Chapter 7: CONCLUSIONS

This research was designed to establish whether differences between 7.62 x 39 mm ammunition were significant enough for characterisation, and whether this could be used to assist in determining manufacturer. This was achieved by considering the materials and methods involved during ammunition manufacture. In order to fully understand the processes involved, several components were analysed. Ammunition from a selection of manufacturers was characterised according to visual properties, physical characteristics and elemental composition. This research has successfully shown that both palpable and subtle distinguishing features are present, disproving the null hypothesis and allowing for improved efforts at determining ammunition provenance.

This research made three assumptions (discussed in **Section 6**) that are critical to the validity of the results. These are summarised below:

1. The manufacturers for the samples analysed were correctly identified.
2. The manufacturers have produced all component parts and not simply assembled them.
3. The manufacturers/ suppliers use different ‘sources’ for the raw materials.

As previously mentioned, the violation of even one of these assumptions would impact the interpretation of the results. Nonetheless, these are all plausible scenarios and their possibility is discuss in **Section 8.**

Some of the differences between projectiles and cartridge cases were nominal. Variation in colour, material, and presence/absence of components such as a steel core or air pocket can be categorised with as much ease as they can be recognised. Such evident disparities should not be disregarded by practitioners as they are the initial characteristics that can assist in establishing manufacturer. The level of assessment should be proportional to the difficulty in determining provenance.

7.1 Projectiles

It was possible to group projectile based initially on their colour, shape (M43 or Type 56), and whether there was lacquer present. Serbia (PPU/94), Serbia (PPU/85), South Africa (13/88), and Bosnia (IK/83) all displayed the Type 56 shape whilst the other 13 of the projectiles exhibited an M43 type shape. There was no lacquer present on the aforementioned Type 56 projectiles as well as three M43 shaped projectiles: Czech (bxn/83), Poland (21/91) and Russia (WOLF) had no lacquer present on the projectiles.

Upon sectioning the projectiles, the jacket and core materials could be predicted. The Type 56 projectiles all appeared to be brass jacketed projectile, as well as Albania (11/89/3). Furthermore, this manufacturers projectiles were the only ones with a brass jacket and a steel core. These characteristics were unique to Albania (11/89/3) who's distinction may be more obvious due to its departure from the Warsaw Pact after 13 years, in 1968. Albania became dependant on Communist China – however, the prevalence of the 7.62 x 39 mm calibre remained unchanged. An agreement between the Albanian Government and MANHURIN (a French firm), may have been influential in developing the unique Albania (11/89/3) projectiles observed [143]. Projectiles of this nature were known to be discovered in Rwanda prior to 1990 could not be identified by French Intervention Forces [143]. Understanding that the combination of materials used was unusual (compared to other manufacturers observed in this study) may have assisted in understanding the path taken by this ammunition.

The aforementioned core material could be classified as lead or steel. The Type 56 shape projectile all displayed a lead core as expected due to the reduced length of the projectile. For the M43 shaped projectiles, all but one manufacturer displayed a steel core with a lead sheath. The exception was the projectiles from Russia (WOLF). This variation in core material could suggest that this ammunition was produced after the BATFE ban on "armour piercing rounds" in 1994 [62]. Whilst initially the core was replaced entirely with lead, the increase in weight lead to lower muzzle velocities and Russian manufacturers released a new design of projectiles in the 1990s with an 'air pocket' present [64].

Where current methods are not adequate in identifying the manufacture, the use of established analytical techniques should be considered The elemental results for projectile jackets obtained using XRF analysis were of varying significance. Elemental analysis of the brass jacketed projectiles produced some statistically significant results ($p < 0.05$). Albania (11/89/3) showed lower levels of copper and higher levels of zinc. The variation in colour was identified visually, however, XRF analysis provided justification for this difference. Observation of colour by an examiner is subjective and difficult to express, whereas, objectively quantifying the elements present allows for more definitive, quantitative comparison of results. Variation in (wt.%) of Mn, Ag and Ni was observed between samples from Serbia (PPU) from different years (1985 and 1994). Analysis of P, Bi and Co was not beneficial. Examination of Al ((wt.%)) only showed two statistically significant differences between manufacture: between South Africa (13/88) – and Serbia (PPU/94) and Bosnia (IK/83) and similarly Fe ((wt.%)) showed a statistically significant difference between Serbia (PPU/85) and South Africa (13/88). These variations were shown to be statistically significant ($p < 0.05$), however, as only four samples were analysed this conclusion should be approached with caution and supported by the analysis of additional samples in order to be representative of the size of a 'batch' produced. This would require details of the ammunition produced by each manufacturer and how these are separated. The inability to obtain this information, as well as a restricted ability to obtain such large quantities, are key limitations of this research.

Steel jacketed projectiles showed some stark disparities between manufacturers. The most beneficial elements analysed proved to be Mn, Cr, Fe, Mo and Nb. These elements showed statistically significant differences ($p < 0.05$) for 62%, 35%, 26%, 23% and 21% of comparisons between manufacturers. In contrast, there were no statistically significant differences ($p < 0.05$) between manufacturers for Al ((wt.%)). Analysis of Czech (bxn/83) showed that this manufacturer could be uniquely identified by its statistically significantly different ($p < 0.05$) Mo levels. Whilst statistical analysis showed that variation was statistically significant ($p < 0.05$) across most of the additional elements, literature presents many different grades of mild steel – all with large acceptable ranges of 'impurities'. The results were within 'permissible' tolerances of mild (carbon) steels [144], therefore, it cannot be concluded that the differences are due to production specifications without determining the composition of steel at 'source'. Though possible, it is unlikely that the manufacturer would have detailed the precise quantities of impurities as this is prohibitively expensive and likely to outweigh any benefits. The tolerances within ASTM standards provide approximations on the range and maximum of weight percentages that should be present, however, as **Table 6.3** shows, these ranges can often overlap, making identification of the steel grade a challenging task [18].

XRF analysis of the steel cores (where present) showed statistically significant divergences between elements ((wt.%)) and manufacturers. The most beneficial element analysed proved to Nb, which is associated with increased strength as a result of grain refinement [139]. Bulgaria (10/99a), Hungary (23/86) and Ukraine (270/60) all showed statistically significant differences ($p < 0.05$) with the same four manufacturers: Bulgaria (10.99b), Romania (324/94), Hungary (23/84) and Russia (539/76). This number increased to seven and included Poland (21/91), Albania (11/89/3), China (61/64) when the Bonferroni post-hoc test was used. The relevance of considering this post-hoc test is included as an increase in sample size could prevent violation of the assumption of homogeneity – therefore allowing for use of this method. XRF analysis was useful in individualising the projectiles from Albania (11/89/3). The Cr levels ((wt.%)) present in these steel cores was approximately double that for any other steel core. Additionally, the Ni levels ((wt.%)) were approximately five times the average ((wt.%)) for any other manufacture. Albania's irregular composition was obvious. The elevated levels (wt.%) suggests that the hardness level for these steel cores would be higher than the other manufacturers examined, however, microindentation hardness testing revealed conflicting results

The average hardness values (gF) for the steel cores were beneficial and showed a range of 143.87 (gF). Albania (11/89/3) was expected to have the highest hardness (gF) due to its aforementioned levels (wt.%) of Cr and Ni, however, this manufacturer proved to have the second lowest average hardness values (gF). The lowest average hardness values (gF) was observed in the steel cores for the projectiles from China (61/64) at 134.09 (gF). This value was statistically significantly different ($p < 0.05$) to all other manufacturers examined in this study. Romania (324/94) bore the highest average hardness value at 277.88 (gF) and was also statistically significantly different ($p < 0.05$) to all other manufacturers examined in this study. Three additional manufacturers showed mostly statistically significant ($p < 0.05$) differences in hardness values (gF) with one or two exceptions (shown below):

- Albania (11/89/3) – except Poland (21/91)
- Poland (21/91) – except Albania (11/89/3) and Russia (539/76)
- Czech (bxn/83) – except Bulgaria (10/99a), Bulgaria (10/99b), and Ukraine (270/67)

As well as the deviation in elemental composition ((wt.%)), variation in averages hardness values (gF) may be attributed to physical processes involved during manufacture. The microstructure for selected samples was explored and displayed promising support for the theory based on metallurgical principles. With the majority of manufacturers displaying relatively low standard deviations this method may prove to assist in determining the manufacturer and is discussed in **Section 8**.

The images of the steel jacketed projectiles obtained using the SEM showed one discernible difference; for the samples from Czech (bxn/83) the inner plating was absent entirely. Even without the use of statistical analysis, this distinction is indicative of a variation in manufacturing process as discussed in **Section 6.1.2**. The inner plating widths also diverged between Ukraine (270/67) and three manufacturers: Poland (21/91) and the two Russian sample sets (WOLF and 539/76). Statistical analysis did show some significant differences for the steel portions between Czech (bxn/83) and Hungary (23/84 and 23/85) however, not Hungary (23/86). Hungary (23/85) also differed from five sample sets in regard to the outer plating. This technique has shown fluctuating success in differentiation of projectiles based on jacket component widths. SEM operation requires a relatively high skill level and time to obtain high quality images with good contrast. Moreover, measuring the images produced manually is time consuming and introduces the potential for bias. This method could prove useful, however, improvements have been suggested in **Section 8** that could progress its implementation.

The examination of projectiles allowed for characterisation of 7 out of 17 manufacturers without the use of the GeNIe model. These are outlined below with brief summaries of the variables used for differentiation

- Albania (11/89/3) had a distinctive colour, was the only brass jacketed M43 shape projectile, and was the only brass jacketed projectile to have a steel core. Variations were also present in elemental analysis of the jacket (Cu and Zn) and the steel core (Cr and Ni).
- Russia (WOLF) exhibited no lacquer, with a steel jacket M43 shape projectile. It was the only steel jacketed projectile to have a lead core. Additionally, it was the only projectile with an ‘air pocket’ present.
- Poland (21/91) also exhibited no lacquer, with a steel jacket M43 shape projectile. Moreover, projectiles from this manufacturer showed statistically significant variation ($p < 0.05$) in hardness values (gF) with all other manufacturers apart from Albania (11/89/3) and Russia (539/76). The projectiles from Russia (539/76) did have a red lacquer present and could be distinguished from projectiles from Poland (21/91).
- Czech (bxn/83) also exhibited no lacquer, with a steel jacket M43 shape projectile. The elemental analysis for Mo ((wt.%)) revealed statistically significant differences ($p < 0.05$) with all other manufacturers apart from China (61/64) - as projectiles from China (61/64) did have a red lacquer

present, they could be distinguished from projectiles from Czech (bxn/83). In addition to this, the three manufacturers (mentioned above) where Czech (bxn/83) did not show statistically significant differences ($p < 0.05$). in the hardness value (gF), all had red lacquer present, and could therefore be distinguished from projectiles from Czech (bxn/83). Projectiles from this manufacturer were also the only projectiles to display no inner plating during SEM analysis.

- Romania (324/94) exhibited a red lacquer, with a steel jacket M43 shape projectile. Projectiles from this manufacturer showed statistically significant variation ($p < 0.05$) in hardness values (gF) with the average values being much higher than all other manufacturers examined.
- China (61/64) also exhibited a red lacquer with a steel jacket M43 shape projectile. Projectiles from this manufacturer showed statistically significant variation ($p < 0.05$) in hardness values (gF) with the average values being much lower than all other manufacturers examined.
- Ukraine (270/67) also exhibited a red lacquer with a steel jacket M43 shape projectile. Identification of projectiles from this manufacturer was possible by utilising the SEM images taken of the steel jacket in order to analyse the copper plating widths (µm). The results observed showed that there were only two statistically significant differences ($p < 0.05$) for the inner plating widths; between Poland (21/91) and Ukraine (270/67) and Russia (WOLF). The knowledge that Russia (WOLF) has no lacquer present allowed use of the process of elimination in order to determine that the only manufacturer with a statistically significant different ($p < 0.05$) inner plating width (µm) from Poland (21/91), that had a red lacquer present on the projectile, was Ukraine (270/67).

The GeNIe model was considerably successful at differentiation between projectiles from different manufacturers – especially when considering the small sample size. Interestingly, the model was able to differentiate between sample who

With an 88.24% success rate for identification of the correct manufacturer, the model has the potential to be expanded with additional samples from known manufacturers. Practitioners who are currently familiar with software such as ‘CartWinPro’, will appreciate the potential of this resource. CartWinPro is a “database [that] contains a huge number of calibre measurements, color code, headstamp, manufacturer and complete cartridge records” [145]. Whilst this software boasts “over 24,890 headstamps”, it still has limitations in the absence of a headstamp or where only fragments of a projectile may be recovered. The GeNIe model created has the potential to supplement such a software and allow practitioners to use analytical methods to increase the possibility of identifying the manufacturer. This could prove particularly useful where fragmented projectiles have been recovered or where differentiation is not possibly based on observation. Theoretically, with increased levels of automation (discussed in **Section 8)** practitioners could submit their own samples to the database, increasing the value of this resource exponentially.

7.2 Cartridge Cases

Variations in the colours of cartridge cases suggested that alternative materials were used. Steel cartridge cases proved to be magnetic and the following cartridge cases were found to be brass:

- Serbia (PPU/85)
- South Africa (13/88)
- Bosnia (IK/83)

The fact that the cartridge cases from former Yugoslavian countries were both made of brass reflects Yugoslavia’s reluctance to conform to USSR pressure and the fact that it never joined the Warsaw Pact. Variations were also present in the lacquer. The cartridge cases from South Africa (13/88) showed a unique green lacquer around the primer annuli whilst the primer annulus for cartridge cases from Romania (324/94) were completely coated in a red lacquer. An additional disparity was present for Czech (bxn/83) which was the only manufacturer not to have a brass coloured primer. This suggested that the primer cap may be manufacturer of steel, however this proved untrue (as shown in **Section 6.4.1**).

For cartridge cases made of brass, there was no statistically significant variation observed. This result was anticipated as the tolerances of elements must be rigorously controlled in order to prevent malfunctions which can be dangerous, even fatal. XRF results for the primer caps showed that some significant differences were present in the levels of phosphorus and nickel, however, due to the small sample size and the reduced sensitivity of non-parametric tests, it was not possible to identify which manufacturers had statistically significant ($p < 0.05$) levels of elements ((wt.%)) present. Analysis of the elemental composition of brass cartridge cases and primer caps was not particularly beneficial for characterisation and would not be recommended for use in differentiation between manufacturers. This is likely due to the required properties of cartridge case brass – both for production of cartridge cases and primer caps, and to correctly perform the function of cartridge cases during ‘firing’, [3], [17], [40].As shown in **Section 6.3.1.1**, there were no statistically significant differences ($p < 0.05$) for elements present ((wt.%)) between the manufacturers.

For the steel cartridge cases, there were statistically significant differences ($p < 0.05$) in the levels ((wt.%)) of Cr, Mo, Ni and Cu. Mann-Whitney U tests were conducted in an effort to identify where these variations occurred, however, as with the brass cartridge cases, the small sample size ($n = 2$) meant that running an ANOVA test would have violated too many assumptions to have produced reliable data. Moreover, the elements observed ((wt.%)) were all within the tolerances of mild steel. Any variation may be representative of the materials supplied to the manufacture as opposed to being specified by them. This consideration links one of the key limitations of this research: considering that several manufacturers may a) have obtain their raw materials from the same ‘source’ (this could be a supplier of mild steel or cartridge brass), and b) have obtained their components, already made, from the same source and simply marked them with their manufacturers headstamp. Conversely, the lack of statistically significant differences could also be the result of stringent manufacturing tolerances in order for cartridge cases to function correctly under extreme temperatures and pressures. Elemental analysis (wt.%) of cartridge cases as a stand alone or supplementary technique is unlikely to allow for unique identification of manufacturer.

The variation in hardness values (gF) provides some weight to the speculation that raw materials may be come from the same 'source'. The graphs presented in **Section 6.3.2** showed cartridges cases increase in hardness (gF) at 6 mm, 8 mm or 10 mm from the cartridge case mouth. With manufacturers separated into three groups:

- **Group 1** – 6mm: Ukraine (270/67), Russia (539/76)
- **Group 2** – 8mm: China (61/64), Russia (WOLF), Poland (21/91)
- **Group 3** – 10mm: Czech (bxn/83), Romania (324/94), Hungary (23/84), Albania (11/89/3), Bulgaria (10/99b)

Variations in where the increase in hardness occurred may be useful in identifying manufacturing techniques, especially when considering countries with previous alliances (USSR or Warsaw Pact). **Group 1** consists solely of former USSR nations which is consistent with the years of manufacture (1967, and 1976). Analysis of the results for the hardness values (gF) showed that Ukraine (270/67), Russia (WOLF), Russia (539/76), and China (61/64) have no statistically significant variation ($p < 0.05$) from each other which is understandable considering historical context [120]. The aforementioned four manufacturers also showed statistically significantly disparities ($p < 0.05$) in hardness values (gF) from all of the other manufacturers – bar Poland (21/91). This result indicates that cartridge cases produced by former USSR members can be differentiated from cartridge cases produced by Warsaw Pact member countries. This has the potential to assist in conflict zones where a significant portion of ammunition originates from both. As previously iterated, although this does not provide a definitive answer as to where the supply has come from, it may assist in determining where trade routes digressed and ammunition entered the 'black market'.

Analysis of the web of case showed five statistically significant differences for both the distance between the flash holes and the diameter of the bolster mark (where present). There were no bolster marks present for the three sets from Hungary as well as Bosnia (IK/83). This absence of the bolster mark for both allow them to be uniquely identified as the only steel/brass cartridge cases for which this feature is absent. This is valuable in determining manufacture and analysis could be undertaken with relative ease, providing that the cartridge case can be sectioned/a camera can move down into the cartridge case to determine if it is present. The distance between the flash holes and the diameter of the bolster mark could prove to be beneficial, providing that obtaining this information was less labour intensive. Automating the process (as discussed in **Section 8**) could assist with this.

The results from SEM analysis of the primer residues are qualitative in nature and showed that the compositions for most sample sets resembled a mercuric, corrosive primer type. Typical compositions are shown in **Section 6.4.2** with two obvious differences. For the Russian sample sets (WOLF and 539/76) disparities are present in primer ‘type’. Russia (WOLF) showed an alternative composition that diverged from the majority of other manufacturers observed; a nonmercuric, corrosive type primer This is suggestive of this ammunition being for commercial rather than military use, and may also be an indication that this ammunition was produced at a later date [62]. This theory is supported by the headstamps: with WOLF being a well-known (in the United States) commercial ammunition brand. South Africa (13/88) could clearly be identified as this was the only sample set with a nonmercuric, noncorrosive, Sinoxyd type primer and this allows primers from this manufacturer to be uniquely identified. Analysis of this component alone would allow for differentiation between South Africa (13/88) and the other manufacturers examined throughout this research.

Examination of primer residue is comparable to (but not interchangeable with) examination of gunshot residue (GSR). Whilst primer residue contains the inorganic components that would be present in GSR, they are unlikely to be present in the same morphology, nor quantity. This is due to dispersion as well as prolonged exposure to increased temperatures. Furthermore, identification of Pb in primer residue is is suggestive of Pb present in the primer mix. In contrast, if Pb is present in GSR, there is a possibility that this is the result of Pb from the base of the projectile [57]. For the primer residue examined in this study, mercury was observed in relatively high quantities and this result is particularly unlikely for GSR particles examined during casework [40], [141], [119]. A conclusion that should be recognised when considering interpretation of the primer residue results.

The examination of cartridge cases (including primers) allowed for characterisation of 8 out of 15 manufacturers/years. These are outlined below with brief summaries of the variables used for differentiation

- Czech (bxn/83) had a grey steel case with a grey coloured primer – and no lacquer present on the primer annulus.
- South Africa (13/88) had a brass cartridge case with green lacquer around the primer annulus. The primer residue analysis displayed a unique combination of elements – indicative of a primer containing lead styphnate, barium nitrate, and antimony sulphide.
- Romania (324/94) had an olive green, steel cartridge case, with the primer cap covered in red lacquer. Additionally, Romania (324/94) was one of two manufacturers to have P present when examining the primer residue. The other manufacturer was Poland (21/91).
- Poland (21/91) had a greenish brown cartridge case with the aforementioned P present in the primer residue. Another distinguish feature was that this manufacturer also had no bolster mark present. The only other manufacturer with a steel cartridge case and no bolster mark was Hungary (23/all years).
- Hungary (23/all years) had a greenish brown cartridge case with the aforementioned absence of a bolster mark.
- Bosnia (IK/83) had a brass cartridge case with no bolster mark present.
- Serbia (PPU/85) had a brass cartridge case with a gradual increase in hardness (gF) profile along the wall of the cartridge case.

- Russia (WOLF) had a grey steel case. The primer residue analysis displayed a unique combination of elements – indicative of a primer containing phosphorus sulphide, magnesium and calcium carbonate, and potassium chlorate

7.3 Key Findings

For the projectiles analysed there are distinguishing features for 7 of the manufacturers. This in combination with the 8 manufacturers that can be uniquely identified from their cartridge cases (including the primer), allows for a total of 11 possible identifications based on a combination of results (there are some manufacturers that are identifiable by both components). Not all of these features require the use of analytical equipment. Observations such as material and lacquer colour are possible outside of a laboratory. If resources are available, sectioning the projectiles and removing the base of cartridge cases to examine the web of case provides valuable information; projectile jacket material, presence of an ‘air pocket’ and whether there is a bolster mark can all be inspected without specialist equipment. Hardness testing proved beneficial for both components (projectiles and cartridge cases), whereas XRF analysis results for cartridge cases showed no advantages in differentiation. For those equipped to use analytical techniques for further analysis, the examination of primer residues can be labour intensive, but provides information that can aid differentiation where other techniques are not able (i.e P in Hungarian ammunition).

Whilst it may appear obvious that the most obvious differentiating physical feature should be used as an initial identifier, it must be considered that the probability of finding a complete round of ammunition may not always be the case. Thus, the individual physical and chemical analysis of component parts may assist in determining the provenance of ammunition which has been fired with only distorted or compromised fragments remaining.

8 Chapter 8: FUTURE WORKS

The ammunition in this study has been investigated in many capacities by a range of specialities. This thesis has provided some useful results and highlighted avenues that should be further explored in order to assist in differentiation and characterisation of ammunition components. Further work in this area should be conducted in a multi-disciplinary capacity.

Analysis was conducted in order to compare ammunition from known manufacturers and quantify the significance of such variations. The sample size is small compared to the population of 7.62 x 39 mm ammunition that has been/is produced and should be taken into consideration when interpreting the results, particularly in areas where only two samples per manufacturer were analysed. This does not mean that the results should be disregarded, however, an increase in the number of samples would increase the reliability of parametric testing and allow for increased confidence when reporting the results. Furthermore, adding additional data (from the same manufacturers analysed) to the GeNIe model is likely to improve its ability to identify the ammunition manufacturer.

One concern that became apparent during the elemental analysis (of projectiles in particular) was the higher than expected copper values observed in steel jacketed projectiles. This may have been as a result of the preparation process – despite being conducted in line with recognised standards [128]. Alternatively, XRF is known to penetrate several layers and could have accounted for elements used in coating the cartridge cases. Two potential changes could be implemented: 1) To use an unorthodox sectioning technique (such as sawing or laser cutting) in order to mitigate the chances of contamination of the steel. 2) To utilise an analytical technique that is not susceptible to the same risks as XRF. Sectioning samples in this way could increase the confidence of reported results, however, these may remain within the tolerances for mild steel.

Analysis of microstructure could prove invaluable in terms of understanding the manufacturing processes. This metallurgical technique is relatively simple to conduct, is both time and cost effective, and can provide information regarding heat treatments and cold working processes. This was minimally explored for the steel cores present within the projectiles (see **Section 6.2.1**) and indicated that these had undergone cold working. As the elemental analysis of the steel cores yielded few obvious differences, it is reasonable to assume that the hardness was a result of the cold working processes. There are several recognised techniques for redrawing (double action, reverse drawing and single action) all of which require calculations based on the cross-sectional and diameter reductions [41]. A greater understanding of the wire extrusion and redrawing operations could prove useful in discriminating between manufacturers. Supplementary to the analysis of steel cores would be the comparison of steel cores from projectiles which have and have not been discharged. As the projectiles are subject to high temperatures and pressures during the firing process, it would be reasonable to assume that this could have an affect on the physical properties of the steel cores. This may be of particular interest to defence industries who face the threat of 7.62 x 39 mm ammunition, in order to ensure protection against ammunition available from a range of manufacturers.

Microstructure examination could also provide further insight in to the variation in H_v values shown for cartridge cases. The hardness profiles indicate the possibility of alternative manufacturing methods, however, this is speculative based on one observed property. Examination of grain size and directionality could potentially support theories based on H_v values. Future work should consider the fact that values are likely to vary if cartridge cases have been ‘fired’ as a result of obturation. Analysis could compare disassembled and fired cartridge cases from the same manufacturer to quantify difference or analyse behaviour. Microstructural analysis also has the potential to replace the requirement for hardness testing; a technique that may be deemed prohibitively time consuming and vulnerable to operator subjectivity. Conversely, etching is a simple, rapid technique that could be conducted in remote areas – an important consideration for conflict zones.

Throughout this research, some attempts have been made to determine whether there are temporal differences between ammunition from the same manufacturer/year. The projectiles for Serbia (PPU) were analysed nine years apart (1985 and 1994) and showed variations in wt % of several elements: Sn, Cr, Mn, Ag, and Ni. These disparities support the considerations that manufacturers will modify their source/manufacturing processes over time and could potentially assist in differentiation. Unfortunately, not all components were available and the cartridge cases, primer caps, and primer mixture could not be compared.

Similarly, for the samples from Hungary (23), ammunition components were analysed from three consecutive years. There were variations present in the levels of Mn and Ni ((wt.%)) in the steel jackets of the projectiles between Hungary (23/84) and projectiles from the succeeding two years. There were also differences in the widths of jacket components: Hungary (23/85) varied from 6 manufacturers, whilst there were no observed differences for the other two years. Furthermore, Hungary (23/86) showed statistically significant differences in Nb (wt.%). There were no variations in hardness values (gF) for the steel cores, nor for the hardness values. Finally, Hungary (23/84) was the only year where Sn was not present in the primer residue. These results suggest that whilst practices are unlikely to vary, the materials or components sourced have the potential to do so. This would provide some explanation for the variation in elemental composition but consistency in hardness values (gF). This indicates that manufacturing process are not regularly modified; presumably as there are few novel applications and this process would be expensive to the manufacturer. The high costs involved should not be a deterrent to the concept of analysing sequential ammunition from one manufacturer, however, the results from this study suggest that analysis be conducted at larger intervals (e.g. 10 years apart) to determine if changes are present prior to determining precise years of variation. Ideally, future work would involve contact with the producer to attempt to clarify or compare changes in manufacture.

One focus for ammunition research has been the ability to individualise manufacturer (or batch/year), thus, being able to effectively link ammunition to events/persons. This research briefly explored the concept of ‘batch variation’, analysing two sample sets from Bulgaria (10), both from the same year (1999), known as batch ‘a’ and ‘b’. The Bayesian network involving these two different groups was able to successfully distinguish between seven out of the eight samples analysed showing the potential of such methods. This requires further exploration to ensure that this phenomenon was not an individual occurrence, however, the potential to identify not only the manufacturer but also the batch could prove invaluable when determining the origin of illicit ammunition.

The primer caps were analysed to determine their elemental composition, however, it was not possible to examine unaltered (still in tact) primer caps. There are obvious risks involved as these contain the explosive materials described in **Section 2.2.4**. The opportunity to examine the primer caps could illustrate differences in morphology and may still be possible where primer caps have been ‘popped’. Further work could include techniques such as infra-red (IR) spectroscopy may assist in examining the lacquers present on both the primer caps and the cartridge cases. This technique allows for identification of bonds via absorption. It was observed that for some of the primer caps a lacquer is present both internally and externally and whilst not explored in this study, may prove useful when examining discharged cartridge cases and could demonstrate additional disparities.

This study amalgamated processes common in analytical chemistry and metallurgy however, it would benefit from the input of automated techniques – particularly during image processing and measurements. ImageJ was utilised for measurement of the web of case details, the projectile jacket components and the microstructure of the cores. This process was particularly labour intensive as approximately 50 images were analysed in several points (six, seven, 30 and n/a respectively). Input from a specialist could allow for measurements to occur based on differences in ‘colour’ thresholds, therefore drastically reducing the time required. Thresholds would require validation against operator results, however, analysis of images using automated methods would also assist in removing operator subjectivity and improve the reliability of results for comparison. This would prove particularly beneficial in circumstances which are time sensitive (both casework and conflict scenarios).

Historical and contextual changes discussed in **Section 4** could be reflected in temporal changes in ammunition. Examining whether there is a dramatic change in composition between The privatisation of ammunition manufacturers following the fall of the USSR is one avenue that could be further explored. This is also true for successive states of former Yugoslavia and Czechoslovakia.

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APPENDIX A: XRF ANALYSIS

Elemental results for projectile jackets:

Material	**ORIGIN**	**ELEMENT (WT.%)**																
		Mo	Ni	Nb	Fe	Al	Cr	Mn	Si	Cu	Sn	Pb	Zn	P	Ag	Co	Ni	Bi
Steel	Czech (bxn/83)	0.032	0.141	0.009	98.10	0.030	0.137	0.623	0.664	0.122								
	Bulgaria (10/99)	0.010	0.123	0.008	97.90	0.028	0.115	0.633	0.603	0.436								
	Hungary (23/85)	0.014	0.133	0.010	97.75	0.029	0.129	0.659	0.588	0.539								
	Hungary (23/86)	0.012	0.110	0.010	98.07	0.028	0.138	0.685	0.583	0.221								
	Ukraine (270/67)	0.014	0.140	0.008	97.99	0.029	0.137	0.590	0.557	0.393								
	Bulgaria (10/99)	0.009	0.087	0.006	98.18	0.027	0.095	0.526	0.717	0.208								
	Romania (324/94)	0.015	0.101	0.006	98.29	0.025	0.104	0.477	0.638	0.197								
	Russia (WOLF)	0.009	0.061	0.008	98.47	0.024	0.084	0.365	0.604	0.235								
	Hungary (23/84)	0.011	0.084	0.007	98.09	0.027	0.098	0.582	0.633	0.320								
	Poland (21/91)	0.013	0.090	0.006	98.36	0.025	0.095	0.432	0.409	0.422								
	China (61/64)	0.023	0.071	0.006	98.51	0.028	0.062	0.524	0.441	0.194								

	Russia (539/76)	0.011	0.107	0.007	98.40	0.026	0.084	0.469	0.471	0.285								
Brass	PPU (PPU/94)				0.111	0.280	0.006	0.006	0.047	90.04	0.033	0.176	9.20	0.051	0.014	0.006	0.010	0.017
	PPU (PPU/85)				0.084	0.281	0.013	0.006	0.029	89.20	0.028	0.167	10.07	0.052	0.032	0.006	0.001	0.019
	South Africa (13/88)				0.103	0.336	0.013	0.007	0.033	88.41	0.028	0.175	10.77	0.055	0.034	0.007	0.002	0.015
	Bosnia (IK/83)				0.087	0.261	0.012	0.007	0.027	89.05	0.028	0.173	10.25	0.043	0.031	0.007	0.000	0.018
	Albania (11/89/3)				0.137	0.291	0.014	0.007	0.029	79.05	0.028	0.076	20.26	0.037	0.031	0.007	0.002	0.018

Table Apx 1.1 Average weight percent (wt.%) of elements present in steel and brass projectile jackets.

Elemental results for projectile steel cores:

ORIGIN	ELEMENT (WT.%)								
	Mo	Ni	Nb	Fe	Al	Cr	Mn	Si	Cu
Czech (bxn/83)	0.018	0.093	0.004	98.40	0.034	0.121	0.526	0.492	0.177
Bulgaria (10/99)	0.017	0.052	0.004	98.44	0.024	0.073	0.523	0.580	0.149
Hungary (23/85)	0.020	0.098	0.004	98.27	0.040	0.105	0.619	0.507	0.194
Hungary (23/86)	0.023	0.121	0.005	98.24	0.039	0.122	0.590	0.557	0.167
Ukraine (270/67)	0.013	0.058	0.004	98.42	0.028	0.083	0.588	0.587	0.081
Bulgaria (10/99)	0.016	0.045	0.002	98.20	0.029	0.112	0.501	0.770	0.116
Romania (324/94)	0.036	0.141	0.002	97.97	0.025	0.162	0.557	0.762	0.210
Hungary (23/84)	0.020	0.080	0.002	98.10	0.026	0.099	0.598	0.775	0.162
Poland (21/91)	0.020	0.069	0.002	98.49	0.022	0.091	0.474	0.559	0.129
Albania (11/89/3)	0.013	0.964	0.002	97.12	0.024	0.408	0.518	0.664	0.151
China (61/64)	0.015	0.032	0.002	98.53	0.024	0.070	0.597	0.537	0.056
Russia (539/76)	0.020	0.116	0.002	98.17	0.022	0.112	0.621	0.669	0.128

Table Apx 2 Average weight percent (wt.%) of elements present in steel core.

Elemental results for brass cartridge cases:

ORIGIN	ELEMENT (WT.%)													
	Sn	Pb	Zn	Fe	Al	Cr	Co	Mn	Si	P	Ag	Cu	Ni	Bi
Serbia (PPU/85)	0.006	0.022	28.17	0.027	0.214	0.010	0.010	0.026	0.008	0.004	0.014	71.48	0.001	0.000
South Africa (13/88)	0.005	0.004	30.20	0.040	0.221	0.010	0.011	0.026	0.006	0.004	0.014	69.45	0.002	0.000
Bosnia (IK/83)	0.004	0.021	28.42	0.025	0.228	0.011	0.008	0.026	0.018	0.004	0.013	71.22	0.001	0.000

Table_Apx 3 Average weight percent (wt.%) of elements present in brass cartridge cases.

Elemental results for steel cartridge cases:

ORIGIN	ELEMENT (WT.%)									
	C	Si	Mn	Cr	Mo	Ni	Al	Cu	Nb	Fe
Czech (bxn/83)	0.14	0.66	0.57	0.10	0.02	0.04	0.02	0.04	0.01	98.40
Hungary (23/85)	0.14	0.60	0.58	0.15	0.03	0.06	0.02	0.04	0.01	98.36
Hungary (23/86)	0.14	0.64	0.56	0.09	0.02	0.04	0.03	0.03	0.01	98.43
Ukraine (270/67)	0.14	0.69	0.55	0.09	0.02	0.06	0.02	0.10	0.01	98.31
Bulgaria (10/99)	0.14	0.72	0.45	0.08	0.02	0.06	0.02	0.07	0.01	98.42
Romania (324/94)	0.14	0.72	0.54	0.07	0.02	0.02	0.03	0.02	0.01	98.43
Russia (WOLF)	0.14	0.71	0.49	0.08	0.02	0.04	0.02	0.06	0.01	98.42
Hungary (23/84)	0.14	0.72	0.55	0.12	0.03	0.05	0.03	0.04	0.01	98.30
Poland (21/91)	0.14	0.90	0.69	0.11	0.02	0.05	0.03	0.07	0.01	97.98
Albania (11/89/3)	0.14	0.83	0.50	0.08	0.02	0.03	0.02	0.02	0.01	98.35
China (61/64)	0.14	0.69	0.59	0.06	0.02	0.02	0.02	0.12	0.01	98.32
Russia (539/76)	0.14	0.70	0.57	0.12	0.02	0.11	0.03	0.24	0.01	98.05

Table_Apx 4 Average weight percent (wt.%) of elements present in steel cartridge cases.

Elemental results for brass primer caps:

ORIGIN	**ELEMENT (WT.%)**													
	Sn	Pb	Zn	Fe	Al	Cr	Co	Mn	Si	P	Ag	Cu	Ni	Bi
Czech (bxn/83)	0.0082	0.0041	28.695	0.1654	0.3039	0.0079	0.0086	0.0253	0.1121	0.2868	0.0145	70.36	0.0020	0.0000
Serbia (PPU/85)	0.0065	0.0092	26.474	0.0333	0.2591	0.0120	0.0093	0.0288	0.0838	0.0099	0.0142	73.059	0.0008	0.0000
Hungary (23/85)	0.0066	0.0052	28.833	0.0411	0.2898	0.0077	0.0082	0.0228	0.1512	0.0564	0.0143	70.557	0.0055	0.0000
Hungary (23/86)	0.0054	0.0024	28.727	0.0641	0.1905	0.0110	0.0101	0.0252	0.2287	0.1892	0.0132	70.516	0.0167	0.0000
Ukraine (270/67)	0.0049	0.0039	27.920	0.0428	0.2487	0.0096	0.0090	0.0267	0.0580	0.0723	0.0140	71.588	0.0015	0.0000
South Africa (13/88)	0.0036	0.0030	30.269	0.0433	0.2222	0.0102	0.0106	0.0266	0.0480	0.0524	0.0140	69.294	0.0026	0.0004
Bulgaria (10/99b)	0.0047	0.0006	28.863	0.0305	0.1639	0.0081	0.0098	0.0258	0.0571	0.1045	0.0145	70.715	0.0010	0.0000
Romania (324/94)	0.0070	0.0194	29.695	0.1704	0.2635	0.0088	0.0220	0.0256	0.0876	0.1246	0.0152	69.558	0.0022	0.0000
Bosnia (IK/83)	0.0056	0.0305	28.994	0.0523	0.2567	0.0104	0.0129	0.0242	0.1283	0.0830	0.0136	70.385	0.0031	0.0000
Russia (WOLF)	0.0043	0.0171	29.680	0.0497	0.2105	0.0104	0.0101	0.0279	0.3567	0.0105	0.0128	69.609	0.0003	0.0000
Hungary (23/84)	0.0053	0.0034	28.934	0.0382	0.2037	0.0101	0.0102	0.0259	0.1753	0.0805	0.0138	70.492	0.0069	0.0000
Poland (21/91)	0.0072	0.0024	30.182	0.0521	0.2061	0.0129	0.0105	0.0266	0.0586	0.0530	0.0136	69.374	0.0007	0.0000
Albania (11/89/3)	0.0022	0.0101	28.589	0.0611	0.2690	0.0099	0.0093	0.0264	0.1999	0.0382	0.0137	70.770	0.0011	0.0000
China (61/64)	0.0065	0.0025	27.334	0.0415	0.2960	0.0113	0.0103	0.0281	0.1259	0.0437	0.0147	72.084	0.0004	0.0000
Russia (539/76)	0.0056	0.0043	29.002	0.0284	0.2067	0.0113	0.0099	0.0296	0.0553	0.0125	0.0133	70.619	0.0013	0.0000

Table_Apx 5 Average weight percent (wt.%) of elements present in brass primer caps.

APPENDIX B: JACKET COMPONENT WIDTHS

Results for components of steel jackets measured using SEM images:

ORIGIN	WIDTH (µm)			
	Total	**Steel Jacket**	**Inner Plating**	**Outer Plating**
Czech (bxn/83)	575.65 **(29.44)**	549.14 **(29.33)**	0.00 **(0.00)**	26.51 **(5.25)**
Bulgaria (10/99a)	564.80 **(12.27)**	502.56 **(10.77)**	39.08 **(4.24)**	23.16 **(2.25)**
Hungary (23/85)	559.26 **(26.16)**	477.43 **(32.85)**	48.47 **(4.99)**	33.36 **(6.60)**
Hungary (23/86)	582.55 **(23.92)**	509.24 **(21.75)**	42.95 **(4.75)**	30.36 **(2.78)**
Ukraine (270/67)	565.48 **(29.90)**	515.19 **(28.32)**	28.48 **(7.59)**	21.81 **(3.04)**
Bulgaria (10/99b)	573.17 **(9.89)**	507.23 **(6.25)**	43.11 **(4.42)**	22.83 **(3.90)**
Romania (324/94)	567.92 **(13.66)**	507.12 **(12.03)**	39.06 **(3.28)**	21.75 **(3.34)**
Hungary (23/84)	546.87 **(19.78)**	469.03 **(14.26)**	48.39 **(8.81)**	29.46 **(3.85)**
Poland (21/91)	592.80 **(7.58)**	509.40 **(8.27)**	52.98 **(6.40)**	30.42 **(4.19)**
China (61/64)	572.75 **(43.22)**	514.57 **(28.77)**	34.61 **(15.91)**	23.57 **(4.14)**
Russia (539/76)	560.57 **(45.62)**	500.06 **(43.22)**	33.85 **(6.90)**	26.66 **(4.91)**

Table Apx 6 Average width of components within steel jacketed projectiles.

APPENDIX C: SEM IMAGES OF STEEL PROJECTILE JACKETS

See electronic Appendix F. Must be opened using ImageJ in order to observe areas measured

.

APPENDIX D: SEM-EDX PRIMER RESULTS

Elemental results for brass primer residue:

ORIGIN	ELEMENT (%)																									
	S	K	Cl	Sb	Ba	Pb	Sn	Fe	Cu	Zn	Hg	Al	O	C	Ni	Na	Si	P	Zr	Mg	N	Ca	Br	Mo	Cr	Ti
Czech (bxn/83)	12.76	10.85	10.70	10.26	0.00	0.00	9.97	8.94	3.08	1.03	3.96	0.00	10.26	9.53	0.00	4.99	2.49	0.29	0.00	0.00	0.00	0.29	0.29	0.00	0.29	0.00
Serbia (PPU/85)	12.02	12.31	12.16	11.17	0.00	0.00	10.33	8.20	10.04	1.41	2.26	6.08	4.67	3.82	0.28	0.28	4.67	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hungary (23/85)	12.48	12.63	12.63	10.98	0.00	0.75	1.50	11.73	3.01	3.46	3.61	3.01	9.47	7.52	0.00	0.45	4.66	1.80	0.00	0.15	0.15	0.00	0.00	0.00	0.00	0.00
Hungary (23/86)	12.70	12.70	12.55	10.70	0.00	0.14	5.71	11.55	4.99	3.85	2.14	1.57	7.42	6.13	0.00	1.43	2.71	3.00	0.43	0.00	0.00	0.00	0.29	0.00	0.00	0.00
Ukraine (270/67)	13.78	11.54	11.54	12.02	0.16	0.32	7.37	9.29	5.61	1.76	2.56	1.44	7.37	9.78	0.16	1.12	2.72	1.12	0.00	0.00	0.00	0.32	0.00	0.00	0.00	0.00
South Africa (13/88)	10.98	0.39	0.65	9.93	10.07	10.33	0.13	7.45	7.97	1.96	0.00	0.13	11.11	11.50	0.00	1.31	9.93	0.26	0.00	0.00	0.52	4.97	0.00	0.39	0.00	0.00

Bulgaria (10/99)	12.43	12.29	12.29	11.43	0.86	0.00	10.00	10.29	3.43	0.43	3.57	1.43	7.86	8.00	0.14	1.14	4.14	0.00	0.00	0.00	0.14	0.14	0.00	0.00	0.00	0.00
Romania (324/94)	10.24	10.12	10.48	9.52	0.00	0.00	8.92	9.64	3.86	4.10	5.30	0.36	8.19	8.55	0.00	2.17	4.82	3.61	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.00
Bosnia (IK/83)	10.88	11.00	11.13	10.25	0.00	0.00	9.88	8.25	9.25	1.13	2.38	6.13	8.63	6.38	0.00	0.00	3.63	0.13	0.00	0.00	0.00	0.00	0.13	0.00	0.00	0.88
Russia (WOLF)	7.57	4.47	1.75	6.60	0.00	15.53	2.52	9.71	2.52	0.19	0.00	0.39	15.92	16.70	0.00	0.78	4.85	0.39	0.00	0.00	9.32	0.78	0.00	0.00	0.00	0.00
Hungary (23/84)	9.47	11.77	11.91	10.42	0.00	0.54	0.14	11.77	1.89	3.52	5.82	2.44	10.55	7.98	0.00	2.30	4.33	2.57	0.00	0.14	2.03	0.27	0.00	0.00	0.14	0.00
Russia (539/76)	10.23	10.23	11.55	10.62	0.00	0.00	9.43	7.70	8.63	1.20	5.71	0.40	9.96	9.16	0.00	0.00	4.78	0.00	0.00	0.13	0.00	0.13	0.00	0.00	0.13	0.00

Table_Apx 7 The percentage (%) of particles analysed where elements were observed.

APPENDIX E: HARDNESS VALUES

Projectile steel cores:

ORIGIN	H_v VALUE (gF)	
	Average	Standard Deviation
Czech (bxn/83)	200.71	4.22
Bulgaria (10/99a)	205.79	11.47
Hungary (23/85)	219.33	3.38
Hungary (23/86)	219.78	2.93
Ukraine (270/67)	192.25	4.38
Bulgaria (10/99b)	201.75	13.49
Romania (324/94)	277.87	3.87
Hungary (2384)	220.55	1.736
Poland (21/91)	178.33	19.53
Albania (11/89/3)	157.55	10.86
China (61/64)	134.08	3.99
Russia (539/76)	210.63	4.41

Table_Apx 8 Average hardness values and standard deviations for projectile steel cores.

Cartridge case profile:

DISTANCE FROM CARTRIDGE CASE MOUTH	ORIGIN												
	Czech (bxn/83)	Serbia (PPU/85)	Ukraine (270/67)	South Africa (13/88)	Bulgaria (10/99b)	Romania (324/94)	Bosnia (IK/83)	Russia (WOLF)	Hungary (23/84)	Poland (21/91)	Albania (11/89/3)	China (61/64)	Russia (539/76)
2	201	115	210	134	206	212	127	207	213	229	201	196	227
4	203	118	211	134	206	208	129	207	214	220	198	197	226
4.5			209	136			134						
5			210	135			134						
5.5			221	137			132						
6	194	118	235	169	203	202	150	208	212	212	190	187	223
6.5			241				161					190	229
7			249				170					195	248
7.5			252				170					210	257
8	178	120	255	171	182	186	164	208	189	204	174	217	257
8.5		120	254				163	218		206		221	
9		124	258				166	225		214		233	
9.5		131	262				172	235		221		240	
10	176	136	269	168	175	177	170	249	183	227	165	245	265
10.5		143				177	171	257		236			
11		147				184	171	258		244			
11.5		154				199	173	261		248			
12	194	161	273	176	177	229	171	264	188	248	193	250	270
12.5	205	167			177	246			196		194		
13	217	170			186	252			230		205		
13.5	227	174			195	255			242		219		
14	233	177	280	175	216	253	172	264	251	254	231	257	269
14.5	236	178			245								
15	241	178			249								
15.5	246	178			249								
16	246	177	274	171	255	251	168	259	256	257	239	253	256
18	243	176	262	175	258	242	170	247	255	257	241	251	253
20	237	181	246	180	252	240	156	246	249	251	243	249	250
22	231	173	245	177	236	228	162	234	237	242	233	249	249
24	223	175	238	180	228	240	158	238	236	235	227	240	240
26	225	166	235	178	226	223	159	230	234	229	219	240	240

28	217	178	225	180	223	225	149	230	225	225	221	241	229
30	218	171	225	166	216	216	152	224	225	221	202	232	229
32	199	147	223	160	217	213	142	213	213	213	203	227	230
34	195	214	222	174	207	211	198	207	205	216	187	214	219

APPENDIX F: WEB OF CASE IMAGES

See electronic Appendix F. Must be opened using ImageJ in order to observe areas measured.

APPENDIX G: WEB OF CASE MEASUREMENTS

Distance between flash holes:

ORIGIN	DISTANCE (mm)	
	Average	St. Dev
Czech (bxn/83)	3.69	0.09
Serbia (PPU/85)	3.88	0.02
Hungary (23/85)	3.76	0.22
Hungary (23/86)	3.59	0.05
Ukraine (270/67)	3.78	0.18
South Africa (13/88)	3.62	0.18
Bulgaria (10/99b)	3.62	0.06
Romania (324/94)	3.69	0.06
Bosnia (IK/1983)	3.83	0.02
Russia (WOLF)	3.59	0.13
Hungary (23/84)	3.67	0.14
Poland (21/91)	3.96	0.04
Albania (11/89/3)	3.78	0.11
China (61/64)	3.73	0.04
Russia (539/76)	3.62	0.09

Table_Apx 9 Average distance between flash holes.

Diameter of bolster mark (where present):

ORIGIN	DIAMETER (mm)	
	Average	St. Dev
Czech (bxn/83)	5.81	0.13
Serbia (PPU/85)	6.81	0.79
Ukraine (270/67)	6.57	0.04
Bulgaria (10/99b)	6.24	0.06
Romania (324/94)	6.33	0.11
Russia (WOLF)	6.24	0.24
Poland (21/91)	6.46	0.09
China (61/64)	6.43	0.06
Russia (539/76)	6.31	0.04

Table_Apx 10 Average diameter of bolster marks.

APPENDIX H: SPSS ANALYSIS

The *Output* files from SPPS analysis conducted have been attached as Microsoft Word documents. These can be found in electronic Appendix H.

APPENDIX I: GENIE CONFUSION MATRICES

GeNIe Model 6C:

MANUFACTURER

	Bulgaria (10/99a)	Bulgaria (10/99b)	Albania (11/89/3)	Poland (21/91)	Hungary (23/84)	Hungary (23/85)	Hungary (23/86)	Ukraine (270/67)	Romania (324/94)	Russia (539/76)	China (61/64)	Czech (bxn83	Bosnia (IK/83)	South Africa	Serbia (PPU/85)	Serbia (PPU/94)	Russia (WOLF)
Bulgaria (10/99a)	**3**	0	0	0	**1**	0	0	0	0	0	0	0	0	0	0	0	0
Bulgaria (10/99b)	**1**	**3**	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Albania (11/89/3)	0	0	**4**	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Poland (21/91)	0	0	0	**4**	0	0	0	0	0	0	0	0	0	0	0	0	0
Hungary (23/84)	**1**	0	0	0	**3**	0	0	0	0	0	0	0	0	0	0	0	0
Hungary (23/85)	0	0	0	0	0	**3**	**1**	0	0	0	0	0	0	0	0	0	0
Hungary (23/86)	0	0	0	0	0	0	**4**	0	0	0	0	0	0	0	0	0	0
Ukraine (270/67)	0	0	0	0	0	0	0	**4**	0	0	0	0	0	0	0	0	0
Romania (324/94)	0	0	0	0	0	0	0	0	**4**	0	0	0	0	0	0	0	0
Russia (539/76)	0	0	0	0	**1**	0	0	0	0	**3**	0	0	0	0	0	0	0
China (61/64)	0	0	0	0	0	0	0	0	0	0	**4**	0	0	0	0	0	0
Czech (bxn83	0	0	0	0	0	0	0	0	0	0	0	**4**	0	0	0	0	0
Bosnia (IK/83)	0	0	0	0	0	0	0	0	0	0	0	0	**3**	0	**1**	0	0
South Africa (13/88)	0	0	0	0	0	0	0	0	0	0	0	0	0	**4**	0	0	0
Serbia (PPU/85)	0	0	0	0	0	0	0	0	0	0	0	0	**1**	**1**	**2**	0	0
Serbia (PPU/94)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**4**	0
Russia (WOLF)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**4**

Table_Apx 11 Confusion matrix for projectiles in Model 6C.

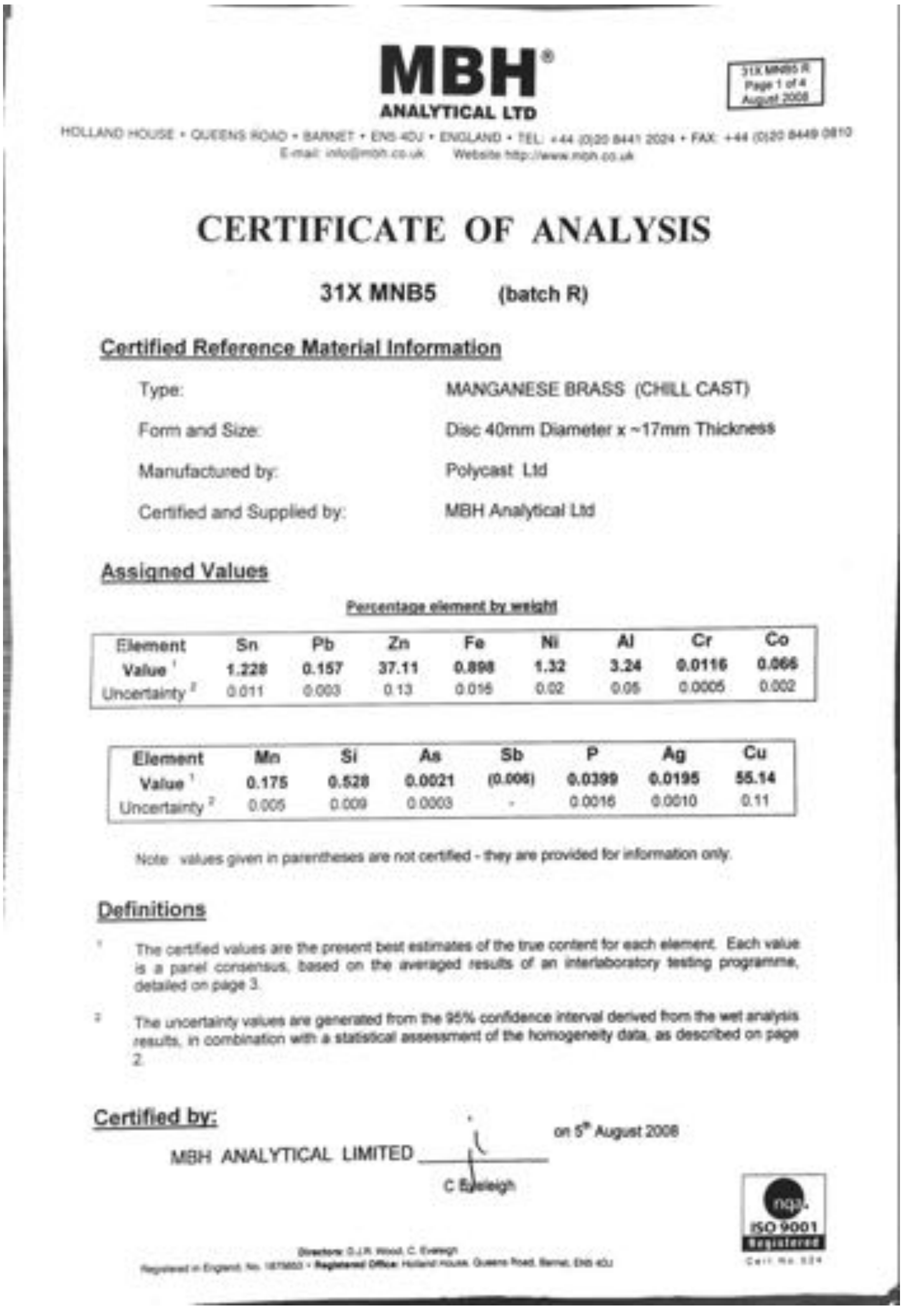
GeNIe Model 6B:

MANUFACTURER

	Bulgaria (10/99b)	Albania (11/89/3)	Poland (21/91)	Hungary (23/84)	Hungary (23/85)	Hungary (23/86)	Ukraine (270/67)	Romania (324/94)	Russia (539/76)	China (61/64)	Czech (bxn83	Bosnia (IK/83)	South Africa	Serbia (PPU/85)	Serbia (PPU/94)	Russia (WOLF)
Bulgaria (10/99b)	**7**	0	0	**1**	0	0	0	0	0	0	0	0	0	0	0	0
Albania (11/89/3)	0	**4**	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Poland (21/91)	0	0	**4**	0	0	0	0	0	0	0	0	0	0	0	0	0
Hungary (23/84)	**1**	0	0	**3**	0	0	0	0	0	0	0	0	0	0	0	0
Hungary (23/85)	0	0	0	0	**3**	**1**	0	0	0	0	0	0	0	0	0	0
Hungary (23/86)	0	0	0	0	0	**4**	0	0	0	0	0	0	0	0	0	0
Ukraine (270/67)	**1**	0	0	0	0	0	**3**	0	0	0	0	0	0	0	0	0
Romania (324/94)	0	0	0	0	0	0	0	**4**	0	0	0	0	0	0	0	0
Russia (539/76)	0	0	0	**1**	0	0	0	0	**3**	0	0	0	0	0	0	0
China (61/64)	0	0	0	0	0	0	0	0	0	**4**	0	0	0	0	0	0
Czech (bxn83	0	0	0	0	0	0	0	0	0	0	**4**	0	0	0	0	0
Bosnia (IK/83)	0	0	0	0	0	0	0	0	0	0	0	**3**	0	**1**	0	0
South Africa (13/88)	0	0	0	0	0	0	0	0	0	0	0	0	**4**	0	0	0
Serbia (PPU/85)	0	0	0	0	0	0	0	0	0	0	0	**1**	**1**	**2**	0	0
Serbia (PPU/94)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**4**	0
Russia (WOLF)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**4**

Table_Apx 12 Confusion matrix for projectiles in Model 6B.

APPENDIX J: REFERENCE STANDARD FOR XRF ANALYSIS



MBH®
ANALYTICAL LTD

31X MNB5 R
Page 1 of 4
August 2008

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CERTIFICATE OF ANALYSIS

31X MNB5 (batch R)

Certified Reference Material Information

Type:	MANGANESE BRASS (CHILL CAST)
Form and Size:	Disc 40mm Diameter x ~17mm Thickness
Manufactured by:	Polycast Ltd
Certified and Supplied by:	MBH Analytical Ltd

Assigned Values

Percentage element by weight

Element	Sn	Pb	Zn	Fe	Ni	Al	Cr	Co
Value [1]	**1.228**	**0.157**	**37.11**	**0.898**	**1.32**	**3.24**	**0.0116**	**0.066**
Uncertainty [2]	0.011	0.003	0.13	0.016	0.02	0.05	0.0005	0.002

Element	Mn	Si	As	Sb	P	Ag	Cu
Value [1]	**0.175**	**0.528**	**0.0021**	**(0.006)**	**0.0399**	**0.0195**	**55.14**
Uncertainty [2]	0.005	0.009	0.0003	-	0.0016	0.0010	0.11

Note: values given in parentheses are not certified - they are provided for information only.

Definitions

[1] The certified values are the present best estimates of the true content for each element. Each value is a panel consensus, based on the averaged results of an interlaboratory testing programme, detailed on page 3.

[2] The uncertainty values are generated from the 95% confidence interval derived from the wet analysis results, in combination with a statistical assessment of the homogeneity data, as described on page 2.

Certified by:

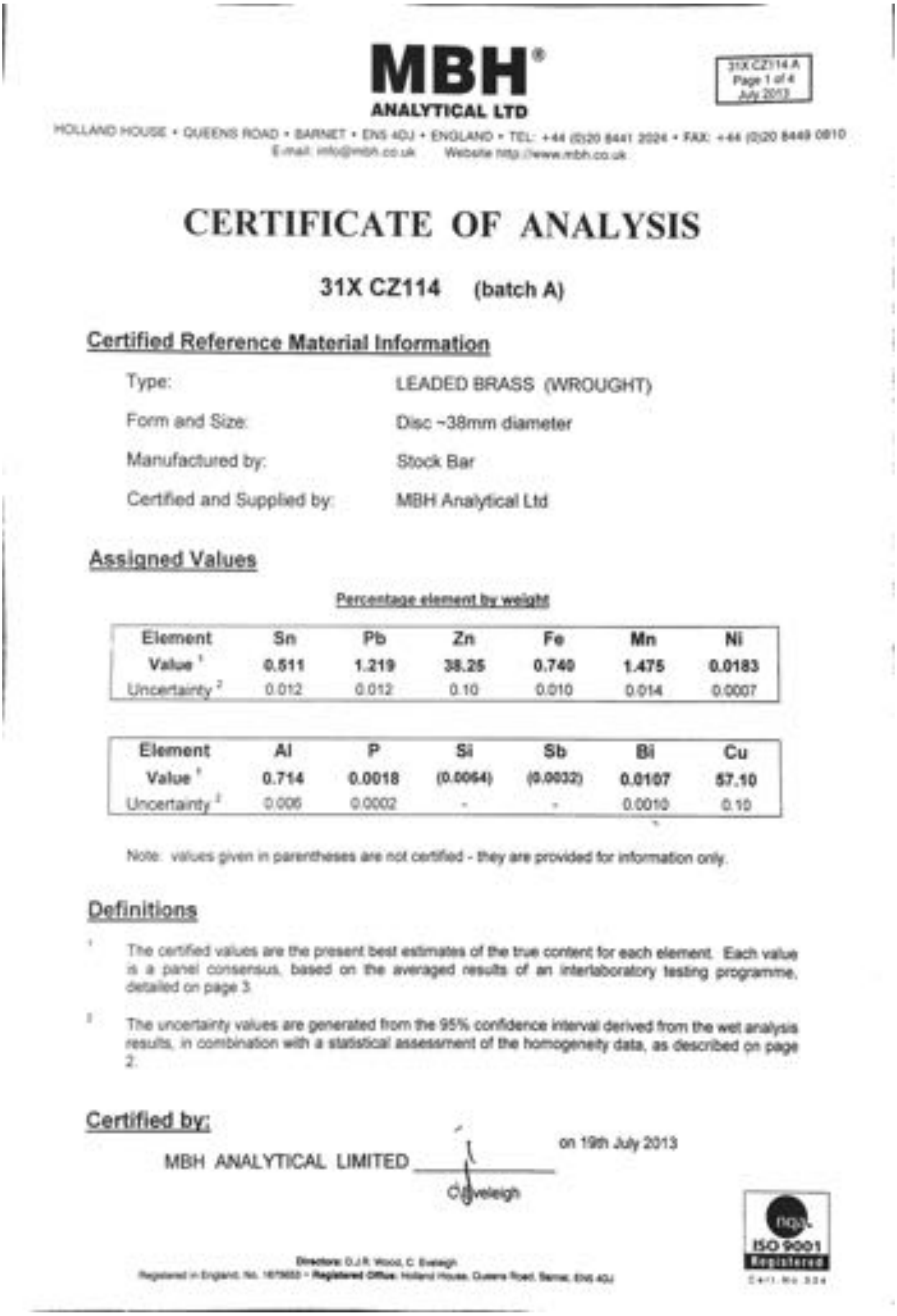
MBH ANALYTICAL LIMITED ____________ on 5th August 2008

C Eveleigh

ISO 9001 Registered
Cert No. [illegible]

Directors: D.J.R. Wood, C. Eveleigh
Registered in England, No. [illegible] • **Registered Office:** Holland House, Queens Road, Barnet, EN5 4DJ

Figure_Apx 1 Copy of reference standard for XRF analysis.



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31X CZ114 A
Page 1 of 4
July 2013

CERTIFICATE OF ANALYSIS

31X CZ114 (batch A)

Certified Reference Material Information

Type:	LEADED BRASS (WROUGHT)
Form and Size:	Disc ~38mm diameter
Manufactured by:	Stock Bar
Certified and Supplied by:	MBH Analytical Ltd

Assigned Values

Percentage element by weight

Element	Sn	Pb	Zn	Fe	Mn	Ni
Value [1]	**0.511**	**1.219**	**38.25**	**0.740**	**1.475**	**0.0183**
Uncertainty [2]	0.012	0.012	0.10	0.010	0.014	0.0007

Element	Al	P	Si	Sb	Bi	Cu
Value [1]	**0.714**	**0.0018**	(0.0064)	(0.0032)	**0.0107**	**57.10**
Uncertainty [2]	0.006	0.0002	-	-	0.0010	0.10

Note: values given in parentheses are not certified - they are provided for information only.

Definitions

[1] The certified values are the present best estimates of the true content for each element. Each value is a panel consensus, based on the averaged results of an interlaboratory testing programme, detailed on page 3.

[2] The uncertainty values are generated from the 95% confidence interval derived from the wet analysis results, in combination with a statistical assessment of the homogeneity data, as described on page 2.

Certified by:

MBH ANALYTICAL LIMITED ______________ on 19th July 2013
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Figure_Apx 2 Copy of reference standard for XRF analysis.

APPENDIX K: GUNSHOT RESIDUE ANALYSIS

GSR is useful in many aspects of investigation. It may be used to identify where holes were caused by ammunition, calculate firing distances, and most frequently, to determine whether or not a person was present during the discharge of a firearm [31] – [34], [38] – [40]. GSR is primarily composed of organic compounds from the propellant and inorganic elements resulting from the primer and the base of the projectile: e.g. lead, antimony, barium.

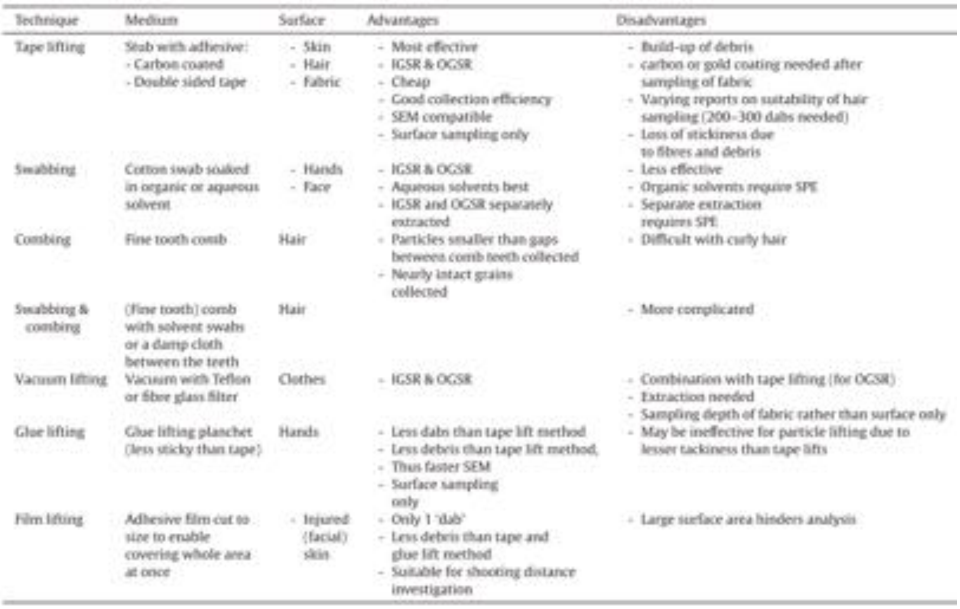
The Locard Exchange Principle refers to the notion of trace and transfer of evidence [60]. Schwoeble uses this principle when referring to the transfer of GSR however, then contradicts this statement articulating how “no direct contact is made between the hands and the airborne particle” [61]; thus, describing how GSR contrasts with most other types of transfer evidence. The principle of secondary transfer is still applicable here and contact between skin, clothes, and surrounding areas can facilitate the transfer of GSR. The possibilities of primary and secondary transfer must be taken into account when examining and evaluating GSR. Furthermore, it is susceptible to environmental conditions such as wind, rain and snow – providing results inconsistent with that of test fired ammunition under controlled conditions [61].

Understanding how GSR is created and deposited is fundamental to the collection process; predictably found on the hands, face, clothing of persons in the vicinity of a discharged firearm, and nearby objects [61]. Four areas on the hands are usually considered – the back and palm of each hand. When using rifles and shotguns, considerable amounts of GSR are deposited on the firer towards the face, hair and chest – the latter often landing on clothing where it will remain for longer than on skin [61].

GSR is time-sensitive and literature suggests that is should be collected as soon as possible after an incident. The standard time is between three and six hours as the quantity of particles will begin to decrease – particularly in relation to samples collected from skin [38], [40], [61]. GSR is more persistent on clothing, thus, any clothing suspected to have GSR present should be handled with caution in an effort to minimise the loss of evidence. It is important to note that physical activity and basic cleaning techniques (such as washing hands or clothes) will remove GSR [61].

Appropriately classed as trace evidence, the size of GSR particles can range from <1 µm to >100 µm. Typically, particles are between 1µm and 10 µm however, the range indicates the importance of not omitting the search for GSR particles because they are not visible [61].

There are several protocols available for gathering GSR evidence depending on the analytical technique that will be utilised. In any case, sterile gloves must be worn. The method of collection is dependent upon the analysis that will be conducted: For atomic absorption (AA) and inductively-coupled plasma (ICP) techniques, GSR it is collected using a cotton swab with a 5% nitric acid solution present. For scanning electron microscope (SEM) an adhesive disc known as a *stub* is used [27], [61]. The adhesive tapes used on the end of SEM stubs may be double-back tape, double-back carbon tape, or multiple-adhesive-layer tape. Goudsmit provides a summary of collection techniques for both organic and inorganic components of GSR (IGSR and OGSR, respectively) shown in **Fig_Appx_ 1.**



Technique	Medium	Surface	Advantages	Disadvantages
Tape lifting	Stub with adhesive: - Carbon coated - Double sided tape	- Skin - Hair - Fabric	- Most effective - IGSR & OGSR - Cheap - Good collection efficiency - SEM compatible - Surface sampling only	- Build-up of debris - carbon or gold coating needed after sampling of fabric - Varying reports on suitability of hair sampling (200–300 dabs needed) - Loss of stickiness due to fibres and debris
Swabbing	Cotton swab soaked in organic or aqueous solvent	- Hands - Face	- IGSR & OGSR - Aqueous solvents best - IGSR and OGSR separately extracted	- Less effective - Organic solvents require SPE - Separate extraction requires SPE
Combing	Fine tooth comb	Hair	- Particles smaller than gaps between comb teeth collected - Nearly intact grains collected	- Difficult with curly hair
Swabbing & combing	(Fine tooth) comb with solvent swabs or a damp cloth between the teeth	Hair		- More complicated
Vacuum lifting	Vacuum with Teflon or fibre glass filter	Clothes	- IGSR & OGSR	- Combination with tape lifting (for OGSR) - Extraction needed - Sampling depth of fabric rather than surface only
Glue lifting	Glue lifting planchet (less sticky than tape)	Hands	- Less dabs than tape lift method - Less debris than tape lift method, - Thus faster SEM - Surface sampling only	- May be ineffective for particle lifting due to lesser tackiness than tape lifts
Film lifting	Adhesive film cut to size to enable covering whole area at once	- Injured (facial) skin	- Only 1 'dab' - Less debris than tape and glue lift method - Suitable for shooting distance investigation	- Large surface area hinders analysis

Fig_Appx_ 1 Collection techniques for deposited GSR [59].

The literature on GSR is extensive and its significance has been reviewed periodically. Meng, Romolo, Dalby and Mahoney have all published reviews that not only cover the key facts, but also detail the progression involved in analysis [57], [62]–[64]. Error! Reference source not found. has been adapted from Dalby et al. and separates compounds based on their origin as well as whether they are organic or inorganic.

Table_Appx 1 Organic and inorganic compounds that may contribute to gunshot residue [63].

Organic Compounds

Propellant Powder

2,4,6-Trinitrotoluene (TNT)
2,4-Dinitrodiphenylamine (2,4-DPA)
2,3-Dinitrotoluene (2,3-DNT)
2,4-Dinitrotoluene (2,4-DNT)
2,6-Dinitrotoluene (2,6-DNT)
2-Nitrodiphenylamine (2-NDPA)
4-Nitrodiphenylamine (4-NDPA)
Akaridte II (AKII)
Butyl phthalate
Butylcentralite (N,N-Dibutylcarbanilide)
Camphor
Carbanilide
Carbazole
Cresol Dextrin
Dibutyl phthalate
Diethyl phthalate
Dimethyl phthalate
Dimethylsebacate
Dinitrocresol
Diphenylamine (DPA)
Ethyl centralite (N,N-Diethylcarbanilide)
Ethyl phthalate
Ethylene glycol dinitrate
Methyl cellulose
Methyl centralite (N,N-Dimethylcarbanilide)
Methyl phthalate
Nitrocellulose (NC)
Nitroglycerine (NG)
Nitroguanidine

Primer Mix

2,4,6-Trinitrotoluene (TNT)
Dextrin
Diazodinitrophenol
Diazonitrophenol
Gum Arabic
Gum tragacanth
Karaya gum
Nitrocellulose (NC)
Nitroglycerine (NG)
Pentaerythritol tetranitrate (PETN)
Rubber cement
Sodium Alginate
Tetracene
Tetryl

Nitrotoluene
N-nitrosodiphenylamine (N-NDPA)
Pentaerythritol tetranitrate (PETN)
Picric acid
RDX (Cyclonite) Resorcinol
Starch
Tetracene
Tetryl
Triacetin

Inorganic Compounds

Propellant Powder

Barium nitrate
Calcium carbonate
Potassium nitrate
Sodium sulphate

Primer Mix

Aluminium
Aluminum sulfide
Antimony sulfide
Antimony sulfite
Antimony trisulfide
Barium nitrate
Barium peroxide
Boron
Calcium silicide
Copper thiocyanate
Gold
Ground glass
Lead azide
Lead dioxide
Lead nitrate
Lead peroxide
Lead styphnate
Lead thiocyanate
Magnesium
Mercury
Mercury fulminate
Potassium chlorate
Potassium nitrate
Prussian blue
Silicon
Sodium nitrate
Strontium nitrate
Sulphur
Tin
Titanium
Zinc peroxide
Zirconium

Projectile/Case/Primer Cap

Aluminium
Antimony
Arsenic
Bismuth
Brass
Bronze
Chromium
Copper
Cupro-nickel
Iron
Lead
Nickel
Phosphorus
Red brass
Steel
Tungsten
Yellow brass
Zinc

The result will be a complex mixture of organic and inorganic particles which are driven out of the firearm and deposited onto surfaces or people. Goudsmit details the analytical techniques utilised for analysis of organic components and a comprehensive review on the application of mass spectrometry is also provided by Taudte [59], [65]. It was intended in this research to analyse the propellants, however, practical limitations prevented this from being possible. As such, these techniques shall not be discussed here.