FORENSIC ANALYSIS OF TRACE ELEMENTS FROM SMOKELESS POWDERS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS)

by

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Sincerely,

Nurul Athirah Binti Zailan

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LIST OF ABBREVIATIONS

AC	Alternating current
Al	Aluminium
amu	atomic mass unit
Ba	Barium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Cr	Chromium
Cu	Copper
DC	Direct current
Fe	Iron
Ge	Germanium
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometry
GSR	Gunshot residue
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HF	Hydrogen fluoride
HNO_3	Nitric acid
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
IED	Improvised explosive device
IGSR	Inorganic gunshot residue
In	Indium
K	Potassium
Li	Lithium

Lu	Lutetium
m/z	mass-to-charge ratio
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
NC	Nitrocellulose
NG	Nitroglycerin
Ni	Nickel
OGSR	Organic gunshot residue
Pb	Lead
Rh	Rhodium
Sb	Antimony
Sc	Scandium
SEM-EDX	Scanning Electron Microscopy-Electron Dispersive X-ray
Tb	Terbium
Th	Thorium
Tl	Thallium
U	Uranium
V	Vanadium
Zn	Zinc

ABSTRAK

Serbuk bahan api tanpa asap ialah sejenis bahan api yang digunakan dalam amunisi. Serbuk tersebut juga boleh ditemui pada peranti letupan terubah suai. Analisis forensik terhadap serbuk bahan tanpa asap kebiasaannya bertumpu kepada komposisi organik yang kebanyakannya membentuk kandungan serbuk tersebut. Dalam kajian ini, unsur tak organik dalam serbuk tanpa asap dikaji dengan menggunakan teknik analitikal Plasma Gandingan Aruhan-Spektrometri Jisim (ICP-MS). Enam jenis serbuk tanpa asap telah dipilih dan setiap jenis serbuk ini akan digandakan dua menjadikan keseluruhan jumlah sampel sebanyak dua belas. Bagi proses penyedian sampel, teknik pencernaan asid dengan teknik plat pemanas telah digunakan bertujuan untuk melarutkan serbuk dalam bentuk larutan. Sampel yang diproses kemudian dianalisis menggunakan ICP-MS. Hasil kajian ini telah mengesan kehadiran unsur-unsur natrium (Na), magnesium (Mg), aluminium (Al), kalium (K), kalsium (Ca), kromium (Cr), mangan (Mn), ferum (Fe), nikel (Ni), kuprum (Cu), zink (Zn), molibdenum (Mo), kadmium (Cd), antimoni (Sb), barium (Ba) dan plumbum (Pb) dalam kesemua dua belas sampel yang telah diuji. Unsur-unsur utama yang ditemui pada kesemua sampel termasuk Na, Al, Ca, Cu, Zn dan Pb manakala unsur-unsur minor yang dikesan ialah Mo, Mg dan Cd. Untuk unsur-unsur yang lain, kepekatan yang dikesan adalah berbeza bagi setiap sampel yang diuji. Hasil kajian ini mencadangkan bahawa perbezaan serbuk-serbuk tanpa asap kepada jenis masing-masing adalah sukar berdasarkan unsur-unsur tak organik yang dikesan sahaja. Namun begitu, kajian ini berjaya membuktikan idea kajian sebelum ini yang menyatakan bahawa sisa-sisa bahan api tak organik juga berkemungkinan berasal daripada sebuk bahan api tanpa asap, dan bukannya hanya daripada primer dan anak peluru dengan bukti kehadiran unsur-unsur tak organik dalam serbuk tersebut.

ABSTRACT

Smokeless powders are a class of propellants found in ammunition, which could also be encountered in improvised explosive devices. The analyses of smokeless powders are usually focused towards organic constituents that mostly made up their composition. In this study, inorganic elements of smokeless powders were aimed to be explored using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique. Six types of smokeless powders were chosen in which each type was duplicated into two samples, making a total of twelve samples. Hot plate procedure was used in acid digestion to dissolve the powders in acid solutions before analysed by ICP-MS. This study found the presence of elements of sodium (Na), magnesium (Mg), aluminium (Al), potassium (K), calcium (Ca), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), cadmium (Cd), antimony (Sb), barium (Ba) and lead (Pb) in all samples. The major elements detected in all types of samples were Na, Al, Ca, Cu, Zn and Pb while the minor elements detected were Mo, Mg and Cd. For other elements detected, they showed varying concentrations in every sample tested. This study suggested that it was difficult to differentiate the smokeless powders into their types based on inorganic elements alone. However, it has successfully strengthened the previous idea stating that it was possible that inorganic gunshot residue could also be originated from smokeless powder and not only from primer and bullet, with proof on the presence of inorganic elements in smokeless powders.

CHAPTER 1: INTRODUCTION

1.1 Ammunition

Ammunition or 'ammo' is propellant and projectile, or anything that can be used in combat including handguns, bombs, missiles, landmines and anti-personnel mines (Behymer, 2015). The entire live round of ammunition used in handguns, such as revolvers and pistols is composed of a cartridge case, primer, propellant, and a bullet or projectile (Hueske, 2015). Figure 1.1 illustrates the components of an ammunition for handgun (Scholasticus, 2013).

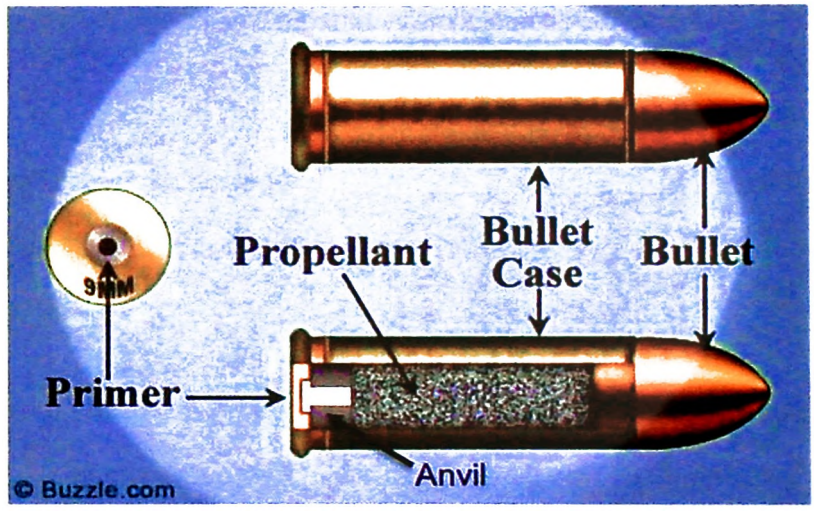

Figure 1.1: Components of an ammunition

The cartridge case or bullet case is a metal cylinder that houses the bullet, propellant, and primer in separate compartments. They are commonly composed of metal alloys, such as brass or steel, where brass is a copper (Cu) and zinc (Zn) alloy and steel is an alloy composed primarily of iron (Fe) (DiMaio, 2015). The primer, an explosive compound, is packed into the primer cup locating at the base of the cartridge case. Common primers are composed of lead styphnate, antimony sulfide and barium nitrate which act as initiator, fuel, and oxidiser, respectively (Hueske, 2015). The

combination of the primer metals, lead (Pb), antimony (Sb), and barium (Ba), in one gunshot residue (GSR) particle is the characteristic feature of GSR (Trimpe, 2011).

The propellant is loaded into the cartridge case on top of the primer compartment, beneath the bullet (Hay, 2013). There are several types of propellant used in small firearms. The early type of propellant used was black powder which was composed of charcoal, sulphur and potassium nitrate (Hay, 2013). Nowadays, the most commonly used propellants in small firearms are smokeless powders. The discharge of the weapon starts when firing pin of a firearm strikes the primer cup. The primer is compressed between the primer cup and an anvil causing the primer to explode. Anvil which is located between the primer and the propellant has vents that allow the flame to contact and ignite the propellant. The propellant deflagrates causing an increase of gas pressure inside the cartridge case. The tightly sealed cartridge case then builds up the pressure of gases causing the bullet to be ejected from the cartridge and move down the barrel of the firearm (Heard, 2011).

A cloud of gas, soot, primer residue and metallic components stripped from the bullet and cartridge case emerge from the barrel along with the bullet itself and these are deposited as GSR on surfaces in the proximity of firearms (DiMaio, 2015). Gunshot residue (GSR) originated from primers commonly contributes to Pb, Sb and Ba elements while GSR came from cartridge cases contains copper (Cu), zinc (Zn) and iron (Fe) elements (Hay, 2013). Propellant powders on the other hand, can contribute to both organic gunshot residue (OGSR) and inorganic gunshot residue (IGSR), (Miyauchi *et al.*, 1998, Heramb and McCord, 2002). The study of the contribution of organic constituents from smokeless powders in GSR has been explored viably for the past years (Heramb and McCord, 2002), while their inorganic elements are still in developing study (Miyauchi *et al.*, 1998).

1.2 Smokeless powders

Smokeless powders are a class of propellants found in ammunition and they may also be encountered in improvised explosive devices (IED) (de Perre *et al.*, 2012). They were developed in late 19th century to replace black powder as burnt materials in ammunitions. Smokeless powders provide much more propellant force than the same amount of black powder, which made it possible for weapon ranges to increase (Heramb and McCord, 2002). 'Smokeless' means the minimal residue left in the gun barrel following the use of smokeless powders (Heramb and McCord, 2002). Since smokeless powders do not leave behind as much residue as black powder does, the weapons require less cleaning after use (Bruno, 2001).

All smokeless powders are divided into three different classes based on their chemical composition of primary energetic ingredients (Dennis *et al.*, 2016). Single base powders contain nitrocellulose (NC) only, double base powders consist of a mixture of NC and nitroglycerin (NG), while triple base powders contain NC and NG with an addition of nitroguanidine (de Perre *et al.*, 2012). NC is a polymer that gives body to the powder and allows extrudability (Heramb and McCord, 2002). In double base powder, the NG raises the energy contents while the addition of nitroguanidine in triple base powder reduces flame temperature and so improves the energy-to-flame properties of propellant (Tilstone *et al.*, 2006).

Single base and double base powders are commercially available in markets as ammunitions in small firearms and rifles for application such as hunting and competitive target shooting (de Perre *et al.*, 2012), however the triple base powders are primarily used in large caliber ammunitions which typically limited to the military ordinance (Roberts *et al.*, 2015). The easy accessibility of smokeless powders in the markets contributes to their abusive in the production of IEDs (de Perre *et al.*, 2012). In addition

to energetic ingredients, the smokeless powders may also contain a myriad of additives, including stabilisers, lubricants, plasticisers, flash suppressants, deterrents and opacifiers which their functions are to improve stability, efficiency and also the burning properties of the smokeless powders (Joshi *et al.*, 2009). Beside the main organic compounds (single base, double base and triple base) and the additives, smokeless powders may also contain trace elements as a result of its manufacturing process (Douse and Smith, 1986).

The process of manufacturing smokeless powders gives sources of inorganic elements that are present in gunshot residue or in post blast residue (Heramb and McCord, 2002). Although not unique to propellant, the presence of the inorganic ions detected can be used in forensic analysis to aid in the identification of unknown powders (Heramb and McCord, 2002). A few elements may be added during the processing of the powder such as potassium sulphate, sodium sulphate, potassium nitrate, and barium nitrate (Heramb and McCord, 2002). Other compounds for examples nitrate, sulphate, hydrogen sulphide, chloride and nitrite may also appear as a result of chemical reaction for treating cellulose to obtain nitrocellulose (Radford Army Ammunition Plant, 1987 in Heramb and McCord, 2002).

1.3 Forensic analysis of smokeless powder

In forensic analysis, examination on the composition of smokeless powders and ammunition can be beneficial as they are able to deliver probative information concerning powder type and possible source attribution (Roberts *et al.*, 2015). Smokeless powders are often encountered as OGSR or as the explosive charge in IEDs (Heramb and McCord, 2002). Thus, forensic analysis of smokeless powders was mainly was carried out to investigate on the constituents of organic compounds in the powders. In a study by Miyauchi *et al.* (1998), they sparked an interest that there could be inorganic trace

elements from smokeless powders produced in GSR besides the elements that were originated from bullet and/or a primer.

Their idea meant that propellant powders could also contribute to IGSR to a greater degree than was previously thought. A study by Miyauchi *et al.* (1998) was one of the limited studies aimed to investigate the inorganic compounds, focusing on the contribution of trace elements originated from smokeless powder to post firing residues. They used scanning electron microscopy with energy dispersive X-ray (SEM-EDX) spectroscopy as their analytical methods to analyse smokeless powder which they then acknowledged that the approach of the discrimination each other only by SEM-EDX was difficult due to their large standard deviation (SD) (Miyauchi *et al.*, 1998). Besides, SEM-EDX requires a considerable amount of analyst time and expensive maintenance, and therefore, its implementation as a routine technique in forensic laboratories has come into question (Vanini *et al.*, 2015).

In this study, inductively coupled plasma-mass spectrometry (ICP-MS) was used as the analytical technique to analyse inorganic trace elements in six different kinds of smokeless powders. As ICP-MS requires liquid samples or aerosol samples for sample introduction, therefore it is a requirement for solid samples to undergo digestion process prior to ICP-MS.

1.4 Acid digestion

Acid digestion procedures are employed for elemental determination in solids subsequent to sampling and mechanical sample preparation to completely transfer the analytes into solution (ISO, 1972). They can then be introduced as liquid into the determination step in which ICP-MS is the instrumental technique used. The goal of every digestion process is to prepare a complete solution of analytes with complete decomposition of solid while avoiding loss or contamination of analyte (ISO, 1972). In

this context, wet chemical digestions utilising various mineral acids such as hydrochloric acid (HCl), nitric acid (HNO_3), hydrogen fluoride (HF), sulphuric acid (H_2SO_4) were carried out in either an open system or in closed vessels (ISO, 1972).

Aside from the various mineral acids, other reagents such as hydrogen peroxide, potassium peroxide sulphate and boric acid were also employed (ISO, 1972). Generally, the selection of specific reagents or the preparation of a reagent mixture highly depends on the sample to be digested (ISO, 1972). Open acid digestions are performed either with a reflux system or in a beaker on a laboratory hot plate (ISO, 1972). Open vessel acid digestions, one of the oldest techniques, are undoubtedly the most common method of sample decomposition or dissolution of organic and inorganic sample materials used in chemical laboratories. This technique is of inestimable value for routine analysis because it is inexpensive and can easily be controlled (ISO, 1972).

1.5 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is an analytical method applied for elemental determination (Santos *et al.*, 2015). The study of Houk *et al.* (1980) was the first to demonstrate the viability of ICP-MS for determination of elemental concentrations and isotopic abundance ratios, which was then all used in the different analytical fields since its commercial introduction in 1983 (Potter, 2008). For the past years, ICP-MS has been massively accepted as the "golden standard" for trace elemental analysis due to its high sensitivity (very low limits of detection) and also because of its high speed analysis (Santos *et al.*, 2015). In addition, it is also known to have unique facet compared to other similar functioning analytical techniques which is to provide isotopic information for elements detected in sample, making the technique useful in forensic analysis including in gunshot residue (GSR) analysis (Santos *et al.*, 2015).

A large range of elements can be detected using an ICP-MS, which are summarised in Figure 1.2. ICP-MS system is capable in quantitatively measure the coloured elements (yellow, blue and pink) in Figure 1.2, and give a measurement of the total amount of that specific element of interest (Bazilio and Weinrich, 2012). Figure 1.2 illustrates elements that can be detected by ICP-MS (Bazilio and Weinrich, 2012). An ICP-MS combines a high-temperature ICP source with a mass spectrometer (MS) (Wolf, 2005). The ICP source converts the atoms of elements in the sample to ions which are then separated and detected by mass spectrometer. The commonly ICP sources used are argon gas, helium gas and hydrogen gas (Wolf, 2005).

Figure 1.2: Elements detected by ICP-MS

The mechanism process of ICP-MS is broken down into four stages, namely sample introductions, ICP torch, interface, and mass spectrometry (MS) (Bazilio and Weinrich, 2012). First, the sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebuliser or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced the ICP torch, it is completely desolvated and the elements in aerosol form are converted first into gaseous atoms and then are ionised towards the end of the

plasma (Bazilio and Weinrich, 2012). When the sample arrives at the analytical zone of the plasma, at approximately 6000–7000 K, it exists as excited atoms and ions, representing the elemental composition of the sample. The excitation of the outer electron of a ground-state atom, to produce wavelength-specific photons of light, is the fundamental basis of atomic emission (Bazilio and Weinrich, 2012).

There is also enough energy in the plasma to remove an electron from its orbital to generate an ion. It is the generation, transportation, and detection of significant numbers of these positively charged ions that give ICP-MS its characteristic ultra-trace detection capabilities (Bazilio and Weinrich, 2012). Once the elements in the sample are converted into ions, they are then brought into mass spectrometer via the interface cones. The interface region of ICP-MS transmits the ions that travel in the argon sample stream at atmospheric pressure (1-2 torr) into a low-pressure region of mass spectrometer ($<1 \times 10^{-5}$ torr). Once the ions enter mass spectrometer, they are separated by their mass-to-charge ratio (m/z).

The most common mass spectrometer is the quadrupole mass filter. In a quadrupole mass filter, alternating alternate current (AC) and direct current (DC) voltages are applied to opposite pairs of the rods. These voltages are then rapidly switched along with a radio frequency field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/z) pass through the rods to the detector at a given instant in time (Bazilio and Weinrich, 2012). The quadrupole mass filter can separate up to 2400 amu (atomic mass units) per second, allowing it to perform simultaneous multi-elemental analysis (Wolf, 2005). The ability to filter ions based on their mass-to-charge ratio enables ICP-MS to provide isotopic information, since different isotopes of the same element have different masses (Wolf, 2005). Figure 1.3 illustrates the schematic of ICP-MS (Hay, 2013).

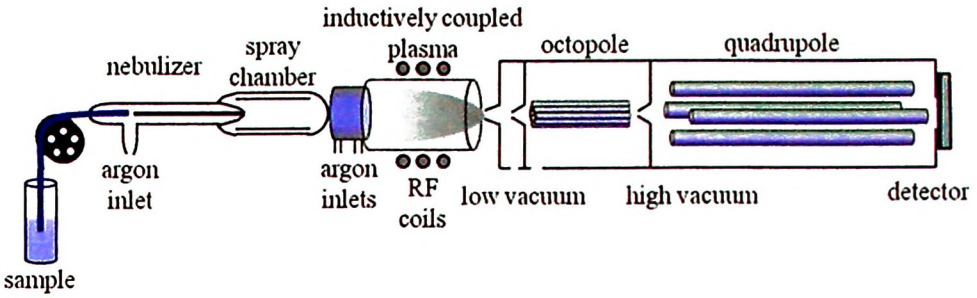

Figure 1.3: Schematic of ICP-MS

1.6 Aim and objectives

To the extent of literature review, an idea on the possible source of trace elements from smokeless powder that could contribute to GSR was generated. As there were only limited studies that have been carried out to prove and to expand the idea, this study was aimed to analyse trace elements from smokeless powders using ICP-MS. To achieve the aim, the objectives of the study are as follows:

i. To detect the presence of trace elements from six different types of smokeless powders,

ii. To quantify the trace elements detected for each type of smokeless powder.

iii. To differentiate smokeless powders on the basis of their manufacturers

The findings of this study could reveal trace elements (if any) from six different types of smokeless powders, which could be used for identification of smokeless powder and determination of product origin, which may greatly provide information during criminal investigation. This study could also suggest the presence of inorganic compounds in GSR which could potentially originated from smokeless powders.

CHAPTER 2: LITERATURE REVIEWS

2.1 Smokeless Powders

Previously, forensic analyses of smokeless powders mainly focused on the constituents of organic compounds using various types of analytical techniques including Gas Chromatography-Mass Spectrometry (GC-MS) (Andrasko *et al.*, 2003, Joshi *et al.*, 2011), Raman Spectroscopy (López-López *et al.*, 2012) and Fourier Transform Infrared Spectroscopy (FTIR) (López-López *et al.*, 2012). The process of manufacturing smokeless powders could introduce sources of inorganic elements into the composition of smokeless powders, which were detected in post blast residue (Heramb and McCord, 2002). These elements could be used in forensic analysis to aid the identification of the unknown powder (Heramb and McCord, 2002).

Despite knowing its importance, there were only limited studies about inorganic elements of smokeless powders that had been done previously. Miyauchi *et al.* (1998) study was one of the limited studies about the inorganic compounds of smokeless powder, focusing on the contribution of trace elements from smokeless powder to post firing residues. The study was done using twenty-two types of smokeless powders, classified from more than 2000 illegal rounds of ammunition, seized from Japanese gang group. Part of the samples was burnt while others remained in the original state. The samples were collected using SEM stub before being manually searched using back scatted electron imaging mode. The particles of interest on the stub were analysed subsequently by EDX.

The findings of the study stated that copper (Cu), sulphur (S), potassium (K), aluminium (Al), calcium (Ca), iron (Fe), chlorine (Cl) and barium (Ba) were found from burnt and unburnt smokeless powders using SEM-EDX (Miyauchi *et al.*, 1998). However, the burnt smokeless powder was lacked of Al due to its relatively easy vapourisation,

which showed that Al in GSRs has likely from primer and not smokeless powder. Apart from Al, other elements that were Si, S, Cl, K, Ca, Ba, Fe and Cu proved to be originated partly from smokeless powders. They also stated that the approach of the discrimination each other only by SEM-EDX was difficult by means of their large standard deviation (SD) (Miyauchi *et al.*, 1998).

2.2 Sample Digestion

As mentioned before, solid samples need to undergo digestion process to change them into liquid or aerosol forms before they can be introduced into ICP-MS. To the extent of literature review, there was lacking in literature that had done digestion process towards smokeless powders prior to elemental analysis performed. However, there were studies that stated the digestion process of gunshot residue from variable types of samples, in which the most popular digestion process was using acid digestion followed by microwave-assisted digestion (LaGoo *et al.*, 2010).

Nitric acids and hydrogen peroxide have been used by LaGoo *et al.* (2010) for the digestion of tissue and larvae samples containing GSR before proceeding to microwave digestion. The reagents used for digestion were not defined specifically for all tissue or other biological samples. However, the combination of an acid, such as nitric acid, and an oxidising agent, such as hydrogen peroxide, was well-documented (Sandroni and Smith, 2002). Nitric acid is a strong acid that does not form insoluble products, which means it can be used with a number of biological samples and analytical techniques (Hay, 2013). Hydrogen peroxide is commonly used as an oxidant to enhance the complete decomposition and solubilisation of the sample.

High burning rate and easily explode in confined space are the nature of smokeless powder. These characteristics make it a suitable burning material for ammunition and explosive devices (Bruno, 2001). Therefore, it is unsecure to proceed

digestion process using microwave-assisted digestion for smokeless powder samples. In this study, sonication and hot plate technique have been used to dissolve powders into acid. These techniques were used as they worked in opened-system which was suitable for smokeless powder.

2.3 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

To date, the author was unaware of any studies in the peer-reviewed literature that has demonstrated analysis of inorganic elements of smokeless powders using analytical ICP-MS. However, ICP techniques including ICP-MS have been used widely all around the world to study on the inorganic gunshot residue elements of lead (Pb), barium (Ba), and antimony (Sb) originated from primer residues (Schwoeble and Exline, 2000).

In 1998, a study by Koons reported the application of ICP-MS for the purpose of identifying gunshot residue originating from primers by the analysis of cotton-tipped swabs spiked with Sb, Ba, and Pb. Koons (1998) admitted the advantages of using ICP-MS compared to other instruments with its superior detection limits than Inductively Coupled Plasma-Atomic Emission Spectromentry (ICP-AES) and Graphite Furnace-Atomic Absorption Spectrometry (GF-AAS). He also stated that ICP-MS has faster analysis times than in GF-AAS. Besides, the use of MS for ICP has allowed the detection of several isotopes for each of the elements of interest which in the case were Pb, Ba and Sb (Koons, 1998).

The potential of ICP-MS for the determination of Sb, Ba and Pb has also been investigated in a study by Roeterdink *et al.* (2004) in which their study focused on the detection of GSR in larvae feeding on beef into which test shots had been previously fired. The larvae were digested in nitric acid on a hot-plate before the levels of elemental interests (Sb, Ba and Pb) in the digest were successfully determined by ICP-MS

(Roeterdink *et al.*, 2004). This approach was said to have potential for detecting GSR in cases where the visual assessment of gunshot wounds is problematic (LaGoo *et al.*, 2010). The study was conducted indoors under controlled conditions using beef contaminated with GSR, and hence an outdoor study using larvae collected from decomposing tissue was then being pursued by LaGoo *et al.* (2010).

In the study by LaGoo *et al.* (2010), the researchers had conducted both indoor and outdoor studies. An indoor study was initially conducted to demonstrate detection of the three elements (Sb, Ba and Pb) in larvae. In the study, beef contaminated with GSR was left to be deposited by medicinal maggots, and larvae were collected over the course of nine days. The larvae were microwave-digested and then analysed by ICP-MS. Then, two outdoor studies were conducted in two different climate conditions, one during late summer and one during the winter. In each study, one pig was shot eleven times and a second, stabbed pig was used as a control. Wound tissue and also larvae from the wounds were collected from each pig at the same time interval throughout the sampling period.

The GSR and control tissue samples were initially analysed by SEM-EDX to confirm the presence of GSR (LaGoo *et al.*, 2010). Then, the tissue and larvae samples were digested using microwave digestion method before being subsequently analysed by ICP-MS, investigating the persistence of the three elements through the decomposition process (LaGoo *et al.*, 2010). ICP-MS has also been reported as highly useful in the determination of levels of additional elements associated with the handling of a firearm or ammunition component, or elements which may be present in specific ammunitions for instance; strontium in some non-toxic primers, cobalt in Nyclad bullets, or copper, nickel, or zinc in jacketed bullets (Dalby *et al.*, 2010).

As far as the author concerns, there was no literature that was available in which ICP-MS was used to detect inorganic residue in smokeless powder. Miyauchi *et al.* (1998) in their paper showed the presence of trace elements detected from smokeless powders using SEM-EDX. In this research, the potential of ICP-MS for the detection of trace elements in smokeless powders is investigated.

CHAPTER 3: METHODOLOGY AND EXPERIMENTAL

3.1 Sampling

Six different types of smokeless powders were chosen in this study. These samples were sourced from four different manufacturers, namely Winchester (WCC, Alton, IL), Giulio Fiocchi-Leccon (G.F.L, Lecco, Italy), Sellier & Bellot (S&B, Prague, Czech Republic) and SME Ordnance Ltd. (SME, Malaysia). Amongst, two types of powders were obtained from SME and S&B, respectively. From SME manufacturer, two types of smokeless powders of two different ammunitions which were .38 and 9 mm were used. Similar to S&B, two types of smokeless powders were also chosen as samples which was 9 mm and 9x19 ammunition, respectively. Visual examination of all six types of smokeless powders was conducted and the observations were then noted.

3.2 Materials and Reagents

Concentrated nitric acid (HNO_3) of suprapure quality (65%, Fisher Scientific, Waltham, MA), ultrapure water (18.2MΩ·cm), prepared by a reverse osmosis system (PURELAB Mk2 Ultra, UK), and hydrogen peroxide (H_2O_2) (30%, Merck KGaA, Darmstadt, Germany), were used for sample preparation. All reagents and solvents were used as received.

3.3 Sample Preparation

All six types of smokeless powders were weighed twice to 0.2 ± 0.01 g in weighing boats making a total of twelve samples. The samples were labelled S1 to S12 as shown in Table 3.1. All the samples were then transferred to 100 mL beakers and clearly labelled. Then, 6 mL of HNO_3 were added to samples followed by 2 mL of H_2O_2. The samples were then proceeded to digestion process. The digestion began with sonication for 10 minutes, followed by heating using hot plate for approximately 30 minutes until all

powders dissolved in the acid solutions. Then, all the prepared solutions were filtered to obtain clear liquids for ICP-MS analysis. Prior to analysis, each filtrate was diluted in 50 mL volumetric flask using deionised water until 50 mL mark. After that, diluted solution of each sample was transferred to Teflon tube.

Table 3.1: Sampling of smokeless powders

Source of Manufacturer	Type of smokeless powder	Sample Name
Winchester	WCC 9 mm	S1 S2
Giulio Fiocchi-Lccon	GFL 9 mm	S3 S4
SME Ordnance	SME .38	S5 S6
Sellier & Bellot	S&B 9x19	S7 S8
SME Ordnance	SME 9 mm	S9 S10
Sellier & Bellot	S&B 9 mm	S11 S12

3.4 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

3.4.1 Instrument

Agilent's 7700 Series ICP-MS equipped with Agilent Integrated Autosampler (I-AS) and ICP-MS MassHunter Workstation software, Version 1.6 were used (Agilent Technologies, Santa Clara, California). Microsoft Excel® 2010 was also used for tabulating results from ICP-MS. Figure 3.1 illustrates the ICP-MS and autosampler in laboratory.

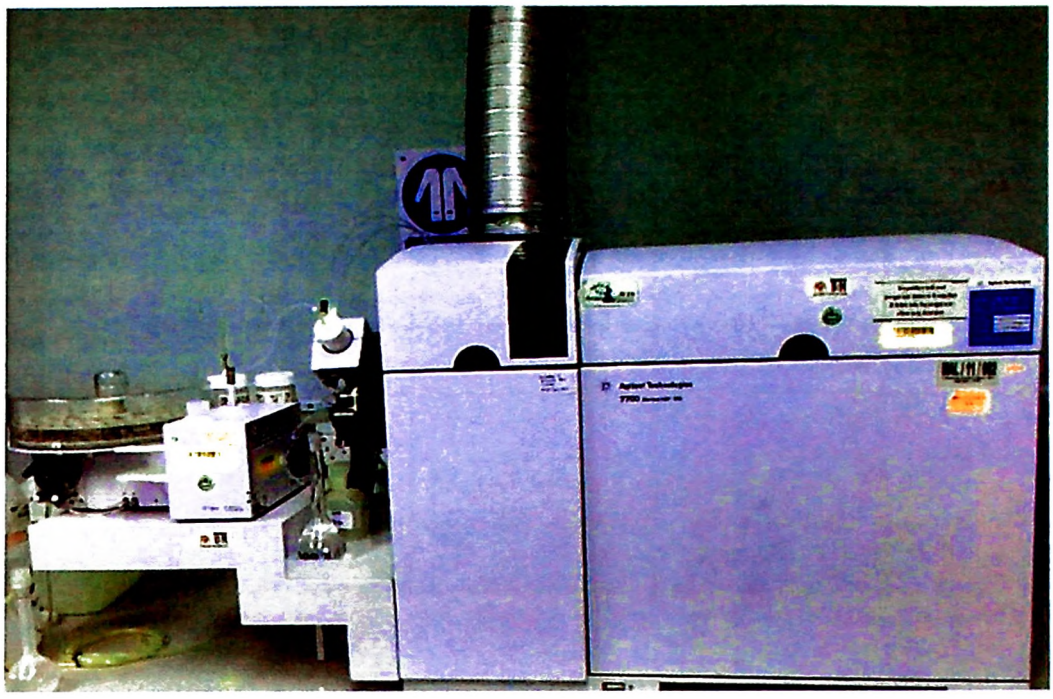

Figure 3.1: The ICP-MS and autosampler

3.4.2 Calibration and Standards

Internal standard solution (ISTD), containing 100 mg/L of Bi, Ge, In, Li, Lu, Rh, Sc and Tb was used in the experiment. Environmental calibration standards, containing 1000 mg/L of Ca, Fe, K, Mg, Na and 10 mg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V and Zn solution in 5% HNO_3 was also used as standards. Working stock solution was prepared with 1 to 10 dilution using the environmental calibration standards. Five mL of Environmental Calibration standards is diluted to 50 mL with reagent water containing 1.0% (v/v) HNO_3 and 0.5% (v/v) HCl. Care must be taken in the preparation of multi-elemental stock standards to ensure the elements are compatible and stable to be used in ICP-MS. Freshly prepared standards were then transferred to acid-cleaned flasks, and monitored periodically. Note that the working stock solution only can be stored in the refrigerator for 2 weeks. Calibration standards (CAL) were then prepared into different concentration as shown in Table 3.2.

Table 3.2: Calibration Standards Preparation

CAL ID	Calibration level	Calibration concentration (ppb)	Volume of working stock solution	Final volume (mL)
CalBlnk	0	0	0	50.0
CAL1	1	10	0.5	50.0
CAL2	2	20	1.0	50.0
CAL3	3	40	2.0	50.0
CAL4	4	80	4.0	50.0
CAL5	5	160	8.0	50.0

3.4.3 Quality Control Sample (QCS)

To verify that the calibration standards were within the determined mean concentration, three analyses of the QCS was conducted. The measurements should not exceed ±10% of the established QCS value.

3.4.4 ICP-MS Operating Parameters

ICP-MS was operated using the parameters as stated in Table 3.3.

Table 3.3: Inductively-Coupled Plasma-Mass Spectrometry Operating Parameter

Acquisition Parameter	
Acquisition mode	spectrum analysis (multi tune)
Total acquisition time	112 sec
Number of repetition	3 times
Plasma Condition	
RF power	1600W
RF matching	1.7 V
Torch-H	-0.3mm
Torch-V	-0.1mm
Carrier gas	0.8 L/min
Dilution gas	0.17 L/min
Nebulizer pump	0.1 rps
Ion Lenses	
Extract 1	0 v
Extract 2	-180 V
Omega bias	-80 V
Omega lens	8 V
Octopole Parameters	
Octp RF	180 V
Octp Bias	-18 V
Detector Parameters	
Discriminator	4.5 mV
Analog HV	1752 V
Pulse HV	1026 V

3.5 Statistical Analysis: Principle Component Analysis (PCA)

PCA was the statistical test chosen in this study to investigate the pattern of different types of smokeless powders on the basis of elemental profiles. The elements that were detected in all samples were used for data interpretation and analysis. Minitab 16.2.3 (State College, Pennsylvania) was used as statistical software in this study.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Visual observation of smokeless powders

All six types of smokeless powders were observed by naked eyes for their physical characteristics. The results of visual observation were showed in Table 4.1.

Table 4.1: Visual Observation of smokeless powders

Smokeless powder type	Visual observation of smokeless powder
SME .38	Ball shaped, black colour and shiny feature.
SME 9 mm	Flattened ball shape, grey colour and shiny feature.
S&B 9 mm	Lamella shaped, green colour and has presence of red kernels among the flakes.
S&B 9x19	Flattened ball shape, grey colour and shiny feature.
WCC 9 mm	Thin disc shaped, green colour.
GFL 9 mm	Lamella shaped, black colour.

Visual examination of smokeless powder revealed a variety of different characteristics including general morphology, lustre, colour and the presence of coloured kernels. Flattened ball shape morphology could be seen in SME 9 mm and S&B 9x19 types of smokeless powders. S&B 9 mm and GFL 9 mm types have lamella shaped powders. Lamella shaped powders have a tablet or plate dimensions whose general morphology is rhombic, diamond and square shaped. S&B 9 mm consisted of varied lamella shaped kernels while GFL 9 mm contained kernels of square-shaped. Only SME .38 type has ball shaped morphology as it made up of primarily ball shaped kernels and no flattened ball was observed. WCC type on the other hand was believed to have thin disc shaped powder as it showed potato chip and taco shapes indicating by specific characteristics of thin disc shaped. Morphology of smokeless powder could be used for

brand determination besides lending clues to whether a powder is single base or double base (Beveridge, 1998).

In term of colour, varying colours were observed in all types of smokeless powders. By naked eyes, the colour of SME .38 and GFL 9 mm types were black, SME 9 mm and S&B 9x19 were grey while the other two types (S&B 9 mm and WCC) were green in colour. Lustre represents the shininess of the kernel in reflected light. Among six types of smokeless powders observed, only three of them have lustre feature namely SME .38, SME 9 mm and S&B 9x19. These smokeless powders showed shiny features when observed under light, different from the rest of powder types that showed dull characteristic. The finding of a coloured kernel such as red, white, blue or green might point to a specific brand or narrow down the brands of smokeless powders. From the observation, red coloured kernel has been detected from S&B 9 mm type of smokeless powder. This red kernel could possibly been added intentionally by manufacturer for identification purpose for S&B 9 mm.

4.2 Detection of trace elements

ICP allowed the detection of certain trace elements from six different types of smokeless powders. The results from ICP-MS analysis was given in ppb unit as shown in Table 4.2 which was then converted to µg/g unit as shown in Table 4.3. It showed that ICP-MS analysis allowed the detection of sodium (Na), magnesium (Mg), aluminium (Al), potassium (K), calcium (Ca), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo), cadmium (Cd), antimony (Sb), barium (Ba) and lead (Pb) in all twelve samples.

Table 4.2: Elemental profiles of smokeless powders by ICP-MS analysis in ppb

	Type of smokeless powder											
	WCC 9 mm		GFL 9 mm		SME .38		S&B 9x19		SME 9 mm		S&B 9 mm	
	Concentration of elements [ppb]											
Element/Sample	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**
Na	203.40	92.13	110.54	107.50	92.48	109.26	111.19	108.13	118.64	101.40	103.95	115.74
Mg	26.98	12.49	15.48	14.85	12.33	13.91	13.19	14.02	15.19	13.16	13.39	14.83
Al	376.10	181.30	248.44	187.66	220.45	162.04	175.12	238.77	321.28	101.09	390.56	110.15
K	14.89	6.99	73.43	74.50	73.32	73.60	93.97	82.59	69.65	68.62	7.43	5.72
Ca	127.93	54.76	60.96	60.95	65.93	72.95	92.71	96.11	73.03	66.58	57.65	61.34
Cr	63.29	25.28	29.58	29.90	49.85	24.96	30.07	46.60	372.95	97.65	2101.20	37.47
Mn	18.71	19.42	15.70	30.64	26.73	21.11	14.82	17.81	54.05	20.92	162.40	22.77
Fe^{2+}	11.87	14.84	6.58	11.18	8.32	5.31	6.18	7.06	19.19	6.86	97.05	4.39
Fe^{3+}	12.24	15.06	6.73	11.44	8.12	5.58	6.26	7.16	19.60	6.84	96.59	4.27
Ni	52.03	16.10	28.66	23.24	14.70	18.76	24.54	42.11	330.80	77.31	1135.17	20.05
Cu	237.09	218.35	57.07	49.74	99.90	129.30	55.85	36.55	67.01	98.87	167.16	171.53
Zn	660.85	360.99	366.61	226.34	371.70	390.61	446.43	256.18	391.77	328.78	412.34	267.25
Mo	6.30	2.21	2.52	2.06	2.58	2.97	1.53	1.74	7.30	7.27	37.35	1.61
Cd	2.46	1.37	0.74	1.25	2.08	2.55	1.48	0.67	1.51	0.95	2.72	3.67
Sb	56.20	35.26	2.44	0.64	24.89	4.48	19.57	0.62	12.87	1.57	3.61	20.02
Ba	194.37	182.88	284.67	19.54	53.65	10.44	12.40	22.38	14.34	6.34	28.90	18.89
Pb	305.82	272.79	118.92	142.55	469.76	452.70	4164.48	97.46	258.23	149.63	251.95	191.30