THE USE OF SURFACE FUNCTIONALISED SILICA NANO-PARTICULATE POWDERS FOR THE IDENTIFICATION OF GUNSHOT RESIDUES FROM FINGERPRINTS

by

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ABSTRACT

Gunshot residue (GSR) mixture consists of partially burned particles of propellant and characteristic particles of elements originating from the primer, bullet, propellant and some additives in the propellant. Since Harrison and Gillory [1] drew forensic scientists' attention to the fact that GSR contained trace amounts of inorganic compounds such as lead, barium and antimony, a number of analytical techniques have been tested trying to find and establish sensitive, selective and reliable methods to identify and analyse gunshot residues. The standard procedure for the analysis of gunshot residues involves imaging these small metallic particles using scanning electron microscopy (SEM) and subsequent compositional analysis using Energy Dispersive X-ray Analysis (EDX).

This study focuses on the analysis organic compounds in GSR. It is motivated by the increasing need to overcome the problems with the analysis of lead-free ammunitions. A comprehensive literature review was performed in order to determine the most commonly encountered organic compounds in GSR. These compounds include diphenylamine, methylcentralite, ethylcentralite, nitroglycerine, 2-nitrodiphenylamine and 4-nitrodiphenylamine. It has been clearly demonstrated using standard materials and appropriate calibration curves that gas chromatograph and mass spectrometry (GC/MS) is capable of providing limits of detection that are consistent with the concentrations of the key organic constituents found in gunshot residues. Furthermore, we have demonstrated that the relative concentrations of seven key components can be used to provide branding information on the shotgun cartridges.

A strong relationship was found between the chemical composition of fired and unfired powder. Therefore, it is possible to differentiate between two ammunition brands through the analysis of the organic constituents.

Traditional fingerprint powders such as titanium dioxide, aluminium, carbon black, iron oxide, lycopodium spores and rosin are used to enhance fingerprint left at the scene of crime. More recently nanoparticles have been demonstrated to be highly effective for the enhancement of the fingerprints [2].

Silica nano-particulates of defined size and shape were synthesised and functionalised with two different functional groups (phenyl and long chain hydrocarbon) using a Tri-

phasic Reverse Emulsion (TPRE) method. These nano-particulates were characterised using scan electron microscope (SEM), transmission electron microscopy (TEM), elemental analysis, particles size analyser, BET surface area and solid-state nuclear magnetic resonance (NMR) spectroscopy. These powders were used as an effective agent to visualise latent fingerprints on different surfaces. Furthermore, they have been utilised to absorb any organic materials within the fingerprint from the discharged of weapon. Analyses of the adsorbed organic residues were performed using GC/MS and Raman spectroscopy.

The results showed that the synthesised silica nano-particulate fingerprint powder gave better result in term of their ability to absorb organic materials in GSR and enhance the visualisation of the latent fingerprint compared to a single commercial powder.

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LIST OF ABBREVIATIONS

AAS:	Atomic Absorption Spectroscopy.
AFIS:	Automated Fingerprint Identification System.
AK II:	Akardite II.
BET:	Brunauer-Emmett-Teller.
BJH:	Barrett–Joyner–Halenda.
CC:	Cartridge Cases.
CCD:	Charge-Coupled Devices.
CE:	Capillary Electrophoresis.
Cu:	Copper.
CI:	Chemical Ionisation.
CSI:	Crime Scene Investigation.
CZE:	Capillary Zone Electrophoresis.
CPMAS:	Cross Polarization Magic Angle Sample Spinning.
DART:	Direct Analysis in Real Time.
DBP:	Dibutylphtalate.
DC:	Direct Current.
DESI-MS:	Desorption Electrospray Ionization and Mass Spectrometry.
DLAS:	DL-amphetamine sulphate.
DPA:	Diphenylamine.
EC:	Ethylcentralite.
ECD:	Electron Capture Detector.
EDAX:	Energy Dispersion Analysis by X-Ray.
EI:	Electron Impact Ionisation.
ESIMS:	Electrospray Ionization Mass Spectrometry.
FBI:	Federal Bureau of Investigation.
FT:	Fourier Transform.
GC:	Gas Chromatography.
GC/MS:	Gas Chromatograph/Mass Spectrometer.
GC-NPD:	Gas Chromatography and Nitrogen Phosphorus Detector.
GC/TEA:	Gas Chromatograph/Thermal Energy Analysis.
GC-NPD:	Gas Chromatography and Nitrogen Phosphorus Detector.
GSR:	Gunshot Residue.
HPLC:	High Performance Liquid Chromatography.
LC:	Liquid Chromatography.
LOD:	Limit of Detection.
LR:	Long Rifle.
IAFIS:	Integrated Automated Fingerprint System.
ICP-MS:	Inductively Coupled Plasma-Mass Spectrometry.
IS:	Internal Standard.
IMS:	Ion Mobility Spectrometry.
IR:	Infrared.
MECE:	Micellular Electrokinetic Capillary Electrophoresis.
MC:	Methylcentralite.
MS:	Mass Spectrometer.
MRM:	Multiple Reaction Mentoring.
M/z:	Mass to Charge ratio.
Min:	Minute.

NAA: Neutron Activation Analysis.
NC: Nitrocellulose.
NG: Nitroglycerine.
NIR: Near-infrared.
Ng: Nano gram.
-NO2: Nitro group.
Nm: Nano meter.
NMR: Nuclear Magnetic Resonance.
MS/MS: Tandem Mass Spectrometry.
OGSR: Organic Gunshot Residue.
Pb-Ba-Sb: Lead – Barium – Antimony.
PCA: Principle Components Analysis.
PDA: Photo Diode Arrays.
pg.: Pico gram.
Ppm: Parts per million.
Ppb: Parts per billion.
PMT: Photomultiplier Tubes.
RF: Response Factor.
RT: Retention Time.
SEM: Scanning Electron Microscope.
SFE: Supercritical Fluid Extraction.
SIM: Selected Ion Monitoring.
S/N: Signal-to-Noise ratio.
SRM: Standard Reference Material.
SPE: Solid Phase Extraction.
SPME: Solid Phase Micro Extraction.
SD: Standard Deviation.
TEM: Transmission Electron Microscopy.
TIC: Total Ion Chromatogram.
TLC: Thin Layer Chromatography.
TNT: Trinitrotoluene.
TOF/MS: Time-of-Flight Secondary Ion Mass Spectrometry.
UV: Ultraviolet.
USE: Ultrasonic Solvent Extractions.
Zn: Zink.
2-NDPA: 2-nitrodiphenylamine.
4-NDPA: 4-nitrodiphenylamine.
2, 4-DNT: 2,4-dinitrotoluene.
2, 6-DNT: 2,6-dinitrotoluene.

1 INTRODUCTION

1.1 Gunshot Residues

During the last two decades, the number of countries where gun crimes have been committed has increased significantly [3-8]. That said, there has been a decrease in the number of incidents involving firearms in England and Wales between 2011 and 2012 compared to the previous year [9], due to the strict law on the possession of weapons. However, this decline does not diminish the importance of the risk of this type of crime. The increase in such crimes has brought about significant challenges to forensic scientists in determining whether or not a particular person has fired the gun.

In a case where firearms have been involved, there are a variety of things that an investigator has to look for. The firearms investigators will look for markings on the bullets or on cartridge cases. In addition, the investigator looks for and collects gunshot residues left on a target or hand of a person who is alleged to have fired the gun [10].

Physical and chemical examinations of evidence have provided solutions in a significant number of crimes committed involving firearms [10]. Comparison microscopy is one of the most reliable methods for the identification of a cartridge case or bullet that has been recovered from the crime scene or from a body. This technique relies on matching unique marks on the cartridges or bullets with the suspect firearm [11]. When a bullet or cartridge case is highly damaged, the quality of characteristic marks may not be sufficient to link them to particular weapon. In such cases additional evidence is essential. Another means of linking a suspect to the discharge of a firearm is through the detection and analysis of characteristic gunshot residues (GSR) [12].

GSR is a type of physical evidence that falls into the category of trace evidence [13], which is frequently invisible without the use of magnification or analytical techniques. GSR has become one of the most highly examined sources of trace evidence at crime scenes involving shooting incidents [14]. There have been many cases where individuals who were not previously considered suspects were tied to the scene of a crime through the analysis of a weapon’s discharge residue [13].

A number of factors must be taken into account in order to ensure the significance of GSR evidence [13]. One of these factors is the area in which the residue is found. The

GSR can be located on the clothing or hands of individuals who were near a firearm when it was discharged [15]. Depending of atmospheric conditions the estimated contamination range for discharged GSR is 60 cm in the case of handgun and 2 m for rifles [16]. The residue can also be found on objects that were near a weapon when it was fired [13].

In order for law enforcement investigators to make full use of the advances in GSR analysis it is important that they understand how the residue is deposited [13]. These investigators can include a wide range of personnel, including evidence collection officers, forensic examiners, police officers and medical staff [17]. A variety of other individuals also come in contact with victims or suspects of a violent crime who need to understand the implications of GSR collection [18], in terms of the different types of media that can be used for collection of the trace evidence at crime scenes. A variety of important questions can be answered by careful analysis of GSR [19], as described in Section 1.3.3. For example, one can frequently determine who fired a gun by analysing the residue of the gunshot [13].

1.1.1 Ammunition

The calibre of ammunition is normally determined by measuring the diameter of the bore inside the firearm. The ammunition of a weapon can either be rim fire or center fire. In rim fire ammunition, the materials of the primer are concentrated around the outer edge of the base of the cartridge, making the rim the most susceptible to detonation. On the other hand, center fire priming is concentrated at the center of the base of the cartridge, making this the most susceptible to ignition [20].

The type of cartridge used as ammunition is an important part of how the GSR is formed [21]. The components of the cartridge casing frequently become part of the GSR, such as brass (copper/zinc), steel, nickel and aluminium.

A round of ammunition, as illustrated in Figures 1.1 and 1.2, consists of the casing, primer, gunpowder, and projectile. This group is known as the cartridge. If the cartridge is being used in a shotgun, there is also a wad [20].

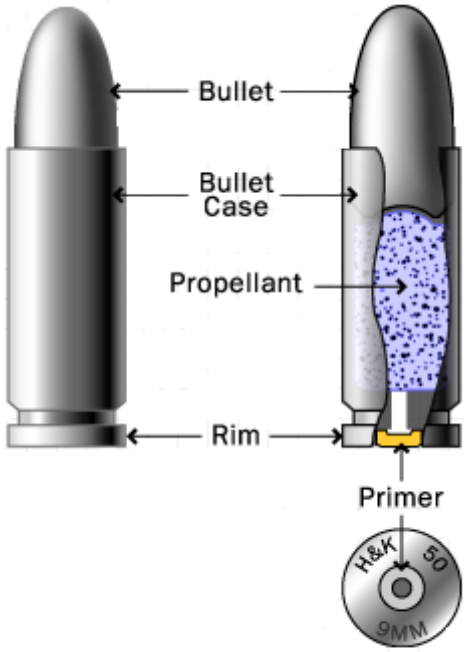

Figure 1.1. The composition of small arms ammunition [22]

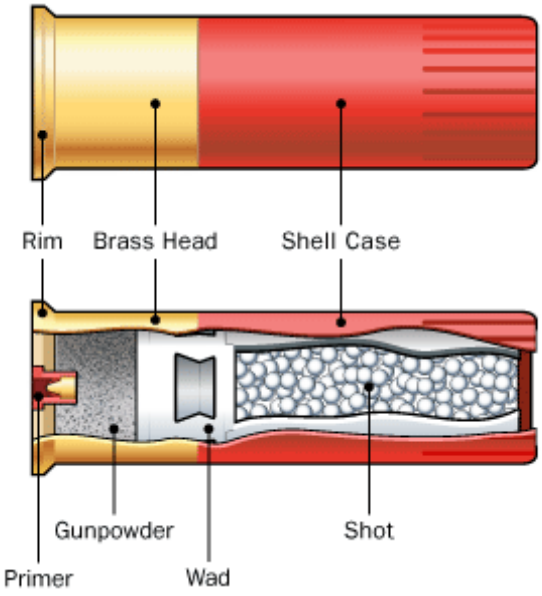

Figure 1.2. The composition of shotgun ammunition [23]

1.1.1.1 The Cartridge

The casing of the cartridge, except for shotgun cartridges, is usually metal and holds together all the different materials. The most common material used for cartridge casings is brass. Brass consists of 30% zinc (Zn) and 70% copper (Cu). This type of brass is also known as cartridge brass. Brass is used in the majority of cartridge casings for a number of reasons, including low cost, high performance, and ease of manufacture [10]. Other materials used to form cartridge casings include steel, aluminum, Zn, and plastic. Steel casings were used for 0.45 calibre ammunition and some German 8 mm ammunition during World War II. Steel cartridge casings are still used for a few types of ammunition such as 7.62 x 39 mmR for AK47 and its variants [10]. While steel is cheaper than brass, it can cause abrasions and rust in the chamber of the weapon; this can also produce unique GSR particles. It should be noted that a number of different ratios of brass and Cu have been experimented with to produce cartridge casings. The use of Cu alone is rare for a cartridge casing due to its insufficient strength to handle the high pressure involved with smokeless powder [20]. There are not presently any cartridge casings made completely of Zn (as this metal does not have the required properties). However, a few manufacturers combine Zn and Cu in specific proportions to produce high-quality brass casings. These casings are less common and more expensive than standard “cartridge brass”. They often create a distinctive GSR, which can be used to identify this type of ammunition [24]. If an unusual material is used as part of the cartridge casing, this can be used to identify a particular type of ammunition, such as silica (Si), calcium (Ca), aluminium (Al), iron (Fe), sulfur (S), phosphorus (P), nickel (Ni), potassium (K), chloride (Cl) and copper and zinc (Cu and Zn) together [20].

1.1.1.2 The Bullet

The bullet is the projectile that travels from the barrel of a gun towards a target after it has been fired (Figure 1.1). The majority of bullets used in an automatic pistol cartridge consist of a lead core enclosed within a full metal jacket. The jacket may be made from copper alloyed with 5 to 10% zinc (known as “gilding metal” or bronze), or ether brass, nickel or aluminium. The lead is alloyed with antimony, tin, or both. Some Russian bullets have a copper “wash” over a steel core, while some bullets contain a copper jacket covering the base and cylindrical portion, leaving soft metal at the tip [14].

Revolver bullets are lead or lead with a thin layer of copper (copper "wash"). The presence of lead or a combination of lead with brass or copper is often revealed in GSR particles associated the bullet [25]. Some bullets are coated with nylon (Federal "Nyclad®" brand) or black copper oxide (Winchester "Black Talon®"). Lead-free bullets are becoming more common, including all copper, or polymer-tungsten matrix [16].

Shotgun pellets are traditionally made of lead or lead alloyed with antimony or tin, or both. Lead-free shotgun loads are now widely available, including steel, tungsten and bismuth and a variety of alloys of these metals with tin, nickel, and bronze (e.g. Lyalvale "Hevishot™", which is an alloy of tungsten, nickel and soft iron [26, 27]). Polymers such as nylon have also been used [16].

The bullet itself can often provide important components of the GSR [6]. Lead is volatilised from the base of the bullet by the burning propellant at high pressure. Cu or Cu/Zn jacket bullet coatings can similarly release particles during firing. Furthermore, each shot fired results in contact between the bullet and the rifling, which will cause surface material to be stripped away from the bullet and released; residues left in the barrel from previous shots may also be driven out. Lead will be deposited on cloth as the bullet passes through before impacting with the target. If the bullet is jacketed it may have acquired primer residues while passing through the bore, which may also be left on any surface through which it passes. Bullets will often pass completely through an object or body leaving an entrance and exit hole. In general, the entry hole will test positively for lead, as will the inner surface of the exit hole. In addition to lead, bullets may acquire Zn or Cu from the inside of the cartridge case, which is transferred to the GSR on the bullet entry hole [6].

1.1.1.3 The Propellant

Over recent decades, smokeless powder has become more acceptable as a propellant of bullets instead of traditional black powder. Smokeless powders are classified as single, double, and triple based powder. The classification depends on the type of energetic materials that have been used. Single' based powders consist of nitrocellulose (NC), double base powders incorporate both nitrocellulose and nitroglycerine (NG), while triple base powders also include nitroguanidine [28].

Nitrocellulose and nitroglycerine are the most common propellants used in identifying gunshot residues; however, care must be taken as these compounds are not unique to GSR. NC can be found in lacquers, varnishes, and celluloid films, while NG is used in pharmaceutical preparations [29].

Most smokeless powder compositions contain a number of additives. These additives are used as stabilisers, plasticisers, flash inhibitors, coolants, moderants (burning rate moderators) and surface lubricants. Depending on its use, a particular powder propellant consist of one or more of these additives [14].

Diphenylamine (DPA), centralite and resorcinol are the most frequently used stabilisers in smokeless powder, particularly in single base powder, and form 1% of the total content of smokeless powder. DPA absorbs any free nitrogen dioxide (NO_2), keeping the propellant stable in long term storage; calcium carbonate is sometimes also used for this purpose. In addition, the main reaction products of nitrous oxide gases and DPA are 2-nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA), and N-nitrosodiphenylamine (N-NDPA), which have been reported to be the most common stabilisers in gunpowder [14, 30]. The use of DPA is not unique to smokeless powder; it is commonly used in rubber products and in the food industry [31], however the use of DPA in these industries is not normally associated with nitrating agents [30], which is considered to be unique to GSR [30, 32]. Care should be taken while linking the presence of DPA to the discharge from a weapon.

The centralites are another group of stabilisers and burning rate moderators that may be used in smokeless powder. Ethylcentralite (EC) is the most frequently used, although methylcentralite (MC) can also be used. In some cases, methylcentralite and Akardite II (AK II or 1-methyl-3,3-diphenylurea) are found in double base propellant powders [14].

Nitrocellulose or nitroglycerin decomposes in the air spontaneously, producing nitrous and nitric acids. This in turn causes further decomposition. The function of the stabiliser is to slow down the decomposition of nitrocellulose and nitroglycerine by removing the nitrous and nitric acids produced [30]. It is rare to find EC and MC compounds in the normal environment, so they are considered to be credible organic GSR [29].

During the process of making powder grain, plasticisers (also called gelatinizers) are combined with powder mixtures provide reinforcement and flexibility to the grains [31]; they also slow the rate of burning [16]. The most common plasticisers used are

glyceryltriactate (triactin), diethylphthalate (DEP), and dibutylphtalate (DBP) [31]. Calcium carbonate, resorcinol (*m*-dihydroxybenzene) and dinitrotoluene are also used [16]. However, plasticisers such as the phthalates, resorcinol and triacetinetc are common place in the environment and therefore do not form good indicators of GSR. In some smokeless powder, dinitrotoluenes and nitroguanidine have been employed as flash suppressers. The function of the flash suppresser in smokeless powder is to produce nitrogen gas to reduce the ignition of gases at the muzzle [14].

Normally, the powder grains are coated by a graphite to prevent any hazards that may arise from static electricity. Another function of using graphite is that it acts as a low friction surface to improve the flow properties of powder during cartridge manufacture [14]. Graphite also acts as a burning rate moderator, delaying the ignition of the propellant particles [16].

1.1.1.4 The Primer

The primer is made of a brass cup, which is frequently nickel plated [25]. The primer cup generally has a thin layer of primer compound on top, kept in place by a foil seal. The primer cup also has an anvil that is usually made of brass. In general, pistol primers are manufactured for small and large calibre pistols. The primers for small pistols are 0.175 inches. Those designed for larger pistols are 0.210 inches [25]. Primer mixtures consist of four basic chemical components: the initiating explosive, oxidizing agent, fuel and sensitiser. Each component can contribute some elements to the gunshot residues after a gun has been fired [1].

Lead styphnate is the most commonly used standard explosive initiator in the primer. In the past, lead azide and mercury fulminate were used as initiators of the primers. However, they are no longer commonly used, since the intensity of flame produced is insufficient, and a corrosive effect is imparted by mercury fulminate to gun barrels. They are still found in some Chinese and Russian ammunition. On occasion, potassium chlorate is also used in ammunition despite also being corrosive [33]. To increase the heat of ignition in the primers, an oxidizing agent is used [1]. Barium nitrate, barium peroxide, lead nitrate, or lead peroxide are usually used as the oxidizing agent.

The compound antimony trisulfide is commonly used as fuel in primers, but calcium silicide, lead thiocyanate, powdered aluminum, powdered zirconium, magnesium and titanium are increasingly being utilised. In small-arm primers, the standard sensitiser

material used is the explosive tetracene (1-(5-tetrazolyl)-4-guanyltetrazene hydrate), however trinitrotoluene (TNT) is also used [1]. There is increasing concern about the toxicity of lead and other GSR compounds in indoor shooting ranges. Many manufacturers are now producing heavy-metal free compositions. This includes lead-free “Sintox” primer made by the manufacturer RUAG. This uses tetrazine and Dinol (diazodinitrophenol) as the initiator and NC, Zn peroxide and titanium as the oxidizer and fuel [34]. The brands GECO®, RWS®, Rottweil®, Norma® and Hirtenberger® ammunition CCI International, Speer, Blazer, Winchester, Remington and Federal have all introduced their own non-toxic lead-free formulations [16, 33].

The elements most commonly found in GSR that originated from the primer are Sb, Ba, and Pb [35]. Some other ingredients of GSR such as Cu, iron, and some nonspecific particles (e.g. aluminum, silicon, sulphur, potassium and calcium) can also be found associated with the primer mixtures. These elements usually originate from bullets, cartridge casings and barrels [14]. Furthermore, lead can also originate from the bullet itself [36]. According to Heard [16], in a study of toxicity hazards to shooters in firing ranges, the US National Bureau of Standards determined that 80% of the airborne lead residues detected in American firing ranges originated from the lead bullets, and only 20% from the primer composition [16].

The primer is a major contributor to the elements of the GSR [25], therefore experiments have been conducted to isolate the effect which primer alone has on the composition of GSR. This involved loading primers into new cases with jacketed bullets. New cases were used to eliminate any contamination from previous primer residue. These studies indicated that it is difficult to determine the type of firearm and ammunition used based solely upon the particulates created by primer residue [25]. Despite the primer being the major component of GSR, the other elements present are often important in determining the type of weapon and ammunition used. For this reason, GSR analysis must consist of using the broadest range of techniques possible [25].

1.1.2 Gunshot Residues (GSR)

When a weapon is fired, the primer and propellant burns and escapes through openings in the weapon as a plume [37]. This plume soon solidifies and is deposited as particles of varying sizes on clothing, skin, and surfaces near the weapon. Some of these particles may be so small that they can only be observed through a powerful microscope. A variety of organic compounds are in the GSR, which were part of the gunpowder or primer [38]. The distance travelled by these particles depends upon the type of weapon [39, 40], its condition and the way in which it is configured, in addition to factors such as calibre, manufacturer and other aspects of the ammunition being used. Environmental conditions such as air turbulence can also affect particle distribution of GSR [41]. Differences in the design of weapons such as semiautomatic pistols or revolvers significantly influences plume patterns [20]. The patterns are also influenced by elements of the ejection port [37].

1.1.2.1 Formation of GSR Particles

Interior ballistics is the science that investigates how chemical energy from the propellant and the primer is converted to kinetic energy that propels the bullet or other projectile [42]. Only about 30% of the energy in the propellant and primer chemicals is converted to kinetic energy. The remaining 70% of this energy becomes heat, light, and GSR. The firing of ammunition from a weapon produces an extremely high pressure and temperature for a short period of time. The average time between the striking of the firing pin and a bullet leaving the weapon is 0.03 seconds. This short period of time only allows for a partial mixing of the GSR components, which accounts for the wide variety of GSR [42].

A great deal of information is known about how GSR is formed [20]. While the components of GSR particles vary, the way in which they are formed is relatively standard and accepted in the community of forensic science. The way in which GSR particles are formed enables the investigator to determine if particles of Ba, Sb, or Pb are part of the GSR, or whether they were merely produced by other environmental sources [20]. The rapid cooling of Ba, Sb, and Pb vaporised particles in the GSR [20] occurs during the high temperature burning of the primer [20].

There are a number of irregularly shaped particles which make up GSR with sufficient frequency to be routinely seen in laboratories [43]. This is a significant fact since it was previously believed that all GSR particles were spherical. These laboratories confirm that GSR particles frequently are not spherical, and may consist of shapes which are in no way considered round. The morphology and characteristics of the GSR particles are determined by this burning. GSR primer particles can be classified as occurring in three general shapes. One type of shape is a regular spheroid, which is smooth and ranges from 1 to 10 μm. A second type of shape is irregular particles, which are formed when large and small particles fuse to form nodules. The third types of particle is present as a lead layer surrounding a core of Sb and Ba, and may or may not be spherical [43].

GSR particles formed inside a firearm or present inside the cartridge may contain different shapes from those three characteristic ones previously described [21]. Most of these particles are bullet derived. This is an important consideration, because the morphology of GSR particles and the way in which they are formed from known cartridge casings can help determine the guilt or innocence of an individual suspected of shooting a firearm [21].

1.1.2.2 Plume Concentrations

A number of studies have been performed to investigate the shape of the plume created by different types of weapons when they are fired [44, 45]. These plumes create distinctive deposition of GSR on the surrounding surfaces (Figure 1.3). This can be an important factor in determining what type of weapon was used during a crime [19, 44]. Whilst a large proportion of the expanding gases escape from the muzzle end of the barrel, a significant amount vents from the breech end, particularly when the cartridge case is ejected.

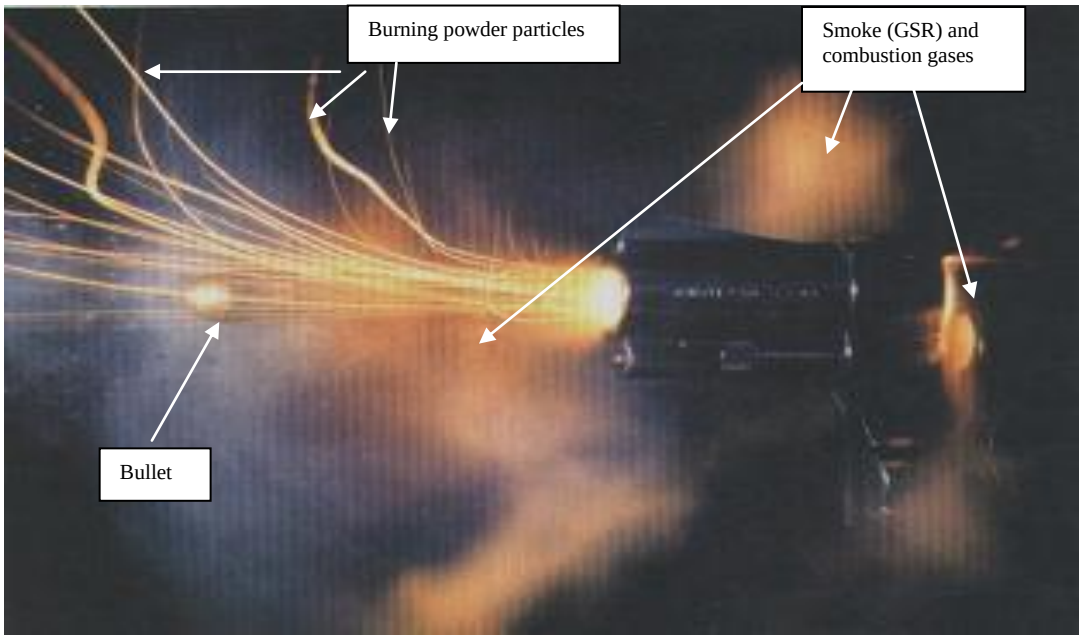

Figure 1.3. A discharging revolver showing gunshot residue components [46]

Plume studies are generally conducted under strictly controlled circumstances [44]. Indoor firing ranges are frequently used, and all possible drafts are eliminated. Backdrops are placed to catch the plume spreading in any direction. Floodlights are frequently used to enhance the viewing of the plume development. Video recordings of the firing are essential. High-speed motion analysers of up to 10,000 frames per second are frequently used to produce clear slow motion pictures [47].

Semiautomatic handguns, which are smaller in calibre, and have forward or high cartridge ejection, create plume concentrations near the tips of the fingers [44]. Frequently, the GSR from these weapons is more prevalent near the fingertips than the wrist areas. Usually, the plume is determined by the direction in which the cartridge is ejected (top or right hand side). Revolvers create lateral plumes to both sides of the weapon due to gases escaping from the cylinder gap at the rear of the barrel, as shown in Figure 1.3. The thumb, forefinger, knuckles and back of the hand become contaminated with GSR. Revolvers of higher calibre weapons have a plume which is spread wider than those of the large calibre semi-automatic weapon, which has ejection ports. The ejection port serves to concentrate the GSR plume in a more compact area [44]. It is noteworthy that the distribution of GSR on the hands of handgun shooters also depends on whether they shoot one-handed or two-handed, left-handed or right-handed, and whether they cup the shooting hand or wrist with the supporting hand.

A common area of plume concentration for shotguns and rifles is in the crook of the arm supporting the weapon [44]. The drift or blowback from the plume is directed toward the shoulder, chest, face, and hair [48]. Many of these types of weapons have heavy concentrations of GSR in these areas, but there is a significant variance between weapon types, ammunition, and even manufacturers. The ejection of the cartridge is a major factor in the GSR plume for many of these weapons. There will be differences between the plumes created by breech loading side-by-side and over/under shotguns (which eject the cartridge when the barrel is "broken" open), and the action of self-loading shotguns and pump-action shotguns both of which have ejection ports. In the case of self-loading shotguns the cartridge will be ejected as part of the firing cycle. However, in the case of break-barrel and pump action shotguns, and also bolt action rifles, significant GSR will only be released as a plume if the cartridge is ejected shortly after firing. However, the plume from shotguns and rifles expands rapidly in all directions from the end of the barrel, regardless of the way in which the cartridge is ejected. The way in which this plume expands can be influenced by air turbulence [44].

1.1.3 The Forensic Importance of GSR

Forensic science consists of applying scientific disciplines to aid the criminal justice system, and the analysis of GSR is an important part of this scientific reference [13]. In spite of the high rate of firearms related offences, there have been fewer textbooks and scholarly articles written on the subject than many other scientific disciplines applied to criminal justice [13].

GSR can be a valuable part of the trace evidence at a crime scene in which a gun was fired [49]. The analysis of GSR can aid the firearms examiner to estimate the shooting distance, identify bullet holes, estimate the time since the latest discharge and determine whether or not a person has fired a gun [14, 39, 50-56].

Frequently, this residue is not visible to the naked eye and sensitive analytical techniques must be used in order to properly characterise the sample. This residue has often been used to link subjects to a crime who would otherwise not be under suspicion. For example, there is commonly a question regarding who has fired the gun used to commit the crime. This can often be answered by GSR and it makes a difference whether a subject is considered the primary perpetrator or merely an accomplice. There may be questions regarding some victims if a homicide or suicide has occurred [49]. In

these cases, an analysis of the GSR can frequently answer the question about who fired the gun.

A correctly performed forensic analysis begins with the evidence being collected properly at the scene of the crime [57]. Proper collection requires the individuals involved to have knowledge regarding the appropriate collection techniques regardless of whether the residue is being collected from an individual or the scene of a crime. When the collection of GSR is involved it is particularly important that those collecting data understand the best ways for preserving both the organic and inorganic components of the GSR. Part of this data collection involves properly cataloging where evidence has been collected and in what manner. This makes later GSR analysis easier to interpret [57]. After the GSR data has been properly collected, the next phase involves laboratory examination [57]. This begins with preparing the samples [58]. However, great care must be taken when interpreting the detection of GSR on a person.

The interpretation of the GSR data can be quite complicated and involves more than simply comparing concentrations of chemicals or finding particles. The individual interpreting the GSR must understand the effect of environmental forces [41], primer formulation, and a variety of other factors that can influence the components and deposition of the residue [58, 59]. After the GSR has been subjected to the appropriate laboratory examination, the next phase is the preparation of a good report [49, 60]. The GSR examiner must help the law enforcement individuals involved in the case understand the meaning and interpretation of the analysis. This part of the GSR analysis is just as essential as the proper collection of the data and its analysis. Valuable information will be lost if the results are not communicated clearly to the appropriate individuals [60].

It is reasonable to expect that the distribution of GSR on the back of one hand or both hands of a person is indicative that they recently fired a weapon. Since the firearm itself will probably become contaminated on its external surfaces with GSR when it is fired, the handling of a recently fired weapon may transfer GSR to the fingers and palms of the hands of the handler who has not fired it. Therefore, this person is not necessarily the shooter. Likewise the absence of GSR on a person requires careful interpretation; the wearing of gloves that are later discarded or thoroughly washed may successfully prevent detection of GSR on a shooter's hands. According to Bowen [49], a suicide victim will have significant GSR on their hand. If an apparent suicide is found with a

gun in their hand but no GSR, then the gun is likely to have been placed in the victim's hand to make a murder appear as a suicide [49]. However, this depends on whether or not the suicide victim was using a short or long-barrel weapon. Rifle and shotgun suicides sometimes involve triggers pulled by the feet or by the use of sticks, rods, string or other devices where the victim cannot reach the trigger with the barrel pointing at their own chest or head. There have even been cases where the suicidal person has constructed an elaborate system to cause another person to trigger the firearm, for example by opening a door; in such cases, their hands may be free of GSR.

It is the responsibility of the GSR examiner to ensure that the most clear facts in the case are provided, along with all necessary information enabling the clearest possible interpretation. Individuals that may be provided with GSR evidence are juries, judges, grand juries, attorneys, or law enforcement personnel [60].

1.1.4 Degradation, Persistence and Transfer of GSR

The components of GSR are both organic [29] and inorganic [61] particles. The inorganic components consist of heavy metals that were part of the ammunition. These particles are durable and last in most environments for an indefinite period of time; however, they are often dislodged with time and activity [61].

The particles are deposited on clothing, skin, and areas surrounding the weapon which is fired. The physical principle which explains the exchange of GSR is known as the Locard Exchange Principle [6]. According to this principle, when two objects come into contact with each other, there is an exchange of materials. When a weapon is fired, particles are formed during the combustion of the propellant [6]. The particles transfer onto items in the surrounding area, including skin, clothing or furniture. In order for this transfer to occur, there does not need to be any direct contact between the weapon and the target material; the particles are diffused' as airborne particulates [6]. This makes GSR different from the majority of trace evidence, which requires transfer through direct contact, although explosives' residues, glass fragments from the breakage of windows and airborne blood droplets also fall into this category. However, the residue created by a gunshot is often transferred to other items in the area through direct contact. For example, an individual firing a gun may have GSR residue on their hands, which is transferred to a door handle when they open or close it. This is known as "secondary transfer". Another frequent area where GSR is found through direct transfer

is in the pockets of clothing. This occurs when an individual fires a weapon and has GSR on their hands. The shooter then places their hands in the pockets of clothing, transferring the GSR to the fabric. It may also happen when they put a handgun in their pocket [33]. In a similar fashion, GSR is frequently found on the interior of automobiles inside which weapons have been fired, for example in drive-by shootings.

GSR is readily removed from the skin by washing. Metallic GSR particles, though persistent in the environment, are lost from the skin. Positive detection of GSR on a person's hands indicates that the person fired a gun within about six hours of the collection of samples from their hands [62]. Warlow [33] is more conservative, suggesting two to four hours persistence of GSR on a shooter's hands, with up to twelve hours for swabs taken from hair. Heard [16] suggests that GSR is lost from the hands at an exponential rate, however GSR may be detected in clothing for several days or even weeks [33].

1.1.5 Constituents of GSR

1.1.5.1 Inorganic Compounds in GSR

The inorganic components of the GSR frequently consist of Ba, Pb, and Sb [61]. These arise from the bullet core, cartridge case [21], anvil, propellant, primer mixture, sealing disc, bullet jacket, propellant additives, lubricants, lacquers, and debris, which are present within the barrel of the weapon [61]. Impurities present in any of these components can make the GSR of a particular weapon unique. The largest amount of GSR inorganic components is produced by the primer and the bullet [61]. Table 1.1 shows a list of different inorganic compounds that may contribute to gunshot residues.

Table 1.1. Inorganic compounds that may contribute to gunshot residues [63]

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

1.1.5.2 Organic Compounds in GSR

The organic components of GSR can arise from a variety of sources [29]. These organic compounds are produced by the propellant, primer mixture, lubricants, sealers, lacquers, and ammunition. Organic compounds can also be produced by debris present in the weapon before it is fired. The primary source of organic compounds in GSR is the propellant [29]. Table 1.2 shows a list of organic compounds that may contribute to the GSR.

Table 1.2. Organic compounds that may contribute to gunshot residues [63]

Compound	Source of Compound
2,4,6-Trinitrotoluene (TNT)	Propellant powder/primer mix
2,4-Dinitrodiphenylamine (2,4-DPA)	Propellant powder
2,3-Dinitrotoluene (2,3-DNT)	Propellant powder
2,4-Dinitrotoluene (2,4-DNT)	Propellant powder
2,6-Dinitrotoluene (2,6-DNT)	Propellant powder
2-Nitrodiphenylamine (2-NDPA)	Propellant powder
4-Nitrodiphenylamine (4-NDPA	Propellant powder
AkarditeII (AKII)	Propellant powder
Butyl phthalate	Propellant powder
Butylcentralite (N,N-Dibutylcarbanilide)	Propellant powder
Camphor	Propellant powder
Carbanilide	Propellant powder
Carbazole	Propellant powder
Dibutyl phthalate	Propellant powder
Diethyl phthalate	Propellant powder
Dimethyl phthalate	Propellant powder
Dimethylsebacate	Propellant powder
Dinitrocresol	Propellant powder
Diphenylamine (DPA)	Propellant powder
Ethyl centralite (N,N-Diethylcarbanilide)	Propellant powder
Ethyl phthalate	Propellant powder
Ethylene glycol dinitrate	Propellant powder
Methyl cellulose	Propellant powder
Methyl centralite (N,N-Dimethylcarbanilide)	Propellant powder
Methyl phthalate	Propellant powder
Nitrocellulose (NC)	Propellant powder/primer mix
Nitroglycerine (NG)	Propellant powder/primer mix
Nitroguanidine	Propellant powder
Nitrotoluene	Propellant powder
N-nitrosodiphenylamine (N-NDPA)	Propellant powder
Pentaerythritoltetranitrate (PETN)	Propellant powder/primer mix
RDX (Cyclonite)	Propellant powder
Resorcinol	Propellant powder
Starch	Propellant powder
Tetracene	Propellant powder/primer mix
Tetryl	Propellant powder/primer mix
Triacetin	Propellant powder

1.1.6 GSR Collection Techniques

A variety of methods have been developed for collecting and preparing GSR for analysis [64]. These techniques involve protocols that depend upon the type of testing being performed. The protocols also vary depending upon the surface from which the residue is collected, with different protocols regarding skin, clothing, vehicles services, furniture, concrete, blacktop, metal, glass, wood, leather, vinyl and plastic. These procedures may also differ according to the policy of the agency collecting the evidence; however, it is effectively universal that organisations require that GSR evidence collectors wear clean gloves [64].

The media used to collect GSR data varies depending on the type of analysis to be performed and the surface from which it has been collected [64]. Several methods have been used in the collection of gunshot residues from the clothing, hands, hair and face of the shooter.

1.1.6.1 Tape Lifts

Tape lifting is widely used for the collection of inorganic compounds in gunshot residue samples from skin surfaces [65]. It has also been used for clothing [66, 67] and hair [68]. A number of studies have been carried out to verify the efficiency of using tape lift method for collection GSR samples. Experiments were carried out by Wrobel [67] to compare the efficiency of a number of different adhesive tapes for the collection of inorganic GSR particles. Fifteen assorted adhesive were studied, including double-sided tapes, adhesive tabs, liquid adhesives, a glue stick and carbon conductive cement. Several criteria were used to assess the appropriateness of each adhesive. Sellotape® 404 double-side tape was chosen as the best performer [67].

The comparison between tape/sticky lifts and swabs (isopropanol as solvent) for the collection of inorganic GSR sampling for scanning electron microscopy has been investigated. The results illustrated that tape lifting is more powerful for the collection of inorganic GSR sample than swabbing [66]. Another comparative study was conducted by DeGaetano [69] to investigate the differences between tape lift (3 M brand adhesive), glue lift and a centrifugal concentration technique. The samples of GSR were collected and analysed using scanning electron microscopy (SEM) with energy dispersive X-ray detection (EDX). The number of inorganic GSR particles lifted

from the surfaces within one hour for each method was used as the criterion to determine the most appropriate method [69]. Tape lifts were found to be the most effective method; they are inexpensive, have good collection efficiency and performance in the SEM. However, tape lifting can cause problems, including the large surface area to be searched, the requirement to carbon coat sample prior to analysis, and the collection of debris that can mask GSR particles.

In theory, the sample concentration technique should reduce the search area; however, the high variability of results generated by this method render it less efficient than tape lifting [63]. Zeichner [70] found that the use of sample concentration technique was associated with problems such as the build-up of debris on the filter surfaces which affects the efficiency of detecting GSR particles, this makes the tape or glue lift technique preferable [70].

A novel method was reported by Zeichner for the extraction of organic compounds in gunshot residues from tape stubs following SEM/EDX analysis [71]. Extraction was performed with an aqueous solution of (0.1% w/v sodium azide)/ethanol mix (80/20) at 80 ^{o}C for 15 minutes, followed by further extraction with methylene chloride. Concentration by evaporation was shown to be the optimal procedure for gas chromatography with thermal energy analysis (GC/TEA) and ion mobility spectrometry (IMS). The results revealed that there are variations in the single base powder and recovery level for NG and 2,4-DNT, ranging from 30% to 90% [71].

Reducing the number of organic materials (skin cells etc.) normally found on the surface of a tape lift has been successfully achieved by using oxygen plasma ashing, which has made the analysis of GSR particles easier [72]. However, the combination of contamination by the electron beam of the SEM and oxygen plasma ashing essentially destroys the cells of the epidermis, leaving only thin filaments; thus plasma ashing alone will not be effective [73].

Using tape lifts for collecting GSR samples from clothing may create some problems with fiber and other debris. This debris is likely to be nonconductive and may hold charge during SEM analysis. Thus the sample may require coating by carbon/gold, which involves extra time and expense [74].

The collection of inorganic GSR particles from hair is considered to be of great value for forensic analysis. Hair retains GSR particles for longer period of time than hands. In

contrast tape lifting was found unsuitable for the collection of GSR sampling from hair [19]. Conversely, study conducted by Zeichner and Levin [68] found tape lifting to be an adequate method to locate GSR on hair (both curly and straight). There was no significant difference between tape stubs, and the more complicated hair comb swab or solvent dampened cloth. However, 200-330 dabs (60–120 dabs for hands) were required in order to perform maximum collection efficiency from hair [68].

1.1.6.2 Vacuum Lifts

Vacuum lifting is one of the most common methods used to collect the GSR sample from different surfaces. Zeichner et al. [75] used a vacuum to collect gunshot (propellant) residues from a shooters' clothing [75]. The collected samples were examined by different analytical techniques, such as gas chromatography/thermal energy analyser (GC/TEA), ion mobility spectrometry (IMS), and gas chromatography/mass spectrometry (GC/MS) [75].

Zeichner et al. [75] investigated the capability of using a vacuum for the collection of organic compounds in GSR. Two different types of vacuum filter (fiber glass and Teflon) were utilised. Four solvents (acetone, methylene chloride, ethyl acetate and chloroform) were investigated in order to determine their ability to extract the residues collected on the fiber. The results showed that there is no significant difference between the solvents in their extraction efficiency of the propellant components. The levels of collection were highly variable, with between 30-100% yields for the same solvent. Teflon filters were found to have better collection efficiency compared to fiber glass. The use of tape lifts for the collection of inorganic residues on clothing was found to be preferable to vacuum lifting to collect organic residues, although both methods were effective [75].

Using double filtration vacuum system for the collection of GSR samples was considered by Andrasko and Pettersson [76]. A filter with a pore size of 20 µM was used in order to allow the separation of residue particles from debris and fibers. GSR samples were collected on the second filter (0.8 µM), and concentrated onto a tape stub for SEM analysis. However, using the protocol described in this study could potentially have led to the loss of inorganic GSR particles larger than 20 µM [76].

Mastruko reported problems in using vacuum lifts used to collect GSR particles from cloth [74], including that other materials may be lifted from the depth of the surface,

which increased the difficulty of interpreting sample analysis [74]. In this case, tape lifting has an advantage as it only lifts particles settled on the surface of a material [74]. On the other hand, using tape lifting has been found to be unsuitable for the collection of GSR from clothing. This is the result of the loss of tape stickiness, which restricted the area that could be sampled. Also, fibers and other unwanted particles were transferred to the tape. Therefore, the analysis of GSR sample using SEM will be more difficult when using tape to remove GSR from clothing [76].

1.1.6.3 Swabbing

Swabbing is the most commonly used procedure technique used for collecting organic residues from the hand of the suspect [14]. The efficiency of eight solvents for the collection of nitroglycerin sample from the hands of a shooter has been studied. Different criteria have been used to determine the efficiency of the solvents, including the amount of NG removed from the hands, the amount of interfering material removed from the hands, as well as the stability of NG within the solvent [77]. The best recoveries were accomplished with aqueous solvents, when thin layer chromatography was used for partial purification. However, NG was degraded by micro-organisms that grew in the solutions. Ethanol was found to be the best performing solvent with the most complete, stable and consistent recovery [77].

Using organic solvents to dissolve collection residues may cause some problems such as dissolving some other unwanted materials. This leads to a complex sample matrix that can interfere with the analysis and therefore affect in the performance of the instrument. To resolve these issues, Thompson [78] suggested using water as an extraction agent and adding an additional step, SPE. Water extraction followed by SPE was reported to be an effective process for treating organic explosive residues on cotton swabs. The extracted sample analysis was accomplished with liquid chromatography (LC) or GC–MS and fast GC-TEA [78]. With the direct injection method, the water/SPE was shown to be just as effective at removing organic explosive compared to solvent extraction (acetone) method. In addition, water extraction followed by SPE also gave much greater selectivity in most cases [78].

Swabbing has been used for the collection of explosive and firearm residues [79]. The samples were extracted and cleaned up by SPE in the containers issued for the return of samples to the laboratory (sample recovery was between 63-75%). Following the

extraction of the organic compounds, the remaining particulates of inorganic GSR in the swabs could also be recovered for characterisation by SEM. This was achieved by sonication in an organic solvent followed by membrane filtration of the extract [79].

Two novel methods for extracting smokeless powder are supercritical fluid extraction (SFE) and ultrasonic solvent extractions (USE). This was performed to determine if a reliable quantitative extraction technique for smokeless powder could be achieved. In double based powder, SFE was found to be unsuitable method for quantitative extraction (which contains stabiliser plus an additional propellant, NG). On the other hand, it was shown a successful for the extraction of single base smokeless powder (containing only a stabiliser, such as DPA). Even after optimisation of the extraction process, the extraction efficiency was below 90% with smokeless powder standards. Furthermore, under the condition of SFE, NG was shown to readily react with stabiliser. The most efficient solvent for USE was found to be 2-butanol:methanol (1:3), and the most desirable extraction time was determined to be 15 minutes (handgun powders), and 75 minutes for ball type rifle powder [80].

1.1.6.4 Glue Lifts

A number of studies have reported the use of glue lifts for the collection of GSR from the hand of the suspect [81, 82]. Glue lifting was reported as very usable technique for the collection of GSR from the surface of hands [82]. This technique required less dabs on the skin surface and collected less debris compared to tape lifts, which increases the speed of SEM analysis. In addition, there are no elements of high atomic number in the glue lifts, which may cause potential interference with the GSR particle analysis using a SEM [82]. DeGaetano et al. reported that the glue lifts were found to be an ineffective lifting medium of GSR [69]. This could be as a result of using different types of glue lifting planchet employed by Basu and Ferriss [82].

1.1.6.5 Collection of GSR from Hair

When a weapon is fired, the primer burns and escapes through openings in the weapon as a plume [37]. The plumes normally extend posterior to the face and head of the shooter. Furthermore, GSR particles can also be deposited in the hair [83]. A number of studies have been published to investigate the appropriate method for

collecting GSR from the hair of the suspect. These include a swab and comb method as well as tape lifting [68, 84].

A fine toothed comb was used by MacCrehan et al. [83] to collect gunshot residue samples from hair. Using handgun firing, most intact grains of unburned powder approaching 0.1 mm diameters were recovered, even if they were smaller than the gaps of the teeth of the comb. Of the 23 tests conducted in this study, 20 positive results were reported for human hair wigs. However, there were difficulties with curly hair when using a fine toothed comb. NG showed a positive result for all three different shooters tested. With rifles and revolvers, NG and ethyl centralite were found to be the major compounds. There were variations in the amount of unburned powder between the GSR that was collected inside the cartridge and the residues collected from the hair using the comb. However, the sample and the combed residue were in agreement [83].

The final results showed that even if EC was detected in some of residues samples, it was found to be an ineffective extraction method and could not be reliably used with capillary electrophoresis (CE). It was also shown that more stringent requirements are needed for an effective protocol regarding hair residues collection. This will enable the reliable detection of stabilisers such as EC, which are present in organic gunshot residue (OGSR) [83].

1.1.6.6 Solid-Phase Micro Extraction (SPME)

Solid-phase micro-extraction (SPME) can be used to help prepare GSR for analysis [42]. This is a relatively inexpensive and simple technique for sample preparation, which can be used without solvents. SPME can be understood as being similar to a shortened gas chromatography column turned inside out [42]. This technique uses a fiber coated with extracting phase. This phase can be a liquid form of polymer or a sorbent in a solid phase. The technique extracts elements of the GSR from the gas or liquid media. This technique has become popular because it can be done in the absence of solvents and detection limits in the parts per trillion are possible [42].

Seven types of SPME fibers were investigated to evaluate the most appropriate fiber for the detection of gunshot residues compounds originating from unfired propellant powders. The assessment was based on the ability of different fibers to extract the desirable compounds' DPA, 4-NDPA, EC, NG and dibutyl phthalate (DBP) from four ammunition types across three calibres (9 mm, 5.56 mm and 7.62 mm). The extracted

samples were analysed by gas chromatography/mass spectrometry (GC/MS). The results showed that 65 polydimethylsiloxane/divinylbenzene (PDMS/DVB) was the most suitable fiber type for the extraction of these compounds, with an optimal extraction time of 35 minutes [85].

1.1.7 Analysis of Inorganic Components

1.1.7.1 Paraffin Test

An early method of detecting GSR was developed in Mexico by Gonzales in 1931 [10], and demonstrated in the US in 1933. The test now has a variety of names, including the Gonzalez test, diphenylamine test, and the dermal nitrate test [10].

The Gonzales test consists of placing melted paraffin wax on the back of the hand of an individual hand suspected of firing a weapon [10, 13]. The back of the hand is coated with paraffin wax with a brush. After the wax solidifies it can be peeled from the back of the hand. The surface of the wax has been in close contact with the subject's skin. After the wax is removed from the hands it is treated with a diphenylamine sulfuric acid reagent. This is applied by spraying or dropping it lightly on the wax. When the reagent is added to the wax, the particles of nitrites and nitrates turn blue [86], indicating that the individual fired a weapon [13].

The Gonzalez test is no longer considered accurate [13]. The Federal Bureau of Investigation (FBI) in the US questioned the technique as early as 1935 and pointed out that it was not specific enough to be used in law enforcement. Later evaluations indicated that the technique was unreliable as an indicator of GSR. The problem with this test is that a variety of substances also produced a blue spot, including fertilizers, pharmaceuticals, urine, paint and tobacco. There are also a number of reagents that cause oxidizing reactions, which turn blue. The oxidizing agents consisted of bromates, chlorates, iodates, vanadates, antimony, ferric salts, and permanganates. During an international conference in 1968 the recommendation was made that the Gonzalez test should no longer be used as a part of law enforcement investigations [13].

1.1.7.2 Harrison and Gilroy Method

Harrison and Gilroy [1] introduced a new method of analysing GSR in 1959. Their method consisted of detecting the components of GSR, which contained metal.

The majority of these metals were barium, lead, and antimony. These were the components of the residue, which were formed by the bullet and primer. A suspect's hands were swabbed with a cotton cloth that had been dampened with a solution of 0.1 m hydrochloric acid (HCl). This allowed a colorimetric spot test to be done. After the swab was dried it was treated with a few drops of a solution composed of 10% alcohol and triphenylmethylarsonium iodide. When antimony is present, an orange ring appears. After the orange ring appears, further analysis is performed [1, 87] consisting of allowing the swab to dry and then treating the center of the orange ring with 5% sodium rhodizonate mixture [88]. If a red colour appears it can be assumed that barium or lead is also present. When this occurs the swab is dried again and a few drops of an HCl solution are added to the red area. If a purple colour appears inside the ring of orange then lead is present. If the red colour remains, the presence of barium can be confirmed [1, 87].

Harrison and Gilroy's method [87] was found to be inconclusive; the colorimetric reagents used were found to lack sufficient sensitivity to detect low concentrations of the metals. Unfortunately, these low concentrations are those generally present in GSR [87]. This method also identified the individual components Pb, Ba and Sb rather than the presence of discrete particles containing all three together.

A number of bulk analysis methods have been developed to analyse inorganic components of GSR [89]. The bulk analysis methods have proven useful in determining the inorganic components of GSR such as lead, barium and antimony. However, the problem with these inorganic components is that they are present in many environments prior to the introduction of GSR [61]. Copper and mercury are also found in GSR, but can frequently be found in trace amounts as background debris of an environment. The lack of specificity regarding the bulk analysis methods has led to a search for methods, which are more sensitive to components more specific for indicating GSR.

1.1.7.3 Neutron Activation Analysis (NAA)

In 1964 there was a breakthrough in neutron activation analysis for use in detecting barium and antimony in GSR [90]. Antimony is an important indicator of GSR because barium is frequently present in environmental and occupational survey samples. The antimony can be used as a clear indicator that residue is from a gunshot rather than some other environmental factor [91].

Neutron activation analysis is a bulk analysis method based on the knowledge that a sample can be irradiated in a nuclear reactor for a specified length of time [91]. During this time the atoms of the sample absorb neutrons. The nuclei, which have additional neutrons, are known as radionuclides. The nuclei in the radionuclide emit the excess energy as gamma rays. These irradiated samples can then be placed into a system capable of recording and detecting the gamma rays [91]. This allows for quantification and identification of the elements comprising the sample. The identification of the elements is performed by measuring the decay lifetimes and emissions of the gamma rays. The quantity of elements within a sample can be measured because the number of gamma rays is in direct proportion to the amount present within the sample [91].

Neutron activation analysis provides a tool that is successful for determining antimony and barium amounts in GSR [91]. This type of analysis has been used to detect gunshot residue on suspects. It is also useful for identifying holes made by bullets in a variety of materials. The test is so sensitive it can be used as a way to estimate the range of fire. Neutron activation analysis can determine when there is mercury or copper in the GSR. This can serve as an identifying feature in some cases [91]. However, despite the many advantages of neutron activation analysis, it does have disadvantages [91]. The equipment for this type of analysis is very costly and requires highly trained staff, as a nuclear reactor is necessary. The samples must be irradiated, cooled, and prepared for radio chemical separation, which can be a time-consuming process. Additionally, neutron activation analysis has shown that it is not sensitive in regard to lead content [91].

1.1.7.4 Atomic Absorption Spectrophotometry (AAS)

Another bulk analytic method used to determine the components of GSR is atomic absorption spectrophotometry (AAS) [65]. This technology is similar to neutron activation analysis in relation to its ability to detect components. However, you can also determine the lead content of GSR [92]. The instruments necessary for this type of testing are present in the majority of analytical laboratories, and equipment costs are significantly lower than those of neutron activation analysis [65]. This technology is valuable for analysing a wide range of metallic elements even if they are present in the minutest of quantities. In addition to GSR analysis, it is used for a variety of other forensic applications. The speed of analysis, simplicity and ability to do the entire procedure in most laboratories is an advantage of atomic absorption spectrophotometry.

The primary disadvantage of this technology is its inability to simultaneously analyse more than one element [93].

Atomic absorption spectrophotometry has become one of the most popular techniques for determining the level of metallic elements in GSR [93]. These elements frequently include barium, antimony [94], lead, mercury and copper [95]. A wide variety of other elements can also be detected by this technique.

Both atomic absorption spectrophotometry and neutron activation analysis are considered bulk analysis methods [93]. They have the disadvantage of determining elements which are present but not specific to GSR [96]. These elements may have occurred due to environmental or occupational inputs [97]. In other words, many environments contain a background level of barium, lead and antimony. It is also common to find mercury or copper in areas in which no GSR is present. This has led to the search for methods more specific to particles created by GSR [96].

1.1.7.5 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Inductively coupled plasma mass spectroscopy is a bulk analysis method that is used to analyse trace amounts of Sb, Pb, and Ba, which are frequently present in the primer residue of GSR [98-100]. This procedure consists of combining an electromagnetic field produced by a radio frequency with argon plasma [25]. This is done at a normal atmospheric pressure [101]. The samples are analysed in a liquid form. This test is highly sensitive and the detection limits are often in the parts per billion [98].

1.1.7.6 Scanning Electron Microscopy (SEM)

One of the most widely used tools for modern GSR analysis is the scanning electron microscope [14]. This instrument can analyse each particle in a sample, therefore it is much more selective than the bulk analysis methods. The electron microscope can detect the presence of Ba, Sb or Pb in a sample and isolate its presence on a single particle. This method is also able to find a single GSR particle with picogram level sensitivity [37].

The scanning electron microscope is useful in GSR studies for a variety of reasons [37]. It has excellent performance in regard to imaging, magnification, composition analysis,

and most recently automation. While many associate a scanning electron microscope with high magnification, it can also be used in applications that require lower magnification. Even samples that only require magnification of 100 X can be analysed. The robust versatility of the instrument makes it useful in a wide variety of circumstances [37].

A common mistake made by those working at crime scenes is that they assume GSR is not present if it is not visible [64]. Many GSR particles are between 1 µM and 10 µM in size and are not visible without magnification. This is one reason GSR is considered as trace evidence [64].

Particle analysis allows the scanning electron microscope to analyse elements and determine if they are part of GSR or have been added to the sample by the environment [102].

1.1.8 Analysis of Organic Components (OGSR)

This section concentrates on organic rather than the inorganic components of GSR due to the relatively higher frequency of the latter in the environment when a weapon has not been fired [57]. The inorganic particles of GSR can be generated in a variety of other heated processes. For example, fireworks often disperse many of the inorganic components of GSR into the environment. This is because the colour fireworks produce is obtained with chemical compounds such as strontium nitrate, potassium chlorate, aluminium, magnesium and barium nitrate. Antimony is often used as a way to produce an effect of glittering, while lead produces a crackling sound [57, 103].

In addition to fireworks, there are other significant contributors to environmental inorganic compounds similar to GSR, such as automotive brake linings [57]. Many automobile mechanics have high levels of inorganic compounds similar to GSR on their work uniforms. Another example is provided by carpenters working with nail guns utilising blank cartridges, who frequently have residue on their clothing resembling inorganic GSR. This presumably also applies to slaughterhouse staff in countries where livestock are killed using captive bolt guns utilising blank cartridges. On the other hand, there are organic components of GSR which are rarely found except when a weapon has been fired [57].

1.1.8.1 Gas Chromatography (GC)

One of the most common methods for determining organic compounds in GSR are chromatographic techniques [104]. These laboratory methods have been used to detect, separate, and identify organic compounds present in samples of GSR. A variety of other methods have also been used such as infrared spectroscopy, molecular luminescence, electron spin spectrometry, Raman spectroscopy, ultraviolet spectroscopy, micro chemical crystal tests, and nuclear magnetic resonance [104].

There is a wide variety of explosive compounds in the organic components of GSR [29, 105]. Analysis previously performed on explosive residues provides information that is applicable to the organic compounds in GSR [106]. Chromatographic techniques are an effective way for analysing the explosive residues in GSR [104]. Chromatography consists of several methods that separate compounds in a mixture by causing them to distribute between a stationary or mobile phase. The stationary phase is frequently a solid, or it can be a liquid supported by a solid. The mobile phase is liquid or gas and flows continuously. The flow is around the stationary phase of the compound. The components are physically separated due to their different affinities for the stationary phase of the compound [104].

While mass spectrometry is a useful tool, it cannot be used independently for GSR analysis due to the impure nature of the sample [107]. The sample of GSR, which is taken from clothing or skin, consists of a complex mix of molecules with unknown contaminants associated with the background in which the weapon was fired. For this reason, mass spectrometry is combined with gas chromatography, which separates the compounds of interest from the contaminants prior to analysis with the mass spectrometer [108].

A feasibility study was performed by Mach et al. [109] using gas chromatography-chemical ionisation mass spectrometry for detection, making use of the organic constituents in gunshot residues. Two packed columns were used. The first was operated isothermally at 175 ^{o}C and the other was programmed from 160 to 250 ^{o}C at a rate of 15 ^{o}C min^{-1}. In the first part of this study, 33 smokeless powder sources were analysed. The results indicated that nitrocellulose, nitroglycerine, 2, 4-dinitrotoluene, diphenylamine, dibutyl phthalate and ethylcentralite were the most common components found in gunshot residues [109].

Forty different smokeless powders were examined the organic constituents from fired and unfired. Samples were analysed using pyrolysis GC. The results confirmed that each smokeless powder has its own chemical compositions and it was distinguished from the other powder. Furthermore, there is similarity between partially burned powders residues taken from the barrels of fired weapons, and the original powders [110].

Jane et al. [111] successfully used GC to detect NG, NC and DPA on the clothing of the shooter up to six hours after discharging a gun. They also reported that the skin surface (such as the face and throat) might be very useful as a source of gunshot residues [111].

Gas chromatography with a thermal energy analyser (GC/TEA) has been applied to the determination of nitroglycerine in gunshot residue samples. The samples were vacuumed from the clothing of the suspect without any pre-treatment. GC/TEA was found to be a selective and sensitive for detection of trace amounts of organic compounds in gunshot residues [112]. Further study performed by Douse confirmed the high selectivity of GC/TEA in determining organic compounds in gunshot residues [113].

The procedure for the analysis of forensic explosives and firearms traces using GC/TEA as a confirmatory technique has been reported [114]. This procedure involves the purified extract of the trace amount of explosive materials from debris of a hand-swabs and clothing using high performance liquid chromatograph (HPLC). The extracted sample was injected directly into GC. Using this method, it is possible to detect nitroglycerine in the articles of clothing recovered from a person who has already fired a gun [114].

The combination of infrared micro spectrophotometry and GC/MS was introduced as an unequivocal technique for the identification of propellant particles [115]. This method involved two stages. Preliminary infrared micro spectrophotometry was used to identify smokeless powder grains and detect nitrocellulose. The extraction samples were then subjected to gas chromatography analysis [115]. The results showed that the IR technique was able to successfully determine nitrocellulose in smokeless powder. However, there is a limit for the detection of minor constituents in propellant grains. The result obtained using GC/MS indicated that partially burned propellant grains contained nitroglycerine, diphenylamine and ethylcentralite, while the fully burned grains contained only nitroglycerine and diphenylamine [115].

A new method was developed for the analysis of inorganic and organic compounds in GSR from the clothing of the shooter [116]. This method required extraction of the organic substances and their concentration using SPE, followed by analysis of the recovery samples using gas chromatography-mass spectrometry method and a modified automated high-performance liquid chromatography pendant mercury drop electrode system. The inorganic gunshot residues were analysed by SEM/EDX analysis [116].

GC/TEA followed by GC/MS was reported by Andrasko et al. [117] for the determination of different compounds in smokeless powder. The protocols involve the use of SPME in the extraction of GSR samples from the barrels of weapons after test shootings, as well as extraction of the soot deposited inside the barrels of the weapons. GC/TEA was used for the analysis of samples while GC/MS was employed for the identification of some organic compounds in GSR [117].

Zeichner et al. [75] assessed the effectiveness of using GC/TEA and GC/MS along with IMS for the analysis of organic compounds in gunshot residues. The results indicated that with GC/TEA the level of the sensitivity for some OGSR was very high. Limits of detection were: 0.2 ng for NG, 0.05 ng for 2, 4 DNT and 0.05 ng for 2, 6 DNT. The considerably lower sensitivity of GC/TEA for NG compared to DNT was a result of the thermal decomposition of NG in the GC columns. This also results in nonlinearity of the NG peak heights as a function of concentration, in particular approaching the limit of detection. Increasing the length of the column resulted in two peaks for NG. The smaller peak was determined to be the result of a thermal decomposition product of NG as 1, 2 glycerol dinitrate (1, 2-GDN), which was reported as a drawback to sensitivity. On the other hand, the presences of two peaks increase the likelihood of identifying NG using GC/TEA [75].

Two GC/MS systems were employed for the analysis of standard mixture of GSR, but neither of them was optimised for the explosive analysis. The limits of detection of the desirable compounds were reported at several nanograms. GC/MS was reported to be sensitive enough for the examination of shooters clothing.

IMS is widely used for the detection of trace explosive evidence due to its high sensitivity (compared to GC/TEA), selectivity and speed of analysis. Therefore, the combination of the GC and IMS method may increase selectivity for the detection of organic compounds in gunshot residue [75].

A double-sided adhesive coated stubs method was utilised to collect gunpowder residues (propellant) from the clothing of shooters. Samples were extracted from the stubs using water/ethanol mixture (80/20) at 80 °C with sonication for 15 minutes, followed by further extraction with methylene chloride and concentration by evaporation. The extracted samples were analysed by gas chromatography/thermal energy analyser (GC/TEA) and ion mobility spectrometry (IMS). The extraction efficiencies of nitroglycerine and 2, 4-dinitro toluene were reported to be 30-90%. The method offers extra analysis for primer residues collected on a double-side adhesive coated stub. Prior to the analysis of organic constituents, it was also analysed by scanning electronic microscopy/energy dispersive X-ray (SEM/EDX), which in turn may increase the probative value of evidence [71].

A novel method was developed by Muller et al. [118] for the analysis of gunshot residues in order to determine the intermediate-long firing range shooting. The experiments were designed based on the characterisation and chemical analysis of the smokeless powder particles on the target. An adhesive lifter was used to collect the GSR sample from the surface of an object. Modified Griess Test (MGT) was carried out after alkaline hydrolysis on the adhesive lifter. Two different analytical techniques are utilised; GC/TEA and GC/MS. NG, 2,4-DNT, DNT and some other stabilisers were identified. The estimated intermediate long firing distance was found to be 0.75-3 m [118].

Solid-phase micro extraction (SPME) followed by GC/MS method was utilised to identify organic components in empty cartridges. With the help of MS database comparison and reference substance analyses, the existence of 32 organic compounds was confirmed. However, the major problem of using this method based on SPME is the reproducibility of measurements of low quantities (in the nanograms range), even when using an auto sampler [21]. The degradations of six target substrates were investigated over more than 32 hours to estimate their particular potential for determining the time of the shooting [21]. The diminution of benzonitrile, phenol, 2-ethyl-1-hexanol and naphthalene was very quickly seen two hours after the shooting, whereas 1,2-dicyanobenzene and diphenylamine decreased more slowly over 32 hours [21].

The extraction of organic gunshot residues from a single particle of unburned gunpowder has been achieved using solid phase micro-extraction (SPME). The

unburned particle gunshot residues were lifted from the target areas. Smokeless powder additives such as diphenylamine (DPA), methyl centralite (MC), ethyl centralite (EC) were successfully extracted by SPME and tested using gas chromatography coupled to a nitrogen phosphorus detector (GC/NPD) [108]. The results indicated that this method is capable of detecting methylcentralite and ethylcentralite at a level of 10 ng, which are considered as signature molecules for the detection of gunshot residue [108].

A comprehensive study was conducted by Joshi et al. [119] to analyse 65 smokeless powder samples. SPME was used as a sampling and pre-concentration technique. GC/MS, GC/GC-micro electron capture detector and IMS were used as analytical techniques to determine the presences of a list of target compounds in smokeless powder. These compounds include nitroglycerine, diphenylamine, ethylcentralite and methylcentralite, 2,4-dinitrotoluene, diethyl and dibutyl phthalate. The results showed that this analytical technique (GC–MS, GC-μECD and IMS) allowed more significant detection for both qualitatively and quantitatively data of smokeless powder samples [119].

1.1.8.2 Liquid Chromatography (LC)

Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) was developed by Laza et al. [29] for the analysis of common organic compounds in gunshot residues [29]. GSR samples were collected by swabbing the hand of shooters. The extracted samples were concentrated and purified using SPE. LC/MS analysis using Multiple Reactions Monitoring (MRM) modes to determine the existence of akardite II, ethylcentralite, and diphenylamine, methylcentralite, N-nitrosodiphenylamine, 2-nitrodiphenylamine, and 4-nitrodiphenylamine. The limit detection of these compounds ranged from 5 to 115 μg. This method was found to be very sensitive for the determination of the centralities (EC and MC) [29].

LC-MS/MS techniques were developed by Perret et al. [120] for the simultianeous determination of highly explosive compounds (trinitrotoluene, cyclotrimethylenetrinitramine (RDX), pentaerythritoltetranitrate (PETN) and nitroglycerin (NG)) as well as two stabilisers (diphenylamine and ethylcentralite). The samples were collected from the hand of the suspects using cotton swabs pre- treated with isopropanol, followed by elution with methanol. The extracted samples were directly injected into the LC-MS/MS system without any pre-treatment. The result

illustrated that the recovery samples from spiked swabs were between 78 to 96%, and the limit of detection ranged from 0.04 and 1.8 ng per injection [120].

High performance liquid chromatography (HPLC) with electrochemical detection has been used for the analysis of gunshot residue components. Using reductive mode, nitroglycerine and 2, 4-dinitrotoluene were detected. The oxidative mode was required to detect diphenylamine, 2-nitrodiphenylamine, and 4-nitrodiphenylamine. Results indicated difficulties in the detection of diphenylamine in gunshot residues compared to nitroglycerine, due to low concentration levels of diphenylamine in smokeless powder, and the complication of using oxidative mode to detect these compounds [121].

Lloyd [122] reported the detection of nitroglycerine on the clothing of a shooter several days after the firing of a gun using high performance liquid chromatography-pendent mercury drop electrode (HPLC/PMDE) methods. [122]. Using HPLC with PMDE detector showed the possibility for the detection of nitroglycerine on the hands of shooters down to 1 ng/swab [122].

Another approach which has shown promise for detecting minute amounts of GSR has been reported by Lloyd [123], who was able to discriminate nitrocellulose using HPLC and a size-exclusion column coupled to (PMDE). The results showed the possibility of detecting nitrocellulose in amounts as small as 100 pg [123].

Lloyd [124] utilised size-exclusion and HPLC with electrochemical detection to identify nitrocellulose, nitroglycerine and diphenylamine from the hand and clothes of the shooter. The results showed that some swabs collected from people not involved with firearms contained different amount of diphenylamine.

Three studies by Lloyd [124-126] investigated gunshot residues compounds, employing HPLC/PMDE technique to determine diphenylamine and nitroglycerine, and size-exclusion chromatography/PMDE to determine nitrocellulose in gunshot residue samples. The results demonstrated that the amount of nitrocellulose that remained after discharging the gun tends to decrease and may not be distinguishable from the large amount of environmental nitrocellulose that is normally present in clothing debris [124-126].

A sequence of studies investigating gunshot residues was published by Dahl and Lott [127-129]. They suggested a method for distinguishing between black and smokeless

gunpowder residues. This method involved chemical spot tests, microscopic examination, X-ray diffraction, and HPLC with electrochemical detection. Their results illustrated that X-ray diffraction confirmed the existence of black powder whilst HPLC with electrochemical detection determined diphenylamine in smokeless powder residues [127-129].

In the second part of their study, they applied HPLC with oxidative electrochemical detection to analyse gunpowder stabilisers such as diphenylamine, ethylcentralite, and 2-nitrodiphenylamin. They concluded that diphenylamine can be obtained from other sources, such as the handling of tyres [127-129].

Other applications of Size-exclusion and HPLC with electrochemical detection technique were achieved by Dahl et al. [127] in the analysis of diphenylamine and ethyl centralite in gunshot residues samples. Gunshot residues samples were recovered from different handgun calibres and various types of ammunition [127].

Wissinger et al. [130] compared smokeless powder additives by means of reversed phase gradient HPLC. They utilised this method to separate geometric isomers of nitrotoluene and nitrodiphenylamine that are usually found in the additives and stabiliser degradation of smokeless powders [130].

Cascio et al. [131] compared two techniques for the analysis of organic compounds in gunshot residues. The results showed that reversed-phases HPLC and Micellar Electrokinetic Capillary Electrophoresis (MEKC) with UV detectors were capable of determining the components of OGSR. Statistical analysis indicated that the patterns from the two systems were highly correlated. Due to the wide range of analysis, better suitability for diode array detection, and lower cost to operate MEKC, diode array UV detection become one of the most acceptable techniques within forensic sciences [131].

1.1.8.3 Capillary Electrophoresis (CE)

Compositions of gunpowder additives such as nitroglycerine, diphenylamine, and ethyl centralite in seven reloading smokeless gun powders were evaluated, both in bulk and as single particles by means of ultrasonic solvent extraction/capillary electrophoresis technique [132]. Generally, there is a similarity between the composition of the residues and the component of unfired powder. It was reported that individual particles may not be sufficient to represent the sample bulk, as a result of

potential blending in finished smokeless powder. The ratio of propellant/total amount of stabiliser (p/s) for both residue and gunpowder sample was revealed to be a more robust way of linking residues to powders. The analysis of 49 of 60 samples enabled reliable comparison to bulk samples. In addition, it was indicated that the combination of quantitative and qualitative information with other details such as particle shape, colour, and size could help associate unknown powders or OGSR with a known samples [132].

A new approach reported by Reardon and MacCrehan [80] uses the propellant to stabiliser ratio to link handgun fired OGSR with unfired powder using Ultrasonic Solvent Extraction/Capillary Electrophoresis. Of seven Gunpowder samples analysed, four could be easily distinguished. However, when the visual examination of particles morphology is combined with the result of the p/s ratio, all seven powders could be reliably distinguished [80].

A capillary electrophoresis method was developed by Morales and Vazquez [89] for the simultaneous detection of 11 organic and 10 inorganic components of gunshot residues. This method is cheaper and more specific method compared to traditional techniques. However, the limit detection of some inorganic and organic compounds in GSR was not sufficient to give detection. Pre-concentration of the sample solved this problem by increasing the OGSR levels sufficiently for detection. It was suggested that using two separation systems for inorganic and organic residues may be a better option (e.g. using CE for inorganic compounds and GC with organic compounds [89]).

Hopper and McCord [133] reported the use of capillary zone electrophoresis (CZE) for the analysis of inorganic ions present in smokeless and muzzle loading powders. Seven smokeless powders were analysed as unburned powder and burned residue. Results demonstrated that ionic profiles can be used to characterise smokeless powders [133].

1.1.8.4 Micellar Electrokinetic Capillary Electrophoresis (MECE)

Adhesive film was used to lift gunshot residue materials from the hand of the shooters. The lift films were investigated under a stereomicroscope and suspect materials eliminated and extracted with methanol. The extract particles were subjected to Micellar Electrokinetic Capillary Electrophoresis analysis after evaporation to dryness and reconstitution in buffer solution. A range of gunshot residue compounds have been detected including, nitroglycerine, diphenylamine, N-nitrosodiphenylamine, 2-nitrodiphenylamine, ethylcentralite and dibutylphtalate from different types of

handgun ammunitions. The results showed that it is possible to distinguish between different ammunitions manufacturers based on their chemical compositions. The results also illustrated that unfired gunpowder and the gunshot residue materials from the same ammunitions contained similar materials [134].

The analysis of organic gunshot residue compound in two spent ammunition casings was achieved using MECE technique. Ethylcentralite and nitroglycerine were found in both casings. Also other plasticiser components such as dibutylphtalate (DBP) were detected [134]. MECE was shown to be the most reliable technique to investigate organic components in gunshot residues. Furthermore, the variety of methods for collecting gunshot residues samples where external contaminants such as grease or blood have been evaluated. The results showed that tape lifts are not a suitable method for positive identification of nitroglycerine and diphenylamine in blood contamination [134-137].

Northorp [138, 139] assessed the use of MECE in the case of GSR. SEM and MECE were used together to provide information on both inorganic and organic compounds in gunshot residues and smokeless powder. The samples were collected using adhesive stubs and analysed using both SEM and MECE. The limit detection of thirteen organic compounds that were detected (2, 3-DNT, 2, 4-DNT, 2, 6-DNT, 3, 4-DNT, 2-NDPA, 4-NDPA, DBP, diethylphthalate, DPA, EC, MC, NG, N-NDPA) ranged from 0.9–3.8 pg for standard solutions. In order to produce a reference library, 100 commercial smokeless powders were studied. The results showed that the detection of characteristic organic gunpowder components was a strong indication of the presence of OGSR, with little likelihood of the presence of these compounds in a normal environment. MECE was found capable of detecting residues from different ammunition types, except 0.22 calibres, which is due to the small size of the weapon and ammunition. There are some factors that affected the outcome of OGSR analysis, such as firing condition and collection method. In this study, both inorganic and organic compounds were successfully determined [138, 139].

1.1.8.5 Tandem Mass Spectrometry (MS/MS)

Mass spectrometry/mass spectrometry (MS/MS) was developed by Wu et al. [140] to be a simple, rapid, sensitive and selective method to identify methyl centralite (MC) in a sample of gunshot residue. To increase the sensitivity, MRM mode was

employed. The results have illustrated the reliability for determining MC on the hands of the shooter. This was true even after eight hours has elapsed since the suspect fired the gun and also if the shooters had washed his hand three times. The detection limit was 60 pg of MC per injection. Since the structure of ethylcentralite is similar to MC, this method can be suitable for analysis EC in gunshot residues [140].

Methylcentralite and ethylcentralite exist in relatively low levels compared to compounds such as nitroglycerine and nitrocellulose. Therefore, MC and EC are considered to be excellent determinates regarding the presence of OGSR. The MS/MS technique has been developed as a highly sensitive and simple method to detect the existence of methyl centralite in gunshot residues. As a result of using MRM mode of the tandem MS, no interference was observed [141].

The quantitative analysis of diphenylamine and its four derivatives, including N-NO-DPA, 4-NO2-DPA, 4-NO-DPA and 2, 4-2NO2-DPA has been reported by Tong, Wei et al [32]. Tandem MS/MS was utilised in the determination of these compounds in gunshot residues. MRM mode was employed to improve sensitivity and avoid interference. The limit detection of DPA, NDPA and 4-NDPA were shown to be 1.0, 0.5 and 2.5 ng ml^{-1} respectively. The method was found to be highly selective and sensitive [32].

1.1.8.6 Desorption Electrospray Ionisation (DESI) with Mass Spectrometry

Desorption electrospray ionisation (DESI)-tandem mass spectrometry technique has been demonstrated by Zhao et al. [31] to be a direct and sensitive method for the determination of stabiliser compounds in smokeless powder. Gunshot residue samples were detected without any sample preparation procedures. The improvement of the sensitivity was achieved using typical transitions for methylcentralite and ethylcentralite, *m/z* 241 to *m/z* 134 and *m/z* 269 to *m/z* 148, respectively. The results confirmed the possibility of detection for MC and EC from various surfaces, with detection limits of 5–70 pg/cm^2 and a detection window of up to 12 hours [31].

1.1.8.7 Time-of-Flight Secondary Ion Mass Spectrometry (TOF/MS)

A technique which has proven useful in analysing gunshot residue is time of flight mass spectrometry (TOF/MS) [142]. This type of mass spectrometry uses a time measurement to determine ions mass to charge ratio. An electric field of a specified

strength is used to accelerate the ions. After the ions have been accelerated they will have the same kinetic energy as other ions having the same charge. The ion's velocity is dependent upon the mass to charge ratio. The ions are accelerated and the time it takes them to reach a detector is measured; heavier particles travel at slower speeds [142].

TOF-SIMS has become a valuable technique in investigating gunshot residues. With the aid of principle components analysis (PCA), TOF-SIMS was able to distinguish between different smokeless and black powder samples by comparing the additives composition in the gunpowder. It is also possible to obtain mass spectral characteristics of each individual gunpowder sample consistent with known gunpowder compositions [142].

TOF-SIMS technique has some advantages over other techniques, such as surface sensitivity, low detection limits, and imaging capabilities, however it has some disadvantages, for example it requires operation under ultrahigh vacuum condition, which will increase the difficulty of analysis and expense of operation. Furthermore, TOF-SIMS is not a suitable technique for more volatile explosives such as nitroglycerine [143].

1.1.8.8 Ion Mobility Spectrometry (IMS)

West et al. [144] reported the first application of using ion mobility spectrometry (IMS) for the detection of ethyl centralite, DPA and its major nitrose and nitro derivatives in smokeless powder. IMS provides a rapid, simple and sensitive screening method for the detection and identification of organic components in smokeless gunpowder. Since the structure of methylcentralite is similar to ethylcentralite, IMS can be used to detect methylcentralite [144].

Detecting some explosive compounds in the hair of the suspects can be achieved with IMS. Three different modes were used to introduce the sample to the IMS: direct insertion, swabbing of the hair, or extraction of the organic materials from a hair using organic solvent. The IMS was run in two different modes: E-mode and N-mode. In E-mode, 2,4,6-trinitrotoluene (TNT), NG and ethylene glycol dinitrate (EGDN) were detected by all three sample introduction methods. In N-mode, TPAT extracted from hair was the only compound detected. The results showed that running the IMS in N-mode is more sensitive and required a lower amount of the sample for detection relative to E-mode [145].

Joshi et al. [28] reported the first application for the detection of odour signature in gunshot residues compounds. The methodology involved the extraction and pre-concentrate of smokeless powder additives from the headspace of commercial powder using solid phase micro extraction (SPME) fiber. The compounds of interest were detected by means of IMS. Diphenylamine and nitrated derivatives of diphenylamine such as dinitrophenylamine were found to be the most common volatile odour chemical in all the powder tested [28].

The evaluation of the persistence of organic gunshot residues was studied by de Perre et al. DPA was used as a target compound and IMS as the detection system. The method involved the extraction of the GSR sample from the hand using a solvent swabbing technique and the swab was introduced into IMS using direct thermal desorption. The results showed the persistence of the OGSR for at least four hours after discharging a weapon [146].

1.1.9 Conclusion for Gunshot Residue

GSR is an important type of trace evidence that can help forensic scientists to solve often complex crimes involving firearms. A variety of analytical techniques have been used to analyse the components of this residue. A number of issues are important in regard to the components of GSR. This residue consists of both inorganic and organic particles. The inorganic components are heavy metals, which do not degrade, but are frequently dislodged with activity. The tendency to move towards ammunition which does not contain heavy metals is increasing the need to develop robust techniques for the analysis of OGSR. However, as discussed later in this thesis, the analysis of OGSR is not without inherent problems associated with analyte stability [29, 147].

1.2 Fingerprints and Crime Scene Investigation

This section contains an examination of fingerprinting and related technology, especially with regard to crime scene investigations.

A fingerprint (epidermal ridge) is an impression which is left by finger ridges located on human fingers [148]. These friction ridges are raised portions of the skin on fingers. They are also present on the hand, the sole of the foot, and toes. They exist due to the interface between the dermis and dermal papillae, as well as the epidermal pegs (Figure 1.4). The epidermal ridges have the effect of amplifying vibrations when the fingertip is moved over a surface. This allows for better transmission of information to the sensory nerves. Fingerprint ridges also assist humans when grasping objects with their hands [148], hence they are also known as friction ridges [149].

Fingerprints are used in crime scene investigations because they are unique and permanent [148]. Fingerprints are formed when a foetus is in the twelfth week of gestation. After this time, the fingerprints are permanent, unless they are altered by accident or surgery. They remain on a person until their bodies completely decompose following death [150].

The fingerprints are uniquely valuable for criminal investigations as there have never been any fingerprints between individuals which have ever been found to be alike [150]. This is true even for identical twins, who have distinct individual fingerprints; even 21st century DNA technology cannot differentiate between identical twins. Fingerprints have been used in law enforcement for more than 100 years; research as well as empirical testing has proven their permanence and uniqueness [151].

Fingerprints contain ridge characteristics known as minutiae [150]. Fingerprints are linked with individuals by an examination of the characteristics of impressions. Ridge characteristics which are sufficiently similar can be judged to be from a certain person, therefore fingerprints left at a crime scene can implicate an individual as having been recently in the area [150].

Fingerprints are usually left at a crime scene due to sweat and other natural secretions from the eccrine glands located in the friction ridges of the skin [148]. When these substances are present on the surface of the skin, touching a smooth object will leave an

impression of the fingerprint. They may also be left as transfer marks in blood or other liquids, or as impressions in soft surfaces, such as fresh window putty or chewing gum.

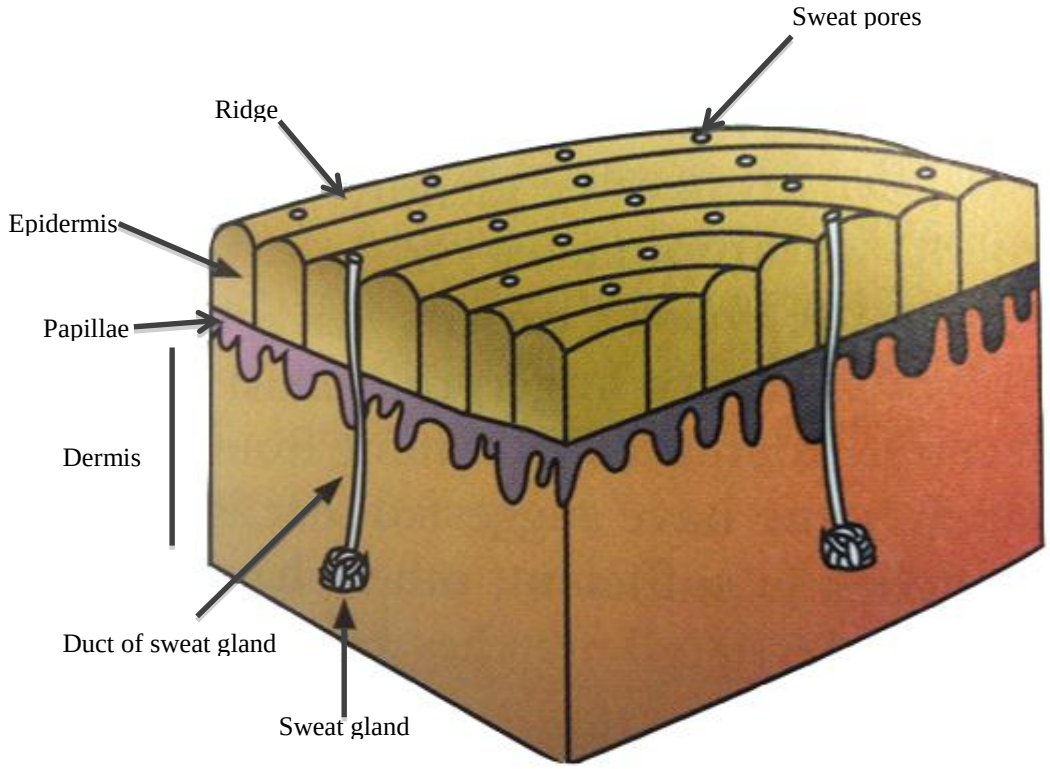

Figure 1.4. Friction ridge skin-diagram of longitudinal section [148]

1.2.1 History of Fingerprints

Fingerprints have been used for identification throughout the ages. They were used as signatures in ancient Mesopotamian civilization in clay seals for business transactions [152], and they were used in 14th century Persian government papers (Persian physicians noted that no two fingerprints were the same). The first modern use of fingerprints was in 1880 [152], when the surgeon-superintendent of a hospital in Japan, Dr. Henry Fauld, suggested a classification system for recording the ink impressions of fingerprints [152]. He published a paper in the journal *Nature* explaining how fingerprints could be used to identify individuals by taking impressions with printer's ink.

In 1888 the British anthropologist Sir Francis Galton (cousin of Charles Darwin) began studying fingerprints as a possible way to identify people [152]. He developed a system

which could be used to identify individuals by use of their fingerprints. The first person to use fingerprints for identifying an individual as being associated with a crime was an Argentine policeman named Vucetich. He began saving fingerprint files, which were based on the pattern types identified by Galton[152].

The world's first bureau of fingerprinting was known as the Anthropometric Bureau and was located in Calcutta, India [152]. The Bureau was formed after it had been approved by the Governor General of India in 1897. Bose and Haque were working at this Bureau when they developed the Henry System of classifying fingerprints. They named this after their supervisor, whose last name was Henry. This classification is still in use in many English-speaking countries in which there is a non-digitised paper archive of files [152].

1.2.2 Classification and Storage of Fingerprints

Prior to the modern practice of digitising information and storing it in computers, there were several different filing systems used to store and classify fingerprints [153]. These classification systems were based on the ridge formations and circular patterns present in fingerprints. This allowed for the filing and later retrieval of fingerprint records even in the case of large collections, enabled by using the ridge patterns. One of the most popular systems of classification was the Roscher System. Other systems included the Vucetich system of classification and the Henry system [148].

There have been a number of advances in how fingerprints are stored [154]. Many of these databases use compression technology. For example, one of the most common compression technologies used by law enforcement agencies located in the US is Wavelet Scalar Quantization. This is a system which can efficiently store compressed fingerprint images with 500 pixels per inch. This approach to storing fingerprints was developed by the Los Alamos National Lab of the FBI and the National Institute for Standards and Technology [151].

1.2.3 Types of Fingerprints

There are a number of different types of fingerprints, which include plastic, patent, latent, exemplar, and most recently electronic [155, 156]. The plastic fingerprint is made by a friction ridge pressing on the material and leaving the shape of the print

(similar to the fingerprint left by a finger pressed down on a piece of wet chewing gum or clay). There are a number of ways in which these can occur at a crime scene. For instance, an individual might touch melted candle wax. There can also be fingerprints left on automobiles in the grease deposits. Plastic fingerprints can be left near the edges of windowpanes in the putty. These prints are visible to the naked eye and can be photographically recorded [157].

Patent prints are those which are left by chance due to the material being transferred from a finger on to some surface [148]. An example of this might be a finger which is coated with flour being touched to a pane of glass. Like the plastic fingerprints, these types of prints are visible and lend themselves to be photographed as a means of recording [148]. There is also a wide variety of techniques that can be used to store the patent prints for later use, such as in a court presentation. One of the most common patent prints is made through the transfer of dirt from the fingers on to a smooth object [148].

Exemplar fingerprints are those which are purposely recorded [150]. This is routinely done after the arrest of a subject by placing ink on the fingers and rolling them on paper. This is also done in a wide variety of other situations, such as enrollment in the military. Usually a single print is taken from each of the fingers. Historically, exemplar prints were stored on paper cards. Many fingerprints are now collected using Live Scan technology, which stores the fingerprints as digital impressions [150].

Latent prints are those which are invisible to the eye [155, 158]. These are the most common types of prints found at a crime scene by forensic investigators. They are the result of a chance impression left from the friction ridge of a finger on to a surface. A wide range of chemical and electronic processing techniques have been developed to allow visualisation of latent prints [155]. This is true regardless of whether the prints are left due to natural body oils on the skin or contaminants such as blood or dirt [159].

1.2.4 Visualisation of Fingerprints

There are a number of different ways in which fingerprints can be obtained [153]. The most common method at a crime scene is latent detection. This has been performed for more than 100 years by police agencies throughout the world. Both victims of crime and suspected perpetrators have been successfully identified by fingerprints [153].

In order to have an effective fingerprint, a wide range of inorganic salts and organic materials are used [148]. Fingerprints usually consist of water-based secretions from the eccrine glands located on the palms and fingers. There may also be material from the sebaceous glands located on the forehead (after the person has wiped their forehead with their hand). Fingerprints which are left from any of these materials will have a significant amount of water as well as chlorides, amino acids, triglycerides, and fatty acids [150].

Latent prints at a crime scene are usually visualised using powders [148]. Items from the crime scene, such as a weapon, can be removed and studied in a laboratory using more complicated chemical enhancement techniques. This means using chemicals. Examples of chemical developers are ninyhydrin, gential violet, Amido Black, Sudan Black, DFO (1,8-diazafluoren-9-one), iodine fuming, cyanoacrylate fuming ("superglue"), and vacuum metal (gold) deposition [149].

While there is still widespread use of obtaining fingerprints through the use of ink and paper, there is an increasing tendency to use Live Scan devices [150]. These are electronic methods of recording the fingerprints. Information is recorded regarding the valleys and ridges on the fingers, which are stored in a digital database [160].

1.2.4.1 Recovery of Fingerprints from Firearms

There are different types of fingerprints, which can be recovered from firearms [2]. The prints which are visible are known as patent prints. These can be viewed without any type of enhancement. They can be seen without applying any type of chemical. Plastic prints are fingerprints, which are visible due to being an impression on a pliable material such as putty or paint [161]. This would be the case if a firearm had one of these substances on the handle or trigger. The most common type of fingerprints associated with firearms is those which are latent. These types of fingerprints can only be detected through the use of some type of enhancement technique such as a chemical, powder, or special lighting [162].

1.2.5 Structure of Fingerprint Powders

A traditional technique in the detection of fingerprints is to powder a smooth surface [163] The articles of powder adhere to the greasy, sticky, or humid substances, which are contained in the latent fingerprint deposits. While powdering for fingerprints is inexpensive and simple, it can be insensitive as only fresh fingerprints will be

detected by this method. This is due to the fingerprint deposits drying over time. There are various powders used in different situations [164].

While there is a wide variety of fingerprint powders, most have a color which is used for contrast as well as some type of resinous material, which yields adhesion [165].
Common colorants consist of sulfides, metal oxides, and carbonates. These can allow for different colors. Both mercury and lead were common formulations historically but are now used only on rare occasions due to problems related to toxicity [166].

Magnetic powders are made through mixing iron grit with copper or aluminum flake powder [167]. This type of powder is applied with a magnetic wand. The magnetic particles which are coarse make a type of brush, while the finer powder serves to develop the prints. By using magnetic powders, the traditional type of brushing is not necessary [168]. This is important as it can prevent the destruction of latent fingerprints, which are fragile. Unfortunately, the process is difficult when attempting to lift fingerprints from a vertical surface. A magnetic powder which is easier to use on an upright surface is one, which has had the iron grit passed through a ball mill which gives iron flakes in a range of 10 to 25 μM. These particles act in a more efficient manner and tend to stick even to vertical surfaces [2].

1.2.6 Nanoparticles Powder

There has been a trend during the 21st century to make use of gold nanoparticles as a dusting powder [162]. The gold nanoparticles have aliphatic chains attached to them. Silver and gold nanoparticles have been coated with oleylamine which is a long chained lipophilic molecule [168]. The nanoparticle produced by this procedure is preferentially deposited on latent fingerprints, which have lipid containing components. This type of powder has good performance on glass as well as painted wood. However, fingerprints on aluminum or plastic surfaces were more problematic. This is especially true when the fingerprints were older [166].
The advantage of the fingerprint powders based on gold-based nanoparticles is that they produce clearer and sharper images for the latent fingerprints [169]. This is true even when background staining is not done. It is also the case when there is less contrast relative to the more conventional black powders. Classical magnetic fingerprint powders have flakes, which are in the 5 to 25 μM range. This is more than 2000 times the size of the nanoparticles [170].

One of the most common techniques with respect to nanoparticles for fingerprint powder is that which is based on a reagent using a silver-palladium (ag-PD) mixture [169].

This is a reagent that can be used on water insoluble parts of the latent fingerprint which may be expressed as a residue on a porous surface. Latent fingerprints have been obtained from paper using the silver-palladium nanoparticle technique [164].

1.2.7 Fingerprint Powder Application Techniques

The most common method used in the development of latent prints is the brush and fingerprint powder method [171]. The materials for this consist of a writing implement, latent lift cards, lifting tape, a squirrel hair brush, a fiberglass brush, and fingerprint powder. The powder is applied over the area in a thin layer with the brush. When the latent pattern appears, the brush strokes should begin to follow the rich contour of the print. An attempt should be made to clean the fingerprint powder from the valleys in order to enhance the clarity of the print. The print can then be lifted using tape and placed on the card. It can also be covered with the tape and remain at the surface on an object [167].

It is important that the brush be used in a gentle manner. Many latent prints can be dissipated by the brush. Only the smallest amount of powder possible should be used. It is easier to add powder than removing any excess. The surface should be dry so that the powder does not smear the print [163].

Fluorescent powders require a different application technique [2]. They are finer and will produce better results when a feather duster is used instead of the squirrel hair brush. The advantage of a fluorescent powder is that it is finer and there is less effort required in order for the latent prints to be developed [161]. This decreases the chance that the print will be destroyed. A disadvantage is that the technique requires the use of an alternative light source in order for the powder to be observed. If an alternative light source is not available, a laser can be used. More traditional light can be used if there is a proper culture barrier available [167].

1.2.8 Enhancement Techniques

While latent fingerprints are the most common at a crime scene, they can also be difficult to detect and process [165]. For this reason, a number of techniques have been developed for enhancing latent fingerprints. One of the most popular methods is cyanoacrylate fuming [168]. Cyanoacrylate is known to the public through its use in

superglue. The fuming of the cyanoacrylate is a physical process in which the gas adheres to the impressions or a substrate by which it is surrounded. This approach has better success when there is moisture associated with the impressions. Dyes such as Rhodamine 6G can be used to enhance the impression even more [162].

The cyanoacrylate fumes interact with the latent fingerprints by polymerizing in situ to the residue [171]. This produces a rich impression which is stable and of off-white color. The process is done in the fuming cabinet in which the cyanoacrylate vapors are infused. There must be sufficient relative humidity and there is a moisture source in the fuming cabinet. While the fuming can be done in a cabinet which is closed, this is a slow process. To accelerate the fuming heat or a strong alkali is used. The latent residue development within the cabinet is monitored through the placement of a test latent print on aluminum foil within the cabinet in a location for easy viewing. If the latent prints are not fully developed with the cyanoacrylate, they can be fumed a second time [163].

Another enhancement method is known as a physical developer[171]. This is a process which is photographic in nature and relies on silver being deposited on the latent fingerprint residue. This residue is formed by a silver salt mixture and ferric redox couple. A similar procedure is to use colloidal gold and add it to the silver salt [164].

1.2.9 Automated Fingerprint Identification System

The FBI uses an integrated automated fingerprint system for identification (IAFIS) [153]. This system is automated and stores the fingerprints of more than 70 million people. These people may have been involved with a criminal investigation or the military. Fingerprints are also available for more than 70,000 people suspected of terrorism in the United States or by international agencies [148].

Fingerprints which are entered into the IAFIS can come from Live Scan technology or the traditional prints taken using ink and paper [151]. For the Live Scan technology, the fingers are placed on a plate of glass above the camera unit. When the prints are taken using paper and ink, which is scanned at high speeds, the process is known as Card Scan [160]. In order to determine if a fingerprint is a match with one stored in the IAFIS system, a technician will scan the suspect’s prints and a computer algorithm will be used to record the deltas, cores, points and minutiae [172] of the fingerprints. Many systems will require the technician to do a review of the points which is then identified by the software and submit these features for search. However, a number of commercial

systems are fully automated. These systems will usually assign some type of quality measure, which indicates the level of certainty. There were over 60 million submissions to the AFIS in the year 2010 [159]. In the UK the Automatic Fingerprint Identification System is NAFIS (National Automatic Fingerprint Identification System) [149], which is now called Ident One [173].

2 INSTRUMENTATION

Introduction

Research within the field of forensic sciences in general demands the use of assorted instrumentation for the collection and analysis of evidence necessary for decision making. Some of the instruments are highly technological and prohibitively expensive while others are affordable and easier to use. It is therefore prudent to examine the key instrumentation necessary for this research to be carried out.

This chapter therefore examines the necessary instrumentation for the current research starting with gas chromatography and mass spectrometry (GC/MS), Automated Fingerprint Identification System (AFIS) and Raman spectroscopy.

2.1 Gas Chromatograph and Mass Spectrometry

Gas chromatograph and mass spectrometry (GC/MS) is one of the most powerful techniques available for the analysis of complex mixtures. It is simple to use and provides both qualitative and quantitative data. GC/MS is a combination of two instruments: gas chromatography (GC), where volatile materials of a mixture are separated, and mass spectrometry (MS), which helps to identify individual molecules that are present in an unknown sample [174].

2.1.1 Gas Chromatograph

This thesis made use of a gas chromatograph (GC) (see Figure 2.1). This type of chromatography allows the separation of components within a mixture [175]. After the components are separated, they can be quantified. A gas chromatograph separates volatile components of small samples. The minute sample sizes can be analysed, making this an excellent technique for researching GSR components [176].

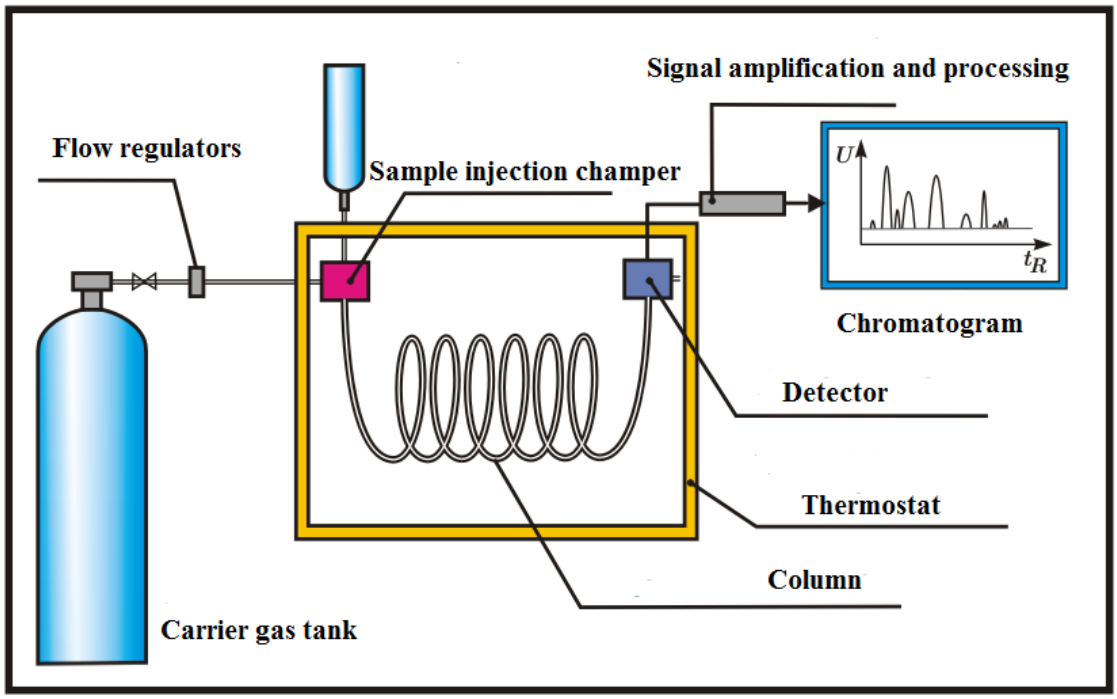

Figure 2.1. Block diagram of a typical gas chromatography[177]

Several components are necessary in order to perform gas chromatography. The sample is introduced into the instrument through the injector port using microliter syringe. The injection part is heated, usually 50-100 °C above the maximum column temperature

(typically 250 °C). The primary function of the injection port is to provide effective volatilisation of the sample [175]. Once in the gas phase, the sample is carried by the carrier gas onto the column.

The carrier gas (mobile phase) is usually an inert gas typically nitrogen or helium, although hydrogen is sometimes used as carrier gas. All the work presented in the thesis used helium as the carrier gas.

The function of the column is to provide separation of the analyte molecules in the mixture. The temperature of the column must be controlled accurately throughout the experiment. This can be performed at constant temperature (isothermal) or by using a predetermined temperature regime (temperature programmed). Sometimes it is necessary to reduce the volume of the sample entering the column, this can be accomplished using a split injection system [178].

Columns can be packed or capillary; both have been used for OGSR analysis, though capillary columns are more usual [107]. The capillary columns have a stationary phase which is coated on the walls of the tubular column (which is of a small diameter, typically 0.25 µ M). A variety of different materials have been used for the stationary phase, depending on the GSR components being examined [176].

Due to differences in the partition coefficient of the analyte between the stationary and mobile phase, the chemicals which interact aggressively with the stationary phase will generally spend less time in the mobile phase. This means they will travel through the column at a slower rate [178].

The column is generally chosen so that it will have a polarity which is similar to that of the sample [175]. This allows for the elution and interaction times of to be calculated according to Raoult's law. The relationship between enthalpy of vaporisation and vapor pressure can also be calculated accurately. Generally, the boiling points will correlate with the retention times. There will not be an exact quantitative correlation yielding an R-value of one, but it will often be close [175].

The interaction of the compound being analysed with the column is not the only variable affecting how the sample moves through the column [178]. Both the carrier gas flow rate and the column temperature are also important. Due to this phenomenon, a first run is often necessary in order to determine the appropriate column temperature

and gas flow rate in order to achieve the best separation of the sample. It is important not to allow elution times to become excessively long. This will result in a broadening of the peaks, which makes resolution poor. It should be remembered that the square root of the elution time is a measure of the width of a peak. The best results will be obtained by a gas flow rate and column temperature, which allows for separation of the peaks in the least amount of time [178].

When the proper column conditions have been chosen, the sample components will leave the column flowing past the detector as single compounds [176]. In other words, they will be appropriately separated. There are a number of different types of detectors, such as flame ionisation (FID), electron capture (ECD) and thermal conductivity (TCD), which can be used for gas chromatography. The specific type of detector will be determined by the type of sample being analysed. Flame ionisation detector has been used as a detector for all the works presented in this thesis.

When the peaks are well separated, the number of molecules from each component will be in direct proportion to the area which is beneath the peak. The software will determine the area under each peak and display the results in a table. The factor of proportionality regarding the amount in the area must be determined through a calibration experiment [176].

In this study, the analyses were carried out on a Gas Chromatograph/Mass Spectrometer (Focus GC, Thermo Fisher Scientific). Separation was carried out on forte GC, BPX5 capillary column (SGE).

Two different columns were used in this study, GC, BPX5 capillary column (SGE), and fused silica capillary column (SUPELCO). The column was 30 m long and had an internal diameter of 0.25 mm and film thickness of 0.25 µM.

The temperature program used an initial temperature held at 50 °C for 5 minutes, then the temperature was ramped to 150 °C at 10 °C min^{-1} and ramped at 20 °C min^{-1} to a final temperature of 250 °C and held for 5 minutes. The carrier gas was helium with a constant flow of 1.2 ml min^{-1}. To improve sensitivity, the sample was injected in the splitless mode with no solvent delay. The injector temperature was maintained at 250 °C for desorption and conditioning. Initially, 5 µ L of each sample was manually injected into the GC for preliminary tests and composition determination.

2.1.2 Mass Spectrometer

Mass spectrometry is used to quantitatively understand the characteristics and identify individual molecules that are present in an unknown sample. Mass spectrometry has undergone continuous technological improvements in terms of ionisation methods, allowing for its application in forensic science, as it facilitates analysis of biologically relevant molecules such as proteins, peptides, carbohydrates, DNA and drugs [174].

A mass spectrometer determines the mass of a molecule by measuring the mass-to-charge ratio (*m/z*) of its ion. The ions are generated by stimulating either the loss or gain of a charge from a neutral species. Once these ions are formed, they are directed into a mass analyser using electrostatic fields where they are separated according to *m/z* and finally detected. The result of the molecular ionisation, ion separation, and ion detection is a spectrum that can provide molecular mass and even structural information.

The modern mass spectrometer has four essential functions. Each function is carried out by a related component. These are listed below (Figure 2.2).

1. **Inlet:** where a sample introduced into the MS.
2. **The Ion Source**: where a minute amount of an unknown sample is ionised usually to positive ions by loss of an electron.
3. **The Mass Analyser:** where the ions are sorted and separated according to their mass and charge.
4. **The Detector:** where the separated ions are finally detected and the results are shown.

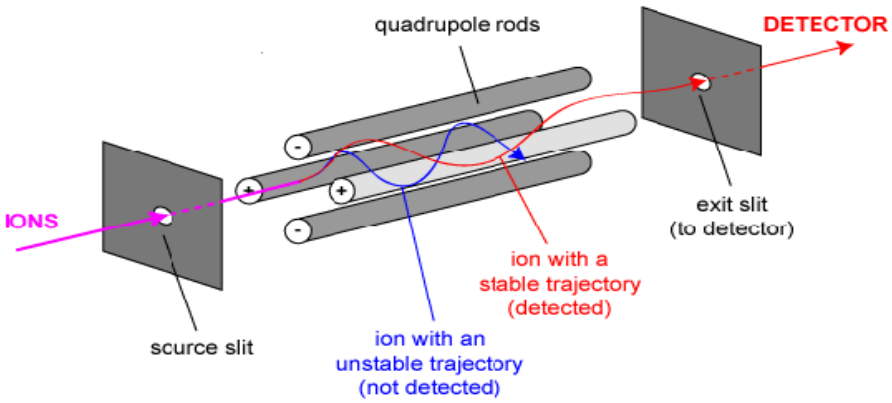

Figure 2.2. Basic Operation of a mass spectrometer[179]

There are four fundamental components inside a mass spectrometer that are standard in all mass spectrometers [174]. These are a sample inlet, an ionisation source, a mass analyser and an ion detector. There are some instruments that combine the sample inlet and the ionisation source, while other instruments combine the mass analyser and the detector. In spite of this, all sample molecules undergo the same processes irrespective of instrument configuration. Sample molecules are injected into the instrument through a sample inlet. Once inside the instrument, the sample molecules are converted to ions in the ionisation source and are fired into the mass analyser using electrostatic forces. Hard ionisation methods are suitable for sample molecules that do not decompose due to heat, whereas soft ionisation methods are suitable for sample molecules that easily decompose with heat. As mentioned previously, the ions are then separated according to their *m/z* inside the mass analyser. Finally, the detector converts the ion energy into electrical signals, which are then transmitted to a computer, and we see the mass spectrum.

2.1.3 Vacuum System

Mass spectrometers usually use either oil diffusion pumps or turbo-molecular pumps to achieve the high vacuum required to operate the instrument [180]. Diffusion pumps are quieter and are cheaper, but they take longer to reach maximum pumping speed and there is a possibility of instrument contamination in case of a leak. Turbo-molecular pumps are more expensive but quicker with regard to reaching ultimate pumping speed. It can also reach a higher vacuum compared to the diffusion pump.

A roughing pump system will also be needed to produce a roughing vacuum. It depends on the instrument size. For example in a bench top instrument, one mechanical pump may serve as both the roughing and fore line pump while in more sophisticated instruments a dedicated roughing pump may be present to allow pumping of inlet ports while the instrument is pumped to high vacuum using the turbo-molecular pump [180].

2.1.4 Inlet System

Depending upon the sample being analysed, there are various methods to insert the sample inside the ionisation source. Each mode can be coupled to a complementary ionisation mode [181]. Gas chromatograph with electron ionisation mode was used in this study.

Correct sample introduction into the mass spectrometer is very important. The choice of the inlet system and the ionisation mode depends on the sample being analysed. As mentioned, different inlet systems are appropriate for different ionisation modes. The factors that define the choice of the inlet system are the solubility, volatility and thermal stability of the sample [181].

2.1.5 Ionisation Mechanisms

There are a number of ion sources or ionisation mechanisms that work with mass spectrometry. The main factors that help choose the ionisation method are the thermal stability, polarity and molar mass of the sample being analysed [181]. The correct choices of ionisation method are important because inappropriate ionisation method will result in the poor spectrum being obtained or even no spectrum at all.

Ionisation methods such as electron impact (EI) ionisation are known as hard ionization, and cause more fragmentation of the sample molecule and less of the molecular ion. Soft ionisation methods such as electrospray ionisation cause lesser fragmentation and more of the molecular ion. Therefore, the molar mass and thermal stability of the sample molecule help us choose the correct mode of ionisation. The one used in this work is electron impact (EI) ionisation.

2.1.5.1 Electron Impact Ionisation (EI)

Electron Impact ionisation is a hard ionisation technique. This means that this ionisation method is suitable for samples that are thermally stable and volatile. Volatile sample molecules in vapor state are bombarded by fast moving electrons, usually with energy of 70 eV. This results in the analyte molecules forming ions. An electron from the highest energy orbital is removed from the sample molecule and as a result molecular ions are formed. Since high energy is used, some of these molecular ions decompose and fragment ions are formed. The fragmentation of a given ion is due to the excess of energy than it requires for the ionisation. Fragment ions can be odd or even electrons depending on their stability. Molecular ions formed in electron impact ionisation are odd electron ions [182]. Odd electron fragment ions are formed by direct cleavage of a covalent bond whereas even electron fragment ions are often formed by rearrangement to form a more stable structure (e.g. proton transfer). As previously mentioned, the sample can be introduced to the EI source through a gas chromatography

device or directly via a solid insertion probe. The amount of sample needed for an experiment is usually less than a microgram of material.

2.1.5.2 Chemical Ionisation (CI)

Chemical Ionisation (CI) is an especially useful technique when no molecular ion is observed in EI mass spectrum, and also in the case of confirming the mass to charge ratio of the molecular ion [182]. Although chemical ionisation technique uses almost the same ion source device as in electron impact, CI uses tight ion source and reagent gas. Reagent gas (e.g. ammonia, methane) is first subjected to electron impact. Sample ions are formed by the interaction of reagent gas ions and sample molecules. This phenomenon is called ion-molecule reactions [182]. Reagent gas molecules are present in the ratio of about 100:1 with respect to sample molecules. The main advantage of CI over EI is that CI is a soft ionisation technique that is able to provide information about the molecular mass of the sample in cases where EI fails to do so.

In CI, the interaction between the reagent ions (G) and neutral sample molecules (M) occur that are known as ion molecule reactions to produce analyte ions. Stable ions such as pseudo-molecular ion MH+ (positive ion mode) or [M-H]- (negative ion mode) are observed in CI [182]. Unlike molecular ions obtained in EI method, MH+ and [M-H]- detection occurs in high yield due to them being more stable, and less fragment ions are observed. CI is normally used to determine the molecular weight of sample, in mixture analysis and in obtaining structural and stereochemical information.

2.1.6 Mass Analysers

After ionisation, the vaporised ions must be separated according to the difference in their mass to charge ratio (*m/z*). Since there are a number of ion sources available, there are also many corresponding mass analysers. Each mass analyser works on its own principle of operation, but all use static or dynamic electric or magnetic fields that can be used in combination or on their own [183]. The five main factors that help measure the performance of a mass analyser are the mass range limit, the analysis speed, the transmission, the mass accuracy and the resolution [183]. The three most common types are the quadrupole MS, the Ion trap MS and the TOF MS. A quadrupole mass analyser was utilised in this study.

2.1.6.1 Quadrupole Mass Analyser

The quadrupole mass analyser is an instrument that utilises the stability of the paths traced by the ions inside the electric field and separates them according to their *m/z* ratio [183]. There is no magnetic field present in the quadrupole mass analyser. These analysers are made up of four parallel rods of circular or hyperbolic cross section (Figure 2.2). Two opposite rods are set at a positive electrical potential, and the other one at a negative potential. A combination of direct current (DC) and radio frequency (RF) voltages is applied to each set. The positive pair of rods acts as a high mass filter, while the negative pair acts as a low mass filter. The resolution of the mass filter depends on the direct current value in relationship to the radio frequency value [184]. The quads are operated at constant resolution, which maintains a constant RF/DC ratio. A given ion with an appropriate *m/z* ratio will make it through while all other ions with *m/z* not matching the requirements will hit the rods. A mass range up to 4000 Da can be detected using this analyser [183]. The quadrupole mass analyser is more sensitive than the double sector analyser [183].

GC/MS quadrupole mass analyser can be operated in two different modes: full scan and selected ion monitoring (SIM) [175]. In the full scan mode, the quadrupole mass analyser will monitor a range of masses and it will detect the fragmentations of a compound within that range over certain period of time. The full scan mode is very useful to identify unknown compound in the complex mixture. In SIM mode, specific ion fragments can be selected to pass through the instrument and then be detected by the mass spectrometer. In SIM mode the instrument will look only for small number of fragments which will increase the sensitivity and therefore increase the limit of detection [175].

2.1.6.2 Ion Trap Mass Analyser

An ion trap mass analyser uses the concept of an oscillating electric field to store ions [183]. It is compatible with the gas chromatograph. It works by using a quadrupole field to trap ions in 2D or 3D. In this system, ions of different masses are present together inside the trap and are expelled out depending on their *m/z* ratio in order to get the spectrum. As the expelled ions repel each other in the trap their paths expand as they come out depending on time. Masses up to *m/z* = 6000 Da can be detected using this

system and it is very sensitive, although only as much as half of all the ions are detected [183].

2.1.6.3 Time of Flight Mass Analyser

The time of flight mass analyser is well suited to the pulsed nature of laser desorption ionisation such as MALDI [183]. This instrument separates ions after they are initially accelerated by an electric field. The separation is based on their velocities in a field free region called a flight tube. The ions are emitted from the ion source in clusters that are produced by a plasma or laser desorption [183]. These ions are then accelerated towards a flight tube using an electrostatic potential difference and an ion extraction system. All the emitted ions acquire the same kinetic energy but the momentum of each ion is different depending on mass and velocity. Depending on this mass and velocity distribution, the ions are separated in the field free region before reaching the detector kept at the other end of the flight tube. This is the most sensitive mass analyser, but it requires a very low pressure to work (10-9 Torr) [183].

2.1.7 Detectors

There are many types of detectors. Most of them work by producing an electronic signal when hit by charged species. Timing mechanisms are involved which integrate those signals with scanning voltages that allow the instrument to report which *m/z* value strikes the detector. It is the mass analyser that sorts the ions according to *m/z* and the detector records the abundance (the number of hits) of each *m/z*. It is important to maintain regular calibration of the *m/z* scale to maintain accuracy in the instrument. As usual, calibration is performed by introducing a well-known compound into the instrument and tuning the circuits so that the compound's molecular ion and fragment ions are reported accurately [183]. The most common type is called the electron multiplier tube. In this section, the ions are measured and the results displayed in chart (called a chromatogram) or table form [185].

2.1.8 Fragmentation

The majority of organic compounds will yield mass spectra, which includes molecular ions. The most stable molecular ions in the majority of simple organic compounds are those with aromatic rings. Some of these compounds may also contain cycloalkanes or conjugated pi-electron systems [183].

The complexity of fragmentation during mass spectrometry allows for the pattern to be used as a type of fingerprint to identify specific compounds [186]. Mass spectral library databases are used to help do this. This is particularly useful for GSR analysis. It has also been used to identify a number of compounds often found at crime scenes, such as flammable liquid residues, controlled substances (drugs), certain explosives, in forensic toxicology, and in the analysis of food residues, pesticides, or environmental pollutants. Substances which are found in minute quantities of even a microgram or less are often sufficient to do a determinative analysis with mass spectrometry [186]. This makes the technique particularly valuable for analysing the components which are present in GSR. The majority of GSR samples are quite small and may be invisible to the naked eye.

While mass spectrometry is a useful tool, it cannot be used independently for GSR analysis due to the impure nature of the sample [107]. The sample of GSR, which is taken from clothing or skin, consists of a complex mix of molecules with unknown contaminants associated with the background in which the weapon was fired. For this reason, mass spectrometry is combined with gas chromatography. The gas chromatograph separates the compounds of interest from the contaminants prior to analysis with the mass spectrometer [108].

2.2 Automated Fingerprint Identification System (AFIS)

Traditionally, individual prints were compared to prints on file by fingerprint examiners to discoverer minutiae details such as ridge dots, ridge endings and bifurcations [187]. The process was time-consuming, taking weeks or months for a fingerprint to be processed due to the long process of examination by the central fingerprint bureau. Information technology has brought remarkable changes to fingerprint identification. Fingerprints can now be scanned and digitally encoded using high-speed computer processing systems.

Automated fingerprint identification system (AFIS) is a biometric identification (ID) technique introduced in the mid-1980s. AFIS applies digital imaging technology to attain, stockpile, and examine fingerprint data [188]. The system database constitutes fingerprint images collected from people either by using manual fingerprint cards or electronic capture using devices with similar features as a scanner, and also from a latent fingerprint [187]. AFIS is a very robust technique which enables law enforcement agencies to identify criminals more quickly, and also has access to a large database with information on fingerprints. This alone has greatly enhanced the efficiency of the criminal justice system and also increased the conviction rate of offenders [187].

2.2.1 History

Modern fingerprinting technology was introduced to tackle crime in the early 1960s, when the FBI in the United States, the Home Office in the United Kingdom, Paris Police in France, and the Japanese National Police initiated projects to develop automated fingerprint identification systems. All these departments used emerging electronic and digital computers to assist or replace the manual labor-intensive processes of classifying, searching, and matching ten-print cards with ink and roll systems, as used for personal identification. On December 16, 1966, the FBI issued a Request for Quotation (RFQ) “for developing, demonstrating, and testing a device for reading certain fingerprint minutiae” [152]. The FBI’s efforts to automate the fingerprint matching process were perceived to be successful, so state and local law enforcement agencies began to evaluate this new fingerprinting technology for their own applications in collecting and storage of fingerprints. The United States developed the AFIS technology in the 1960s, however it took over two decades for the technology to be completely introduced in all states. France, the United Kingdom, and Japan also

conducted research into automatic fingerprint image processing and matching. AFIS initiatives spread across Japan, France, United Kingdom and the United States from the 1960s to the 1990s.

The Automated Fingerprint System (AFIS) was the most definitive computerised and digital system introduced in certain US states in 1997 and fingerprint technicians were provided the capability to scan fingerprint images for storage, comparison and retrieval. In 2008 AFIS upgraded their systems to eliminate the scanning process and decrease processing time to allow instantaneous links of data and information to the FBI for criminal investigations. The database consists of information on criminal arrests and fingerprints of offenders that allows for identification of suspects in real-time. It is possible to compare latent fingerprints against the stored ten-print images [189]. An automated fingerprint identification network enables processing and storing of live-scan transmittals and connects with FBI's integrated automated fingerprint system (IAFIS) to share arrest information that could replace ink and roll arrest cards. The AFIS technology introduced in 1997 was expanded in 1999 to several law enforcement contributors, and by 2009 AFIS lives-can helped in the transmission of 90% of arrests in the US [189]. Live-scan machine used in automated fingerprint identification system replaces and ink and roll fingerprints and provides a paperless environment wherein the prints are converted to digital form for electronic transmission to workstation for identification.

2.2.2 Main Components and Processes

Principally, there are four components of AFIS system, namely scanner, the recognition algorithm, database search a query algorithm and the data compression algorithm [190]. The scanner traces the fingerprint at a low resolution of about 500 pixels in both column and row. The image of fingerprint is converted to digital minutiae (the ridge characteristics) by the scanning devices. The digital minutiae contain data showing ridges at their points of termination (ridge endings) and the branching of ridges into two ridges (bifurcations). The scanning converts the spatial relationship of a fingerprint's ridge endings and ridge bifurcations (minutiae points) into a digitised representation of the fingerprints [191]. Regardless of the type of the technique and media applied by the scanner, the generated electronic image must be of sufficient quality to provide convincing fingerprint comparison, prosperous fingerprint sorting and characteristic detection, and should enhance AFIS search credibility [192].

Fingerprint matching (Figure 2.3) pursues scanning, whereby the image quality is improved. The fingerprint matching entails two tasks: ridge improvement; and segmentation and restoration of fingerprint images. In this step a binary fragmented fingerprint ridge image is generated from grey scale image input, with the ridge possessing a value of 1, and the rest of image possessing a value of 0. Moreover, the fingerprint matching entails computation of direction field, background/foreground division, ride segmentation and ridge directional smoothing [193].

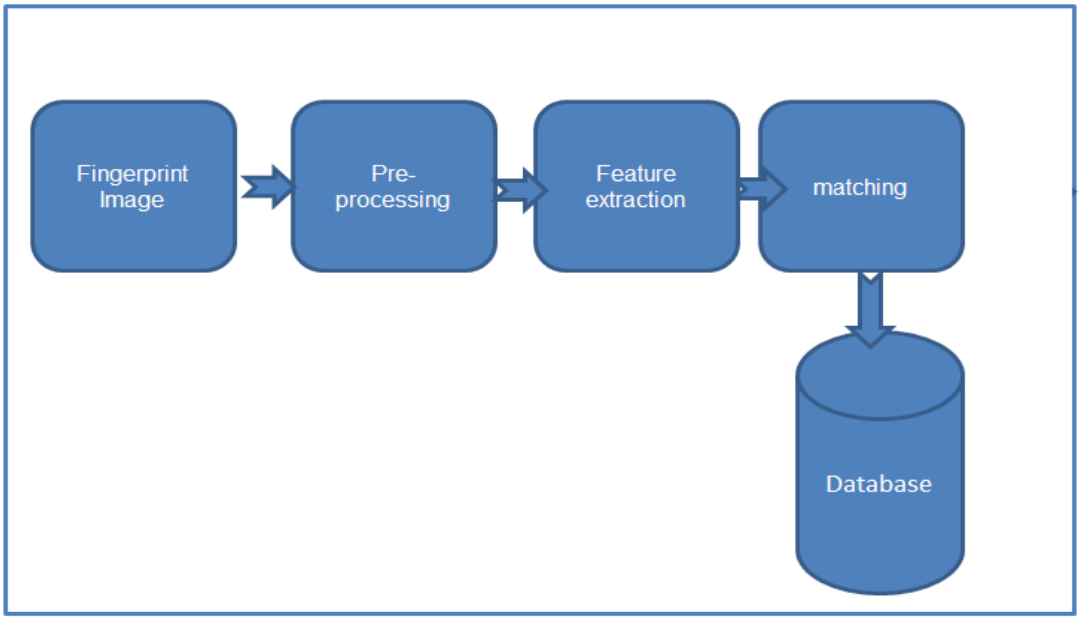

Figure 2.3. Matching block diagram in AFIS [193]

Fingerprint classification pursues fingerprint matching, whereby the fingerprints are classified into five main categories [193]: arch, tented arch, right loop, left loop and whorl [194]. Figure 2.4 illustrates classification process of fingerprints. In case of partial print or noisy fingerprint, ridge density count and singular point detection is used as an alternative classification method [193].

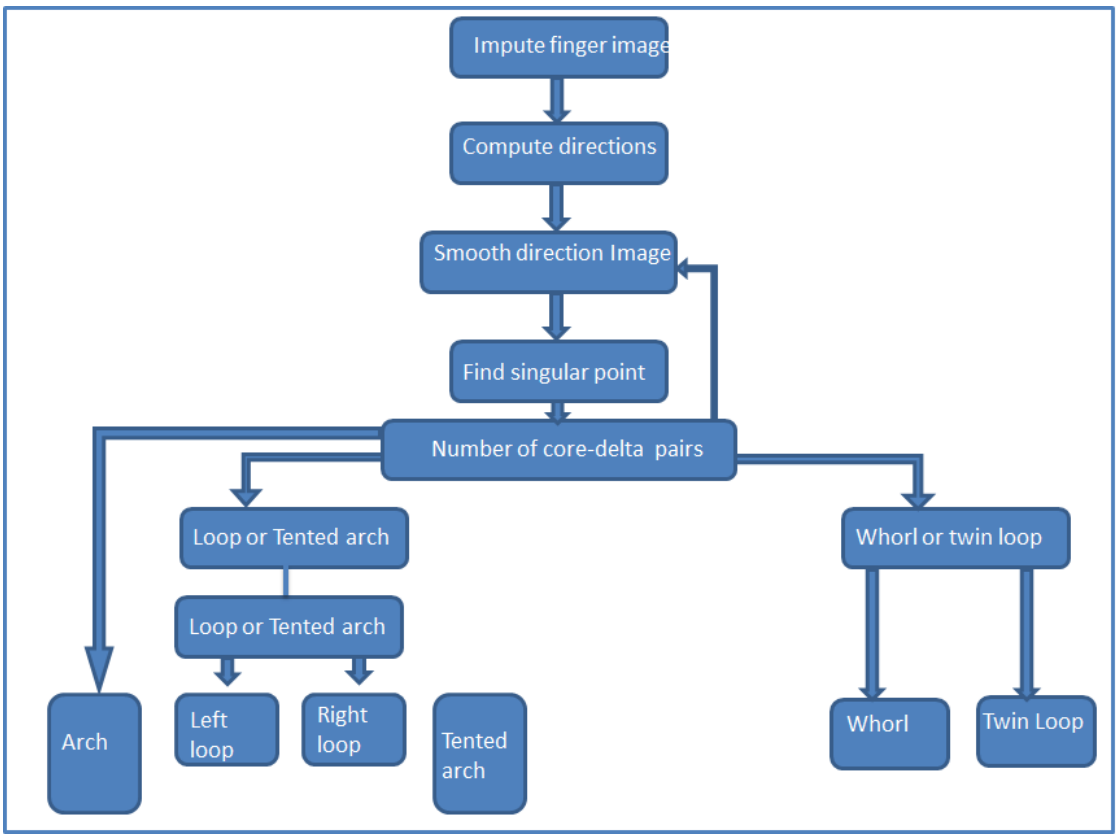

Figure 2.4. Block diagram of the fingerprint classification algorithm[193]

2.2.3 How AFIS Works

When a person is arrested, the police take the suspect into police custody where their fingerprints are taken as part of the booking process. The suspect's fingers and palm are rolled on a glass plate placed on a Live Scan or inked prints are used which are later scanned [187]. The scanner and terminal placed below the plate read the prints information, which is stored digitally in a computer's memory. The computer then generates a spatial map of the unique ridge patterns of the prints and then translates into a binary code [191]. This information is later conveyed electronically to the identification section, where the trained officer in charge of identification checks the prints for the purpose of quality control [195]. After checking the prints using the AFIS approval station, the technician coveys the data to the AFIS, wherein the fingerprints are searched against a database that contains over 50 million individuals' fingerprints. The AFIS submits information based on three-closest match of the searched prints. When the search is complete, the computer produces a list of file prints. Trained fingerprint experts compare the fingerprints with those of the arrested suspect to determine whether

the latter has previously been arrested or has provided fake recognition information[187].

The identification part of the system occurs when the fingerprints are searched against the fingerprints database on a local or national database. The term system is coined from the computerisation of fingerprint identification process, application of software and the fact that it can be integrated with other identification systems and subsystems [187].

2.2.4 AFIS Operations and Proliferation

The AFIS has been viewed as a system that encompasses all aspects of identification and brings identification from the crime scene to the courtroom. The AFIS operations work on a budget that includes laboratory, crime scene equipment, training of forensic evidence and purchase of vehicles. The new system was organised and introduced in 1983 and significant organisational changes commenced when AFIS was used on a large scale by all law enforcement agencies. The AFIS provided a search database where all latent prints could be searched and a new unit for Crime Scene Investigation (CSI) was created and staffed to work 24/7. Patrol officers were required to notify crime scene investigators after referring to latent prints [196].

AFISs that are used with law enforcement units are composed of two interdependent subsystems: the ten-print (i.e., criminal identification) subsystem and the latent (i.e. criminal investigation) subsystem. Each subsystem is autonomous, and yet these are interdependent subsystems and important for public safety. The ten-print subsystem identifies sets of inked or live-scan fingerprints incident to an arrest to determine whether a person has an existing record and is the first step to definite identification [196].

Within law enforcement units, identification personnel are responsible for maintenance of the fingerprint and criminal history databases and AFIS provides the necessary infrastructure for such regulations. Identification bureau personnel comprise fingerprint technicians who perform automated ten-print fingerprints with sufficient clarity so searching of more than two fingers in a criminal investigation is usually unnecessary, as one fingerprint provides considerable detail. Generally, a search on AFIS can return a million records in under a minute. The AFIS databases have expanded in time across the world, and although search one finger is sufficient, AFIS engineers have expanded to searching four fingers or more within a database, in an effort to increase accuracy [196].

The latent print or criminal identification subsystem helps in solving crimes though the identification of latent prints. These prints are developed from crime scenes and provide physical evidence of criminals. The search for identifying evidence using latent prints is more tedious and time consuming than a ten-print search because latent prints are fragmentary and have poor image quality than a ten-print [196].

2.2.5 Benefits of AFIS

Although there is no national reporting mechanisms, gathering of AFIS data or latent print statistics, undetermined benefits of AFIS seem to exist. Based on one survey, an estimated 50,000 suspects are identified in the United States every year through AFIS latent searches. However the contribution of latent print identification on public safety is largely unmeasured [196]. One AFIS hit prevents at least 100 crimes in a year if a criminal is convicted with fingerprint identification for five years in prison. Community safety is one of the major benefits of AFIS identification systems [196].

2.2.6 AFIS – Errors and Validation

In the past 100 years, many theoretical models have been used to test the theory of two friction ridge and images from different areas of palmar surfaces determine the minimum number of minutiae that could be sufficient to support individualisation decision [196]. AFIS tested the practical applications of identification theory every day for more than 20 years following being introduced in the 1980s. The applications of the AFIS systems tend to validate the friction ridge principles initially propounded when AFIS first came into effect [196]. AFIS has served as a catalyst to help expand image processing knowledge and skills of investigation personnel. However errors can happen in manual and automated systems and the systems can be improved in the future when there is continual study of errors. According to Wayman, “Error rates (in friction ridge identification) are difficult to measure, precisely because they are so low” [197]. This would suggest that AFIS systems and fingerprinting technologies and applications have considerable reliability and validity and are generally subject only to minor or very occasional errors [197].

2.3 Raman spectroscopy

Raman spectroscopy is a method which is employed in chemistry as well as condensed matter physics to study the low-frequency modes, such as rotational and vibrational modes in systems. The effect was discovered during 1928 by the Indian physicist Chandrasekhara Venkata Raman [198]. This spectroscopic technique relies on Raman scattering (inelastic scattering) of monochromatic light in the near infrared, near ultraviolet or visible spectrum. The scattering of light can then give information about the symmetry, bonding, electronic environment and the symmetry of the involved molecule [198]. This facilitates both qualitative and quantitative analysis of the compound [199]. The latest advancements in technology have led to Raman spectroscopy being a useful analytical tool used in studying forensic materials. Raman spectroscopy is applied in forensic science because of its non-destructive and non-contact nature [200]. The technique can be used to analyse inorganic and organic compounds, either non-volatile or volatile species.

2.3.1 Theory of Raman Spectroscopy

When monochromatic light is directed onto a sample, the radiation interacts with the sample such that it can be reflected, scattered or absorbed. The scattered light consists of several components, namely the Anti-Stokes scattering, Stokes scattering and Rayleigh scattering [198]. Figure 2.6 below shows the radiations scattered from the sample.

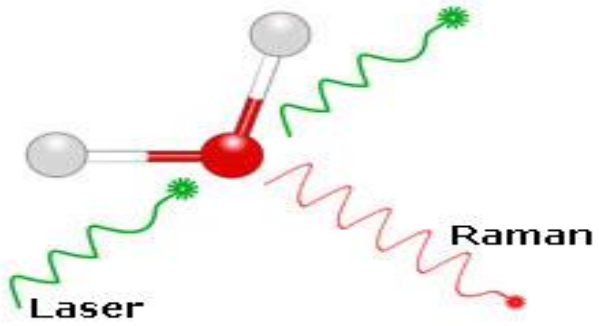

Figure 2.5. Radiation scattered from the molecule

When a molecule is irradiated with a monochromatic light, two types of light scattering takes place: elastic and inelastic (Figure 2.6) [199]. In elastic scattering, the

interaction of the incident radiation with the compound or molecule is not associated with exchange of energy between the photon and the molecule, therefore the net energy exchanged is zero. On the other hand, inelastic scattering takes place when the interaction of the incident radiation with a molecule causes the single molecular vibration net energy exchange, in which either the photon may lose or gain some amount of energy. Consequently, three types of phenomena can occur [199].

Rayleigh scattering takes place when the incident light intricate with a molecules but the net exchange of energy (E) is zero, therefore the frequency of the scattered photon is the same as that of the incident light($E= E_o$).

Anti-Stokes Raman Scattering occurs when the interaction of the incident radiation with a molecule causes the single molecular vibration net energy exchange. In this case, the photon could gain energy and thus making the scattered radiation to have a greater frequency than the incident radiation ($E = E_o + Ev$). Conversely, in Stokes scattering, the photon transfers energy to the molecule and thus the scattered radiation will possess a higher frequency compared to the incident radiation ($E = Eo - Ev$)[199].

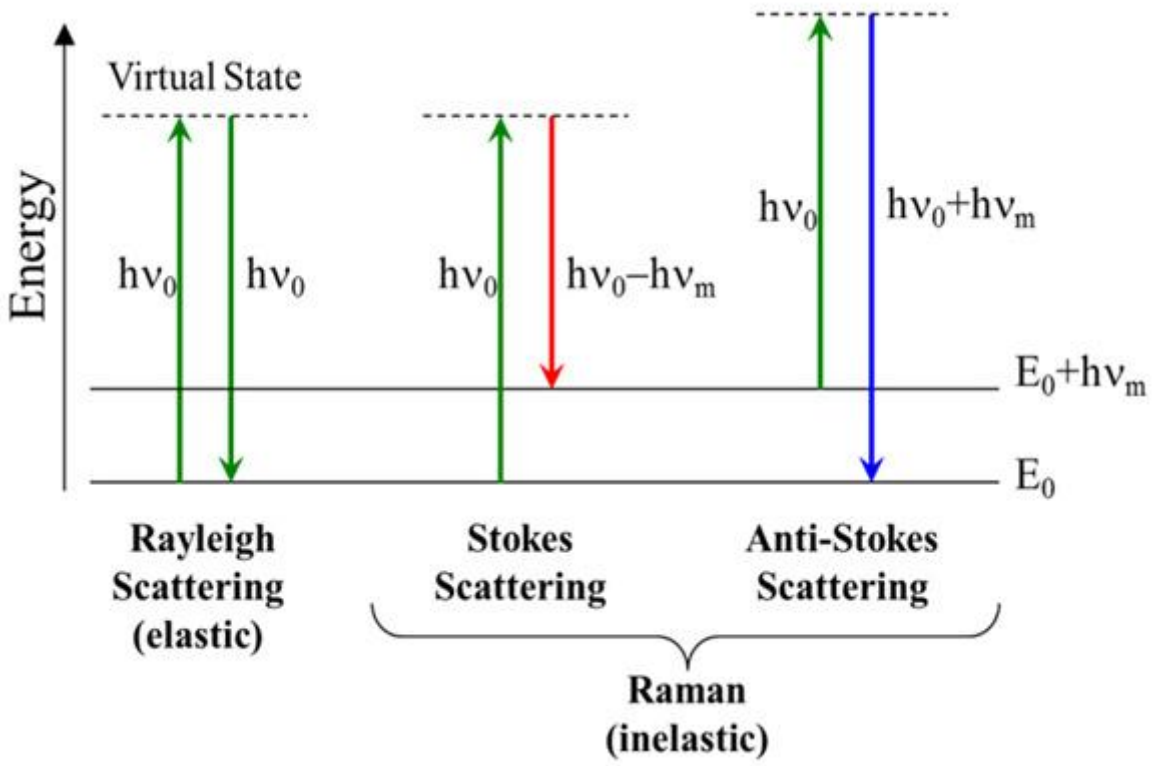

Figure 2.6 Jablonski energy diagram [201]

2.3.2 Instrumentation

The Raman spectrometer consists of an excitation source (laser), sample illumination system and light collection optics, wavelength selector (filter or spectrophotometer) and detector (Figure 2.7).

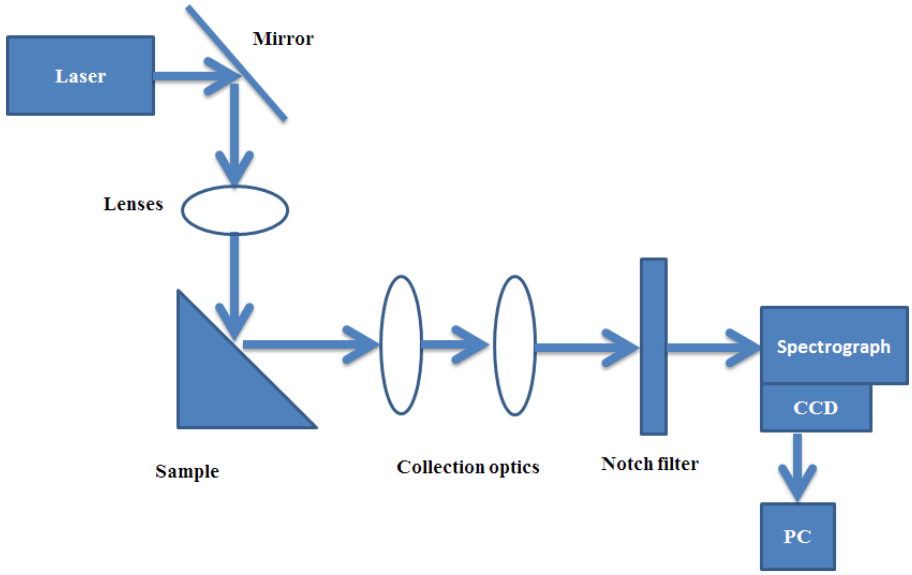

Figure 2.7. Schematic diagram for Raman spectroscopy [202].

The sample is illuminated by using the laser light in the visible, near-infrared (NIR) or ultraviolet (UV) range. The light scattered from the sample is then focused by the lens through the spectrophotometer. The spectrophotometer separates the Raman modes. Spectrometers are of various types: non-dispersive, dispersive and Fourier Transform (FT) [203]. Non-dispersive spectrometers do not allow the selection of variable wavelengths. On the other hand, in dispersive spectrometers, the variable wavelengths could be selected by using filters or gratings. The optical mechanism contained in the spectrometer is utilised in transmitting light to the detector. The lens system, which is made of either quartz or glass, could only be used in the visible or ultra violet range. The lens system cannot be used in the infrared range because the lenses absorb the incident radiation, which is below 5000 cm^{-1} [204]. Therefore, the IR spectrometers consist of mirror optics.

The intensity of Rayleigh scattering could be greater than that of Raman signals, which makes it difficult to separate the two. This problem can be solved by the use of interference filters to cut off the spectrum within the range of ± 80 to ± 120 cm^{-1} away

from the line of the laser [203]. This technique is very efficient in eliminating the stray light, but cannot detect low-frequency Raman scattering within ranges less than 100 cm^{-1} [203]. Stray light depends on the quality of the grating, since it occurs during light dispersion. Normally, Raman spectrometers utilise holographic gratings because they have less structural defects compared to the ruled gratings. The stray light generated from the holographic grating is less intense in magnitude compared to that generated by ruled gratings. Utilising multiple dispersion phases is also another technique of reducing stray light. Double as well as triple spectrometers allow Raman spectra to be taken without using notch filters [203].

The use of single-point detectors like PMT (Photomultiplier Tubes) require longer exposure periods. This is because the Raman signal is very weak. Currently, multichannel detectors such as Charge-Coupled Devices (CCD) and Photo Diode Arrays (PDA) are used for detecting signals in the Raman spectroscopy. The two major techniques that are employed in collecting Raman spectra are dispersive Raman and Fourier transform Raman. Each technique has its own unique advantages which are ideally suited to specific types of analysis [205].

Dispersive Raman utilises visible laser radiation including a wide range of laser wavelengths (780 nm, 633 nm, 532 nm, and 473 nm). The intensity of the Raman scatter is proportional to $1/\lambda 4$, therefore short excitation laser wavelengths provide a much stronger Raman signal. In order to observe the Raman spectrum in dispersive Raman instruments, it is necessary to separate the collected Raman scattered light into its composite wavelengths. This was performed by focusing the Raman scattered light onto a diffraction grating. The grating separates the wavelengths of light in the spectral range and directs each wavelength individually through a slit to the detector to produce a spectrum [205].

In FT-Raman spectrometer a laser in the near infrared is usually used at 1064 nm, where fluorescence wavelength is almost completely absent. FT-Raman employs sensitive, single-element, near-infrared detectors. These include indium gallium arsenide (InGaAs) or liquid nitrogen-cooled germanium (Ge) detectors [205].

An interferometer-based system converts the Raman signal into an interferogram. This will allow the detector to collect the entire Raman spectrum simultaneously. Generally at low signal levels the spectral noise is mostly detector dark noise and is independent

of the intensity of the Raman signal. The entire spectrum is delivered at once onto the detector, which greatly improves the signal to- noise ratio [205].

It should be noted that the FT spectrometers have several advantages over dispersive interferometers. Firstly, in the FT spectrometers the wavelengths can be measured simultaneously, while in the dispersive interferometer they can only be measured one at a time [204]. Secondly, FT spectrometers have higher wavenumber stability than the dispersive ones. Next, the measurement times are shorter in FT interferometers than in the dispersive ones using the same signal-to-noise ratio [204] Again, the FT interferometers' light throughput is higher than that of the dispersive ones.

In this study Raman spectra were collected using a Horiba JobinYvon HR 800 Raman spectroscope. The Raman scattering was excited with a 532 nm near infrared diode laser and a 50X objective lens, giving a laser spot diameter of approximately ~ 1 μ M. Spectra were obtained for a 10 s exposure of the CCD detector in the wavenumber region 100 – 4000 cm^{-1} using the extended scanning mode of the instrument. With 100% laser power, five accumulations were collected for the sample and the total acquisition time of the spectra was about 10 min. Spectral acquisition, presentation, and analysis were performed with the HORIBA Scientific's LabSpec 6 software.

2.3.3 Application in Forensic Science

Forensic scientists in the 21st century are required to deal with a wide range of challenges from terrorist groups as well as organised crime [206]. They must be able to have selective and sensitive method for the identification of substances such as toxins, explosives, poisons, biological warfare agents and drug mixtures. Unfortunately, many of the available identification and detection techniques involve individuals coming into close contact with harmful substances. In these instances, Raman spectroscopy has been used to significant advantage [200].

Raman spectroscopy allows the detection and analysis of compounds without an individual coming into physical contact with them [207]. This is especially true due to the recent advances in allowing the technique to be more portable. The residents and service enhancements for the Raman signal now allow the Raman spectrometer to be one of the most compact and sensitive instruments available for detecting and assessing dangerous substances. This type of spectroscopy provides a molecular fingerprint which is highly selective, detailed, reproducible, and unique to the substance being measured.

This technique can be used for nearly any type of optically accessible sample. Samples which are organic, biological, or inorganic can be assessed. The samples can also be transparent, non-transparent, gaseous, liquid, or solid. Unlike many forensic techniques, Raman spectroscopy does not require specialised preparation of the samples. The scanning can be done in a noninvasive and relatively clandestine manner [206].

Raman spectroscopy has proven to be exceptionally useful to the field of forensic science for a number of reasons [200]. There are detection configurations that can be used to accommodate extremely small particles of 1 μm up to several dm^2. The molecular fingerprint provided by Raman spectroscopy is unaffected by the excitation wavelength. This means that nearly any laser wavelength of excitation can be used, which allows for flexibility of the instrument. This type of spectroscopy can be done at night, during the day, and in any other lighting condition. It can also be carried out in the ultraviolet spectrum [207].

2.3.3.1 Gunshot Residue

As described in Chapter 1, gunshot residues consist of unburned and burned particles, which are usually a complex mixture of multiple inorganic and organic compounds. Raman spectroscopy has proven to be a useful technique in the analysis of gunshot residues (GSR) [206]. It has significant advantages over other analytical techniques for the analysis of OGSR such as a faster analysis without any sample preparation.

Raman spectroscopy was used by López-López et al. [208] for the analysis of OGSR sample. The firing was carried out using six different types of ammunition into cloth targets at a close distance. The Raman spectra from unfired ammunition were obtained to use as reference and compare with fired ammunition. The results showed high similarity between fired and unfired ammunition. However, the presence of some other substances that might be found in victims or shooters, such as sand, dried blood or black ink might cause confusion in the GSR sample.

López-López et al. [209] assessed the influence of using different types of ammunition fired from the same weapon in giving mixed results for the analysis of organic GSR samples. This is known as the memory effect. The experiment procedures involved two different types of ammunition. Twenty shots were fired using the same weapon into a paper target at close range. Shots 1, 3, 9 and 20 were fired with the first type of

ammunition, the rest with a second type of ammunition. The paper targets were introduced into Raman stage without any preparation.

The GSR constituents for each types of ammunition were identified. The results clearly showed that there was greater variability between spectra each time the type of ammunition was changed. Ethyl centralite was determined in SB96+ (type 1) ammunition, whereas Diphenylamine and derivatives were detected in the composition of SB-T93+ (type 2) ammunition. After the type of ammunition was changed 1.5% to 7% of type 1 residues were detected amongst the type 2 GSR. Identification of GSR compounds for each type of ammunition was made based on the presence or absence of such bands by visually examining the Raman spectrum. The authors concluded that there is no significant difference in the chemical composition of the GSR when different types of ammunition were used, even after an immediate change of type used in the same weapon [209].

3 AIMS OF THIS RESEARCH

The overarching aim of this project was to develop nano-particulates fingerprint powders which had dual functionalised that they were highly efficient at visualising finger marks and also facilitating the retrieval and analysis of organic residues produced from the discharged of weapons.

This overarching aim was achieved through following objectives.

- The review and development of analytical procedures based on GC/MS for the analysis of the organic components of GSR.
- The identification of the key organic components of unfired and fired shot gun cartridges and blank handgun ammunition.
- The synthesis and surface modification of silica nano-particulates to produce a bio-functional fingerprint powder.
- The development of techniques for the use of the functionalised nano-particulates for the visualisation and concentration of organic GSR prior to analysis by GC/MS.
- The development techniques based on non-destructive spectroscopic techniques involving functionalised nano-particulates for the identification of organic GSR.

4 METHOD DEVELOPMENT

4.1 Determination of Limit of Detection for Gunshot Residues' Major Organic Constituents

The determination of the limit of detection is normally required for methods intended to measure analytes that are present in very low concentrations. However, there is no need to determine the limit of detection for analytes that have much greater concentration than limit of detection (LOD). The LOD is defined as the lowest quantity of a substance that the instrument can measure with a specified precision or reproducibility [210]. Most commercial laboratories report the LOD for any analyte using their given analytical procedures [211]. This is important in ascertaining the confidence to which low levels of particular analyte can be reported. In forensic casework the presence of analyte can only be confirmed if it is present above the LOD [212]. Different analytical techniques have been used to determine the organic constituents of GSR. These techniques and their reported limit of detection are summarised in Table 4.1.

Table 4.1. Limit detection of organic compounds in GSR.

Compound	Technique	Limit of detection	Reference
Diphenylamine	MS/MS	1.0 ng ml^{-1}	[32]
2-nitrodiphenylamine	MECE	1.9 ng ml^{-1}	[138]
4-nitrodiphenylamine	MECE	2.1 ng ml^{-1}	[138]
Diphenylamine	MECE	0.9 ng ml^{-1}	[138]
Ethel centralite	MECE	1.8 ng ml^{-1}	[138]
Methylcentralite	MECE	1.1 ng ml^{-1}	[138]
Ethel centralite	HPLC	1.0 to 0.5 ng ml^{-1}	[130]
Diphenylamine	HPLC	1.0 to 0.5 µg ml^{-1}	[130]
Ethel centralite	IMS	0.5–1 ng ml^{-1}	[144]
Diphenylamine	IMS	2 ng ml^{-1}	[144]
Ethel centralite	LC-MS/MS	5 to 115 pg ml^{-1}	[29]
Diphenylamine	LC-MS/MS	5 to 115 pg ml^{-1}	[29]
Methylcentralite	LC-MS/MS	5 to 115 pg ml^{-1}	[29]
2-nitrodiphenylamine	LC-MS/MS	5 to 115 pg ml^{-1}	[29]
4-nitrodiphenylamine	LC-MS/MS	5 to 115 pg ml^{-1}	[29]
Methylcentralite	DESI-SMS	5–70 pg/cm2	[31]
Ethel centralite	DESI-SMS	5–70 pg/cm2	[31]
Diphenylamine	LC–MS–MS	1.8 ng ml^{-1}	[120]
Ethel centralite	LC–MS–MS	0.04 ng ml^{-1}	[120]
Diphenylamine	SPME/IM)	0.12 ng ml^{-1}	[28]
Ethel centralite	SPME/IMS	1.2 ng ml^{-1}	[28]

For the purpose of this study, a review of the literature was performed to determine the most commonly encountered organic components in GSR, with the additional criteria

that the compounds must be present at very low levels in the normal environment to avoid any contamination from other sources.

Applying these criteria, it was decided to focus on diphenylamine, methylcentralite, ethylcentralite, nitroglycerine, 2-nitrodiphenylamine, and 4-nitrodiphenylamine. Determination of the detection limits for these organic residues using the equipment available (GC/MS) was a key step in ensuring that the limits of detection of this instrument was in line with the levels normally encountered from fire arms discharges and comparable to the levels determined by other workers in this field.

Standard materials of diphenylamine (DPA), ethyl centralite (EC), methyl centralite (MC), 2-nitrodiphenylamine, and 4-nitrodiphenylamine, were purchased from Sigma-Aldrich (UK). Aqueous solution of nitroglycerine was obtained from VWR International, UK. Acetone - CHROMASOLV plus, for HPLC, ≥99.9%, was purchased from Sigma-Aldrich (UK). Samples were injected using an electronic syringe (SGE EVOL) obtained from VWR.

4.1.1 Determination of Retention Window for Selective Ion Monitoring Studies

A total ion chromatogram (TIC) was recorded for a standard containing all the substances described in Section 3.1.2 at a concentration of 2 $x10^{-3}$ mg ml^{-1}. DSQ II MS with a quadrupole mass analyser was used. The mass spectra of the individual components were matched against the software library (NIST, version 2), so that a positive identification of each peak could be made. This information was then used to develop an analytical method based on selective ion monitoring (SIM) (Table 4.2). This was necessary as analysis using SIM mode not only improves the selectivity of the analytical method but equally as important increases the sensitivity. This increased sensitivity is necessary for the analysis of the organic compounds of GSR where very low concentrations are involved.

4.1.2 Preparation of Calibration Standard Samples

Standard solutions of Diphenylamine (Aldrich), Ethylcentralite (Aldrich), Methylcentralite (Aldrich), 2-nitrodiphenylamine (Aldrich), and 4-nitrodiphenylamine (Aldrich) were prepared by dissolving 0.1 g of each compound in 50 ml of acetone. This solution then underwent a series of serial dilutions to produce a solution of concentration 2 $x10^{-6}$ mg ml^{-1}. This solution was then further diluted to construct the

calibration series which contained solutions of concentrations 1.5 $x10^{-6}$, $1x10^{-6}$, $5x10^{-7}$ and $2x10^{-7}$ mg ml^{-1}. Five micro liters of each concentration were injected manually in triplicate into the GC/MS for the analysis.

4.1.3 The Calculation of the Limit of Detection

The formula for the determination of LoD is given by:

$$\mathbf{LoD} = \frac{\mathbf{k} * \mathbf{s}}{\mathbf{S}}$$

Equation 1. Calculate the limit of detection

Where k is a numerical value that is chosen according to the level of confidence which is 95%, **s** is the standard deviation and **S** is the slope of the curve obtained on plotting of peak area/A.U. against concentration of the sample [213, 214].

4.1.4 Results from Analysis of Calibration Standards

In the first phase of this experiment, a relatively high concentration 2 $x10^{-3}$ mg ml^{-1} of the sample was introduced into the instrument using the mass spectrometer in full scan mode. The TIC of the compounds chosen to be representative of organic components of GSR is shown in Figure 4.1. The mass spectra for the individual compounds are shown in Figure 4.2. From the retention time and the mass spectra, the analytical protocol in terms of retention and ion where chosen to provide the condition for the SIM analysis. The analytical conditions derived for the SIM experiments are contained in Table 4.2.

A typical SIM chromatogram is shown in Figure 4.3. The calibration curves used to determine the limit of detection and potentially provide some quantification are shown in Figures 4.4-4.8. The limits of detection determined using the method described in Section 3.1.3 are recorded in Table 4.3.

Figure 4.3 clearly shows that despite of the compounds all being present at the same concentration, EC displays the highest response factor compared to the other standard compounds used in this study, Whereas 4-NDPA displays the smallest response factor.

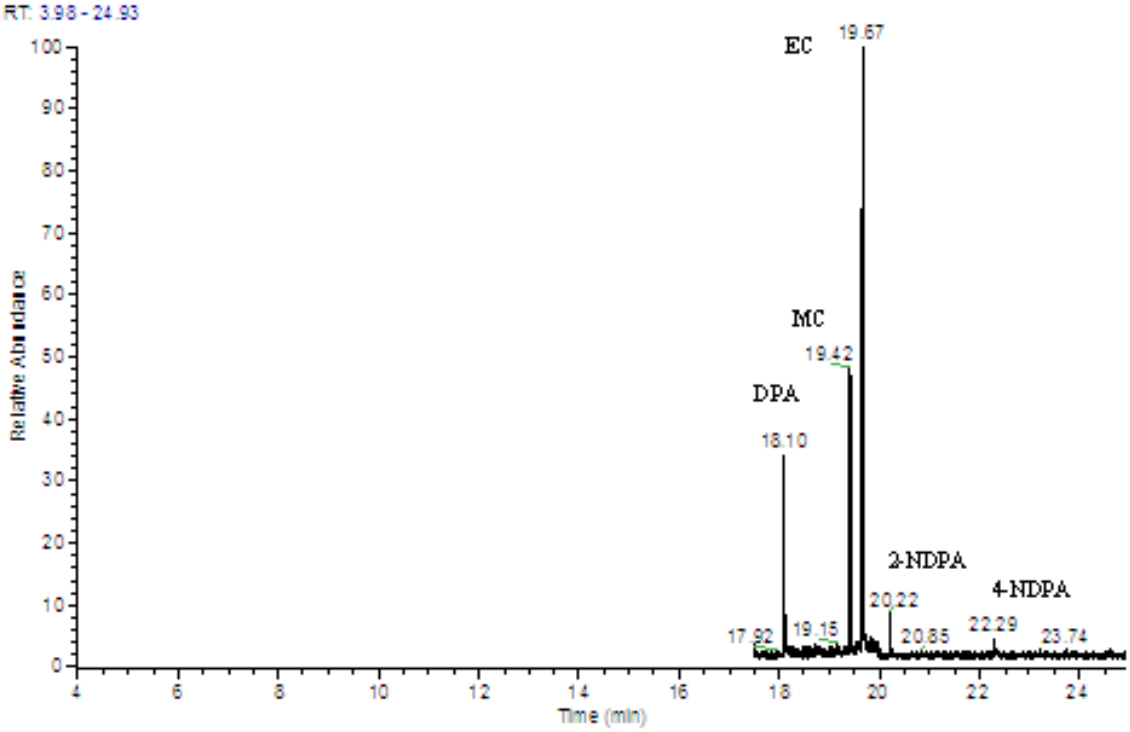

Figure 4.1. TIC of DPA, EC, MC, 2-NDPA and 4-NDPA (2 x10^{-3} mg ml^{-1})

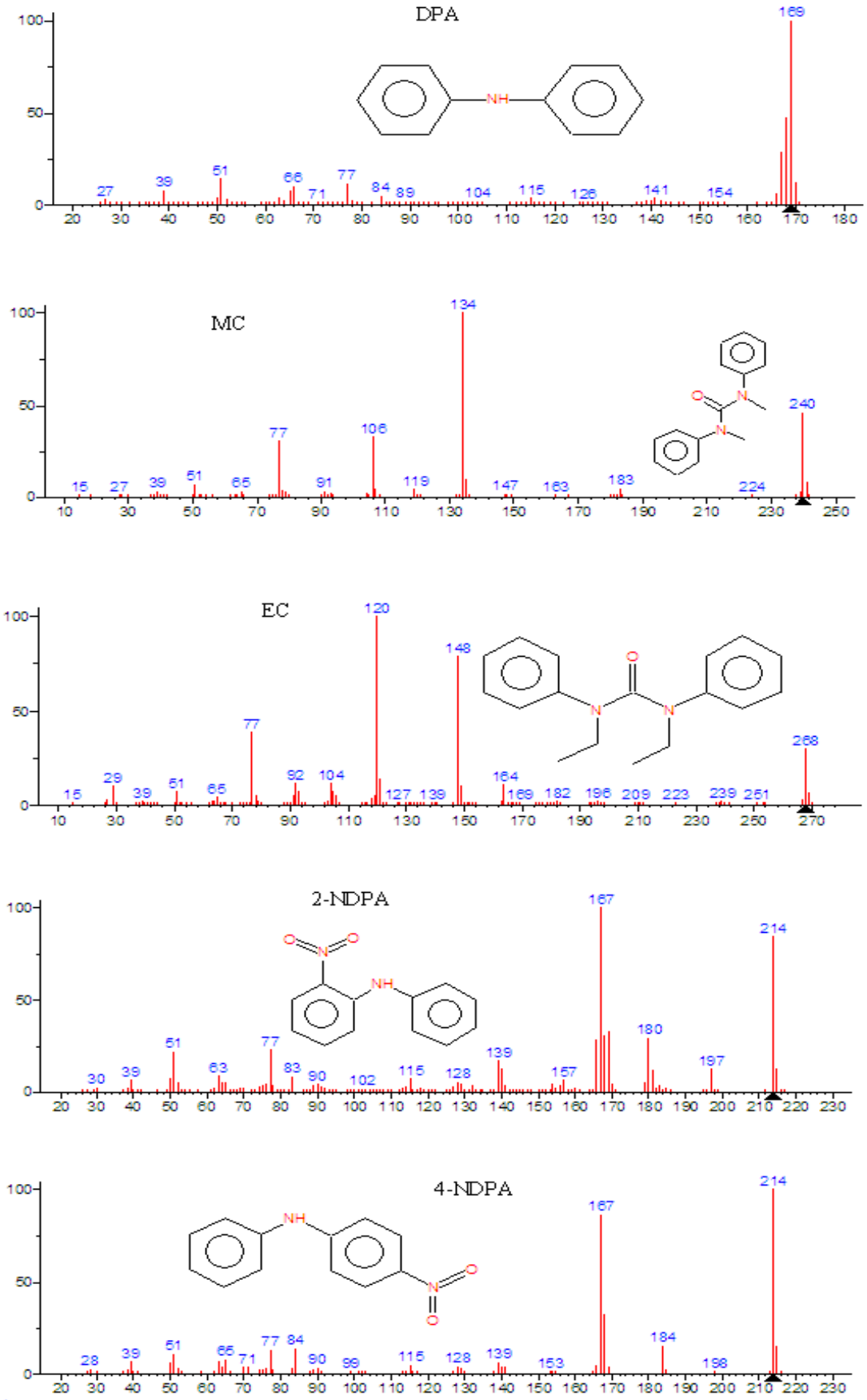

Figure 4.2. The mass spectra for the individual compounds being used in this study

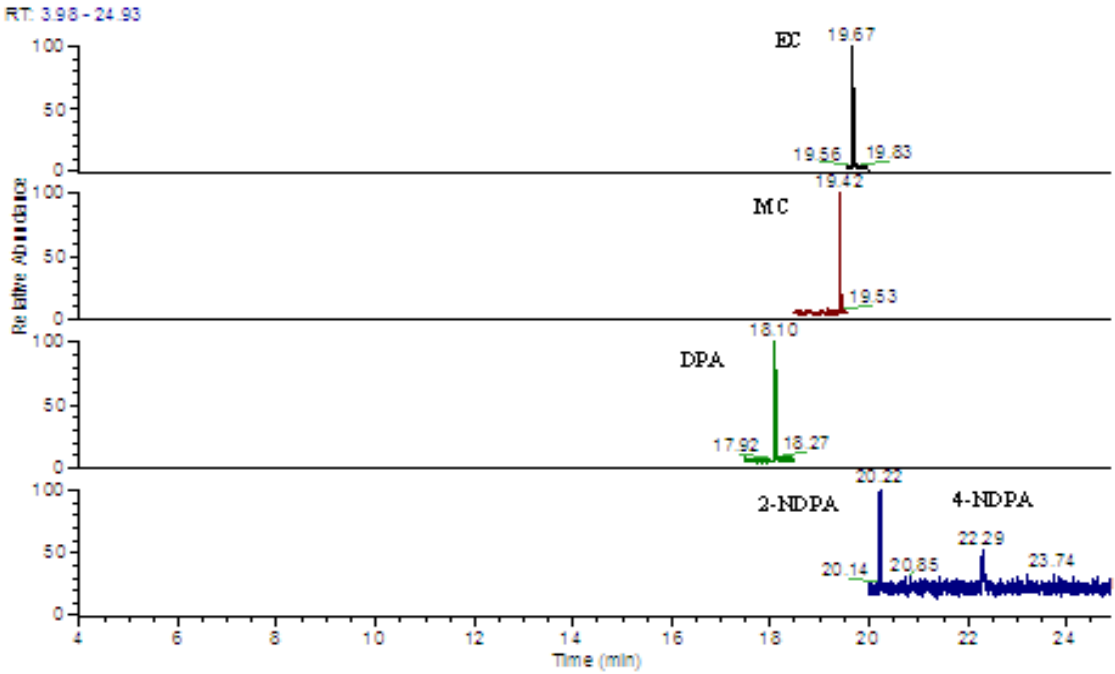

Figure 4.3. SIM of EC, MC, DPA, 2N-DPA, AND 4-NDPA

Table 4.2. Retention Window for use in Selective Ion Monitoring studies

Start Time	Substance	Mass
12:00	4-nitrotoluene	137
13:00	2,6-Dinitrotoluene and 2,4-Dinitrotouene	165
17:60	Diphenylamine	169
19:00	Methylcentralite	134
19:60	Ethel centralite	120
20:00	2-Nitrodiphenylamine	214
22:00	4-Nitrodiphenylamine	214

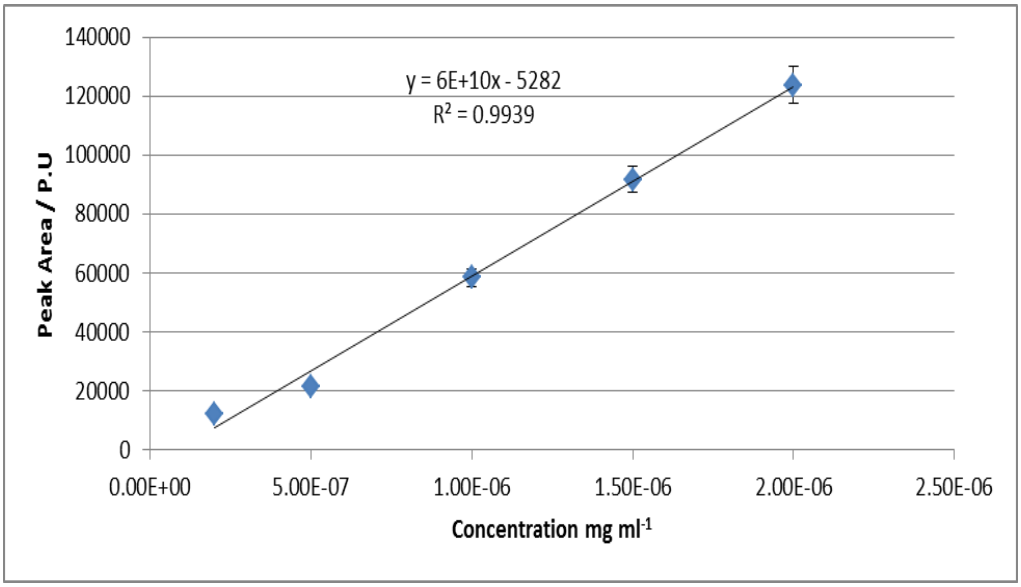

Figure 4.4. Calibration curve of Diphenylamine

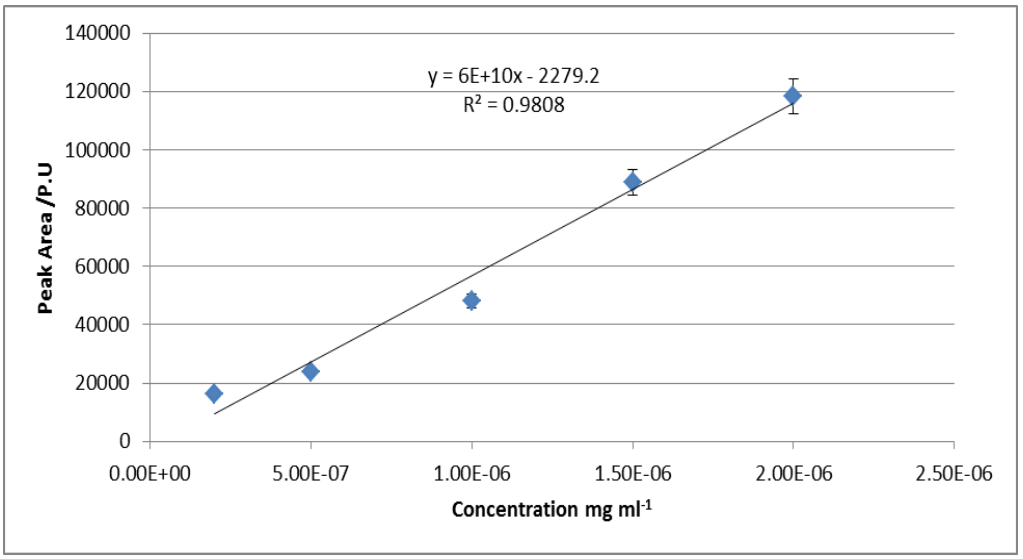

Figure 4.5. Calibration curve of Methylcentralite

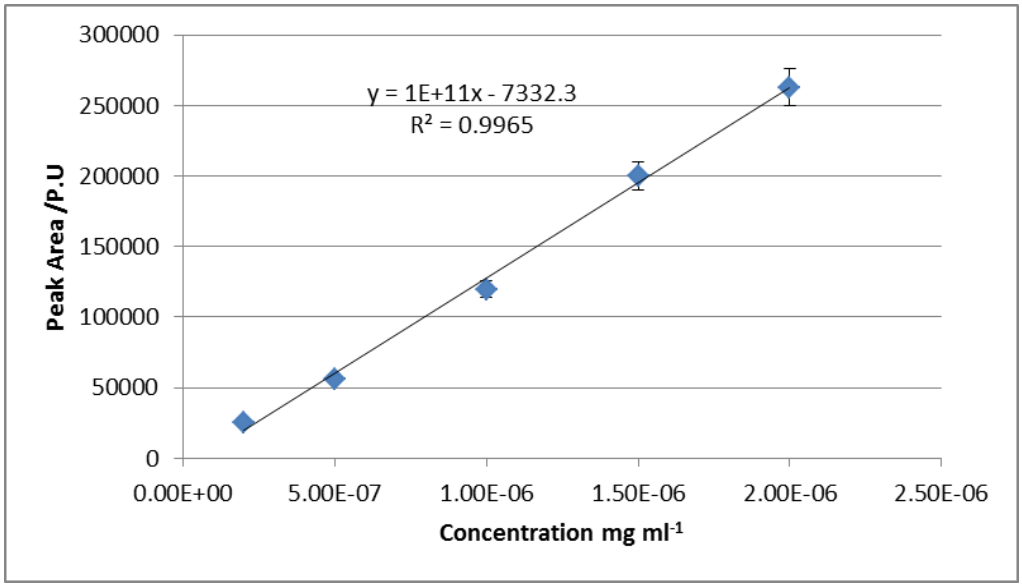

Figure 4.6. Calibration curve of Ethylcentralite

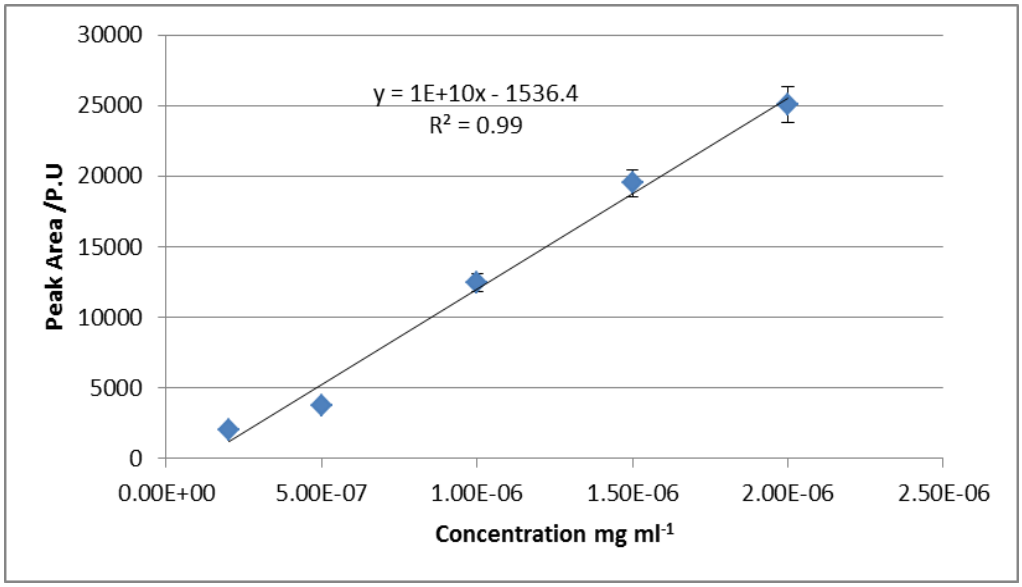

Figure 4.7. Calibration curve of 2-Nitrodiphenyalamine

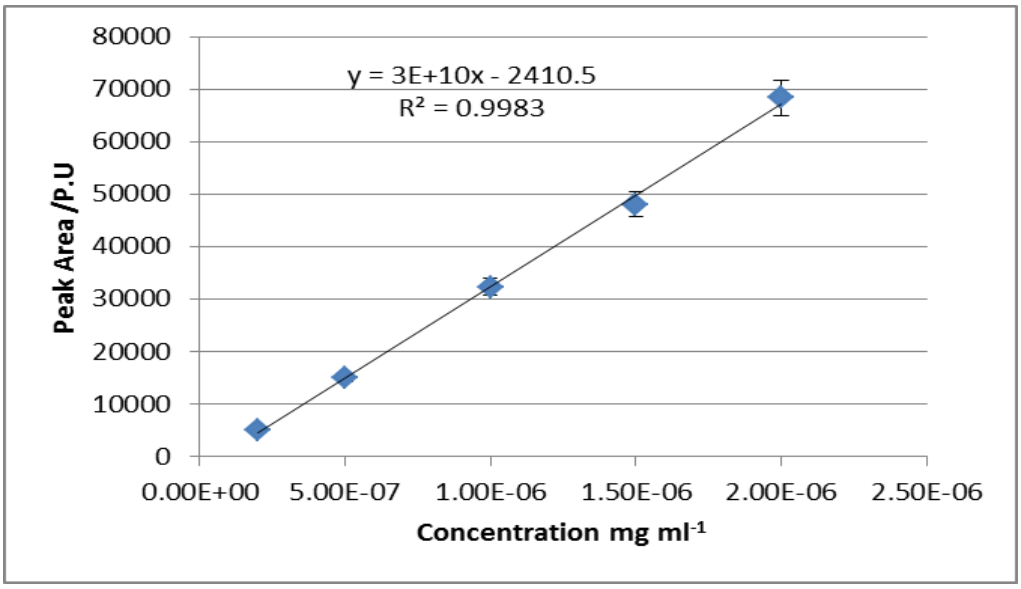

Figure 4.8. Calibration curve of 4-Nitrodiphenylamine

Table 4.3. GSR standard's detection Limit

Compound	Detection Limit/ng ml^{-1}
Diphenylamine	2.2
Methyl centralite	0.39
Ethyl centralite	0.16
2,Nitrodiphenylamine	0.28
4,Nitrodiphenylamine	0.11

4.1.5 Discussion

Determination of the detection limits for these organic residues using the equipment (GC/MS) available was a key step. The LODs of the GC/MS employed in this study for diphenylamine, ethylcentralite, methylcentralite, 2-nitrodiphenylamine, and 4-nitrodiphenylamine are in the range of 0.11–2.2ngml^{-1} (Table 4.3). This shows the capability of GC/MS to identify these materials at levels consistent with those found in actual GSR. Furthermore, it is in line with other work in the field (Table 4.1).

4.2 Experiments to Determine the Effect of Storage Conditions on the Determination of Organic Gunshot Residues.

Variations in the observed concentration of GSR in forensic samples are due to a number of well recognised reasons [215], including time since discharging weapon, the person's behavior after the shooting incident, the characterisation of the offender's skin composition, the amount of the GSR particles recovered as well as the firing distance [215].

Most of the organic materials detected in GSR are relatively volatile. In addition, they are initially present at a very low level [14]. Therefore, maintaining the concentration of organic residue within the GSR sample prior to performing appropriate analysis is a significant challenge for forensic scientists. In this study the effect of storage time and temperature on the analysis of organic residues from GSR has been investigated.

4.2.1 The Determination of the Relative Response Factor of the Analytes

Standard solutions of 4-nitrotoluene (Aldrich) (Internal Standard), Diphenylamine (Aldrich), Ethylcentralite (Aldrich), Methylcentralite (Aldrich), 2-nitrodiphenylamine (Aldrich), and 4-nitrodiphenylamine (Aldrich) were prepared by dissolving 0.1 g of each compound in 60 ml of acetone. This solution then underwent a series of serial dilutions to produce a solution of concentration 1.67 $x10^{-5}$ mg ml^{-1}. Five micro liters was injected manually in triplicate into the GC/MS for the analysis.

The relative response factor for each compound was identified experimentally by analysing a known quantity of the substance into the GC/MS and quantifying the area of the relevant peak. The relative response factor was calculated using the following formula:

$$\mathbf{RF} = \frac{((\mathbf{A_X})(\mathbf{C_{IS}}))}{((\mathbf{A_{IS}})(\mathbf{C_X}))}$$

Equation 2. Calculate the response factor [216]

Where RF: response factor, $A_{X:}$ area of the analyte, C_{IS}: concentration of the internal standard, A_{IS}: area of the internal standard and C_X: the concentration of the analyte.
Using the known response factor, the unknown concentration (quantity) of each substance can now be calculated by modifying the previous formulas

$$C_X = \frac{((A_X)(C_{IS}))}{((A_{IS})(RF))}$$

Equation 3. Calculate the quantity of the known analyte [216]

The sample preparation process involved first preparing stock solutions of each material (DPA, EC, MC, 2,4-DNT, 2-NDPA, 4-NDPA) in acetone at 0.1gm/10 mL and then combining each one to form a mixture. Working solutions were prepared by diluting aliquots of the solution mixture to the appropriate concentrations equivalent to the actual GSR ($2x10^{-6}$ mg ml^{-1}).

4.2.2 Effect of Storage Conditions on the Determination of Standard Materials Found in Gunshot Residues

Stock solution (0.2 ml) was injected on to the cotton fabrics (1 cm^2) and left to dry. After the cotton fabric had dried, they were placed in sealed in nylon bags for predetermined times at either at 4 °C or room temperature.

A solution of internal standard was prepared by dissolving 0.1gm of 4-nitrotoluene in 10 ml of acetone. This solution then underwent a series of serial dilutions to produce a solution of concentration 1 $x10^{-5}$ mg ml^{-1}. Once the sample had been aged for the predetermined time, the cotton fabrics were transferred to a test tube and internal standard (0.2 ml) was added immediately. The sample was then sonicated for 15 minutes, after which the sample was left to stand for one hour to ensure complete leaching of the organic material. After one hour, this solution was transferred to test tube to concentrate using nitrogen gas at 30 °C. Five microliters of the concentrated solution were then injected into the GC/MS for quantitative analysis using the SIM condition described previously, and the GC condition described in Section 2.1

4.2.3 Results

Standard materials of the five most common organic constituents that normally found in gunshot residues were utilised. These compounds include DPA, EC, MC, 2-NDPA, and 4-NDPA. 4-Nitrotoluene was used as an internal standard.

Table 4.4. The response factors of six substances were used in this study

Analyte	Response factor
Diphenylamine	27.66
Methylcentralite	16.50
Ethyl centralite	35.27
2-Nitrodiphenylamine	31.14
4-Nitrodiphenylamine	2.91

A baseline experiment was performed at day zero to provide information concerning the ability to quantitatively extract the organic components of gunshot residue from a piece of cotton fabric. The results from the study are shown in Figure 4.9. The amount of each component dosed on the cotton fabric was $4x10^{-7}$ mg. Therefore, if there is no loss of materials within the extraction process, there should be $4x10^{-7}$ mg extracted. As can be seen from the data in Figure 4.9, the retrieval of MC, EC and 2-NDPA fall with a 95% confidence interval of the true value ($4x10^{-7}$ mg) when subjected to a t-Test. However, the retrieval amount of DPA and 4-NDPA are well outside this range.

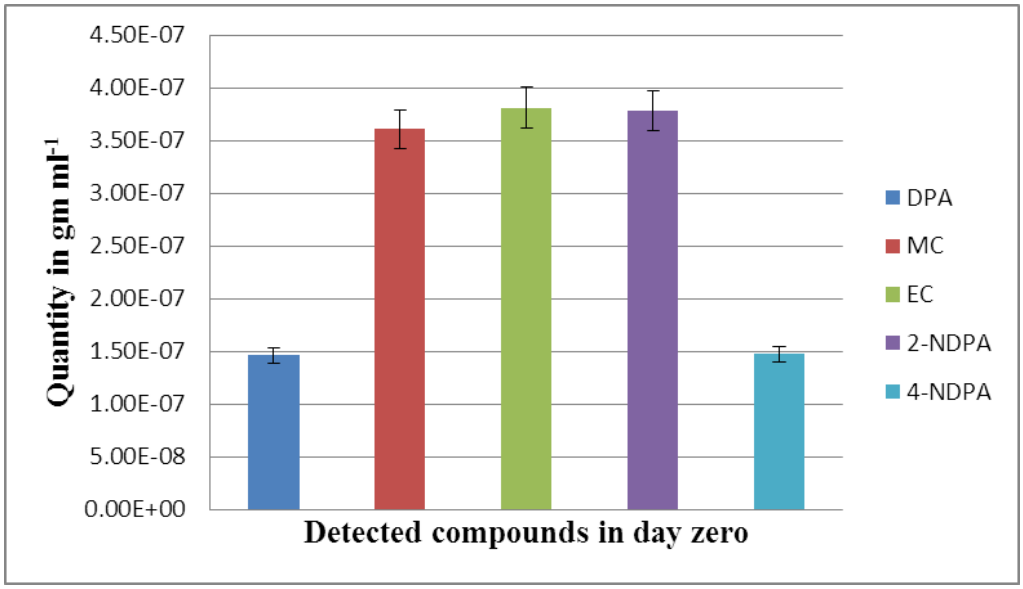

Figure 4.9. Detected compounds in cotton fabric at day zero

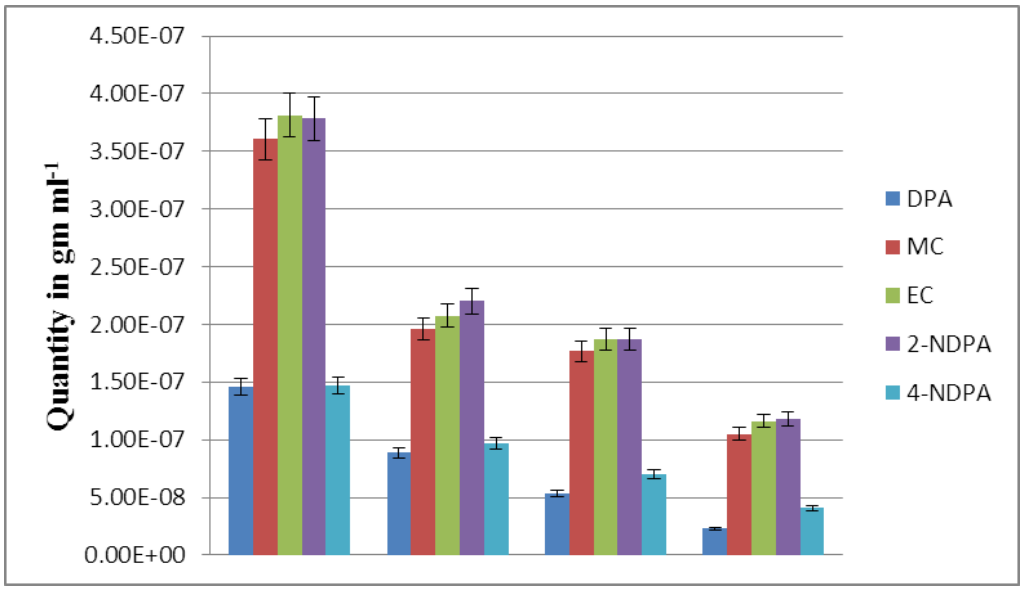

Figure 4.10. Detected compounds at day 0, 1, 5 and 10 at ambient temperature

The effect of storage for a period of 5 and 10 days at two temperatures, ambient and 4 ^{o}C, was determined. The data from these lists is shown in Figures 4.10 and 4.11.

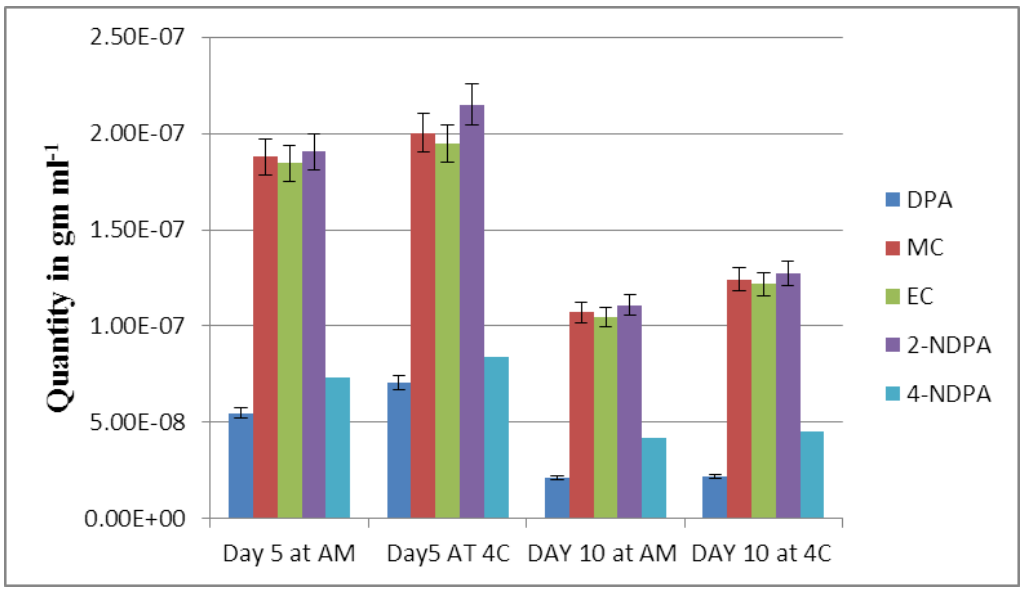

Figure 4.11. Detected compounds in day 5 and 10 at ambient and 4 ^{o}C temperature

4.2.4 Discussion

A series of experiments were performed to investigate the effect of storage time and temperature on the preservation of the organic components of GSR. A quantitative study was performed to show how critical the storage time and temperature are upon the concentration of organic residues retrieved when the samples are stored in nylon bags. This result will potentially be important in influencing storage protocols for the storage of this type of evidence.

In order to perform quantitative analysis with sufficient accuracy it was necessary to adopt a method that employed an internal standard. 4-Nitrotoluene was chosen because it has similarity in structure and physical properties to the target substances.

The data from day zero of the study produced some interesting results. The initial amount of each organic loaded onto the cloth was $4x10^{-7}$ mg. Extraction at time zero shows that all the materials cannot be extracted without loss. However, the recovery of MC, EC and 2-NDPA is relatively good with the amount recovered being $3.61x10^{-7}$, $3.81x10^{-7}$ and $3.78x10^{-7}$ mg respectively. Surprisingly, the recovery of DPA and 4-NDPA is not as good, with only $1.46x10^{-7}$ and $1.47x10^{-7}$ mg of these materials being recovered (respectively). While 4-NDPA and DPA do have the lowest boiling points of the materials utilised in this study (Table 4.5), they still have relatively high boiling points and it is not thought that the low recovery of these two components is due to loss through evaporation due to their increased volatility.

Table 4.5. Physical properties for key organic compounds in GSR

Compound	Flash point	Boiling Point	Melting/freezing Point
Diphenylamine	153 °C	302 °C	53 °C
Ethyl centralite	325-330 °C	325-330 °C	73 °C
Methylcentralite	142.6 °C	350 °C	122 °C
2-Nitrodiphenylamine	346 °C	346 °C	74 °C
4-Nitrodiphenylamine	190 °C	211 °C	132 °C

The reduced recovery of DPA could be a result of a reaction with the acetone used for the extraction. DPA can react with acetone to produce 9,9-dimethyl-10H-acridine (Figure 4.12).

In theory both 2-NDPA and 4-NDPA can also react with acetone. However, because 2-NDPA (Figure 4.14) is a much weaker base than 4-NDPA (Figure 4.13), due to intra-molecular hydrogen bonding between the secondary amine and nitro groups, the reaction with acetone will be much slower with 2-NDPA compared to 4-NDPA. This is therefore postulated as a potential explanation as to why the recovery of 2-NDPA is significantly greater than 4-NDPA.

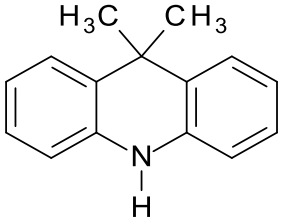

Figure 4.12. The structure of 9,9-dimethyl-10H-acridine compound

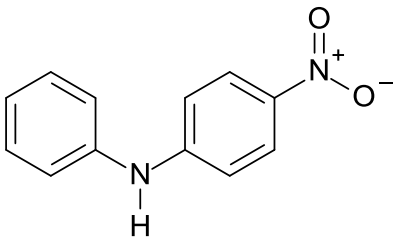

Figure 4.13. The structure of 4-Nitrodiphenylamine

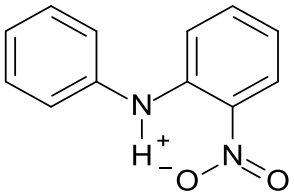

Figure 4.14. The structure of 2-Nitrodiphenylamine

The effect of increased time and storage temperature is to reduce the concentration of all components. The MC, EC and 2-NDPA are always retrieved in larger concentration than the DPA and 4-NDPA. Several studies reported the influence of the time being a factor in the detection of GSR [14, 54, 124, 217, 218]. Time is the major factor that the forensic scientist must take into account while performing any examination of gunshot residues. This factor may directly affect whether a positive or negative result for gunshot residues analysis is produced [14]. After a certain period of time, detection of

GSR becomes extremely difficult in terms of detecting the compounds within the limit of detection.

The issues associated with the time delay between discharge of a weapon and swabbing to collect GSR are well documented [14, 124]. The amount of GSR on the hand of the suspect has been shown to decrease rapidly with time as a consequence of environmental exposure [219, 220]. The environmental exposure can contribute to degradation of the organic materials in gunshot residues [139] In addition to the time alone, the consequences of environmental exposure need to the taken into account [139, 219]. Physiochemical processes such as diffusion through air and absorption metallic surfaces play a role.

This study differs from those previously described in the literature. In this study the sample was stored in sealed nylon bag throughout the experiment. The natural assumption is that under these conditions the sample will be preserved. However, these results clearly show that the time delay between collection of the sample and analysis is also an equally important factor in the analytical protocol, and not just the time between discharge of the weapon and collection/storage of the sample.

The results presented here clearly show that the storage temperature is a key factor. Storage of the samples at $4^{o}C$ results in significantly greater recovery of all of the organic components. While it is known that the long-term storage of ammunition results in it degradation and associated changes to its chemical composition due to oxidation processes [29]. Storage of the sample at $4^{o}C$ is likely to result in a lower rate of degradation through oxidation reactions and would provide a plausible explanation of the data presented within this study.

Different container types have been used in to store GSR evidence [139]. The nylon bags used in this study are widely accepted as being the method of choice due to their low permeability to volatile materials [221].

Studies have been conducted to determine the best container for the storage of volatile materials, including GSR. Paint can, mason jar, and nylon bag containers were utilised. Nylon bags have been found to have better performance compared to the other containers due to their low permeability to volatile materials [221]. The findings from this study clearly show that there is a strong relationship between storage, time and temperature when analysing the organic residues from GSR. The data clearly shows that

minimising storage time and refrigeration samples during storage are highly recommended in order to minimise the loss of the organic GSR during this phase of the process.

4.2.5 Conclusion of Method Development

Based on the limit of detection and storage experiment, it can be concluded that GC/MS is able to detect DPA, EC, MC, 2-NDPA and 4-NDPA compounds at very low level The approximate LODs of the GC/MS employed in this study for Diphenylamine, Ethylcentralite, methylcentralite, 2-nitrodiphenylamine, and 4-nitrodiphenylamine, are in the range of 0.1–1 ng (Table 4.3). This shows the capability of GC/MS to identify these materials at levels consistent with those found in actual GSR. Furthermore, it is in line with other work in the field. Storage of the sample in nylon bags at low temperature can be a very useful technique to maintain the integrity of the sample.

5 BRANDING OF SHOT GUN AND BLANK HANDGUN CARTRIDGES PRE- AND POST-FIRING FROM THE ANALYSIS OF THE ORGANIC CONSTITUENTS

5.1 Introduction

The traditional methods for the analysis of GSR involve measurement of metals such as lead, barium, and antimony using scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDX) [14]. This method is becoming less useful to identify GSR as result of the introduction of new ammunition that is less toxic (lead-free) and of non-metallic composition [132, 222].

The analysis of the organic materials in GSR provides very useful information for the forensic scientist. This information can aid the forensic investigators to link a suspect to the discharge of a firearm [14, 132]. One of the main aims of forensic science is to correlate between the crime scene evidence and the suspect or victim [76, 132, 139]. The analysis of the organic composition in GSR from pre- and post-firing is one such example. Generally, the organic constituents of the propellant and stabiliser additives in the unfired powder are retained in the residues after the weapon has been fired [223, 224]. The organic particles in GSR appear as result of incomplete combustion of smokeless powder. Therefore, the resulting composition of GSR will depend on the variability in the chemical composition of unfired powder [224].

This chapter discusses the use of GC/MS to determine the relationship between the additives composition in unfired propellant, and fired residue remaining in the spent cartridge casings after discharge of a shotgun as well as from a blank handgun. While there are a number of studies on the organic components of handgun and rifle cartridges, there are no previous studies on the organic composition of shotgun cartridges reported in the literature.

Given the greater availability of shotguns within the UK compared to handgun and rifle, this adds to the relevance of this study. Additionally, there is significantly less physical information that can be obtained from a discharged shotgun cartridge in comparison to a bullet linking in to a particular weapon due to the lack of rifling marks produced during the discharge of the weapon.

5.2 Unfired Shotgun Cartridge Experiments

5.2.1 Materials and Methods

A sample of 12 bore calibre (12 gauge) shotgun cartridges from five brands produced by three manufacturers were used, as indicated below (Table 5.1).

Table 5.1. List of type of ammunition used

Brand	Wad	Muzzle Velocity	Case length	Shot size	Shot load (g)	Group number
Eley Olympic Trap	Plastic	1400fps	70mm	7.5	28 g	1
Eley Blues	Fiber	1400 fps	70 mm	7.5	28 g	2
Hull Comp X	Fiber	1375 fps	65mm	7.5	28 g	3
Lyalvale Express – "world cup"	Fiber	1500 fps	70 mm	8	28 g	4
Lyalvale Express – "Excel Olympian	Plastic	1450 fps	70 mm	7.5	24 g	5

These are three very well-known UK brands of shotgun ammunition. The Eley Hawk ammunition was donated by the company upon request. No other manufacturer was prepared to engage with the project. For reasons of shotgun licensing legislation in the UK it was not possible to purchase any ammunition. This explains the limitation in the number of manufacturers and brands used. The Lyalvale and Hull ammunition was supplied by a shooting club.

5.2.2 Collecting the Sample

The cartridges in each group were assigned numbers from 1 to 5. The shotgun cartridges were opened by cutting the plastic shell casing with a single edged razor. The powder contents were weighed and then emptied into a 2 mL GC vial for storage. All samples were handled with gloves to avoid any contamination.

5.2.3 Preparation and Analysis of the Samples

The bulk composition of the five ammunitions was determined using a procedure developed in house. This consisted of taking one milligram of unfired powder from each cartridge in all groups. The sample was dissolved in a volumetric flask with 10 mL of acetone (CHROMASOLV plus, for HPLC, ≥99.9%). The solution was taken

and placed into a separate GC vial. The vial was sonicated for 15 minutes to dissolve the powder completely.

Following sonification, 5 μL of each sample was injected in triplicate into the GC/MS for analysis to give a total of fifteen measurements. Total ion chromatograms were recorded as described in Section 2.1.1.

5.2.4 Results from the Analysis of Unfired Shotgun Cartridges

The average weight of propellant in each group was recorded; the results are contained in Table 5.2. The chemical composition of each brand of cartridge was determined by GC/MS. The TICs are shown in Figure 5.1, and the data are summarised in Table 5.3 to aid analysis.

Table 5.2. The average weight of the propellant from 5 types of 12 bore shotgun ammunition

Group	Average weight of propellant
1	1.380 gm
2	1.217 gm
3	1.329 gm
4	1.400 gm
5	1.216 gm

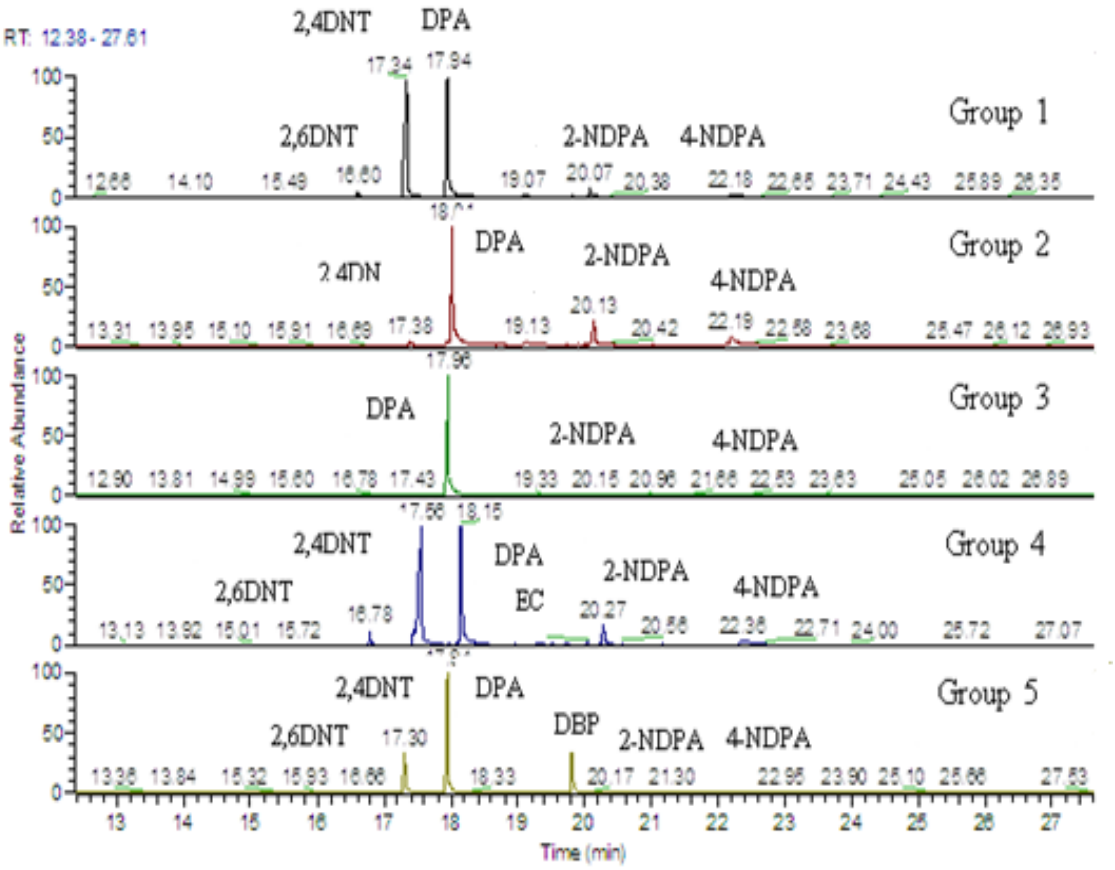

Figure 5.1. GC/MS analysis of unfired shotgun cartridges

Analysis of the data in Table 5.1 shows that each brand of ammunition contained three or more substances of the seven components listed in Table 5.3. The following bar charts (Figures 5.2-5.6) depict the relative concentration of each constituent within the smokeless powder. The absolute concentrations in the unfired cartridges are irrelevant as these will change dramatically upon firing.

Table 5.3. The present components in each group of unfired shotgun ammunition

Ammunition	2.4-DNT	2.6-DNT	DPA	EC	DBP	2-NDPA	4-NDPA
Group 1	X	X	X			X	X
Group 2	X	x	X			X	X
Group 3			X			X	X
Group 4	X	X	X	X		X	X
Group 5	X	X	X		X	X	

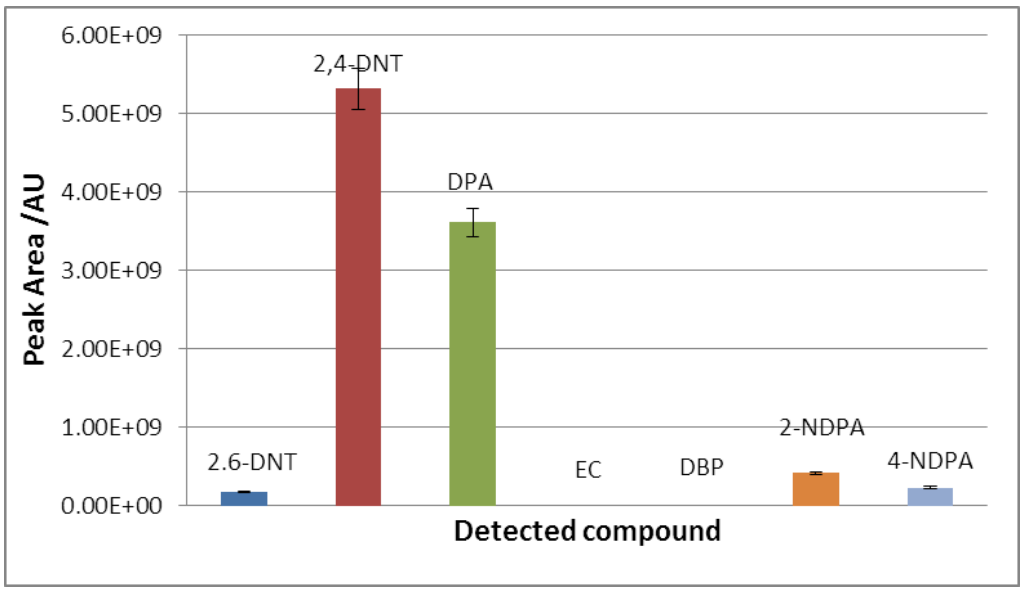

Figure 5.2. Bar chart of detected compounds in Group 1 ammunition

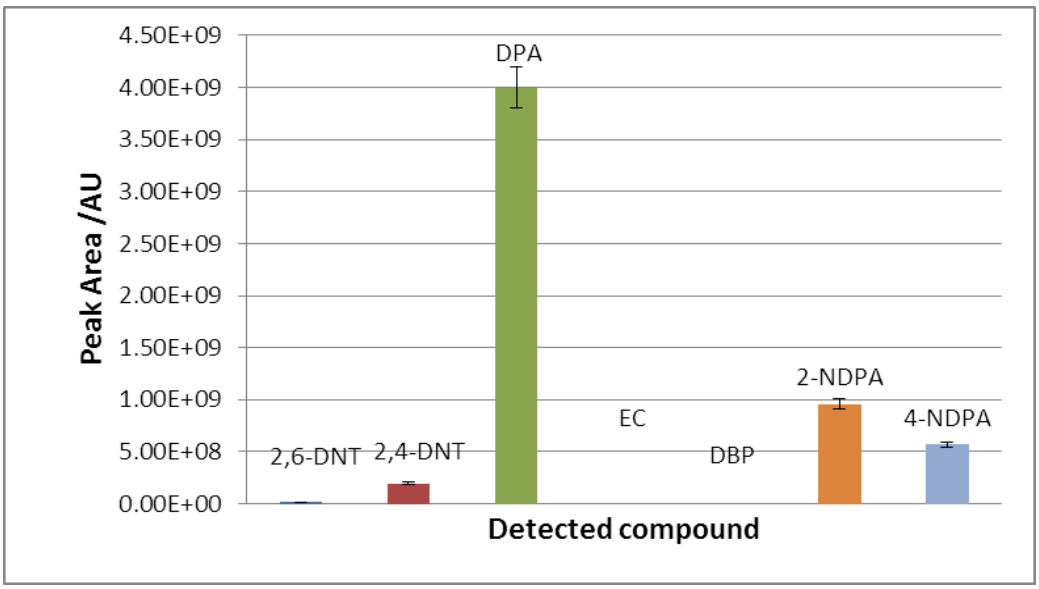

Figure 5.3. Bar chart of detected compounds in Group 2 ammunition

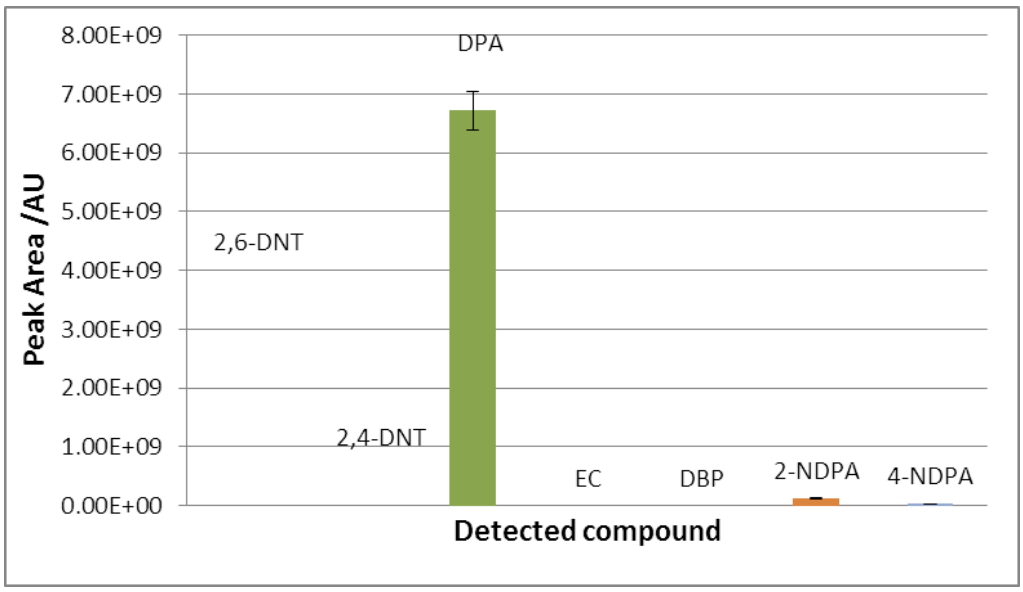

Figure 5.4. Bar chart of detected compounds in Group 3 ammunition

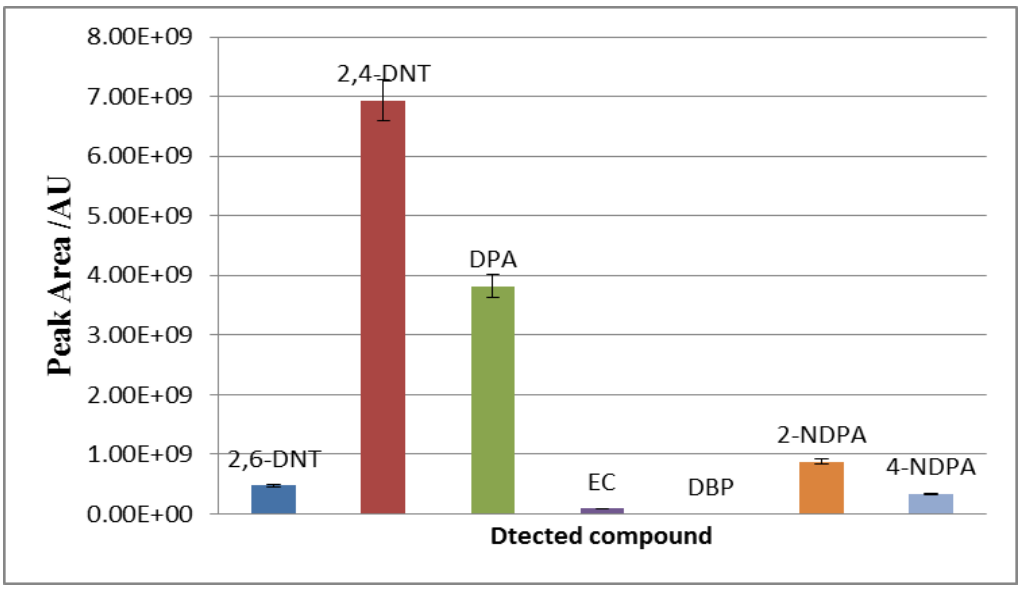

Figure 5.5. Bar chart of detected compounds in Group 4 ammunition

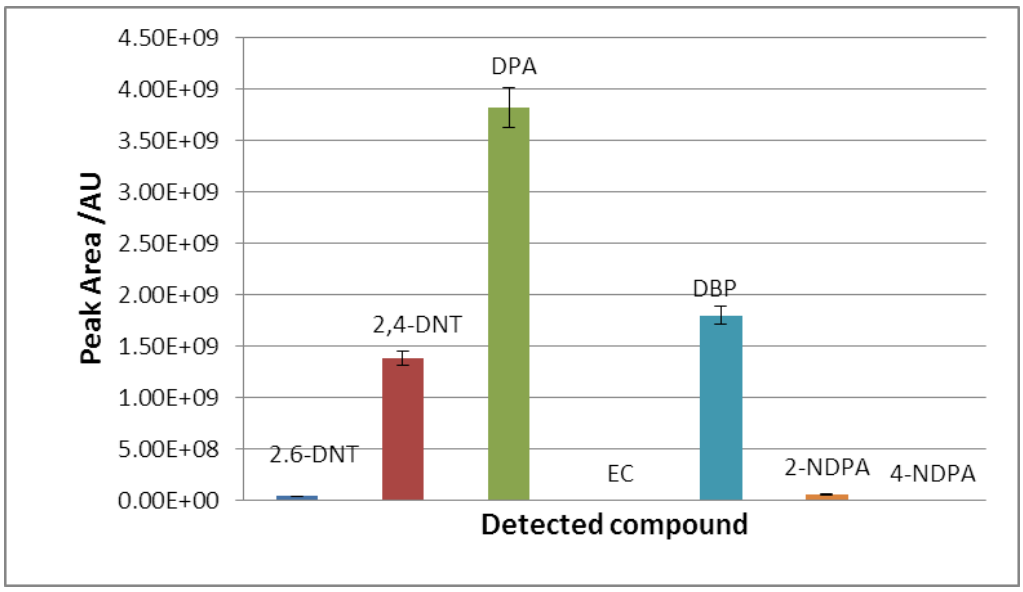

Figure 5.6. Bar chart of detected compounds in Group 5 ammunition

The bar charts clearly show that there are notable differences in composition depending upon the brand of shotgun cartridge. While this study is limited to only five brands and samples of three cartridges for each brand, it is clear that the differences have the potential to identify brands based on their chemical compositions.

5.2.5 Discussion

In general, smokeless shotgun powders are composed of nitrocellulose (NC) (i.e. they are single-base propellants). Therefore, it is necessary to dissolve the nitrocellulose pellets using an appropriate organic solvent in order to release the organic components.

The combination of GC/MS was used for the analysis of organic materials in GSR. GC allows for rapid and sensitive separation of the mixtures while MS provides identification of the resulting peaks from the chromatogram [14].

Gas chromatograph is not an ideal technique for the analysis of non-volatile materials such as nitrocellulose. In this study the nitrocellulose, which is the major component, was ignored and the analysis focused on the minor components which provide a means of determining the origin (brand) of shotgun cartridges.

Identification of a bullet that has been used by matching it to a batch of ammunition is not possible based on its physical characterisation and visual inspection. Likewise, it is not possible to predict smokeless powder composition based on the calibre or bullet type [225]. However, since each ammunition manufacturer has its own unique chemical

composition of the smokeless powder [107]. The discrimination between different types of small arms ammunition can be achieved by the presence or absence of certain organic compounds in smokeless powder [226].

In this study, the analysis of the smokeless powder samples was achieved by determining the constitution of each brand and comparing the result with the compounds that were detected in each group.

The composition of each brand of ammunition analysed contained three or more substances of the seven components mentioned in Table 5.3; DPA, 2-NDPA and 4-NDP were found to be the most common compounds detected in all groups.

DPA is the most frequent stabiliser used in smokeless powder, particularly in single base powder. In addition, the main reaction products of nitrous oxide gases and DPA are 2-nitrodiphenylamine, 4-nitrodiphenylamine and n-nitrosodiphenylamine [30]. The addition of the stabiliser to the smokeless powder has the effect of slowing down the decomposition of nitrocellulose, by removing the nitrous and nitric acids that are produced [30].

Most of the components detected in Group 1 were 2,6-DNT, 2,4-DNT, DPA, 2-NDPA and 4-NDPA. In contrast, most of the organic compounds that were found in Group 1 were found in Group 2. DBP is used as a plasticiser in smokeless powder to maintain powder shape during the manufacturing process by improving flexibility [14, 220]. It is widely used in products other than smokeless powder. Therefore, the presence of DBP alone has lower value in forensic science. On the other hand, the combination of DBP with EC, MC, and DPA adds further certainty that the unknown samples being analysed are smokeless powder [227].

Lyalvale Express - “world cup” was the only smokeless powder in which ethylcentralite (EC) was detected. The presence of EC in this group even at trace level can be used as indicator to identify the type of manufacturer that i.e. Lyalvale express-“world cup”. It is common to use EC as a stabiliser and burning rate moderator in smokeless powder, but rare to find it in a normal environment, thus it is considered to be credible organic GSR [29].

There are some similarities between the compounds that were found in all groups, which may be attributable to the number or type of organic compounds, although some

differences in the concentration of these compounds were noted from one group to another. The degree of variation in the concentration of smokeless powder additives could be interpreted to varying amounts of these additives in the propellant [107, 228]. This gives further evidence that each brand may contain different concentrations of the main constituents. In general, results showed that there is a similarity in the components of the propellant that was made from the same manufacture.

From the results, no NG or MC was detected in any type of ammunition. The absence of NG may be an indication of the type of smokeless powder that was used (i.e. single-base propellant). However, NG is commonly found in the environment, particularly in certain pharmaceutical preparations. Notably, no methylcentralite was detected in any types of ammunition. That could be due to the place of powder manufacture.

It could be possible to discriminate between ammunition based on the concentration of their chemical compositions. GC/MS results confirmed that it is possible to distinguish between different types of ammunition based on the organic compounds in the propellant.

5.3 Fired Shotgun Cartridges Experiments

5.3.1 Materials and Methods

The series of cartridge types used in this study was identical to those previously described in Section 5.1. Test firing was performed in conjunction with the Greater Manchester Police Firearms unit in their indoor range in Great Manchester using the following shotgun weapons (Table 5.4).

Table 5.4. List of the weapons that were used

Number	Weapon	Calibre
1	Browning 325- O/U	12 bore
2	Parker Hale – S/S	12 bore
3	Beretta A 302 12 – self loading	12 bore
4	Smith & Wesson – 3000 – Pump action	12 bore
5	Brno ZB132- S/B	12 bore

All the weapons were kindly provided by the forensic science services of Manchester Police. In this procedure, each shooting was carried out using five different types of weapon and five different types of ammunition. Five shots were made from each weapon using a different brand of ammunition for each shot.

5.3.2 Preparation and Analysis of the Samples

Once the weapon was fired, the spent cartridges were sampled immediately after shooting and closed in hermetic 10 ml vials with screw caps and transferred to the laboratory for the analysis. The spent cartridges were washed with 1 ml of acetone. The solution was transferred into the test tube. The sample was concentrated using sample concentrator (Techne, DRI-BLOCK DB.3) using nitrogen. Five microliters of the concentrated sample was injected in triplicate into the GC/MS for the analysis using the conditions described in Section 4.11.

5.3.3 Result From the Analysis of Fired Shotgun Cartridges

The selective ion chromatograms (SIM) of the fired cartridges are shown in Figure 5.7. The data obtained from the fired cartridges displayed a marked similarity to their unfired counterparts. Therefore, every brand of ammunition contained more than two substances of each of the seven components listed in Table 5.1. The relative concentrations of each component detected are represented by the bar charts in Figures 5.8-5.12.

While an initial hypothesis was made that the weapon type my influence the chemical compositions of the fired cartridge, this proved to be a false hypothesis as no discernible differences in the chemical composition of the GSR was observed when different weapons were used. Consequently the data in Figures 5.8-5.12 are an average of five discharges from different weapons.

Figure 5.7 showed the detected substance in each brand of ammunition used in this study. In Group 1 and 2, 4-DNT, DPA, DBP, 2-NDPA were identified. DBP was also detected in all fired shotgun cartridges that were used in this study (Figure 5.7). DBP was present in all groups at a relatively high concentration compared to other substances that were detected. DPA was also determined in all groups as a second major compound.

In group 4, 2-4DNT, DPA, EC, 2-NDPA and DBP were present regardless the variation in their concentration. The range of compounds detected from the fired shotgun cartridges is more limited than in the unfired cartridges. However, all brands produced a signal for at least two of the test substances. In addition, fired cartridges displayed chromatograms containing a peak from DBP. This originated from the plasticiser used in the manufacture of the cartridge case. The bar charts in Figures 5.8, 5.9, 5.10, 5.11, and 5.12 depict the relative concentration of each constituent within the smokeless powder.

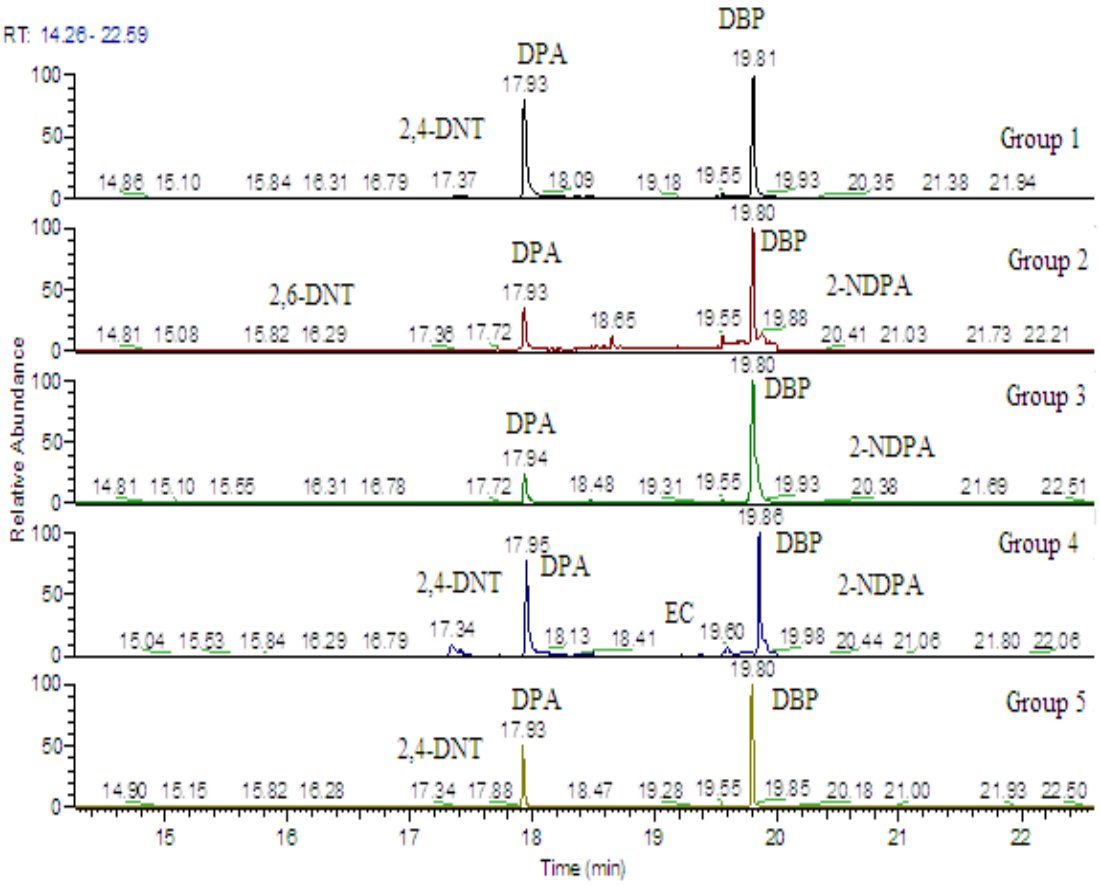

Figure 5.7.GC/MS analysis of fired shotgun cartridges

Table 5.5. The present components in each group of fired shotgun ammunition

Ammunition	2.6-DNT	2.4-DNT	DPA	EC	DBP	2-NDPA	4-NDPA
Group 1		X	X		X	X	
Group 2	X		X		X	X	
Group 3			X		X	X	
Group 4		X	X	X	X	x	
Group 5		X	X		X		

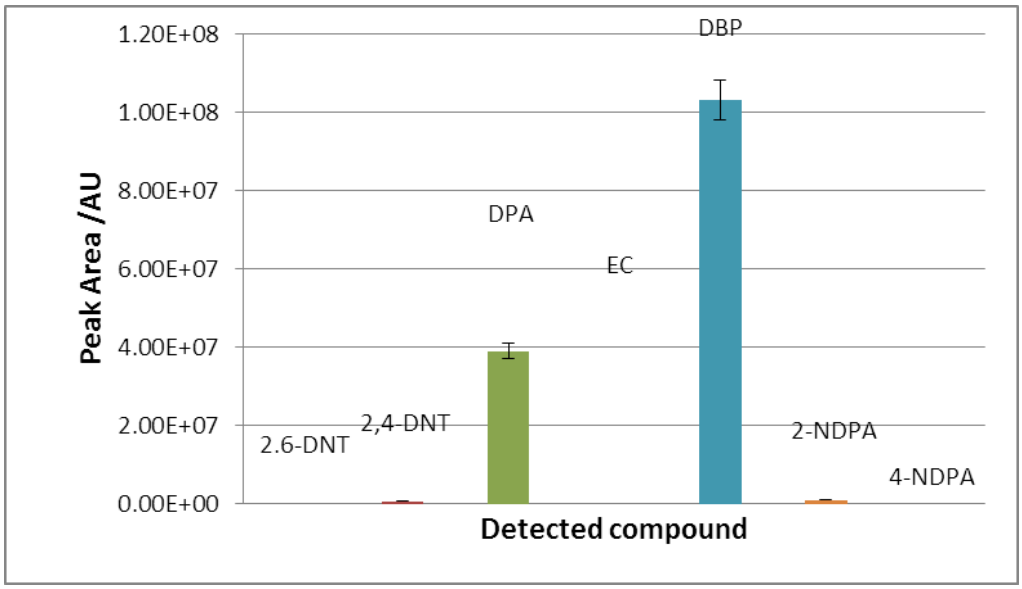

Figure 5.8. Bar chart of detected compounds in Group 1ammunition

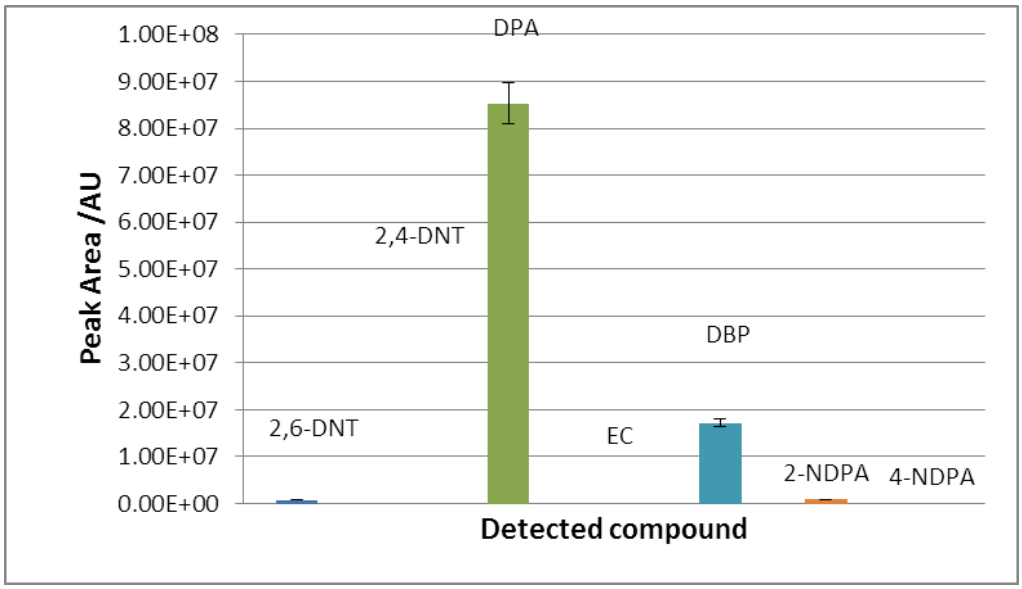

Figure 5.9. Bar chart of detected compounds in Group 2 ammunition

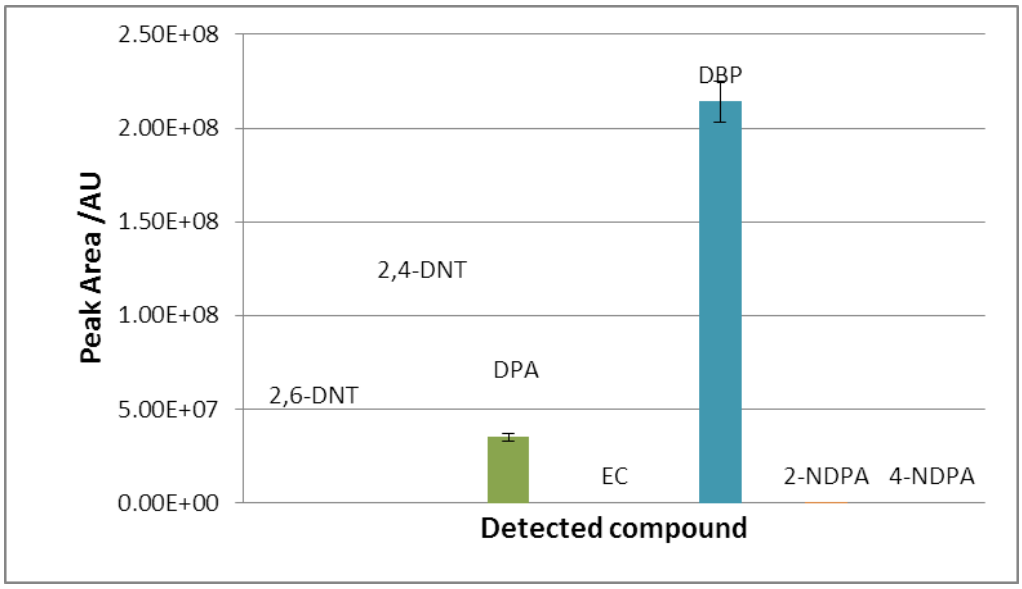

Figure 5.10. Bar chart of detected compounds in Group 3 ammunition

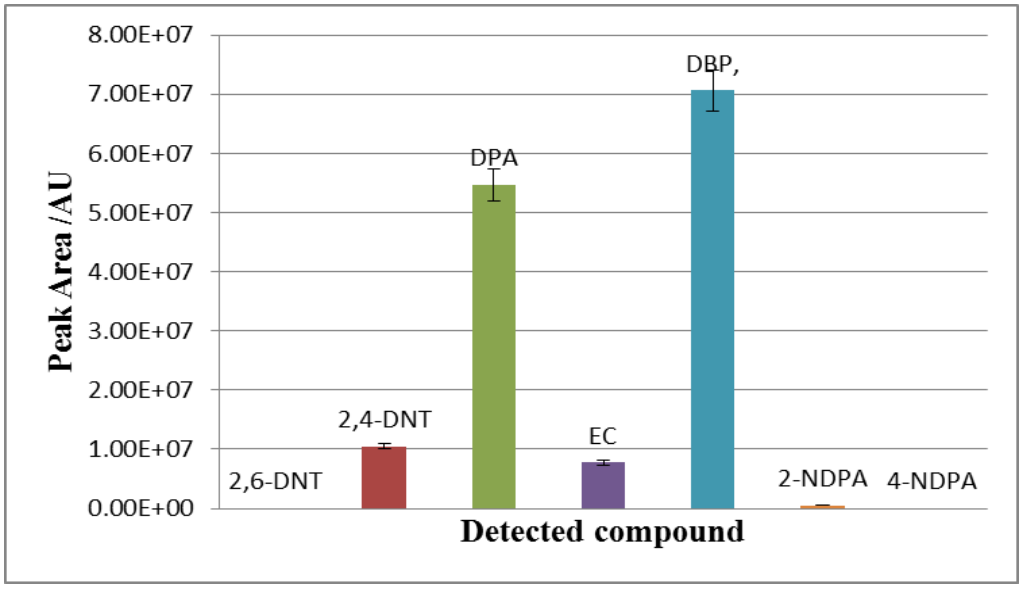

Figure 5.11. Bar chart of detected compounds in Group 4 ammunition

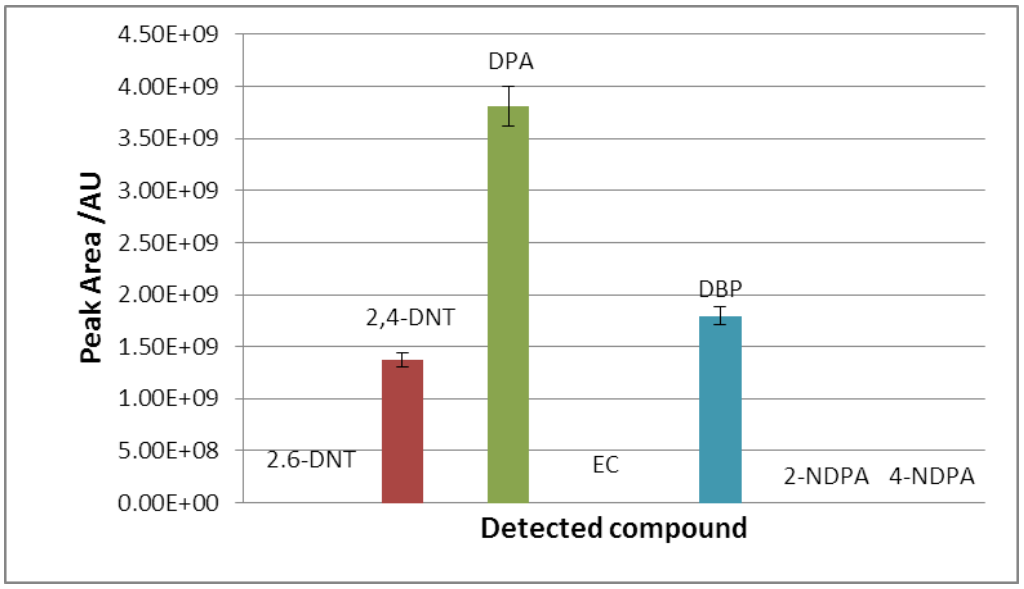

Figure 5.12. Bar chart of detected compounds in Group 5 ammunition

5.3.4 Discussion

Dibutyl phthalate was detected in all the residues from all five cartridges. It is interesting that it is not present in all the analyses of the unfired propellant. However, the explanation of this is relatively straightforward: it is released from the plastic casing during the firing process as a consequence of the exposure to high temperature. The presence of the dibutyl phthalate in fired shotgun cartridge residues has been previously reported by other researchers [119, 137].

The concentrations profiles of the organic constituents of the propellant change markedly upon firing the cartridge. Therefore, unlike in the case of unfired shotgun cartridges, branding cannot be carried out merely in terms of the constituents that are present. Table 5.5 clearly indicates that this is no longer the case, as it would be appear that Group 1 and Group 2 are the same. However, if the concentrations of the components of the residues are considered, comparing Figures 5.8 and 5.9 it is clear that there are significant differences. The residue from the Group 2 cartridges contains significantly more DPA than Group 1.

While the peak areas associated with some of the materials are relatively small, they all exceed the limit of detection previously determined and consequently this data can be repeated with confidence.

The conclusion from this limited study is that it would appear that shotgun cartridges can be branded from the analysis of the fired residue. This is independent upon the type of the weapon used to make the firing and this serves to increase the significance of this finding.

5.4 Blank Handgun Cartridges

5.4.1 Analysis of Unfired Blank Handgun Cartridges

The procedure of collecting the powder from the unfired cartridge involved the holding of the cartridge vertically in a small milling vice placed beneath a pillar drill fitted with a narrow angle bit. The drill was lowered to press open the crimped brass end of the cartridge and to widen the orifice (non-rotating drill). The internal fiber wad was removed and the powder poured into glass vial.

One milligram of unfired powder (0.380 NC-knall calibre , manufactured by Lapua GmbH., Schönebeck, Germany) from each cartridge was accurately weighted and dissolved into volumetric flask with 10 mL of acetone in order to break the nitrocellulose pellets. The solution was taken and placed into a separate GC vial. The vial was sonicated for 15 minutes to dissolve the powder completely. Following sonification, 5 μ L of each sample was injected in replicate into the GC/MS for analysis, as described in Section 2.1.1.

5.4.2 Results from the Analysis of Unfired Blank Handgun Cartridges

Figure 5.13 shows the organic compositions that were found in 0.38 NC-knall cartridges. These consisted of DPA, 2-NDPA and 4-NDPA. Figure 5.14 shows the different concentration between the detected constituents. The relative concentration of DPA is markedly higher than that of 2-NDPA and 4-NDPA.

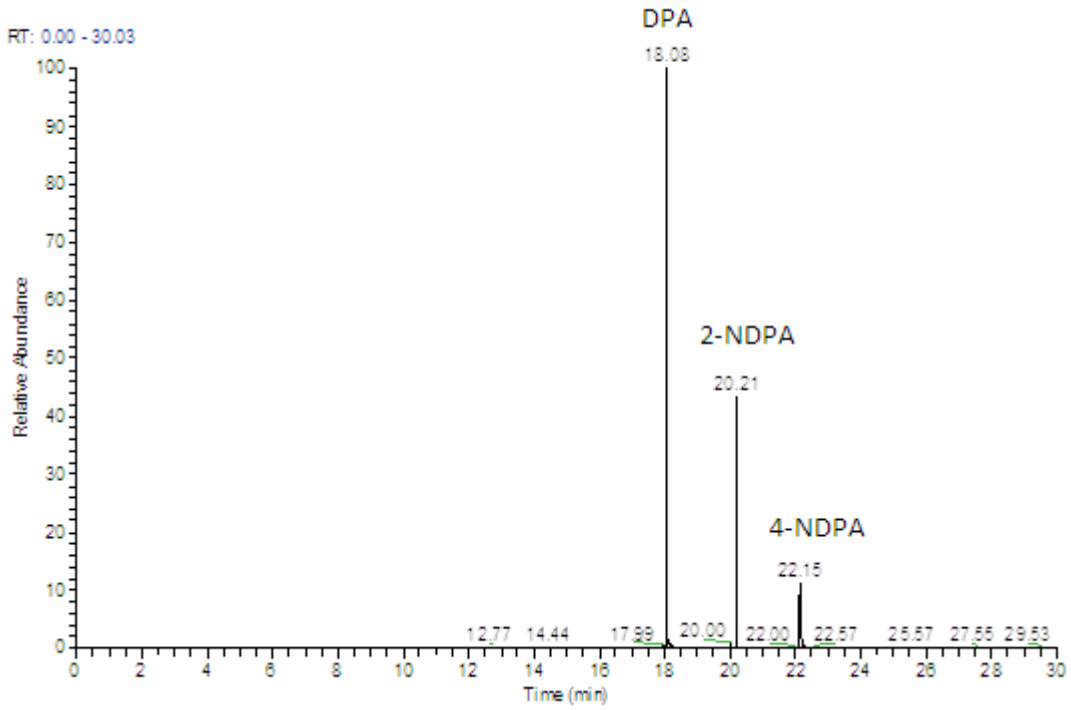

Figure 5.13. GC/MS analysis of unfired blank handgun cartridge (NC-Knall 0.38)

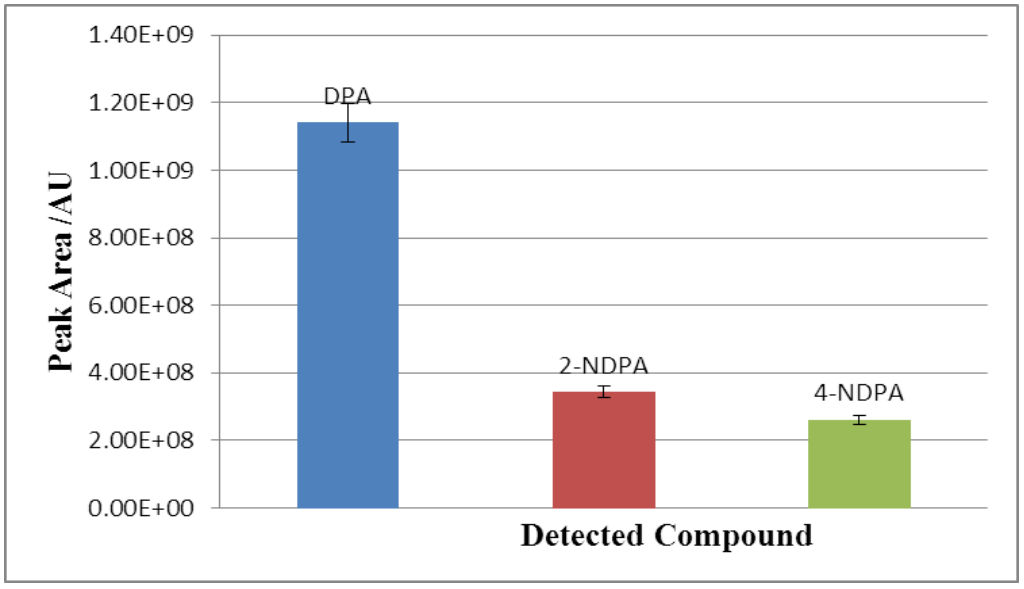

Figure 5.14. Bar chart for unfired blank handgun cartridge (NC-Knall 0.38)

5.4.3 Discussion of the Analysis of Blank Handgun Cartridges

This study was designed to determine the main organic constituents that are present in blank handgun ammunition. The results showed that DPA is present in the highest of the organic substances that was detected. In addition to DPA, 2-NDPA and 4-NDAP are also present.

It is easier to differentiate between different types of unfired ammunition by analysing their organic constituents. In addition to the absence or presence of any organic substance being used, it is also be possible to differentiate by the relative percentage between all the organic substances. Generally, each manufacturer used their own concentration to manufacture their ammunition. These concentrations vary in terms of different compounds.

5.5 Fired Blank Handgun Cartridges Experiments

5.5.1 Analysis of Fired Blank Handgun Cartridges

The blank firing handgun (ME38 Competitive Alarm revolver, manufactured by Cuno-Melcher ME Sport-Waffen, Italy) was fired three times into a dust bin. Swabs (VWR) were taken from the hand of the shooter after each discharge. Every kit was packed into a cylindrical plastic pot with sealable lid. Each kit and each sample were processed separately, taking care to avoid cross-contamination

Swabs kits were removed from the cylindrical plastic pot and a fresh set of laboratory test tubes were labeled to correspond with the sample vials. 0.5 ml of acetone was added to the swab vial and kept in the fridge at room temperature for two hours, after which the swab was squeezed and pressed against the inside wall of the vial using forceps. The solvent was then removed to another vial and concentrated down to approximately 100 μ L under a stream of dry nitrogen at 30 ^{o}C. 5 μ L from the sample was injected into the GC/MS. Analysis was performed using the conditions previously described in Section 4.1.1.

5.5.2 Results from the Analysis of Fired Blank Handgun Cartridges

The ion chromatogram from firing a blank handgun using swab methods is shown in Figure 5.15; diphenylamine, 2-NDPA and 4-NDPA were detected. The results showed that the residues did not change significantly from the original gunpowder composition (Figure 5.16). However, the concentration of DPA, 2-NDPA and 4-NDPA was relatively lower compared to unfired cartridges (Figure 5.17).

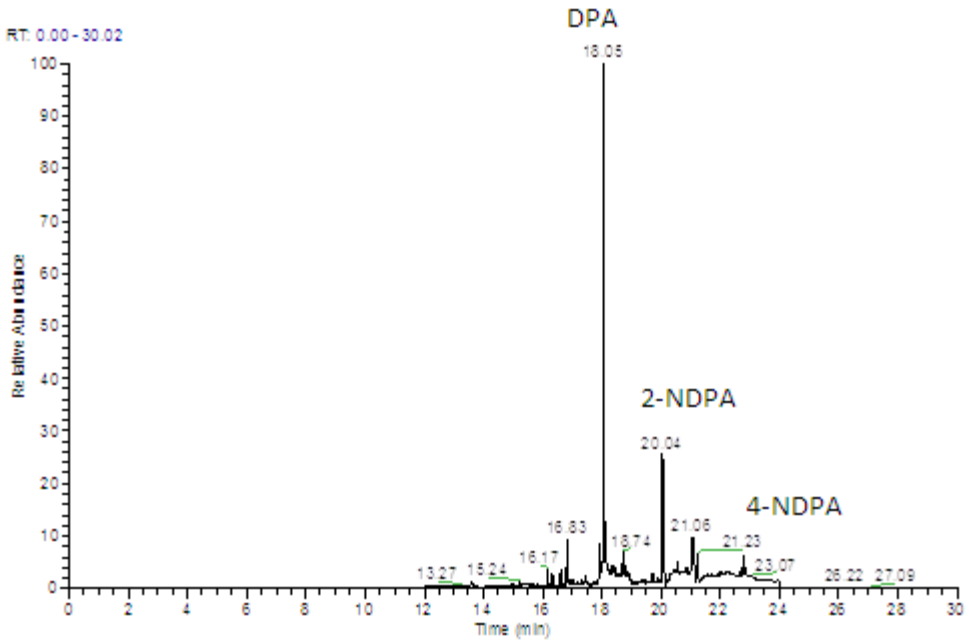

Figure 5.15. GC/MS analysis of the Collecting of GSR from the hand of the shooter using swab method

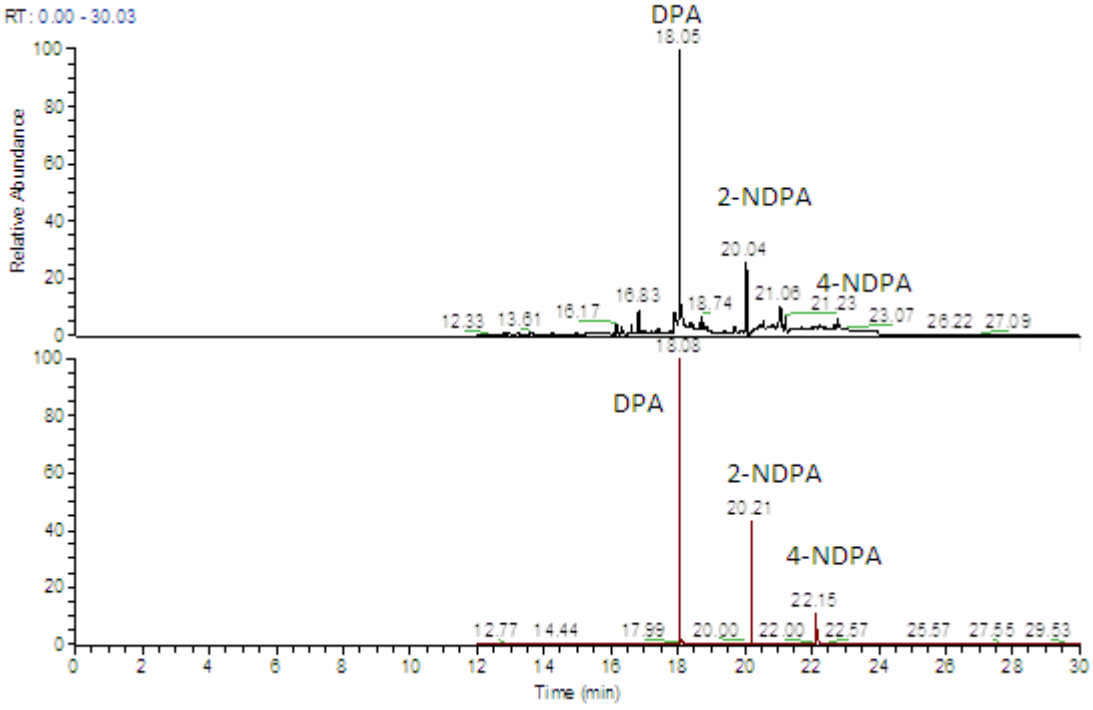

Figure 5.16. GC/MS analysis of unfired and fired blank handgun cartridge

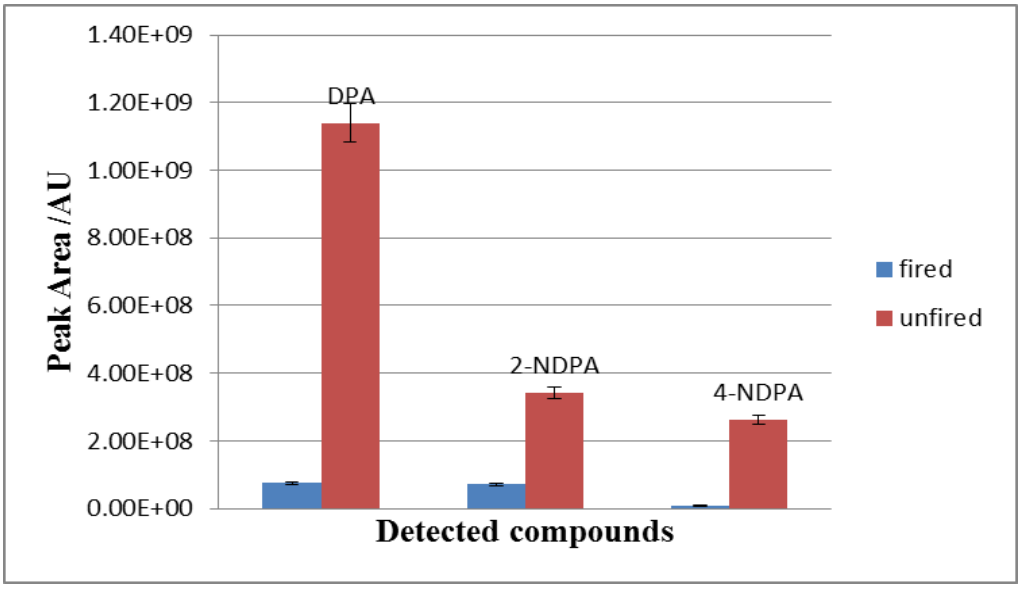

Figure 5.17. Bar chart of detected compounds in fired and unfired blank handgun ammunition

5.5.3 Discussion

The results presented in Figure 5.17 clearly show that the major constituents of the unfired ammunition , namely DPA, 2-NDPA and 4-NDPA are still present in the analysis of the residues after firing, this is consistent with the findings of previous workers[139]. However, there relative concentrations of the detected compounds are seen to vary significantly between the unfired and fired samples. In the unfired materials the component present in the largest amount is DPA while in the fired sample the relative amount of DPA and 2-NDPA are very similar. These results indicate that any branding exercise which is reliant upon the relative concentration of the key components must be based on fired samples as the relative concentrations can vary significantly during the discharge of the weapon.

5.6 Conclusion from the Analysis of Shotgun and Blank Handgun Cartridges

Smokeless powders additives from pre- and post-firing of shotgun and blank handgun cartridges were determined. The methods involved the extraction of the organic materials via solvent extraction and analysis using GC/MS. Five different brands of shotgun ammunition manufactures were studied. The chemical composition of each manufacturer was identified. There are some similarities between the compounds that were found in all brands in terms of the number or type of organic compounds found. A strong relationship was found between the chemical composition of fired and unfired powder. Therefore, it is possible to differentiate between two ammunition brands through the analysis of the organic constituents. The results provide very useful information that may aid in associating an unknown sample of powder or residue to known samples.

A more extensive study of blank handgun cartridges is needed to confirm that the OGSR analysis could provide branding information. Interestingly, very little difference was observed in the relative composition of the constituents in residues from handgun cartridges compared to shotgun cartridges.

6 DEVELOPMENT OF NANO-PARTICULATES MATERIALS TO USE AS FINGERPRINT POWDER

6.1 Introduction

A fingerprint is one of the most common types of physical evidence found at crime scenes. It is basically a complex mixture of natural secretions of the body from three types of glands: eccrine, apocrine, and sebaceous glands. It also contains contaminations from the environment. The chemical compositions of the deposit are mostly water (99%), with a minor amount (up to 1%) of inorganic and organic compounds [229, 230]. A number of studies have been undertaken to develop materials for use in lifting fingerprints. In general, the impressions made by fingermarks found at the crime scenes fall into three categories: plastic (or impression), visible (patent) and latent prints; the latter require enhancement in order to be visualised and identified.

Since the 1990s there has been significant development in the visualisation methods of latent fingerprints [163]. This includes the combination of optical, physical, and chemical methods. In spite of all of the current methods for detecting latent fingermarks, there is a strong demand for new and more efficient reagents to visualise latent fingerprints. In this context, nanotechnology has a great influence on modern day applications relating to forensic science. It is one of the fastest growing technologies in all fields of science and technology, such as electronics, aerospace, defense, medical and dental. This involves the design, synthesis, characterisation and application of material and devices on the nanometer scale.

In recent years, a number of studies have utilised the use of nanotechnology applications in the field of forensic science [231, 232]. These have been limited to the enhancement of latent fingerprints. However, they differ from the work included in this thesis as they did not focus on the added retrieval of chemical information. In 1968, Stöber et al. developed a protocol for the synthesis of silica nano-particulates [233]. Since that time, researchers have conducted several studies to investigate and understand the reaction mechanism for controlling the sizes and shapes of nano-particulates.

In this chapter, the synthesis of novel fingerprint powders based on silica nano-particulates of various sizes with three different surface functionalities (OH, - longer

chain hydrocarbon (C12) and phenyl) is reported. Functionalised nano-particulates were used to enhance latent fingermark deposited onto different non-porous surfaces (glass and wood) and the results have been compared with currently available commercial powders (K9 Scene of Crime Equipment Limited)

6.2 Silica Nanoparticles: Synthesis and Characterisation

6.2.1 Synthesis of Silica Nanoparticles

Silica nano-particulates were synthesised following Stöber method [233] and the surfaces were functionalised in multistep processes. Stöber and his team published a simple process for synthesising spherical and monodispersed silica nano-particulates via sol-gel method[233].

The synthesis takes place in two steps; hydrolysis and condensation of Tetraethyl orthosilicate e (TEOS) in an ethanol solution in the present of ammonia as a catalyst, as shown below.

$$\text{Hydrolysis: } Si(OR)_4 + H_2O \rightarrow Si(OH)_4 + 4R\text{–}OH,$$

$$\text{Condensation: } 2Si(OH)_4 \rightarrow 2(Si\text{–}O\text{–}Si) + 4H_2O$$

Synthesis of silica nano-particulates by the following method: ethanol (125 ml, Thermo Fisher UK) and concentrated ammonium hydroxide (125 mL, 5 M, Aldrich) were added to a reaction flask and the mixture was stirred using ultrasonic vibration (ultrasonic bath) for five minutes. Tetraethyl orthosilicate (TEOS) (17.5 mL, Aldrich) was added to the reaction flask and the mixture was kept under ultrasonic vibration for a further 30 minutes. The nano-particulate suspension was placed inside a dialysis tube (cellulose) and placed in a beaker of deionised water. The deionised water was changed a number of times and the dialysis was continued until the pH of the deionised water was measured to be less than 7. Samples were then transferred from the dialysis tube and kept in glass bottle at room temperature.

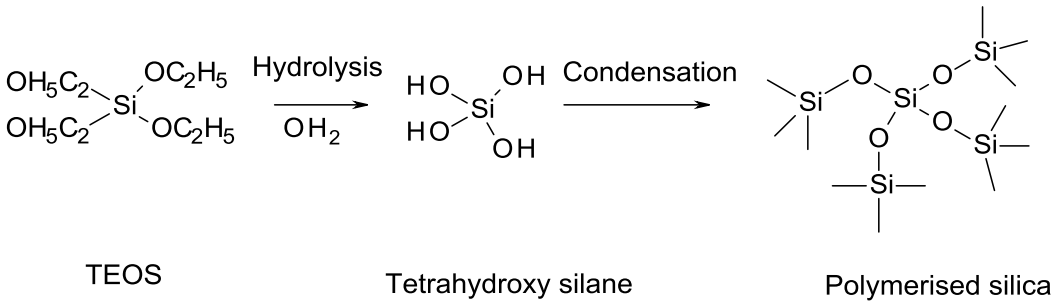

Figure 6.1. The reaction mechanism of surface functionalisation

6.2.2 Functionalisation of Silica Nanoparticles with N-Dodecyl Trimethoxysilane

Silica nano-particulates (300 mg) were collected by centrifugation from a silica suspension (7.4 mg ml^{-1}). Toluene (40.5 mL, Aldrich) and triton X100 (5 mg, Aldrich) were added and the mixture was shaken to form a tri-phasic reverse emulsion (TPRE) (Figure 6.2). n-Dodecyl trimethoxysilane was added to the emulsion at two different concentrations (10% and 20% v/v) (Figure 6.3). The mixture was allowed to react in 100 ml glass reactor fitted with condenser attached at 50 °C in an oil bath for 16 hours with continuous stirring using a magnetic stirrer bar. After sixteen hours the suspension was centrifuged in order to separate out the nano-particulates, which were then washed three times (25 mL each) with coupling solution (0.8% (v/v) glacial acetic acid (Aldrich) in dry methanol (VWR)) by centrifugation. The sample was stored at room temperature in 20 mL of coupling solution. The fingerprint powder was prepared by centrifugation of known amount of the silica suspension for five minutes at 3000 rpm. The supernatant was removed and the particles allowed to dry in an oven at 60 °C for 24 hours. Once the particles were dry, they were crushed in a mortar and pestle and kept in glass vial for further use.

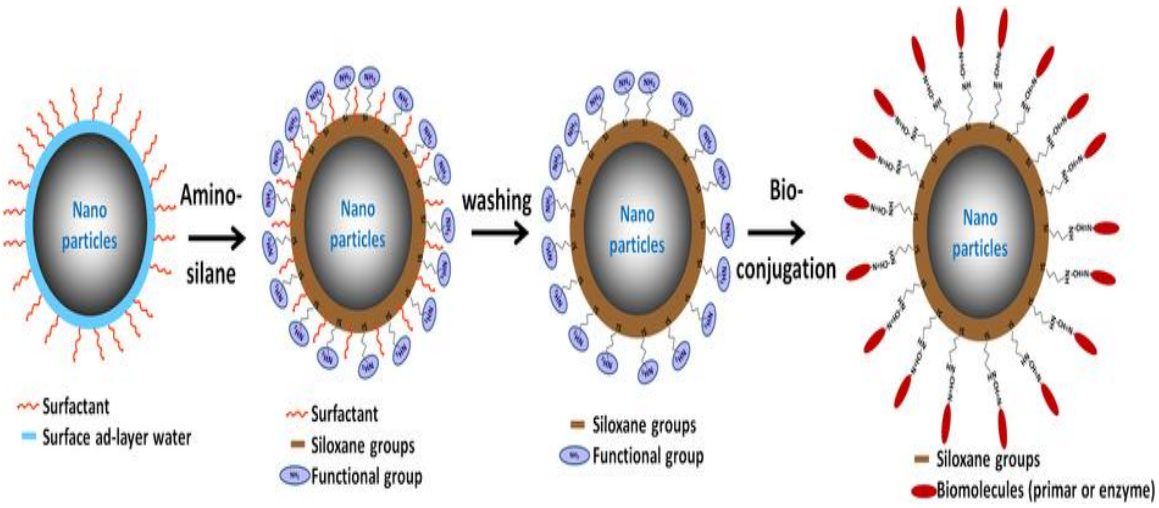

Figure 6.2. A schematic diagram of TPRE for surface patterning of nano-particulates in suspension [234]

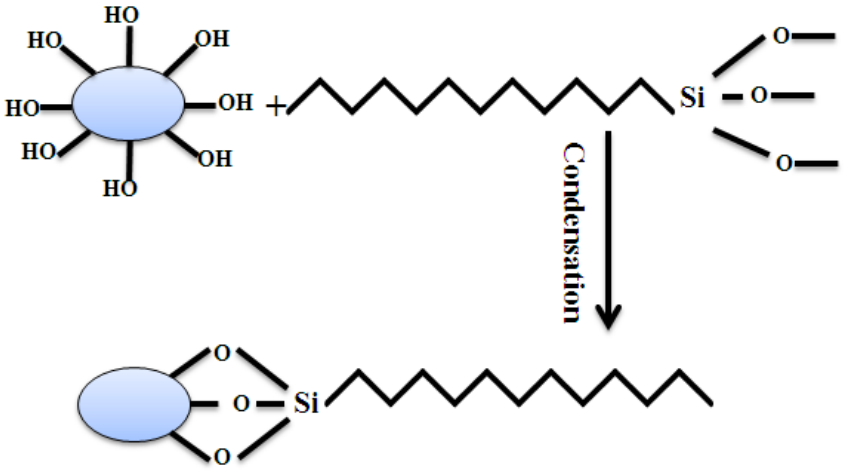

Figure 6.3. Surface modification of nano-particulates by n-Dodecyl trimethoxysilane

6.2.3 Functionalisation of Silica Nanoparticles with Triethoxyphenylsilane

Silica nano-particulates (300 mg) were collected by centrifugation. Toluene (40.5 ml, Aldrich) and triton X100 (5 mg, Aldrich) were added and the mixture shaken to form a tri-phasic reverse emulsion (Figure 6.4.). Triethoxyphenylsilane (3.5 mL, Aldrich) was then added to the mixture, which was allowed to react in 100 mL glass reactor fitted with condenser attached at 50 °C in oil bath for 16 hours with continuous stirring by a magnetic stirrer bar. After 16 hours the nano-particulates were removed by centrifugation and washed three times (25 mL each) with coupling solution followed by centrifugation. The sample was stored at room temperature in coupling solution (20 mL).

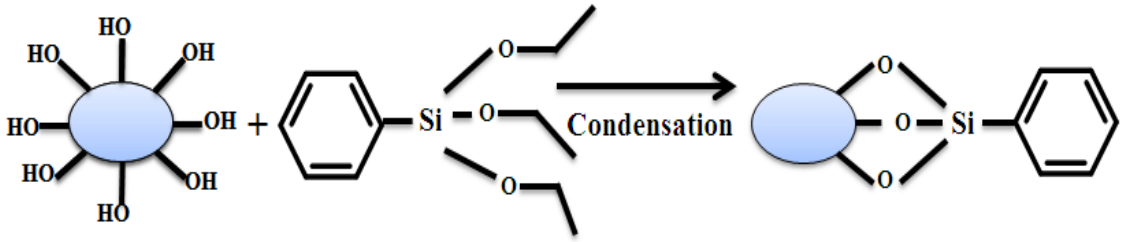

Figure 6.4. Surface modification of nano-particulates by Triethoxyphenylsilane

6.2.4 Determination of Solid Content of Nanoparticle Suspensions

Nanoparticle suspension densities were determined by drying 0.1 mL of each sample at 60 °C under vacuum overnight to obtain a dry mass estimation. This process was carried out in duplicate to obtain an average value.

6.2.5 Laser Particle Size Analyser

The measurement of the particle sizes in suspension was performed by dynamic light scattering (DLS) using Zetasizer Nano-ZS (Malvern, UK), and the data were analysed with Malvern DTS version 5.00 computer software.

6.2.6 Scanning Electron Microscope (SEM)

The morphology of the silica nano-particulates was determined by scanning electron microscope (FEI Quanta 200, USA). A drop of particle suspension was placed on a carbon coated SEM stub and dried at 60 ^{o}C for an hour. The dried samples were coated with gold before analysis by SEM.

6.2.7 The Brunauer-Emmett-Teller (BET) surface Area Measurement by Nitrogen Adsorption

The surface area of non-functionalised silica nano-particulates and commercial white fingerprint powders (titanium dioxide) was determined by the BET method (nitrogen gas as an adsorbent) using a Micromeritics ASAP 2010. All samples were degased at 90 °C for one hour followed by 250°C for four hours. Each dried sample was weighed accurately to four decimal places and placed in a sample tube (an identical empty tube was used as a reference). Analyses were performed using an automatic adsorption programme, measuring the volume of nitrogen adsorbed by the sample at the following pressures: 76, 114, 152, 190, and 228 mm Hg.

6.2.8 Transmission Electron Microscopy (TEM)

Particle suspensions were placed onto a carbon-coated copper grid using a dropping pipette and dried at room temperature before inserting into the TEM. The samples were imaged with a JEOL JEM-2000EX Transmission Electron Microscope at 200 kV.

6.2.9 C, H and N Element Analysis:

Elemental analyses (C, H and N) were performed by an external research organization (Manchester University) using Redox Spa (Milan, Italy).

6.2.10 Solid State Nuclear Magnetic Resonance (NMR)

^{13}C-^{1}H solid state cross polarization magic angle sample spinning CP-MAS NMR spectra were recorded on a BRUKER Ultra Shield magnet spectrometer operating at 400 MHz. Solid materials (phenyl, long chain hydrocarbon and OH terminated) were loaded into 4 mm zirconia rotors which were then tightly closed. Cross polarization with magic-angle spinning (CP MAS) was applied using a spin speed of 6000 Hz. 20000 scans were used to achieve sufficient signal to noise ratio.

6.3 Results and Discussion

6.3.1 The Particle Size Distribution

The particle size distribution of the synthesised materials is presented in Figure 6.5. The average size of silica nano-particulates was around 450 nm. This result indicates that the nano-particulates are well dispersed in suspension (see SEM and TEM results in Sections 6.3.2 and 6.3.3).

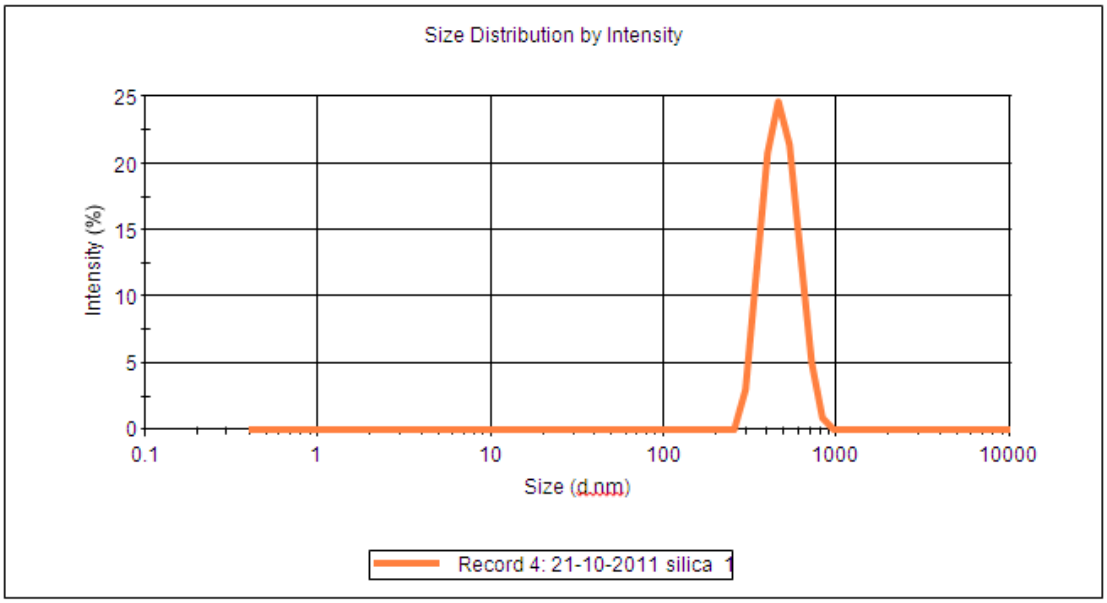

Figure 6.5. Laser particle size data of silica nano-particulates synthesised

6.3.2 SEM

The morphology of synthesised silica nano-particulates was characterised using scanning electron microscopy. The SEM images of silica nano-particulates and TiO_2 powder are shown in Figure 6.6.and Figure 6.7 respectively. The results show that the particles are spherical in morphology, of sizes 450 nm and nearly monodispersed, whereas TiO_2 particles exhibited irregular morphology.

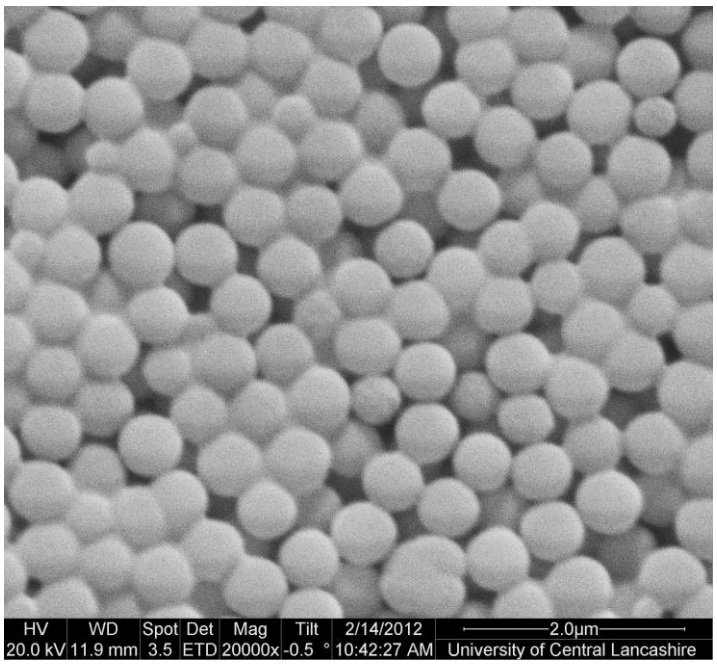

Figure 6.6. SEM image for the silica nano-particulates powder

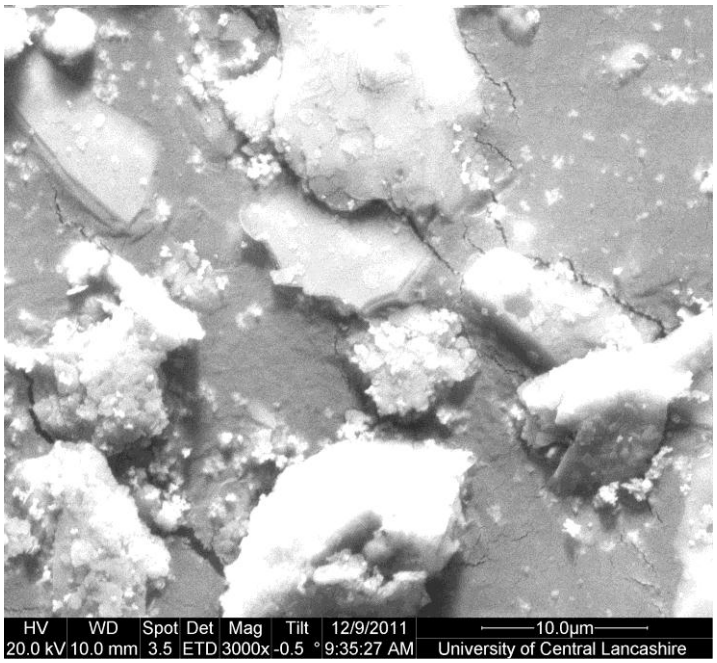

Figure 6.7. SEM image for theTiO_2 powder

6.3.3 TEM

Figure 6.8 shows the transmission electron micrographs of non-functionalised silica nano-particulates, whereas Figure 6.9 shows the TEM images of modified silica nano-particulates with phenyl groups. The results show that the particles are monodispersed and spherical in nature and have a well-defined spherical shape. The

diameter of the particle was measured to be around 419 nm with small mesopores. The pores which are disordered have an approximately 3 nm repeating distance.

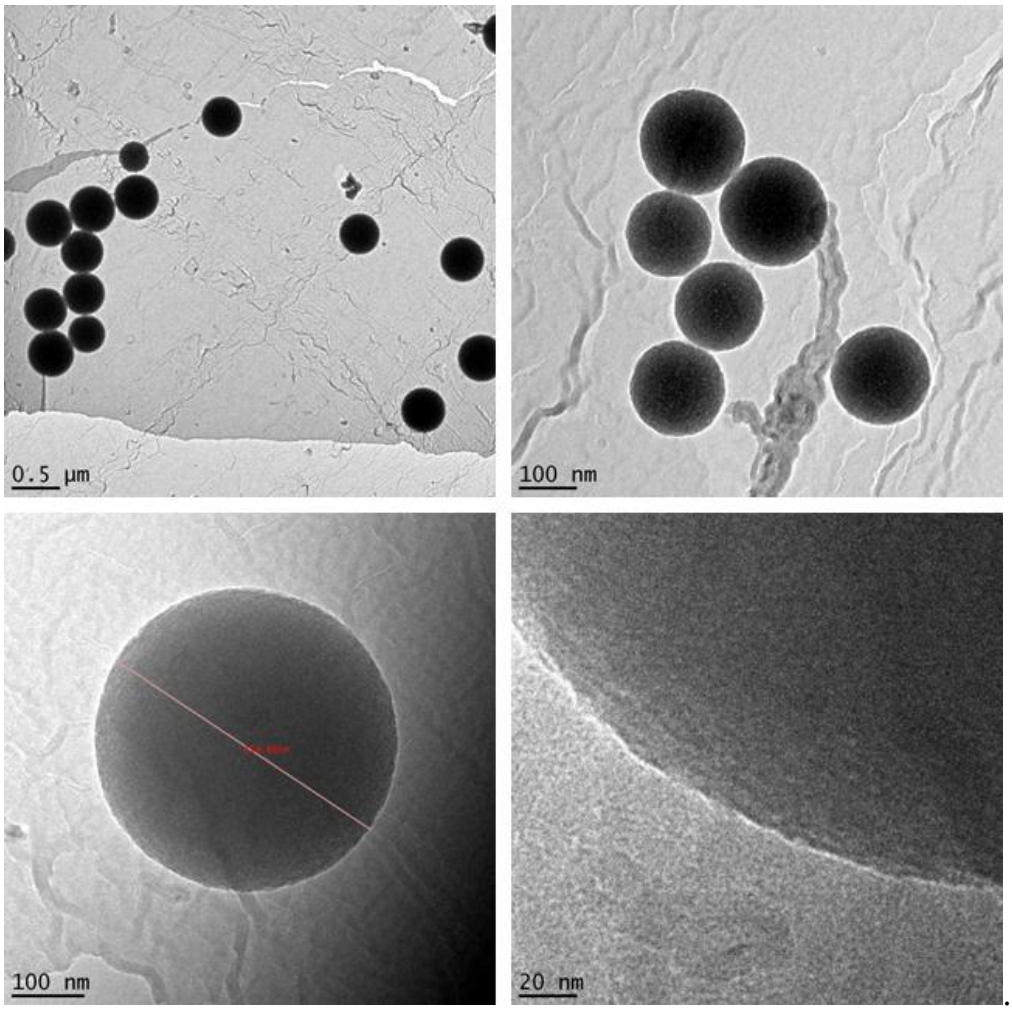

Figure 6.8. TEM images for un-modified silica nano-particulates powder

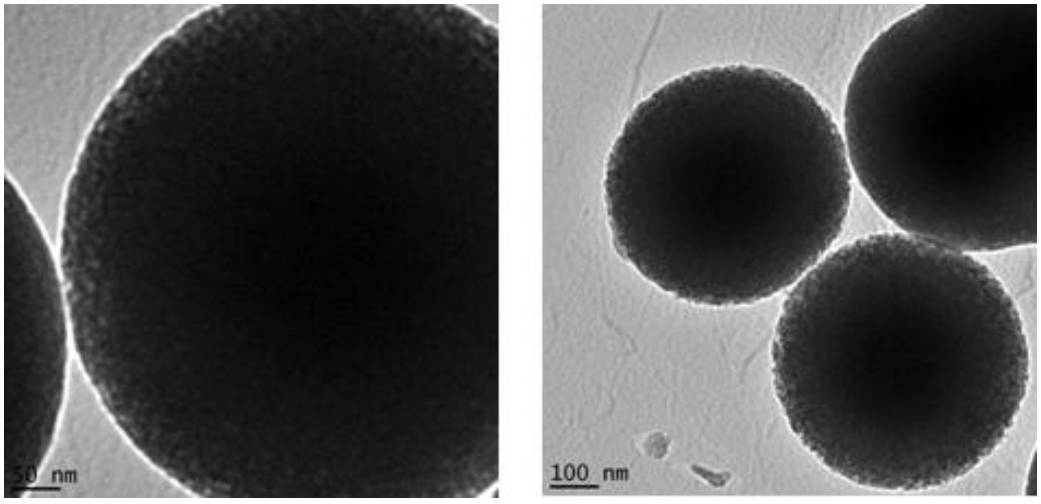

Figure 6.9. TEM images for modified silica nano-particulates with Triethoxyphenylsilane

6.3.4 The Brunauer-Emmett-Teller (BET) Surface Area Measurement by Nitrogen Adsorption

The Brunauer-Emmett-Teller (BET) adsorption isotherm analysis of silica nano-particulates and commercial fingerprint powders are shown in figures 6.10 and 6.12. The silica nanoparticles exhibited very high specific surface area (402 m^2 g^{-1}) compared to commercial fingerprint powder (6 m^2 g^{-1}). Furthermore, the adsorption isotherm for the silica nano-particulates powder clearly shows desorption hysteresis, which is indicative of mesoporosity. No such hysteresis was observed from the adsorption/desorption isotherms produced from the commercial fingerprint powder (Figure 6.12). Hysteresis phenomena is commonly observed for porous materials where in the shape of the pores causes the absorption and desorption gas molecules which is shown on the isotherms to have different path [235].

The determination of the pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) method. Figure 6.11 shows the pore volume and BJH pore size distribution for the silica nano-particulates which have a median pore diameter of 26.04 Å. This indicates that lots of pores are spread over the surface of the nano-particulates, which confirms the observation made using TEM.

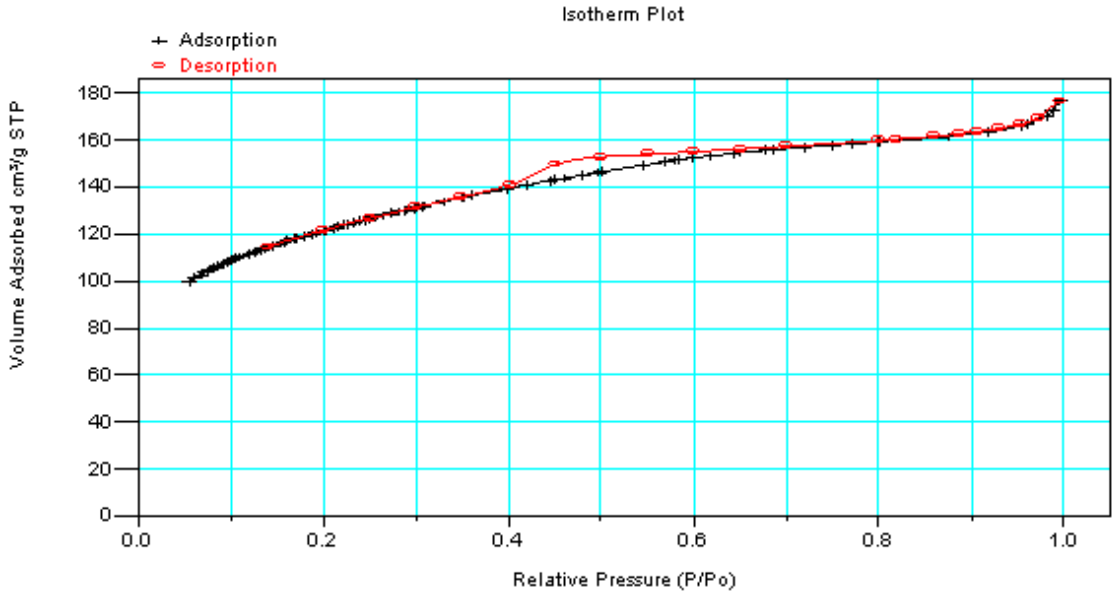

Figure 6.10. Nitrogen adsorption-desorption isotherm (BET) for silica nano-particulates powder.

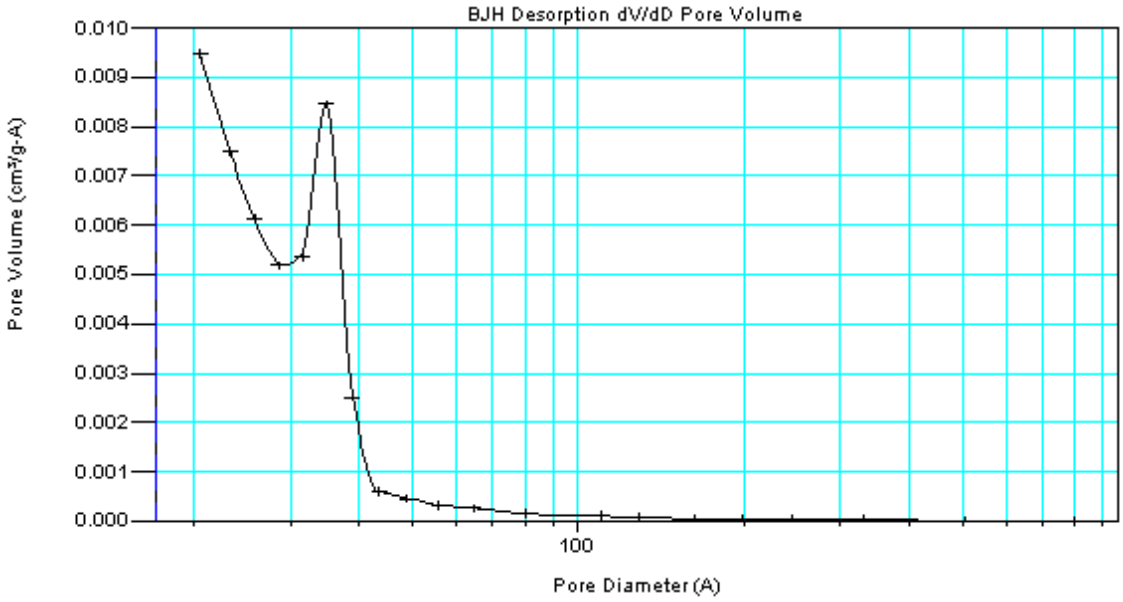

Figure 6.11. Differential pore sizes distribution of silica nano-particulates

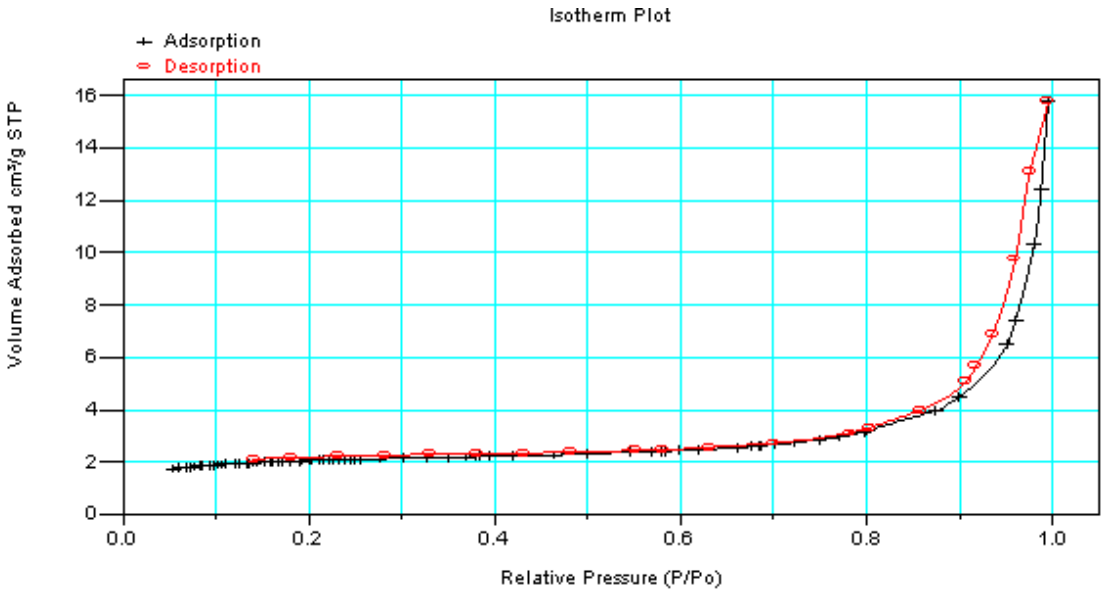

Figure 6.12. Nitrogen adsorption-desorption isotherm (BET) for TiO_2 powder.

6.3.5 C, H and N Element Analysis

Table 6.1 contains the percentage of carbon, hydrogen and nitrogen in the synthesised materials. It is clear that from the C,H and N values obtained the organic content of the materials is very low.

Table 6.1: C H and N element analysis (wt%)

Types of modification	C	H	N
Unmodified silica nano-particulates (OH terminated)	0.25	1.56	0
Modified silica nano-particulates with long chain hydrocarbon	1.03	1.28	0
Modified silica nano-particulates with phenyl group	3.59	1.38	0

In the unmodified particles the hydrogen content is relatively high compared to the modified particles, while the carbon content is relatively small. In theory there should be no carbon associated with the unmodified particles. However, the small amount of carbon observed could be the result of unhydrolyesed ethoxy group or from the hydrolyisation of ethanol during the synthesis of silica nano-particulates.

6.3.6 ^{13}C-^{1}H-CPMAS NMR

The ^{13}C-^{1}H CPMAS solid state NMR spectra of unmodified silica and functionalised silica nano-particulates with long chain hydrocarbon (C12) and phenyl groups are shown in Figures 6.13-6.15 respectively. No characteristics signals were obtained from unmodified silica nano-particulates (Spectrum A), indicating the absence of carbon atoms (as anticipated).

The silica functionalised with long chain hydrocarbon (Figure 6.14) displays three peaks at 31, 61 and 63.27 ppm. The peak at 31ppm is due to the CH_2 being connected with silica. There are small peaks around 20 ppm which are related to long chain hydrocarbon. This may result in the lower concentration of the N-Dodecyl Trimethoxysilane attached to the surface of silica nano-particulates. The two peaks at 61 and 63.27 ppm were assigned to CH_2O from surfactant (Triton X100).

The resonances from 139.35 ppm to 145.82 ppm correspond to carbon atoms associated with phenyl groups on functionalised silica nano-particulates with Triethoxyphenylsilane (Figure 6.14). In theory there are four peaks, but due to the resolution of the technique all peaks are not resolved; indeed the peak at 139.35 does appear to have a contribution from more than one peak. The two peaks at 85 and 205 ppm correspond to spinning sidebands for CPMAS spectra, whereas the peak at 61 ppm is due the surfactant (Triton X100).

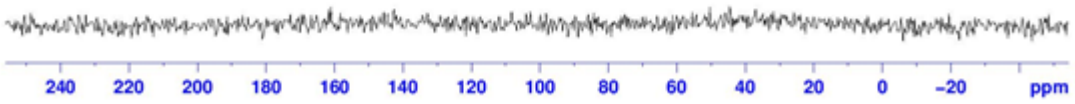

Figure 6.13. 13C - 1H-CPMAS NMR spectra of un-unmodified silica nano-particulates

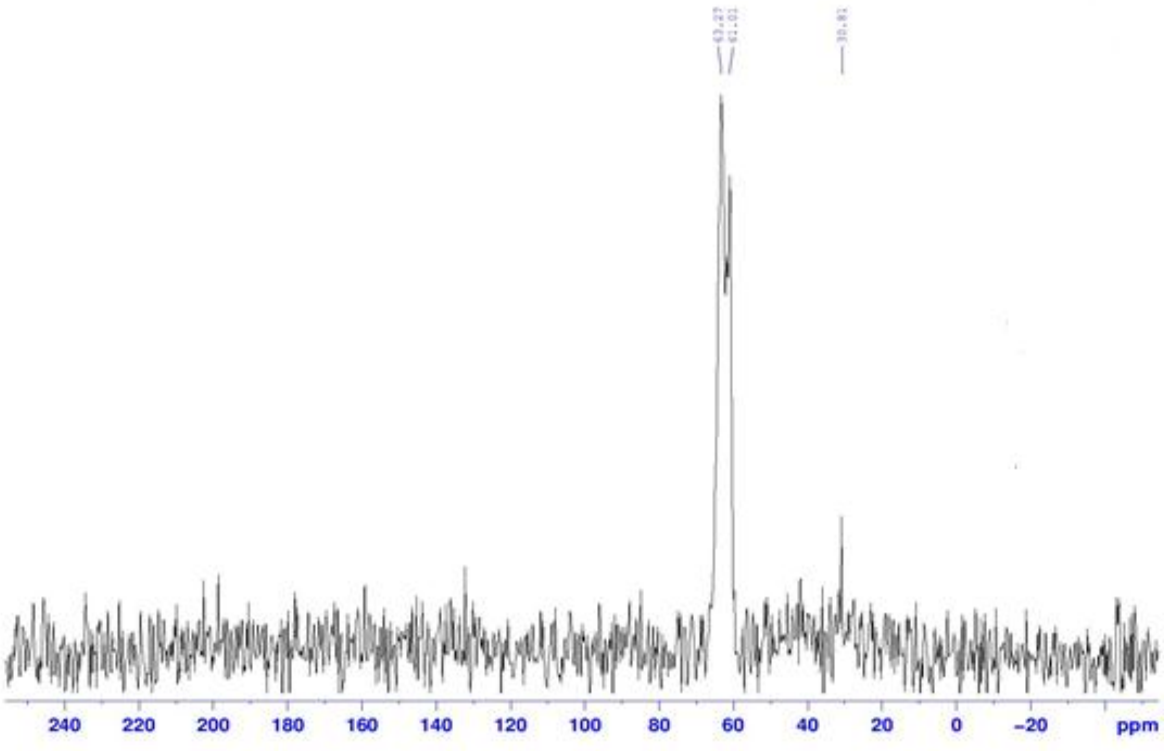

Figure 6.14.^{13}C - ^{1}H-CPMAS NMR spectra of functionalised silica nano-particulates with long chain hydrocarbon

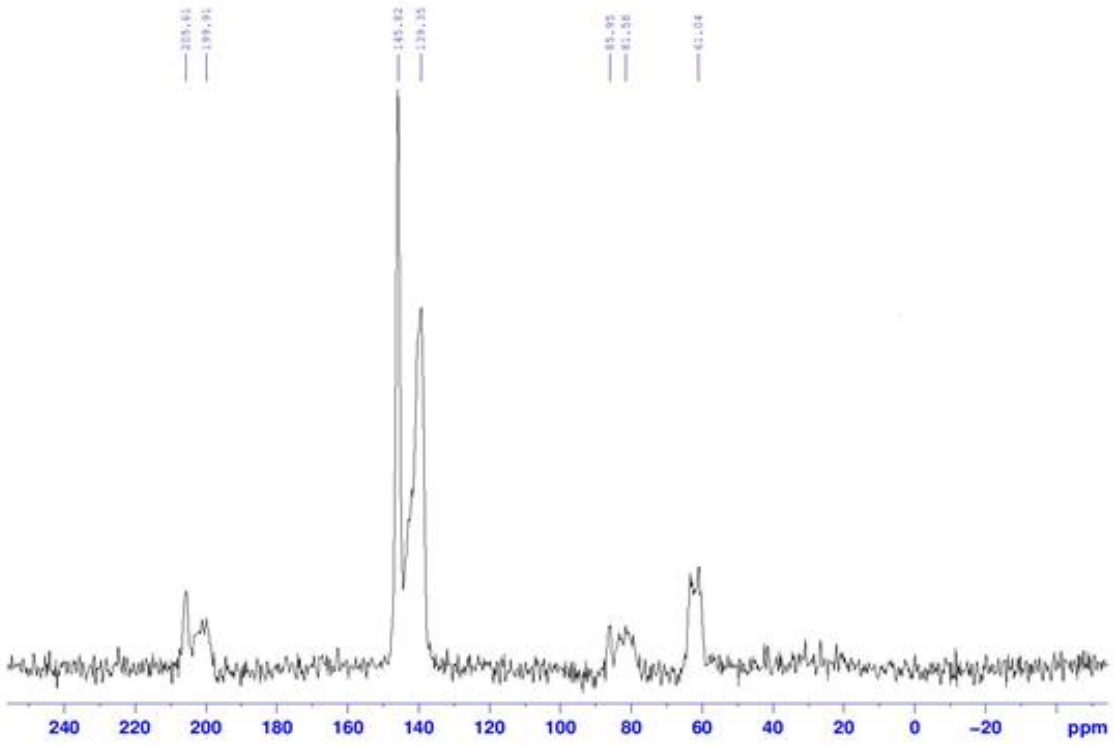

Figure 6.15.^{13}C - ^{1}H-CPMAS NMR spectra of functionalised silica nano-particulates with phenyl groups

The results confirm that the surfaces of silica nano-particulates were successfully functionalised with phenyl groups. These particles will subsequently be used for detection of different types of forensic evidence, including latent fingerprint, and GSR.

6.4 Conclusion

Silica nano-particulates of defined size and shape have been successfully synthesised. These silica nano-particulates have been functionalised with two different functional groups, namely phenyl and long chain hydrocarbon, using TPRE method.

The modification of the surface particles in aqueous suspension is usually associated with a number of fundamental problems such as particle aggregation, variable density and a non-uniform distribution of surface functional groups. TPER organised the function groups on the surface of the particles by controlling the surface condensation of the aminosilane. TPRE was introduced as a simple and efficient protocol to overcome such problems [234].

These nano-particulates were characterised using scanning electron microscope (SEM), transmission electronic microscopy (TEM), elemental analysis, size particles analyser, BET surface area and solid-state nuclear magnetic resonance (NMR) spectroscopy. The silica nano-particulates materials are monodispersed and spherical in nature, having a well-defined spherical shape. The diameter of the particle was measured to be around 412 nm. BET surface area measurement confirmed the surface area of the particle, which was around 402 $m^2 g^{-1}$.

7 APPLICATION OF NANO PARTICULATE MATERIALS AS FINGERPRINT POWDERS

7.1 The Use of Nano Particulate Fingerprint Powders for Fingermark Enhancement

A number of techniques have been developed to enhance the detection of latent fingerprints, including the combination of optical, physical, physical/chemical and chemical methods [163, 229]. In spite of all the existing techniques, there is still a strong demand for more efficient reagents to detect latent fingerprints.

Nanotechnology involves the creation of functional materials, devices and systems using matter with dimensions on the nanometer length scale (1–100 nm), and the exploitation of properties unique to the nanoscale. The main advantage of using nanotechnology is an increased ratio of surface area to volume present in many nanomaterial compared to the bulk material. This provides new possibilities in surface-based science including forensic fingerprint detection [236]. Nanoparticles are much smaller than most of the particles currently used in fingerprint detection, which are in the order of 1–10 μ M in size [237]. In this chapter, the use of nano-particulates as an agent for detection of latent fingerprint on the surfaces is investigated.

7.1.1 Experimental Procedures for the Enhancement of Latent Fingerprints

All fingerprint samples were taken from a single donor. Hands were cleaned with water and ordinary soap and dried with a paper towel prior to the experiment. The fingerprints from the donor were deposited on clean surface of black wood. The donor pressed their fingers down onto a horizontal surface, with contact time of 2 to 5seconds, without rolling the fingers. Care was taken when producing the latent fingerprint impression to ensure standardization of the applied pressure and length of time for deposition. A single donor was used to gauge a constant procedure during the production of the fingerprint. However, no scientific measurement of pressure was made. The fingermarks were then enhanced by the three different types of nano-particulate powders described in Chapter 5 and a commercial white coloured (titanium dioxide) fingerprint powder (K9 Scene of Crime Equipment Ltd.) using fingerprint brushes (Squirrel powder Brush, K9 forensic services Ltd, Media House, 31 Freehold Street, Northampton, Northamptonshire, NN2 6EF, England.). This powder was chosen

because it is a standard product used widely by police services in the UK. Four different fingerprints brushes were used to eliminate any possible contamination that might have happened between the fingerprint powders during the enhancement of the fingermarks on the surfaces. The enhanced fingerprints were photographed (Nikon D80 Digital SLR Camera). The photographed fingerprints were then printed and scanned into the Automated Fingerprint Identification System (AFIS) using the scanning plate provided with the system. This was then used to determine the quality of the fingerprints, as described in Section 2.2.

7.1.2 Results

The results from using the three different types of silica nano-particulates that were used are able to detect latent fingerprint powder on black wood surface are shown in Figure 7.1. Figure 7.1-A shows the recovered fingerprint from black wood surface using phenyl terminated nano-particulate powder. The image produced from enhancements using the C12 terminated powder is shown in Figure 7.1B. The images presented in Figure 7.1C and 7.1D were produced using unmodified silica (OH terminated) and commercial fingerprint powder respectively.

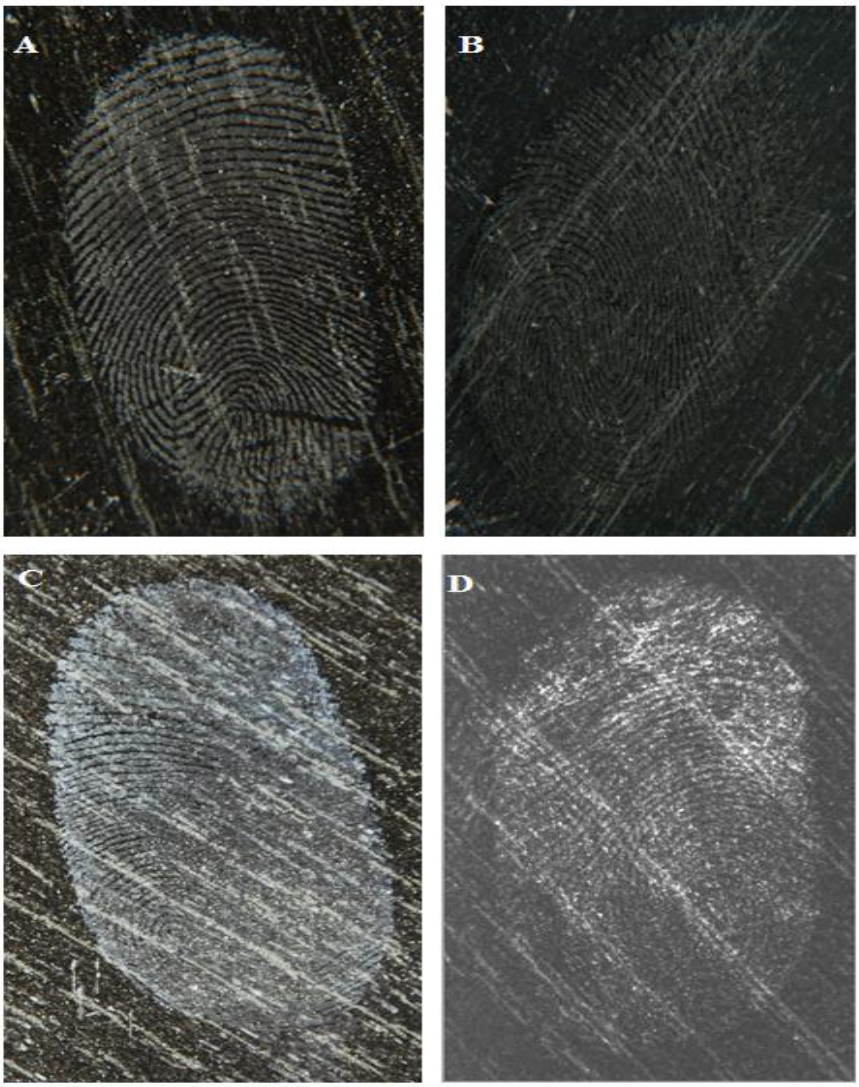

Figure 7.1. The visualisation of latent fingermarks using different fingerprint powders (Phenyl -A, C12- B, OH –C - and commercial powder D

Table 7.1. AFIS confidence rate and minutiae point for different fingerprint powder

Type of fingerprint	Confidence rate	Minutiae
Phenyl (A)	10000	64
C12 (B)	10000	30
OH terminated (C)	4289	57
Commercial fingerprint (D)	3103	10

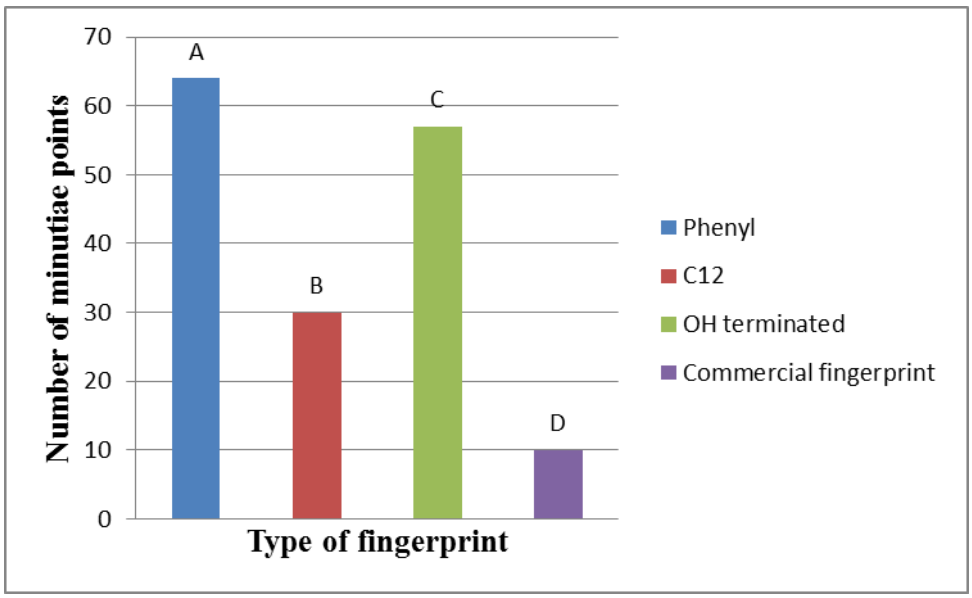

Figure 7.2. The number of minutiae points in different fingerprint powder used in this study

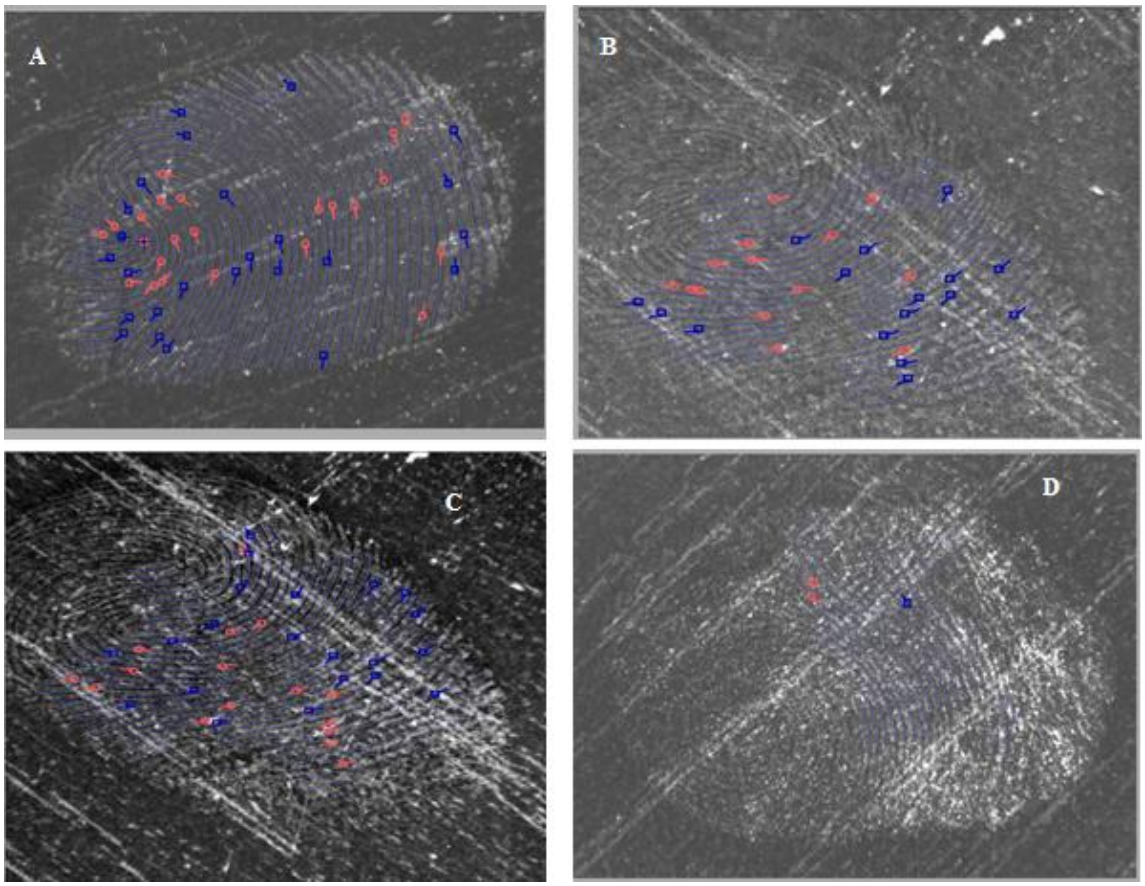

Figure 7.3. The number of minutiae points that were detected using AFIS from different fingerprint powders (phenyl terminated (A), C12 (B), OH (C) and commercial (D))

Table 7.1 and Figures 7.2-7.3 summaries the results obtained from the AFIS, which showed the minutiae confidence rate and minutiae points for different fingerprint powders. A functionalised silica nanoparticle with phenyl group has the highest minutiae confidence rate and minutiae points for all the different types of powder tested. The minutiae confidence rate for modified particles with long chain hydrocarbon is 10000, while the minutia is 30 points. OH terminated has 4289 minutiae confidence rate and 57 point of minutiae. Commercial fingerprint powder presented at very low minutiae point (10) compared to the rest of the types of powder.

The confidence rate value is based on a collection of intermediate algorithm quantities used in the detection process. The numbers of minutiae points provide useful information that can be used in the later matching stages to improve the fingerprint-matching accuracy. Therefore it is important to associate feature mediated by minutiae points and confidence in order to properly qualify detected minutiae and associated features.

Raman spectroscopy has also been used as a confirmatory tool to measure the enhancement of the fingerprint. This has been based on the assumption that a strong interaction between the fingerprint powder and the lipid is necessary for good enhancement. The results from this study are presented in Figure 7.4.

The absorption bands centered around 2888 cm^{-1} result from lipid. Strong absorption bands in this region are an indication of strong attraction between the fingerprint powder and the lipid consequently a high level of enhancement is attained. The spectra shown in Figure 7.4 indicates that the attraction of lipid to powder is in the order phenyl > C12 > commercial > OH

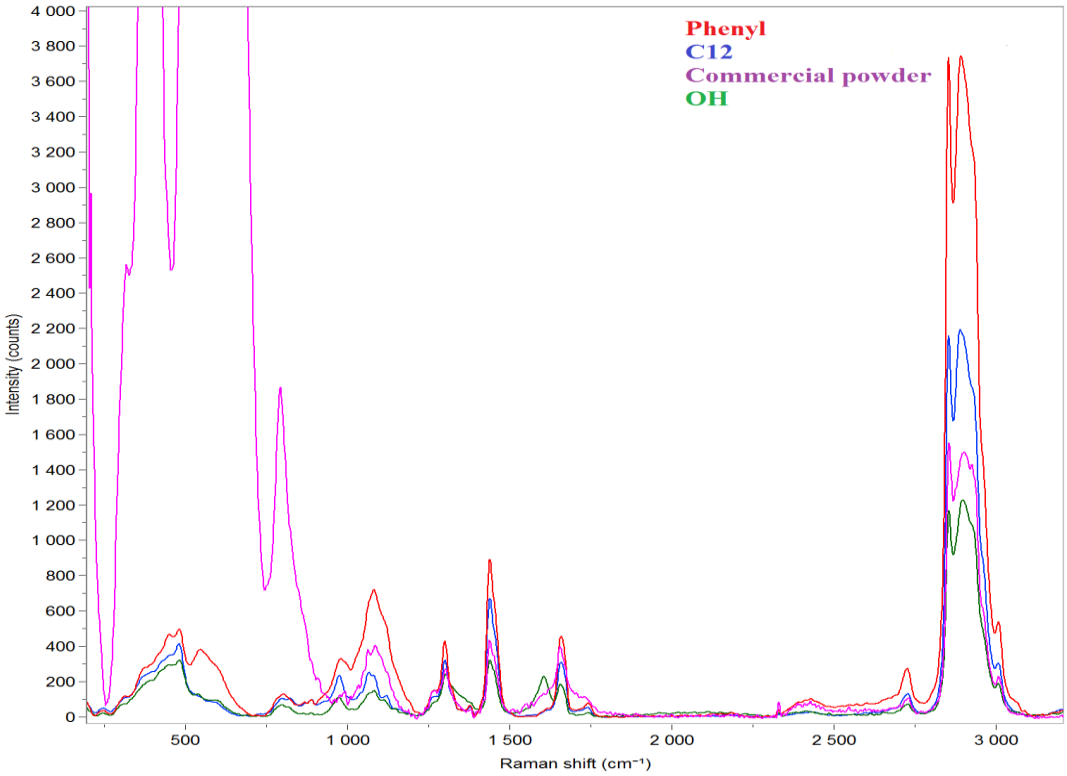

Figure 7.4. Comparison the performance of three different fingerprint powders (Phenyl, C12 and OH) and commercial powder

7.1.3 Discussion

A comparison has been made between functionalised nano-particulates and commercial fingerprint powder in terms of the fingerprint image quality, sensitivity, and adhesion to friction ridges.

The results clearly show that the performance of phenyl, OH, and long chain hydrocarbon terminated powders are much better than a single commercial powder. As described in Chapter 5, these powders (phenyl, C12 and OH terminated) have very large surface area compared to the commercial fingerprint powder. Furthermore, the particulates are spherical in morphology of sizes 412 nm, and are nearly monodispersed. In contrast, the commercial fingerprint powder that was used in this study has very large particles size and ununiformed shape.

The size and shape of the powder particles has a significant impact on the extent of adhesion to fingerprints [237]. The smaller and finer the particles, the better is the adhesion to the fingerprint [237]. The number of minutiae points and the minutiae

confidence rate of three nano-particulate fingerprint powders are significantly higher than commercially available fingerprint powder.

Usually, the determination of the similarity between two different fingerprints is made by computing the total number of matching minutiae. This process is called minutiae based [194]. Therefore, increasing the number of minutiae points detailed has the potential to increase the quality of the match [194].

7.2 The Application of Nano Particulate Finger Print Powders for the Detection of Organic GSR in Finger Marks

7.2.1 Introduction

Physical and chemical analysis of latent fingerprints can provide information regarding the donor of the fingerprint [238]. This can take the form of standard information produced via visualisation of the pattern and comparison with patterns of suspects and patterns stored in data bases. However, fingerprints offer the potential to provide significantly more detailed information through chemical analysis.

The composition of latent fingermarks contain numerous compounds such as naturally occurring chemicals from the body (e.g. amino acids, cholesterol, squalene and fatty acids etc.), but may also contain compounds which may be left on the latent fingermark from prior contact with foreign matter (e.g. gunshot residue or drugs of abuse) [189, 239, 240]. Several studies have been published showing the applications of GC/MS to detect different residues in latent fingerprints. These residues include squalene, cholesterol, drugs of abuse and metabolites. The residues from latent fingermarks can be extracted into a solvent and analysed using GC/MS [239, 240].

The analysis of gunshot residue is a critical step in forensic studies of firearms and related criminal cases. However, there is an urgent need to improve the extent of research in this area [241]. Nanotechnology is starting to make a significant impact across a broad range of scientific areas, yet few studies have been conducted looking at the use of nanotechnology applications within the field of forensic science [2, 163, 167-169, 171, 242, 243], with the exception of a review of the application of nano-particulates in this field has been published by Dilag et al. [2]. Nanotechnology is likely to play a major role in the future to deliver more selective and more sensitive ways to detect and enhance fingermarks.

In this chapter the application of the novel nano-particulates fingerprint powder described in Chapter 6 will be investigated for their potential application in the detection of GSR from the fingerprint of a shooter.

7.2.2 Experimental Procedures for Determining Organic Component of GSR in Fingermarks Using Nano Particulate Fingerprint Powders

Prior to discharge of the weapon the firer ensured no pre contamination had occurred by washing hands thoroughly with soap and water. The blank handgun (ME38 revolver (Cuno-Melcher ME Sport-Waffen) was discharged three times into a clean plastic dust bin, the top of which was partially sealed to prevent loss of GSR and increase the likelihood of contamination of the hand of the firer.

Individual fingerprints were then made on the three different surfaces (polycarbonate-black and white and a glass microscopy slide). The fingerprints were then enhanced with the fingerprint powders as described in Section 7.1. The fingerprints were photographed (using a Nikon D80 Digital SLR Camera) prior to extraction. The process was repeated in turn for each of the fingerprint powders. Comparison data was produced using a commercial fingerprint powder (white coloured titanium dioxide), (K9 Scene of Crime Equipment Ltd.). Extractions were also performed from fingermarks which had not been enhanced with any fingerprint powder.

Extraction of the organic GSR was performed by washing the surface with 0.2 ml of acetone using a pipette, and the solution was allowed to drain into a 15 ml centrifuge tube. The collected solution was sonicated for 15 minutes and concentrated to 100 μ L using nitrogen gas. Five microliters of the solution was injected into the GC/MS and the analysis was performed as described in Section 2.1.1.

7.2.3 Results from the Analysis of Organic Gunshot Residues from nano-particulates Fingerprint Powders

Data was presented from the fingermarks produced on both glass and polycarbonate surfaces. These two surfaces were chosen because they provided a contrast in terms of surface polarity. The glass is OH terminated and provides a polar surface. Conversely the polycarbonate contains aromatic moieties and is therefore significantly less polar. It should be noted that only data from one of the polycarbonate materials has been displayed, as both the black and white poly carbonate yielded very similar results in terms of the extraction data.

The results produced from the study are shown in Figures 7.5-7.6. The data is based on five replicated experiments. The errors on the measurement are shown as error bars.

However these are consumed within the data points but never exceed 5%. The data clearly shows that the nano-particulates powders synthesised during this study are effective in absorbing the organic residues from the GSR. The ability to absorb follows the pattern phenyl > C12 > OH termination. All the nano-particulates powders provide data enhancement compared to both commercial fingerprint powder and no fingerprint powder.

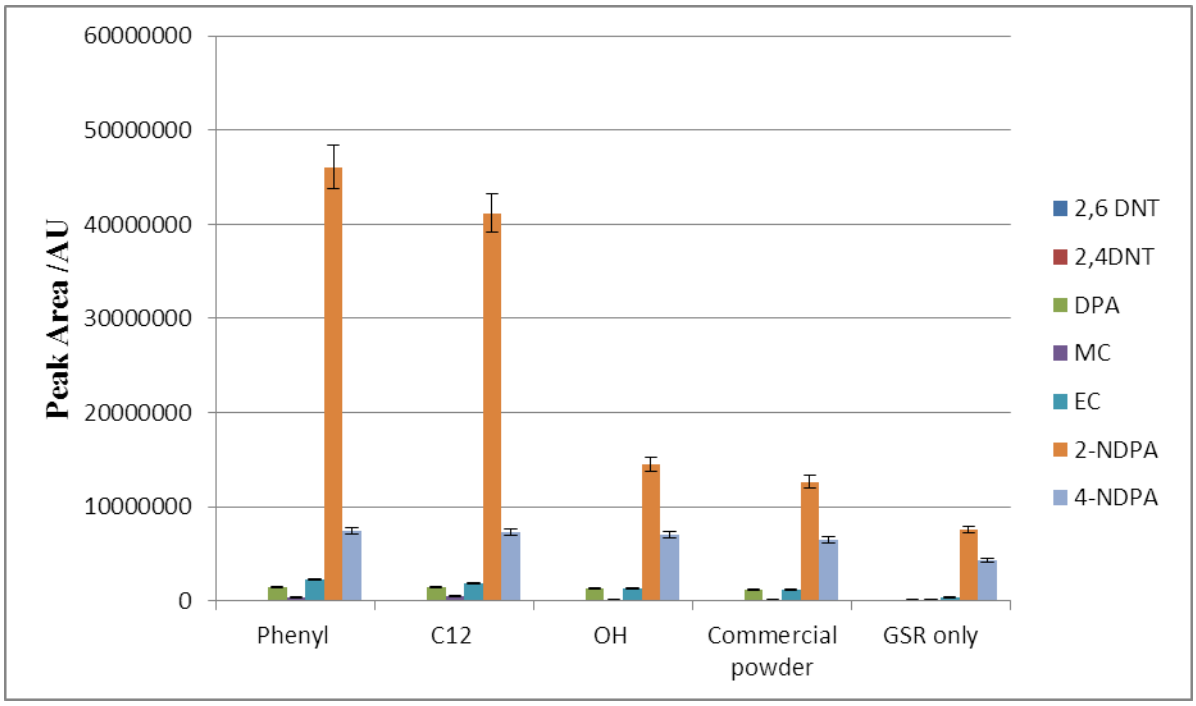

Figure 7.5. Comparison of the extraction of organic GSR from different fingerprint powders and non-powder on polycarbonate white surfaces

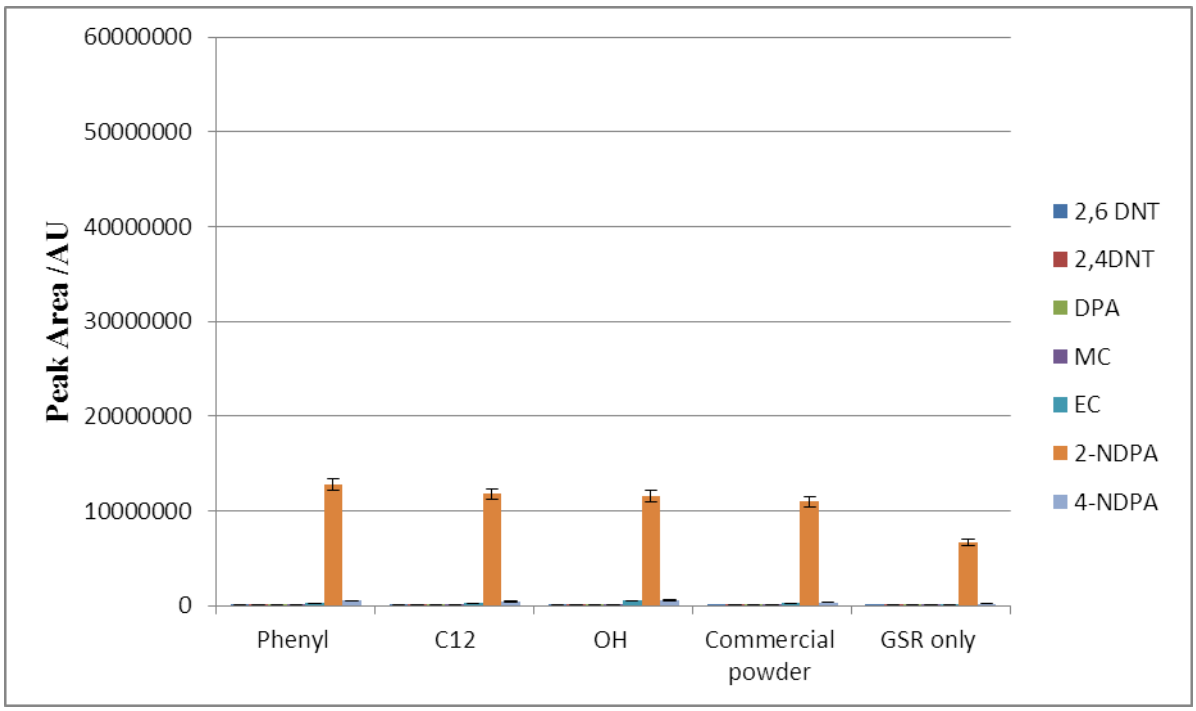

Figure 7.6. Comparison the extraction of organic GSR from different fingerprint powders and non-powder on glass surfaces

The absorbed organic materials from the fingerprint were identified by GC/MS. These compounds are 2, 6-DNT, 2, 4-DNT, DPA, MC, EC 2-NDPA and 4-NDPA. However, there is variation in the amount of these compounds recovered from the fingerprint. The profile of concentrations was similar to that reported in fired cartridges in Section 4.4.

7.2.4 Discussion of the Analysis of Organic Gunshot Residues Extraction from nano-particulates

A comparison of the organic constituents from an unfired and blank handgun cartridge is shown in Figure 7.17. The data shows that during firing the relative percentage of DPA is significantly reduced compared to 2-NDPA and 4-NDPA. The data presented in this chapter confirms that there is a significant decrease in the concentration of DPA. However, the relative percentage of DPA is greater than that observed from the hand swab experiments (Chapter 5).

The storage experiments (Chapter 4) show that even in a sealed nylon bag the organic components of GSR are lost (Figures 4.10 and 4.11), and this needs to borne in mind when interpreting the data in this Section (Figures 7.5 and 7.6).

The least OGSR is extracted when no fingerprint powder has been used. The reason for this is that there is nothing to prevent the organic components being lost through

evaporation into the environment. The phenyl terminated nano-particulates powder performs the best facilitating the extractions up to five times the amount of 2-NDPA compared to when no powder is used. The C12 terminated powder performs a little less well than the phenyl terminated but significantly better than the OH terminated nano-particulates powder and the commercial TiO_2 powder, which will also be OH terminated.

If these results are considered in terms of the interactions at a molecular level then it is not surprising. The aromatic molecules which make up the organic components of GSR will be absorbed more strongly by the phenyl terminated fingerprint powder. The C12 will have weaker attractive forces and the OH terminated considerably less.

When a more polar substrate is used (i.e. glass as opposed to polycarbonate) (Figure 7.6), the first thing to note is that less organic materials is extracted. This is undoubtedly due to the fact that the glass will not retain the organic GSR as well as the polycarbonate. Comparing the efficacy of the fingerprint powders, the phenyl terminated powder is the best for the reason previously stated. However, in this case, where the concentrations are presumably lower, the performance enhancement of phenyl and C12 terminated powders is not as significant.

7.2.5 Conclusion

The study demonstrates the possibility of obtaining very useful information from latent fingerprints, in addition to the standard information derived from the visible patterns associated with such fingerprints. Three different types of novel fingerprint powders that were synthesised in the laboratory were successfully used as agents to detect GSR from the fingerprints left on the surface by the firer. These materials included DPA, EC, MC 2-NDPA and 4-NDPA. This process involves the dusting of fingerprints contaminated with GSR using different fingerprints powder followed by extracting the organic materials in fingerprint using a solvent extraction method. The extracted solvent was analysed using GC/MS. The results were compared with single commercial powders available in the market. Significant differences were observed between the two. The synthesised fingerprint powder gave better result in term of their ability to absorb organic materials and enhance the visualisation of the latent fingerprint.

The potential problem with the technique described in this chapter is that the fingerprint is destroyed during the collection of the chemical information. Ideally, it would be better to obtain the chemical information using a nondestructive analytical technique.

8 THE USE OF RAMAN SPECTROSCOPY FOR THE DETERMINATION OF CHEMICAL EVIDENCE FROM FINGERPRINTS

8.1 Introduction

As described in Chapter 1, a fingerprint is a reproduction of the friction ridges in the fingers. When a finger touches any surface, the natural skin secretions from the eccrine glands present in the friction ridge skin, and other materials present on the finger, such as skin residue, sebum GSR, drugs and petrol, are deposited on the contact surface. In the previous chapter the ability of the fingerprint powders that were described in Chapter 6 to absorb the organic materials within the fingerprint was demonstrated. The absorbed material was extracted using a suitable solvent and analysed using GC/MS. However, there are potential problems with the approach adopted, as the fingerprint is destroyed during the collection of the chemical information. It is therefore beneficial to investigate the use of other techniques that can analyse the sample without destruction.

Raman spectroscopy has proved a valuable analytical tool in various fields of research including surface science, electrochemistry, biology, and material science. Raman spectroscopy has a number of advantages over other analysis technique. It is a non-destructive analytical technique, requires a small amount of sample and does not need any sample preparation. A number of studies have been performed using Raman spectroscopy for the analysis of forensic evidences, as reviewed by Das and Agrawal [199].

In this chapter the use of Raman spectroscopy in conjunction with nano-particulate fingerprint powders for the detection of organic GSR will be discussed.

8.2 Determination the Organic Constituent of GSR

8.2.1 Experimental Procedures

2-NDPA was used as a standard material to replicate the organic compounds of GSR, as it has been previously identified as being the major constituent (Section 4.4). The analysis of the organic materials from the fingerprint was performed using the instrument described in Section 2.3.

A solution of 2-NDPA (sigma Aldrich, UK) was prepared by dissolving 0.1 g in 10 ml of acetone. This was then further diluted to provide a 0.001 % w/v solution. A reference Raman spectrum of 2-NDPA was obtained by placing a drop of the 2-NDAP solution on to a glass microscope slides, which had previously been cleaned with acetone. This spectrum was recorded when the complete evaporation of the solvent was achieved.

A fingerprint contaminated with this substance was prepared on a glass microscopy slide, which had previously been cleaned with acetone before use and subsequently handled as little as possible. Hands were washed using ordinary soap and water and dried with a paper towel prior to the beginning the experiment. Contaminated fingerprints were prepared by drying known amount of 2-NDPA onto a clean microscopy slide surface (VWR) and touching it with a clean finger in order to contaminate the fingertip with 2-NDPA.

The substance was left on the finger for 10 minutes to allow sweat to accumulate on the fingertip, during which time nothing was touched with the contaminated finger. The contaminated fingertip was then pressed onto a clean glass microscopy slide in order to deposit a doped fingerprint. The fingerprints were then enhanced by three different types of powders of nano-particulate powder using fingerprint brushes (squirrel powder brushes from K9 Forensic Services Ltd).

8.2.2 Result from Standard Materials

The Raman spectra of 2-NDPA and a blank glass microscopy slide are shown in Figure 8.1. The spectra clearly show that the absorption bands associated with 2-NDAP are observed at 1354 and 1603 cm^{-1}. The absorption bands at 564 and 1003 cm^{-1} are the predominant features associated with glass microscopy slide (Table 8.1).

The Raman spectrum of fingerprint on glass microscopic slide is shown in Figure 8.2 and the absorption bands associated with the fingerprint are observed at ~2900, 1666 and 1437 cm^{-1}. These absorption bands result from the lipid and other residues associated with fingerprints (Table 8.2). The Raman spectrum produced from the fingerprint contaminated with 2-NDPA in conjunction with the phenyl terminated fingerprint powder is shown in Figure 8.3. The fingerprint powder exhibits absorption bands at 793 and 1821cm^{-1}, however the bands associated with 2-NDPA are clearly visible at 1349 and 1591 cm^{-1} (Table 8.3). The Raman spectra obtained from a fingerprint previously contaminated with 2-NDPA and dusted with the C12 and OH terminated nano-particulate powder are shown in Figure 8.4. It can be clearly seen that better of these powder perform as well as the phenyl terminated powder.

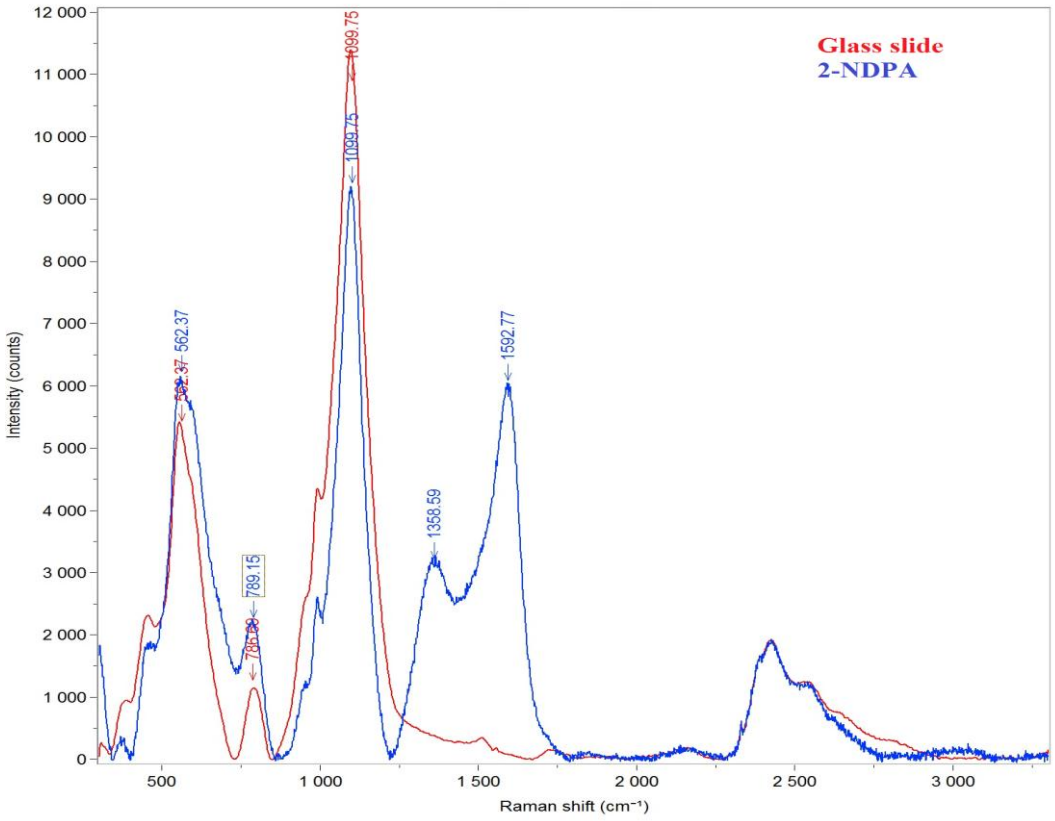

Figure 8.1. Raman spectrum obtained from standard materials of 2-NDPA (a) and a glass microscope slide (b)

Table 8.1. Wavenumbers (cm^{-1}) and assignments of bands seen in the Raman spectra of 2-NDPA only in microscope slide

Raman Shift (cm^{-1})	Assignment	Vibrational modes
526	Glass microscopy slide	Si-O stretching
798	Glass microscopy slide	Si-O bending
1009	Glass microscopy slide	Si-O stretching
1359	2-NDPA	C-N-O stretching
1593	2-NDPA	C-C aromatic ring stretching

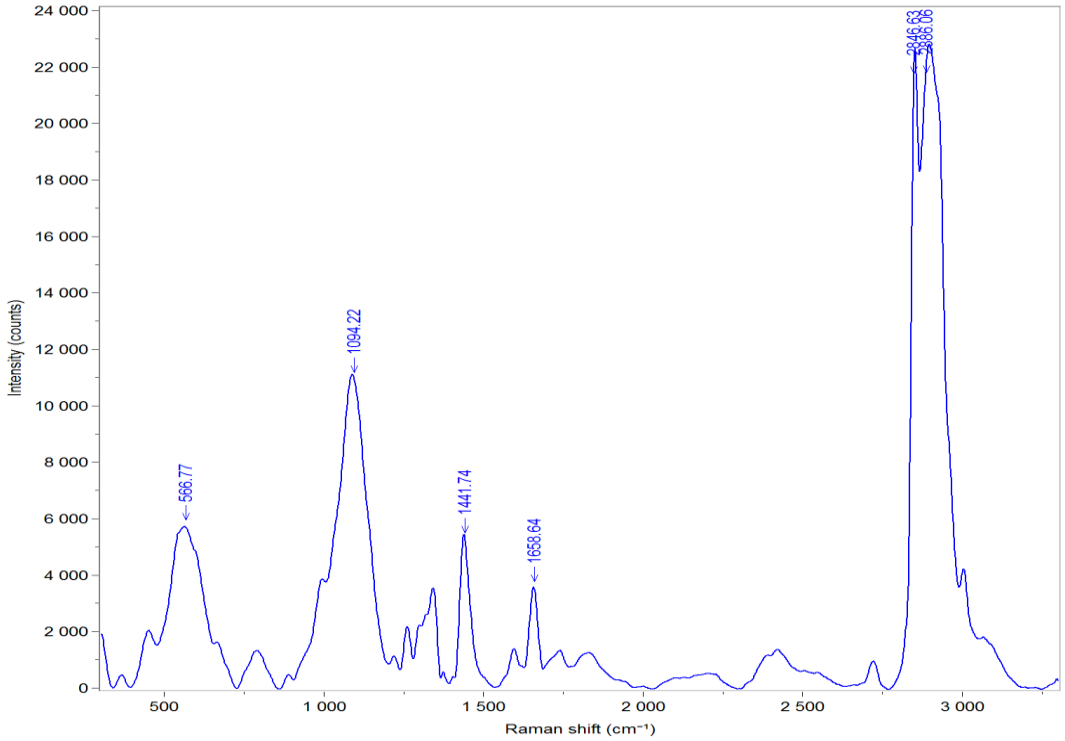

Figure 8.2. Raman spectrum obtained from fingerprint only in a glass microscope slide

Table 8.2. Wavenumbers (cm^{-1}) and assignments of bands seen in the Raman spectra of fingerprint only in microscope slide

Raman Shift (cm^{-1})	Assignment	Vibrational modes
567	Glass microscopy slide	Si-O stretching
1094	Glass microscopy slide	Si-O bending
1442	Fingerprint	CH_2 bending
1659	Fingerprint	C=C stretching
2886	Fingerprint	C-H stretching

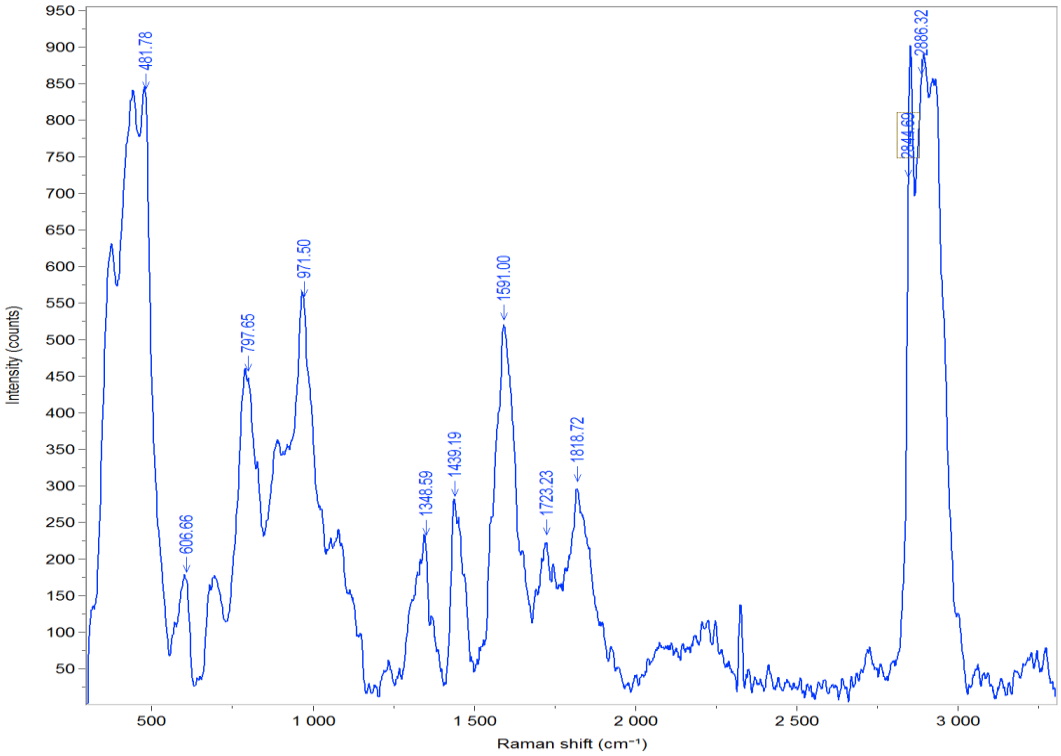

Figure 8.3. Raman spectrum obtained from a fingerprint contaminated with 2-NDPA and dusted with phenyl terminated powder

Table 8.3. Wavenumbers (cm^{-1}) and assignments of bands seen in the Raman spectra of fingerprint contaminated with 2-NDPA and dusted with phenyl powder

Raman Shift (cm^{-1})	Assignment	Vibrational modes
481	Glass microscope slide	Si-O stretching
606	Glass microscope slide	Si-O bending
797	Fingerprint powder	C=C Ring
971	Glass microscope slide	Si-O bending
1349	2-NDPA	C-N-O stretching
1439	Fingerprint	CH_2 bending
1591	2-NDPA	C–C aromatic ring stretching
1723	Fingerprint	C=O stretching
1821	Fingerprint powder	C=C Ring
2886	Fingerprint	C-H stretching

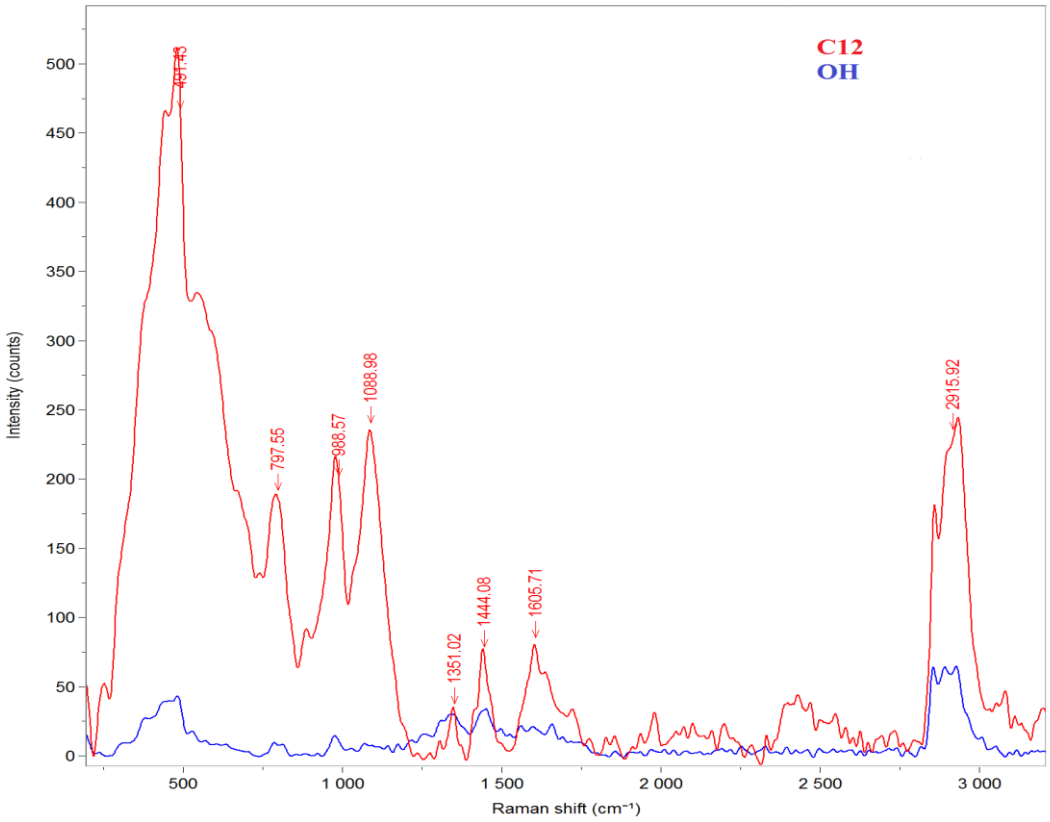

Figure 8.4. Raman spectrum obtained from a fingerprint contaminated with 2-NDPA and dusted with C12 and OH terminated powders

8.3 Experiments Using GSR

8.3.1 Experiment Procedures

The hand of the shooter was contaminated with GSR using the methodology described in Section 5.5.1. The procedures involved firing the gun three times into the dust pine. Following the firing, the contaminated fingerprint with GSR was pressed into a clean microscopy glass slide. The samples were then placed into Raman stage for the analysis.

Due to the far superior performance displayed by the phenyl terminated powder during the tests using the model compound (2-NDPA), experiments involving GSR were limited to the use of phenyl terminated powder.

The GSR samples were also collected from the shotgun ammunition (Eley Olympic Trap cartridge). The procedure involved burning shotgun powder in the laboratory because there was no longer any available access to the Forensic Science Service Northern Firearms Unit in Manchester by this time. The procedures involved opening the cartridge by cutting the plastic shell casing with a single edged razor. The powder (0.8 g) was placed into small watch glass and ignited using a lighted wooden taper. The clean hand was exposed to the smoke at a height of 30 cm above the burning powder and then a fingertip was pressed into a microscope slide. The fingerprints were dusted with phenyl terminated nano-particulate powder using squirrel powder brushes (from K9 Forensic Services Ltd) as described in Section 8.21. This process was repeated in triplicate in order to produce represented data.

8.3.2 Results from GSR Experiments

The Raman spectrum produced from a fingerprint contaminated with GSR in conjunction with phenyl terminated powder is shown in Figure 8.5. The spectra clearly show that the absorption bands associated with GSR are observed at 1343 and 1642 cm^{-1}. The absorption bands at 452 and ~1115 cm^{-1} are related to the glass microscopy slide, while the absorption bands at ~2930 cm^{-1} is related to the fingerprint lipids and other residues associated with fingerprints (Table 8.4). Figure 8.6 shows the spectrum produced from the contaminated fingerprint with GSR from shotgun in conjunction with phenyl terminated fingerprint powder. All the detected bands are presented in Table 8.4.

The absorption band at 812cm^{-1}is related to fingerprint powder. The bands associated with GSR are observed at 1349 and 1598 cm^{-1}.

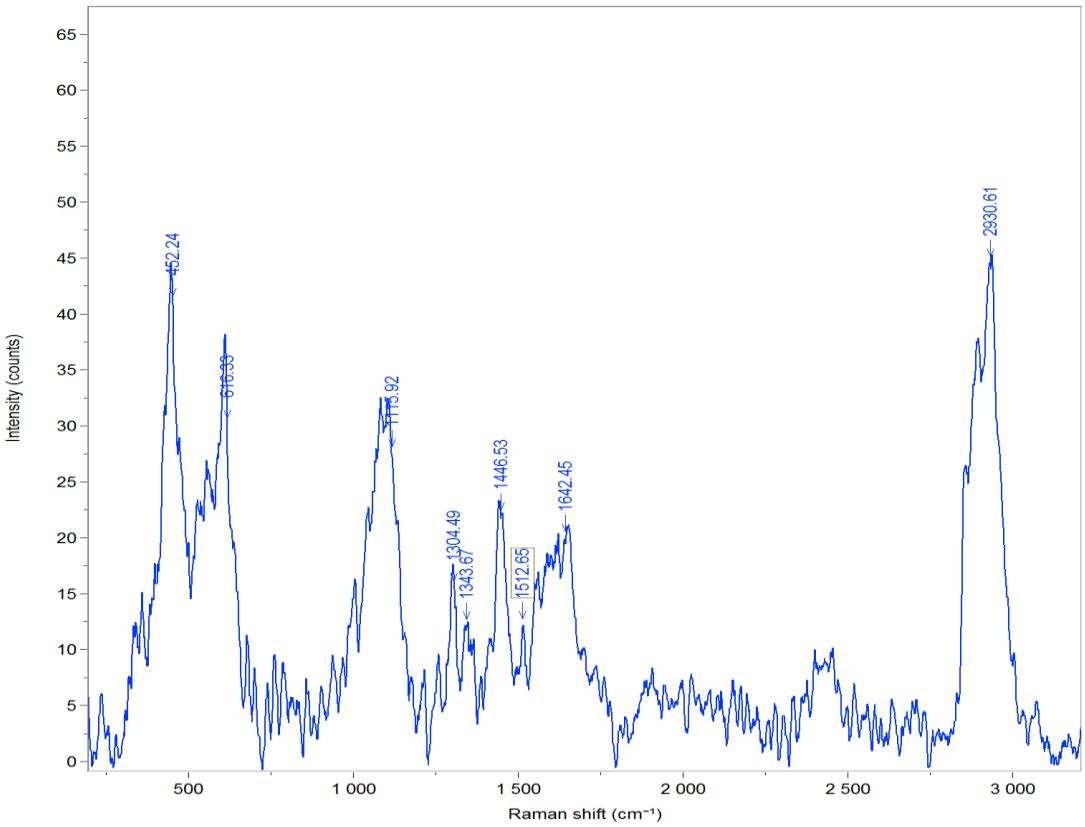

Figure 8.5. Raman spectrum for fingerprint contaminated with organic GSR (handgun) dusted with phenyl terminated powder

Table 8.4. Wavenumbers (cm^{-1}) and assignments of bands seen in the Raman spectra of fingerprint contaminated with organic GSR (blank handgun) and dusted with phenyl powder

Raman Shift (cm^{-1})	Assignment	Vibrational modes
452	Glass microscope slide	Si-O stretching
616	Glass microscope slide	Si-O bending
793	Fingerprint powder	C=C Ring
1115	Glass microscope slide	Si-O bending
1343	2-NDPA	C-N-O stretching
1446	Fingerprint	CH_2 bending
1642	2-NDPA	C-C aromatic ring stretching
2930	Fingerprint	C-H stretching

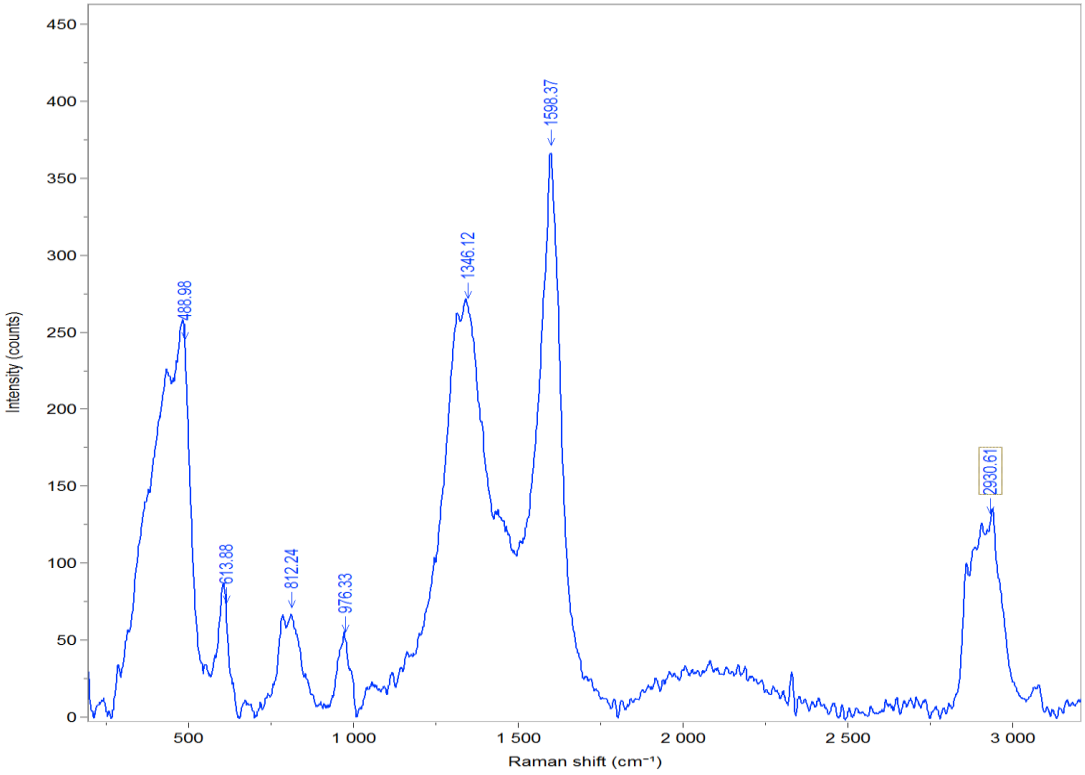

Figure 8.6. Raman spectrum obtained from the fingerprint contaminated with organic GSR (shotgun) and dusted with phenyl powder

Table 8.5. Wavenumbers (cm^{-1}) and assignments of bands seen in the Raman spectra of fingerprint contaminated with organic GSR (shotgun) and dusted with phenyl powder

Raman Shift (cm^{-1})	Assignment	Vibrational modes
489	Glass microscope slide	Si-O stretching
812	Fingerprint powder	C=C Ring
1346	GSR	C-N O stretching
1598	GSR	C-C aromatic ring stretching
2930	Fingerprint	C-H stretching

8.3.3 Discussion

The data produced from this study are very encouraging as they clearly confirm that the novel fingerprint powder can be used to detect the presence of the organic compounds associated with GSR. Raman spectroscopy has been shown to be a suitable analytical tool for the non-destructive detection of the GSR. However, some concern remains surrounding the sensitivity of the technique. The results from the discharge of the handgun (Figure 8.5) shows relatively weak peak intensity, and contamination of the hand of the shooter was carried out under somewhat artificial conditions so as to

increase the level of contamination. However, there is a scope to improve the signal to noise ratio through further optimisation of the instrumental parameters used to collect the spectra.

The data from this study compliment results from the extraction studies using these fingerprint powder (Section 7.2). Both sets of data clearly show that the phenyl terminated nano-particulate powder is the preferred powder for elucidating the organic residues (mainly 2-NDPA) associated with GSR. As previously discussed, this is a result of increased molecular attraction between the phenyl terminated on the silica and the aromatic ring of the 2-NDPA.

8.4 Conclusions

The nano-particulate fingerprint powders have proved to be highly versatile in enhancing the production of chemical evidence from fingerprints when used in conjunction with Raman spectroscopy. The phenyl terminated powder has consistently performed best, however the relative performance is dependent upon the evidence type. The possibility of the other powders outperforming the phenyl cannot be overruled with other evidence.

9 GENERAL DISCUSSION

This study has focused on the analysis of organic GSR. The forensic value of inorganic GSR has been called into question, for a number of reasons. These include persistence, secondary and tertiary transfer, the increasing use of lead-free primer compositions, and the potential for false positive results due to creation of similar particles from alternative sources.

Gas chromatography-mass spectrometry has been found to be very useful in analysing organic components of GSR. The limit of detection of GC/MS was in line with the levels normally encountered from fire arms discharges and comparable to the levels determined by other workers in this field.
According to the UK Office for National Statistics [9], shotguns were used in only 5% of firearms offences in England and Wales in 2011/12. However, they were actually fired more commonly than any other weapon, apart from airguns and imitation firearms. Furthermore, shotguns were fired in 50% of the offences in which they were used. This is more than handguns or rifles.

There is very little individual characteristic information available for material discharged from shotguns, other than striation marks on plastic wads. This is due to the lack of rifling, and the use of shot pellets rather than solid slugs, except in rare cases. The analysis of organic GSR from shotgun ammunition has the potential to provide valuable evidence to link a particular weapon and/or cartridge, with a shooter and/or a scene. This would support the physical evidence obtainable from any recovered cartridge cases.

While the work focused on the branding of shotgun ammunition is a limited study and needs to be expanded in order to determine its full potential impact. The initial results indicate that it is possible to determine the organic (brand) of the ammunition from the organic residues which remain after the discharge of the weapon.

This study has significantly expanded on the body of knowledge relating to the use of nanoparticles to enhance the visualisation of fingerprints. Previous studies had not concerned themselves with the modification of the surface to develop hydrophobicity, they had merely utilised the benefits afforded by using smaller particles of a more

uniform dimension. This study clearly shows that rendering the surface of the particle hydrophobic improves the interaction with the fingerprint and this leads to improved visualisation.

Surface functionalised nanoparticles can also interact strongly with organic residues which may also be present within a fingerprint. These residues could provide valuable forensic information, particularly if the fingerprint has been taken from someone who has discharged a weapon, handled drugs of abuse or handled accelerant. This research has shown that the surface modified fingerprint powders trap these organic residues making them easier to analyse via analytical techniques such as GC/MS. However they can also be used in conjunction with spectroscopic techniques such as Raman spectroscopy to provide a non-destructive analytic procedure which not only enhances visualisation of the fingerprint but also provide chemical evidence.

10 FUTURE WORK

The preliminary studies reported in this thesis have shown that OGSR analysis using GC/MS can be used to provide branding information for shotgun cartridges. Further studies could include further expansion of the number of brands involved within the study which would serve to make it more complete.

This work on branding ammunition could be extended to cover other calibre weapons and ammunition.

Since the analysis of the organic constituents in GSR from a blank gun and shotgun ammunition in this study was performed through solvent extraction methods, it would be worthwhile to investigate different methods of sample preparation.

The sample preparation techniques proposed for the analysis of OGSR could be used to improve the sensitivity of specific target compounds found in GSR to perform trace detection.

Several studies have applied for the extraction of the OGSR samples using SPME, which would be an alternative method for the collection of the GSR sample from the target and spent cartridges. Different types of SPME fibers could be utilised in order to have better efficiency for collecting OGSR sample.

Silica nano-particulates of defined size and shape have been successfully synthesised. These silica nano-particulates have been functionalised for two different functional groups (phenyl and long chain hydrocarbon) using TPRE method. The functionalisation of silica nano-particulates with other functional groups would be very useful to improve sensitivity and selectivity in absorbing the organic materials in OGSR and other types of forensically important organic residues. These functional groups should including cyano, amine and carboxyl groups.

Other studies have reported the use of MALDI-TOF in conjunction with fingerprint powders [244]. It would be interesting to compare the performance of the powder produced in this study using MALDI-TOF analysis.

Ideally, it would be desirable to be able to analyse the organic residues trapped within the fingerprint at the scene of the crime. Fingerprints are often left on large pieces of furniture (e.g. doors) and hence transport can itself be difficult even before considering

the logistics of getting the exhibit into the instrument for analysis. One of the latest developments in Raman spectroscopy is the production of a hand-held spectrometer and this could be used at the crime scene. It would be interesting to compare results produced with this type of instrument to determine if it has sufficient sensitivity to analyse chemical information from fingerprints enhanced with nano-particulate fingerprint powders. An alternative strategy could be to perform tape lifts of the nano-particulate powder used to perform the fingerprints enhancement. This could then be analysed using laboratory based spectroscopic technique, including Raman and GC/MS.

The application of the nano-particulate powder should be extended to cover different areas of forensic evidence, such as an explosives and a greater range of drugs of abuse, including cannabinoids.

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12 APPENDICES

12.1 Poster and Oral Presentations Related to this Work

2012 Forensic Science Society - Autumn Conference & AGM, 10th November, Coventry, UK. *Poster presentation.*

2012 OMICS Group Conferences International Conference on Forensic Research &Technology, 15th-17th October, Chicago (USA). *The abstract for this conference was accepted for Oral Presentation but due the VISA process of the US Embassy I was unable to attend the Conference.*

2012 UCLan Graduate School Research Conference – June, University of central Lancashire. *Poster presentation- shortlisted for the best poster.*

2011 10th International symposium in forensic sciences- 27th -30th September, Slovak Republic –Bratislava. *Poster presentation.*

2011 UCLan Graduate School Research Conference – June, University of Central Lancashire. *Poster presentation.*

2011 7th National FORREST Conference (FORensic RESearch and Teaching), 29th-30th June, Nottingham Trent University. *Poster presentation- awarded the third prize for the best poster.*

2011 Centre for Material Science (UCLan) - February, University of Central Lancashire. *Oral Presentation.*

7th National FORREST Conference 2011

29th June – 30th June 2011
Nottingham Trent University

Student Poster Prizes

At this year's FORREST conference there was a poster competition for the posters presented by students. The posters were judged on visual impact, organisation, ease of understanding and also the discussion with the presenter.

The following posters were chosen to receive the poster prizes:

1. **Book tokens donated by smcs Limited**
   P21. WGA (Whole Genome Amplification): Evaluation and Analysis of Crowded MDA
   Waseeh Chaudhry and Graham Williams, *University of Huddersfield*

2. **Student Fingerprint kit donated by SciChem**
   P25. Evaluation of a new fingerprint enhancement technology based on coloured polymers, RACHEL M. Brown, Ann L. Beresford, A. Robert Hillman and John W. Bond, *University of Leicester, Leicester, LE1 7RH*

3. **Student Fingerprint kit donated by SciChem**
   P17. Branding of Shot Gun Cartridges Pre- and Post- Firing From the Analysis of the Organic Constituents
   Mohammad Alrashidi, Stephen Andrews, Gary Bond, and Allison E. Jones, *University of Central Lancashire*

4. **Copy of 'Forensic Science Laboratory Manual and Workbook, 3rd Edition', Kubic and Petraco, donated by CRC Press**
   P8. An Investigation on the Colour Fading of Fibres at a Microscopic Level, Roslyn DeBattista, Helen Tidy and Matthew Clark, *Teesside University, University of Leeds*

5. **Copy of 'Forensic Science Laboratory Manual and Workbook, 3rd Edition', Kubic and Petraco, donated by CRC Press**
   P9. The impact of male hair products on the enhancement and recovery of fingerprints from common surfaces, Jacqueline Green, Ian Parker and Helen Tidy, *Teesside University*

6. **Copy of 'Essential Forensic Biology, 2nd Edition', Gunn (2009), donated by Wiley-Blackwell**
   P18. The effect of temperature on the phytochemistry of the ethnomedicine *Aconitum*
   Hannah Barber and Olivia Corcoran, *University of East London*

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OMICS Group Conferences
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Forensic Research & Technology

October 15-17, 2012 DoubleTree by Hilton Chicago-Northshore, USA

Novel nano-particles and their application as fingerprint powders

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A Fingerprint is one of the most common types of physical evidence found at crime scenes. It is basically a complex mixture of natural secretions of the body from three types of glands: eccrine, apocrine, and sebaceous glands. It also contains contaminations from the environment. The chemical compositions of the deposit are mostly water (99%) with minor amount (up to 1%) of inorganic and organic compounds. There have been number of studies undertaken to develop materials used in lifting fingerprints. In general, the impressions made by finger marks found at the crime scenes fall into three categories, such as plastic (or impression), visible (patent) and latent prints; the latter require enhancement in order to be visualised and identified.

Since the 1990's there has been significant development in the visualisation methods of latent fingerprints. This includes the combination of optical, physical, and chemical methods. In spite of all of the current methods for detecting latent finger-marks, there is a strong demand for new and more efficient reagents to visualise latent fingerprints.

In this study, we report the synthesis of novel fingerprint powders based on silica nanoparticles of various sizes with three different surface functionalities. Functionalised nanoparticles have been applied to detect latent finger-mark deposited onto different non-porous surfaces and the results have been compared with currently available commercial powders (K9 Scene of Crime Equipment Limited).

Biography

Mohammad has worked in Forensic Department in Saudi Arabia police for more than ten years. He has completed his master degree in forensic materials from Heriot-Watt University. Now, he is in his final year of PhD at the School of Forensic and Investigative Sciences, University of Central Lancashire. He has attended 3 National conferences and 1 International conference in the area of Forensic Science.

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