

UNIVERSITI SAINS MALAYSIA



EXAMINATION OF GUNSHOT RESIDUE  
DISTRIBUTION PATTERN FROM 9 MM  
SEMI-AUTOMATIC PISTOLS ON COTTON, COTTON  
POLYESTER BLEND, SATIN AND JERSEY FABRIC IN  
RELATION TO FIRING DISTANCE

Dissertation submitted in partial fulfilment for the Degree of Bachelor  
of Science (Hons) in Forensic Science

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## **LIST OF ABBREVIATIONS**

AAS – Atomic Absorption Spectroscopy

CDR – Cartridge Discharge Residue

cm – centimeter

FDR – Firearm Discharge Residue

g – gram

GSR – Gunshot Residue

IPD – Ibu Pejabat Polis Daerah

kg – kilogram

m – meter

mL – millimeter

MGT – Modified Griess Test

NAA – Neutron Activation Analysis

NC – Nitrocellulose

NG - Nitroglycerine

ppm – Parts per million

SEM – Scanning Electron Microscope

SEM-EDS – Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy

XRF – X-ray Fluorescence

## ABSTRACT

Firearm-related crime is classified as violent crime and surely it has given an impact to general public safety. Study of gunshot residue (GSR) becomes important in investigating shooting incidents. Detection of GSR can estimate firing distances. This study focused on GSR distribution pattern deposited on four different types of fabrics, shot at three distances by four different types of pistols. 9 mm pistols and 9 mm ammunition were used in test firing. All shooting tests were performed at Ibu Pejabat Polis Daerah (IPD) Kota Bharu, Kelantan. Physical observation, microscopic examination and chemical enhancement methods were used in detection of GSR. Results showed that, as shooting distance increased, GSR particles decreased and dispersed widely. There was not much difference in diameter of bullet and soot if the shooting distance more than 1 m. For close range shot, GSR distribution pattern was quite useful to characterise the pistol used but not strong enough to identify pistol. As muzzle-to-target increased, type of pistol cannot be determined because the result showed no observable difference in term of GSR pattern and bullet hole diameter. Chemical enhancement involving the application of Modified Griess Test (MGT) in detection of nitrite residues as a by-product of combustion of gunpowder was performed. The presence of dark-purple colour indicated positive result of nitrite. Careful examination showed the decrease in the intensity of the colour in which the colour was too fade to observe as the shooting distance increased. Nitrite can still be detected up to 3 m on some fabric used and certain type of pistols. It is believed that, different pistols act differently during firing the cartridge and discharge the GSR. Mesh size of fabric is important in attachment persistency of residues. GSR distribution pattern from 9 mm semi-automatics pistols on fabrics could be established by visual and chemical enhancement method.

## ABSTRAK

Jenayah berkaitan senjata api tergolong sebagai keganasan jenayah dan telah memberi satu impak kepada keselamatan orang awam. Kajian sisa tembakan (GSR) penting dalam siasatan kes-kes tembakan. Pengesanan GSR dapat menganggarkan jarak tembakan. Kajian ini fokus pada pola taburan GSR yang terdapat atas empat jenis fabrik yang berlainan, ditembak dari tiga jarak daripada empat jenis pistol. Pistol-pistol 9 mm dan peluru 9 mm telah digunakan dalam ujian menembak. Semua ujian menembak dijalankan di Ibu Pejabat Polis Daerah (IPD) Kota Bharu, Kelantan. Pemerhatian secara fizikal, pemeriksaan mikroskopik dan kaedah peneguhan kimia telah digunakan dalam pengesanan GSR. Keputusan menunjukkan bahawa, apabila jarak tembakan bertambah jauh, zarah-zarah GSR berkurang dan tersebar dengan meluas. Tidak begitu banyak pembezaan dari segi diameter peluru dan jelaga jika jarak tembakan lebih daripada 1 m. Untuk tembakan dekat, pola taburan GSR berguna untuk menyatakan pistol yang telah digunakan tetapi belum cukup kuat untuk mengenal pasti jenis pistol. Apabila jarak dari muncung laras ke sasaran bertambah, jenis pistol tidak dapat ditentukan kerana keputusan menunjukkan perbezaan yang tidak ketara dari aspek corak GSR dan diameter lubang peluru. Kaedah kimia melibatkan ujian Griess diubahsuai (MGT) telah dilakukan untuk pengesanan sisa-sisa nitrit yang merupakan satu hasil sampingan pembakaran serbuk letupan. Kehadiran warna ungu gelap menunjukkan keputusan positif untuk nitrit. Pemeriksaan teliti dititikberatkan kerana warna tersebut semakin pudar untuk dilihat apabila jarak tembakan semakin bertambah. Nitrit masih boleh dikesan sehingga jarak 3 m bergantung fabrik dan pistol yang telah digunakan. Dipercayai bahawa, pistol yang berbeza bertindak dengan cara yang berbeza semasa menembak kartrij dan pelepasan GSR. Saiz lubang net fabrik sangat penting untuk sisa tembakan melekat kepada fabric. Pola taburan GSR daripada pistol-pistol berkaliber 9 mm boleh ditonjolkan melalui kaedah pemerhatian dan peneguhan kimia.

## CHAPTER ONE

### INTRODUCTION

Firearm-related crime is classified as violent crime and surely it has given an impact to general public safety. Out of 314,675 cases of violent crimes reported in between 2004-2013 in Malaysia, 5,284 criminal cases involved firearm (Amin *et al.*, 2014). The number accounted for 1.68% of total crimes during ten years duration, therefore forensic investigation regarding firearm is important and should not be neglected (Amin *et al.*, 2014).

According to Firearm Act 206 1960 (revised 1978), firearm is defined as any fatal barreled weapon of any description from which it can discharge any shot, bullet or other missile by means of an explosive charge, and includes a bomb or grenade containing an explosive charge (Arms Act 1960). The same Act define ammunition (including blank ammunition) for any arm as hereinafter defined, and includes grenades, bombs and others like missiles, whether capable of use with arms or not, and any ammunition containing, or designed or adapted to contain, any noxious liquid, gas or other thing (Arms Act 1960).

In forensic firearm investigation, firearm identification (spent bullet or spent cartridge examination) and analysis of GSR are the common procedures performed. Firearm identification comparison method is performed to determine if a particular firearm was related to the shooting incident while GSR analysis on the other hand is useful in firing distance estimation, bullet holes identification and determination of a person who might be responsible in discharge of the firearm (Ananth *et al.*, 2011). The link between the shooter, firearm, victim as well as the crime scene can be established by GSR analysis (Chang *et*

*al.*, 2013). GSR may acts as crucial evidence in court. Thus, variety of techniques have to be choosen wisely based on its functioning in analysing GSR.

### **1.1 Gunshot Residue (GSR)**

GSR is one of the trace evidence. GSR may be found on shooter hand and clothing, as well as any object that proximity to the discharge (Schwoeble and Exline, 2000; Arndt *et al.*, 2012; French and Morgan, 2015; Vanini *et al.*, 2015). Cartridge discharge residue or firearm discharge residue (FDR) also refers to gunshot residue (GSR) and they are used interchangeably. In general, GSR is gaseous plume discharges from muzzle of barrel that accompanied the bullet during shooting. By definition, GSR is particles resulting from combustion of propellant and primer mixtures during firing a firearm (Zeichner and Glattstein, 2002; Wallace, 2008; Rijnders *et al.*, 2010). Burned, partially burned and unburned gunpowder and particles from primer along with the smoke, grease, lubricant, cartridge case and firearm itself are part of GSR (Pun and Gallusser, 2008; Sharma and Lahiri, 2009; Dalby *et al.*, 2010; Lopez-Lopez *et al.*, 2012; Turillazzi *et al.*, 2013; Lopez-Lopez and Garcia-Ruiz, 2014;).

General misconception among the public refers to ammunition as the bullet alone. Bullet however is actually a component within an ammunition. The schematic representation of ammunition are showed in Figure 1.1.

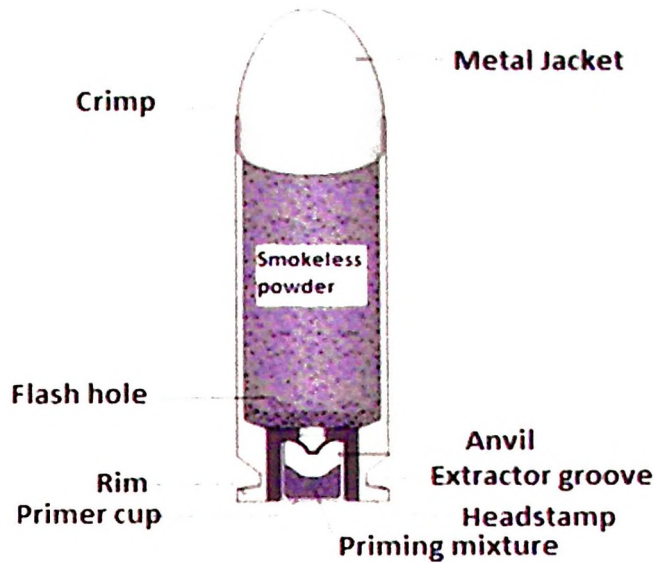


Figure 1.1: Schematic representation of 9 mm ammunition showing primer and propellant sections (Basu *et al.*, 1997).

Formation of GSR occurs in a sequence of events. Firstly, when a trigger is pulled, hammer delivers a blow to the firing pin and strikes the primer cup. Next, primer cup which contains a mixture of chemical sensitive to sudden compression burns rapidly causing rapid ignition of propellant also known as gunpowder (Ditrich, 2012).

Gaseous plumes generated from the propellant burning created enough heat and pressure to push the bullet out of barrel. Bullet emits from the muzzle of barrel and also release gaseous plume simultaneously at all firearm openings as shown in Figure 1.2.

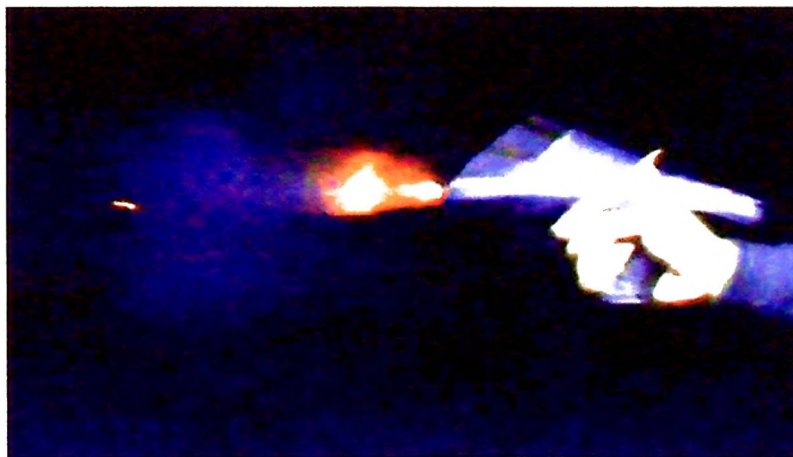


Figure 1.2: Ejection of bullet along with GSR discharge from 9 mm semi-automatic pistols (Aryantee *et al.*, 2015).

A step by step diagram in Figure 1.3 illustrates GSR plume progression once it exits the muzzle of the gun in detail.

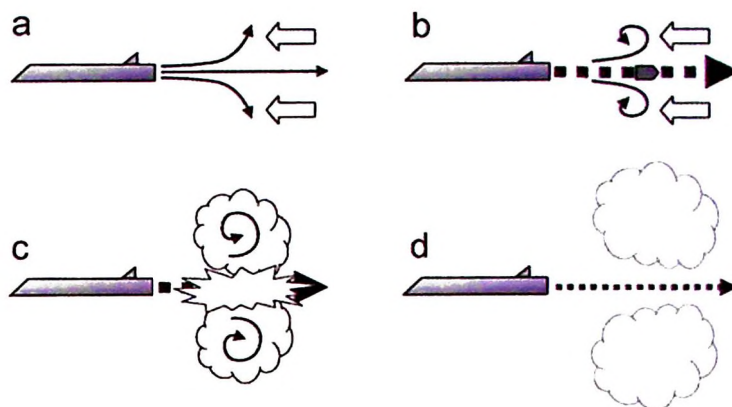


Figure 1.3: Generalized schematic sequence of formation of gaseous plume at the muzzle of barrel of handgun (Ditrich, 2012).

At the beginning of shooting gaseous plume emits from muzzle of barrel at about the size of caliber. Later, cone-shaped gas formed from stream of gas consisting of substantial amounts of unburned gunpowder and GSR particles due to resistance of surrounding air. Next, ring-like cloud formed and further increased in size by internal expansion and from additional gases from the barrel. Lastly, gaseous plume condensed thus is decreased in speed and amount (Fojtasek and Kmjec, 2005; Ditrich, 2012).

GSR travels outward from muzzle in circular pattern and embeds themselves onto target material at close range (Hodges, 2008). Roughly, GSR projected in conical pattern, travelled in some distance and stops either by resistance or target (Chang *et al.*, 2013). A study also showed that GSR particles suspended in the air at a certain time before deposit onto the target (Fojtasek and Kmjec, 2005; Schwoble and Harrison, 2006). Thus, person those show up in the shooting area after the shooting incident may be contaminated with GSR (French and Morgan, 2015). Detection or the presence of GSR pattern on target material is able to shed valuable information regarding the shooting activity.

GSR can be further classified into two classes, organic and inorganic GSR (Dalby *et al.*, 2010). Organic GSR are the unburned and partially burned propellant and some products of hydrocarbon (mainly originated from the propellant lubricants and other parts of live cartridge). Meanwhile, nitrates, nitrites, and metallic particles originate from primer and propellant, bullet core or jacketed and weapon itself are constituents of inorganic GSR (Wallace, 2008; Dalby *et al.*, 2010; Turillazzi *et al.*, 2013).

## **1.2 Composition of GSR**

The three main components of GSR are products from combustion of high explosive primer mixture located in the cap at the base of ammunition. Primer mixture comprises of four important components which are;

- (i) high explosive initiating chemical such as lead styphnate, lead azides and fulminate,
- (ii) oxidizing agent to increase heat of ignition *i.e.* barium nitrate and potassium chlorate,
- (iii) fuel that sensitive to compression *i.e.* antimony sulphide, calcium silicide and aluminium powder and
- (iv) sensitizer.

The presence of barium, antimony and lead are unique for elemental identification of GSR. Nonetheless, in forensic firearm investigation, identification of one or two elements from uniqueness of GSR are considered as consistent or indicative to GSR and sufficient for GSR identification (Brozek-Mucha, 2009; Chang *et al.*, 2013).

## **1.3 Problem Statement**

Plume line, soot and particles of GSR distribution pattern are useful to estimate muzzle-to-target distance. As a rule of thumb, as distance increased, GSR dispersed on target reduced in amounts. However, detection of GSR pattern on target material is influenced by many

factors such as distance, air movement and also the target such as fabric texture, namely cotton, cotton polyester blend, satin and jersey fabric.

Cloth texture of various fabrics may retain GSR differently, thus showing different GSR distribution pattern and intensity (Ananth *et al.*, 2011) .However, correlation between GSR originate from similar type of handguns to similar target is rarely discussed.

#### **1.4 Significant of the study**

GSR is valuable in linking a person, the place and the time with firearm involved. It is important to understand several factors that may influence the GSR distribution pattern such as the types of firearms, fabrics and distances, so that the knowledge can contribute positively to GSR sampling strategy. In addition, estimation of shooting range from GSR analysis is vital in reconstruction of firearm-related offenses, either by murder, suicide, or accident.

#### **1.5 Objectives of Study**

This study is conducted to qualitatively examine the effect of GSR distribution pattern on different fabrics when the types of pistols and shooting distance are varied.

Specifically, the study looked upon the physical and microscope characteristics of each fabric type. Next, the study aims to use Modified Griess Test to examine GSR distribution pattern when different types of fabric are used as target material *i.e.* cotton T-shirt, cotton polyester blend, satin and jersey. The relationship between firing distance (0, 1 and 3 meters) and types of 9 mm semi-automatic pistols (Walther P99<sup>®</sup>, Baretta<sup>®</sup>, Styer<sup>®</sup>, Vector<sup>®</sup>) are also discovered.

## CHAPTER TWO

### LITERATURE REVIEW

This chapter discussed on the development of colometric studies for rapid detection of GSR. Contributing factors that influence GSR distribution pattern on target was also discussed. Other techniques pertaining to characterisation of GSR particle were also briefly discussed.

Common practice for GSR analysis is carried out in a sequence of events. GSR analysis is carried out using visual inspection, followed by colour or spot test and then by instrumental technique. Colour test is a qualitatively test for visual inspection. Colour test is used for estimation firing distance by examining the distribution pattern of GSR (Dalby *et al.*, 2010). Intensity of GSR surrounding bullet hole on various targets also has a correlation to firing distance (Ananth *et al.*, 2011). However, the distribution pattern of GSR influenced by various factors including ammunition type, barrel length, muzzle-to-target angle and distance and weapon parameters (Glattstein *et al.*, 2000; Halim *et al.*, 2010; Lopez-Lopez and Garcia-Ruiz, 2014).

There are numerous colour test employed for GSR detection depending on the target residue material. Table 2.1 lists the chemical test employed for GSR detection.

Table 2.1: Lists of presumptive test for GSR detection (Romolo and Margot, 2001; Dalby *et al.*, 2010; Halim *et al.*, 2010; Ananth *et al.*, 2011; Arndt *et al.*, 2012; Chang *et al.*, 2013).

No.	Colour Test	Chemical Detect
1.	Modified Griess Test	Nitrite
2.	Sodium Rhodizonate test	Lead
3.	Diphenylamine test	Nitrate
4.	Dithioamide test	Copper
5.	Rubeanic acid test	Copper
6.	Lunge test	Nitrocellulose
7.	Zincon reagent	Applied to Pb lead ammunition / copper
8.	Marshall and Tewari test	Nitrites
9.	Harrison and Gillroy test	Lead, barium, antimony

There are pro and cons in choosing colour test as each tests serve specific purpose. All the tests were different in techniques, chemicals and reaction chain.

Among variety of colour tests carried out for studying GSR pattern, Griess test is the most commonly used in estimation of firing distance. The test detects by-products of combustion process double base propellant, nitrite residues (Ananth *et al.*, 2011). Double base propellant consists of nitrocellulose (NC) with small amount of nitroglycerine (NG). Double base propellant is modern ammunition besides single and triple base powder which replaces black powder (Chang *et al.*, 2013).

Griess test is commonly used as the reagent does not applied directly to the exhibit. Instead, the colour reaction can be observed on treated paper. Thus, GSR can be detected although there is dark background or dark design. However, the behaviour of Griess test as spot test made it as a presumptive nature but there are still certain countries that used it in case work in determining the presence of GSR (Dalby *et al.*, 2010).

Sodium Rhodizonate test and Diphenylamine test can also be performed for detection of lead residues and nitrate inorganic compound, respectively. Distance of firing from muzzle to target can be estimated by observing the intensity and distribution of colour as a product of chromophoric test (Ananth *et al.*, 2011). GSR distribution pattern is represented by the appearance of the colour. Previous study showed that, as the distance of muzzle-to-target increased, the intensity of colouration decreased (Halim *et al.*, 2010).

## 2.1 Tests for GSR.

In forensic laboratory, it is a standard practice to perform GSR analysis in a sequence of events for example examination by visual inspection, followed by colour or spot test and then possibly by instrumental technique. GSR chemical testing analysis sequences involving visual and colour test examinations are shown in Figure 2.1.

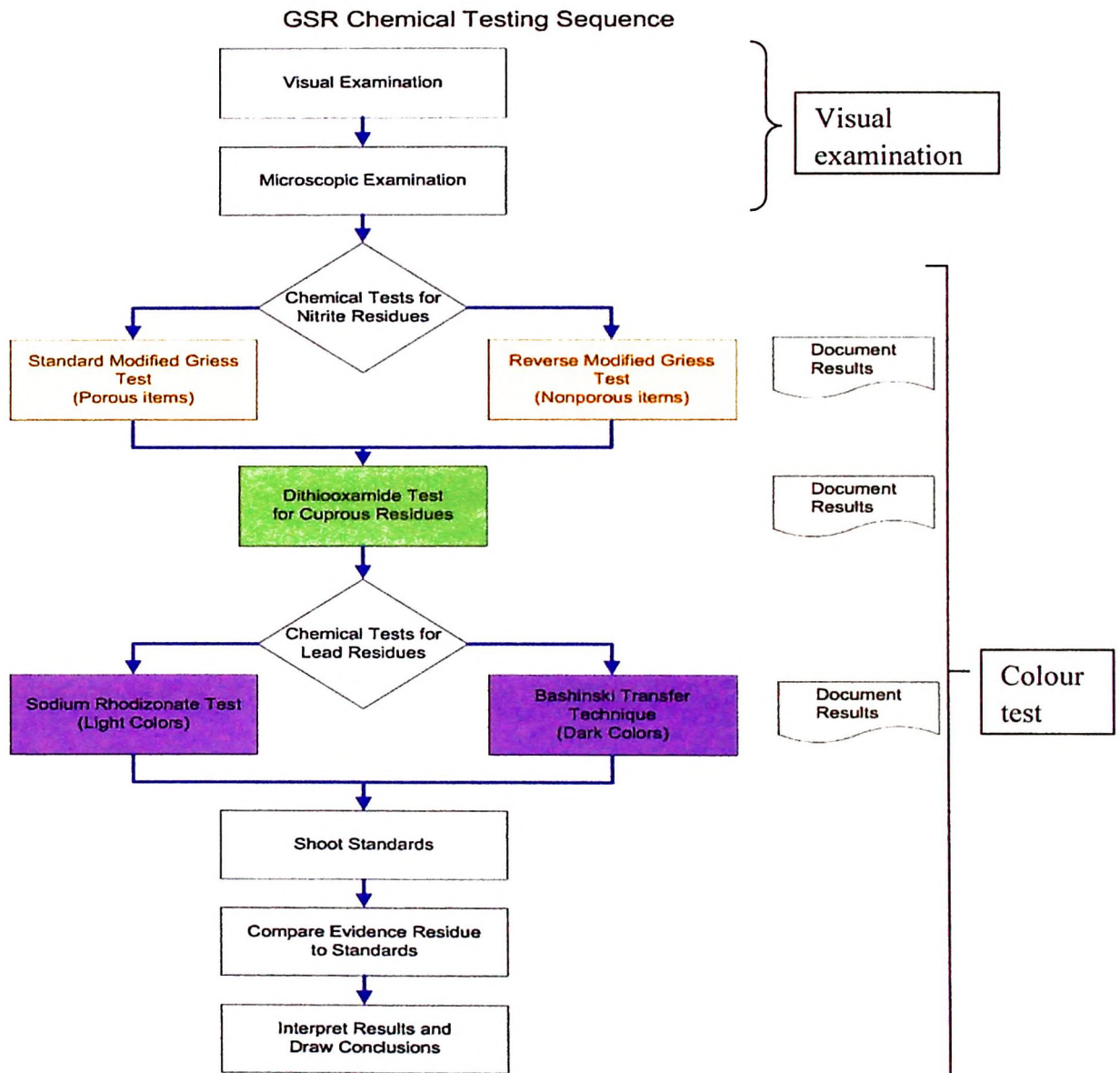


Figure 2.1: Schematic diagram on the flow of GSR analysis (National Forensic Science Technology Center (NSFTC), Science Service Justice Florida, 2008).

### 2.1.1 Modified Griess Test

Modified Griess test is a qualitative test for detection of nitrite compounds, products of combustion of nitrate such as from smokeless powder (Dalby et al., 2010; Chang et al., 2013; Vanini et al., 2015). It is colour-producing test (chromophoric) which will form different colour result based on reagent used for Griess solution. Griess test focus on distribution of nitrite residues on victim's clothing or other objects for shooting range estimation, therefore useful in shooting reconstruction (Glattstein *et al.*, 2000). Griess test is not specific and defined test. Any modification to the existing Griess test called Modified Griess test (Zeichner and Glattstein, 2002).

Modified Griess test was first proposed by German chemist, Goroncy in 1928 (NFSTC Science Service Justice Florida, 2008). He proposed the use of alpha-naphthylamine and sulphanic acid (Figure 2.2) in acetic acid solution for detection of nitrite residues. Initially, a portion of victim's clothing bearing GSR was cut out and extracted in a solution. The indicator of detection was based on the intensity of colour of the solution for muzzle-to-target distance estimation at the time of discharge. However, major weakness or disadvantages of this test were the nature of destructive and no indication of GSR distribution pattern around bullet hole can be made (NFSTC Science Service Justice Florida, 2008).

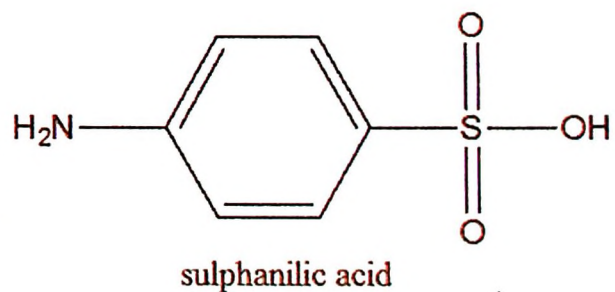
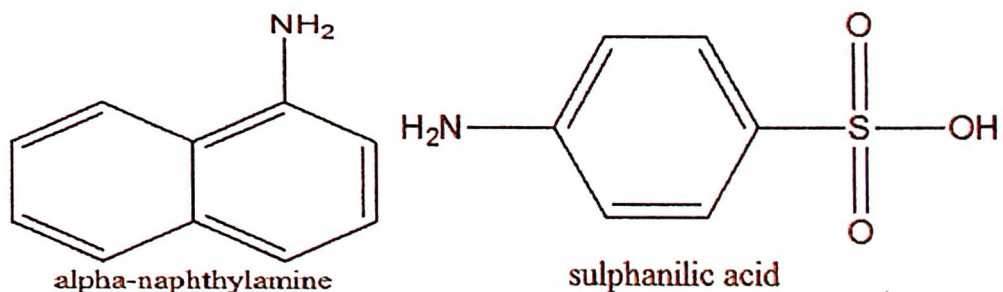


Figure 2.1: Chemical structure of alpha-naphthylamine and sulphanic acid used in Griess test.

The proposed technique was improved in 1937 (NFSTC Science Service Justice Florida, 2008). Goroncy's technique was enhanced by Joseph Walker by using C-acid (2-naphthylamine-4, 8-disulfonic acid) or H-acid (alpha-naphthylamine and sulphanilic acid). Next, this reagent was used to treat a special paper *i.e.* emulsion coated desensitized photographic paper. The treated paper then side up, victim's clothing bearing residues side down (bullet hole centered on treated paper), and layers of towelling containing moistened acetic acid solution was put on top of cloth (NFSTC Science Service Justice Florida, 2008). This sandwich's formation was heated using uncontaminated iron for few minutes such as illustrated in Figure 2.3.

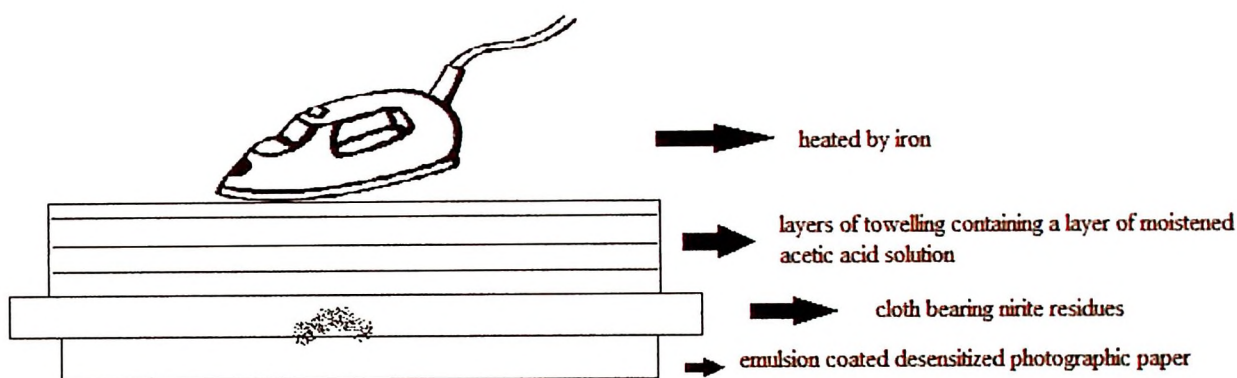


Figure 2.3: Illustration diagram on procedure of Griess test proposed by Joseph Walker, 1937 (NFSTC Science Service Justice Florida, 2008).

Positive result for the presence of nitrite residues was indicated by the formation of reddish specks pigment found on the treated paper. This test was accepted widely as confirmatory test for nitrites because no other chemicals reacted to give reddish pigments before (NFSTC Science Service Justice Florida, 2008). Advantage of this protocol was the application of treated paper which was not sensitive to light but instead sensitive to nitrite residues. Distribution pattern of nitrite residues was directly visualised which be recorded

as permanent graphic and later preserved as evidence. In addition, pattern appeared can be compared with known shooting test that carried out in laboratory.

Further modification to Griess test was made in 1970's due to health and safety issues as alpha-naphthylamine was recognised as carcinogen. The reagent was replaced with Marshall's reagent which actually is combination of equal ratio of sulphanilic acid solution in water and solution of N-(1-naphthyl)-ethylenediamine dihydrochloride in methyl alcohol (NFSTC Science Service Justice Florida, 2008).

Through the 1970's when Marshall's Reagent also was classified as carcinogen, practicing forensic laboratory in Canada introduced alpha-naphthol or naphthoresorcinol as substitute in these Griess test (NFSTC Science Service Justice Florida, 2008). Chemicals were not carcinogenic and had mild antiseptics properties. The protocol employed by the Canadian laboratory was treated the clothing with the reagent directly.

As mention before, different chemicals that had been used in the solution of Griess test gave different colour reaction when they react positively with nitrites. Alpha-naphthol formed an orange-azo dye when react with nitrites while naphthoresorcinol formed yellow azo dye. The employment of alpha-naphthol was preferable as the formation of orange colour is brighter and is more cost effective. The use of photographic paper is also preferable as the medium can reflect the size and nitrite distribution pattern for side-to-side comparison purposes (NFSTC Science Service Justice Florida, 2008).

MGT detects only nitrite ions from burnt or partially burnt smokeless powder. To increase the sensitivity of nitrite ions of unburn smokeless powder source, alkaline hydrolysis was performed as preliminary step prior to MGT test (Glattstein *et al.*, 2000).

Alkaline hydrolysis cause unburned smokeless powder particles *i.e.* nitrocellulose and nitroglycerine to change to carbonyl compound and free nitrite ion. This resulted in availability of higher concentration of free nitrite ions, resulting in the increase of the sensitivity of MGT.

Glattstein *et al.* (2000) stated that for MGT, nitrite distribution pattern around bullet hole was obtained by sheet printing method using fixed photographic paper soaked with reagents before use. Total nitrite consists of free nitrite ion and smokeless powder residues were transferred to an adhesive lifter or blotting paper from the target. Alkaline hydrolysis of smokeless powder residues on the adhesive lifter (blotted paper) carried out first, followed by MGT.

MGT can either be performed directly onto target material or by performing blotting technique. Direct application of MGT onto target sample may interfere with visualisation especially if it involves dark colour target, which can mask visualisation of positive reaction. Some problems have been identified detected if MGT was applied directly on clothing. As Griess test employed a hot press, some types of clothing is prone to damaged. Other than that, colour reaction obtained from Griess test may cause false positive results on some surfaces, for example on fixed photographic paper which obtained uniform colour range on woolen surfaces. As a result, MGT was carried out on the transfer medium of nitrite residues (Glattstein *et al.*, 2000).

Blotting technique uses adhesive lifter (similar to blotting paper) to lift GSR from the target. Most of GSR is lifted onto the adhesive surface and upon reaction with MGT reagent; distribution pattern of nitrite (a component in nitrite) is visualised (Glattstein *et al.*, 2000). Adhesive lifter is not absorbing materials, unlike fabric. Alkaline solution sprayed lightly on the adhesive lifter during hydrolysis step. After lifting of gunpowder

carried out, lead and copper residues visualised directly on the target using sodium rhodizonate and rubeanic acid test, respectively (Zeichner and Glattstein, 2002).

Advantage of hydrolysis step followed by MGT test is that adhesive lifter (blotted paper) can be repeated without original target sample losing much information because there is stoichiometric excess of hydrolysable nitrite compound in a particle compared to the available quantity of its base (Glattstein *et al.*, 2000). The procedure cannot be employed again if the MGT is treated directly on the cloth target because photographic paper lifts up part of the particles from the target. Visualisation of gunpowder distribution pattern on adhesive lifter is important in re-examination of exhibit bearing GSR (Zeichner and Glattstein, 2002).

Figure 2.4 shown below showed that there was huge different in colour intensity of MGT for gunpowder residue distribution pattern. Hence, in such cases, alkaline hydrolysis is an important step. However, not all firearm types will show such different pattern (Zeichner and Glattstein, 2002).

9 mm, Winchester Super X, FMJ, 50 cm



Figure 2.4: Visualization of target after application of MGT: without hydrolysis before MGT (left), with hydrolysis before MGT (right) (Zeichner and Glattstein, 2002).

### 2.1.1.1 Mechanism of Griess Reagent

Colour test is needed to evaluate distribution pattern of GSR as it detects nitrite residues; the combustion product of propellant. As proposed by Walker (1937) in the Goroncy's (1928) Griess test, Griess reagent consists of alpha-naphthylamine and sulphanilic acid in acetic acid solution was used. Mechanism applied in this reaction is sulphanilic acid reacts with the presence of nitrite to form diazonium ion. Diazonium ion later reacts with alpha-naphthylamine to form an orange azo dye (Zeichner and Glattstein, 2002). The reaction was shown in Figure 2.5 and Figure 2.6.

Step 1: Nitrite + sulphanilic acid  $\rightarrow$  diazonium ion

Step 2: Diazonium ion + alpha-naphthylamine  $\rightarrow$  azo dye (orange)

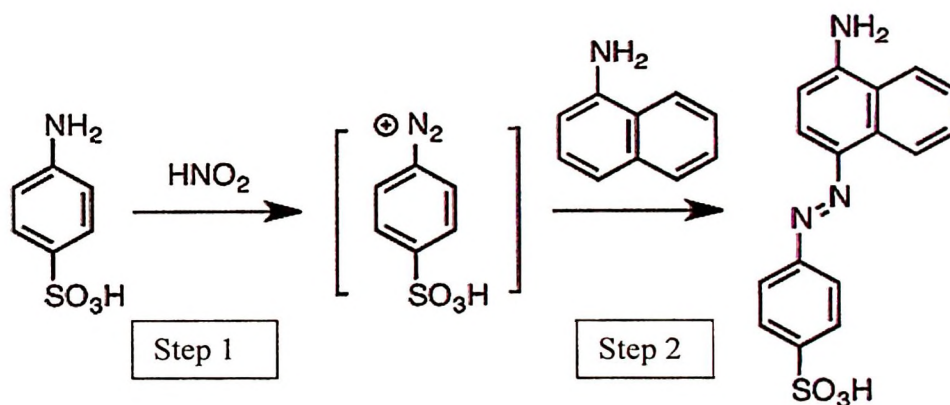


Figure 2.5: Chemical reaction of Griess test (Zurcher *et al.*, 2014).

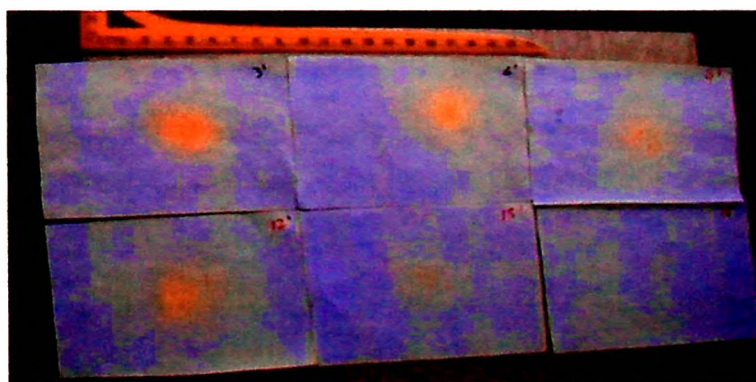


Figure 2.6: Formation of orange colour indicate positive result of MGT in detection of nitrite (Ananth *et al.*, 2011).

Later, modification made to original Griess test after alpha-naphthylamine was identified as carcinogen which replaced by alpha-naphthol (NFSTC Science Service Justice Florida, 2008). At that time, N-(1-naphthyl)-ethylenediamine dihydrochloride also was listed as carcinogen. However, Zeichner and Glattstein (2002) stated that N-(1-naphthyl)-ethylenediamine dihydrochloride was not carcinogen based on literature on chemical safety data. Instead, they use N-(1-naphthyl)-ethylenediamine dihydrochloride with sulphaniamide for Modified Griess Test (Zeichner and Glattstein, 2002).

### **2.1.2 Diphenylamine Test**

Diphenylamine (DPA) test detect nitro compounds as a combustion products of nitrocellulose (NC) and nitroglycerine (NG) (double base propellant particles). Positive reaction will appear as dark blue colouration. The intensity and distribution of the colour depends on the intensity and distribution of nitrates inorganic compounds. The intensity and distribution colour will be used to estimate firing distance because intensity colour increased as distance decreased and the distribution of the nitrates (dark blue) is not sparsely distributed (Ananth *et al.*, 2011). However, the test may give false positive result because other oxidisers may also give the same reaction making the test is unreliable for GSR (Lopez-Lopez and Garcia-Ruiz, 2014).

Differ from Griess test, diphenylamine test is applied directly onto exhibit. Reagent consists of sulphuric acid and glacial acetic acid could destroy the sample thus is not preferred technique and blotting technique for this test is unavailable. GSR distribution failed to be detected on dark background and dark design. The reason is production of dark blue colour of diphenylamine test will mask the presence of GSR (Ananth *et al.*, 2011). Hence, the test should be carried out in sequence, which Griess test applied first, follow by Sodium Rhodizonate test or Diphenylamine test (Glattstein *et al.*, 2000). The presence of dark blue colour as a positive detection of nitrates was shown in Figure 2.7.

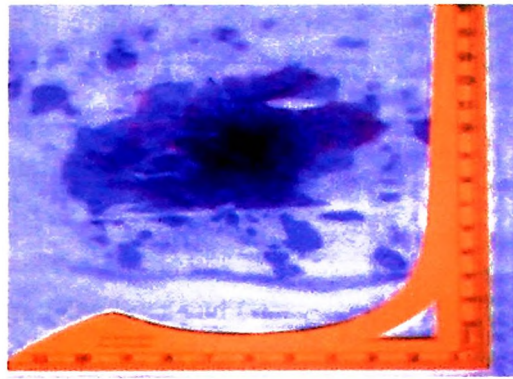


Figure 2.7: Formation of dark blue colour as a positive reaction of diphenylamine test in detection of nitrates (Ananth *et al.*, 2011).

### 2.1.3 Sodium Rhodizonate Test

Sodium rhodizonate test is one of the proposed chemical test other than nitrite test (Chang *et al.*, 2013). The test detects lead that may come from lead-jacketed/bearing bullet and lead residue from the primer mixture (lead styphnate). Sodium rhodizonate test implies the application of weak solution of sodium rhodizonate and buffer solution to the target directly. Formation of pink colour from dark yellow colour showed positive detection of lead (Azman *et al.*, 2014; Lopez-Lopez and Garcia-Ruiz, 2014; Vanini *et al.*, 2015). Same principle with other colour test, the intensity of colour (pink) decreased when the distance increased (Halim *et al.*, 2010). The formation of pink colour showed detection of lead residue detection shown in Figure 2.8.



Figure 2.8: Formation of pink colour showed positive reaction to lead residue in sodium rhodizonate test (Doyle, 2014).

Advantages of application sodium rhodizonate test are cost-effective, easy and can be applied to human tissue (Andreola *et al.*, 2011; Turillazzi *et al.*, 2013). It is advocated to conduct MGT first, followed by sodium rhodizonate test. Besides this test is destructive, it also due to the reason that the lead particles is a nonreproducible phenomenon. Lead may only found at a closer range (Zeichner and Glattstein, 2002). In addition, the test may give false positive result as it also reacts with other heavy metals.

Due to health concern and environmental issue, lead-free ammunition is introduced (Romolo and Margot, 2001). Airborne lead exposure may risk the employees (shooter) with much serious and fatal disease (Martiny *et al.*, 2008; Chang *et al.*, 2010). The introduction of lead-free ammunition makes the sodium rhodizonate test cannot be relying upon anymore. Thus, a method was established in detection of lead-free ammunition (Berendes *et al.*, 2006; Weber *et al.*, 2014). Zincon reagent is used to detect the constituents of the lead-free ammunition primer which are zinc and titanium. Another test in Lunges test which detects nitrocellulose (Dalby *et al.*, 2010; Lopez-Lopez and Garcia-Ruiz, 2014).

## **2.2 Other GSR Detection Techniques**

In some cases, GSR can be detected by naked eyes or using microscope if the colour background of cloth is light enough colour (Zeichner and Glattstein, 2002). Otherwise, most procedures employed colour enhancement test before further analysis using instrumental carried out to estimate muzzle-to-target distance estimation.

Scanning Electron Microscope (SEM) instrumental analysis is preferable in analysis of GSR morphologically and its microstructure (Fojtasek *et al.*, 2003; Zadora and Brozek-Mucha, 2003; Sharma and Lahiri, 2009; Lopez-Lopez and Garcia-Ruiz, 2014; Weber *et*

*al.*, 2014). SEM analysis is useful to reveal the morphology of GSR whereby the shape can be determined (spherical or irregular) and size can be measured. The analysis is powerful to prove the proximity of the shooter to the gun that had been fired (Brozek-Mucha, 2011). Particles that still molten upon impact on the target due to close range tend to have irregular shape while spherical GSR particles shape were said to be solidified upon contact as travelled at longer range (Dalby *et al.*, 2010).

The interpreted result can determine whether if the residue was the combustion of primer or other possible sources (Romolo and Margot, 2001). Non-conductivity of GSR leads to the application of low vacuum mode (Halim *et al.*, 2010). Electron bombarded onto sample creates a three-dimensional image (Chang *et al.*, 2013).

Shape of GSR can vary due to different process that took part in formation of solidified particulates as the gas vaporised and escaped from opening of different firearms. Different kinds of ammunition involved were also factor to different geometrical shape of GSR. Using SEM-EDX, GSR can be seen in spherical (Halim *et al.*, 2010) or irregular shape (Dalby *et al.*, 2010). Colour of particles tends to change original gray-black to greenish-yellow when fired (Muller *et al.*, 2007). Dockery *et al.* (2010) stated that size of GSR about 20  $\mu\text{m}$  to 40  $\mu\text{m}$  in diameter but up to 100  $\mu\text{m}$  have been reported by Dalby *et al.* (2010). However, irregular shapes of the particles that exceed 40  $\mu\text{m}$  are uncommon (Oommen and Pierce, 2006).

Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscopy (SEM-EDS) is non-destructive and capable in identification of single particle of GSR (Meng and Lee, 2007). Other than that, SEM-EDS is a well-known method for identification of GSR particles as the sample preparation does not undergo a complex process (Brozek-Mucha, 2009). Plates or sphere shape have same elemental composition.

Fusing of fibres as bullet pass through the fabric also can be seen through the image appeared (Palenik *et al.*, 2013).

Instrumental analysis such as neutron activation analysis (NAA), atomic absorption spectroscopy (AAS) and X-Ray fluorescence (XRF) still has been apply to estimate firing distance although there are many advance techniques had been introduced (Sharma and Lahiri, 2009; Zeichner and Glattstein, 2002). XRF is a technique of application of excitation X-ray source to the sample to generate a fluorescence emission of the sample (Berendes *et al.*, 2006; Lopez-Lopez and Garcia-Ruiz, 2014). The technique is non-destructive and no sample preparation needed. NAA can measured barium and antimony (Zeichner and Glattstein, 2002). AAS is a technique that can also detect lead, barium and antimony (Lopez-Lopez and Garcia-Ruiz, 2014) and can support visual inspection of GSR on clothing or other surfaces (Chang *et al.*, 2013). Instrumental analysis is not possible for shooting distance determination although some of the techniques measured GSR quantitatively.

### **2.3 Factors Affecting GSR distribution.**

As mentioned in the previous section, GSR distribution and retention of shot target were influence by a number of factors. Successful detection of GSR around bullet hole do not rely 100% upon enhancement (colour test) techniques. The following sections discuss briefly those contributing factors.

#### **2.3.1 Shooting Target Material**

In many shooting cases, bullet may penetrate different surfaces such as garment, wall, glass, wood and so on. The outcome of this incident may show different appearance of entry and exit bullet hole as well as GSR distribution pattern because of different material

composition and arrangement (Azman *et al.*, 2014). Thus, GSR behave differently depends on the type of shooting target (Brozek-Mucha, 2011).

### **2.3.1.1 Porous Type (Cloth fibres)**

Fabric is important in everyday life. It is used for clothing, furnishing, symbolic communication and business. Fabrics originate from natural and synthetic sources (Needles, 1986). Cotton from plant fibers is an example of fibers from natural source. Cotton is most commonly used in textile materials. Factors such as type of cotton, fiber length, and strand degree of twist contribute to the diversity of this fabric. Cotton polyester blend is the combination of the best properties of components where cotton is major substrate. Quality of cotton made the fabric more valuable in addition to other substitution of other alternative materials (Bel-beger *et al.*, 1999). Meanwhile, satin can be produced by combination or mixture of different fiber contents but always produced a smooth and lustrous surface. Its flexibility depends on types of yarn used such as rayon, acetate, polyester and silk multifilament. Jersey made into T-shirt is from single jersey fabrics either by woven structure or knit fabric. However, in improving single-knit fabrics, Lycra is used to co-knit with cotton yarn. Lycra consists of 85% polyurethane (Sadek *et al.*, 2012).

Textile or publicly known as cloth is defined as any material composed of fibers (Johnson, 1991). Composed textile can be arranged in 4 levels, usually starts with fiber, yarns, fabric and textile. Fibers are formed into yarns, then yarns is interlace into fabrics either by weaving, knitting, braiding or even knotting (e.g nets), producing textile or cloth as the end product (Johnson, 1991).

Physical damage found on textile can give indicators as to what cause the damage. Bullet entrance hole, cut, punctured by sharp and blunt object can be characterised by

observation of the fabric under microscope. Generally, examination is carried out by looking at fabric level, followed by yarn level then at the fiber level (Johnson, 1991).

At the fabric level, examiners look for distortion of fabric and changes to thread spacing. At yarn level, damage is shown at yarn end which may look frayed or in chaos disorder. Fiber end can sometimes give valuable information. The end of the fiber such as formation of mushroom up suggests damage by heat for example giving useful information for further investigation (Johnson, 1991).

Type of fabric influences penetration of bullet. Some fabric that stretchable gives an impact to the size of bullet hole (Azman *et al.*, 2014). Cloth texture affects intensity of GSR deposited on fabric which imprints to residual attachment persistency (Ananth *et al.*, 2011). Persistency of the residue possibly due to residue embedded into the weave of the fabric (Charles *et al.*, 2013). In addition, dark background or multicoloured fabric prohibit examination of GSR intensity and distribution visually (Bailey *et al.*, 2006).

#### **2.3.1.2 Non-Porous Type and Others**

Most in the shooting cases, victim's clothing is examined for shooting distance estimation. The exhibit can be examined in laboratory. However, in some cases, there is a need in estimation of exhibit that cannot be processed in the laboratory such as cars, walls, doors, windows or furniture.

Some study by Glattstein *et al* in Zeichner and Glattstein (2002) examined other materials *i.e.* galvanized steel, glass, plywood and high-pressure laminated plastic sheets of melamine and phenolic materials using same method that developed for clothing. Result showed that amounts and density of discharged residues that detected visually without any treatment were smaller than those obtained after chemical treatment (Zeichner and Glattstein, 2002). Example is glass, which showed no blackening around bullet hole even

though it was a contact shot. Study found that total nitrite distribution pattern around bullet hole for others material than clothing which visualised on adhesive lifter were similar to those obtained from cotton cloth at short shooting ranges. The pattern shared relatively similar characteristic in terms of the amounts of particles and its density around bullet hole (Zeichner and Glattstein, 2002).

The greater the shooting distances, amounts and density of nitrite spots on the lifter of all the tested materials decrease. Recommendation made for method in estimating shooting distance for exhibit that cannot be processed in laboratory is as follow:

- a) Adhesive lifter lifts the discharged residues from target.
- b) Rhodizonate test applied on target to determine lead residues. It is preferable to take photograph the lead pattern due to instability of the colour formed.
- c) Rubenic acid applied on target for copper deposits.
- d) MGT test on adhesive lifter for total nitrite distribution pattern in the laboratory.

To get more accurate results, it is recommended that test firings carried out using materials as similar as possible to the evidence being examined. If there is no possibility to conduct test firings on similar materials to the evidence, then cotton cloth is preferable to be used. Visualisation of total nitrite pattern will be sufficient enough to demonstrate shooting distances of the evidence either equal or slightly below to the total nitrite distribution by the cotton cloth (Zeichner and Glattstein, 2002).

Most shooting cases involving the bullet strike surfaces of various body parts directly without any intermediate medium such as clothing are happened. In such case, to assess shooting distance, only visual or microscopic examination of the appearance of the wound and gunshot residues pattern can be described (Turillazzi *et al.*, 2013; Lopez-Lopez and