Journal of
Emerging Investigators

The Relationship between Close-range Shooting Distance and Nitrite Patterns on Cotton and Polyester Clothing

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Summary

At a crime scene, the presence and pattern of gunshot residue can help forensic scientists piece together the events that occurred. To assist this, we determined the relationship between shooting distance and nitrite residue patterns left on fabric targets. Using the Modified Griess Test, we also investigated whether fabric type plays a role in gunshot residue (GSR) amounts. Cotton and polyester targets were shot from five different distances, and the targets were processed using the Modified Griess Test to measure the nitrite components of the GSR particles. An image processing program called ImageJ was used to approximate the total area of the residue. Results show that from 0 cm to 25 cm away, there was a rapid increase in GSR, but beyond 25 cm, there was a decrease in GSR, which is consistent with previous studies. Also, fabric type played a significant role in GSR patterns, with polyester fabrics holding more GSR on average than cotton at 25 cm, but less than cotton at 0 cm. The results of this study can potentially provide new and innovative ways to determine shooting distances and GSR patterns on different fabric types.

Received: March 15, 2016; **Accepted:** May 30, 2016; **Published:** September 5, 2016

Introduction

The materials found at the scene of a crime can provide an abundance of trace evidence. An example of this is gunshot residue, which consists of chemical compounds often found on the victim or the shooter as the result of the combustion of gunpowder (1). There are various chemical tests that show the presence and patterns of gunshot residue (GSR) and provide critical clues for forensic examiners. Examiners can use GSR on the victim to estimate the shooting distance (2), either supporting that the shooter was in close proximity or further away. For example, in a hypothetical crime scene, a victim lies dead and it is indeterminable whether it was a murder or a suicide. The forensic examiner is called to the scene to recover GSR evidence from the victim and uses it to estimate the distance from which the gun was fired. The purpose of this study was to investigate the relationship between shooting distance and GSR patterns on a victim's clothing, using the Modified Griess Test to measure the presence of nitrite residue on both cotton and polyester fabrics.

Gunpowder, also known as smokeless powder, is an explosive consisting primarily of combustible nitrocellulose, a highly flammable substance made through the exposure of cellulose fibers to nitric acid (1,3). Nitrocellulose acts as a fuel and as an oxidizer. The oxidizer, due to its burning properties and high heat levels, often acts as a propellant in firearms (3). Gunpowder also contains additives such as stabilizers that prevent the nitrocellulose from decomposing, plasticizers to reduce the need for volatile solvents to colloid nitrocellulose, flash inhibitors that reduce the flash when the gun is shot, coolants that prevent overheating of the muzzle, moderants to slow down the rate of combustion, surface lubricants that lubricate the muzzle, and anti-wear additives (3). All types of smokeless gunpowder contain nitrogen, and its oxidation during the discharge of a firearm causes nitrites to form patterns of GSR at crime scenes. The most common test that forensic labs use to identify nitrite patterns when estimating shooting distance is the Modified Griess Test (2,3).

The Modified Griess Test (MGT) is an indicator test that detects the presence of nitrite ions in a solution (1, 2, 4). This detection is marked by the formation of a pink violet color called an azo dye. When the solution is applied to an entry hole in a victim's clothing, the MGT's two components, N-(1-naphthyl)ethylenediamine and sulfanilamide, react with the GSR to create the pink color, due to the nitrite ions in the GSR.

Numerous studies have investigated GSR and shooting distance using the MGT. One study used shooting distances of 7.6, 15.2, 22.9, and 30.5 cm away from the target and found that, with increasing distance from the target, the "intensity" of the pattern decreased. However, the study also found that there was no pattern beyond 38.1 cm (4). Another study aimed to address problems with the MGT and found that an air press could be used as an alternative for capturing the nitrites without damaging the fabric (5). This is useful when multiple types of tests need to be performed on the same fabric. Another study reviewed previous shooting distance research and concluded that the MGT was the most common and accepted way to analyze nitrite patterns on fabric (2).

Other studies have investigated the effect of various types of interference on nitrite particles on either clothing or shooting victims' bodies. One study tested the effect of machine washing and brushing on GSR patterns and concluded that machine washing had a more significant effect on the disruption of GSR patterns than brushing (6). The last study sought to determine the reliability of using bullet wipe and fiber direction metrics in a forensic investigation (7). Bullet wipe is a form of GSR that commonly consists of a visible dark deposit that is carbonaceous, located around the perimeter of the bullet hole (7). The results showed that fiber direction is not the most reliable indicator of an entry or exit hole in cloth or human tissue, whereas bullet wipe is a more reliable method (7). This is important because GSR is typically only found on the entry hole of a victim's fabric. Research on different fabric types is limited; one study found that polyester will hold more GSR than cotton, but that study measured GSR particles on fabric near targets, as opposed the target material itself (8). While many studies have investigated the relationship between shooting distance and nitrite patterns, none have described the pattern quantitatively. This study will contribute to the current field of research by suggesting new ways to predict shooting distance from GSR patterns.

The purpose of this study is to describe the relationship between shooting distance and the nitrite pattern on fabric using the MGT. Because other studies have found that the spread of the nitrite residue becomes larger as the shooting distance increases, (2, 4, 5, 7), we hypothesized that, as the shooting distance increased, the nitrite residue area will decrease. We also hypothesized that there will be a significant difference between different fabric types, in this case, cotton and polyester.

Results

In order to investigate these hypotheses, we shot a total of 30 targets made of cotton and polyester fabrics from distances of 0 cm, 25 cm, 50 cm, 75 cm, and 100 cm using a Ruger 9mm handgun. Then, we used the Modified Griess Test (MGT) to visualize the particles from the targets after they were transferred onto photo paper. Photo papers were analyzed visually and numerically using the particle analysis program ImageJ. We hypothesized that the polyester and cotton would hold different amounts of GSR and that, as the distance increased, the amount of GSR would decrease.

For the polyester targets, from 0 cm to 25 cm, the particle area increased, but at 25 cm and beyond, the particle area decreased (**Figure 1 and 2A**). This pattern was consistent across all of the targets except for the second shot at 100 cm, which was unusually high for no clear reason. Because the targets were handled only with rubber gloves and sealed individually in plastic bags, contamination was unlikely. It is possible that the target was shot from the wrong distance due to uncooperative weather conditions, but this is also unlikely due to the shooter and lab assistant constantly checking and re-measuring the distance. At 0 cm, almost no residue was visible except the amount that surrounded the large entry hole. At 25 cm, on the other hand, there was vibrant color change, which suggested a high amount of residue (**Figure 2A**). At 50 cm, the particles were spread out around the target, but were clumped together around the entry hole. For targets at 75 cm to 100 cm, there were little to no noticeable particles. Some of the targets shot at 100 cm exhibited a spiral pattern near the entry, perhaps due to the bullet spinning as it entered the target.

For the cotton targets, the same general pattern occurred. Between 0 cm and 25 cm, the particle area increased and then decreased after 25 cm (**Figure 1 and 2B**). When comparing cotton and polyester, the general relationships were the same. From 0 to 25 cm, there was a dramatic increase in the total area of residue, and beyond 25 cm there was a rapid decrease; cotton exhibited a 98% decrease and polyester exhibited a 94% decrease. However, the difference between the two fabrics was that cotton at 0 cm covered a larger area of GSR residue than polyester. Their total averages were 189.138 mm^2 for cotton vs. 0.746 mm^2 for polyester (**Table 1**). The polyester targets at 25 cm had near triple the area of residue: 689.503 mm^2 vs. 217.456 mm^2.

These results partially supported our first hypothesis that, as the distance increases, the particle area

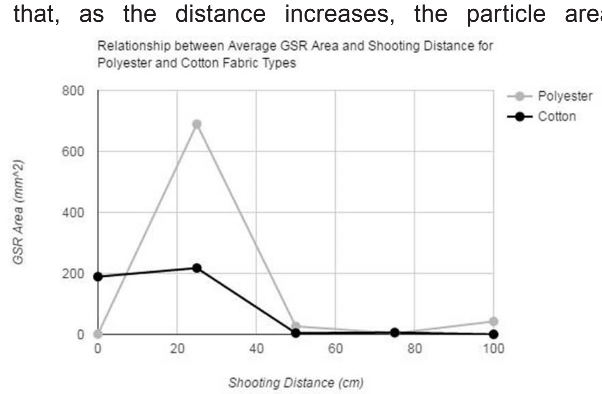

Figure 1. Relationship between the area and the shooting distance for two types of fabrics. As shown, polyester held more at 25 cm but cotton held more GSR at 0 cm. Beyond 25 cm, both fabric types had a rapid decrease.

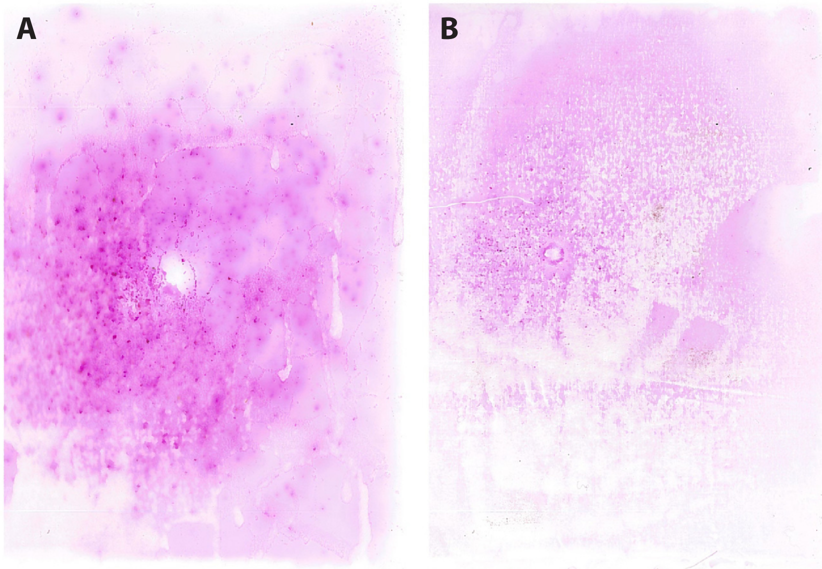

Figure 2. Photo paper after the MGT was performed on the cloth target. A: The target was polyester from a distance of 25 cm. **B:** The target was cotton from a distance of 25 cm.

decreases, because from 0 to 25 cm the amount of residue increased significantly. Beyond 25 cm, the amount of residue began to rapidly decrease the further the distance from the target. The second hypothesis was also partially supported; there was a difference between the two fabric types because polyester retained a larger area at 25 cm compared to cotton, although the cotton contained more at 0 cm.

Discussion

This study investigated the relationship between shooting distance and GSR patterns on cotton and polyester targets. The results partially supported the first hypothesis, from 0 cm to 25 cm, there was a rapid increase in GSR, but then from 25 cm and beyond, the GSR began to decrease on the targets. The second hypothesis was also partially supported; while both fabric types followed the same basic distance relationship, the polyester held less GSR than cotton at 0 cm, but more GSR from 25 cm and beyond (**Table 1, Figure 1**).

One possible limitation with the results could have been that the distances were not in closer proximity with each other. The shooting distances were evenly spaced at 25 cm intervals, but instead could have been measured at 5 cm intervals. This would have helped to describe the drastic change between 0 cm and 25 cm for polyester (**Table 1**) and would indicate if the change was gradual or rapid. It is possible that the GSR area had zero particles at 0 cm, but was otherwise much higher than the 25 cm average just beyond 0 cm. However, it is also possible that the GSR gradually increased to a maximum area at 25 cm. Future studies should include finer gradations. For example, one previous study found maximum nitrite GSR residue at a distance of 7.62cm, which is a distance not included in this study (4). A final limitation is that two targets were removed from the original sample because the shots were not centered. However, the other two shots from these distances were consistent with each other, suggesting the results are still reliable.

Table 1: Total Average Area of GSR (mm^2) for each shot of Cotton and Polyester

Distances	0cm (mm^2)	25 cm (mm^2)	50 cm (mm^2)	75 cm (mm^2)	100cm (mm^2)
Cotton 1	182.793	233.097	7.194	0.369	*
Cotton 2	195.482	327.853	0.445	5.161	0
Cotton 3	*	91.387	4.804	0.549	0
Cotton Average	189.138	217.456	4.147	6.079	0
Polyester 1	0	548.6	21.371	6.910	6.240
Polyester 2	0.246	880.285	23.949	0.323	116.362
Polyester 3	1.992	639.624	33.361	3.224	4.262
Polyester Average	0.746	689.503	26.227	3.486	42.288

Table 1. Total GSR area (mm2) for targets at different shooting distances and fabric types. Two trials were discarded (*) because they were shot too far off center, and there were concerns that too much of the GSR would have missed the target or would have demonstrated an inaccurate amount of GSR particles on the target.

A possible reason that polyester held more GSR than cotton beyond 25 cm was due to polyester having a negative electrostatic affinity, whereas cotton has a positive electrostatic affinity (10). This suggests that polyester was able to electrostatically attract more GSR particles from the air than cotton, thus offering a potential explanation for the differences in GSR amounts. However, this does not explain the reversal of the pattern where cotton exhibited a larger GSR area at 0 cm. This explanation does not apply to the GSR area at 0 cm, because cotton had more bullet wipe than polyester, which was counted in the GSR area. Although it is unclear as to why cotton had more bullet wipe, it may be due to the construction of the fabric.

One similarity between the current study and other studies (4-6, 8) is that they all used white cotton to retrieve GSR particles. These studies' data are consistent with the results of the current study in that, beyond contact shooting (0 cm), GSR area decreased as the distance increased. However, these other studies (4-6) used only white cotton, and one study (8) used polyester, but did not use them as targets. The study (8) had the fabric on the floor as the gun discharged, and the fabric collected the GSR particles as they fell. The researchers found that polyester fabric held more GSR than cotton, but the results were determined qualitatively through visual inspection. These results may correspond with the data of our current study in that polyester held more GSR than cotton at distances beyond 25 cm.

Another key difference between this study and past studies (4-6) is that the current study shot from 0 cm while other studies had a starting point from either 7.6 cm, 25 cm, or 10 cm, respectively. While the results of the current study and other studies are consistent beyond 0 cm, at 0 cm there are no other data to compare it to. Gunshot analysis at 0 cm is further complicated because of the gun used. The current study used a semiautomatic pistol (9mm) where the GSR can only go out of the barrel or it is blown back from the receiver onto the shooter. But with a revolver, which was used in one study (4), the GSR may blow out of the sides, causing more GSR to be present on the targets.

One unique aspect in this study was that a computer program was used to find the GSR area measurements. This is a potentially beneficial method because the computer is consistent; it applies the same methodology to every sample unlike the forensic scientist who relies on visual analysis for every sample. However, there were only five data points, which provide limited evidence to conclude the method proposed here is better than the method that forensic scientists use. We recommend that future researchers consider using this method to investigate additional distances and weapon types to compare it to other methods for measuring GSR to see if it has any practical value. We also recommend the addition of a control fabric target, not receiving a gunshot, for the Modified Griess Test, to allow for increased precision in processing the images in ImageJ. These results are intended to suggest a new way to detect GSR and determine distance. In addition, fabric type should be taken into consideration when trying to determine gunshot distance and amount. For example, if someone is shot and they were wearing a polyester and cotton blend t-shirt, the results may be different than a just cotton shirt.

Materials and Methods

Targets

The targets were pieces of 100% cotton and 100% polyester fabric cut into 8 x10 inch rectangles then stapled to 9 x 12 of a piece of foam board. The foam board was hung from a target stand with large binder clips. Then, the distance from the end of the gun barrel to the piece of fabric was measured and marked on the ground. After taking one shot at the target, the clips were removed by a lab assistant wearing nitrile gloves, and the target was placed into a large plastic zip-loc bag, labeled with the distance and sample number. Once all the shooting had taken place, the targets were taken from the bags one by one and tested using the Modified Griess Test.

Modified Griess Test

The Modified Griess Test is a chemical test that indicates the presence of nitrites on a sample. In the first part of the chemical reaction, described in **Figure 3**, the $NO2^-$ (nitrite) is sprayed with a strong acid that provides excess hydrogen ions. Then the acid begins to break apart the nitrite, freeing the nitrogen anions, which are attracted to and bond with the sulfanilamide. This creates a diazonium salt, which acts as an intermediate. An intermediate is the product half way through the reaction that helps produce the final product. This intermediate is positively charged due to the missing electron in the N=N complex. The intermediate desires to share electrons, which it finds via its bond to the N-(1-naphthyl) ethylenediamine. Next, the intermediate bonds to the N-(1-naphthyl)ethylenediamine through an electrophilic-aromatic substitution. It bonds to the para position of the ethylenediamine benzene ring due to the ethylene diamine's role as an ortho-para director. It bonds in the para position rather than the ortho because the structure of the N-(1-naphthyl)ethylenediamine makes the ortho position sterically hindered. This new aromatic ring is a violet pink colored azo dye – a nitrogen-based dye that gets its color due to delocalized electrons in the new benzene ring. The pink color confirms that there are nitrites, which are present in the GSR.

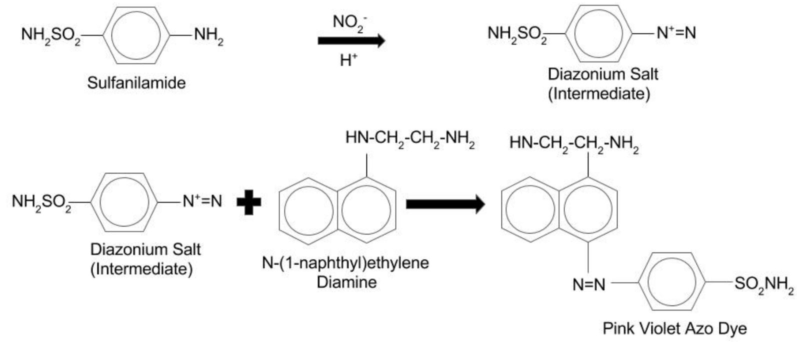

Figure 3. Chemical reaction of Modified Griess reagent to GSR nitrites. The nitrites in the GSR are sprayed with acid that contains extra hydrogen atoms, and the acid breaks apart the nitrite, freeing nitrogen anions that bond with the sulfanilamide. This then creates the diazonium salt known as the intermediate. Next the intermediate bonds with the N-(1-naphthyl)ethylenediamine through electrophilic aromatic substitution. This creates a new ring, which is a violet pink color, indicating there are nitrites present in the GSR.

The Modified Griess reagent was made by dissolving eight grams of sulfanilamide in 1000 mL of 10% (v/v) phosphoric acid. Then, 4 g of N-(1-naphthyl) ethylenediamine was dissolved in 1000 mL of 10% (v/v) phosphoric acid, and a fresh mixture was prepared by mixing equal volumes of each solution to create the final solution (1). After making the reagent, it was applied onto 8 x 10 pieces of photo paper, previously treated with photographic fixer, by soaking for one minute. Photo paper is commonly used to extract the nitrite particles from the fabric, making the resulting image easier to analyze, especially when more than one type of GSR test is done to a fabric sample (1). The treated photo paper was placed down on the targets and a hot iron applied on top for several minutes until dry to transfer the nitrite particles onto the paper. Then the photo paper was used to examine and calculate the area the nitrite residue covered at each distance.

Image analysis

Finally, ImageJ, a computer software program, was used to calculate the number and total area of particles on the pieces of photo paper, measuring the area that the particles covered. Prior to calculating, the settings for saturation, brightness, and hue had to be adjusted using the Particles function to omit the background nitrite residue present on the fabric, which was a light pink. These settings allowed the program to count the number of distinct circular particles and measure their combined area.

Acknowledgements

We would like to thank George Francis for helping with gun safety while performing the experiment and collecting the data. Thank you also to Alexis Wright for her safety supervision in the lab. Finally, we thank Alexis Jackson for help in taking photographs of samples.

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