

# The SCIENCE behind Testing for GUNPOWDER RESIDUE

## What is GUNPOWDER RESIDUE ?

Gunpowder residue is composed of two substances a propellant and a primer. Each of these is a mixture that has a unique function and chemical composition.

**Propellant:** (gunpowder) The two types of propellents are **black powder** or **smokeless powder**.

**Black powder:** consists of charcoal (15%), sulphur (10%) and potassium nitrate (75%). When ignited, it produces a lot of smoke.

**Smokeless powder:** contains either nitrocellulose alone (*single base powder*) or nitrocellulose mixed with nitroglycerine. These compounds are known as nitrites.

**Primer:** The cartridge also contains some special chemicals called the **primer**. These chemicals have the special property of igniting when subjected to great pressure. Several types of primers may be used, but the most commonly used are lead azide, lead styphnate, mercury fulminate, barium nitrate, potassium chlorate and antimony sulphide.

## How do the Propellant and Primer mixtures cause a gun to FIRE ?

When the trigger of a gun is pressed, the firing pin strikes the cartridge at a point where the primer is kept. This causes the primer to ignite. The flames thus produced ignites the propellant charge. The burning of the propellant charge produces large amounts of gases, which finally propels the bullet.

## How is gunpowder residue DETECTED ?

When a gun is fired, the products of combustion (propellant + primer) come out of the barrel of the gun. Some may leak through the back of the gun and may get deposited on the hands of the person who has fired. Depending of whether the gun was handled by the right or the left hand, the products of combustion get deposited on certain specific areas of the hand which are exposed. This is known as gunpowder residue and Forensic Scientists can test for this on a person's hands to determine if they have fired a gun.

Because there are so many different types of chemical compounds found in both gunpowder residue and primer residue (ie. *gunpowder = charcoal, sulphur, potassium nitrate, nitrocellulose, nitroglycerine; primer = lead azide, lead styphnate, mercury fulminate, barium nitrate, potassium chlorate and antimony sulphide*) - there are many of types of chemical tests that can be performed to detect gunpowder residue. The following section outlines some of the common types of gunpowder residue chemical test techniques that Forensic Scientists will perform...

## Various Types of Gunpowder Residue Test Techniques...

### PARAFFIN test (a.k.a. dermal nitrate test or diphenylamine test)

The first gunpowder residue test was done by Teodoro Gonzalez of the Criminal Identification Laboratory, Mexico City police headquarters in 1933.

In this test, the hands of the suspect are coated with a layer of **paraffin**. After cooling, the paraffin 'casts' are removed and treated with an **acid solution of diphenylamine**. This solution detects nitrites and nitrates that originate from gun powder and are deposited on the hands of the criminal. A positive test is indicated by the presence of blue flecks in the paraffin.

The downfall to the paraffin test is that it reacts specifically to nitrites and nitrates - however there are many household products that contains nitrites and nitrates such as: fertilisers, tobacco, fingernail polish, urine and matches.

(diphenylamine + sulfuric acid) + nitrites or nitrates ---> **BLUE flecks**

### MODIFIED GRIESS test

The Modified Griess Test is a test that detects the presence of nitrite residues. Nitrite residues are a by-product of the combustion of smokeless-gunpowder.

The Modified Griess Test is performed by first treating a piece of desensitized **photographic paper** with a chemical mixture of **sulfanilic acid** in **distilled water** and **alpha-naphthol** in **methanol**. The photographic paper will now no longer be light-sensitive, but will be reactive to the presence of nitrite residues.

This piece of photographic paper is then placed face down against a suspected bullet hole centered on the paper. The back of the photographic paper is then steam ironed with a dilute **acetic acid** solution in the iron instead of water. The acetic acid vapors will penetrate the paper and a reaction takes place between any nitrite

### MODIFIED GREISS test (con't)

residues on the exhibit and the chemicals contained in the photographic paper. The resulting reaction will appear as orange specks on the piece photographic paper.

**photographic paper + acetic acid + nitrites ---> RED/ORANGE specks**  
(soaked in sulfanilic acid, water,  
alpha-naphthol, methanol)

### SODIUM RHODIZONATE test

This chemical test is designed to determine if barium or lead residue are present on the hands of a suspect. First any residue is 'picked up' by rubbing the hand with a gauze wet with dilute hydrochloric acid. The gauze is then cut into small pieces, and some drops of sodium rhodizonate, distilled water and buffer solution are added to each piece.

A **brown-pink** color means that there was barium on the hand, if the color is **scarlet red** then there was lead, and a mixture of these colors tells you both were present.

These are the colors developed when a salt between rhodizonate and lead or barium is formed. These characteristic color changes are positive proof - however the absence of color does not mean the hand is innocent. The killer could have already washed hands.

**sodium rhodizonate + barium --> BROWN-PINK color change**  
solution

**sodium rhodizonate + lead --> SCARLET RED color change**  
solution

### HARRISON-GILROY test

The Harrison-Gilroy Test checked for the presence of barium, antimony, and lead on the hands. These substances are common in most of the primers used in cartridges.

In this test, a square of white cotton cloth is moistened with dilute hydrochloric acid. This cotton cloth is used to swab the hands of the suspect. If the suspect has fired the gun, the particles of the chemicals mentioned above will get transferred to the cotton. The cotton swab is allowed to dry and then treated with a special chemical triphenylmethylarsonium iodide. The cotton swab is dried again and then treated with sodium rhodizonate. After the addition of each of these chemical compounds the color is noted.

If antimony is present on the swab, the first reagent (triphenylmethylarsonium iodide) turns a **orange** color, if lead or barium were present, the second reagent (sodium rhodizonate) turns a **red** color.

## HARRISON-GILROY test (con't)

triphenylmethylarsonium iodide + antimony --> ORANGE color change

triphenyl- + sodium + lead or barium --> RED color change  
methylarsonium rhodizonate  
iodide

## NEUTRON ACTIVATION ANALYSIS test (NAA)

The Neutron Activation Analysis test (NAA) detects barium and antimony. To collect samples for it, use cotton swabs with plastic handles. Dip the swabs in a mild **hydrochloric acid** or **nitric acid** solution and wipe the hands with the swabs in the area where residue is expected to be present.

Unfortunately this test requires the use of nuclear reactor and is not available in all areas. It is relatively harmless to gather samples for it, however, and in extremely important cases, they might be gathered against the possibility that the samples could be submitted elsewhere.

## FLAMELESS ATOMIC ABSORPTION SYSTEM (FAAS)

The Flameless Atomic Absorption System (FAAS) detects antimony, lead, barium, and copper. The sampling method is similar to that for the NAA system except that **5% nitric acid solution** must be used. Four swabs should be taken from various parts of the hand. One sample of just the acid should be submitted also, for control.

Unfortunately the FAA method, does not differentiate between the various elements that it tests for. It only tests for the amount of all four elements that are present. Because barium is present in the soil, the results can be misleading. Furthermore the test has a 50% false negative rate and obviously is not extremely reliable.

## SCANNING ELECTRON MICROSCOPE

The Scanning Electron Microscope method using **x-ray analysis**. It is considered to be the most reliable test, but requires the use of a scanning electron microscope which is a very expensive piece of equipment.

Samples are taken from the hands with tape. The Scanning Electron Microscope looks for individual particles on the tape. It looks for the distinctive shape of gun powder residue and then x-rays the particles to determine the elements present within the particle. The false negative rate is only 10% for pistols but 50% for long guns. One of the nice things about the SEM method is that it is still possible to take a valid sample 12 hours after the shooting.

Worksheet: The SCIENCE behind testing for GUNPOWDER RESIDUE

PLEASE ANSWER ON A SEPARATE SHEET OF PAPER!

1. Gunpowder residue is made up of a propellant and a primer: TRUE FALSE
2. Another name for propellant is black powder: TRUE FALSE
3. Smokeless powder contains charcoal, sulphur & KNO<sub>3</sub>: TRUE FALSE
4. The primer in the cartridge ignites when exposed to pressure: TRUE FALSE
5. A gun's firing pin strikes the propellant causing it to ignite: TRUE FALSE
6. Flames from the primer cause the propellant to produce gases: TRUE FALSE
7. Forensic scientists will usually test a culprit's face for gunpowder residue: TRUE FALSE
8. The Paraffin test tests for nitrates only: TRUE FALSE
9. The + test for the Paraffin test is the appearance of blue flecks: TRUE FALSE
10. Fertilizers, nail polish & tobacco on a persons hands will test positive for the Paraffin test: TRUE FALSE
11. The Modified Greiss test will determine if smokeless powder has been used: TRUE FALSE
12. The Modified Greiss test uses normal photographic paper: TRUE FALSE
13. The positive test for the Modified Greiss test is the appearance of green specks on the photographic paper: TRUE FALSE
14. The Sodium Rhodizonate test tests for primer residue: TRUE FALSE
15. The Sodium Rhodizonate test tests for the presence of sulphur: TRUE FALSE
16. sodium rhodizonate + barium --> brown/pink color change TRUE FALSE
17. sodium rhodizonate + lead --> deep purple color change TRUE FALSE
18. The Harrison-Gilroy test tests for propellant residue: TRUE FALSE
19. The Harrison-Gilroy test will turn orange for antimony & red for lead or barium: TRUE FALSE
20. The results of the NAA test should support the results of the Harrison-Gilroy test: TRUE FALSE
21. The FAAS test tests for the presence of propellant residue: TRUE FALSE
22. The Scanning Electron Microscope test uses x-ray analysis: TRUE FALSE