Gunshot Residue Analysis

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In this Forensic Science Newsletter we will discuss the analysis of gunshot residue (GSR).

General Information

GSR is the residue deposited on the hands and clothes of someone who has discharged a firearm; was in proximity to the firearm when it was discharged; handled a firearm that has recently been fired; has touched an object that has been handled by a person who recently fired a firearm; on an entrance and exit wound; or other targeted materials.

GSR is composed of burnt and unburnt particles from the **cartridge primer, cartridge propellant (gun powder), minute fragments from the cartridge case, the surface of the missile and lubricants used on the firearms.** It is important to keep in mind you may not see the GSR. Because you cannot see it, do not assume it is not there. GSR particles are usually in the 1-10 μ range, although they may range in size from <1 μ->100 μ (a micron is 0.00038 inch), hence you may not see them. Even if the hands of the shooter are clean or the skin or clothing on the victim are clean in appearance do not assume GSR is not present. Likewise, because the alleged shooters hands are black or the skin or clothes of the victim are black do not assume this is from GSR. It may be from another source.

GSR are composed of **inorganic** and **organic components**. The **inorganic residues** primarily come from the **primer**, whereas the **organic residues** originate from both the **propellant (gun powder)** and the **primer**.

Inorganic residues typically consist of the chemical elements **lead, barium** and **antimony**. **Organic residues** consist of **explosives** and **additives**. An example of explosive is **nitroglycerine** and or **nitrocellulose**. Additives are chemical compounds which are added to the propellant to improve its performance. For example, **deterrents** are added to the powder grains of the propellant so that it burns slower, proceeding in a progressive fashion. Another example of an additive is **graphite**, which eliminates static electricity and helps the flow of the powder during the process of loading the cartridge. **Stabilizers** such as diphenylamine, ethyl centralite and or methyl centralite are also added to the propellant. The purpose of a stabilizer is to help prevent degradation of the gun powder. The nitrocellulose and nitroglycerine in gun powder will on standing, especially in hot conditions, deteriorate, releasing nitrate. Free nitrate will in turn cause nitrous and nitric acid to form, which will further degrade the gun powder. In the United States and Great Britain, diphenylamine is the most common stabilizer. Some of the other stabilizers used are petroleum jelly, calcium carbonate, magnesium oxide, sodium bicarbonate, beta-naphthyl methyl ether, resorcinol, ethyl centralite and methyl centralite.

The amount of GSR identified at the scene usually decreases as you get further from the muzzle of the firearm. The furtherest distance you can detect GSR is very variable. In the literature. For example, some of the literature quotes 20 cm (7.9 inches); some 3-5 feet (0.9-1.5 meters); others report 20-26 feet (6-8 meters) forward of the muzzle and up to 20 feet (6 meters) lateral to the muzzle.

Before continuing it is important we review the fundamentals of what occurs when you pull the trigger of a weapon. When a firearm is discharged by pulling the trigger, the firing pin strikes the primer cap, which in the centerfire cartridge consist of a brass or gilding metal cup. Within the metal cup is a pellet containing approximately 1 grain of a very explosive material, nitrocellulose and or nitroglycerine and a brass anvil. When the firing pin strikes the primer cap, it compresses the explosive material between the primer cup and the overlying anvil. This compression causes the explosive material to explode. The flame resulting from the explosion passes through holes in the anvil to ignite the propellant in the cartridge case. The ignition of the propellant results in a high temperature and pressure reaction, which propels the bullet from the barrel.

As the primer composite burns, it escapes from the gun as vapor or plume through all available openings in the firearm. It then condenses into fine particles, which settle on any surface in the immediate proximity of the discharged firearm. Factors which influence how far the particles travel is determined by the firearm and its condition, type of ammunition and air turbulence. Revolvers and semiautomatics with left and right ejection ports produce different vapor or plume patterns. As discussed above, the airborne particles consist of inorganic components, such as lead, barium and antimony and organic components from the primer and propellant.

Small arms cartridges consist of a primer, propellant (gunpowder), cartridge case, and a missile (bullet).

Primer Case & Primer

The **primer case** is typically composed of copper and zinc, both of which can be detected.

Small arms cartridges are divided into two categories based on the location of the primer: **centerfire** and **rimfire.** In centerfire cartridges the primer is located in the center of the base of the cartridge case. The chemical composition of the **centerfire**

primer in the United States and much of Europe consist of lead styphnate, barium nitrate and antimony sulfate. It is these three major components in the primer compound, which play a major role in the formation and identification of GSR:

1. Lead styphnate, serves as the **initiator**, which is set off when the firing pin strikes the primer cap.
2. Barium nitrate, serves as the **oxidizer**, which gives up its oxygen readily. The oxygen is needed to help burn the fuel.
3. Antimony sulfide, serves as the **fuel**, which burns at a very high rate. It is this initial burn, which ignites the gun powder, which in turn propels the bullet.

Besides these major components of the primer compound there are other components, which play an important role. For example, a **senstizer** is added to lead styphnate to make it more irritable and thus enhancing syphnate as an initiator. Common senstizers used are tetracen or guanylnitrosoaminoguanyltetracene. Another additive are **binders,** which hold the various components of the primer together. Various gums, such as gum arabic and gum tragacanth, starches, polyvinyl alcohol serve as binders.

Some of the newer primers are lead and or barium free. For example, there is a German company that produces cartridges that do not contain either lead or barium. You can find a mercury-fulminant based primer in ammunition made in Eastern Europe, which is also used the Middle East. Primer compounds originally were made of fulminate of mercury, however, on firing they would release free mercury. Ammunition referred to as “lead free” may contain one or more other elements including tin, titanium, zinc, aluminum, sulfur, calcium, potassium, chloride, copper, barium, antimony, strontium or silicone.

In **rimfire** cartridges, the primer is located within the rim of the cartridge case. In rimfire ammunition, the composition of the primer varies with the manufacture. Originally, rimfire ammunition made by Winchester and CCI contained only lead and barium. Before 1989 Remington rimfire ammunition contained only lead, and Federal ammunition contained lead, barium and antimony. In 1989 Remington Arms Company went from lead to lead, barium and antimony, whereas Federal went from lead, barium and antimony to lead and barium (Bryan Burnett). Currently, most U.S. manufactures and many foreign manufactures of .22 ammunition use lead and barium in their primer (Bryan Burnett). The only exception to this is Remington for U.S. manufactures ,which has stayed with a primer composed of lead, barium and antimony (Bryan Burnett). Along with antimony being a component of the primer compound it can also be found on the surface of .22 ammunition (Bryan Burnett). Rimfire primers contain a **frictionater,** the most common of which is ground glass. The sharp coroners of the ground glass provide a force to the sensitizer and initiator that compresses and ruptures the explosive crystals.
When the firing pin strikes the face of rimfire ammunition, the rim collapses, causing the back and forward edges to crush the priming compound. This reaction ignites the priming compound and initiates a flame that ignites the propellant.

Rimfire ammunition is the most common ammunition used today. The term rimfire is associated with .22 caliber ammunition.

Propellant & Cartridge Case

The **cartridge case** is the container that holds all the cartridge components together. It is usually made of copper and zinc as is true of the primer case. Some cartridge cases have a nickel coating.

Today, the gun powder used as a propellant contains as many as 23 organic compounds. Nitrocellulose is typically present along with other compounds containing nitrate or nitrogen. What must be remembered, these organic compounds can be identified. For example, one of the stabilizers used in gun powder is diphenylamine. This can be detected using reagents containing sulfuric acid.

The gun powder used today, which is known as **smokeless powder**, was first synthesized in 1884 by Vieille, a French Chemist. In 1887, Alfred Nobel developed a different form of smokeless powder. Nobel used a form of nitrocellulose, which was not as highly nitrated as Vielle's. The physical appearance of either Vielle's or Nobel's smokeless powder can be **flakes, disk,** or **cylinderical**.
There are two types of smokeless powder, **single-base** and **double-base**. Single-base is smokeless powder in which the primary ingredient is nitrocellulose, whereas double-base contains in addition, 1-40% nitroglycerine. You can differentiate between them by using mass spectrometer.

In 1933, Winchester developed **ball powder** in which the nitrocellulose instead of being colloided is dissolved completely, with the resultant lacquer being formed into small balls that constitute the powder grains. A colloidal mixture is one in which the particles are suspended in liquid or a gas and are not completely dissolved.
There are differences in how ball powder burns versus flake powder. Ball powder initially burns due to loss of surface area as it diminishes equally from all sides, until it is consumed. It burns evenly and can be very accurate in pistol and rifle loads, and some are used in shotguns. Burn rates can be from very fast to moderately slow. Flake powder burns steadily due to its thin profile, which keeps the overall surface area about the same until the burn is complete. They typically are the fastest burning and are used in shotguns, pistols, and "lite" or reduced rifle loads in small to very large volume cartridges.

There are other propellants besides nitrocellulose and nitroglycerin such as nitroguanidine, DINA (bis-nitro-ethylnitramine), Fivonite (tetramethylolcyclopentanine tetranitrate), DGN (di-ethylene glycol dinitrate) and acetyl cellulose.

Missile (Bullet)

As stated earlier, one of the components of GSR are minute fragments of the missile. Missiles fall into two categories: **lead bullets** and **metal jacketed** bullets.

Lead bullets are primarily constructed of lead to which antimony may be added to increase the hardness of the alloy. Some bullets have a ferrous alloy core. The bullets are also lubricated with grease or a lubricating compound. The purpose of lubricating compounds is to prevent lead fouling of the barrel. A cup made of hard metal, such as copper, is placed at the base of the bullet, which is called a gas check, to decrease lead deposits by protecting the rear of the bullet from melting when fired at high pressures. Bullets may also be coated in nickel, copper or a copper alloy. The purpose of this coating is to harden the bullet. Such coatings are referred to as “gilding.” Again, all of these components can be detected using appropriate analysis.

Jacketed bullets are usually copper, however some may be brass (90% copper with 10% zinc) with a lead or steal core. Some are covered by gilding metal clad steel, copper-nickel, or aluminum. There are types of small ammunition bullets with a wash of copper (luballoy). Frangible bullets are usually composed of copper and a synthetic polymer.

Particle Formation

Understanding how GSR particles are formed aids the forensic scientist in differentiating GSR particles from environmental sources of lead, barium and antimony. Because GSR primer particles are formed by rapid cooling of the vaporized lead, barium, antimony, gilding metal or lubricating compounds following high temperature burn of the primer compounds, etc., particles of GSR take on characteristic morphologies. In reference to GSR primer particles there are three fundamental types:

1. **Regular spheroids,** which are uniformly round particles ranging in size from 1-10 µ.
2. **Irregular particles**, which are formed by the fusion between small and larger particles resulting in nodular spheroids.
3. **Particles** that form as a layer surrounding the inner core of barium and antimony.

Particles formed from the cartridge or bullet contain other types of formation. Knowledge of types of particles derived from the primer, cartridge and bullet is of great importance when examining the particles on the hand of the suspected shooter.

Detection of GSR

Today, the primary techniques used for the detection of GSR are **Flameless Atomic Absorption Spectrometry (FAAS)** and **Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)**, which are **bulk analytic techniques**. For particle analysis the primary technique used is **Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS)** because of its ability to obtain both morphologic information and the elemental composition of the particles. This technique is referred to as **particle-by-particle analysis.** One of the factors that has enhanced the use of the

SEM/EDS system is it has become automated, which has made automated GSR by computer-controlled SEM the method of choice among laboratories doing these analysis.

Bulk Analytic Technique: This analytic technique can detect trace amounts of elements, such as lead, barium and antimony at the nanogram range (one billionth of a gram). Finding of these elements suggest GSR. The reason it is only suggestive is although the elements, such as lead, barium and antimony are present, it does not say where they originated from. Therefore, the finding of these elements in of themselves is nonspecific; it does not say they came from a single source, such as the discharge of a firearm.

FAAS is used in many crime labs in this country due to its reasonable cost, ease of analysis and adequate sensitivity. It will identify lead, barium and antimony from the primer and copper vaporized from either the cartridge case or the surface of the bullet.

Atomic Absorption Spectrometry uses the principle that energy absorbed by a sample can be used to assess its characteristics. When the sample absorbs energy it causes light to be released from the sample. This light is then measured by a technique, such as fluorescence spectroscopy.

Some of the older literature lists **Neutron Activation Analysis (NAA)** as a generally accepted method for analyzing GSR. NAA is a bulk method of analysis in which the inorganic components of the primer residue can be determined. NAA involves irradiation of the GSR using neutron bombardment, which forms radioactive isotopes by combining neutrons with elements within the GSR. The neutron induced radioisotopes emit x-rays, which are characteristic of the individual elements. The elements and their trace level amounts are determined by peak radiation intensities. Although NAA is very sensitive and accurate, it is not widely used due to the required reactors, the time required for the analysis and the cost.

Inductively Coupled Plasma-Mass Spectroscopy is a bulk method of analysis, which is used to measure the trace amounts of lead, barium and antimony in the primer residue. It uses a process which involves coupling an argon plasma to a radio frequency electromagnetic field at atmospheric pressure. The samples are in liquid form. Typically, the detection limits are given in parts-per-billion level.

In a study of wound samples microwave-digested and analyzed using ICP-MS to detect all elements present at measurable levels in GSR, shot versus normal, uninvolved tissues could be distinguished. Also, jacketed and unjacketed bullet types could be distinguished.

Particle-by-particle Analysis: SEM in contradistinction to FAAS and ICP is a particle-by particle analysis. It looks at the individual characteristics of each particle. Consequently, it can identify the presence of lead, barium and antimony, to a single particle. SEM can detect a single, micron-ranged GSR particle, which is picogram (one trillionth of a gram) level analytical sensitivity.

SEMs usually have an EDS, which determines the elements present in the sample being analyzed. The EDS unit measures very minute amounts of ionization current when x-ray is absorbed in a silicon sensing element (silicon diode). To put this simplistically, a EDS detector measures the amount of energy carried by an x-ray photon. Successive x-rays from a single element is represented by a finite peak for that element. Each element has its own peak in a sense, hence, the ability to identify each element. It should be kept in mind the heavier elements commonly have additional peaks not present in the lighter elements.

Detection of Gunshot Residue

Any hand body part that was close to the discharged firearm can have GSR. This also applied to the clothing not only of the victim, but the shooter, as well as those in proximity to the scene. The clothes on the victim should be kept on the body until it is removed immediately before doing the autopsy. Removal of the clothing before the autopsy may modify the GSR on the body, most especially near the entrance wound and or exit wound. Typically, the entrance wound will have more GSR than the exit wound. In one study a fifth of exit wounds showed microscopic evidence of GSR.

Clothing from the victim, the alleged shooter and other persons present at the time of discharge of the firearm should be retained for examination. Clothing from the victim, most especially that clothing perforated by the bullet should be examined with a dissecting microscope.

Thorough recovery and analysis of GSR should reveal the quantity of lead, barium and antimony on the four surfaces of the hands. Such careful collection and analysis should also show the distribution of these elements on the hands. With such data one can then determine that these metals were deposited due to firing of the weapon. The distribution of these metals is important for it provides information whether the person was the shooter or victim. For example, finding these metals on the palms of the hand instead on the back of the hand, or only a minimal quantity on the back of the hand, suggest the person was the victim as they raised their hands in a defensive posture rather than firing the weapon. However, there is another possibility, the person could have recently handled a firearm, which had been fired, and thus picked up the GSR still remaining on the surface of the weapon. What may be helpful in determining which scenario took place is to quantify the amount of lead, barium and antimony present on the palm versus the back of the hand. Typically, the palms of the hands of the victim will have a greater quantity of these elements than the back of their hand. If the victim had handled a recently fired weapon, GSR will be found only on the palm.
In one lab, for these metals to be significant lead must be at or above 800 ng, barium 150 ng and antimony 35 ng (nanogram). One gram contains 1,000,000,000 nanograms. What is important to keep in mind, the lab test must include all elements present in that primer to be valid. As an example, if the involved primer contained lead, barium and antimony, all three elements must be present and at least lead must be elevated. Should you only find barium, then the person may have had their hands recently in dirt rich in barium. **For this analysis to have scientific validity you must determine not only the presence of the primer elements, but also their distribution and quantity.**

If you are dealing with GSR from the discharge of a rifle or shotgun, GSR will typically not be found on the hand used to discharge the weapon. It is however, usually found on the non firing hand or in the crook of the support arm.

Other Determinations

It is important to remember, when a bullet passes through an object, whether that be an intermediate or the victim, it may carry with it minute fragments of the object. For example, if the bullet passed through a metal screen before entering the victim, it may contain minute fragments of the screen. The bullet on passing through the victim may contain fragments of bone, other tissue or blood, which on DNA or RNA analysis can confirm it was this bullet which passed through the victim. You can also type the blood from that on the bullet and compare it to the victim. There are instances in which a single missile has passed through a person and entered another person. DNA or RNA analysis of the tissue on the tip of the missile determined it was this single missile that struck both victims, perforating the one and penetrating the other. There are also occasions in which determination of blood types from blood on the tip of the missile showed it came from both victims.

In firing the weapon blood from the victim may splattered on to the firearm and or hand of the shooter. DNA or RNA analysis of this blood splatter can show it came from the victim.

DNA can also be identified on the firearm, clothing or objects touched by the alleged shooter due to cells from their hands being left on these surfaces.

Petroleum based products found in lubricants used on firearms can be identified by gas chromatography.

Fingerprints may be found on cartridges and shell casings as well as the firearm.

Summary

For GSR analysis to be meaningful and make a significant scientific contribution to crime scene analysis it must be accomplished in a thorough, pains taking fashion. The thoroughness not only applies to the collection of evidence at the scene, and at the time of the autopsy, but also by those who are doing the technical analysis of the evidence. They must be thoroughly trained, have appropriate equipment, and the knowledge of the capabilities of their equipments and most especially their limitations. If properly done GSR analysis can make a significant contribution to the resolution of a crime scene.