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Analysis of Gunshot Residues Deposited on Different Fabrics (Ammunition and Firearm Effect)

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ABSTRACT

Gunshot residues (GSR) are the particulate matter that exits a firearm after the shot. Studying their deposition, morphology, and chemical content, it is possible to reach some conclusions regarding the shooting distance, the type of ammunition utilised, the recognition of entrance and exits holes and, most importantly, the guiltiness or not of a suspect from which the residues are collected. This thesis investigates the morphology and the chemical composition of the residues expelled from different ammunitions, showing the main differences and peculiarities between them by means of the Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray (EDX) detector; moreover, also a statistical analysis on the persistence and sampling efficiency of the residues expelled in a close range frontal shot on different substrates and with different ammunitions is performed, showing how the polyester is largely the best fabric to collect and sample GSR with respect to the other substrates utilized which are the cotton and the wool and that the M4 Benelli utilized with the Fiocchi calibre 12 ammunition which contains pellets produces the largest number of residues with respect to the other ammunitions used, the Fiocchi calibre 9x21 shoot with a Glock, the Hornady 50 AE shoot with a Desert Eagle and the Royal Buck calibre 12 containing buckshot shoot with the M4 Benelli.

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1. Introduction

The analysis, study and characterization of the gunshot residues (GSR) are all part of the branch of the forensic science which task is to discover the shooting distance, the ammunition utilized, the recognition of entrance and exits holes and most importantly if a suspect has fired or not a firearm in the hours before the sampling by analysing the residues expelled from the firearm at the moment of firing and deposited on the shooter, the bystanders and all the surrounding objects; this method is probably the only existent one able to correctly fulfil this very difficult task. Since from a report on the GSR a court can judge a suspect to be guilty or not, it is possible to immediately understand how difficult could be such analysis which is full of variables and influencing factors which could modify the final results. Moreover, this science is in constant evolution; when a discovery is made, all the precedent methods need to be revised and changed according to the most recent trends. Last but not least, it is a very young science, which was born around the middle of the twentieth century because before that time there weren’t the technologies able to effectively fulfil the needs of the investigators, and it is still today full of unexplored fields which can bring in future additional information to the GSR analysis, helping to reach unequivocal conclusions about the guiltiness or not of a suspect, which is probably the most important aim of the entire branch. This is why this thesis deals with the analysis of GSR, trying to aid additional information to this evolving science and hoping to throw light to the newest fields that have not been analysed before.

2. Aim of the Thesis

This thesis deals with the identification, analysis and characterization of the GSR by using the most recent methodology and technology, the analysis with a SEM equipped with an EDX detector. The residues are deposited on different substrates, which in practice are different fabrics, utilizing different types of ammunitions fired with different firearms. The aim is to characterize the different GSR both morphologically and chemically trying to differentiate them according to the ammunitions from which they are generated. Moreover, thanks to the exceptional magnification capacities of the utilized SEM, via the images of the residues, also a nano-characterization is performed in order to aid some information and better understand the GSR formation. Last but not least, also a statistical analysis is conducted trying to demonstrate that the persistence and the sampling efficiency of the GSR changes according to the fabric on which they deposit and are sampled and according to the ammunition from which they are generated.

3. State of the Art

3.1 What are the Gunshot residues?

Gunshot residues (GSR) are burnt and unburnt particles that are deposited on the hand of a shooter when a firearm is fired and that mainly come from the primer mixture, as well as the propellant, the bullet, the cartridge case, the firearm itself and are also composed of particles coming from grease and lubricants [1][2]; since their origin is quite variable, they can also be called firearm discharge residues (FDR) or cartridge discharge residues (CDR) [2]. The analysis of GSR is probably the most promising practice used to try to determine if a suspected individual has fired or not a firearm and can also fulfil needs like estimation of firing distance, time since discharge, and relating a bullet with an injury [3]. In general, collection of evidence materials from people and subjects related to a shooting incident and detection of GSR may contribute to establishing some of its circumstances and possibly to the reconstruction of its course [4].

GSR are highly characteristic and uncommon with respect to everyday life particles that can be found on hands of people. The most common characteristics of the GSR particles are a specific chemical composition, in which it is common to find lead, antimony and barium, which are the particles from which usually the primer of the ammunitions is formed, and a specific shape and morphology, since they are usually sphere like and not crystalline on the surface [4]. These combustion materials from the primer, propellant, and other sources escape from weapon openings as vaporized materials and solidify into particulates, with size ranging from 0.5 μm or 10 μm or even more [2]. The science that is concerned with the primer ignition, the burning of the propellant powder, and the resulting internal pressures and torques as the bullet is forced through the barrel is called interior ballistic [5].

From this brief introduction about the GSR is already possible to understand how difficult and full of variability is such a phenomenon, especially considering that there are a lot of manufacturers in the world, which use a lot of materials and chemical compositions to produce firearms and its related components; environmental conditions, type of substrate on which GSR deposit, environmental source of GSR-like particles, the transfer phenomenon and many other issues that are exposed later on in the thesis make understand why this branch of the forensic science is in constant evolution.

3.2 The Formation of Gunshot Residue particles

Before explaining the formation of the GSR it is mandatory to give an overview on the phenomenon that stand on the basis of the gunshot residues ejection from a firearm, which basically is the explosion. Moreover, it's not possible to understand why GSR form and their classification without giving an overview on the firearms and ammunitions.

3.2.1 The Explosion

It's called explosion whatever phenomena which deals with a rapid formation of a great quantity of gas, at high temperature, and the consequent increase of pressure and volume of the gas, according to the ideal gas law, which simply directly relate temperature with the product of pressure and volume. This means that depending on the volume, an explosion could be very destructive or not; if the explosion happens in a closed volume, it means that the volume in the ideal gas law is fixed, so when the temperature increases, the pressure increases a lot and this produces strong mechanic actions on the walls of the closed volume. Obviously also the contrary stands, since if an explosion happen in a completely open volume, the pressure will not increase at all. Usually there are four parameters that characterize an explosion which are the maximum pressure reached, the velocity at which that pressure is reached, which is the main parameter that describes the strongness of an explosion, the volume in which the explosion happens and the flame propagation speed. The latter two parameters are directly related as showed in (1), in which K is a constant. This simply means that smaller the volume, the higher the strongness of the explosion. Depending on the strongness of the explosion, the effects on the bystander things could be of different types, like the fragile fracture, the ductile fracture with deformations and usually the projection of parts.

$$\left(\frac{dP}{dt}\right)_{max} \cdot \sqrt[3]{V} = K \tag{1}$$

According to the flame propagation speed an explosion could be divided into two categories, the deflagration and the detonation. If the flame propagation speed is smaller than the speed of sound, the explosion is called deflagration. It is considered the less rapid form of explosion and it is possible to discern three different phases, which are the ignition, the inflammation of the all mass of the explosive and the combustion. The deflagration is the main phenomenon that happen in the firing chamber of a firearm when the trigger is pulled and, in some types of firearms, makes the expulsion of the used cartridge possible. If the flame propagation speed is a lot bigger than the speed of sound, the explosion is called detonation, typical of disruptive explosives and involves huge pressures, also in an open environment, in a very small time; this is why in this case, no phase can be distinguished [6]. It is important to notice that these two types of explosions are not two different things but are simply two aspects of the same phenomenon. In fact, all the fuels can deflagrate or detonate, according to the volume in which the explosion happen. For completeness, there is also another type of combustion, which is called slow combustion or calorific conductivity, which happens in the order of some seconds or minutes. With the slow combustion, using a great amount of fuel, it is possible to generate a burst, but is not possible to obtain an explosion [6].

In general, to make an explosion happen, it is needed a fuel, an oxidizer and a primer to start the explosion. The latter is a very small amount of energy compared to the one released by the subsequent explosion, and could be a small heating, a small shock, a rubbing, an electric discharge, an adiabatic compression and so on. Obviously, the decomposition of the oxidizer substance will happen more or less easily according to its chemical stability, which determines also the entity of the priming action. When an explosion starts, it is not possible to stop it since the heat generated fuels the explosion itself.

3.2.2 Classification and Composition of the Explosives

An explosive is a substance, which could be at solid, liquid or gaseous state, that because of an external cause is able to develop a great quantity of gases at high temperature in a very small time. There are two types of explosives; in some cases, the oxygen that makes the explosion happen is given by a substance, which is called oxidizer, that when the explosion happens, release the oxygen which reacts with the fuel substance oxidising it. This explosive is called explosive mixture and the phenomenon described earlier is also called combustion [6]. The most common example is the black powder, one of the first explosive substance used in ancient times in the firearms, which is formed by the potassium nitrate (saltpetre), which chemical formula is KNO_3, the oxidizer, and by two fuels, which are the charcoal (C) and the sulphur (S), respectively in composition of 75 %, 15 % and 10 % [6]. The complete reaction is showed in Figure 1.

$$\begin{aligned}&74KNO_3+30S+16C_6H_2O\ \text{(charcoal)}=56CO_2+14CO+3CH_4+2H_2S+\\&\quad 4H_2+35N_2+19K_2CO_3+7K_2SO_4+2K_2S++8K_2S_2O_3+2KCNS+\\&\quad (NH_4)_2CO_3+C+S+665\ \text{kcal/kg}\end{aligned}$$

Figure 1: Complete combustion of the black powder [7].

In other cases, oxygen and fuel are mixed together in the same molecule. They are called chemical explosives and are oxygenated compounds that are usually obtained via the action of the nitro sulfuric mixture, which is formed by nitric and sulfuric acid, on appropriate organic substances. One of the most common example is the nitroglycerin, which molecule is showed in Figure 2; it contains both the oxidizer, the oxygen, and the fuels, the carbon and the hydrogen and is obtained by the nitration of the glycerine. Another common chemical explosive is the TNT, obtained by nitrating toluene, which formula is $C_7H_5N_3O_6$ [6].

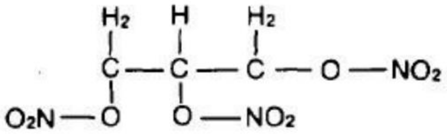


Figure 2: Molecule of nitroglycerin [6].

3.2.3 Firearms

There are a huge number of firearms types, but regarding this thesis, which deals with the identification of GSR in order to try to correlate a suspected individual to a shooting incident, only the submachine guns will be discussed. Notice that a submachine gun is a lightweight machine gun that is handheld as compared to a machine gun that is bipod/tripod mounted for continuous fire.

Between submachine guns, pistols and revolvers are usually described as handguns, and rifles and shotguns as shoulder guns, as this is their normal mode of use [5]. The name "firearm" is due to the flame produced at the muzzle end when a firearm is discharged; the muzzle is the front part where the bullet emerges from the barrel. In general, a firearm is a tool designed to discharge lethal projectiles from a barrel toward selected targets [5].

In general, submachine guns can be divided into two main groups, depending on the type of bore that they have, rifled or smooth bore. In rifled firearms, the bore contains a number of grooves parallel to one another and cut with a spiral twist from the breech to the muzzle. The lands are the high places between the grooves. The calibre is determined by the internal diameter of the barrel, measured between two opposite lands. The rifling of the barrel grips the bullet and causes it to rotate, thereby preventing it from wobbling or turning over in flight and allows it to reach greater distances. Notice that the bullet is usually slightly bigger than the diameter of the bore [5]. In contrast, smooth-bore firearms have a perfectly smooth bore from one end to the other. The gauge of smooth-bore barrels is determined by the number of spherical balls of pure lead that are needed to make up 1 lb, with each ball fitting separately and exactly inside the bore [8]. In Figure 3 is showed a schematic representation of a smooth and a rifled bore.

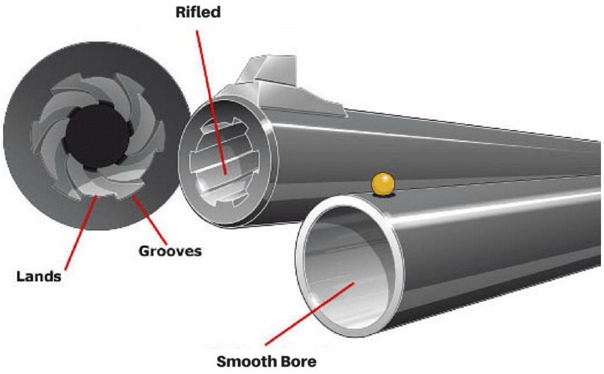


Figure 3: Schematic representation of rifled and smooth bore [9].

Rifles are firearms with a long-rifled barrel and a shoulder stock. They can be manual or semi-automatic, depending on the reloading mechanism. Manual when the ejection of the spent case and loading of a new cartridge is accomplished by hand operation of a bolt, lever, or slide [8]; an example is showed in Figure 4.

Figure 4: Winchester model 70 308 bolt action rifle [10].

On the contrary, a semi-automatic rifle uses the gas or recoil of the gun to eject the spent casing and load a new cartridge into the chamber each time the trigger is pulled [8]; an example is showed in Figure 5.

Figure 5: M1 carbine 30 semi-automatic rifle [8].

Instead shotguns are shoulder-stocked firearms with a long barrel. The difference with respect to the rifles is that the shotgun barrel is usually a larger diameter and not rifled. Moreover, as will be described in 3.2.4, also the type of ammunition used is different between rifles and shotguns. An example of a shotgun is showed in Figure 6.

Figure 6: REM model 58 12-gauge semi-automatic shotgun [8].

Regarding pistols, these are firearms with a short-rifled barrel that is fired with one hand. There are three general types of pistols which are the single shot, the revolver, and the semi-automatic pistol. The single shot pistol allows the shooter to fire one shot at a time and must be manually reloaded each time. The revolver has a revolving cylinder, which contains many firing chambers. After a shot is fired, the chamber revolves, placing another ammunition in line with the firing pin, thus allowing the shooter to fire another shot without manually reloading. This process can be continued until all of the bullets in the chambers are fired. Some revolver models have up to ten firing chambers [8]. An example of a revolver is showed in Figure 7.

Figure 7: An example of a revolver, the S&W model 629 [8].

The semi-automatic pistol is very different from the single shot pistol and the revolver. It contains a magazine that automatically loads the ammunition into the chamber following the discharge. The mechanism of the semi-automatic pistol also discards the expired cartridge casing by means of an extractor. As the breechblock moves back after the firing of the ammunition, the ejector expels the spent casing. In fact, after every shot the semi-automatic pistol expels the spent cartridge, so that they can be recovered from the crime scene, while with the other two types of pistols, this is not possible [8]. An example of a semi-automatic pistol is showed in Figure 8.

Figure 8: An example of a semi-automatic pistol, the colt 1911 A1 [8].

However, whatever type of firearm is considered, the construction of it is quite simple; at the rear of the rifled or smooth bore there is the chamber, whose diameter is normally larger than that of the bore and contains the ammunition. The transition from the chamber to the rifled or smooth section is formed in a cone shape and is called the forcing cone. The tube is sealed at the rear by the breech block, which can be constructed in different ways to suit the type of ammunition to be used, which must be designed to withstand the maximum pressure encountered during firing. With usual ammunitions, the sealing of the breech is provided directly by the cartridge case. With caseless ammunitions, special seals are required [11]. A schematic representation of a rifled loaded gun tube is showed in Figure 9.

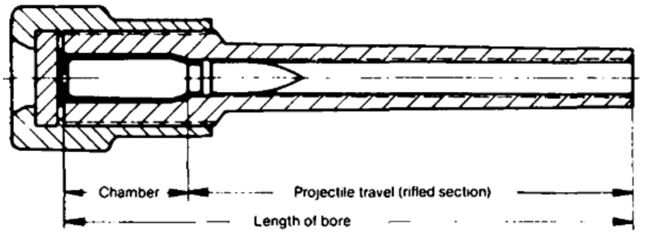


Figure 9: Schematic drawing of a rifled loaded gun tube [11].

Regarding the materials used to build the firearms, chromium–molybdenum steel is the basic material for the modern firearms industry. It possesses good tensile strength, resists wear, and has good machining properties. Also chromium-molybdenum-vanadium steel, carbon steel and stainless steel are used. The general trend is toward lightweight handguns and rifles and increasing use is being made of polymers (plastics) and rubbers for the manufacture of parts such as stocks, grips, frames, magazines, and so forth. These materials have considerable advantages, being lightweight, durable, inexpensive, noncorrosive, and easily molded to any required shape. Other less common materials, like nylon, polyurethane, fiberglass, Kevlar reinforced with fiberglass or carbon fiber, or thermoplastic resin reinforced with glass and ceramics may be used. Moreover, practically all the produced firearms are surface coated, usually to get rid of reflections from bright surfaces which could dazzle the firer and/or reveal the firing position to the enemy or game, to improve the appearance of the firearm, and more importantly to provide a degree of protection against corrosion. The vast majority of firearms currently manufactured are finished by the use of a blackening solution containing sodium hydroxide, potassium nitrate, and sodium nitrate in the typical ratio 65:25:10, respectively, but also electrostatic spray painting, epoxy, zinc chromate, and Teflon are used [5].

3.2.4 Ammunitions

There are a huge amount of types of ammunitions and also a huge number of manufacturers. An entire live round of ammunition is generally constituted by the primer, the propellant, the cartridge casing and the projectile [8]. The next paragraphs will deal with each component listed before, explaining the characteristics and also their most common chemical compositions.

3.2.4.1 The Cartridge

There are two main types of cartridges, one for the rifled bore and one for the smooth bore. Regarding the cartridge used for the rifled bores, it is possible to divide them in two different main categories, which are the rimfire cartridges and the centrefire cartridges. The rimfire cartridges are the most commonly used type of cartridges; the term "rimfire" is associated with .22-caliber ammunition. The priming compound is contained in the rim area of the casing around the cartridge [8], which also serves to correctly place the cartridge in the firing chamber of the firearm. In this type of cartridge, the primer mixture is in direct contact with the propellant. This is extremely important for the GSR analysis since being in contact with the propellant, the primer mixture doesn't need to contain compound like antimony, calcium, silicon or aluminum, because the fuel compounds are already present in the propellant [6]. In Figure 10 is showed a typical rimfire cartridge.

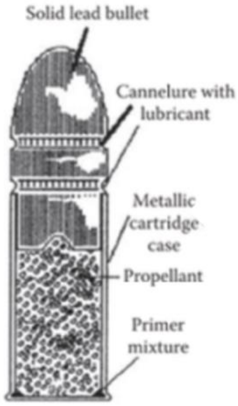


Figure 10: A typical rimfire cartridge [5].

On the contrary, the priming compound of the centrefire cartridge is located in self-contained primer cups in the centre of the head end of the cartridge. Centrefire cartridges are commonly used in .38 Special calibre weapons [8]. In Figure 11 is showed a typical centrefire cartridge.

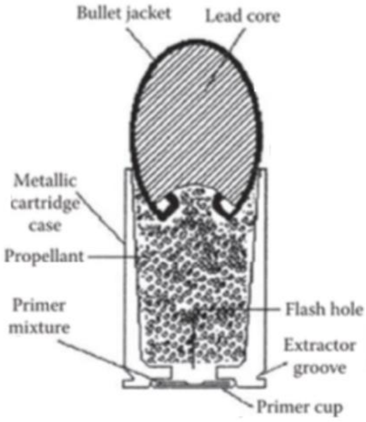


Figure 11: A typical centrefire cartridge [5].

These cartridges can be further divided into two classes, depending on the design of the central primer cup, and they are called Berdan cartridge or Boxer cartridge. Their main differences will be discussed in 3.2.4.3, which is the paragraph related to the primers. Berdan cartridges are used mainly by former Eastern Bloc and Asian manufacturers and Boxer cartridges are used by most European and American manufacturers [12].

Regarding the typical cartridge used for the smooth bores, instead of a single bullet, shotgun ammunition typically contains numerous spherical lead balls which are totally enclosed within the cartridge case and are usually called pellets. These pellets are contained in the upper part of the shotgun cartridge and to prevent distortion during discharge, a shot cup, that encloses the shot as it travels through the barrel, is used, which falls away when it exits the muzzle. Between the pellets and the propellant there are wads, used to provide a gas tight seal as the projectiles pass into the barrel and to close the mouth of the cartridge case. Wads are shoot out from the barrel of the shotgun but due to their shape they only travel a short distance and can provide some information about the primer and propellant types, and physical examination can sometimes reveal the calibre and give an indication of shot size [5]. Since the primer in the shotgun cartridges is in the centre of the metallic base, these cartridges are considered as a third type of centrefire cartridges and are called battery cup.[12] A scheme of a shotgun cartridge is showed in Figure 12.

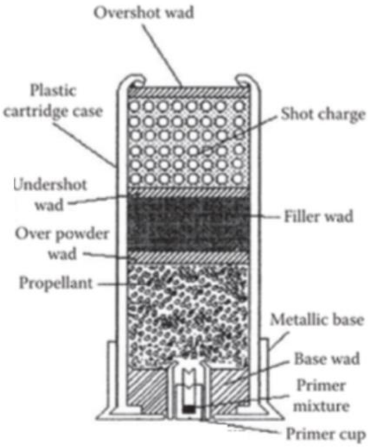


Figure 12: A typical shotgun cartridge [5].

3.2.4.2 The Cartridge Casing

The cartridge casing is the metal casing that holds together all the components of the cartridge. There are five subtypes of cartridge casings: rimmed, semi- rimmed, rimless, belted, and rebated. The shape of the cartridge case may be straight, tapered, necked, or tapered necked. It is not the aim of this thesis to explain all these variants on the shape of a cartridge casing, which mainly depends on the role of the ammunition, the type of weapon, the design of the bullet to be used and the type of ignition system. However, the general purposes of the cartridge casing is to maintain together all the components of the ammunition, to seal the primer and the propellant against moisture and oil, to assure constant performances independently of weather and storage time and to be relatively cheap and easy to manufacture.

Moreover, it needs to retain the bullet for a period after ignition to allow the propelling gas pressure to build up sufficiently to achieve peak performance and to be strong enough to resists to high forces and pressures but also to ensure the hermetic closure of the breech thanks to its elastic expansion against the chamber walls at the moment of firing, which phenomenon is called obturation. This is an extremely important function of the cartridge case as this prevents the rearward escape of gases. Such an escape of gases would reduce the velocity of the projectile and consequently the efficiency of the firearm and could possibly cause a malfunction in the firearm mechanism [5] [13].

On the rifled bores cartridges, the casing is mostly composed of brass, which is 70 % copper and 30 % zinc, mainly due to its performances, since it is strong, sufficiently ductile and nonrusting, cheap, and easy to manufacture, being suited to drawing operations. The type of brass used can change from manufacture to manufacture. Notice that if the brass in the cartridge case is too soft, it will not spring back from the chamber walls, which will probably make extraction of the spent cartridge case very difficult. If the brass is too hard, the cartridge case could crack because it is too brittle and jam the firearm mechanism. The base of a cartridge case must be strong enough to withstand ramming and extraction while the neck of the case must be strong enough to rigidly support the bullet yet flexible enough to expand and seal the chamber during discharge. In fact, the thickness of metal in a cartridge case is carefully controlled and decreases from the base to the neck. High-velocity cartridge cases are tapered and necked to avoid extraction difficulties which would be experienced if cylindrical cases were used in firearms with high chamber pressures. The feeding and extraction mechanism of the firearm coupled with the type of ignition system dictates the design of the base of the cartridge case. The joint between the primer cup and the outside of the cartridge case base is sealed with lacquer to prevent the ingress of moisture and oil. Sometimes the mouth of the case is internally varnished, just before inserting the bullet, to waterproof the joint and to provide resistance to the pressure of the propellant gases [5]. Notice that copper alone is a good material for making cartridges, but it lacks the strength to withstand the high pressures of smokeless powder loadings, while pure zinc is too soft; this is why brass is the most used material. Cartridge casings are obtained with a series of deep drawing and draws from rectangular brass tapes between 3 and 4 millimetres thick [8].

Also steel can be used, but although steel is much cheaper, about a quarter of the cost, steel rusts and also abrades the chamber. Moreover, steel is more difficult to work with and requires special lubrications. This results in increased wear on manufacturing equipment, which offsets the cost of the raw material. Sometimes, cases of ammunitions are also composed by polymer coated steel and in some instances, steel cases are "washed" or electroplated with copper or nickel to prevent corrosion and provide an aesthetic finish. Some .22 calibre ammunitions have cobalt-plated cases [12]. On the contrary shotgun cartridge casings are usually made of plastic with a brass or coated steel base and they have a cylindric shape.

Last but not least, current trends in firearms and ammunition are toward lighter and easier to carry ammunitions. This is why some manufacturers are trying to produce caseless ammunition, meaning with combustible cartridge cases and primers. The disadvantages of caseless ammunition include the very high cost of totally new weapons and ammunition manufacturing systems, relative fragility and sensitivity of the ammunition, and difficulties with weapon maintenance and repair in the field. Advantages of caseless ammunition include space and weight saving, a cost saving over brass-cased ammunition, a material saving since copper is a critical material during wartime, and a higher cyclic rate of fire made possible because the extraction and ejection cycle of conventional firearms is no longer necessary. Caseless ammunition has no cartridge case to serve as a heat sink and barrier between the propellant and the hot chamber walls. The problem of "cook-off," that is, the heat rather than the firing pin causing the cartridge to discharge, has always been a major disadvantage with caseless ammunition. Only changing the propellant composition, it is possible to solve this problem [5]. Since by now disadvantages overcome advantages, caseless ammunitions are still not used nowadays.

3.2.4.3 Primers

Primer mixtures are contained in the primer cup; both the weight, which could vary between 0.013 g and 0.352 g and the designs of the primer cups, usually made of brass or Ni-plated brass [8], differ according to the type of ammunition used [13]. In rimfire ammunition the priming composition is housed inside the cartridge case in the hollow perimeter of the base while for centrefire ammunition is housed in small metal cups which fit into a recess, called the primer pocket, in the centre of the base of the cartridge case and could be Berdan or Boxer. The only difference between the two types is the design because the Berdan primer does not have an integral anvil, as the anvil is part of the cartridge case, whereas the Boxer primer has its own anvil which is inserted into the primer cup. Moreover in the Boxer cartridge there is only one flash hole while in the Berdan one there are two flash holes; the flash holes are the passages that connect the primer cup with the area in which there is the propellant, so they are the passages in which the deflagration of the primer mixture passes and goes toward the propellant. Boxer primers are preferred because they are replace-able [5]. In Figure 13 is showed a schematic representation of the Berdan and the Boxer primer design.

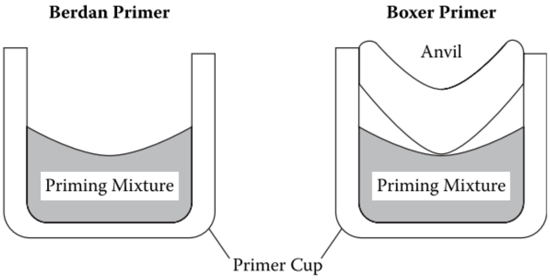


Figure 13: Berdan and Boxer primer designs [5].

In the shotgun cartridges the primer cup is in the centre, exactly like the centrefire cartridges. Generally speaking, primer cups for rifles differ in size, structure, and amount of priming composition from those used for pistols and revolvers, due to the higher amount of propellant used and the heavier blow they receive from the firing pin.

Primer cups are usually made of cartridge brass, although copper, nickel-plated copper or brass, copper alloy, cupronickel, and zinc-coated steel cups are also encountered [8]. A metal, plastic, or paper disc is often placed over the priming mixture inside the primer cup. These discs provide a physical barrier to hold the priming mixture in the cup during transport and protect it. Paper discs are mainly resin coated. Tin foil is also used for this purpose in some ammunition, particularly from eastern Europe [12].

Primers chemical composition is probably the most important aspect in the field of the GSR analysis, since most of the GSR particles come from the primer mixture, specifically the non-volatile species. Priming compositions for firearms ammunition are mixtures which, when subjected to percussion, provide a sudden burst of flame that serves to ignite the propellant within the cartridge case. A priming composition must deliver a relatively large volume of hot gases and hot solid particles without the development of a detonating wave. The ideal priming composition would consist of a cheap, readily available, relatively safe to handle, simple chemical compound of uniform granulation which when subjected to impact would undergo rapid, highly exothermic decomposition. The rate of burning, volume of gases, weight of solid particles produced, and the duration of the flame are the major influences on the efficient functioning of a priming composition. Since in practice no single chemical compound meets all these requirements, modern primer composition are a mixtures of different compounds [8].

Igniting the propellant was a big problem in ancient times. All the ancient means of ignition, from the hot wire to the flintlock, were dependent to a greater or lesser extent on the weather conditions and none offered the reliability of ignition experienced with modern ammunition. The first instant ignition was made of mercury fulminate. With the introduction of brass cartridges, since mercury react with Zinc and embrittle brass, other priming compositions were invented. However, it is rare but is still possible to find some old ammunitions that use as primer this compound but notice that it is rarely found in correspondent GSR probably due to its volatility and the fact that during firing it is expelled away from the firer. Moreover, in parallel with mercury fulminate, also potassium chlorate was used a lot in priming compositions, but problems of firearm rust were largely present, and so it is very rarely used nowadays. However, if found, usually the primer cup is protected from rust and corrosion by a foil of lead in the case of potassium chlorate, or a foil of brass in the case of mercury fulminate, which can react with the zinc of the brass and embrittle the primer cup, resulting dangerous for the shooter. This is very useful for the purpose of the GSR analysis because if zinc is found in the GSR, probably the primer composition contains mercury fulminate. As seen, the objectives were to produce a satisfactory priming composition which was both noncorrosive and non-mercuric (NCNM)[5][12].

The NCNM solution was reached with the production of the Sinoxid type primer which is mostly made by three components: the initiator, lead styphnate ($C_6HN_3O_8Pb$), which is set off with a sharp blow when the firing pin strikes the primer cap, and has substituted the mercury fulminate.

The oxidizer, usually barium nitrate ($Ba(NO_3)_2$) but also potassium chlorate ($KClO_3$) could be used, which gives up its oxygen readily, needed to burn the fuel which usually is the antimony sulphide (Sb_2S_3), but also calcium silicide ($CaSi_2$) and aluminum are used, which burns at very high rate and ignites the propellant; fuel is necessary to prolong the combustion long enough to ignite the propellant. Notice that sometimes, a single component may serve two purposes; for example, antimony sulphide acts as a fuel as well as a sensitizer to friction. Moreover, the sensitivity of priming compositions can vary also by careful control of the granulation of each of the ingredients [13].

Other common components are the sensitizers which are added to the styphnate to make the mix irritable, due to the sluggish nature of the styphnate; one of the most common sensitizer is the tetracene. The frictionators, needed for rimfire primers, commonly composed of ground glass. The sharp corners of the frictionator provide a force to the sensitizer and initiator that compresses and ruptures explosive crystals. Binder gums are used to hold the primer mix in place and they are usually gum arabic, gum tragacanth, glue, dextrin, sodium alginate, rubber cement, and Karaya gum [12]. Explosives such as PETN, TNT, and DDNP, may be used to provide heat and energy to the reaction [8]. The typical composition of the Sinoxid type primer is showed in Table 1. Notice that with the introduction of smokeless powder, used to substitute the black powder, it is needed a hotter primer to ignite it and Sinoxid responds also to this requirement. Propellant will be discussed in 3.2.4.4.

Table 1: Typical composition of a Sinoxid type primer [8].

Lead styphnate	25 % to 55 %
Barium nitrate	24 % to 25 %
Antimony sulphide	0 % to 10 %
Lead dioxide	5 % to 10 %
Tetracene	0.5 % to 5 %
Calcium silicide	3 % to 15 %
Glass powder	0 % to 5 %

It is important to point out that manufacturers of primers do not disclose the information regarding the primer composition so the only way to discover primer compositions is by means of chemical analysis. It is vital that examiners conduct routine analysis on all primers and that they keep abreast of the findings reported by others, since primers change continuously and since most of the GSR particles, as already stated, comes from the primer mixture [8]. For example, since in the rimfire cartridges the primer compound doesn't need to contain the fuel, in the residues expelled during discharge, the antimony sulphide will not be present.

In recent years, since with conventional primers, when discharged, a firearm expels lead, antimony and barium, which are unhealthy especially for people which utilize firearms everyday like firearm instructors, heavy metal-free (HMF) primers were invented. Lead styphnate is replaced by 2-diazo- 4,6-dinitrophenol (diazole) and the barium nitrate and antimony sulphide are replaced by a mixture of zinc peroxide and titanium metal powder.

This type of primer is called Sintox and the use of this primer coupled with a totally jacketed bullet, meaning with the base also enclosed, entirely eliminates the health hazard problems, since in the GSR heavy metals will be no more present. Notice that since lead is the most unhealthy specie for human being, some manufacturers simply built primers without it, using strontium nitrate, potassium nitrate, barium nitrate and elements like boron and aluminum; these are simply called lead-free primers [13]. HMF primers and lead-free primers will be largely discussed in 3.4.

The primer composition of the smooth bore firearms like shotguns obviously contain the same primer mixture of the rifled bore ones, but in a greater quantity since the shotgun cartridges require much more initiating energy with respect to the rifled bore cartridges [6].

Last but not least, some primers, at the moment only in Germany, produced by RUAG Ammotech and MEN, contain in the primer mixture also a very rare element, usually gadolinium, to distinguish these ammunitions, usually given to police forces or institutional clients, from the ones derived from other sources; these are called marked ammunitions. However, it is a very rare practice nowadays [6]. Notice that another practice is to mark ammunitions using gallium in the propellant; however, this element is rarely detected in GSR and it’s far better to mark the primer with gadolinium, which on the contrary is easily detectable [14].

In general, primer composition can be divided into six categories, as showed in Table 2.

Table 2: Classification of primer mixtures [12].

Mercuric and corrosive	Mercury fulminate, potassium chlorate, and antimony sulphide based sealed or not with a tin foil.
Mercuric and Non-corrosive	Mercury fulminate, barium nitrate, and antimony sulphide based sealed or not with a tin foil.
Non-mercuric and corrosive	Potassium chlorate, lead thiocyanate, and antimony sulphide based.
Non-mercuric and non-corrosive	Lead styphnate, barium nitrate, and antimony sulphide based (Sinoxid type), sealed or not with a tin foil. These types of primers could be encountered with some variations: o Aluminum powder as frictionator and fuel. o Calcium silicide in place of antimony sulphide. o Glass frictionators, like borosilicate or soda-lime glasses, in place of antimony sulphide; sealed or not with a tin foil; common to .22 calibre ammunition. o Lead thiocyanate in place of antimony sulphide; mainly in 0.22” rimfire ammunition type. o Only lead styphnate; typical of Remington, “U” or “REM” stamp.
Miscellaneous	Phosphorus-containing Eley (UK) 0.22" rimfire ammunitions. Primer composition is lead styphnate, barium nitrate and lead thiocyanate based, while phosphorous is present in the primer due to the manufacturing process of lead styphnate.
Lead-free/Heavy metal free ammunitions	The primer composition of these types of ammunitions could contain the following elements: Sb/Ba; Al/Ba/Si; Al/Sr; Al/Na; Al/Si/K; K/Cu/Zn; K/Si; Si/Ca; Sr/Cu/Zn; Sr/Al/Si; Cu/Zn; Sb/Ba; Zn/Ti; Al/Si/K/Zr.

Regarding the geographical aspect, modern centre fire ammunitions from Western countries, that is, Europe, America, Sweden, Australia and New Zealand, and so on, all contain a very similar priming composition, the basic elements found being Pb, Ba and Sb with calcium silicide and/or powdered glass giving silicon (Si). With so little variation, it is therefore very difficult to make any differentiation between calibres and origin. Aluminium (Al), or sometimes magnesium (Mg), is also often added to increase the temperature and burn time of the flame produced. This is usually found in the higher-pressure cartridges and can be sometimes useful in identifying the type of ammunition fired. On the contrary, centre fire ammunition from what was previously called the Warsaw Pact countries, that is, Russia, Poland, Czechoslovakia, Hungary, Romania, as well as China and Korea tend to have a completely different primer composition. Generally speaking, the priming compounds are much more corrosive than those found elsewhere in the world. The basic elements found in these priming compounds are mercury (Hg); tin (Sn); antimony (Sb); phosphorous (P); potassium (K); sodium (Na); silicon (Si) and calcium (Ca). Other compounds occasionally encountered include lead (Pb); barium (Ba); silver (Ag); zinc (Zn); copper (Cu); magnesium (Mg); aluminium (Al) and lanthanum/cerium/iron (basically lighter flint) [15].

It is this great diversity of elements which, in some circumstances, enables the identification of calibre, country of origin and sometimes even a factory code from the GSR composition. Moreover, as it is possible to understand from the precedent paragraphs, there are a lot of variants regarding the chemical composition of the primer mixtures, and since most of the GSR particles derive from the primer, as will be discussed in 3.2.5, it is always better to understand what is the primer composition of the cartridge in exam and to search for the GSR particles that are able to derive from such primer. This composition is usually derivable on the spent cartridges or bullets found on the crime scene.

3.2.4.4 Propellants

Propellants, also called gunpowder, powder charges or simply as charges of power, are explosive materials which generate large volumes of hot gases at highly controlled, predetermined rates. Ideally, a propellant would be a single, solid, nontoxic chemical compound that is stable, easy to store, easy to ignite, of compact mass, cheap and simple to prepare from readily available materials and which on combustion produces no smoke or solid residue, that is, is completely converted into hot gas or gases. It must contain its own oxygen supply, which is necessary for combustion in confined spaces, it must burn very rapidly as opposed to detonation, and it must have a satisfactory energy/weight relationship. Moreover, it must be easy and safe to load, non-hydroscopic, and free from combustion products that are difficult to remove or injurious to the firearm or cartridge case and must give consistent performance under varying conditions of storage and climate, and it must not deteriorate with age. Last but not least, it must also not ignite when in the chamber of a very hot firearm for a considerable period of time [8].

Propellant compositions vary according to space available within the cartridge case and gun barrel, the bullet weight, pressure requirements, and the required bullet velocity so many propellant mixtures are available. The burning rate is extremely important because if the propellant releases hot gases too quickly, it detonates, thereby destroying the gun and possibly causing injury to the firer. If it burns too slowly, it is inefficient, and the bullet will lack sufficient velocity. The burning rate can be controlled by the size and geometrical design of the individual granules and also by the use of surface coatings, which are the moderants, on the granules of propellant. It is critically important that propellant granules not contain non-uniformities such as cracks, pores, and cavities, because this could cause internal granule burning, leading to detonation or excessive pressure. The process of delivery of propellant gases at a predetermined rate involves the selection of a propellant composition with the required burning rate at the operating pressure of the firearm, and then designing the propellant granules so that the necessary burning surface is available to provide the required mass rate of gas evolution, that is, the necessary time/pressure relationship [5].

The most used propellant in ancient times was the black powder, commonly called gun powder when used in firearms, which composition is reported in 3.2.1. At the very beginning, gun powder components were simply mixed together, but such gunpowder was unreliable. Improved methods of combining the chemicals evolved and by the fifteenth century a form known as “corned” gunpowder had been developed in which the components were bonded together in small granules. On combustion, black powder produces 44% of its original weight as hot gases and 56% as solid residues in the form of dense white smoke [5]. This is a clear sign of the inefficiency of the gun powder, since most of it becomes a solid residue that does not participate to the boost on the bullet for which a propellant is designed for. Moreover, the dense white smoke that exits from the muzzle of the firearm attracts atmospheric moisture causing rusting of the firearm, can obscure the firer’s view for subsequent shots, and the smoke gives away the firing position.

This is why black powder was gradually replaced by smokeless propellants toward the end of the nineteenth century. Smokeless powders usually give much higher pressures than black powder and are much harder to ignite. Smokeless powders require a much “hotter” primer, which needs a much stronger blow from the firing pin. They can be single-, double- or triple-based powders; single base powders are based around nitrocellulose (NC) as an explosive, while double base powders contain both NC and nitroglycerin (NG), the latter increasing the energy potential of the powder. In triple base powders, a portion of NC and NG is replaced by nitroguanidine; usually they are used in rockets and military ordinance and are seldom encountered in forensic work [12]. All smokeless powders, in addition to explosive ingredients, contain a number of additives, including stabilizers, plasticizers, flash inhibitors, coolants, moderants, surface lubricants, and anti-wear additives [2]. In particular, stabilizers are necessary because nitrocellulose decompose with age; without stabilizers, the shelf life of the ammunition will be greatly reduced. A common stabilizer in single-base propellants is diphenylamine (DPA) or its nitro derivatives. In double based propellants is not so good as it may hydrolyse NG.

A stabilizer usually found in double-based powders is the Ethyl centralite (EC). Regarding the plasticizers, they add strength and flexibility to the propellant granules and usually are triacetin, dimethyl phthalate, diethyl phthalate, and dibutyl phthalate. Muzzle flash suppressor are needed to reduce the heat of the explosion, and so the typical flash that exits from the muzzle of a firearms when it shoots. The most common flash suppressor is dinitrotoluene. Regarding the binders, used to hold the granule shape, they include ethyl acetate and rosin. Last but not least, as anti-wear additives, usually de-coppering additives are used, to decrease the build-up of copper residues in the barrel rifling and include tin metal and compounds such as tin dioxide, and bismuth compounds. After the shot, smokeless powders leave relatively little solid residue on combustion and produce much less smoke than black powder. Combustion of smokeless powders produces primarily nitrogen, carbon monoxide, carbon dioxide, hydrogen, and water vapor. The quantity of smokeless powder varies depending on the calibre, bullet weight/type, required pressure/velocity, space available within the cartridge case/chamber, and so forth [5].

3.2.4.5 Bullets

The bullet is the only part of the cartridge that, at the shot, leave the cartridge case, in which is inserted, and goes towards the target. The first lead bullets were spherical and were used for many years in smooth bore muzzle-loading firearms where the bullet did not have to be a tight fit in the bore. As stated in the previous paragraphs, rifling of the bore was found to improve the accuracy and consequently the effective range of firearms. It is the invention of the rifled bore that changed the shape of the bullet, because it had to be a tight fit otherwise it would not grip the rifling when discharged. After several tests the elongated bullet was invented, which had greater weight for a given diameter and was more stable in flight [5]. In Figure 14 are showed some designs of bullets.

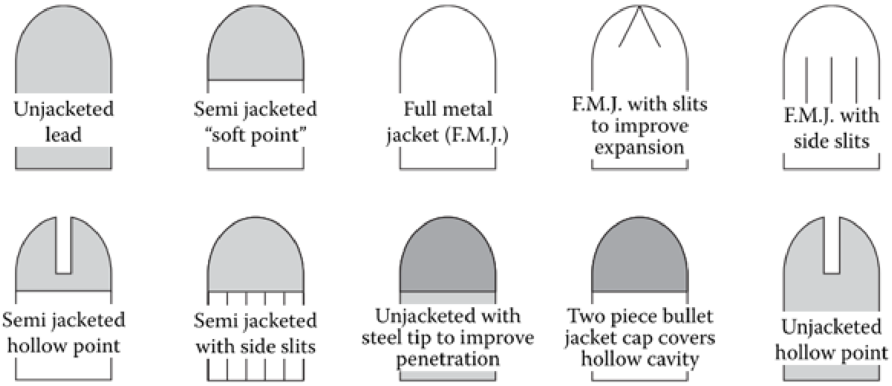


Figure 14: Designs of round-nosed bullets [5].

At the beginning, bullets were all unjacketed; they may have their surface coated with a very thin layer of copper or brass coloured material, which is used as a lubricant, and for cosmetic reasons. Moreover, in order to reduce the leading of the bore and the deformation of the bullet and also slightly reduce the extent of bullet deformation on hitting a target, lead bullets were hardened by tin or antimony. This is referred to as a "coat" or "wash" and is not a bullet jacket in the conventional sense of the word. Another thing that can reduce a lot the leading of the bore is to apply lubricants in the annular grooves, such as tallow and beeswax.

However, un-jacked bullets are very little used nowadays due to melting and fusing of the exposed lead surface causing leading of the barrel, deformation of the bullet, and a loss of accuracy of the firearm. In fact, they are only used nowadays in lower-velocity revolvers [5]. This aspect is really important for GSR analysis since some lead found in the chemical composition of GSR may also come from the erosion of the bullet at discharge, which cannot happen when dealing with full metal jacket bullets.

On the contrary, higher velocity bullets have to be either full or partly jacketed. In the majority of bullets, the lead base is exposed to the hot propellant gases, with except for the full metal jacketed bullets. Some bullets incorporate a gas check in the base to prevent erosion by the hot gases; such erosion can upset the symmetry of the bullet and consequently the accuracy [5]. Some designs of the bases of the bullets are showed in Figure 15.

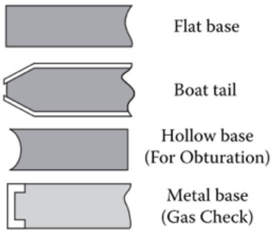


Figure 15: Bullet base designs [5].

The bullet jacket material is almost always harder than the bullet core material, with the one exception of armour-piercing bullet jackets, but soft enough to take up the rifling and not cause excessive wear to the barrel. Bullet jacketing is done either by electroplating or, much more commonly, the jacket is manufactured separately from the bullet, and the bullet then forced into the jacket in a press. Another method is to pour molten lead into the jacket. The edges of the jacket are usually partly rolled over the base of the bullet or attached by some other physical means. This is because if the jackets separate from the bullet after the shoot, the penetration will reduce. Bullet jackets were for a long period made of cupronickel, which is made by 80% copper and 20% nickel, and nowadays especially of gilding metal, which alloy is known as Lubaloy or Nobaloy and is made of 90% to 95% copper, 10% to 5% zinc and a small quantity of tin, which is claimed to have excellent lubricating properties; another less used material is steel, coated both inside and outside with a softer metal to prevent barrel wear and rusting [5]. Some examples of the bullet core/jacket designs are showed in Figure 16.

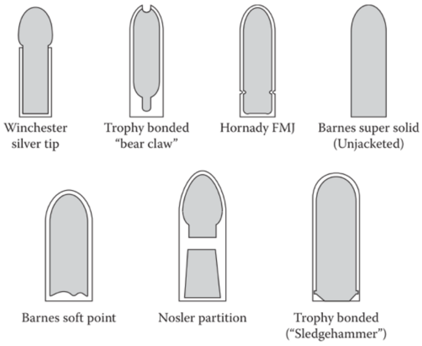


Figure 16: Bullet core/jacket designs [5].

The core of the bullet can be made from a variety of materials; lead is by far the most common because of its high density and the fact that it is cheap, readily obtained, and easy to fabricate but also other high-density materials can be used, such as steel, depleted uranium and so forth. Sometimes a combination of bullet core materials is used to produce a hardness difference between the base and the nose; these are called dual core bullets. Bullet lead can be either soft lead or lead hardened by antimony, by tin, or by both. Bullet tips are usually made from lighter-weight material than that used for the core. Some soft point and unjacketed bullets employ a metal cap over the nose of the bullet either for increased penetration, to protect the nose from damage, or to improve feeding in self-loading firearms [5].

Regarding the bullets for shotguns, also called shotgun pellets, they are round metal balls available in various sizes, degrees of hardness, and materials depending on their intended use. The pellets material is usually lead or steel; pellets are sometimes graphite coated, copper plated, or nickel plated and is usually applied on hard or extra hard shots. Sometimes a single rifled slug, a single lead ball, or a plated steel ball is loaded in shotgun cartridges and are especially used for giving a considerable penetration and stopping power at close ranges [5].

The bullets described above are probably the most common, the ones that most of the firearms cartridges utilize; however, there are many other types of bullets, less used and more specific. A brief summary of some of the most important is reported in Table 3.

Table 3: A brief summary of some of the most important specific purposes bullets [5].

Armor-piercing (AP) Bullets	Called like this because they are especially used in rifles for penetrate vehicles body works and body armours, but it is ineffective against heavy armour plate. They are usually jacketed; the core is not made of lead, which will be too soft, but it's constructed entirely from a combination of tungsten alloys, usually tungsten carbide, steel, iron, brass, bronze, beryllium copper, or depleted uranium. AP rifle bullets usually have a bullet tip filler, usually lead, which is designed to cushion the effect of the impact on the AP core, which is very hard and brittle and can break on impact without a "cushioning" effect. The AP core is also frequently surrounded with a thin sheath of lead between the core and the bullet jacket.
Tracer Bullets	When fired, a tracer bullet leaves a visible trace behind it so that the trajectory can be seen and the aim corrected if necessary. A tracer bullet has a cavity at the base which is filled with a mixture of substances that are ignited by the propellant, called tracer igniter mixture, which consists of potassium permanganate and iron filings.
Incendiary Bullets	Used against flammable targets and have an incendiary composition in the nose portion which is ignited on impact. The best-known incendiary agent is magnesium, which melts about 650°C and once melted is very easily ignited. Also potassium is used, but the manufacturing difficulties of such bullets are a lot.
Exploding Bullets	Bullets designed to explode at the impact; in the jacket of the bullet there is the lead core and also an explosive substance which on target is ignited by a firing pin present between the lead core and the explosive.
Saboted Subcalibre Bullets	A sabot is a lightweight plastic container that encloses the lower portion of a bullet. It is used to produce very high bullet velocities when a smaller calibre bullet, which obviously have a smaller weight, is fired from a larger calibre barrel.

	As the sabot and bullet move down the barrel together, they both start to spin from the twist of the rifling. The substantial centrifugal force generated opens the front end of the sabot. The sabot, as it is light weight and blunt, separates from the bullet by air resistance about 18 inches from the muzzle. These projectiles are useful cause they can travel a lot due to their high velocity and lightweight and they allow a single firearm to shoot also different calibres bullets.
Poisoned Bullets	Utilized because if the bullet itself fails to kill, the backup system of the poison offers a twofold method of attack. Their design is quite simple, there is a cavity in the bullet filled with poison like aconitin or hydrogen cyanide, which breaks and contaminate the target when hits it.
Frangible Bullets	They are designed to disintegrate on hitting the target and consequently will not ricochet. They consist of particles of iron or lead bonded in some synthetic material.

In Figure 17 is showed an example of an explosive bullet while in Figure 18 is showed the mechanism behind the saboted bullets.

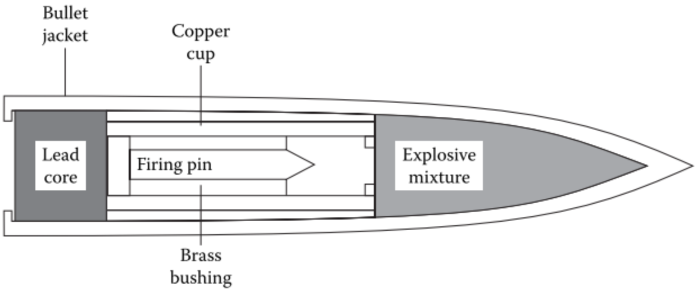


Figure 17: Exploding bullet [5].

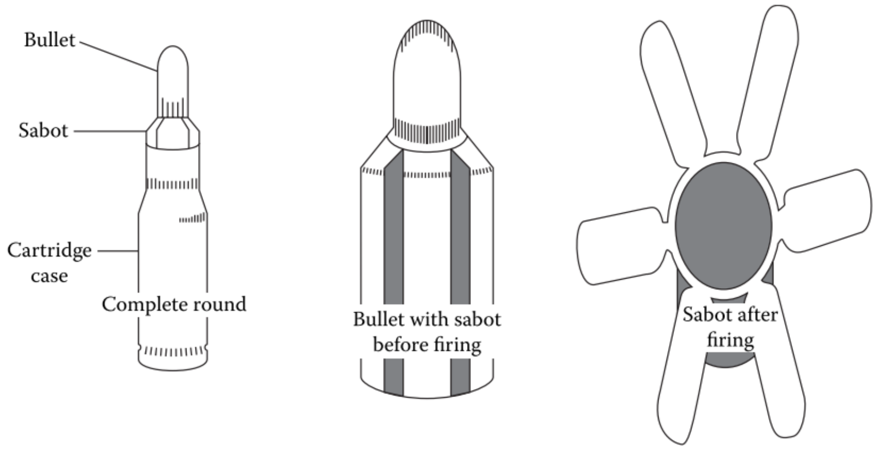


Figure 18: A schematic representation of what happens to a saboted bullet when fired [5].

Lastly, there are also cartridges that do not contain any bullet. They are blank ammunitions and they are not designed to be lethal, but only to simulate the flash and the sound of a gun fire. They can be used only in blank firearms, which normally have a hardened steel blockage in the barrel to prevent them from being converted to fire bulleted ammunition. They can be important for GSR analysis since primer mixture and propellant are the same of the usual ammunitions.

3.2.5 The Gunshot and the Ejection of GSR Particles

The firing mechanism of a firearm consists of a mechanical device which causes a hammer to fly forward and deliver a blow to the firing pin when the trigger is pulled. The firing pin goes through a small hole in the breech face and strikes the primer cup. As the firing pin strikes the primer cap, the primer mixture is ignited because contains chemicals that sensitize each other to percussion, creating an environment of rapid temperature and pressure increases within the cartridge.

This environment melts the primer and within a few milliseconds, the vaporization points of lead, barium and antimony, the main components of the most common primer compositions, which are respectively 1620 C°, 1140 C° and 1380 C°, are exceeded [2]. As the primer mix produces a shower of hot particles and ignites the propellant powder, the controlled burning of the propellant starts, which results in a second rapid increase in pressure and temperature until the bullet is expelled from the firearm barrel. Notice that the initial motion of the bullet is quite slow because the pressure needs to win the inertia of the bullet and the resistance given by the bullet itself crimped in the neck of the cartridge case. Notice that the maximum pressure and temperature of the gases created by the deflagration of the propellant is reached after the motion of the bullet. This phenomenon can be explained by the fact that the pressure in the chamber increases as long as the velocity of production of hot gases is higher than the increase of volume created by the motion of the projectile. When this situation reverses, pressure will start to decrease [6].

These phenomena are better understandable looking at the Figure 19, in which is showed a graph of pressure, velocity and motion of the bullet against time.

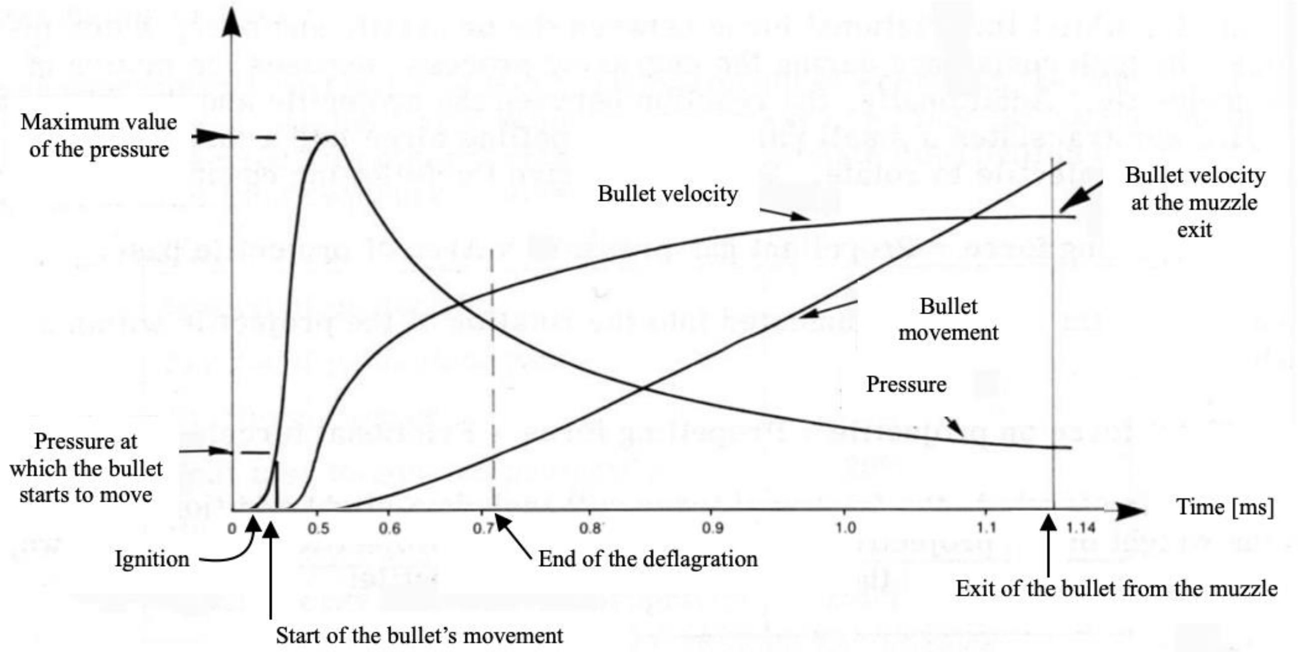


Figure 19: Graph of pressure, bullet speed and motion against time [6].

Notice that the increase of pressure is an extremely fast phenomenon, as seen from the time scale in the graph of Figure 19, in which are shown the typical durations of a rifle; in a handgun, since the bore is shorter, the durations are even smaller. In fact, the time span from the firing pin hitting the primer cup to the bullet leaving the gun is typically in the region of 1 to 1.5 milliseconds. These are the durations at which the material of the cartridge case, the bullet and the firearm are subjected at a very high temperature, largely above the fusion one, but the action of the generated heat is so short, that in the expelled GSR there will still be some contributions from the bullet and the cartridge but negligible contributions from the material of the bore [6]; however, mixtures containing selenium are used to repair surface coatings of firearms, and particles containing selenium are occasionally encountered in GSR, although is a very rare phenomenon. Temperatures and pressures inside a gun during discharge can be in the region of 3,000 C° and 50,000 pounds per square inch [5]. In Figure 20 is showed a schematic representation of a rimfire cartridge when it is fired.

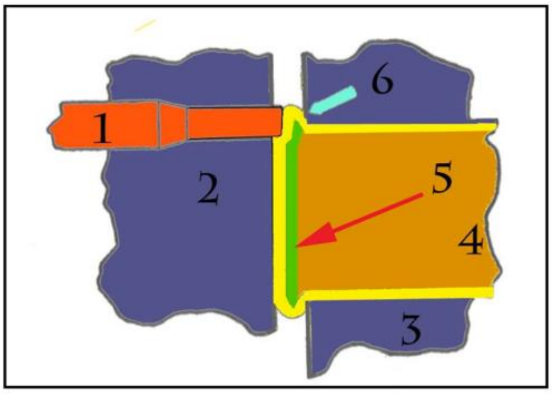


Figure 20: A schematic representation of the firing of a rimfire cartridge. The firing pin (1), which is contained in the breech block (2), strikes the rim (6) of the ammunition (4), supported by the breech (3), in which the primer (5) is contained, and deflagrates it [6].

In Figure 21 instead, is showed a centrefire cartridge when is fired.

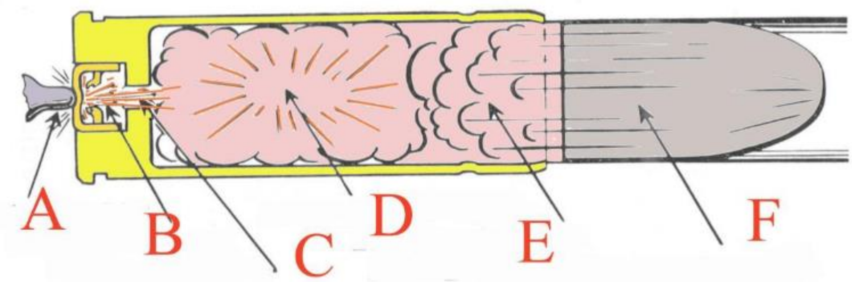


Figure 21: A schematic representation of the firing of a centrefire cartridge. (A) The firing pin strikes the primer cup; (B) the primer is ignited by the strike; (C) the deflagrated primer mixture passes in the flash hole towards the propellant; (D) the propellant is ignited; (E) the deflagration of the propellant creates a stream of hot gases, so the pressure increase as the volume is fixed; (F) the bullet starts its motion towards the target immediately before the pressure reaches the maximum value [6].

The gases, vapours, and particulate matter formed by the discharge of ammunition in a firearm are collectively known as firearm discharge residue (FDR) or gunshot residue (GSR) and are deposited on the skin, head hair, clothing of the firer and on all the other surfaces that get in contact with them during the shot; anything present in ammunition may contribute, especially the primer mixture and the propellant. In Figure 22 is showed the cloud of particulate that escapes from the firearm not only from the muzzle but especially through any available openings of the weapon, like the cylinder gaps and the ejection ports.

Figure 22: The plume of gases that escapes a weapon, in this case a revolver, when it is fired [5].

Gunshot residues consist of a complex heterogeneous mixture that is claimed to be mostly particulate in nature. During the discharge, approximately 30% of the chemical energy of the propellant is converted into kinetic energy; the rest is accommodated in the discharge residues. As a result of the very short time period from the hammer or firing pin striking the primer to the bullet or shot exiting from the muzzle and the nature of the discharge process, only partial mixing of the constituents occurs and this accounts for the very heterogeneous nature of firearm discharge residue [5]. The effects of supersaturation cause vaporized particles to condense back onto the liquefied primer surface as droplets; this, as will be seen in the next paragraph, happen directly inside the firearm. Moreover, primer ingredients are initially compounds and therefore cannot be expected to be reduced to elements in the oxidizing environment of the primer ignition. This is why elemental particle should therefore originate from bullet materials [16].

Moreover, in the vicinity of the muzzle the hot propellant gases ignite and emit light on contact with the surrounding air. This effect is called muzzle flash. The high-pressure propellant gases at the muzzle are released into the air causing considerable turbulence and producing a powerful blast shock. This effect is known as muzzle blast. In fact, muzzle blast residue can be deposited on the target if the muzzle-to-target distance is less than 3 feet, that is, a close-range shooting and nearly always contains unburned or partially burned propellant and soot [5].

Last but not least, also clusters of particles, which consist of from five to several hundred spherical particles attached to each other in a similar fashion to a bunch of grapes, and flakes of unburned smokeless powder, which are organic in nature and range in size from about 50 to 1,000 μm, are expelled and participate to the GSR, but since they are very large in size, they are never found on suspects as they are immediately lost after the shot [5].

3.2.6 The Theory of Basu and the GSR Morphology

What many people interested in this field do not know is that practically all the GSR that deposits on the firer and that are used to try to discover if a suspect has fired a firearm or not, exit from the firearm already solid. One of the best theories that tries to explain the formation of the GSR was made by Samarendra Basu [17]. In Figure 23 is schematised the formation of the GSR according to Basu's theory. In the vertical axis there are the pressure and the temperature, which increase together in a phenomenon like the one that happen inside a cartridge during the shooting, considered for simplicity an adiabatic polytropic phenomenon. Notice that the values shown in Basu's graph for the phase I are referred to the ones of an explosive and not the ones that happen in an ammunition of a submachine gun, which are around 2700 C° and around one third of the pressure indicated by Basu [6].

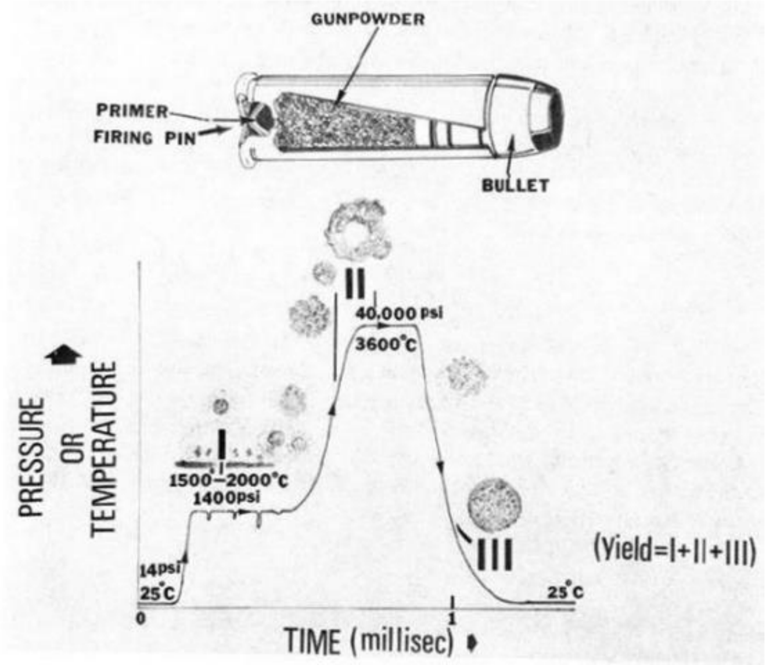


Figure 23: Formation of the three types of GSR particles [17].

Basu divides the formation of GSR particles in three different phases, which corresponds to three different values of temperature and pressure. In the environmental conditions of the phase I the first GSR particles, the ones identified as type I from Basu, born. Their formation happens directly after the ignition of the primer mixture, in the primer cup, and so directly in the ammunition even before the bullet exit from the firearm. This is why the only elements present in the chemical composition of these particles will be the ones present in the primer mixture and represents also most of the particles of the entire population of the expelled GSR. This makes understand instantly why, as will be seen more in detail later on, in all the debris found on a suspect, the analysis concentrates on searching all the particles that contains elements which are present in the primer composition of the shot cartridge. For example, if in the primer cup were present lead styphnate, antimony sulphide and barium nitrate, in the gases produced will be found lead, sulphur, antimony, barium, nitrogen, hydrogen and oxygen.

It’s quite immediate to understand that the lighter elements will go away in the atmosphere while the heaviest ones, like lead, sulphur, antimony and barium, will become liquid and then form solid spherules, the ones that are deposited on the firer. It is worth to notice that these spherules forms when the chemical substances present in the primer mixture sublime, which means even before the ignition of the propellant and passes through the latter at an extremely high velocity, igniting it. Then, due to an homogeneous nucleation in a supersaturate ambient, they become liquid droplets which then solidify, this is why they are nearly perfect spheres of dimension of the order of 2-10 μm. Due to the thermodynamic characteristics of the ambient in which they form, the core of these particles is usually homogeneous and contains a uniform and concurrent mixture of the primer composition dominated by barium, with the possible presence of superficial nodules, in which lead and antimony are usually concentrated. The surface is amorphous, free from any trace of crystallization. Notice that in the nodules it is possible to find also zinc and copper, elements of which the primer cup is made. An example of a type I particle is showed in Figure 24 in which is also present the analytical spectrum, which shows the chemical composition of the particle. Images and spectra are obtained via the SEM/EDX equipment, which will be discussed in 3.5.3.

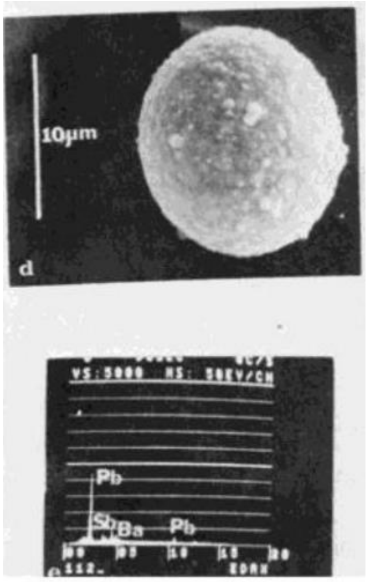


Figure 24: Example of a type I particle and its analytical spectrum [17].

The second GSR particles that chronologically form are the ones that born in the environmental conditions that on the graph in Figure 23 are the ones at the maximum pressure and temperature. In these thermodynamic conditions, type II GSR particles form. They are less common with respect to the Type I particles, always spheroidal but with an irregular shape and a dimension of the order of 15 to 55 μm, and in some rare cases also smaller. The composition is not homogeneous, but they have a discontinuous distribution of the primer elements. Moreover, this category, which comprehend the irregular shaped GSR, may be also formed due to the fact that some particles are still liquid when they exits from the barrel; especially if the firing distance is short, these molten particles can be splattered or flattened on the target, losing the sphere-like shape. This usually happen at muzzle to target distance between 20-30 mm [18].

Notice that Basu describes type I and type II particles as formed in two different instants, and not the evolution of one in the other one [19]. An example of a type II particle and its analytical spectrum is showed in Figure 25.

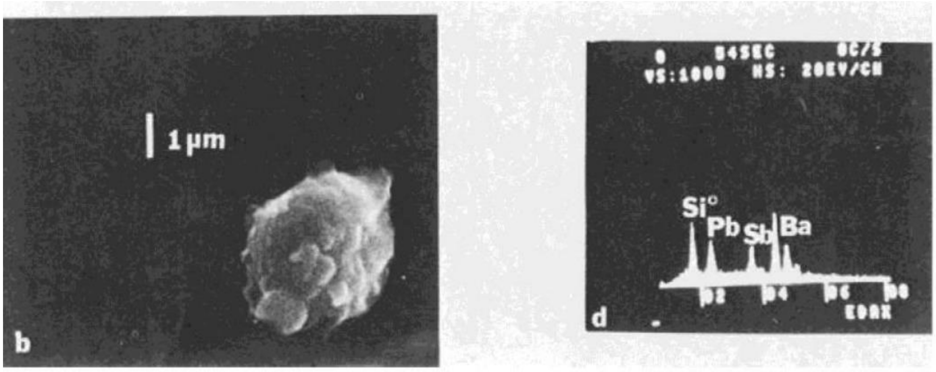


Figure 25: Example of a type II particle and its analytical spectrum [17].

Regarding the last particles formed, type III, they are also the less common between the other two types. They form when pressure and temperatures are decreasing and they are described as peeled orange, with a dimension between 10 and 35 μm. Their layered structure comes from the fact that the elements that compose the primer mixtures have different solidification temperatures; this is why usually type III particles have a lead surface, having the lowest melting point, which condensate on an already formed core made of barium and antimony. Moreover, these particles forms in the bore of the firearm and the lead on the surface may both come from the primer as well as from the eroded bullet, since its base is eroded by the hot propellant gases, it is engraved on the outside by the rifling of the barrel and in general it is subjected to friction [5]. An example of a type III particle and its analytical spectrum is showed in Figure 26.

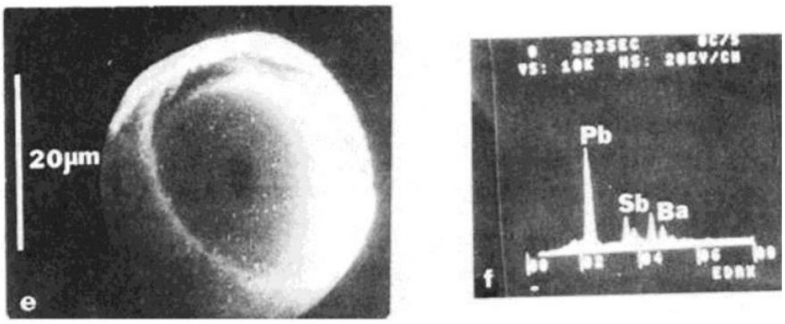


Figure 26: An example of a type III particle and its analytical spectrum [17].

It is worth to notice that categories II and III are larger sized particles that are thought to travel slower through the propellant ignition front and are therefore subjected to a second, greater increase in pressure and temperature. This causes these particles to pass through various metastable states because of boiling, fragmenting, or etching until a stable shape is again reached. Obviously, all the dimensions indicated are indicative, since the mechanism behind the dimension of these particles is that all the particles that have a diameter smaller than 10 μm are formed as droplets in an equilibrium state while bigger particles form due to the coalescence of smaller ones.

These mechanisms of formation do not exclude that some elements coming from the cartridge case and from the firearm itself may participate to a GSR particle, but they cannot be present on type I particles, in which only the primer elements are present. Moreover, if these extraneous particles are found, they mandatorily need to be on the surface of the GSR. Notice that in the case of tin-plated bullets, since some pure tin particles may be eroded from the bullet, it is possible to find these particles splashed on the substrate on which they are found because the cooling process of tin particles is completed after the droplets of liquid metal had collided with the substrate. Obviously, this phenomenon happens more often in close proximity shoots. In fact, GSR dusting of targets greater than 50 cm show that particles may actually shatter and not flatter since they have the time to solidify and become brittle before impacting the target. Obviously, a stationary target appears to enhance the creation of flattened or splattered GSR particles [18]. This throws new light on the process of formation of GSR, since so far it has been believed that the solidification of GSR particles is being completed in the air, before hitting a substrate while in the case of tin particles, since it is a metal of low melting point, an opposite situation took place [20]. Some examples of splashed GSR tin particles are showed in Figure 27.

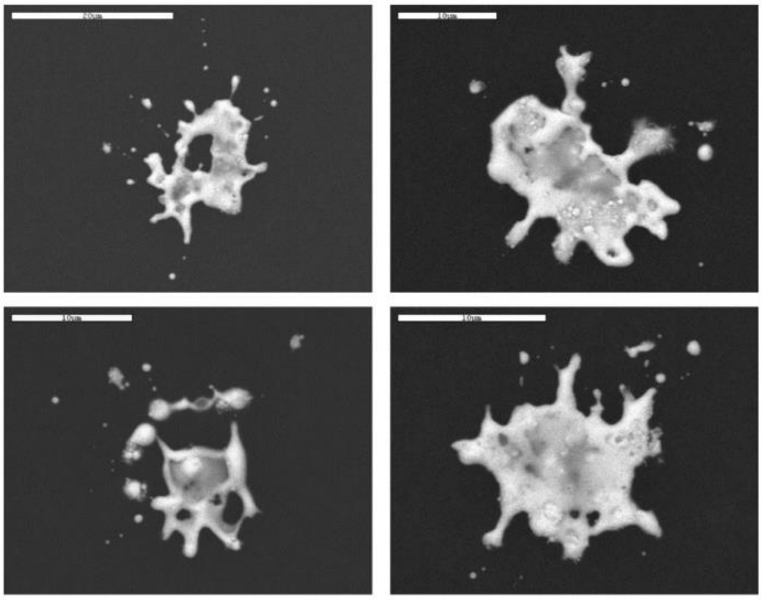


Figure 27: Splashed GSR tin particles [20].

Last but not least, it is possible to find on the spent cartridges some GSR particles that are attached to the internal surfaces of the cartridge casing, important to determine the type of primer mixture used in the analysed case. It is possible that these particles have an irregular shape and a crystalline surface. This could happen since the type I particles are ejected out from the primer cup at a very high velocity in the zone of the cartridge in which the propellant is present. If these particles bump into the walls of the cartridge case, they can be deformed and can assume an irregular shape. The crystalline surface comes from the fact that the walls of the cartridge case are colder than the ambient in which the propellant burns and so these particles solidify slowly [6].

In Table 4 are resumed all the characteristic of the three types of GSR as theorized by Basu.

Table 4: Classification of GSR particles as made by Basu [2][17].

	Characteristics	***Frequency of occurrence***
Type I	Most commonly found type on the hands of a person who has previously discharged a firearm. Small spheroid particles that may have small nodules upon their surfaces. Nodules are usually of single elemental composition, which may originate from the primer or primer cup and may be nonspecific, which means not Pb, Ba, or Sb. Believed nodules are captured by the main particle mass when a degree of cooling has occurred, and the particle is solidifying. The main body of these particles contains a uniform and concurrent mixture of the primer composition, dominated by barium probably due to thermal agitation and Brownian motion. Sizes range from 2 μm to 10 μm in diameter. They are generally solid with no space in the core.	~68%
Type II	Inhomogeneous particles that have a discontinuous distribution of the primer mixture. This heterogeneity may reflect the way in which the particle grows; in fact, they often have air central cavities, which suggest they have been subjected to some form of disturbance during formation, which may explain elemental distribution.	~25%
Type III	This type of particles represents the least commonly found. They are composed by a core made of the primer mixtures usually surrounded by a lead crust. It is believed that the core is in the process of solidifying when it captures Pb vapours from burnt residues and the etched bullet, caused by barrel rifling as the bullet travels down the barrel. The Pb coating may also take on a peeled orange appearance in certain conditions.	~8%

In general it is possible to say that irregular and aggregate particles generally constitute the majority of larger GSR particles produced, ranging in size typically from few μms to several hundred μms, while spherical particles are usually smaller [12].

Notice that the shapes of GSR particles as theorized by Basu happen in an ideal situation. In reality, although most of the particles could be reconducted to one of the types described by Basu, but since all these types of particles interact with each other and with an environment of high temperatures and pressures, some could create agglomerates of particles with irregular and unusual shapes and, when collected, do not pertain to any of the category described by Basu; obviously, the larger the particles the faster they will fall from the hands. Some examples are showed in Figure 28 and Figure 29.

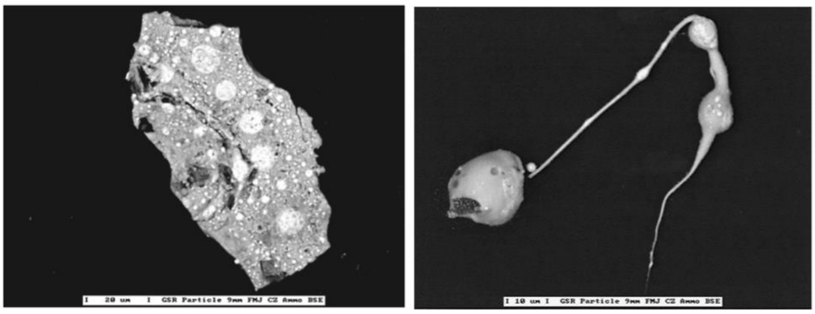


Figure 28: Irregular GSR particle (left) and an unusual GSR shape (right), with a spheroid attached to a channel mostly made of barium [19].

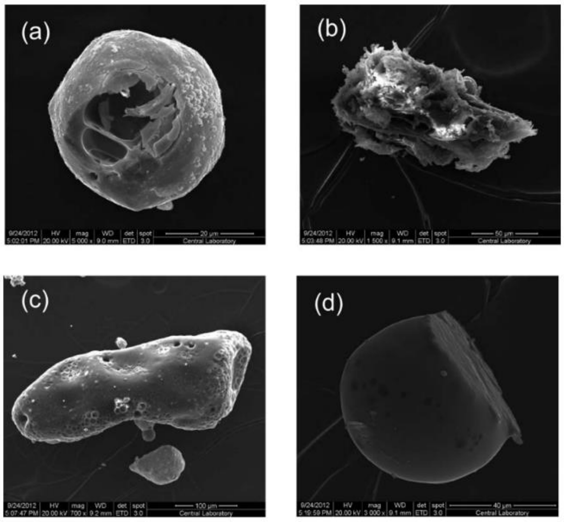


Figure 29: Other types of GSR: (a) hollow, (b) irregular, (c) spongy, and (d) half-spherical [21].

Moreover, the advancement of the technology has brought some new possibilities in GSR analysis that were not available at Basu's years. The focused ion beam (FIB) milling technology for example is able to dissect a GSR particle by means of a focused ion beam of gallium, allowing the analyser to check the internal structure of a particle and to extract more information from the particle's core. In general, the core of the GSR particles is usually solid, whatever types of primer is used. However, it is possible that sometimes the core is not solid but present spherical, elliptical cavities and also ruptures, like the examples showed in Figure 30, in which are showed the sections of three different GSR particles coming from A to C respectively from the GECO Sinoxid ammunition type, which characteristic GSR elements are Pb, Ba and Sb, from the GECO Sintox, which characteristic GSR contains Ti and Zn, and from the X Lead Free, which discharge particles are made mainly of Mn and K [22].

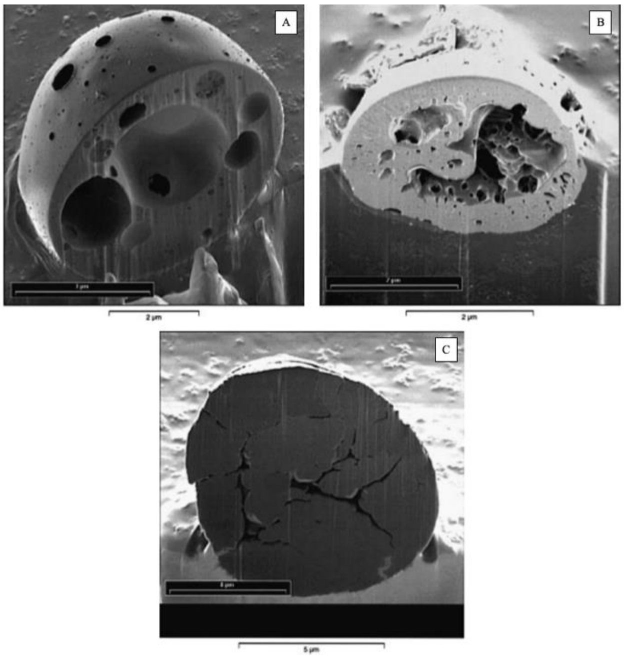


Figure 30: Ion induced secondary electron image of a cross-sectioned GECO Sinoxid particle (A), GECO Sintox particle (B) and X Lead Free particle (C) [22].

Moreover, some studies have investigated the shape of GSR particles in relation to their chemical composition. Kara et al. [23] in their work found out that according to their surface structure, GSR can be divided in to three groups which are the regular spheres, spheroids connected by a bridge, and irregular spheres (elliptical). Spheroids are formed by the combination of small spheres with regular surfaces connected by a sort of bridge, and irregular spheres are formed when larger spheroids are combined together. Looking at this perspective, these three kinds of particles can be viewed as derivatives of each other. However, partially broken spheres, hemispheres, or small parts of a sphere were also observed. It is important to notice that this classification has nothing to do with the classification made by Basu based on the mechanism of GSR formation. The three different shapes are showed in Figure 31.

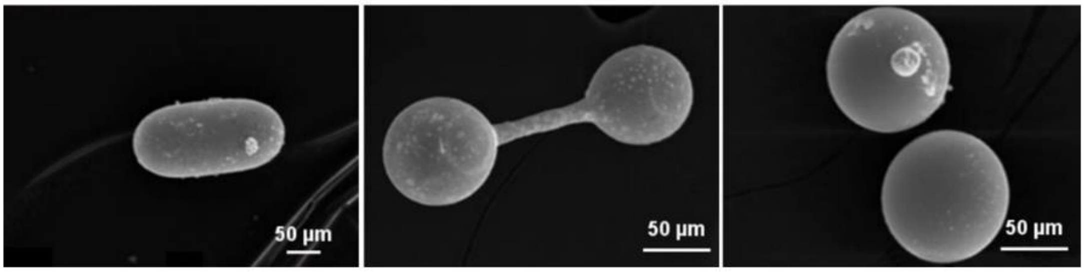


Figure 31: Three different shapes of GSR particles according to Kara et al. An elliptical particle (left), two spheres connected by a bridge (centre) and two distinct spheres (right) [23].

Then, authors state that the chemical composition affects the surface morphology of the particles formed. In general, it seems that decreasing the element content in the GSR particles, make the surface morphology passing from elliptical shape to spherical shape. For example, considering the most common primer composition, the one composed by lead styphnate, barium nitrate and antimony sulphide, decreasing the mole fraction of Sb and Ba, the particles pass from elliptical shape to spheres. These results are resumed in Figure 32.

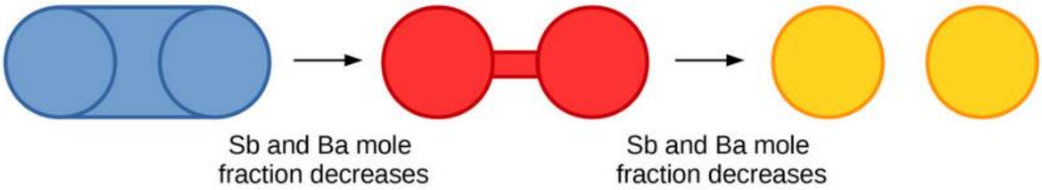
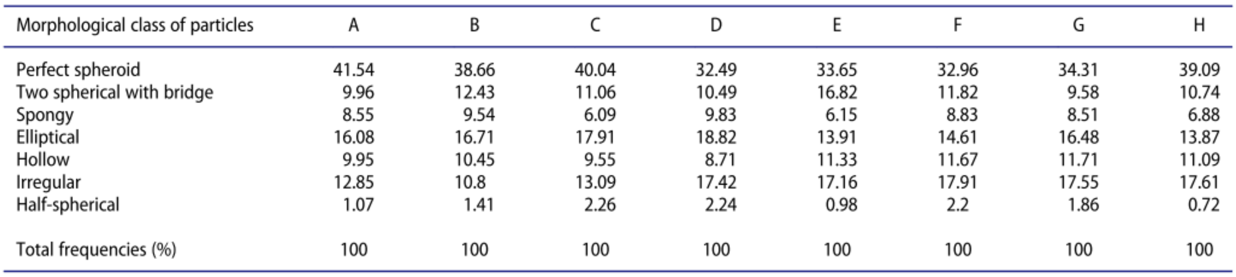


Figure 32: Schematic representation of the change of GSR shape according to the chemical composition [23].

To resume, in Figure 33 is showed the frequency of occurrence of the different shapes of GSR particles in 8 different experiments performed in the same conditions; this to give an idea of the diversity of shapes of GSR that a discharge produce.



Morphological class of particles	A	B	C	D	E	F	G	H
Perfect spheroid	41.54	38.66	40.04	32.49	33.65	32.96	34.31	39.09
Two spherical with bridge	9.96	12.43	11.06	10.49	16.82	11.82	9.58	10.74
Spongy	8.55	9.54	6.09	9.83	6.15	8.83	8.51	6.88
Elliptical	16.08	16.71	17.91	18.82	13.91	14.61	16.48	13.87
Hollow	9.95	10.45	9.55	8.71	11.33	11.67	11.71	11.09
Irregular	12.85	10.8	13.09	17.42	17.16	17.91	17.55	17.61
Half-spherical	1.07	1.41	2.26	2.24	0.98	2.2	1.86	0.72
Total frequencies (%)	100	100	100	100	100	100	100	100

Figure 33: Frequency of occurrence of the different shapes of GSR particles [21].

Particular attention needs to be put on the rimfire cartridges calibre .22. In these ammunitions, as already stated, in the primer the antimony is not present, but it may be present on the bullet to harden the lead core. However, it is quite unusual to find antimony in the GSR, obviously in the type III ones; this shows how the erosion of the bullet when it is hardened by antimony participate really a few in the GSR chemical composition, and shows why many efforts in searching possible GSR particles are put in searching particles with a chemical composition that corresponds to the one used in the primer of the fired ammunition. Notice that regarding the shapes of GSR that can be found on the spent cartridges, useful to correctly apply the so called case-by-case approach which is the approach used today for GSR analysis and interpretation, as will be extensively discussed in 3.4.3, they also reveal features of molten and rapidly cooled matter but their shapes and sizes are different from airborne particles. Some of the particles can be of spherical shape, usually of greater sizes than these of the airborne particles, but the majority of the residue are solid or porous plates and dendrite-like objects. The plates are rather large and some of them can be even seen by a naked eye, except for their fine structure visible only with SEM. Their shapes suggest that the cooling process of the metal droplets completed after they hit the inner surface of the cartridge case. Contrary to that, regular spherical morphology of the majority of airborne particles proves that they solidify in the air before reaching any substrate, with the exceptions seen in the previous paragraphs [20]. Examples of GSR particles originated from interior of cartridge cases are shown in Figure 34.

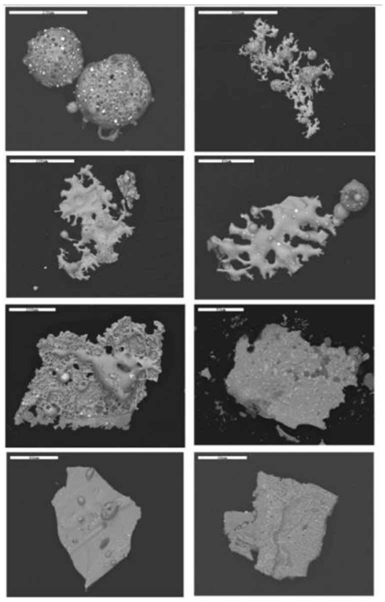


Figure 34: Examples of GSR particles originated from interior of cartridge cases [20].

Last but not least, recent studies have discovered that GSR nanoparticles consist of crystallite agglomerates since a cloud of metallic atoms is immediately generated after the shot; these atoms condensate into metals and metallic oxide crystals, which then agglomerate around each other forming nanoparticles, which subsequently form the usual GSR particles. This is why crystallinity seems to be a characteristic feature for most of the nanoparticles, and, as a consequence, GSR particles are not entirely amorphous, as claimed before, unless considering only the micrometric particles.

Notice that these considerations are done by using a TEM, a transmission electron microscope which is able to provide a much higher resolution than the SEM, with which GSR will always appear amorphous [24][25].

As seen, understanding the mechanism of GSR formation is mandatory if one wants to discern between a real GSR from an environmental source one, which could have the same chemical composition but a different shape and structure.

3.3 GSR uses

Regarding the uses that the forensic scientists made about the GSR expelled from a firearm, they are really a lot. For example, if the firearm is fired perpendicular to the target, the resulting residue pattern will be in a roughly circular area around the entrance hole. The diameter of the circle and the density of residue depend on the distance between the muzzle and the target. The pattern size, shape, and density enable range of fire to be determined, give an indication of the angle of fire, and very occasionally the propellant granules can be identified from physical appearance as originating from a specific type of ammunition and enable a tentative identification of weapon type [5].

During the discharge process some smoke emerges from the muzzle ahead of the bullet and also that just after the bullet leaves the muzzle it is surrounded by a large cloud of smoke over a short distance. This is because the propellant gases expand rapidly on release into the atmosphere, accelerating to velocities much greater than that of the bullet, and this is why the bullet is surrounded by a large cloud of smoke. As a result of these effects, GSR are deposited on the surface of the bullet and also on the perimeter of the entrance hole, irrespective of the range of fire. Notice that GSR on bullet fragments are very rare to be detected, but it is not impossible. At the exit of the hole, no GSR is present, and this can help to discover and differentiate the difference between entrance and exit holes. Notice that also from the size and shape of the wipe produced by a gunshot it is possible to extract some information, since the size of wipe produced by the bullet increases as the angle of fire increases and is also dependent on relative position and attitudes of the firer [5].

Moreover, the presence of GSR at a crime scene, with its location, density, and nature, can often assist in the interpretation of the sequence of events. As seen, there are a lot of uses of the GSR, but without any doubt, the most difficult and important area of analysis of GSR is to use GSR to decide whether a person has fired a gun or not. Usually, organic GSR are used for a better understand of the crime scene, like the estimation of the firing distance, the entrance or exits holes or the identification of the type of ammunition used; inorganic GSR are usually used to understand if a suspect has fired a firearm or not.

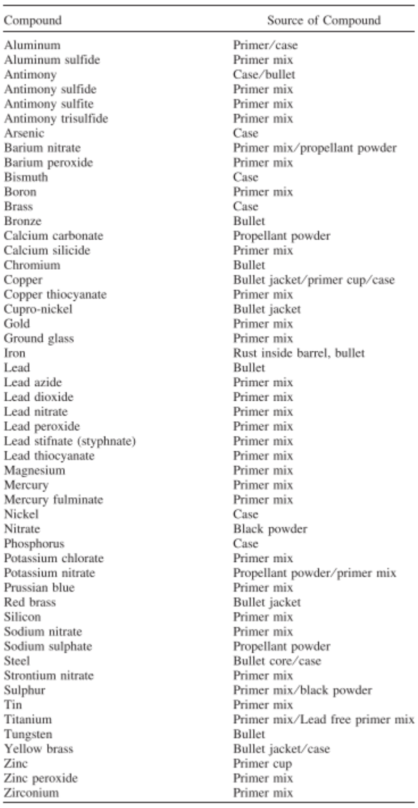
3.4 GSR classification

Classify GSR is probably an impossible task due to the enormous number of ammunition manufacturers in the world and also due to the infinite number of variables from which the ejection of GSR from a fired firearm depends.

However, forensic scientists have tried during the years to fulfil this impossible task, and, as will be shown, as time goes by, they have constantly changed their theories. Nowadays, it is not possible with 100 % sureness to incriminate a suspect of having fired a firearm. The only thesis that it is possible to sustain is that a suspect could be involved in the discharge of a firearm, meaning that he has discharged the firearm itself, he was in the near vicinity of the firing or gets in contact with a person or an object on which GSR are deposited. Moreover, to give a correct answer to the latter questions, it is not possible to rely on only one aspect of the GSR analysis, like the chemical composition, but also the shape and morphologies of the GSR particles, the entire population of particles found, the correspondence of the particles found with the composition of the ammunition used and if possible the parallel analysis of the organic compounds are needed. In the following paragraphs, all these aspects will be treated.

3.4.1 Organic and Inorganic GSR

The gunshot residues that exits from a firearm when it is discharged could be of two types, inorganic and organic. Inorganic constituents are the most used in the GSR analysis on the suspected individuals; they are predominantly nitrates, nitrites, and metallic particles and could originate from the primer mixture, the cup, the sealing disc, the anvil, the cartridge case, inorganic additives to the propellant, the bullet core and jacket, metallic containing pigments in coloured lacquers, sealers, lubricants, inorganic trace impurities in any component, and also from inorganic debris already present inside the firearm before discharge. However, the main sources of inorganic discharge residue are the bullet and the primer [5]. Since from manufacturer to manufacturer the materials composing an ammunition change, the chemical composition of the inorganic compounds will vary a lot. In Figure 35 is showed a list of inorganic compounds that may contribute to GSR.

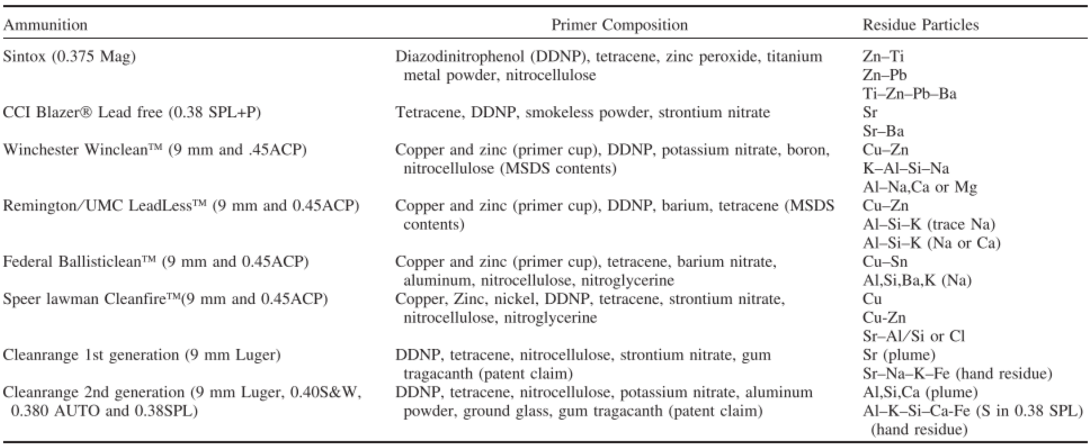


Compound	Source of Compound
Aluminum	Primer/case
Aluminum sulfide	Primer mix
Antimony	Case/bullet
Antimony sulfide	Primer mix
Antimony sulfite	Primer mix
Antimony trisulfide	Primer mix
Arsenic	Case
Barium nitrate	Primer mix/propellant powder
Barium peroxide	Primer mix
Bismuth	Case
Boron	Primer mix
Brass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

Figure 35: A list of inorganic compounds that may contribute to gunshot residue [2].

Nowadays, numerous types of lead- and heavy metal-free primers have been introduced due to response to increased concerns over health problems relating to air-borne pollution and exposure to high levels of heavy metals, such as those found in ‘‘modern’’ primer mixtures [2], especially for the ones that shoot often or professionally. There are some manufacturers that are producing completely lead-free primers, meaning without lead styphnate, but this does not mean that the lead is not present elsewhere, like for example in the bullets, obviously if they are not completely jacketed [26]. This is because aerosolized lead as a result of rapid heating and pressurization during cartridge discharge makes its way into the bloodstream and pose significant health risks. With lead removed, the difficulties for forensic trace analyst to achieve positive identification of these new ammunition types are even more [27].

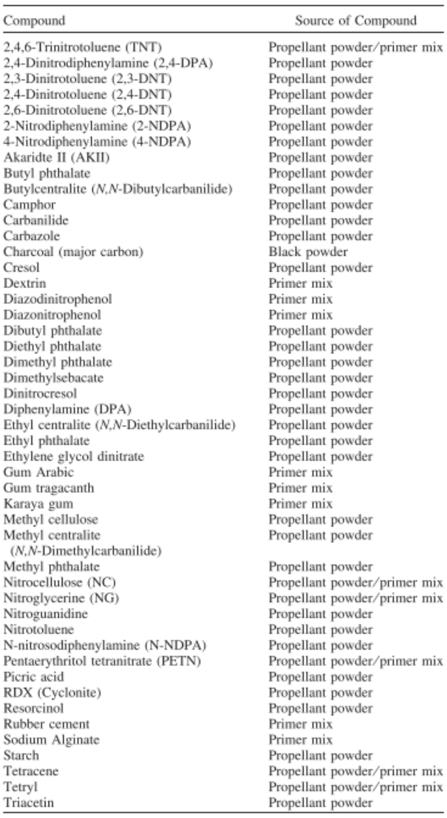
Some other manufacturers are producing completely heavy metal-free primers, completely without Pb, Ba and Sb, which are substituted with other ingredients such as strontium, potassium-based oxidizers, diazodinitrophenol or calcium silicide. With such ammunitions, the analysis of the inorganic constituent of the GSR has become really difficult; they reflect as always the primer composition, but since it contains various compositions such as Ti and Zn for Sintox, Sr for CCI Blazer® Lead Free ammunition, and also Al, Si, Cu, Ca, K, Gd (gadolinium), Ga (gallium), Sn (tin) in all the other lead-free ammunitions analysed in literature, this is a problem, since many elements found in these types of primer can be found also in many other fields, like construction and automobiles. This is why morphology was determined as the only way of truly discriminating such particles from environmental sources. For example, Ti and Zn are found in paint pigments but never as major elements and never with inorganic GSR characteristic spherical morphologies. Moreover, K, Ca, Mg, and Na salt, present in some of the residues are soluble in water and therefore would be expected to be dissolved by human sweat [2]. This is why identification of the organic components in GSR (OGSR) may allow for discrimination between GSR and other deposits [28]. Analysing both inorganic and organic GSR when dealing with the use of lead- or heavy metal-free cartridges or when there are some doubts on the usual analysis on the inorganic GSR can help to prevent false negative conclusions. This is because the analysis of organic GSR is not conclusive, it would only provide complementary information that may strengthen the evidence based on the inorganic residues [28]. Elemental composition of residues from various lead-free/non-toxic primers are showed in Figure 36.



Ammunition	Primer Composition	Residue Particles
Sintox (0.375 Mag)	Diazodinitrophenol (DDNP), tetracene, zinc peroxide, titanium metal powder, nitrocellulose	Zn–Ti Zn–Pb Ti–Zn–Pb–Ba
CCI Blazer® Lead free (0.38 SPL+P)	Tetracene, DDNP, smokeless powder, strontium nitrate	Sr Sr–Ba
Winchester Winclean™ (9 mm and .45ACP)	Copper and zinc (primer cup), DDNP, potassium nitrate, boron, nitrocellulose (MSDS contents)	Cu–Zn K–Al–Si–Na Al–Na,Ca or Mg
Remington/UMC LeadLess™ (9 mm and 0.45ACP)	Copper and zinc (primer cup), DDNP, barium, tetracene (MSDS contents)	Cu–Zn Al–Si–K (trace Na) Al–Si–K (Na or Ca)
Federal Ballisticlean™ (9 mm and 0.45ACP)	Copper and zinc (primer cup), tetracene, barium nitrate, aluminum, nitrocellulose, nitroglycerine	Cu–Sn Al,Si,Ba,K (Na)
Speer lawman Cleanfire™(9 mm and 0.45ACP)	Copper, Zinc, nickel, DDNP, tetracene, strontium nitrate, nitrocellulose, nitroglycerine	Cu Cu-Zn Sr–Al/Si or Cl
Cleanrange 1st generation (9 mm Luger)	DDNP, tetracene, nitrocellulose, strontium nitrate, gum tragacanth (patent claim)	Sr (plume) Sr–Na–K–Fe (hand residue)
Cleanrange 2nd generation (9 mm Luger, 0.40S&W, 0.380 AUTO and 0.38SPL)	DDNP, tetracene, nitrocellulose, potassium nitrate, aluminum powder, ground glass, gum tragacanth (patent claim)	Al,Si,Ca (plume) Al–K–Si–Ca-Fe (S in 0.38 SPL) (hand residue)

Figure 36: Elemental composition of residues from various lead-free/non-toxic primers [2].

Regarding the organic constituents, they mainly come from primer and propellant mixtures, in which additives such as stabilizers, plasticizers, flash inhibitors, coolants, deterrents, surface lubricants, dyes are added and also from lubricants and organic debris already present inside the firearm before discharge. However, the main source of organic discharge residue is the propellant, since the smokeless powder used today are mostly made with organic components. Besides the explosive nitro-glycerine (NG), the stabiliser diphenylamine (DPA), its derivates, ethyl centralite (EC) and/or methyl centralite (MC) are OGSR most commonly detected in GSR samples [29]. Additionally, they can be detected on the hands up to several hours after discharge despite losses due to evaporation and skin permeation [30]. Therefore, these compounds have a quite high evidential value due to their low abundance in the environment and uniqueness when detected in combination [31]. In Figure 37 is showed a list of organic compounds that may contribute to GSR.



Compound	Source of Compound
2,4,6-Trinitrotoluene (TNT)	Propellant powder/primer mix
2,4-Dinitrodiphenylamine (2,4-DPA)	Propellant powder
2,3-Dinitrotoluene (2,3-DNT)	Propellant powder
2,4-Dinitrotoluene (2,4-DNT)	Propellant powder
2,6-Dinitrotoluene (2,6-DNT)	Propellant powder
2-Nitrodiphenylamine (2-NDPA)	Propellant powder
4-Nitrodiphenylamine (4-NDPA)	Propellant powder
Akaridte II (AKII)	Propellant powder
Butyl phthalate	Propellant powder
Butylcentralite (*N,N*-Dibutylcarbanilide)	Propellant powder
Camphor	Propellant powder
Carbanilide	Propellant powder
Carbazole	Propellant powder
Charcoal (major carbon)	Black powder
Cresol	Propellant powder
Dextrin	Primer mix
Diazodinitrophenol	Primer mix
Diazonitrophenol	Primer mix
Dibutyl phthalate	Propellant powder
Diethyl phthalate	Propellant powder
Dimethyl phthalate	Propellant powder
Dimethylsebacate	Propellant powder
Dinitrocresol	Propellant powder
Diphenylamine (DPA)	Propellant powder
Ethyl centralite (*N,N*-Diethylcarbanilide)	Propellant powder
Ethyl phthalate	Propellant powder
Ethylene glycol dinitrate	Propellant powder
Gum Arabic	Primer mix
Gum tragacanth	Primer mix
Karaya gum	Primer mix
Methyl cellulose	Propellant powder
Methyl centralite (*N,N*-Dimethylcarbanilide)	Propellant powder
Methyl phthalate	Propellant powder
Nitrocellulose (NC)	Propellant powder/primer mix
Nitroglycerine (NG)	Propellant powder/primer mix
Nitroguanidine	Propellant powder
Nitrotoluene	Propellant powder
N-nitrosodiphenylamine (N-NDPA)	Propellant powder
Pentaerythritol tetranitrate (PETN)	Propellant powder/primer mix
Picric acid	Propellant powder
RDX (Cyclonite)	Propellant powder
Resorcinol	Propellant powder
Rubber cement	Primer mix
Sodium Alginate	Primer mix
Starch	Propellant powder
Tetracene	Propellant powder/primer mix
Tetryl	Propellant powder/primer mix
Triacetin	Propellant powder

Figure 37: A list of organic compounds that may contribute to gunshot residue [2].

Last but not least, it is important to remember that secretions and other debris from the subject‘s skin or hair can also contribute to the physical form and chemical composition of GSR particles collected as well as some sort of residues of the sampled surface if GSR are collected from a fabric [12].

3.4.2 A brief Historical Overview

Since the forensic science about the GSR is in constant evolution, in order to understand what are the conclusions reached by the forensic scientists nowadays regarding the GSR classification, it’s mandatory to give an historical overview on the evolution of the GSR classification systems.

It has always been thought that the gunshot residues particles expelled from a firearm during discharge contains the elements present originally in the ammunition used, especially in the primer mixture. This is why the firsts classification systems were simply a list of chemical elements that were most commonly found in the primers used in the ammunitions. In 1977, it was thought that 4 chemical compositions were unique of GSR; they are showed in Table 5. In that days, the use of the SEM/EDX method, which will be largely discussed in 3.5.3, for analysing the GSR, was in its infancy.

Table 5: Unique GSR particles in 1977 [26].

Lead, barium and antimony
Barium, calcium and silicon, with sulphur at trace level
Barium, calcium and silicon, with lead at trace level and without copper and zinc
Antimony and barium

This means that if someone was found with some traces of one or more of these combinations of elements, it was considered without any doubt involved in the firing of a firearm. Notice that the work of Wolten and Nesbitt (1977) is still today one of the best manual to learn the method for GSR analysis and interpretation, obviously with the due changes that the discoveries made in 40 years have brought. For example, the authors gave in parallel with the unique particles also a list of elements which are considered permitted in the GSR, collected in Table 6.

Table 6: A list of Permitted elements in the GSR as listed by Wolten and Nesbitt (1977) [26].

Silicon, Calcium	Present in the calcium silicide, a fuel. This is why if in the primer mixture silicon is found, there should be also calcium.
Aluminum	A fuel substance present in some primers.
Copper, Steel	Presents sometimes in the material of the primer cup and of the walls of the cartridge case, not in the primer mixtures.
Sulphur	Present in the antimony sulphide. This is why if sulphur is found, it must be found also the antimony. What is done in practice is the contrary, meaning that if there is antimony in the analytical spectrum, it is expected also a quite high lead peak, since the peak of S and Pb are overlapped.
Zinc	Present only if it is present also copper, since brass is probably the most used alloy for cartridge casings and primer cups.
Nickel	This element is very rare and is present only if brass is present, since sometimes is used in the cartridge casings and the primer cups made of brass.
Potassium, chlorine	Which together made the potassium chlorate. Present only in the ammunitions that utilize this compound in the primer mixture.
Tin	If found, it needs to be very few. Present in old ammunitions.
Phosphorous	Very rare.

From the Table 6 it is clear how they are only the elements present in the zone of formation of GSR, and that some elements are permitted only if coupled with other ones, because they are found in the ammunitions always together for construction purposes. This makes understand that also in 1977, ages in which there were accepted four unique particles, it was well established the fact that before even examining a GSR found on a suspect, the forensic scientists need to know the composition of the substances inside the ammunition used in the analysed crime, which is usually available from the spent cartridges found on the crime scene. This is why these elements are permitted only if there is a justification of their presence in the GSR particle found [6].

When in 1984 were found environmental sources for some of the univocal particles listed by Wolten and Nesbitt, Wallace and McQuillan [32] published another paper in which they revised the GSR classification. In their paper, the unique particles have become only two, while they list also some other particles called indicative, which means that if found alone, one cannot be sure if they come from GSR but if found with the unique ones, they could enforce the thesis that the suspect on which they are found has been involved in the firing of a firearm. Notice that the authors were aware that the use of the term unique is not limited to firearm discharge residue, but must be generally extended to discharge residue of any primer based on a mixture of lead, barium, and antimony compounds [33]. Their classification is showed in Table 7.

Table 7: GSR classification according to Wallace and McQuillan [32].

Unique	**Indicative**
Pb, Sb, Ba	*Ba, Ca and Si-Si*
Sb, Ba	*Pb, Sb*
	Pb, Ba
	Sb (with S)
	Sb (without S)
	Ba-Ba
	Pb

The comments of the authors about this classification were that the indicative particles were listed from the most common to the least; sulphur is acceptable at trace levels only when also barium is present; all the particles listed in the classification can also contain Al, Ca, S, Si at major, minor or trace level; Cl, Cu, K, Fe, and Zn but only if Cu is present and the ratio between zinc and copper is bigger than one, at minor or trace level; Mg, Na and P only at trace level. Last but not least, particles without Pb, Sb and Ba that contains all the elements previously listed can be considered indicative if accompanied by other indicative particles. Major minor and trace levels are referred to the analytical spectra of the particles, which will be discussed in 3.5.3. However, major are all the peaks that are bigger than 1/3 of the highest peak, minor are the ones which height is between 1/3 and 1/10 of the highest peak and trace when the peak is smaller than 1/10 of the highest peak. These is another great advancement in the theory behind the interpretation of GSR; the permitted elements cannot be present indiscriminately, but they need to respect determined peaks height proportions between themselves [6].

After some years, in 1994 Warlow [34] published a work in which on the basis of an experimental work, also the uniqueness of Sb and Ba has fallen and only the triplet Pb, Ba and Sb was considered unique for the GSR. Finally around 1999-2000, Torre et al. [33] published a work in which they found that particles containing Pb, Ba and Sb could be found also from worn brake linings. After this work, it was clear that considering only the chemical composition of the GSR is not a good practice for a correct investigation on the GSR.

3.4.3 The Latest Classification of GSR

As seen, this branch of the forensic science is in constant evolution simply because as time goes by new discoveries are made and the theories are constantly reviewed. However, it is now clear that simply according to the chemical composition, it is not possible to discern between a GSR and an environmental source. In fact, only looking at the chemical composition, particles are nowadays classified as either characteristic of, consistent with or commonly associated with GSR, as described in Table 8.

Table 8: Modern particles classification according to the chemical composition [12].

Characteristic	The chemical composition is rarely found in particles from any other source. Notice that almost all these particles come from the "Sinoxid" type of primer, composed by lead styphnate with possibly other lead compounds, antimony sulphide and barium nitrate. Other elements that can be found are silicon, calcium, aluminum, copper, tin as major, minor or trace levels; iron as minor or trace levels, sulphur, zinc, potassium, chlorine, phosphorus, nickel; Other elements rarely found in "Sinoxid" but that can provide a specific link to ammunition or a specific sub-type of ammunitions are cobalt and zirconium. Gadolinium, titanium and copper can be found when using tagged ammunitions.
Consistent	They have compositions that are also found in particles from a number of relatively common, non-firearm sources. Usually are particles containing one or a combination of two of the three elements, which are lead, antimony and barium, of the characteristic triplet. In addition, many non-Sinoxid primers based on lead styphnate and other lead compounds do not contain both antimony sulphide and barium nitrate. Furthermore, some lead-free ammunition contains barium nitrate and antimony sulphide. As such, ammunition containing these types of primer will not generate characteristic lead-antimony-barium particles. Consequently, particles with the following elemental profiles are considered to be consistent with GSR: o Barium, calcium, silicon, with no more than a trace of sulphur. o Antimony, barium, usually with no more than a trace of iron or sulphur. o Lead with levels of antimony greater than trace amounts. o Barium, aluminum. o Lead, barium. o Lead, barium, calcium, silicon, produced by antimony-free, lead styphnate, barium nitrate, and calcium silicide-based primers. Moreover, there are many variants of primers incorporating 2,4-dinitrophenol that are classified as "Sintox" primers which consistent particles contain titanium and zinc and may also contain copper or tin, which for example come from jacketing material, and/or silicon, calcium, and aluminum or "environmentally safe" primers which consistent particles contain strontium and may also contain copper, from jacketing material, aluminum, potassium, calcium, and/or barium.
Commonly associated	They have compositions that are also commonly found in environmental particles from numerous sources. When present, in addition to particles that are characteristic of, and/or consistent with GSR, these particles can be of significance in the interpretation of a population of particles and, consequently, the likelihood that that population is GSR.

Alone, however, such particles have little significance in examinations of GSR. These particles could include:

- Lead with only trace levels of antimony
- Lead
- Antimony
- Barium; in the absence of sulphur.

These particles may also contain one or more of only the following other elements: silicon, calcium, aluminum, copper, and trace amounts of iron, sulphur, phosphorus, zinc, nickel in conjunction with copper and zinc, potassium, chlorine, and tin.

In general, the distribution of the chemical elements in the GSR is determined by two main factors. The first of them is the direction of the movement of the expanding products of the burning propellant at the stage of internal ballistics and the second one is the kind of materials that were applied to construct the gun and ammunition [20]. Obviously, the classification scheme has to be flexible in order to encompass the wide range of different primer/cartridge case/propellant/bullet combinations. For example, firearms with rusted barrel interiors or the use of steel jacketed bullets can produce discharge particles with iron at major level; primers containing lead hypophosphite can give discharge particles with phosphorus at major level; ammunition with black powder can produce discharge particles with potassium and sulphur at major level [5].

However thanks to the explanation of Basu about to the mechanism of formation of the GSR, in parallel with the chemical composition, also the shape of a GSR particles can be used to discern between them and an environmental source, since the formation of GSR is a specific phenomenon that happen only inside a cartridge. More problem then arises when particles that resemble both the shape and the chemical composition of a GSR particle were found for example from residues left from cartridge operated tools, from fireworks or from brake linings. Besides the chemical composition and the morphology, it is needed another criterion.

This criterion changes the way of analysing a GSR sample. The idea is that, since it is not enough to search for particles with shape and composition typical of GSR, also the entire population of particles found on a suspect need to be analysed, in particular in term of ratios between triple, double and single elemental composition particles. This is because not all primer residue particles formed during the firing of a weapon will contain all the elements present in the original primer mix. Consider for example a lead styphnate, barium nitrate and antimony sulphide containing primer, there will be some particles made of Pb, Sb and Ba, which will be probably identified as GSR particles if also the morphology respect the prerequisites, some others classified as indicative, containing PB/Sb, Pb/Ba or Ba/Sb and lastly other particles of indeterminate origin, containing only Pb, Ba or Sb. There will be, depending on the ammunition type and make, a very approximate relationship between the ratios of these positive GSR particles and indicative GSR particles [15]. However, the general idea is that individual particles within a sample should be considered in relation to all the others that are present and that particles that are individually consistent with GSR should not be found with otherwise similar particles that are in some way inconsistent with GSR [5]. Obviously the fewer the number of particles that are present within a sample, the more difficult is to discriminate from GSR and particles coming from other sources [2].

For example, with a plain lead bullet and a Pb, Sb, Ba primer, the positive/indicative ratio would be in the region of 1:40 or even more; with a jacketed hollow-point bullet will be 1:10. Considering the latter case, if for example the baseline for a positive GSR result is taken as being two positive particles, then there should be at least 20 indicative particles present in the particle population. Hence, one in every 10 fields should contain an indicative particle. If no indicative particles are located in the first 10 fields examined, then potentially, there are no positive particles on the sample stub. Statistically, however, this is a very small number to base any predictive finding of a positive GSR particle. The number of fields examined before a GSR sample population can be eliminated can, therefore, be doubled, or even trebled. Even by trebling the number of fields examined, the sample search time will still be significantly reduced when compared to the time taken to search the whole of the stub. If after searching half of the stub, no positive particles and less than 10 indicative particles have been located, statistically, there is little likelihood of finding a sufficient additional number of indicative and positive particles in the second half to satisfy the 1:10 positive/indicative GSR particle ratio as well as the threshold of two positive GSR particles for a positive result. If 10 or more indicative particles are located in the first half of the stub, the whole stub must be searched as there is still a statistically significant chance of satisfying the requirement for a positive result [15].

Looking for the GSR particle population can also bring another significant contribution to the GSR analysis and interpretation. For example, if the bullet is plain lead, there will also be a distinct Pb/GSR ratio from lead volatilized from the base of the bullet. The ratio of plain lead particles to GSR particles, in ammunition containing a plain lead bullet, will be higher at the muzzle than at the breech end of the barrel. This can be accounted for by the hot gases emerging from the muzzle having had longer to volatilize the lead from the base of the bullet than those emerging from the breech and the fact that particles of lead are torn off the sides of the bullet as it passes down the rifling. This can be extremely useful when determining whether particles found on a suspect’s hands were from actually firing a weapon or whether they were from merely being in front of the weapon, possibly as an innocent bystander, when it was fired. The situation with fully jacketed ammunition is similar, but the Pb/GSR ratio is much lower due to the smaller area of lead which is exposed [15].

Concluding, what the most recent trends in the analysis and interpretation of GSR stand is that for a positive result, in general it would be needed to check the chemical composition of the found GSR, the shape and morphology, the distribution of particles with respect to all the population found, the correspondence of the found GSR with the ones found in the spent cartridge, if available, and also some analysis on the organic GSR can help to reach a safe and sure conclusion. In fact, the combined analysis of both kinds of residue was reported to produce the most useful/powerful results [35]. However, if all these things are checked, the benchmark of a minimum of two confirmed GSR particles, together with associated particles, is considered the absolute lowest limit for a positive result [15].

Notice that in practice the situation is far more complex. If, for example, one is in an area where the police force is issued with ammunition containing Pb, Ba, Sb and Al and the criminals are using ammunition containing Hg, Sn, K and Cl, the finding of only one Hg, Sn, K and Cl particle on the hands of a suspect would have far more significance than if both the criminals and the police were using Pb-, Sb-, Ba-, Al-based ammunition. Moreover, this lower threshold also varies between countries and even between single forensic laboratories. Unfortunately, there is still too much free will in this forensic branch.

As seen from the previous paragraphs, in the years there was an evolution of the method, which is concomitant with the evolution of the technologies used to search and characterize the GSR, which will be discussed in 3.5. At the early stages of GSR examination, the idea is to try to create a formal approach in which samples are interpreted following the rules of a formal general interpretation system. Nowadays the approach is completely different, and is called "case-by-case" approach, meaning that the correct approach is to analyse the GSR collected on hands of suspects controlling the chemical composition, the shape and morphology, the particles population, and compare them with the GSR in the spent cartridges or in the barrel of the used gun [2]. This is why it was concluded that if ammunition that was recovered from a suspect/scene is not available for comparison with residue samples then any conclusions should be drawn with extreme caution [33]. The only drawback is that, as already seen, the shape and appearance of particles in a spent cartridge case are not typical of the particles detected in casework and that GSR particles of exceptional composition are formed using different types of ammunition in the same firearm. The most satisfactory way for analysing primer GSR from spent cartridges is to open the primer cup and analyse the interior. However, this is not practical in casework as it would mean the destruction of evidence and would be time-consuming, tedious, and in the vast majority of instances, unnecessary. In laboratory, the most practical way is to take a new ammunition, remove the bullet and the propellant and to fire the primer; then it is possible to check the interior part of the opened cartridge. Moreover, it is important to notice that it is not possible to decide to not sample a spent cartridge when possible only because it is of the same brand of the previously analysed spent cartridge. This is because manufacturers will use whatever is available at the time, from whatever source, to complete an order, provided that it meets the required ballistics performance and produces no residues that are injurious to the gun. For these reasons it is unwise to make assumptions about ammunition components and composition, even for the same calibre and manufacturer, as they could vary from batch to batch [5].

In general, the residue present inside the cartridge case reveals that the chemical composition directly results from the composition of the primer, while the chemical composition of the airborne particles may also show contributions from materials of the propellant, the core and the jacket of the projectile. Obviously, these considerations depend on the physical and chemical properties of the materials, such as their hardness, the melting points and the reactivity. For examples, tin and lead are soft metals that are greatly eroded by the hot gases of the detonation of the primer and the propellant and contribute a lot in the composition of GSR found on hands of shooters [20].

Notice that whenever no cartridge cases are found, it is also possible to find GSR particles on the bottom of discharged bullets, since it has been showed that the high temperatures and pressures in the firearm on discharge appeared to cause particles to fuse to the base of the bullet, maintain them attached to it also if it is highly deformed, as showed in Figure 38. Moreover GSR could be also found on the gunshot wound area, on the impact site, also at long ranges since some GSR travel with the bullet and are dislodged upon impact with the target, on a surface believed to have been adjacent to the point of discharge, on the firearm used, if found, since sampling directly from the firearm can also establish the contribution of residues originating from previous firings of different ammunition [1][12][36][37].

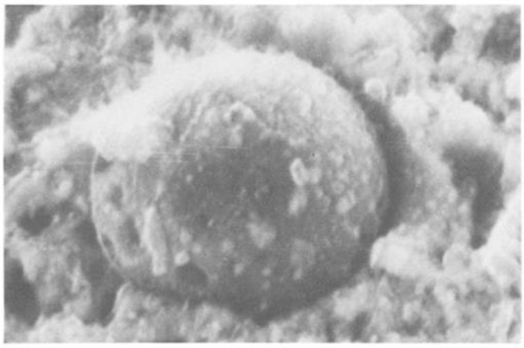


Figure 38: A GSR particle filling a crater-like hole in the bottom of a lead bullet [36].

As seen from the previous paragraphs, the case by case approach is mandatory and acquires also a greater importance if one wants to try to alleviate the main problems of this branch of the forensic science, which are the transfer problem, the time factor and the environmental source of GSR-like particles, which will be deeply discussed respectively in 3.6, 3.7 and 3.8.

Notice that some forensic scientist in the last years have also tried to apply a statistical approach to GSR evidence, in particular a Bayesian approach, to try to discover with certainty if a suspect has fired a firearm or not, based on the particle population. However, statistical quantification of the evidence remains elusive even under a case-by-case approach. This is mainly because the number of GSR particles depends heavily on the type of weapon and ammunition used, and also on the condition of the environment at the moment of the shoot, and consequently, to acquire representative data for likelihood calculations, one should perform experimentation using the same weapon, the same ammunition and the same environment as in the case under investigation, which is practically impossible. Moreover, the subjective choices made by a forensic expert when building a statistical model for the data deeply influence the conclusions in such a manner that small changes in the assumptions can lead to large changes in the quantitative evidence. Hence, an inevitable degree of arbitrariness will remain in the probabilities derived from the observed GSR data even when analysed by an experienced forensic scientist, which may have consequences for the legal process. For these two great drawbacks, statistical models are very rare in the forensic practice [38].

3.5 Identification of Gunshot Residues

There are an enormous number of techniques that can be used to analyse the residues expelled from the firing of a firearm. From a chronological aspect, the identification techniques used to identify and analyse the GSR have changed in parallel with the theories behind the GSR interpretation. At the beginning, as already stated, it was thought that for identifying a GSR, only an elemental analysis would be needed, so the so-called bulk methods were firstly used, which were able only to show what elements are present in the analysed sample. With the advancement of the theories, this was no longer enough and were needed techniques that were able to analyse GSR from a single particle perspective. Nowadays, in order to fulfil all the procedures shown and in order to be able to obtain a positive and univocal result in analysing the GSR, the SEM-EDX method seems the most suitable technology. Before describing it, in the next paragraphs it will be presented some of the most used technologies to analyse and identify both organic and inorganic GSR.

3.5.1 Bulk Analyses

In 1933, the dermal nitrate or paraffine test was introduced. This involved the taking of a cast of the back of the suspect's hand using hot paraffin wax. When cooled and set, the wax was peeled off along with embedded GSR particles. The cast was then sprayed with a 0.25% solution of N, N0-diphenyl- benzidine in concentrated sulphuric acid. The reagent gave a deep blue coloration with nitro-compounds. The great problem of this method is that oxidisers causing a positive reaction are found in fertilisers, pharmaceuticals, fingernail polish, urine and on hands of people after striking a match. This is why the paraffin test was declared obsolete. If one thinks of how many suspects were declared guilty or innocent according to this obsolete test, he could immediately understand of how delicate this branch of the forensic science is [1].

Then, the Harrison and Gilroy method was introduced, which consists of swabs moistened with dilute hydrochloric acid used to collect GSR on hands and to detect lead, barium and antimony. The swabs were dried and treated with triphenylmethylarsonium iodide, then, after drying again, a solution of sodium rhodizonate was added. The first reagent produced orange spots if antimony was present. The second one gave a red coloration with barium and after addition of dilute hydrochloric acid, the spots turned purple due to the presence of lead. However, this test was considered to be inconclusive, and the sensitivities of the colorimetric reagents used were not adequate to reliably detect the low concentrations found in actual firings [5]. Notice that both the paraffin test and the Harrison and Gilroy tests are also called colour or spot tests, since the change of colour gives the indication of the presence of the searched elements. Other colour tests are the sodium rhodizonate test, routinely used in many forensic laboratories for identification of entry and exit holes in clothing and range of fire determinations. In this test, an acidic swab passes on the area to be examined; then the swab is lightly sprayed with a saturated solution of sodium rhodizonate in water and then partially dried and lightly sprayed with dilute hydrochloric acid. Purple spots remaining confirm the presence of lead. If the swab is then placed into an alkaline condition, that is, by exposing it to the fumes of 880 ammonia solution, any pink/orange spots which develop indicate the presence of barium; because of its sensitivity and simplicity, it is still a commonly used test [15].

Another colour test is the Walker test, which is a chemical test for the presence of nitrates in unburned or partially burned propellants and gives information about the range at which a weapon was fired and identification of exit or entrance holes. Others are the modified Greiss test, used to detect nitrites; the diphenylamine test used to detect the presence of nitrates and nitrites; the Marshall and Tewari tests, both of which test for nitrites, helps to determine the firing distance, and the Lunge reagent, which is a chemical used to indicate the presence of nitrocellulose, an organic constituent of the smokeless powders [8].

In 1962 was presented the use of neutron activation analysis (NAA) for the identification of antimony and barium in GSR. Sample preparation involves irradiation of the sample using neutron bombardment, which forms radioactive isotopes by combining neutrons with elements contained within the sample. The neutron-induced radioisotopes emit X-rays which are characteristic of the individual elements, and the trace level amounts are determined by the peak radiation intensities [8]. The drawbacks are that the technique cannot be applied to Pb analysis, samples must be irradiated, it requires a nuclear reactor as a neutron source, trained personnel are required to carry out the analysis procedure, and it is also an expensive and time-consuming technique [2].

Another bulk technique is the atomic absorption spectroscopy (AAS). It Offers similar detection limits to NAA and is suitable for the determination of low levels of lead. Due to lower equipment costs and easy use of the instrumentation, this technique has completely replaced NAA. In AAS the sample is heated by a flame to a high temperature, thus breaking the chemical bonds and enabling individual atoms to float freely in the sample area. These ground state atoms are then capable of absorbing ultraviolet or visible radiation. The wavelength bands that each specific element can absorb are very narrow and different for every element. A detector is used to measure the decrease in signal from the source when absorbing atoms are placed in the light beam. The magnitude of the decrease in signal is dependent on the amount of the element of interest in the sample [5]. If in place of a flame is adopted an heated graphite tube, this technique become flameless AAS [15]. One disadvantage is that it is not capable of simultaneous multielement analysis. Moreover, heavily soiled swabs that potentially prevented effective extractions were also reported as problematic and a large number of false negatives were also reported in literature [2]. Notice that a negative test for gunshot residue is meaningless. It does not prove that an individual did not fire a weapon. Last but not least, in living individuals, the analysis is virtually always negative when the time interval is greater than 2 to 3 hours from the shooting incident to the sampling operations [39].

A more successful method with respect to AAS is the inductively coupled plasma-mass spectroscopy techniques (ICP-MS), which operate by coupling an argon plasma to a radio frequency electromagnetic field at atmospheric pressure [8]. They are always bulk analyses techniques and the advantages with respect to AAS are the lack of interference from common swab constituents, a wide linear dynamic range, a good precision and accuracy, and it is also faster. Moreover, it allows the detection of several isotopes for each of the elements of interest [2].

Notice that the SEM/EDX analysis coupled with this method can offer a very efficient and correct determination of the chemical constituents of the GSR but is a destructive and very time-consuming method. Multiple-collector ICP-MS (MC-ICP-MS) is a good technique in specific type of scenarios, like a shoot-out situation where several firearms and ammunition are discharged. Moreover, it was reported to be possible to link a bullet hole to the firearm that discharged the bullet. Last but not least, sector field, high-resolution-ICP-MS (SF-HR-ICP-MS) can be used to detect elements present in a very small concentration [2].

Other less used bulk analyses are the Graphite Furnace Atomic Absorption (GFAAS), used in the analysis of inorganic materials in primer residue, namely, Ba and Sb. After sample preparation, the Ba and Sb are in a liquid state. The sample is put in a graphite furnace, where it is subjected to a drying stage, an ashing stage, and an atomization stage in which free atoms are generated. The absorption signal measured during the atomization stage is proportional to the amount of element in the sample. However this method is quite difficult and expensive [8]. Other rarely used bulk techniques are the soft X-ray radiography and emission spectroscopy (ES), anodic stripping voltammetry (ASV) technique, Auger electron spectroscopy and selective photoluminescence technique [3].

3.5.2 Particle Analyses

Bulk analyses techniques in general lack of specificity, since results only show elements presence on a surface. Individually, the compounds that are present in most of the primers such as Pb, Ba and Sb can be found in an enormous number of situations, ranging from combustion of leaded petrol, automobile mechanics, brake systems, electrician, professional fireworks technicians and so forth [1]. Bulk analyses can only prove that Pb, Ba, and Sb were present at nanogram levels on the subject without correlating them to a single source; i.e., in principle, it cannot determine if these elements are independent or associated in a compound [8]. In practice, they can detect the searched elements in all the analysed sample but are not capable of found them in only single particles; some threshold are established in order to set a level above which results may be significant and correlated to the discharge of a firearm [5]. The fact that bulk analysis can be done if the levels of the elements present in the analysed GSR are above certain thresholds poses another limitation [2]. These results, by nature, are non-specific. Particle analyses, in contrast, analyse on a particle-by-particle basis, thus retaining the individual feature characteristics lost in a bulk analysis.

With the advancement of the theories on the GSR classification and interpretation, the pure chemical analysis became only a part of the work to be done in order to reach appropriate results from the GSR analysis. The most appropriate particle by particle method used also nowadays for the analysis of the GSR is the scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDX) or a wavelength dispersive X-ray spectrometer (WDX), the only appropriate devices to study GSR chemical composition and morphology on a single particle basis. Notice that most of the other techniques that gives the same results as SEM/EDX does, are destructive, this is why they are not used [15].

3.5.3 How the SEM Works

In a SEM, objects are described and seen in terms of how they interact with energy. The following discussion will be divided into three components, starting from the description of the source of energy, then the explanation of the interaction between the energy source and the specimen, and finally the description of the detectors, which are the devices with which the effects of the latter interaction is detected. A schematic drawn of a SEM is showed in Figure 39.

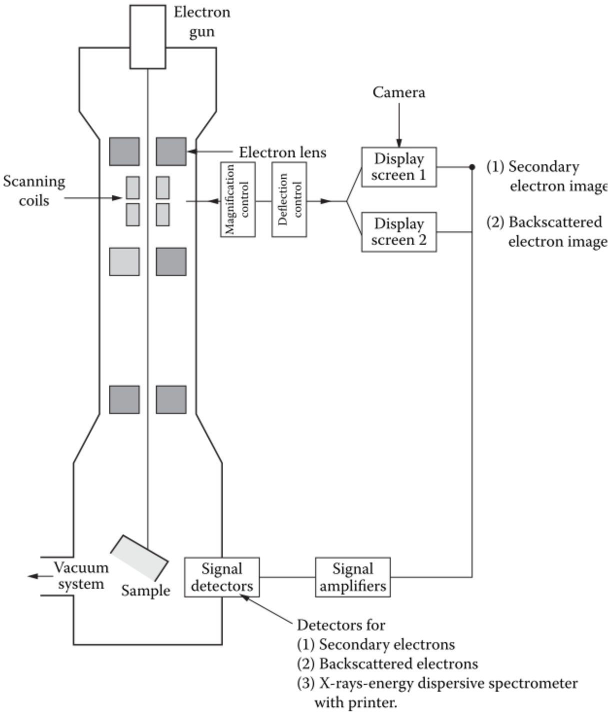


Figure 39: Schematic draw of a SEM with the EDX detector [5].

In general, the outputs of a SEM equipped with an EDX detector are images using both backscattered or secondary electrons, an analytical spectrum created using X-rays and also contrasts and brightness peaks [13]. In Figure 40 is showed a modern SEM workstation.

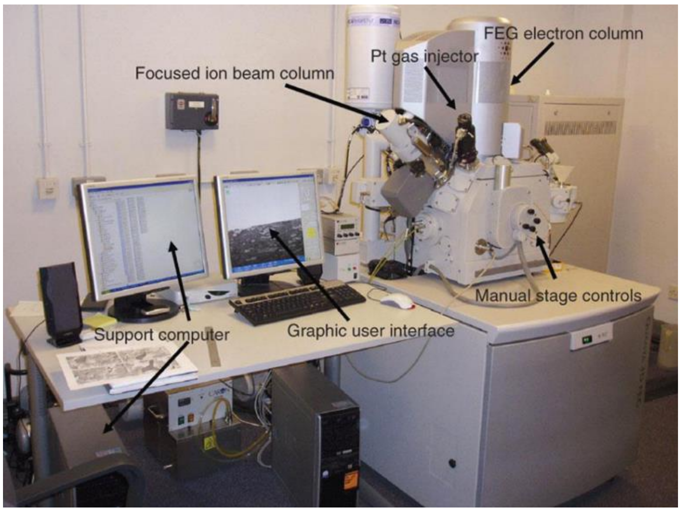


Figure 40: A modern SEM workstation [6].

The images are obtained with an extremely higher resolution that an optical microscope; in fact, the maximum resolution of an optical microscope could reach 200 nm while SEM's one reaches 0.5 nm. This is because the resolution, which is the minimum distance between two points that the microscope is able to observe separated, is inversely proportional to the wavelength of the radiation utilized to create the image. Electrons indeed have a much smaller wavelength with respect to the visible light [6]. In Figure 41 is showed the same object by means of an optical microscope and by means of a SEM utilizing secondary electrons; the differences are enormous.

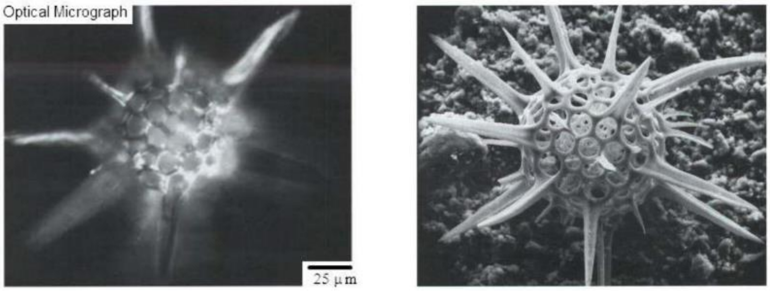


Figure 41: The same object observed via an optical microscope (left) and a SEM (right), which utilizes secondary electrons [6].

In Figure 42 are showed the main structural differences between an optical microscope and a SEM.

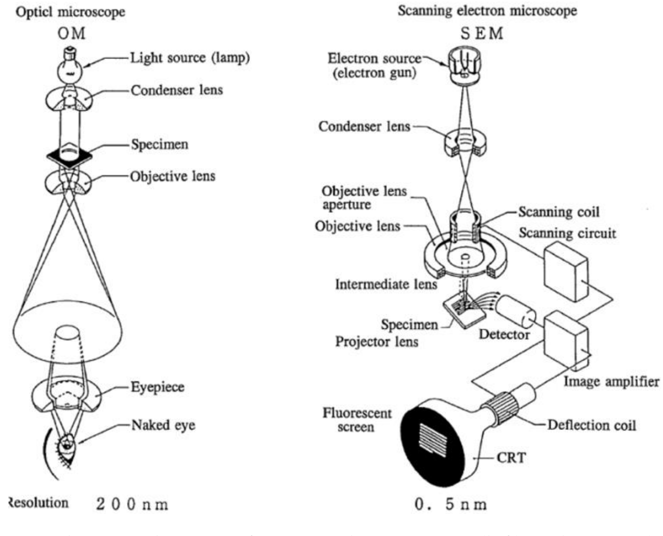


Figure 42: Schematic drawing of an optical microscope (left) and a SEM (right) [6].

3.5.3.1 The Column

To produce the beam of electrons which are sent to the sample that needs to be analysed, usually it is used a heated wire, usually made of tungsten, which is bent at an acute angle, from which the electrons are emitted; this process is called thermionic emission [13]. Also other electron sources exist, like the lanthanum hexaboride (LaB_6) filament or the so-called field emission gun, which both cost more than the tungsten filament but provide extended filament life and stability with superior image resolution. All of them are used with accelerating voltages of at least 20kV for optimum generation of backscattered electrons and X-rays from GSR particles. Commonly, an accelerating voltage of between 20 and 25kV is used for manual and automated searching [12].

Since the electrons are emitted in all directions, under the sharp wire, which is maintained at a negative potential, an anode with a hole is placed in order to let the electrons enter in the column. A bias voltage is applied to the grid structure that encloses the filament, so as to focus the beam to a small point, called the "crossover", which dimension is between 10 and 50 μm. The rest of the column lenses further demagnify this already small beam reaching a diameter of about 5 μm [13]. Below the filament is a Wehnelt, part of a lens that focuses the electrons. Electrons passing through the Wehnelt are accelerated into the column. The anode is positive, as it happens in all electrical devices, relative to the cathode but only because the Wehnelt is operated at a negative voltage. A small negative bias voltage placed on the Wehnelt deforms the anode field to help draw the electrons into the column [8]. A scheme of the just described electron gun is showed in Figure 43.

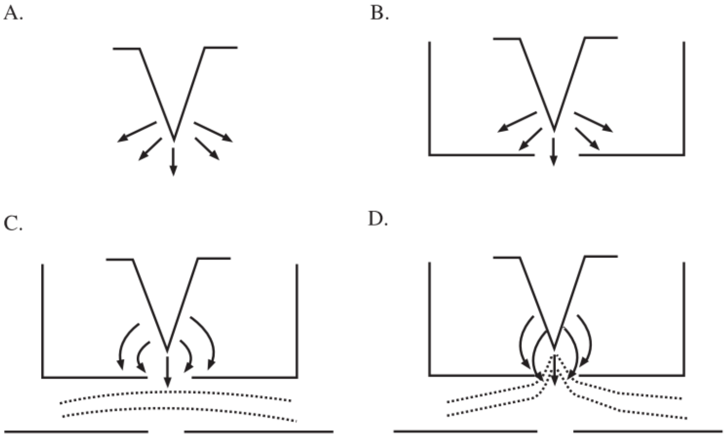


Figure 43: Electron gun configuration. (A) Electrons given off by the heated filaments are scattered in all directions. (B) Electrons directed toward the column by the Wehnelt. (C) Electrons attracted towards the column by a positive charge on the anode. (D) Bias on the Wehnelt deforms the anode field for more efficient collection of electrons [8].

Current in the emitting wire is enhanced till additional filament heating produces no appreciable increase in electron emission. At this point, the filament is said to be saturated, and the beam is energetic and stable. Under the anode hole there is the SEM column, which consists of a central "tube" surrounded by magnetic lenses that produce a small focused beam, circular in cross section, and reduce the scatter of the beam itself.

The dimension of the final aperture through which the electron beam passes is important in that a larger aperture allows more beam electrons to illuminate the sample, resulting in a brighter and clearer image. However, the angle of convergence of individual electrons in the beam will be larger in a wide aperture, and this will reduce the depth of focus, which is related to the angle of the cone of electrons, in turn related to the aperture of the electron microscope. The aperture on the SEM is very small, generally of the order of 100 µm, which results in a depth of field in the order of over 100 µm at 100× and several tens of µm at 500×. In the case of GSR where particle size is generally 10 µm or smaller and that usually these are analysed at about 100×, the entire particle is in simultaneous focus. Such is not the case with optical microscopes [8]. In the entire column, to not hamper the formation of the electronic beam, vacuum is created by a series of pumps; one main pump, one turbomolecular or diffusion pump and one last additional ionic pump [13].

Notice that the optics of the SEM can become dirty, phenomenon that can happen for example when a not perfectly inert sample is placed under vacuum, and so degassing may occur, or due to the unavoidable environmental contamination. When such happen, electron beam could deform and may not be circular in section anymore, but "astigmatic", and this will affect the quality of the image. In fact, to correct the beam's deformations, SEMs are equipped with a special set of crossed focusing elements called stigmators. The general issues of the SEMs columns are that the filament should be aligned in its structure, it should be properly saturated, otherwise too low of a current will make it insensitive to small changes, but too high of a current will reduce the filament life [12], the beam should be aligned with respect to the anode, the proper bias should be placed on the Wehnelt, imaging should be assessed for astigmatism and corrected by applying the stigmators or cleaning the column as needed [8].

3.5.3.2 Beam-Sample Interaction

Matter is made of atoms, which are made by nucleus of protons and neutrons, and electrons that rotate on different shells around it. When a beam of electrons, called primary electrons, hits the specimen, the electrons penetrate a distance directly proportional to the beam energy and inversely proportional to the specimen density. As the primary electrons interact with specimen atoms, the energy is dissipated within an interaction volume. From 20 to 30% of the primary electrons collide with specimen atoms, rebound elastically with little energy loss, and are scattered out of the specimen. The reemergent beam electrons are known as backscattered electrons (BE) and are highly energetic. When the primary electron beam hits the specimen, atoms may be ionized by the forced emission of electrons. The specimen electrons emitted from the sample are referred to as secondary electrons (SE), which are relatively low energy.

When secondary electrons are emitted from an atom, they create "holes" in the electronic configuration. These holes will be filled by the collapse of electrons from any higher order shell. This process is called an "electron jump." Higher order electrons are less tightly bound to the atom than those in inner shells, and when they "jump" to an inner vacancy their excess energy is released as characteristic X-rays, so called because the properties of the X-rays, meaning energy and wavelength, are characteristic of the element from which it was derived [8]. These emitted X-rays are called according to the convention showed in Figure 44.

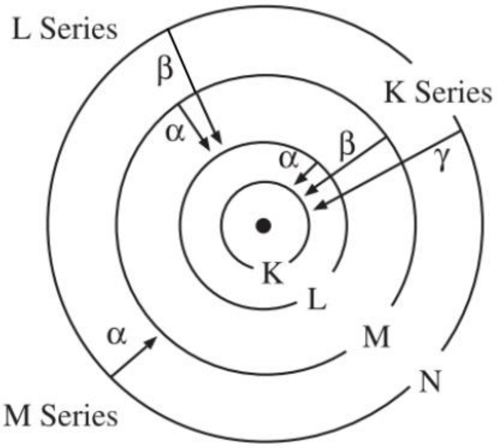


Figure 44: Naming convention for X-rays generated by specific electron jumps [8].

The naming convention showed in Figure 44 is quite easy to understand by making and example. In the name of the X-ray called Lβ, the first character refers to the shell in which the electron hole was created and into which the electron jumps, in this case the shell "L". The second character refers to the number of "jumps" that an electron needs to do to reach the shell with the hole: alpha (α) for one shell, beta (β) for two shells, gamma (γ) for three shells.

Notice that there is also another type of electrons that are emitted from the specimen which are the Auger electrons, not processed by the SEM. Another important aspect are the relative depths from which these four types of electrons can escape the examined sample. In Figure 45 are showed the latter relative depths. It is possible to see how the Auger electrons come from a very thin superficial layer; SE also come from a superficial layer while BE and X-rays come from a deeper layer.

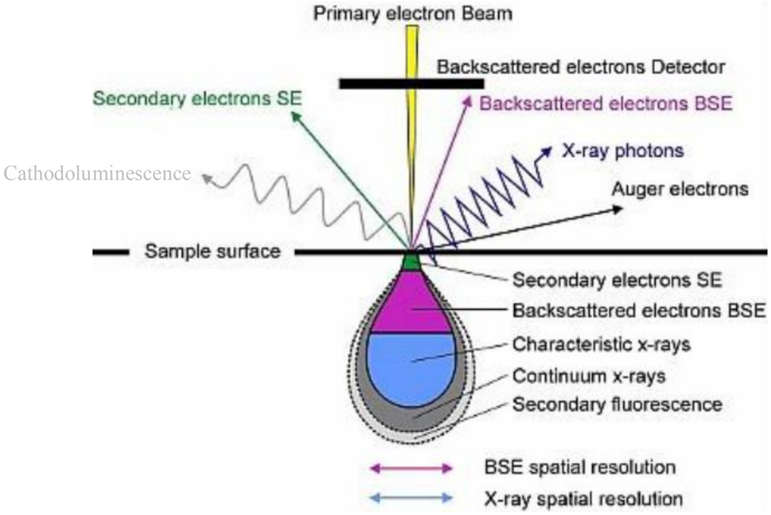


Figure 45: Relative depths of the four types of electrons [6] .

Notice that because the specimen is in a vacuum the electrons cannot be sent into the chamber. Therefore, the specimen should be a conductor of electrons, otherwise, no sort of image will be visible. For non-conductors, the general solution is to give the specimen a thin coating of conductive material, such as gold, gold and palladium, or carbon. Au and Pa are very good conductors and the resulting images may be better than those coated with C. However, these relatively heavy elements interfere with the beam electrons, sample electrons and emitted X-rays, and contribute Au/Pa X-rays that cannot be differentiated from X-rays generated from Au or Pa in the specimen. C does not absorb as much energy and generates fewer interfering peaks, but the problem of differentiating coating from specimen C remains.

There is a solution which can eliminate such charging effect called variable pressure operation. This consists in maintaining a bit of atmosphere in the sample's chamber, obviously maintaining the filament in vacuum, which dissipates charges and reduce these interactions. In fact, in variable-pressure SEM, also called environmental-type SEM, imaging can be performed directly on a nonconductive sample when the chamber pressure is maintained at a level where most of the electrons reach the sample surface, whilst there are enough gas molecules to ionize and neutralize charging.

Another advantage of the variable pressure operation is that non-conducting specimens do not have to be altered by the coating process, thus allowing larger samples, an entire glove, for example, to be accommodated [8]; The variable pressure SEM will be further explained in 3.5.3.6.

Some issues regarding the beam-sample interaction are that to avoid charging effects and to be sure the sample has a continuous path to ground through specimen holder. Moreover, the word “point” is often casually used to refer to the intersection of the beam with the specimen surface. It is important to keep in mind that this region is in fact a small volume. In fact, the distribution of X-rays obtained from a single phase consisting of two elements may be identical to the distribution of X-rays obtained from two closely spaced single element phases. Last but not least, X-rays will not be generated unless there is sufficient energy in the electron beam to excite the elements of interest, practice called “over-voltage”. Make sure to have sufficient accelerating voltage to identify the elements of interest [8].

3.5.3.3 Detectors

What detectors need to detect in SEM are secondary and backscattered electrons, and X-rays for compositional analysis. Before introducing the different types of detectors, it is mandatory to give a brief description of how electrons are emitted or reflected from the specimen. This is because electrons are emitted in all directions from the sample but some differences between a flat surface or an angled surface, or between backscattered electrons (BE) and secondary electrons (SE) exists. These differences are showed in Figure 46.

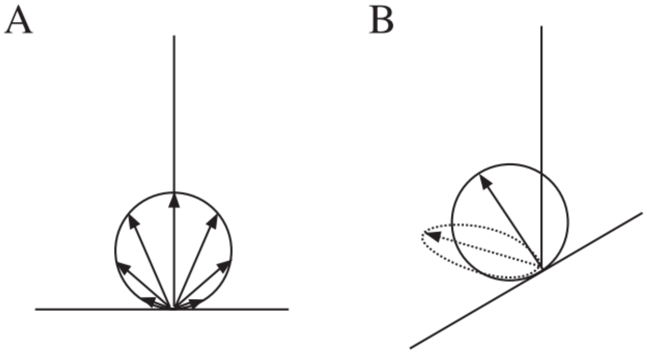


Figure 46: Relationship between incident beam and direction of emitted electrons from a perpendicular surface (A) and from an angled surface (B).

As Figure 46 shows, the BEs and the SEs are emitted in all directions, but most of all in the perpendicular direction, and there’s no difference between them. However on an angled surface, the BEs, represented by the dashed line and the ellipse, behave as if reflected, while the SEs also in this case are especially emitted perpendicularly to the incident surface. Notice that the length of the arrows represents the amount of electrons emitted.

The most commonly used SE detector is the Everhart-Thornley (ET) detector, which consists of a collector, scintillator, light pipe, and photomultiplier. The ET collector has a small positive charge, which attracts the SE.

A scintillator element is provided with a large positive charge that accelerates the electrons toward it; the number of electrons reaching the scintillator are dependent on the topography of the sample surface since this will influence whether or not a particular area on the sample surface is visible to the primary beam and detector and the elemental nature of the sample surface as this will affect the energy of the secondary electrons and consequently their susceptibility to the cage potential [5]. The electrons emit light when they crash into the scintillator, and this light is carried by the light pipe out of the specimen chamber to an external photomultiplier tube where the light energy is converted to an electric current. Notice that the high energy BEs cannot be deflected by the ET collector, so only the BEs emitted in the right direction toward it can be collected [8]. In Figure 47 is showed an image of a GSR particle obtained using secondary electrons.

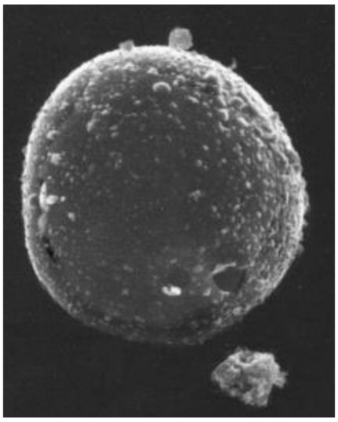


Figure 47: An image of a GSR particle obtained via secondary electrons [40].

To detect BEs, it is always possible to use a scintillator, bigger than the one in the ET detector and positioned so that more BEs strike it, or a solid-state BE detector, which consists of a semiconductor "diode". When struck by a BE, the semiconductor produces an electron-hole pair, the components of which migrate in opposite directions under the influence of a small applied field. These moving charges produce an electrical current. Notice that the BEs have a very high energy and so velocity, and it is not possible to deflect them applying to the detectors a positive charge. What is usually done is to apply a negative charge which is not sufficient to repel the BEs, but it will repel the SEs, resulting in a purer BE signal. In Figure 48 is showed the same GSR particle showed in Figure 47, but using backscattered electrons.

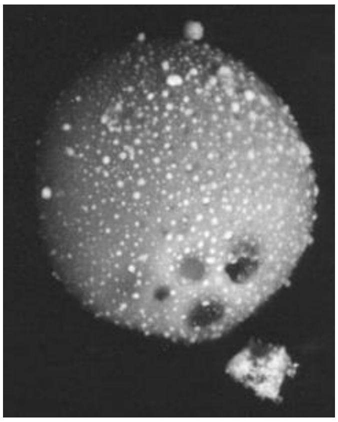


Figure 48: An image of a GSR particle obtained via backscattered electrons [40].

To produce an image, scan coils in the column cause the beam to raster or scan over an area of the specimen, this explains the presence of the word "scanning" in the name SEM [6]. The electrons, either SEs or BEs, are detected at known beam positions in that raster and the image is reconstructed on a display monitor. Regions where electrons were detected in large numbers are displayed as relatively bright compared to regions where electrons were detected in small numbers. When the beam raster is small, the image displayed on the screen shows relatively high magnification and vice versa. Since SEs can be deflected, in the image produced through them, the shadows are considerably softened, and this results in a 3D image very detailed. As a contrary, the path of the BEs cannot be curved, so the image produced appears "flatter".

However, the major advantage of images produced in the backscattered electron mode is that phases can be discriminated. Because like charges repel, electrons "bounce off" the electrons surrounding the specimen atoms and scatter back out of the specimen. The number of BEs scattered back out of the specimen is proportional to the number of SEs surrounding an atomic nucleus. The higher the atomic number, the greater the number of specimen electrons, and the greater the likelihood that beam electrons will strike specimen electrons, resulting in a greater number of electrons that will be scattered back and a brighter image. This is very useful, meaning that the brightness of the zones on the image depends on the atomic number of the atoms that compose a certain zone. Higher the atomic number, brighter the image. Notice that this information cannot be used directly for phase identification, it can be used for phase differentiation and screening. When looking at an entire sample of GSR, examination would be in the BE mode, thus passing up the "haystack" of darker particles while singling out the GSR "needles." This is at the base of automatic research of GSR particles in Computer-controlled SEM (CCSEM) devices, in which usually the threshold for flagging up the promising particles is set at a minimum atomic number of 26, starting for example with iron [13]. The CCSEM will be extensively discussed in 3.5.3.5.

Last but not least, pay attention when working on SEM because the operator should check the size calibration periodically by comparing the measured size of an object to the known size of that object. A variety of size standards are available for this purpose. Keep in mind that the column should be degaussed prior to performing any size measurements [8].

Regarding the X-ray detectors, the most used one is the Energy Dispersive Spectrometer (EDS), also called energy dispersive X-ray spectrometer (EDX), which is a very sophisticated device that accurately measure the very miniscule amount of ionization current produced when an X-ray is absorbed in a silicon sensing element, called silicon diode. To accomplish this feat, the diode must be maintained at a very low temperature, in fact a reservoir of liquid nitrogen at –127 C° is present, and very specialized circuitry must be employed. The detector can process a single X-ray per time. The time during processing is called dead time and the time in which the detector is ready for analysis is referred as live time. For an efficient analysis, it is recommended that dead time reside in the approximate range of 20 to 40%. At lower dead time, the processor is idle much of the time, waiting for the next X-ray.

At higher dead times, the X-rays come in so quickly that there is a high probability that a second event will interfere with the measurement of a first event. This phenomenon, referred to as “flooding” or “swamping” the detector, should be avoided.

Since the energy at which an X-ray is produced changes according to the element that emits it, the EDX can built graph on which on the vertical axis counts the X-rays absorbed while on the horizontal axis reports the different X-rays energies. Such graph is called analytical spectrum and each peak represent a different chemical element. Higher the peak, bigger the amount of the correspondent element presents in the specimen. This permits to do the chemical analysis of the specimen, which is called microanalysis. Certain software put on each peak the name of the correspondent element, but pay attention since some elements share the same peak, as will be discussed in the next paragraph [6]. In Figure 49 are shown some examples of analytical spectra.

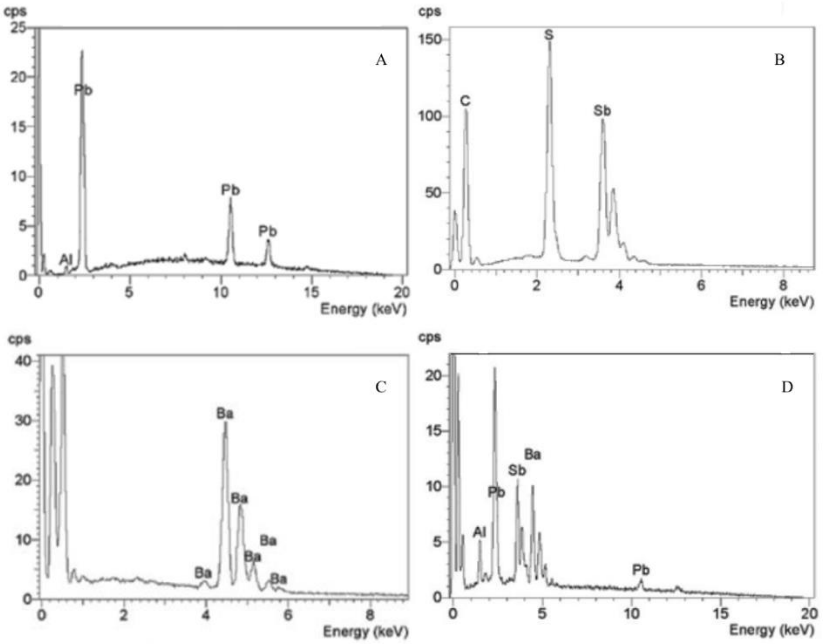


Figure 49: Examples of analytical spectra. (A) Analytical spectrum of lead styphnate crystal with aluminum fine particles attached to it. (B) Analytical spectrum of antimony sulphide crystal. (C) Analytical spectrum of barium nitrate crystal. (D) Analytical spectrum of a GSR residual coming from a typical non-corrosive primer mixture [6].

In Figure 50 is shown an example of an analytical spectrum created from the analysis of GSR coming from a calibre .22 LR Winchester ammunition. This is a rimfire ammunition and is possible to notice the presence of only lead and barium without antimony.

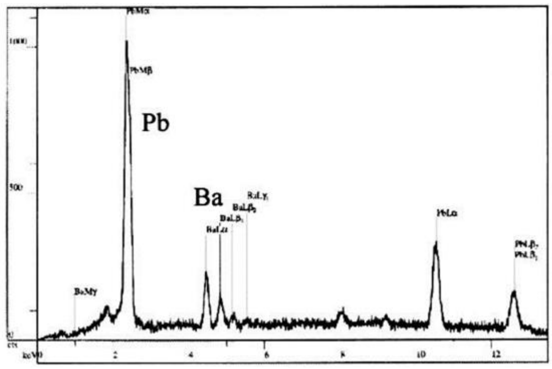


Figure 50: Analytical spectra of a GSR coming from a calibre .22 LR Winchester ammunition [6].

Since in every detector there is a random error, the resulting plot of successive X-rays from a single element is represented by a peak of perhaps 100 to 150 eV wide rather than a single discrete value. Because these peaks are broad, there may be overlap among peaks of various elements, which sometimes makes element identification problematic. This problem is alleviated somewhat by the fact that most overlaps do not involve the exact peak location, that peaks of overlapping elements are not necessarily exactly the same shape, and that not present in the lighter elements. An overlap that usually happens in GSR analysis is the overlap between Pb and S peaks. What could help is that the Pb peak is usually asymmetric due to the overlap and that additional Pb peaks are also present at different X-rays energies. Other typical overlaps in GSR analysis happen between the peak of calcium and antimony and between the peak of titanium and barium [1]. In cases of peak overlap, a well-trained analyst must take care to identify the element responsible for that peak, for example by means of long EDS acquisition time, expanding the scales for detailed inspection, and comparison to known elemental standards. Moreover, since usually each element is reported on the analytical spectra on more than one peak, searching for other peaks that are not overlapped could help to correctly identify the real elements present in the analysed sample [6]. Sophisticated software is also available to deconvolve such overlaps [8]. A typical Pb-S overlap is showed in Figure 51.

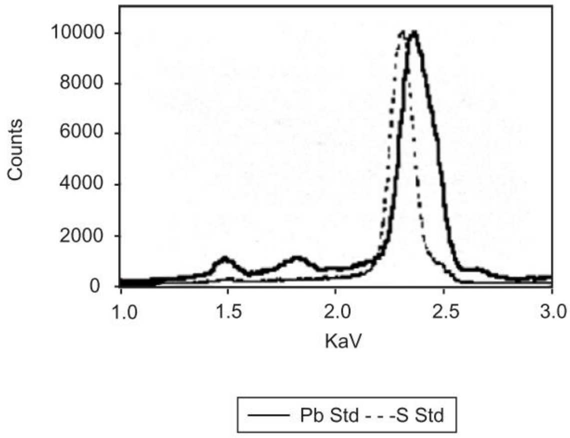


Figure 51: Peak overlaps of Pb and S [8].

Notice that Another solution to resolve ambiguous peaks based on EDS is to use the wavelength dispersive spectrometer (WDS), also called Wavelength dispersive X-ray spectrometer (WDX). Wavelength is inversely related to energy and is thus just another measure of the same property. Wavelength can be more accurately measured using a WDS than can energy using an EDS, and the resulting peaks are very narrow. The peaks that display considerable overlap in EDS are observed as discrete peaks in WDS. However, an entire EDS spectrum for all elements excited in the beam interaction volume can be processed simultaneously and quickly. WDS analysis proceeds on an element-by-element basis and requires many minutes of operator time for each element. WDS units are also considerably more expensive to purchase and maintain. Some SEMs have optional WDS capabilities.

Another problem that can happen with X-ray detectors happens when simultaneously two X-rays strike the detector. This is seen as a sum of peaks, and wrong conclusions are highlighted.

Obviously, it is a very rare phenomenon, except when a very large number of X-rays enter in the detector. However, this can be avoided by reducing the spot size or increasing the working distance. Another problem is the one called "escape peak", in which a silicon X-ray can be excited in the detector material, thereby reducing the energy detected by the amount of energy it took to liberate the silicon X-ray (e.g., 1.74 KeV). Moreover, some high energy X-rays can stimulate the emission of X-rays from the construction material of the chamber, most commonly iron. Paying attention to the geometry of the detector can reduce such phenomena.

Last but not least, the EDS should be calibrated once a month by means of a reference sample, usually of copper, which is greatly conductive. Bear in mind that when particles are analysed, as it happens in GSR, the composition of features on the surface facing away from the detector cannot be determined [8]. Moreover, windowless EDS detectors are not suitable for GSR analysis as samples are often contaminated with biological and other organic matter that can out-gas and deposit on the unprotected detector surface resulting in a decline in performance. Beryllium or organic/polymeric windows are suitable for protection of the detector [12].

3.5.3.4 Working Distance

The working distance is defined as the distance between the bottom of the filament and the surface. It affects image quality and X-ray detection. The strength of the signal is a function of distance, the inverse square law, and the detector geometry. Moreover, the best working distance for a good image may not be the same for a good chemical analysis via EDS, so a compromise must be chosen. Notice that the SEM can measure the working distance from the amount of current needed to drive the final lens so that it focuses the beam on the surface. However, as the lens current is changed repeatedly, residual magnetism may build up in the lens material. This distorts the computations of working distance and thus produces an incorrect magnification value. This residual magnetism can be eliminated by a process known as "degaussing," which should be done on a regular basis, and particularly before the magnification is calibrated [8]. This is because elimination of hysteresis of the magnetic field optimizes accuracy of the magnification and alignment of the electron optical axis [12].

3.5.3.5 Automated SEM Analysis

A serious disadvantage to the use of the SEM for the detection of firearms residue particles was the excessively long time required to search for and locate the particles. The lengthy searching was mainly due to the large sample area, the time spent examining, analysing and rejecting a large number of non-firearms particles and the presence of extraneous material such as fibres and skin debris which could make the particles difficult to find or even conceal them from view [1]. Sample clean-up procedures and the use of an automated SEM have completely solved these issues.

CCSEM or automated-SEM can rapidly screen thousands of particles by using the BE imaging, as described in 3.5.3.3, and store the composition, size, images, and location coordinates of potential GSR particles.

Obviously, to validate results, such flagged particles need to be analysed by an operator by manual microscopy for relocation and confirmation. Automated SEM/EDX is the current method for GSR analysis because is fast, both morphological and chemical characteristics, and without elaborate sample preparation.

GSR samples must be analysed in the "as collected" condition; meaning that it is not possible to uniformly distribute the collected particles. Usually, very little operations of samples preparation are needed, like dissolving the adhesive and redepositing the particulate on an SEM stub, needed only when sample are collected on multiple-adhesive-layer stubs, otherwise it is possible to directly put the stub in the SEM. Notice that if no particles are found in 45 % of the sample, this would indicate with 95% certainty that any further analysis would be unlikely to detect the particles required for a positive result. If 60% of the stub were analysed with no GSR particles detected, the certainty factor that the result would not be positive would increase to 99%. All these percentages are given if the particles are uniformly distributed on the sample, something which rarely happen, so usually is suggested to analyse all the collected stub [8]. In general, an automated SEM/EDS system should provide hard copy output and long-term storage of the sample identifier and stage position, the field of analysis, the stage coordinates of all detected particles, the total number of particles detected, and the total number of particles classified as GSR. Where large numbers of particles of potential GSR are detected, the re-analysis and verification of only a reasonable number of the total particles detected can be sufficient [12].

Notice that the set of parameters used for the automatic research of GSRs on the SEM/EDX are not standard but depend on the sample, so they vary sample by sample and also depending on the time after firearm discharge. For example, a sample collected from a suspected shooter a number of hours after firearm discharge is likely to contain smaller sized particles than a sample collected immediately and a search program would need to be tailored accordingly [41]; also with heavy metal free primers, particles of high atomic number will not be present in the GSR, so a different set of parameters must be used. This gives additional strength to the fact that it is important to know what type of ammunition is used in the analysed crime. Lastly, in automated GSR particle search systems, the extent to which the SEM and EDX communicate and are integrated varies according to the manufacturers involved and the capabilities of the hardware/software architecture. Automated GSR/particle search systems may include a motorized and programmable sample stage, an automated stage and beam control with the ability to recall stage locations for verification of the composition of particles of interest, a saved image of the analysed particle and a software for particle detection and classification [12].

It is important to notice that even if most SEM systems have now fast, fully automated, search routines, these can still take three or more hours per sample. Considering that two samples must be taken from each hand and one blank control for each suspect, the time involved to process each case can be prohibitive. This is why it is mandatory, by using some simple statistical data and the elimination of certain types of particle, to reduce this search time which can, even with a fast-automated scanning routine, be reduced dramatically with even 30 min or less being possible.

In fact, all automated systems now come with a particle recognition system where the elemental composition of expected particles is logged into a database. These databases help the system to eliminate the long scan of non-relevant particles or to 'flag up' certain other particles which require further investigation. For example, the first particles to be flagged up relates to particle size. No GSR particle above 20 μm should ever be present on the hands. Any particle of a size greater than this will fall off almost immediately. Moreover, particles smaller than 1 μm are usually not searched to avoid airborne contamination and reduce errors due to the resolution limitations of SEM. However, it is reasonable to assume that nanoparticles are not only likely to stay airborne for longer periods of time and contaminate the scene and/or non-related bystanders but may also persist longer on any surface. Therefore, it must be clear that the filtering of smaller particles is advisable when one wants to eliminate the chances of a false positive as a result of cross contamination even though the nanometric particles are present and remain undetected, since nanometric particles are very easy to be transferred [24]. Perfectly spherical particles of GSR should also be viewed with suspicion and appropriately 'flagged'. GSR particles are invariably spheroidal, but rarely spherical [15]. These databases also have a list of high atomic number particles that can be eliminated for GSR examination purposes, collected in Table 9.

Table 9: List of high atomic number particles that should be ignored during SEM analysis [15].

Ba	These particles can be ignored, since it is far more probable that Ba only particles come from $\mathbf{BaSO_4}$ particles from paper or even ladies' make-up.
Ce-La-Fe-Al	Large, absolutely spherical particles in the region of 5 μm or more containing these elements can be ignored as these are invariably mischmetal from cigarette lighter flints. Mischmetal gives an extremely strong backscattered electron detector signal and should not be confused with that from a GSR particle.
Fe-Al-Si	Spherical particles containing these elements and ranging in size from 0.5 to 100 μm can be ignored. These particles are boiler fly ash and contain silicon (SiO_2), aluminium (Al_2O_3) and iron (Fe_2O_3) and, like mischmetal, give a strong backscattered electron detector signal.
Sb	Antimony is, for some unknown reason, very rarely encountered alone as a GSR indicative particle. Once again, if a pure antimony particle is located, it is most probably a contaminant.
Pb-Sn	Particles containing these elements are invariably from type metal or plumber's solder and should be ignored.
Th	In some areas where camping is a popular pastime, spherical particles of thorium are sometimes located on the hands. These are from the mantles used in gas or paraffin-powered light sources. Being spherical and of a high atomic number, they give a very strong backscattered electron signal. Any particle containing thorium should be ignored.

Moreover, also a list of detection parameters needs to be appropriately set before conducting the automated analysis. The working distance, electron beam spot size and magnification should be set at the optimum settings for detection of GSR by a particular instrument and should be fixed for all the analysis unless there is a particular reason for modifying parameters, reasons which should be documented in the relevant case record. As already said, automatic research of GSR works looking at the brighter particles on the stub. The magnitude of the brightness is related to electron beam current, in particular increases in intensity as the beam current increases, mean atomic number, and size of the particle.

The beam current can be measured with a Faraday cup, a specimen current meter, or monitored by comparing the integrated counts within the same peak in sequentially collected spectra from a known standard. The sensitivity of the BE detector to changes in mean atomic number of a particle at a given working distance, spot size, and beam current is adjusted using the brightness and contrast settings. Using an appropriate reference or calibration sample, the BE detector response should be adjusted to set a threshold or grey scale that will allow the detection of a particle whose mean atomic number is like that of a typical Pb, Ba, Sb particle [12]. Moreover, notice that if in place of the usual tungsten filament a field emission gun is used, it is possible to provide a higher beam current able to decrease even more the auto-search run time [42].

Notice that if one standardizes the search parameters and the area searched on each lift, then it is possible to express the number of gunshot residue particles per unit of area, permitting comparison of the concentration of particles on the different surfaces on which they are sampled. The distribution may be an additional information which can help to discover if the sample analysed is or is not consistent with firing a gun [39].

The SEM beam stability is crucial for a stable BE signal and is critical in both manual and automated systems while the EDX energy calibration is important for accurate identification of elements and, hence, automated classification of particles. The SEM beam stability and EDX energy calibration can be monitored during analysis by some automated systems, using a suitable reference standard. Moreover, when operating in automated mode, a suitable reference sample/standard, like the ENFSI Synthetic GSR Standard or a prepared GSR standard subjected to repeated analysis with a known particle distribution and/or composition, size and location should be analysed in order to test the accuracy of particle detection and classification. This standard should be analysed regularly to check the detection efficiency of the instrument. It can also be suitable for adjusting the BE detector and setting the SEM/EDX parameters prior to automated analyses [12].

Last but not least, recent trends are now moving toward coupling the automated SEM-EDX technology with an electron backscattered diffraction detector, capable of revealing nanocrystalline domains present in the particles that occur as a result of extreme temperature and pressure conditions and then rapid cooling. In general, the SEM-EDX-EBSD seems to be potentially the most specific method for recognition of post-blast and gunshot residue for its ability to simultaneously answer the question on the chemical content, morphology, and the internal structure [4].

3.5.3.6 Variable Pressure SEM

Since particle loss and possible contamination during preparation are critical parameters in the analysis of GSR, the possibility offered by the variable pressure SEM to not prepare the sample with conductive coating and to analyse also non-conductive samples without any preparation is a great advantage in GSR analysis. In fact, with usual SEM and non-conductive materials, there is no path for electrons to travel away from the sample at the point of beam contact or impact. This causes a charge build up that blooms bright in that localized region and washes out the features of the image. This phenomenon is called “Charging effect”. Moreover, samples may have outgassing problems, caused by oil, grease, or moisture.

Some materials outgas naturally under vacuum due to porosity. Other materials may have high vapor pressure properties. If a sample is outgassing, it may require several hours of evacuation before the electron beam of the conventional SEM can be turned on. Some samples are evacuated for long periods of time in a separate chamber to remove oil vapor or moisture before they can be placed in the microscope for examination. Numerous materials require intricate sample preparation techniques when the examiner uses a conventional SEM. A variable pressure SEM can avoid sample preparation, reducing time consumption and contaminating risks. An example of a variable pressure SEM is showed in Figure 52.

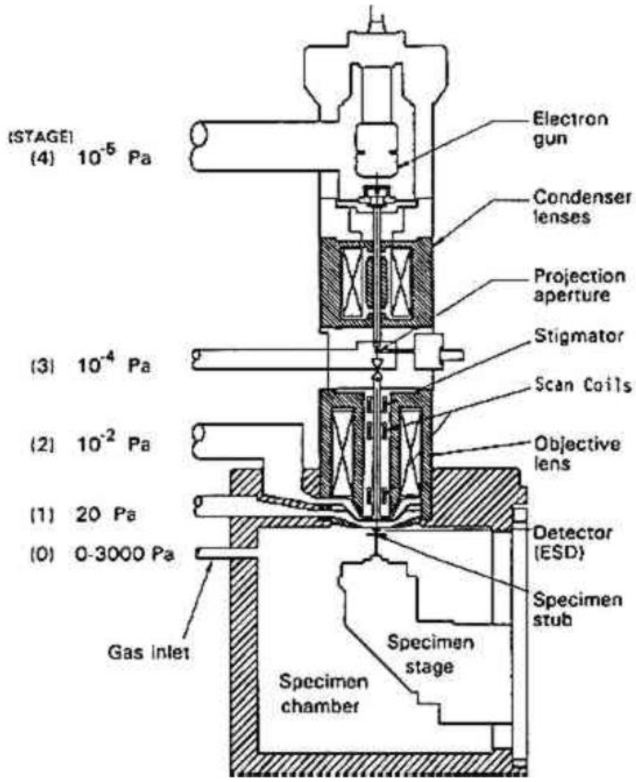


Figure 52: The electron optical column and differential pumping system of the environmental scanning electron microscope [43].

It is possible to maintain the high vacuum required in the gun assembly, thus creating an efficient condition for beam generation, acceleration and control and then, through a series of restrictive orifices, to isolate the sample chamber and regulate the pressure at an elevated level. This bleeding of gas into the sample chamber supplies additional gas molecules, which are ionized by the action of the beam, causing dissipation of surface charge. Various samples that were once considered virtually impossible or extremely difficult to prepare and examine due to charging and outgassing are now being examined with no preparation at all. GSR samples collected on a non-conductive adhesive substrate can be examined routinely at a sample chamber pressure of 0.2 torr and a working distance of 16 mm. Because a sample may not be coated, particles that may be lost in the preparation process are not lost or disturbed. The most difficult mediums to be analysed at conventional SEM are saturated oil filters, concrete and fabrics [8].

3.5.4 Detection of Organic GSR

As already stated in the previous paragraphs, since the early 1990s, inorganic GSR analysis integrity has been challenged with the introduction of lead-free non-toxic primers as a measure to prevent environmental and health hazards and with the discoveries of many environmental sources GSR-like particles. Many researchers started to focus on the organic constituents of GSR, particularly those originating from the propellant for the purpose of identification and to aid in the investigation of criminal cases [3]. For example, if particles in the "indicative" category were accompanied by NG, it would substantially raise the significance level of such particles [8]. Moreover, although DPA is also widely used as an industrial compound and when found it cannot be considered as evidence of GSR, as it might induce to false positives, finding its nitrate derivatives such as 2-NDPA, 4-NDPA or 2,4-DNDPA together with DPA on a suspect's hands could raise a lot the evidence that the person is involved in the manipulation of firearms or explosives. In fact, although the information provided by the analysis of OGSR using several techniques is not conclusive, it would provide complementary information that may strengthen the evidence based on the inorganic residues, also because unlike inorganic GSR, the analysis of organic GSR is not influenced by the memory effect of the firearm when different ammunitions are discharged, because their persistence time is finite [28]. Notice that in general, analysis of organic GSR alone is carried out usually for an estimation of time after discharge [4].

From the start it was realized that the chief problem was the low concentration of detectable constituents present in smokeless propellants which, after combustion, would be present at extremely low levels in the discharge residue. This is why all the techniques used for OGSR examination need to be extremely sensible. Moreover, it would be preferable that methods for detecting organic GSR would not be detrimental to the existing particle analysis method, the SEM/EDX, in order to use them in parallel with the usual analysis of inorganic GSR [8].

Chromatographic techniques are the main methods that have been used to separate, detect, and identify organic components of GSR. Chromatography is the general name given to the methods by which two or more compounds in a mixture physically separate by distributing themselves between two phases: a stationary phase, which can be a solid or a liquid supported on a solid, and a mobile phase, either a gas or a liquid which flows continuously around the stationary phase. The separation of individual components results primarily from differences in their affinity for the stationary phase [3].

In High Performance-Liquid Chromatography (HP-LC) the mobile phase is a liquid. The stationary phase is a solid contained inside a long narrow tube called "the column." Separation of mixtures occurs during passage through the column. The volume of mobile phase at which a component elutes is constant and characteristic of that component, for a given chromatographic system. Thus, the retention volume can be used for qualitative identification. If the detector response is related to the amount of component in the sample, then the area under the chromatographic peak gives a measure of the quantity present.

The components in a mixture separate in the column and exit from the column at different times, called retention times. As they exit, the detector registers the event and causes it to be recorded as a peak on the chromatogram. All materials and conditions used in the instrument are carefully chosen to match the type of sample mixture involved. Detection to nanogram level is quite common and some systems can detect to picogram level using very small volumes of sample. The column efficiency is increased and separation times decreased compared to normal liquid chromatography [3].

Another used technique for analysis of organic GSR is the Gas chromatography coupled with a mass spectrometer (GC-MS). A gas chromatograph is an apparatus consisting of an injection port connected to a column that has a detector at its outlet end. The column is contained in an oven that is electrically heated. A stream of inert carrier gas, usually helium, is introduced into the injection port and flows through the column and detector. Individual sample components are vaporized and travel through the column at a rate dependent on their interaction with the material used to pack the column. The detector registers and records the output from the column. In this case the detector is a mass spectrometer. Mass spectrometers are sophisticated instruments that produce, separate, and detect positively charged gas phase ions. Pure compounds can be identified by their characteristic ions and the result is nearly always unambiguous. Mass spectrometry on its own is not suitable for GSR work because generally speaking “pure” compounds must be analysed. The problem is solved by separation of the constituents using gas chromatography prior to introduction to the mass spectrometer [5]. With gas chromatography-mass spectrometry the presence of GSR on hands by measuring traces of volatile organic compounds in both smokeless powder and residue were demonstrated [3]. Notice that gas chromatography techniques suffer from the inability to analyse NC, as it is not sufficiently volatile, and also nitrate esters, frequently present in GSR, because of their thermal instability [2].

Another used chromatographic method is the Micellar Electrokinetic Capillary Electrophoresis (ME-CE), designed to separate and detect organic and explosive material components. It is a multiple-wavelength analysis technique that generates ultraviolet spectral profiles and selective wavelength monitoring. However, it is a quiet expensive method [8].

Other techniques to detect organic GSR are the pyrolysis GC, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), able to analyse both organic and inorganic compounds, thin layer chromatography (TLC), ultraviolet–visible (UV-vis) spectrometry, high performance liquid chromatography-electrochemical (HPLC-EC), for the detection of stabilizers, Fourier Transform Infra-red Spectrometry (FTIR), for nitrocellulose detection, gas chromatography-thermal energy analysis (GC-TEA), colour test containing sulfuric acid, fluorescence, both to detect stabilizers [3], molecular luminescence, infrared spectroscopy, electron spin response spectrometry, microchemical crystal tests, nuclear magnetic resonance and polarography [5].

Last but not least, notice that since ionic profiles could be used for characterizing smokeless powders, capillary electrophoresis (CE), usually used for OGSR analysis, can also be applied to the analysis of inorganic GSR, such the nitrate and the nitrite. This shows that CE offered a sound potential for forensic GSR investigation as a screening technique prior to more expensive and time-consuming analytical methods. It was also reported that CE could be useful in the detection of residues produced by lead-free ammunition, where the evidential value of analytical results obtained with SEM can be poor [44]. Another noteworthy screening tool for both organic and inorganic residues is the Raman spectroscopy, which also allows to link OGSR spectra to the spectrum of the propellant trying to trace the ammunition used [28].

3.5.5 GSR Deposition and Distribution

A "plume" is the gaseous formation that exits all openings of a firearm following the discharge of a round of ammunition [8], as showed in Figure 53, while distribution of GSR can be defined as the areas where GSR is deposited and the concentration in those area [5][45]. GSR particles deposit onto nearby surfaces via two mechanisms: fallout deposition, meaning particle sedimentation of air-borne residues, and impact deposition. Whilst GSR on the shooters hands is likely to originate from impact deposition rather than fallout deposition, fallout deposition may account for characteristic particles found on bystanders or individuals entering a scene after discharge [8][46]. Notice that upon impact with the target GSR may undergo some modification in the form of splattering or flattening while airborne GSR particles have been shown to take relatively long periods, up to 10 min, after discharge, to settle [47][48]. In fact, particle fallout times can vary widely, based upon the physical characteristics of the subject particle. Given the same size and shape, particles of higher density will settle out faster than those of less dense composition. Factors such as turbulence, temperature, humidity, and pressure would affect the length of time that a particle would remain airborne. Generally, an increase in these factors will increase the entrainment time [8].

Figure 53: The plume that exits a firearm when discharged [39].

The most common area where it is possible to find GSR after a discharge of a firearm are obviously the hands, since GSR that deposits on them are mainly emitted from openings around the breech, the ejection port and the trigger notch in self-loading firearms and from the flash gap between the cylinder and barrel in revolvers.

This fact is mainly due to the backward gases, which mostly come from the primer, since they are generated by the fact that the high pressure that forms in the cartridge case, acts in all directions, so also rearward; this is why the residue exiting from the breech has a higher concentration of small detectable particles than the muzzle exhaust [5]. Another quite common area is the face, which can be sampled on occasions when firearms such as rifles and shotguns are used in the shooting. Using these types of guns causes a condition of blow-back toward the chest, face, and hair of the GSR. Other areas of GSR deposition are the clothes, hairs, which if not washed can contain a lot of GSR, nasal mucus, which is like a storage of GSR particles since it is arguable that shooters may inhale part of the gunshot residues displaced in the surrounding environment anytime a shot is fired [49]; near objects in the vicinity of the shooting incident, since when the plume of the discharging firearm is created, the cloud spreads from all the openings in the firearm and deposits on the areas in the immediate vicinity of the discharge, and also cars, since drive-by shootings are unfortunately common in today's world. Methods have been developed to collect GSR from the interior and exterior of automobiles involved in these types of crimes to check if that particular automobile is used in the investigated crime. Notice that sampling from hair, clothes and nasal mucus is obviously more difficult than from hands, as will be shown in 3.5.6 [8].

Obviously, many factors are thought to influence the amount and nature of GSR deposited on the firer. The type of gun is probably the heaviest factor; smaller calibre semi-automatic handguns with high or forward cartridge ejection have plume concentrations toward the front of the fingers which are heavier than web and wrist areas. In most cases, the plume tends to follow the direction of cartridge ejection. Larger calibre revolvers have a widespread plume as opposed to the more compact plume of larger calibre semi-automatic weapons with ejection ports. The most consistent area of plume concentration for rifles and shotguns is the crook of the support arm; however, blow-back or drift of the original plume formation is toward the chest, shoulder, face, and hair, with heavy concentrations for some weapons and light for others. Cartridge ejection is a factor in many of these weapons; in fact, although the plume expands quickly in all directions, [50] and [51] reported that a larger amount of GSR particles is detected usually on the right side of the pistols rather than on the left side, as showed in Figure 54.

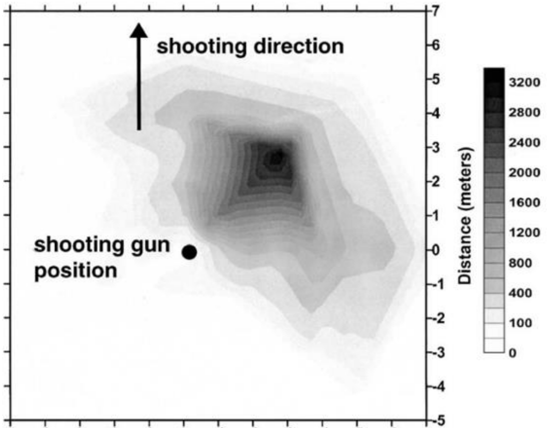


Figure 54: Distribution of GSR in the surrounding of a firearm discharge in a closed environment. The grey shades indicate the number of GSR detected [50].

The same experiment performed in an open environment shows that the distribution of particles is the same as in a closed environment but the concentration were 10 times lower, showing a significant influence of the climatic conditions on amount of particles, but not on their distribution [2]. This widespread distribution of GSR highlights the potential for bystander contamination. Moreover, particle size distribution presents an interesting trend when weapon types are considered. The paths that gases and forming particulate take upon escape from a revolver vs. a semi-automatic weapon create different conditions during the formation of the particles. In the revolver, most of the gases from the primer burn escape in the area around the cylinder, whereas in the semi-automatic, the initial path is the opening provided by the ejection port. A noticeable difference was apparent in the particle size distributions from the two weapon types. Revolvers appeared to generate more smaller particles than semi-automatic weapons [8].

Regarding rifles, if the weapon is of the self-loading variety, then gases will escape from the ejection port as with a self-loading pistol. In this case, residues could be deposited on the hands of the firer depending on the position of the ejection port. Moreover, the increased contact between the bullet and the interior of a rifled barrel is likely to cause a “shaving” of the exterior of the bullet, and an increased proportion of bullet residues [52]. If, however, the weapon is of the bolt action or locked breech, as in a normal break-barrel-action shotgun, then there will be virtually no gas escape from the breech end of the barrel until the action is manually opened. In this case, the deposition of GSR on the hands of the firer will only occur if the action is opened immediately after firing [15]. Lastly, the barrel length may further influence the distribution of GSR particles. When shortening the barrel length of a rifle by 10 cm lead is found to be more sparsely distributed. It is suggested that this was due to a decrease in pressure in longer barrelled firearms [53]. Moreover, intuitively, stance and weapon handling affect GSR distribution on hands. If the hand holding the barrel of the gun is closer to the muzzle of the gun than the hand pulling the trigger, it is possible that the non-shooting hand may be contaminated with a greater amount of GSR [5]. The only thing that do not change between different firearms is the GSR ejection from the muzzle, which in all the case is directed towards the target [54].

Also the mechanical conditions of the gun are an important factor in GSR deposition since a gun in poor mechanical condition is likely to have larger gaps in the firing mechanism, thereby allowing more GSR to escape as well as its cleanliness, because a contact with a “clean” gun is likely to produce less GSR than contact with a “dirty” gun of the same type [3]. In fact, it is important to remember that the gases issuing from the muzzle are projected at great velocity away from the firer and unless there is a very strong wind blowing towards the firer, these GSR-containing gases will not be deposited on the hands; on the contrary, the gases issuing from the breech end of the barrel, whether it is a revolver or a self-loading pistol, are of much lower velocity. Unless the non-firing hand is held within a few inches of the gun during firing, these gases will only be deposited on the back of the firing hand. This is why the palm of the firing hand will be protected from the deposition of any GSR particles during firing as it is wrapped round the grip.

GSR on the palm can be found only if the grip is contaminated with GSR or, in a weapon which has been fired, also on the muzzle end of the barrel [15]. In fact, subsequent manipulation of the gun such as unloading, reloading, cleaning, and also picking up spent cartridge cases can yield more GSR than the actual shooting [5].

As seen, this add another factor in GSR examination and interpretation, since a good forensic analyst needs also to pay attention to the position in which GSR are found. If unique GSR particles were detected on the right back area of a suspected shooter and no other particles were detected on the right palm, left back, and left palm, this would be expected in a right-handed person who has fired a gun. But if high numbers of particles are present on the palms and are absent on the back of the hands, this would lead one to assume that a firearm was handled but may not have been fired by that individual [8]. It is important to remember that with the exception of suicides and dead suspects, the initial distribution pattern will almost certainly have altered markedly between the incident and sampling, which is typically 2,3 or 4 hours after the event. In practice the circumstances of the case dictate the areas to be examined for GSR; moreover, always bear in mind that GSR are loss with time and activity, and the fact that residues are readily transferred from area to area, as will be discussed in 3.7, means that any interpretation based on distribution needs to be approached with caution [5]. A summary of the information that is possible to extract from GSR deposition on hands is reported in Table 10.

Table 10: Information extracted by GSR deposition on hands [15].

Location	***Extracted Information***
Back of the right or left hand	This is highly indicative of the person having fired a weapon in that hand.
Backs of both hands	This is highly indicative that the person fired the weapon in one hand whilst supporting the firing hand with the other.
Back and palms of both hands	This would indicate that the person was standing in front of a weapon when it was fired and was enveloped in the large cloud of gases emanating from the muzzle of the weapon. The person could have been either an innocent bystander doing a defensive gesture or part of the gang carrying out the robbery.
Palm of both hands	This could indicate that the person had merely handled a weapon which had been recently fired.

For GSR deposition, another influencing factor is the type of ammunition; jacketed bullets produce substantially fewer GSR particles than unjacketed bullets. Primer characteristics like size, composition, burning characteristics, can influence the number of primer particles produced. The temperature and pressure achieved by the burning of the propellant determines the power and velocity of the bullet which can influence the number of particles deposited and the age and condition of the ammunition might influence the GSR deposition [26].

Also the meteorological conditions influence the GSR deposition, like wind, rain, humidity and temperature; notice that water does not chemically interact with GSR and it is more likely that it could decrease particle population simply by physical disturbance, like washing away them or moving GSR farther into the fabric of the garment, making them more difficult to be sampled [5]. In general, less GSR are found on the firer in the case of the outdoor tests, mainly because of the wind. In fact notice that GSR have the tendency to stay in air for certain period before depositing on any surface, and since the period is variable, the determination of a general time curve for sedimentation of these particles was found to be impossible [48]. Other factors are the firing location and the duration of the exposure, since firing from confined spaces, for example, doorways, small rooms, vehicle interiors, will tend to expose the firer to a more residue-laden environment for a longer than normal period of time; consequently, it will take the GSR longer to disperse and the chances of GSR from the muzzle being deposited are increased. Last but not least, also the nature of the surface on which GSR deposit, like skin conditions which could be dry, moist, covered with natural oils, the amount of hair, and nature of clothing, meaning smooth or rough, could influence their deposition [3]; in fact, the possibility of vaporized/gaseous products being adsorbed on to skin or clothing surfaces also exists [5].

Notice that repeated firings with the same gun do not necessarily yield progressively increasing levels of residue nor does the same gun/ammunition combination firing the same number of shots under apparent similar conditions necessarily yield comparable levels of residue. To explain anomalies in quantity and composition of GSR deposited under very similar conditions, it has been proposed that most of the mass of the elements detected is contained in a few large particles and that a large variation occurs in the number and composition of these large particles recovered from firing to firing. It has also been suggested that the skin becomes saturated with residue and that the blast from subsequent shots dislodges residue from previous shots [5]. Moreover, if the firearm is not pre-cleaned, the residues of previous firings lodged as fouling in the interior of the gun and are blown-off rather irregularly through the breeches and the muzzle in the subsequent firings; for example, with lead-free ammunition, it is also possible to find the usual triplets Pb, Ba and Sb in the GSR if the gun is not perfectly clean and it has been used with standard ammunitions [1]. Notice that even thorough cleaning of a firearm has been shown not to remove all traces of previous residues and lead to a kind of memory effect within the firearm barrel; this strength even more the mandatory use of a case-by-case approach in the GSR analysis [2][4]. Moreover, it is generally accepted that to characterize the GSR from a particular cartridge, it would be preferable to use a new gun otherwise GSR from previous and current firings may be mixed since particles adhere strongly to the barrel and the interior part of the bullet chamber, and neither mechanical cleaning with copper bore brushes nor chemical cleaning with acid solutions completely removes these deposits from the firearms [28][55]. On the contrary, a very interesting fact is that regarding the organic GSR, compositional analysis of residues from firearms in which ammunition types had been changed showed only trace amounts of organic compounds of propellant powder from previous firings in the first shot and none in subsequent shots [56].

Last but not least, at close ranges, the GSR particles reach the target and cause soiling, the extent of which is dependent upon the proximity of the target to the cloud of residues expelled prior to the bullet. At increased distances, only the heaviest particles like metals and grains from burnt and unburnt propellant as opposed to soot, are expected to reach the target [46]. When the distance from the muzzle was increased, the dimension of the zone of GSR particles on the targets also increased, however, the density of this zone decreased [57], as showed in Figure 55; obviously firing estimations of longer-range shots were less accurate than close range. Notice that no sort of model exists for GSR distribution on target; what it is possible to state is that the time required by the GSR particles to reach a close-range target is smaller than the time needed for development of turbulence [58].

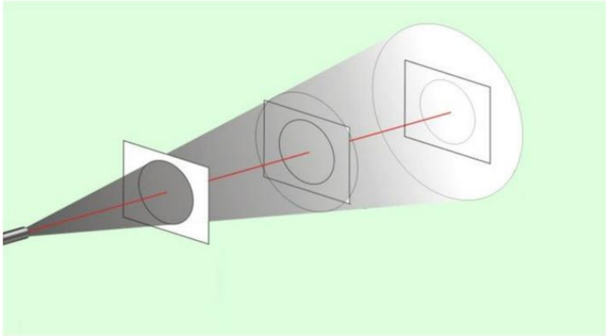


Figure 55: Schematic representation which shows how GSR distribution and concentration can be used to estimate the shooting distance [40].

3.5.6 GSR Collection Techniques

As seen in the previous paragraphs the areas from which GSR may be collected are wide ranging. Skin, vehicles, like seats and seat backs, doors, windows, dashboards, headliners, interiors, and exteriors, the surroundings of an incident, body parts, clothing, any surfaces in the immediate vicinity of a firearm discharge may all be sample target and also other exposed body parts, such as the wrists and forearms can also be sampled if the subject is suspected of having washed their hands after the incident. The main variables in sample collection are the efficiency of the sample collection officer, the efficiency of the sample collection media, environmental conditions, and the time lapse between the incident being investigated and collection coupled with the physical activity of the subject being examined [8]. However, all are in accordance in saying that sterile gloves, boiler suit and hair cover should be worn when collecting any type of trace evidence, in order to avoid any possibility of GSR secondary transfer from the collecting officer and these disposable clothes and gloves should be changed for each suspect examined; this should be done even if the sampler has had no contact with a weapon. If the sampler has any contact at all with firearms, he should, before taking the samples, change his clothes, shower and wash his hair thoroughly [15].

The sampling methods are really a lot and in general fall into two categories since they could be destructive or non-destructive, depending on the effect of the sampling procedure on individual GSR particles, acids tending to breakdown the particles [5]. Tape lift, also called adhesive stub, is a non-destructive method and probably one of the most common and cheap procedure to collect GSR from skin, hair and other mediums.

The ideal collecting device was described as a surface that does not require carbon coating, polished smooth and flat, with no contaminating elements of high atomic number [1]. There are a wide variety of adhesives, like double-back tape, double-back carbon tape, multiple-adhesive-layer tape, freshly activated adhesive sampler and so on. However, after many experiments on 15 different adhesives, the Sellotape 404 double-sided tape was the medium chosen as the best performer [8][59]. Between tape lifting, glue lift and the centrifugal concentration technique all used to analyse GSR at the SEM/EDX, tape lifts were reported to be the most effective, being cheap, having good collection efficiency, and performing well in the SEM [60]; being SEM/EDX the most used technique in GSR analysis, this is why tape lift is the most used sampling method.

Regarding the stub, the most used one is a multi-adhesive-layer stub stuck onto a thin acetate strip; it is usually made of aluminum and it has a diameter of 12.7 mm [12]. These stubs are then individually placed in clean sealed SEM stub tubes under ultra-clean conditions. These tubes have special stub holders in the cap which enable the tube to be simply removed from the cap for sampling. Once the tube is replaced over the cap, it self-seals, preventing any chance of the sample being tampered with [15]. When sampling, the tube is removed from the sampler and the stub is pressed against a specific area of the skin even after the tackiness is gone, usually at least 30 times [27]; notice that when it is decided how many press are needed to cover the area of interest, it is better to maintain this number to ensure consistency. A slight rotation of the stub while it is pressed against the sampling area will expose new adhesive, allowing prolonged sampling. Notice that a control blank taping should also be submitted with the samples; These are also called environmental controls, which in practice are a sample stub exposed to any process in which GSR sample stubs experiences. Examples include sample preparation areas, carbon-coating equipment, or inside the SEM chamber. Moreover, when sampling stub/kit are bought, it is suggested for each batch to test one blank sample [12]. The tapings after sampling should be placed in individual bottles and sealed. The individual bottles should be placed in sealed bags and the sealed bags placed in another sealed bag. Examples of sampling stubs are showed in Figure 56.

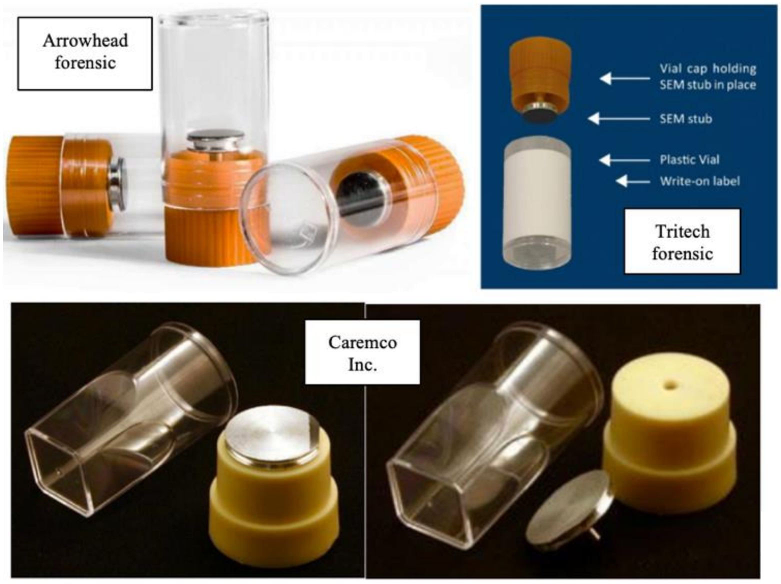


Figure 56: Three different types of adhesives stubs used for GSR sampling and SEM/EDX analysis [6].

When it comes to the SEM examination, the SEM stub is removed from the cap with a pair of SEM stub tweezers and transferred to the SEM stub holder and into the SEM chamber [15]. Exposure of the sample collection stub should be limited to essential procedures only and it should be replaced into its container immediately upon completion of the task, working without all materials that could transfer to the sample surface. Moreover, collection stubs should be labelled. Notice that the collected samples even before analysing them with the SEM/EDX can first be examined with a stereomicroscope to examine the material adhering to the sample. This preliminary examination can, for example, detect the presence of partially burnt propellant grains or other particles of interest [12]. Notice that the examiner need to document any deviations from the instructions and checklist provided [12]. The general scheme of detection of inorganic GSR by means of SEM/EDX is showed in Figure 57.

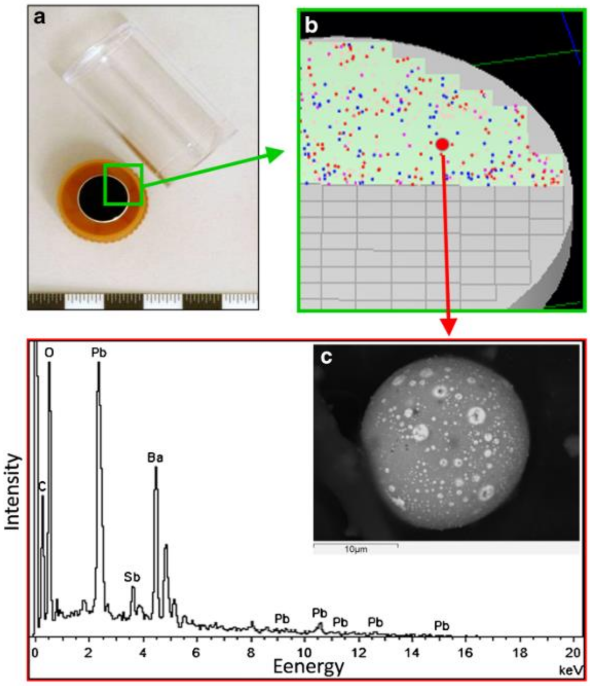


Figure 57: A scheme of detection of inorganic gunshot residue by means of scanning electron microscopy and X-ray spectrometry: SEM stub with micro traces collected, e.g. from hands of a suspect (a), the automatic search for particles of defined properties (b) and the image of the particle with its analytical spectra (c) [4].

Tape lifts works perfectly on the skin, like hands and face sampling. Regarding the hands, collection typically focuses on four regions of the hands which are the right back, right palm, left back, and left palm. Generally, the areas sampled on the back of the hands cover the index finger, the thumb, and the web area between and behind the thumb and index finger and toward the wrist [3]. These areas are showed in Figure 58. Notice that also wrist and forearms can be additionally sampled, remembering that the amount of GSR detected decreases with the distance to the firearm [45]. During the taking of the samples, the skin must be stretched as much as possible to ensure that any GSR particles which may be hidden within the folds of the skin are removed. Moreover, if the hands are wet, they should be allowed to dry naturally. Blow-drying the hands must not be used since it will remove all GSR particles. Sampling from areas of the hand covered with blood should be avoided at all costs; the imaging technique used during the search for the particles, which is the backscattered imaging, is completely overloaded by the iron content of haemoglobin in blood.

It should also be stressed that if the suspect has to be handcuffed, disposable nylon restraints should be used rather than the police issue handcuffs, which may well have been contaminated either from range courses or the gun the officer might be wearing and it is mandatory to not allow the subject to place hands in pockets [15]. To better avoid these problems, it is usually better to sample the suspect prior to handcuffing and fingerprinting [12].

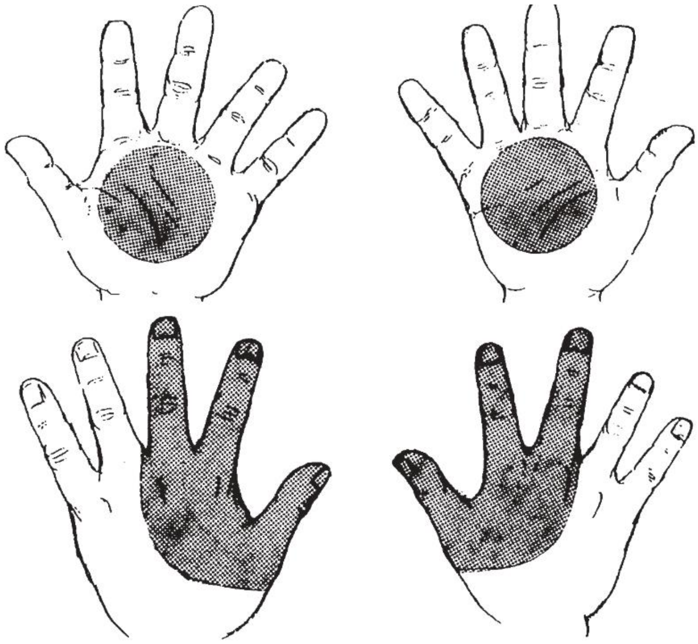


Figure 58: Diagram of areas of the hand to be taped for gunshot residue recovery [15].

However, a number of problems were reported with tape lifts including the large surface area to be searched, obviously dependent on tape size, the collection of debris that may mask particles, and the requirement to carbon coat samples prior to analysis, which is something which can now be avoided by using carbon-coated adhesives, which discs are similar to double-sided tape but the adhesive material, which is specially formulated for SEM use, is pre-impregnated with carbon dust [2]. Notice that to reduce the search area, a sample concentration technique can be used, but the drawback is that potentially helpful particles may be lost during this method, since it maintains only the very small ones, meaning between 0.5 μm to 2 μm. In fact, if possible, a complete analysis of the tape lift is far better. Oxygen Plasma ashing plus the electron beam of the SEM on tape samples is a successful method for reducing organic material, like skin cells, that may be present on the surface of a tape lift, making GSR particles easier to analyse. Notice that particles completely covered in skin cells that could not be detected by the secondary electron image were detected without problem by the backscatter electron image and EDX detector; this to say that for finding the chemical composition of GSR, the organic contamination on the tape are not a problem [61]. Collecting samples from clothing using tape lifts may also create problems with fibers and other debris. This detritus is likely to be nonconductive and may hold charge during SEM analysis. Carbon/gold additional coating of the sample may therefore be required which involves extra time and expense.

Notice that fabric characteristics may influence the GSR collection procedure; for example, the collection efficiency of GSR was more efficient for smoother fabrics such as leather, due to the rate at which the substrate saturated the sampling tape [62].

Moreover, there is also the possibility to simultaneously sample both IGSR and OGSR using tape lifting; a simple SEM stub can be modified, covering half of it with PTFE (Polytetrafluoroethylene), allowing to analyse the non-covered part with SEM/EDX. Advantages of the modified device were the possibility to simultaneously analyse OGSR and IGSR and that the IGSR half of the stub stayed intact and could be re-analysed if required. However, there is also a drawback because separating the sampling device in two areas could raise the possibility of losing important OGSR or IGSR that are collected on the other side of the stub [63]. In order to eliminate this drawback, Taudte et al. [31] developed a protocol that is sensitive and selective for OGSR detection analysing them using Ultra-High Performance Liquid Chromatography (UHPLC) but does not compromise IGSR analysis by SEM-EDX; the only drawback is its destructive nature. Such collection protocol is showed schematically in Figure 59.

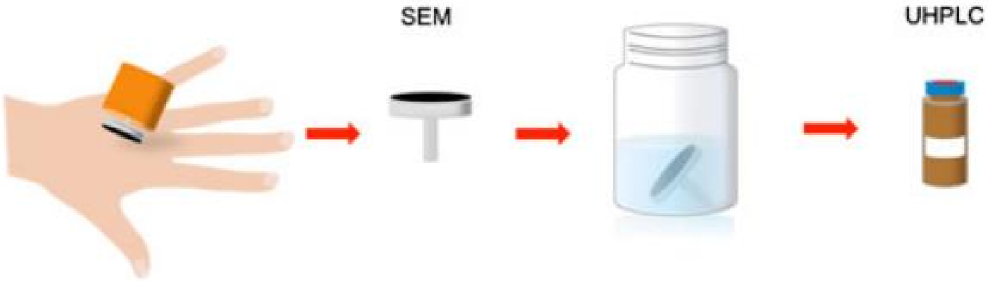


Figure 59: Scheme of sample preparation using GSR stubs as collection device and liquid extraction. After collection, the stubs are analysed for IGSR using SEM-EDX. This is followed by liquid extraction of the OGSR and their analysis by UHPLC [31].

Another used sampling method is the vacuum lift, also called suction sampling. Vacuuming is used primarily for the collection of GSR from clothing, collecting both organic and inorganic residues; notice that more organic than inorganic compound are collected with this method. The main problems with this technique are related to the extraction efficiency, since sometimes is possible that debris and garments are lifted and obstruct the filter , and to the fact that vacuuming on cloth removes particles from the surface but also from the depth of the clothing, and the particles coming from the depth maybe come from a different situation that the one needed for the shooting in exam [34][64]. Zeichner et al. optimize this technique choosing the Teflon filter, with respect to the fiber glass one, and as solvent the Methylene chloride, although one can use every type of solvent possible, this one is chosen because of the advantage of not dissolving/extracting NC [65]. Moreover, a double filtration system is effective, with a first filter to remove large debris and fiber, and a second one to concentrate the wanted GSR to be analysed at the SEM, but as already stated, some useful particles can be lost in the passage into the first filter. Notice that the best technique for GSR sampling on clothes is a combination of both tape lifts, for the collection of inorganic GSR, followed by vacuum lift to collect organic residues, always bearing in mind that the loss of tape stickiness can reduce a lot the potential to trap GSR particles [66]. A scheme of a suction sampling device is showed in Figure 60.

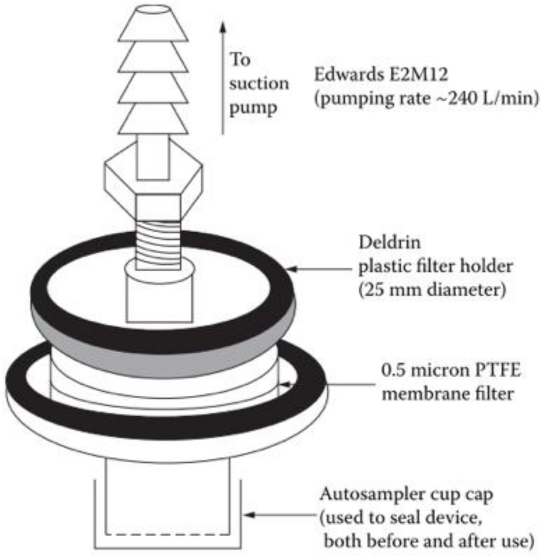


Figure 60: Schematic representation of a suction sampling device [5].

Notice that when possible, it is better to sample clothes in situ at the scene to minimize the loss of GSR; if not possible, clothing should be removed as delicately as possible and then analysed in laboratory [45]. The most likely areas to sample from clothes include right and left cuffs, wrists of long sleeved shirts or jackets, right and left shoulders if a long gun was used, pockets or back waistband, if there is reason to believe that is where the gun was carried, headwear including the underneath side of hat visors, and gloves, which are sampled like hands [12].

Another sampling method is the swabbing, mostly used for the collection of organic compounds from skin surfaces. The best solvent to put on a swab is the ethanol, with the most complete, stable, and consistent recovery [67]. Swabbing is mostly used when GSR will need to be analysed by using Atomic Absorption (AA), Neutron Activation Analysis (NAA) and Inductively Coupled Plasma (ICP). In fact swabs are not usable with the SEM, this is because the acid solution on the swab immediately starts to transform the solid particulate into solution, which is retained in the swab media, this is why it is considered a destructive method [8].

Another sampling method is the glue lift, a very usable technique for the surface of hands. When compared to tape lifts, glue lifts required less dabs on the skin and also contain no elements of high atomic numbers that could potentially interfere with the GSR particle analysis with a SEM surface; this increased the speed of SEM analysis. The great problem with respect to tape lifts is that it collects less debris because of the glue being less tacky than tape lifts, being the glue an ineffective lifting medium [60][68].

Regarding the nasal collection, no one of the methods seen before can be used; the collection methods are quite simple and consist of blowing the nose with paper handkerchief or with the introduction of cotton-like sticks in the nostrils; the great problem is that the preparation of the sample for the SEM analysis is then long and cumbersome [6].

In general, Collecting GSRs from nasal mucus is quite advantageous since the particles stay there for a considerably long time, both because it is harder to wash the nasal cavities with respect to the hands and also because contamination of hands is more likely than in nasal cavities, more preserved from accidental contact and environmental contamination [49]. This however is both a positive and a negative factor, since it will be more difficult to relate the found GSRs particles to the firearm injury under study. Notice that this problem exists also when GSRs are found on clothes and hairs and in general on all the substrates which retain GSRs for a long time [2].

Last but not least, since smoke plumes exiting the breach of a weapon during discharge frequently extend posterior to the face and head, with potentially useful GSRs being deposited in the hair, also the sampling of this zone can bring some useful GSRs particles. To collect GSRs in hairs, the most used method is still tape liftin, with some difficulties [2]. Another used method is to utilize a fine-toothed comb, with which nearly intact grains of incompletely burned propellant powder residues approaching mm diameter are detected. However, problems with this method and curly hair are observed. Another used method in collecting GSR on hairs is the suction sampling, always bearing in mind that it recovers both organic and inorganic GSR [5].

3.6 The Transfer Phenomenon

Above all the problems and precautions that have been already treated in the precedent paragraphs there is another great problem that poses some serious difficulties in GSR interpretation which is the problem of transfer, the main reason why the presence of GSR does not necessarily indicate that a suspect has fired a gun. Rather, material can be acquired as a result of contact with a surface bearing GSR, or via proximity to a firearm discharge. The transfer is the mechanism by which GSR particles can be transferred to a subject which has nothing to deal with a discharge of a firearm, and can be secondary, tertiary or even more, according to the number of surfaces on which GSR deposit before they are sampled and analysed [69]. The basic principle of trace and transfer evidence is the Locard Exchange Principle. This principle states that when two objects come in contact with one another, an exchange of material takes place. Secondary transfer may also occur when trace evidence originally transferred to one object is subsequently deposited on another surface and picked up by a second recipient object [8]. The possibility of finding GSR on a person's hand not only if he had fired a gun adds to the difficulty in the investigation of a firearm involving case [3]. In fact, besides finding GSR with all the shrewdness already explained, it is important also to exclude that such residues have got in contact with the suspect via transfer, or even that these residues are extraneous to the crime scene analysed because they come from another crime [40]. However, notice that the presence of GSR does demand an explanation from the suspect, also if the transfer phenomenon has happened [5].

For example, contamination can be possible when a person walked through the particle cloud of a firearm discharge and not just as a consequence of staying close to a shooter or simply handling a firearm; In general, if GSR are collected immediately after the discharge, it is quite easy to discern between shooters and bystanders since the number of GSR on shooters is much larger than on bystanders but this rarely happen because suspects are usually captured and sampled a few hours after the crime [70]. Moreover, since a part of GSR travels with bullets, it is therefore possible for GSR to be transferred to an individual interacting with a victim/target [58]. GSR may be also transferred from the hands to clothing or surrounding areas by contact for example from the backs and palms of the hands to other items simply by rubbing the hands together or transferred from hands into pockets by placing the hands in the pockets [8][66]. It has also been shown that GSR particles can be transferred from contaminated person to "clean" person, even through the simple act of shaking hands.

Other extraneous source of GSR may be the hands of firearm carrying police officers that are delegate to take samples from the suspects or also on police vehicles; in fact, if police officers are contaminated with gunshot residue through the normal receiving, checking, loading, and securing of their issued firearm, there is the potential for secondary transfer of GSR to anyone those officers arrest during their shift, especially during the frisking procedures, with gloves highlighted as the main source of potential contamination of GSR [46][71]. In fact, a good practice is to change gloves when an arrest needs to be done and also when multiple suspects need to be sampled [72].

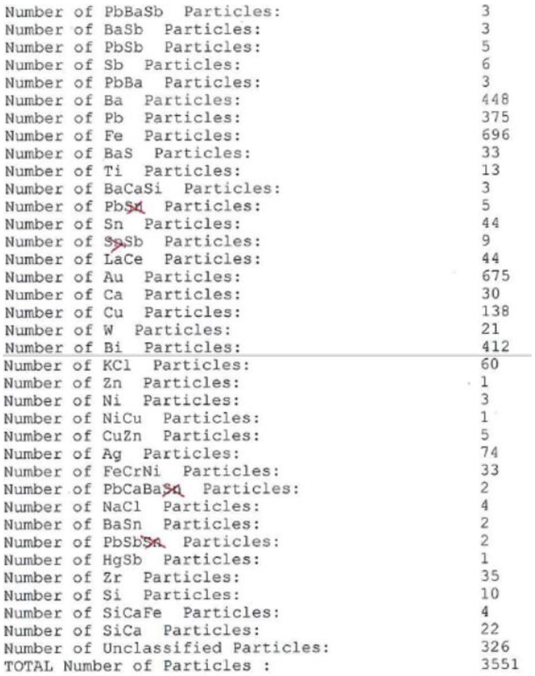
Notice that since the number of found particles on police officers is quite low, is quite low also the probability of transfer between officer and vehicles on the arrested suspects. However, the possibility of even one or two particles of GSR being transferred to a person who is to be tested for GSR must be seen as important, as such a small quantity of GSR has been used in court as evidence of a person discharging a firearm [2]. Another example of transfer phenomenon regards the handling of spent ammunitions and also the unspent ones that are previously loaded in used firearms. As showed by the previous examples, the presence of GSR on the hands does not prove that the suspect fired a gun but does infer recent involvement with firearms or related items [5]. A summary of the different transfer mechanism is showed in Table 11.

Table 11: Transfer processes related to GSR [69].

Transfer type	***Description/Method of Transfer***
Primary transfer (1°)	The initial discharge of a firearm results in the direct deposition of GSR particles onto surfaces in near proximity, for example, the shooters hands; the firearm; a bystander who was in the proximity of firearm discharge.
Secondary transfer (2°)	Contact with surfaces/individuals contaminated with GSR particles during primary transfer may result in subsequent cross-transfer to a surface that was not present during initial discharge. Secondary transfer may occur under an array of circumstances, for example: o Direct contact with a shooter, for example, handshaking immediately after firearm discharge. o An individual not present at the time of discharge handling objects contaminated with GSR during primary transfer, for example, a discharged firearm. o GSR transfer to “clean” clothing from a contaminated garment through direct contact.
Tertiary transfer (3°)	Contact with materials contaminated by secondary transfer.
Quaternary transfer (4°)	Contact with materials contaminated by tertiary transfer.

Notice that all dimension ranges of particles are subjected to secondary transfer mechanism, also the 100 μms ones; however, the majority of particles that underwent tertiary transfer measured <10 μm [73]. This is why it is essential to understand the distribution of GSR in relation to the shooter and their surroundings, not only in terms of sample collection but also minimization of contamination and secondary transfer within samples which could potentially lead to an inaccurate conclusion as to whether a subject has been involved in handling or discharging firearms. An understanding of these processes may also aid in the accurate interpretation of analysis results [2].

Looking at the populations of GSR particles play an important role when one considers or forms an opinion of what is direct deposition and what is possibly the transfer from hands or clothing due to casual contact [8]. In fact, finding GSR in a population of particles that have nothing to do with a discharge of a firearm could be an evidence that the transfer phenomenon has happened; in the following paragraph, there is an example of the latter situation [6]. In Figure 61 is showed an example of GSR analysis at the SEM.



```
Number of PbBaSb  Particles:                  3
Number of BaSb  Particles:                    3
Number of PbSb  Particles:                    5
Number of Sb  Particles:                      6
Number of PbBa  Particles:                    3
Number of Ba  Particles:                      448
Number of Pb  Particles:                      375
Number of Fe  Particles:                      696
Number of BaS  Particles:                     33
Number of Ti  Particles:                      13
Number of BaCaSi  Particles:                  3
Number of PbSn  Particles:                    5
Number of Sn  Particles:                      44
Number of SnSb  Particles:                    9
Number of LaCe  Particles:                    44
Number of Au  Particles:                      675
Number of Ca  Particles:                      30
Number of Cu  Particles:                      138
Number of W  Particles:                       21
Number of Bi  Particles:                      412
Number of KCl  Particles:                     60
Number of Zn  Particles:                      1
Number of Ni  Particles:                      3
Number of NiCu  Particles:                    1
Number of CuZn  Particles:                    5
Number of Ag  Particles:                      74
Number of FeCrNi  Particles:                  33
Number of PbCaBaSn  Particles:                2
Number of NaCl  Particles:                    4
Number of BaSn  Particles:                    2
Number of PbSbSn  Particles:                  2
Number of HgSb  Particles:                    1
Number of Zr  Particles:                      35
Number of Si  Particles:                      10
Number of SiCaFe  Particles:                  4
Number of SiCa  Particles:                    22
Number of Unclassified Particles:             326
TOTAL Number of Particles :                   3551
```

Figure 61: Example of a GSR analysis at the SEM [6].

This is the population of particles that an automated SEM analysis have printed. The three Pb, Ba e Sb are very interesting for the GSR analysis and will need to be further analysed by means of secondary electrons imaging and the analytical spectra. Also binary and single particles are present and their amount is lager that the particles that contain the triad of interest but also an enormous amount of particles that have nothing to do with GSR are present. Supposing that the three Pb, Ba and Sb particles are for sure GSR particles, in the following there is an example of how it is possible to understand if the transfer phenomenon has happened simply looking at the entire population of particles. These particles were collected 6 hours after the investigated crime has happened from a non-smoker suspect who works in the countryside and has taken the shower immediately before the sampling procedures were performed; in the element list, besides the already seen particles, stands out also a great quantity of La, Ce, Fe and W, the typical composition of the residue coming from the flint of a lighter, typical particles found on hand of smoker, which, however, the person subjected to the sampling is not. Moreover, the suspect takes the shower before sampling, and it is impossible to find GSR particles after having washed the hands. The fact that the sampling is taken 6 hours after the crime and all the other facts previously listed make understand that the transfer phenomenon has happened [6].

Besides particle population, also other methods are available to discover if the transfer phenomenon has happened; for example, decreases in GSR content over time on the shooters hand are expected, as will be extensively seen in 3.7, a rise in particle numbers seen on the non-shooting hand at times over t = 0 may be seen due to transfer from the shooting hand and this can help to discern between circumstances [46]; also the particles dimension is an important factor, since bigger particles tend to fall off from the hands immediately after the deposition, with a suspect captured and sampled after one or two hours from the crime, if too big particles are found, it is probably a transfer phenomenon.

Last but not least, also if it seems trivial, the chemical composition of the GSR particles found on a suspect hand need to coincide with the one used in the crime analysed, otherwise it is probably a transfer phenomenon [6]. In fact, if possible, it would be better to analyse both the cartridge cases found on the crime scene and the one used by the police officers to check if the GSR found on the suspect belong to the crime or to the contamination; this is why the use of marked ammunition by police officers would be a great advantage in reducing the problem of cross-transfer [72].

However, the best way to deal with a transfer phenomenon is not to find a method which recognizes it when it has happened but is to avoid it adopting the most efficient procedures in GSR sampling and analysis. In fact, everyone who gets in contact with a person that could be involved in a firearm discharge or with a victim, must understand the potential existence and significance of GSR evidence. For these individuals, education about forensic evidence and training in the area of evidence collection and recognition are essential [8]. The sequence of events associated with GSR examination comprehend usually the initial incident, apprehension of suspects, transporting of suspects to police station, sampling of suspects at police station, submission of items to the laboratory, sampling of clothing at the laboratory, sample preparation, analysis of samples, interpretation of results, preparation of statement of witness report, and the presentation of forensic evidence in court. It is quite immediate to understand that the contamination, which substantially diminish the value of evidence obtained, together with the time delays, which substantially diminish the chances of obtaining evidence and will be shown in 3.7, are the most important factors involved in the processing of suspects for forensic evidence, also because transfer allegations are frequently used as defence in court since it is extremely difficult to demonstrate that has not happened [5].

To avoid transfer and contamination, some precautions need to be adopted; for example, when police forces need to apprehend a suspect, they need to pay attention to the procedures that they adopt. It has for a long time been a source of annoyance and frustration that, at the time of apprehension of a suspect, there are currently no effective measures available to secure potentially crucial evidence. Some police forces throughout the world use bags, usually plastic ones, to cover the hands of persons suspected of firing a gun. The use of plastic bags can have a detrimental effect on GSR, causing the hands to sweat, which in turn causes most of the GSR to be removed from the hands onto the surface of the bag also due to the problem with static electricity [15]. Apart from protection of the hands, no effort has been made to protect other suspect sampling sites. This is why the invention of a kit for protect the suspect hands from losing GSR and also from cross contamination had bring an enormous advantage, but only if it is supplied to all the police forces. Notice that this kit protects the hands and also the suspect's upper outer garment, in which many of the residues are likely to be detected. Moreover, on arrival at the sampling location a suspect should individually be taken directly to a room and be under constant supervision until sampling is completed. A number of "clean" rooms should be provided at each sampling location and the room should be cleaned between suspects; furthermore, assigning one suspect per officer, where possible, would limit the potential for indirect transfer and would ensure that evidence was preserved [69].

The materials storage area, cells, custody offices, medical examination rooms, and police vehicle interiors should also be monitored at frequent intervals to check the presence of GSR. Equipment and other surfaces in the GSR sampling and SEM rooms should be regularly cleaned and samples should be kept in closed containers, and the time they are exposed kept to a minimum. Once the samples have been removed after the SEM analysis, pressurized air may also be used to remove any dust from the chamber and seals [12]. Taking all these precautions will help to reduce a lot the risk of cross transfer. In multi-suspect cases the suspects should be separated immediately and remain separated at all times [5]. Moreover, it would be preferable that all the areas needed for GSR work should not be located close to firing ranges or where firearms, ammunition, or associated accessories are examined and not be connected to the same air conditioning or ventilation system as areas that may be a source of GSR. Obviously, regular firearms users or persons carrying firearms should not be allowed to enter the GSR facilities. Similarly, GSR personnel should not enter the firearms facilities unless it is unavoidable and it's better that should not themselves be a regular firearms user, otherwise many precautions need to be taken before entering the GSR facilities. Additionally, tour by visitors of the GSR facilities should be avoided if possible and if this is not applicable, GSR facilities need to be visited before the firearm facilities [12].

However, notice that the best way for avoiding contamination, rather than paying extreme attention to all the stages of the sampling procedures, is to check more frequently as possible the devices using blank samples. In fact, "Blanks" are included to serve as a check on the apparatus, materials, and reagents used, and the possibility of carryover from sample to sample. For example, processing an unused sample stub at the same time as casework samples so that it passes through all of the handling, packaging, sample preparation and analysis steps will demonstrate extraneous material has not been introduced within the period of testing; this is the co-called "blind negative" proficiency test [12]. Also the random sampling of visiting personnel and personnel submitting evidence is a practice that can help to avoid the risk of contamination. It is in fact highly desirable for a forensic science laboratory engaged in such work to frequently monitor the sampling procedures and sampling environment used by the police in order to be in a position to demonstrate the validity of laboratory results [5]. Suitable areas to be monitored include the GSR kit preparation area, SEM and sample preparation area, bench tops used for bulk item sampling, storage areas and so on [12].

If contamination is detected in control samples, laboratories should have a protocol to follow, which comprehend a general diagnosis of the contamination incident, a review of the impact on the relevant cases, the identification of other cases that might be affected, and remedial actions required if the contamination is believed to have compromised case work, which generally include informing the appropriate authorities and withdrawing the report. On the contrary, if contamination is detected in non-GSR laboratory areas and/or personnel it is usually needed to expand the scope and regularity of this form of monitoring, increase the restricted access zone, introduce new facilities to control the passage of particulate material into critical areas, establishing restrictions on the carrying of firearms into certain areas of the laboratory by attending police members.

Moreover would be preferable to establish more regular and thorough cleaning of common rooms and other areas in which staff may interact, introduce more rigorous personal decontamination and personal protective equipment (PPE), procedures for GSR staff prior to entry into the restricted zone and establish separate areas in common rooms and catering facilities for GSR and Firearms personnel [12].

The benefit of all these procedures and precautions is the ability to effectively refute cross-examination allegations in court, thereby increasing the confidence level of everyone involved and forming a very strong supporting evidence. In general, contamination avoidance must be a priority. If it cannot be shown that contamination is unlikely to have occurred, then the significance of laboratory positive results will be substantially diminished [5][15].

3.7 The Time Factor

It is of importance to understand the potential longevity of GSR particles on hands, other skin, clothing, and other materials from which samples may be collected. Not only is this information useful when determining whether a sample should be taken or not, in cases where the subject is suspected of discharging a firearm several hours, days, weeks or months prior to apprehension, but also in interpreting the results of any given sample analysis. In fact, in GSR collection, time is probably the most important factor; on a living person, GSR persistence decreases with passage of time due to everyday activities. This is why it is very important to collect the evidence as soon as possible after the suspected shooting; time delays greatly reduce the chances of getting a positive result [5].

Regarding hands, GSR are merely lying on the surface of the skin. They are, therefore, readily removed by everyday activities. If there is anything in their favour for being retained on the surface of the skin, it is their exceedingly small size, since they readily become trapped in the microscopic folds of the skin or drop down into hair follicles. Even so, for all practical purposes, all GSR particles will be removed from the hands by everyday activities within 3 hours or, at the very most, 4 hours of a weapon being fired; therefore, sampling a suspect when the investigated crime has been committed more than 4 h before is practically useless [15]. In general, GSR are lost rapidly from the hands, an order of magnitude in the first hour, in which particles larger than approximately 10 μm mostly disappear; only small GSR particles of less than 3 μm were observed after 2 h or more and could still be detected 3/4 h after a single pistol shot had been discharged [1][5]. This increase a lot the evidential values if GSR are found on a person's hand, because it means that have shoot a very short time before the collection of the GSR, excluding suicides and dead suspects on which however it's better to retain and sample the GSR on the scene, because if the body had been placed in the mortuary refrigerator, the skin does become clammy and it is very difficult to take the samples [15].

Notice that also the shape and the texture of the GSR particles found gives some information about the GSR longevity. In fact, when GSR particles are analysed immediately after the shooting action and without washing the hands, not only spherical particles are found, but also large populations of irregularly shaped GSR particles are present in all the primer residues.

In many large particles, the surface cracking shows the potential breakup into smaller particles with straight edges. With physical activity, like rubbing and clenching of hands, these particles may be lost or broken into several sections and redistributed over the skin and clothing of the shooter. Certainly, many spherical particles remain intact and in agglomerated form, but as time goes by, they will be less than the irregularly shaped ones, also because irregular particles remain attached easily to the skin [8].

What decrease a lot the GSR levels are the everyday activities that a suspect does after having discharged the firearm as for example the normal hygiene of a suspect. Washing hands with soap and water then drying on a paper towel effectively removed all traces of inorganic GSR. Rinsing hands for 3 sec under low-pressure water removed substantial amounts of residue, as did wiping hands on clothing, bringing levels close or equal to those levels found on the hands of non-shooters [74]. Also handcuffing suspects behind the back is a source of GSR loss, rubbing the hands together could transfer the residue from one hand to the other and placing hands in pockets could remove residues; however, residues could be subsequently detected within the pocket [2][55]. Great care should also be taken if a suspect requests to be allowed to go to the toilet as urine is also very effective at removing GSR particles. Last but not least, if the suspect requires medical assistance, the officer need to be quick to take the samples before any medical help which will remove any trace of GSR. For example, insertion of drips into the back of the hand by the hospital should also be discouraged as the insertion point is usually scrubbed with a disinfectant [15]. In Figure 62 is showed the decrease of GSR particles and size during time.

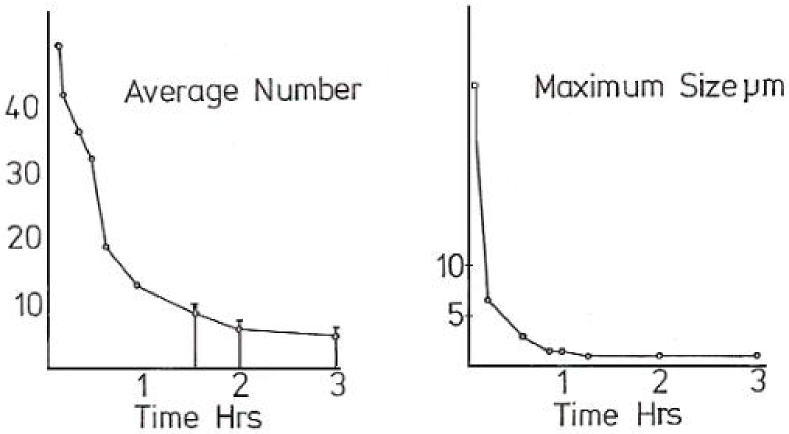


Figure 62: Graphs showing GSR particle count vs time (left) and GSR size vs time (right)[13].

The longevity of GSR on clothing is generally much greater than on skin, the length of time depending on the nature of the material and the extent of physical disturbance of the garment [5]. Particles have been found days or even weeks after firearm discharge. For example, residues deposited on a cotton sheet placed 1 m in front of a revolver that discharged five rounds remained detectable for up to 2 months, if the sheet was undisturbed. Machine washing or brushing of clothing has been reported to decrease considerably the amount and the density of inorganic GSR remaining on clothing [2]. Moreover, if the clothing is worn after deposition, there will be a loss as a consequence of normal activity, namely, motion, transfer, wind, rain, and so forth.

This as already stated does not apply on pockets, which usually are undisturbed and are the most faithful areas of GSR detection, since with time GSR particles gravitate to the bottom of the pocket and become trapped within the folds of material and general pocket fluff and debris which accumulate in this area. The particles are protected so well by this debris that they are not affected by repeated washing and dry cleaning of the trousers. GSR particles have been recovered up to 16 months after a shooting incident. Obviously recovering the GSR particles in this type of site is quite problematic, due to the very high amount of organic material accumulated in there, which need to be eliminated otherwise it will disturb a lot the SEM analysis [5][15].

As already said, also hair and nasal mucus can retain for a longer period the GSR, up to 24 h if hairs are not washed and if the nose is not blown [2]. Moreover, also the GSR on the face can be recovered for more that 4 h after the crime, since commonly the face undergoes fewer physical activities than hands. In general, the police forces should be instructed not to sample the hands if the 4 hours are exceeded but to take the face and head hair samples as normal, while clothes will be subsequently sampled directly at the scene or at the forensic laboratory [5]. Notice that whilst some of these areas showed promise, they all suffered from the same problem, that is, the GSR vented from the breech end of a pistol is of low velocity and as such, particles can only be found on the surfaces immediately surrounding the breech of the weapon, that is, the hands. The likelihood of any GSR particles being found on any of these alternative sites, unless a strong wind is blowing towards the firer, is therefore extremely small [15].

It is important to point out that the fact that some surfaces retain GSR for a longer periods is not always a positive aspect, since as time from the discharge goes by, it will be more and more difficult to relate the found GSR with the crime investigated and link them to a specific shooting incident. On the contrary, the positive aspect is that when residues are found on hands of a shooter, it is certain that the incident has happened not a long time before, if the transfer phenomenon could be discarded. This is why suspects must be sampled as a matter of urgency. Large time delays can occur in certain cases because of geographical locations. Suspects should be taken to the nearest sampling location irrespective of divisional boundaries. At each sampling location there should be trained personnel on site at all times. The more trained personnel available at any location, the greater the chances of reducing time delays to a minimum. Moreover, at each sampling location all the necessary sampling materials should be readily available at all times [5].

These examples suggest that the loss of GSR is caused by physical activity rather than compound degradation. Particles of GSR are very durable and chemically stable; they are composed of heavy metals that originate from the ammunition components. The inorganic particles that are examined can last in a normal environment indefinitely [8]. This was also confirmed by the numerous analysis of GSR made on suicides hands and clothes, which resist much longer time [2].

Unfortunately, both the transfer mechanism and the GSR loss over time are two phenomena that have become increasingly popular during time.

This is showed also from the positive cases of firearm discharge residues, that are decreasing a lot in recent years, despite the fact that the sensitivity of the detecting methods is increased; this in fact is mainly due to the careful planning of terrorist incidents and the precautions terrorists take to prevent leaving any type of forensic evidence at a scene or on their persons [5].

Last but not least, notice that regarding the persistence of organic GSR, due to the lack of a systematic study, no upper time limit for OGSR detection has been proposed yet; nevertheless, the results of Maitre et al. [75] show that the decrease of OGSR over time seems less significant than the loss of IGSR. Studies showed that some OGSR compounds, mainly stabilizers, can be absorbed by the skin due to their lipophilic properties, which could be a positive property for OGSR detection since they might be less susceptible to secondary transfer. However, contrarily to IGSR, OGSR can degrade in time since evaporation could be a mechanism for OGSR losses. Lastly, notice that differences in OGSR retention exist regarding men and women. The main factor regards hairiness; since hair retained residues better, then more residues might be found on men than women. Moreover, the skin of women is usually better hydrated than men’s one, so less skin flakes in which OGSR are trapped are taken from the stubs, and less OGSR were detected on women; notice that this does not apply for IGSR [45].

3.8 Environmental Sources of GSR-like Particles

The environmental contaminations in GSR analysis are probably the biggest problem in this branch of the forensic science, accompanied by the already discussed transfer problem and time delays. Since the early beginnings of the analysis of GSR, awareness of the presence of occupational-environmental particles similar in composition to GSR, which may lead to misinterpretation, prompted the constant change in GSR classification systems, till the latest conclusion, which states that it is not possible to discern between a GSR and an environmental contaminants simply by looking at its chemical composition [33]. It was clear from the beginning that bulk methods could no longer be used for forensic purposes since elements present in the composition of GSR are also found in many forms and combinations in the environment [8]. The metallic elements Pb, Ba, and Sb are used extensively in numerous applications in the commercial world. For example, lead and bromine could be found in the emissions from car exhausts and come from the ethylene dibromide which is used to remove the lead used in the petrol anti-knock compound, lead tetraethyl. Likewise, barium is also utilized in face powders and a filler in paper. In these situations, it is nearly always associated with sulphur (S) and should be readily identified. In fact, with modern non-corrosive ammunition, it is very rare to find sulphur in a priming compound; however, it is not impossible, so always great care should be taken. Zirconium and titanium, used in lead-free primer compounds, are used as fluoro-complexes in the treatment of wool and as pigments in paints. Lead is alloyed with antimony in battery plates and type metal. It is also alloyed with tin and/or antimony in solder. This is a common contaminant especially with anyone working in the printing or car repair trade. Antimony is also used as its oxide as a fire retardant in cotton and polyester blend fibres and is extensively used as a surfactant on most fibres to give them lustre [1][15]. A summary of the common sources of Pb, Ba and Sb is showed in Table 12.

Table 12: Common sources of Pb, Ba and Sb [2][8].

Lead (Pb)	Storage batteries, solder, bearing metals, gasoline, bullets, shot, paint, shielding sheet, cable coverings, glass, matches, dyes and pyrotechnics.
Antimony (Sb)	Hardening alloys, Babbitt metals, paint pigments, safety matches, bearings, pewter utensils, brake pads and pyrotechnics.
Barium (Ba)	Deoxidizing alloys of tin, copper, lead and zinc, radiography, in heat-treating baths for tempering of steel, in laser crystals, dyes, paint, car grease, inks, leather tanning, photographic chemicals, insecticides, paper products, face make-ups and pyrotechnics.

Also the organic GSR can be found in nature from an enormous number of different sources. For example, the stabilizer compound DPA may come from a great variety of environmental sources like the surface of apples, tires, outer garments, solid rocket fuels, pesticides, dyes, pharmaceuticals, and veterinary medicines. Another example regards the EC, which may come from grapefruit, oranges, and pears. As showed, if the analysis of OGSR concentrate on the research of the stabilizers compounds, great attention must be paid since the environmental contaminants are really al lot [76][77].

As already explained, the use of the SEM/EDX technology to search on a particle by particle basis the correct chemical composition and morphology, seemed to have solved all the problem related to the GSR analysis. As time goes by, this was no longer true, due to the constant discovery of particles with both shape and composition similar to GSR but coming from different fields. In fact, if it were found that any other process or activity could produce particles with indistinguishable morphological and/or compositional characteristics to those of GSR then the weight of such particles as forensic evidence would be greatly reduced [2].

Examples of environmental sources of GSR-like particles are a lot; first of all, as it is quite intuitive, there are some areas that are classified as critical, meaning that they are a possible source for GSR-like particles production, and are industrial and commercial areas involving metals or compounds of Pb, Ba, and Sb. Sectors that involved melting and/or vaporization of such elements were of particular interest [2]. An example comes from the ammunitions for the stud guns, which were physically indistinguishable from the GSR; in general, cartridge operated tools produce residues, which are the welding fumes, that are very similar in shape and composition to gunshot residues and can be usually found on hands of general labourers that operate in building sites [32][46][78]. As an example, with the introduction of lead-free ammunitions, the usual chemical composition of the particles found as already explained contain mainly Ti, Zi and Al. On the other hand, considering one of the most used welding techniques, manual metal arc welding (MMA), it requires a consumable shielded electrode, which is an electrode with a covering. Electric arc may generate temperatures of 3000 - 30,000 °C, in which the covering decomposes and produces airborne gases and slag blanket that protects the hot weld metal from the atmosphere as it cools. Both the metal core and the covering of the electrode contribute to welding fume being formed, when the elements and compounds are heated above their boiling points and then condensate from vapours to fine solid particulates, containing for example aluminium or titanium. In fact, a single titanium or aluminum particle cannot be distinguished from the residues produced by the lead-free ammunitions [79]. Two examples are showed in Figure 63.

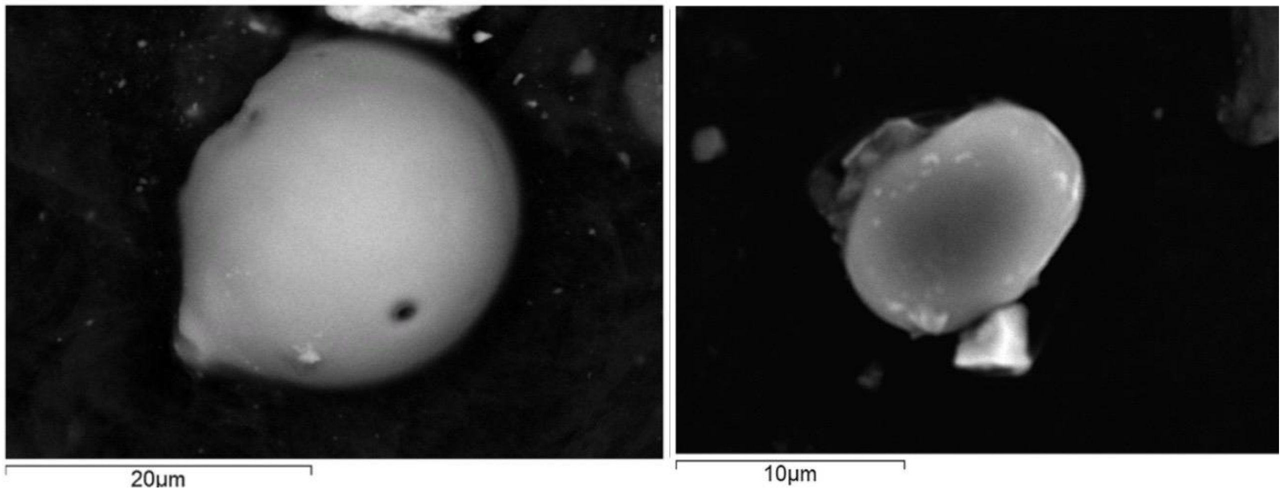


Figure 63: BE image of single element particles produced from residues of welding fumes particles; A titanium particle (left) and an aluminum particle (rigth) [79].

However, when dealing with welding fume residues, the predominant group of particles contain iron and partially crystallized iron oxide, the hematite, on the surface. They are easily distinguishable from GSR not only for the iron content, but also from the fact that they present on the surface a typical crystalline morphology, as showed in Figure 64, which is forbidden on GSR particles [79].

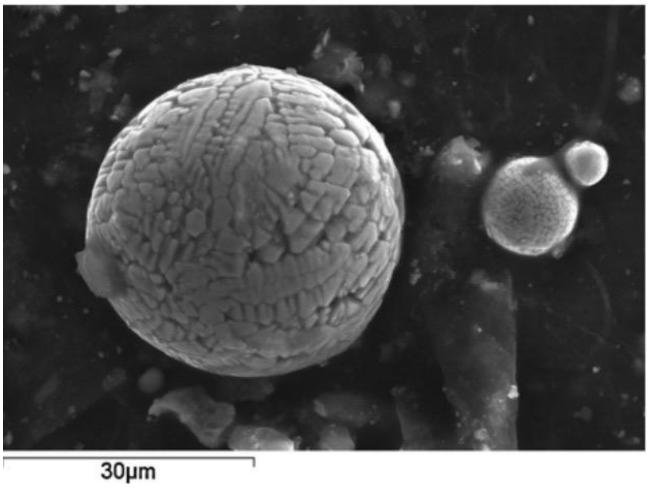


Figure 64: BSE image of iron and hematite welding fume particle [79].

Moreover, particles of Sb and Ba have been found in samples relating to car repair and maintenance activities. Even taking into account the morphology of these particles there were some that were hard to distinguish from genuine inorganic GSR Sb, Ba particles. It was therefore suggested that Ba, Sb particles with iron present can no longer be classed as unique to inorganic GSR and instead be seen as characteristic. Ba and Sb particles in the absence of Fe should be seen as borderline particles between the characteristics ones and the consistent ones [80].

Other GSR-like particles may come also from all the tools and mechanisms that incorporate a primer to initiate a reaction or an action critical to the purpose of the device like fireworks, cartridge-operated nail guns and also airbags. In fact, firework residues could be mistaken with inorganic GSR. Samples collected from the hands of the professional firework display organizers contained some Sb and Ba particles that were morphologically similar to inorganic GSR particles, since they were found to be spheroid, non-crystalline, and between 0.5 - 5 μm in diameter [81]. Other pyrotechnic mixtures can contain aluminum powder and barium nitrate and can produce spherical Al-Ba particles that are similar to GSR [12]. However, the majority of the particles produced are irregular, crystalline, and many large flakes are also present; only a small proportion of particles could be confused with GSR, but never when seen in relationship with the all population of particles [5]. Moreover, the majority of particles generated from the ignition of firework products contain elements not typically found in GSR, such as magnesium, sodium and other elements present in levels not generally seen in GSR like chlorine and potassium [12]. As an example, in the work of Grima et al. [82], a large firework display was used to take sample from people. Then, a standard automated search analysis was performed via the automated SEM/EDX device on the collected sample, flagging out 141 potential GSR.

Between them, 129 particles were discarded simply by looking at their elemental composition, with the criteria showed in Table 13.

Table 13: Exclusion criteria used to discard 129 particles out of 141potential GSR collected from people assisting to a firework display [82].

Exclusion Criterion	***Particle Frequency***
Mg present	21
Na present	85
Mg and Na present	6
Ti with Zn absent	1
Sr with trace elements	2
Ba with Sr	2
Ba with Sb and Sr	1
Ba and S	11
total	129

Only the remaining twelve particles were termed GSR-similar by taking into consideration their elemental profile, shape and morphology. This to show that the particles that were indistinguishable from GSR constituted only a small percentage of the total particle population, which was clearly firework derived. Notice that particles indistinguishable from GSR were also found on crowd assisting the display at a great distance from firework source. This poses other problems, since increasing the distance, the population of particles found could diminish due to environmental factors and it may be more difficult to arrive to a conclusion. The smaller the number of particles, the more neutral the evidence becomes. The best way to handle this situation is as always to adopt a case-by-case approach, comparing the found GSR particles with the ones recovered from spent cartridge casing or bullet left on the crime scene [82].

Regarding cartridge operated nail guns, they use the explosive energy of a blank cartridge discharge to propel a nail into the work piece. Most nail guns use rimfire cartridges that are based on lead-barium component primers although some old tools operate with “Sinoxid” type primers. These types of tool can produce residues similar to GSR. Notice that in some places their use has largely been supplanted by compressed air operated systems. However, they operate exactly like blank cartridges, and so there are some factors that can be used to discriminate between these GSR-like particles and the real ones, as will be seen later on. Also airbags incorporate a primer device that is mounted in the passenger side dashboard of a vehicle. They employ primer initiation to guarantee a sufficient rate of inflation. Most of the air bag primer residue particles obtained from these deployed passenger side devices contain elements unusual to GSR as well as lead, antimony, and barium. Furthermore, many thousands of non-primer particles, characteristic of air bag residues but foreign to GSR, are also expelled from the air bag on deployment, and constitute a signal in order to not confound these particles with GSR [12].

Another environmental source of GSR-like particles are the urban areas rich in metallic particulates such as those exposed to road traffic, like for example the car front rims, on which is quite common to find Sb and Ba particles [33]. In Figure 65 are showed four examples of particles that are considered GSR from many forensic laboratories but in reality, they come from the areas stated before.

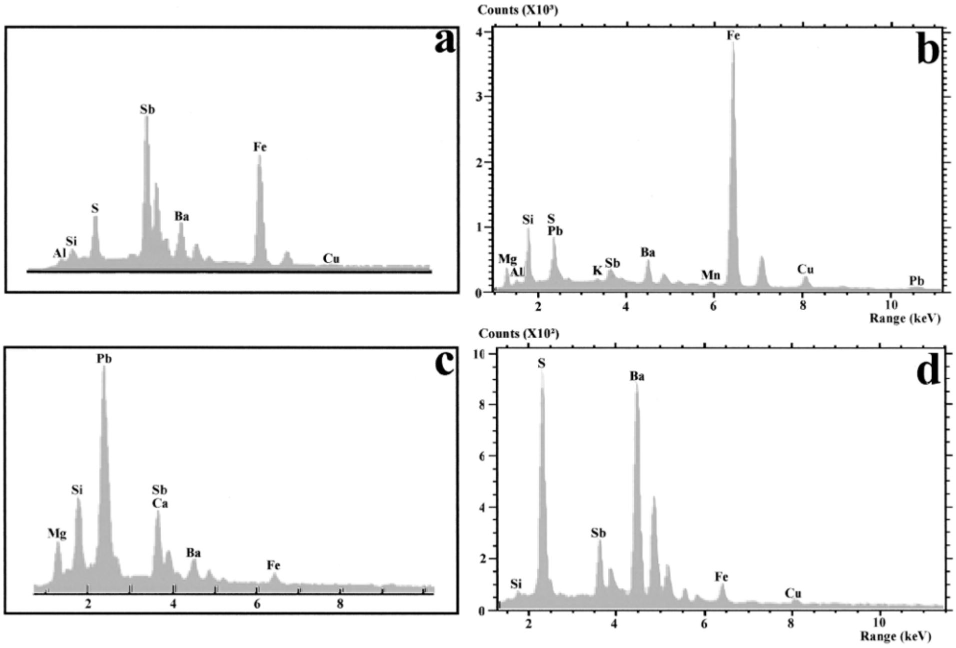


Figure 65: Examples of particles found in urban areas rich in particulate that are easily confused with GSR. (a) There is too much iron; (b) there is too much iron and also manganese and magnesium; (c) there are too much manganese and calcium, both elements permitted only at trace level; (c) sulphur is the strongest peak in the spectra, which is not possible for a GSR, in which sulphur could be present at major, minor or trace levels but never as the highest peak [6][33].

Regarding these areas, probably the most important discovery was made, since from brake linings residue, also the last unique GSR particle, the one with Pb, Ba and Sb chemical composition, was disproved. In fact, brake linings appeared to be an obvious source of GSR-like particles, as many contain in the used friction material lead sulphide, antimony sulphide, and barium sulfate in different combinations and while breaking, disks can reach temperatures in excess of 600 C°, reaching up to 1500 C° in friction spots on the surface, similar temperature to those that occur during a firearm discharge. Heat combines with mechanical action to pulverize and blend the different components of the lining. This is why, through manufacture and wear, brake linings may produce particles containing the most significant elements for the purpose of GSR identification. In their work, Torre et al. [33] divided the particles from brake linings in two different categories calling the particles that could be easily confounded with GSR "clean" particles, which contains Pb, Ba and Sb or only Sb and Ba, and "unclean" the other particles that cannot be confused since they contain the precedent elements but also others forbidden. Notice that the only two compositions that were not found in brake linings were: ''clean'' Ba, Sb particles with no sulphur, or sulphur at trace levels and ''clean'' Pb, Sb, Ba particles with Ba and/or Sb levels higher than lead. These particle types could still in theory be considered ''unique''; nevertheless, previous experience suggests that the classification "unique" should be abandoned in favour of the more prudent "consistent" [2][33].

Looking at the complete population of particles is also in this case the best way of differentiating these environmental source GSR-like particles and the real ones, since residues from brake pads are always accompanied with elevated levels of iron, with sulphur at major level quite constantly also in the "clean" particles, and sometimes with the presence of magnesium, which is rarely found in GSR unless it is used in the ammunition involved in the analysed crime. Moreover, morphology must be re-evaluated, since even the "clean" particles, which resemble the size and chemical composition of GSR, can be distinguished from real gunshot residues by the shape, remembering that the only reliable particles must be considered those with "ideal" morphology, that is to say spherical or globular, with surface either perfectly smooth, pitted with craters, or coated with roundish and smooth nodules, but never, even in part, rough or dusty [33]. Last but not least, notice that the use of lead in brake pads was interrupted in the first years of the 21st century due to health and environmental reasons. Vehicles that still have such brake pads will become less common over time [12].

Other sources of GSR, which are quite more intuitive than the latters, are for example the blank cartridges, used in fake firearms like starting pistols, and toy caps. Regarding blank cartridges, when single particles are considered, their morphology is quite indistinguishable from the GSR, since they usually range in size between 1 to 19 μm, both spherical and irregular particles and all had the appearance of having partially or wholly condensed from a vapor or melt, exhibiting some degree of curvature. They did not exhibit any degree of crystallinity and their surface details were smooth, irregular, cratered, or nodular. However, considering these particles as a whole, the ratio of positive to indicative particles were considerably different that the normal discharge of a firearm, which is about 1:40 with plain lead bullets. In the case of blank cartridges this ratio is of the order of 10:1; this abundance of positive discharge particles suggests a much more homogeneous mixture of discharge residue, since the chemicals are contained within a relatively small volume compared to firearm ammunition, that is, a more intimate mixture contained in a smaller cartridge case, in parallel with a more uniform discharging environment in terms of temperatures and pressures. Moreover, there is no bullet involved to complicate the issue by producing a large number of bullet particles, which would make a substantial contribution to the total number of particles in the indicative category. In fact, unlike GSR, the discharge residue from the blank cartridges contained very few lead-only particles. Last but not least, each of the blank cartridges produced a limited range of discharge particle types [5]. Notice that all these factors can be used also when distinguishing between residues from cartridge-operated nail guns and the real GSR.

Regarding toy caps, used in toy guns, the analysis of discharge particles revealed that both spherical and irregular particles were present, ranging between 3 to 160 μm. The elemental composition comprehends aluminum, calcium, chlorine, copper, iron, potassium, magnesium, phosphorus, lead, sulphur, antimony, silicon, titanium, and zinc, with calcium, chlorine, potassium, phosphorus, lead, and silicon as major elements. Antimony and lead did not occur together and none of these particles would be confused with GSR as their elemental profile differ.

Only a small proportion of the particles containing either lead or antimony met the criteria for “single” element GSR particles. However, if the population of particles is seen as a whole, they cannot be confused with GSR [5].

Notice that both matches and signal flares, which intuitively produce an environment similar to the one of a discharged firearm, in reality do not produce GSR-like particles, both for the morphology, since most of the particles are largely irregular, and also for the chemical composition, since they are always accompanied by elements that are clearly a non-GSR source [5].

As seen, the only solution against environmental contaminants similar both in shape and composition to GSR is to adopt a case by case approach, checking morphology, composition, the spent cartridge and most of all the population of particles, since usually these GSR-like particles are accompanied by a large amount of other particles that cannot be confused with GSR both because of their chemical composition and also because of their morphology. From the particle’s population is also possible to check the ratios between particles, since usually they are different with respect to the ones found in a firearm discharge. Also X-ray mapping technique, able to represent the bi-dimensional spatial distribution of component elements, and the Focused ion beam milling technology can bring some help if needed, since they can analyse the internal elemental structures of particles, reducing the probability of mistakes in inorganic GSR analysis, because true GSR particles and those from other environmental sources in some cases may have very different internal element distributions [2][22][83] .

4. Materials and Methods

In order to fulfil the aims of this thesis, 36 shots with different firearms and ammunitions on different fabrics have been performed in a private shooting range. All the materials and the methods used to produce, collect and analyse the GSR are presented in the following paragraphs.

4.1 Experimental Setup

In a private shooting range, by means of some iron bars mounted specifically for the experiment, three different types of fabrics are arranged so as to shot with different firearms through them and then sampling the produced GSR by using the adhesive stubs. The fabrics used for the experiment are cotton, wool and polyester and are showed in Figure 66.

Figure 66: The three different fabrics used in the experiments; (top) cotton, (down left) wool and (down right) polyester.

The set-up of the experiment is showed in Figure 67. As it is possible to see, the fabrics are fixed to the iron frame by means of two clothespins.

Figure 67: The set-up of the experiment.

In these experiments, three different types of firearms are used, in particular two pistols and one shotgun. The first 9 shots are all performed with a semiautomatic pistol Glock calibre 9x21, showed in Figure 68.

Figure 68: One of the three firearms used in the experiments: the semiautomatic pistol Glock calibre 9x21.

Regarding the ammunition used in the Glock, they are the centre fire cartridges calibre 9x21 produced by Fiocchi with a full metal jacket bullet. The primer of these ammunitions contains the usual Sinoxid mixture which basically contains lead styphnate, barium nitrate and antimony sulphide. The weight of the bullet is 123 grams, with a maximum speed of 375 m/s, a maximum pressure of 2350 bar and an energy of 563 joule. The ammunition and its packaging are showed in Figure 69.

Figure 69: The ammunition used in the Glock, the Fiocchi centrefire cartridges calibre 9x21.

The second firearm used is the shotgun M4 Super 90 calibre 12 produced by Benelli. This firearm can shoot whatever type of calibre 12 shotgun cartridge, ranging from single ball, buckshot and pellets, with or without wads or felts. The Firearm is showed in Figure 70.

Figure 70: The second type of firearm used in the experiments, the M4 Super 90 Benelli, calibre 12.

Eighteen shots are done with this firearm. The first nine, three for each fabric, are performed utilizing the shotgun centre fire cartridge calibre 12 JK6 38 with felt produced by Fiocchi. It assures a maximum speed of 410 m/s and a pressure of 880 bar; the length of the cartridge case is 70 mm and contains pellets. The ammunition is showed in Figure 71.

Figure 71: The first type of ammunition used in the M4 Super 90 Benelli, a Fiocchi calibre 12 JK6 38.

Then with the M4 other nine shots are performed, three for each fabric, changing the ammunition, utilizing the shotgun centre fire cartridge calibre 12 with buckshot produced by the Royal Buck. Notice that both types of shotgun ammunitions used in these experiments contains a Sinoxid type primer, but in a greater quantity with respect to the ammunitions used in the Glock for example. The Royal Buck calibre 12 ammunitions are showed in Figure 72.

Figure 72: The second type of ammunition used in the M4 Super 90 Benelli, the Royal buck calibre 12.

Lastly, another pistol is used, performing the last nine shots with the Desert Eagle which is showed in Figure 73, produced by IMI, the Israel Military Industries. This firearm is a semi-automatic handgun notable for chambering the largest centre fire cartridge of any magazine-fed, self-loading pistol.

Figure 73: The last firearm used in the experiments, the Desert Eagle.

The ammunition used are the centre fire cartridges calibre 50 Action Express (AE) XTP Mag which is a large calibre handgun cartridge produced by the Hornady. The bullet is completely jacketed and weights 300 gr and the primer composition is again a Sinoxid type one. The ammunition is showed in Figure 74.

Figure 74: The ammunition used in the Desert Eagle, the Hornady calibre 50 AE XTP Mag.

In total 36 shots are performed with different firearms, fabrics and ammunitions, considering three replicates for each experimental condition, and 36 sampling stubs are utilized to collect the related GSR on the fabrics. The stubs are the usual aluminum SEM’s stubs of 25 mm in diameter and are showed in Figure 75.

Figure 75: Aluminum SEM's stubs used to collect GSR.

On these stubs, right before the sampling, an adhesive carbon layer is put and then the collection is done by repeated pressing on the fabric on which GSR are deposited till tackiness is gone, usually about 30 times. The adhesive carbon layer is the extra smooth self-adhesive carbon disc produced by TAAB and is showed in Figure 76. Being already coated with carbon, no sample preparations are needed, and the stub could immediately be put under the SEM for the analysis reducing the possibilities of unwanted contaminations and particles loss.

Figure 76: The adhesive layer coated with carbon used on the aluminum stubs to collect the GSR.

The stubs then are inserted in a cardboard and are covered with water caps to protect them. On each cap, an identification number is written; all these precautions are done to protect and to have a safe handling and transportation of the utilized stubs, minimizing possible errors and contaminations. The handling arrangement is showed in Figure 77.

Figure 77: Stubs handling arrangement; each stub is inserted in the cardboard, covered with a cap and fixed with a scotch; in this figure, the first six stubs are showed. .

To resume, the characteristics of each of the 36 shots performed, which correspond to the 36 stubs collected, are showed in Table 14.

Table 14: Experimental conditions of the 36 shots performed.

Shot	***Firearm***	***Ammunition***	***Fabric***
1st ,2nd, 3rd	Glock	Fiocchi Calibre 9x21	Cotton
4th, 5th, 6th	Glock	Fiocchi Calibre 9x21	Polyester
7th, 8th, 9th	Glock	Fiocchi Calibre 9x21	Wool
10th, 11th, 12th	M4 Super 90	Fiocchi calibre 12	Cotton
13th, 14th, 15th	M4 Super 90	Fiocchi calibre 12	Wool
16th, 17th, 18th	M4 Super 90	Fiocchi calibre 12	Polyester
19th, 20ht, 21st	Desert Eagle	Hornady 50 AE	Cotton
22nd, 23rd, 24th	Desert Eagle	Hornady 50 AE	Polyester
25th, 26th, 27th	Desert Eagle	Hornady 50 AE	Wool
28th, 29th, 30th	M4 Super 90	Royal Buck calibre 12	Cotton
31st, 32nd, 33rd	M4 Super 90	Royal Buck calibre 12	Polyester
34th, 35th, 36th	M4 Super 90	Royal Buck calibre 12	Wool

4.2 SEM Analyses

After the collection, the stubs are analysed at the scanning electron microscope of the department of Mechanical Engineering at the Politecnico di Milano. The SEM is produced by Zeiss and the model is the Gemini Sigma 500. It has a field emission gun made of a thin tungsten filament coated with a layer of zirconium oxide, allowing a prolonged filament life and bringing more signal and more detail, especially at very low voltages; it works in high vacuum. The SEM workstation is showed in Figure 78.

Figure 78: SEM workstation of the Politecnico di Milano.

This powerful SEM is able to magnify the images till 1000000x, with a variable working distance, usually maintained between 7 and 14 mm and an accelerating voltage of 20 kV. It has both the backscattered and the secondary electrons detectors, while the emitted X-rays are analysed via an Energy Dispersive X-ray (EDX) detector. The stubs are one by one screwed in the centre of the stub holder, which is showed in Figure 79, which holds them in place.

Figure 79: The stub holder of the SEM; it can receive till 9 stubs.

Since the analysis is not automated, it is obviously impossible to check the entire surface of the 36 stubs and to identify and perform the microanalysis for all the bright particles found.

In fact, for each stub, five zones, showed in Figure 80, are analysed by means of the backscattered electrons at a magnification of 300x, and for each zone, the brighter particles are counted and analysed with the microanalysis to confirm the GSR origin.

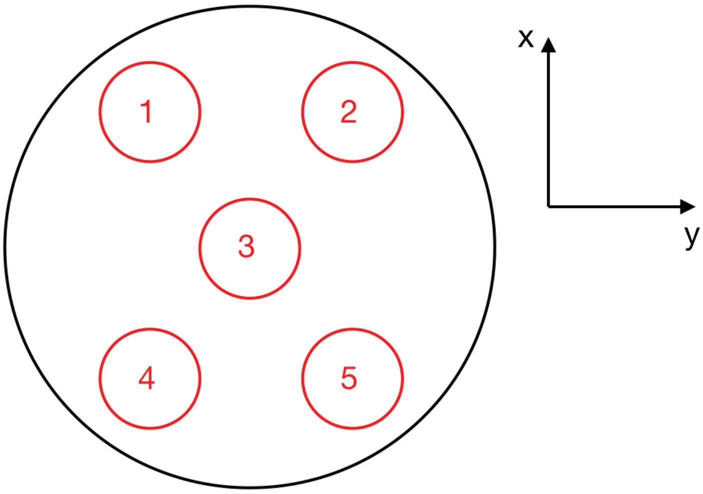


Figure 80: A scheme of the five zones analysed at 300x on each stub.

For completeness, the coordinates of each of the five zones are showed in Table 15, considering that the 25 mm stub is mounted in the central position of the stub holder, as showed in Figure 81.

Table 15: Coordinates of the five positions analysed on the stub.

	Zone 1	*Zone 2*	*Zone 3*	*Zone 5*	*Zone 6*
x	71.901 mm	72.361 mm	65.361 mm	54.223 mm	54.725 mm
y	68.458 mm	61.720 mm	64.381 mm	69.772 mm	59.564 mm

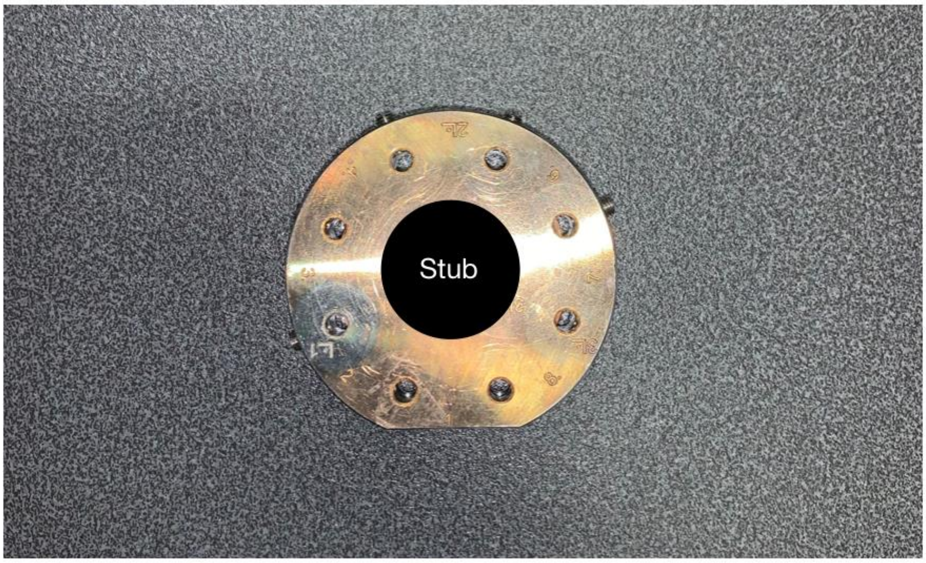


Figure 81: Position of the mounted stub on the stub holder.

For the zones in which there are too much bright particles, only a maximum of 9 particles are analysed and checked for GSR confirmation. An example of a zone in which too much bright particles are present is showed in Figure 82, which is the zone 1 of the 6th stub.

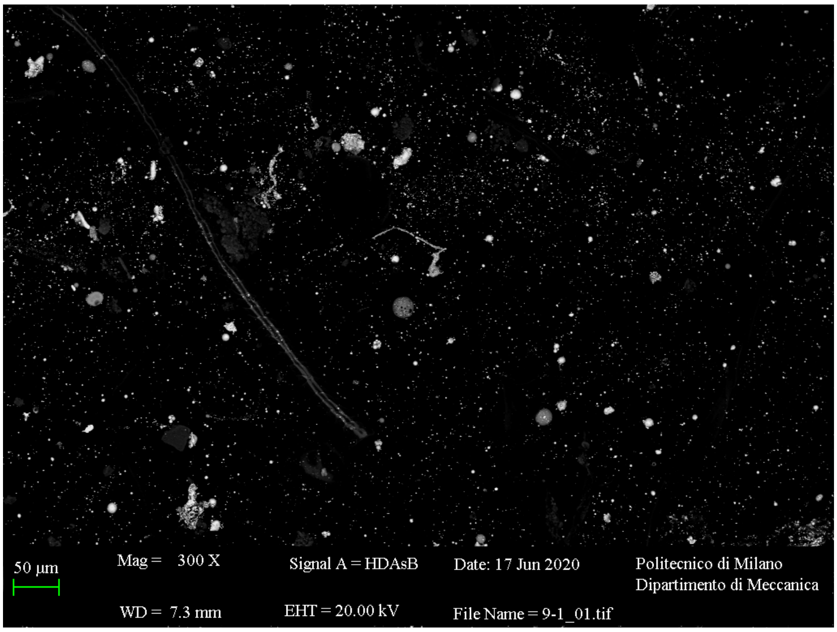


Figure 82: The zone 1 of the 6th stub, magnified at 300x; as it is possible to see, there are a lot of GSR particles.

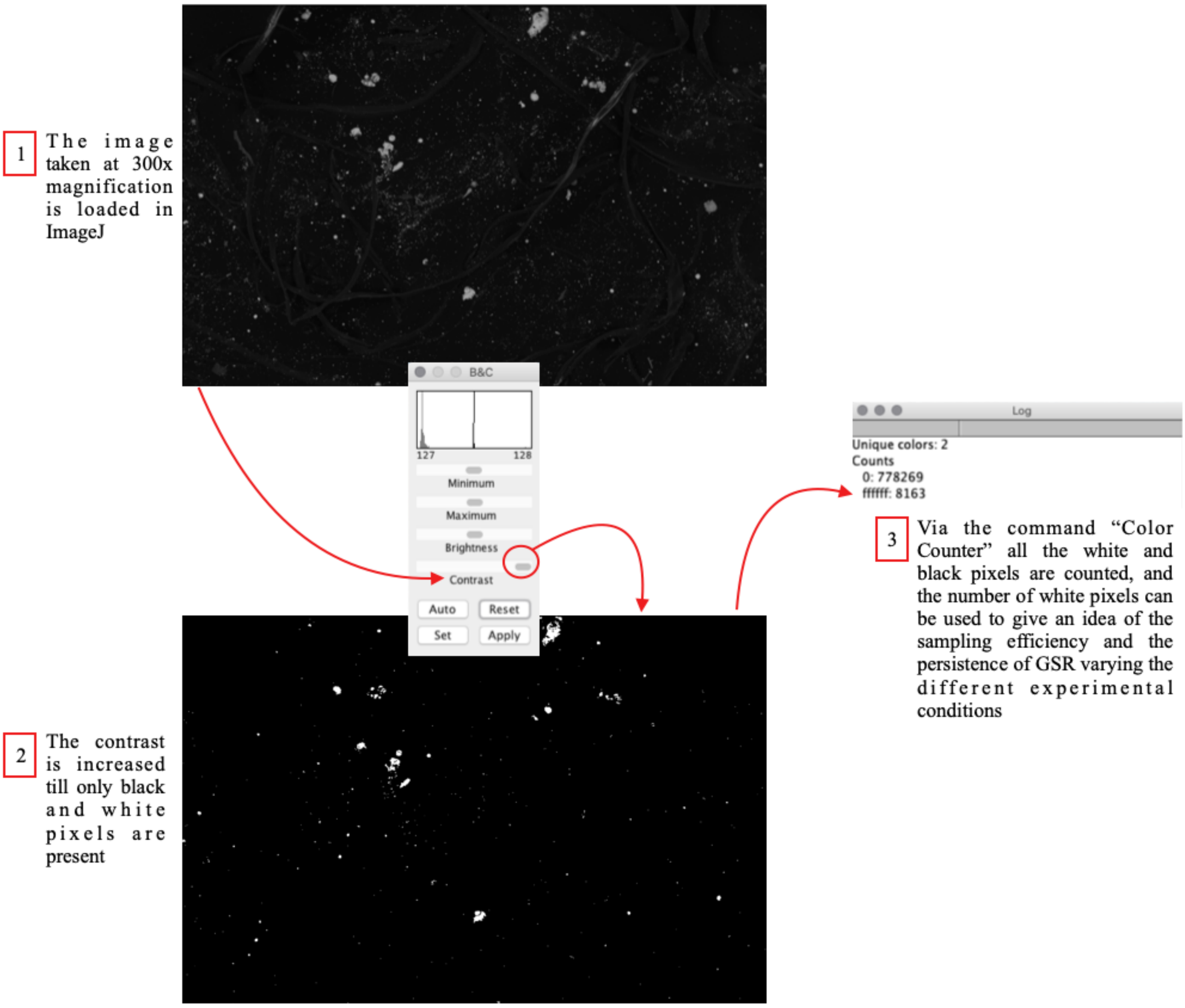
As it is possible to see, the bright particles are a lot, so it would be impossible to analyse all of them without utilizing an automated software that assists the SEM, which however is not available. In fact, in order to reach a conclusion about the persistence and the sampling efficiency of the GSR when using different ammunitions and substrates, which is one of the aims of this thesis, a software for images elaboration is used, explained in detail in the next paragraph.

4.3 GSR Persistence

For checking the GSR persistence using different ammunitions and substrates, since the analysis on the SEM is not automated and being impossible to manually count all the particles present on the five images for each of the 36 stubs taken at 300x magnification, the idea is to use a post-production program to manually count all the particles present on the images.

The procedure is quite simple: for each stub, five images at 300x are taken in the different stub locations already discussed in 4.1; then the contrast of the images is augmented till only black and white pixels are present. All the bright particles became white while the rest of the stub became black. Then with the same program used to increase the contrast, which is a free software called ImageJ, the image is transformed in a RGB color format and then all the different pixels are counted, and the output are the number of white pixels and the number of black pixels; the scheme of the procedure is showed in Figure 83. Lastly the number of white pixels for all the five images taken for each stub is utilized as response in an experimental set-up which could be considered a two-way ANOVA, with 3 replicates for each condition. The factors of the experimental set-up are two: the ammunitions used, which obviously reflects also the firearms utilized to shoot them, and the substrate on which the GSR are deposited and on which they are sampled. The statistical analysis is performed by utilizing a software provided by the Politecnico di Milano to all of its students, which name is Minitab.

The conclusions of the statistical analysis will be on the response, so the number of white pixels which reflects the number of GSR collected on the stubs, and their relationship with the ammunition which produces them and the substrate on which they are recovered.



1 The image taken at 300x magnification is loaded in ImageJ

2 The contrast is increased till only black and white pixels are present

```
Unique colors: 2
Counts
  0: 778269
  ffffff: 8163
```

3 Via the command “Color Counter” all the white and black pixels are counted, and the number of white pixels can be used to give an idea of the sampling efficiency and the persistence of GSR varying the different experimental conditions

Figure 83: Scheme of the procedure utilized to analyse the sampling efficiency and the persistence of GSR varying the different experimental conditions.

5. Experimental

In this chapter of thesis are reported all the results obtained from the experimental campaign performed.

5.1 Results on the Fabrics

After each one of the 36 shots performed, the GSR are collected via the adhesive stubs on the fabrics already mounted on the frame. The results for each condition are reported in the following section; all the photos are taken on the side of the entrance holes, which are highlighted by means of a red circle; obviously, the replicates are not reported. Regarding the 1st, 4th and 7th shots, the fabrics are reported in Figure 84.

Figure 84: The three fabrics used in the first, fourth and seventh shots.

The results of the 10th, 13th and 16th shots are reported in Figure 85.

Figure 85: The fabrics used in the 10th, 13th and 16th shots.

The results of the 19th, 22nd and 25th are reported in Figure 86.

Figure 86: The fabrics used in the 19th, 22nd and 25th shots.

The results of the 28th, 31st and 34th shots are reported in Figure 87.

Figure 87: The fabric of the 28th, 31st and 34th shots.

It is important to point out that during the sampling operations on the wool, a lot of debris and fibres of the fabric itself are also collected and there is no way to avoid this problem.

This complicate a lot the analysis on the SEM, since these debris are non-conductive and it is possible that sometimes useful GSR particles are embedded in them, but could be hardly analysed due to the charging effect of the debris, like the particles showed in Figure 88.

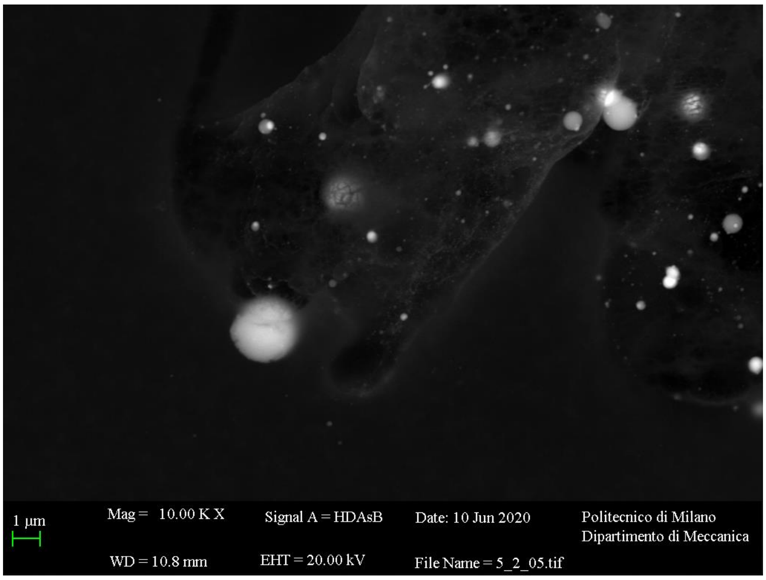


Figure 88: Particles embedded in a micrometric piece of wool.

5.2 Morphology of the GSR

In this chapter, the morphology of the GSR found in each experimental condition is analysed in detail, showing the main peculiarities and differences of the residues produced.

5.2.1 GSR Expelled from the Glock

As expected, most of the confirmed GSR are spherical and are of the type I as theorized by Basu. Their dimension is between 2 to 20 μm, which is a little bit bigger than the type I particles, which according to Basu arrive at maximum at 10 μm. They present an amorphous surface covered with superficial nodules, which quantity could vary a lot, as showed in Figure 89; in particular in the top left and right images there are two particles collected from the polyester, in the down left image there is a particle collected from the cotton while in the downright image there is a particle collected from the wool.

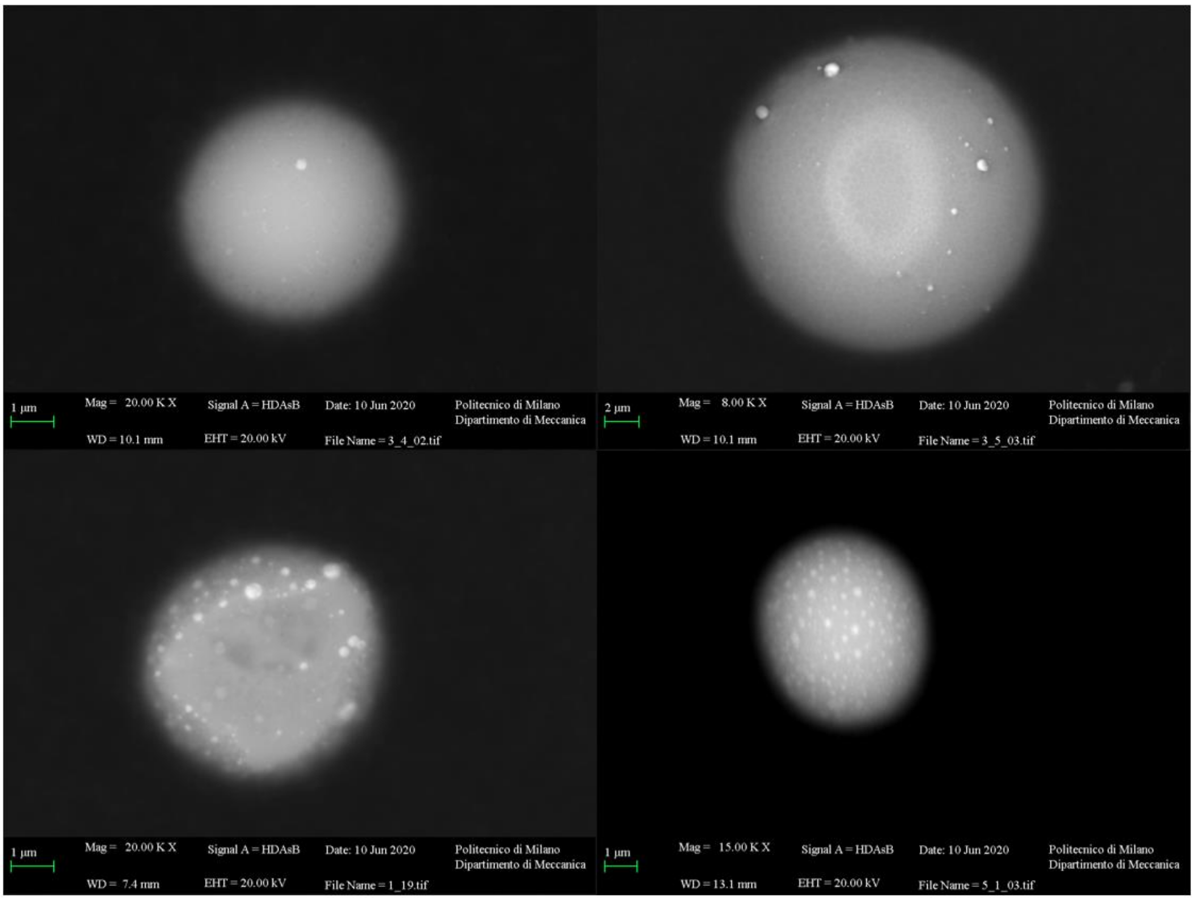


Figure 89: Type I GSR particles with variable number of superficial nodules.

It's important to notice that the type I particles are mostly spherical but it is possible to find also other morphologies, which are obviously more rare and may come from the interaction between these particles with other ones, with the propellant powder, with the projectile, with the cartridge case or with the barrel of the firearm itself. These shapes could be for example elliptical, irregular, but always with a sphere-like form, or a sphere which is clearly disrupted and deformed, as showed in Figure 90, in which is showed a deformed type I particle in the top right collected from the wool, an irregular type I particle in the top left collected from the polyester and an elliptical type I particle in the downward image collected from the cotton.

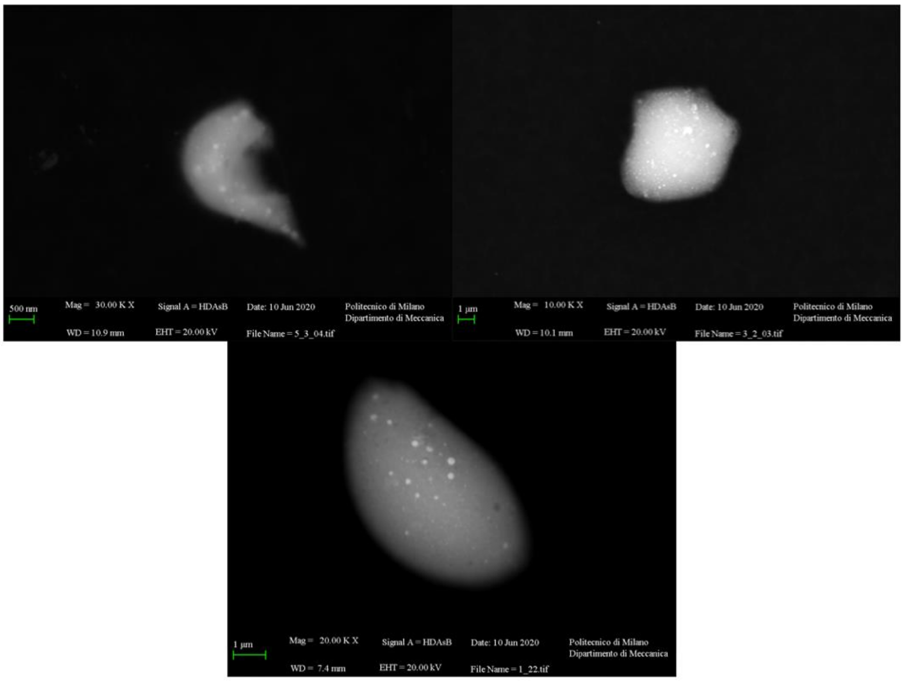


Figure 90: Type I GSR particles with a morphology that it's not spherical.

Also some strange shapes particles are found on the stubs, which resemble type I particles on which have grown some protuberances, which makes their shape irregular and not sphere-like. Two examples are showed in are showed in Figure 91.

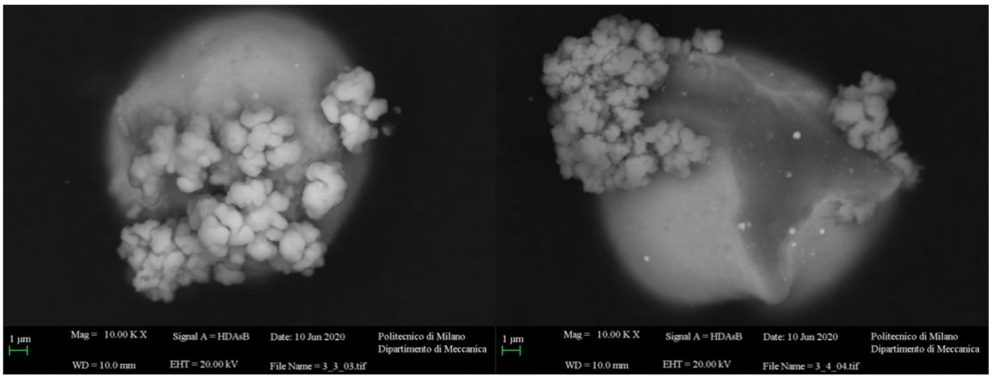


Figure 91: Irregular type I particles on which have grown some protuberances. All of them are collected from the polyester.

Only one single type II particle is found on the stub, probably due to the lower frequency of occurrence of such particles with respect to the type I ones. As theorized by Basu, they have an irregular morphology, as showed in Figure 92.

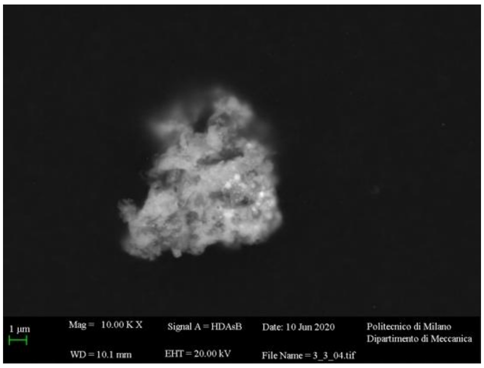


Figure 92: A type II particle collected from the wool.

Notice that no type III particles is found on the stubs, which is not so strange considering that their frequency of occurrence is quite small, even smaller than the one of the type II particles. However, some particles that are not referable nor to the type I nor to the type II are found and some examples are showed in Figure 93. Their shapes are spherical or elliptical. The top one is collected from the wool, the particle in the downright image is collected from the polyester while the particle in the downleft image from the cotton.

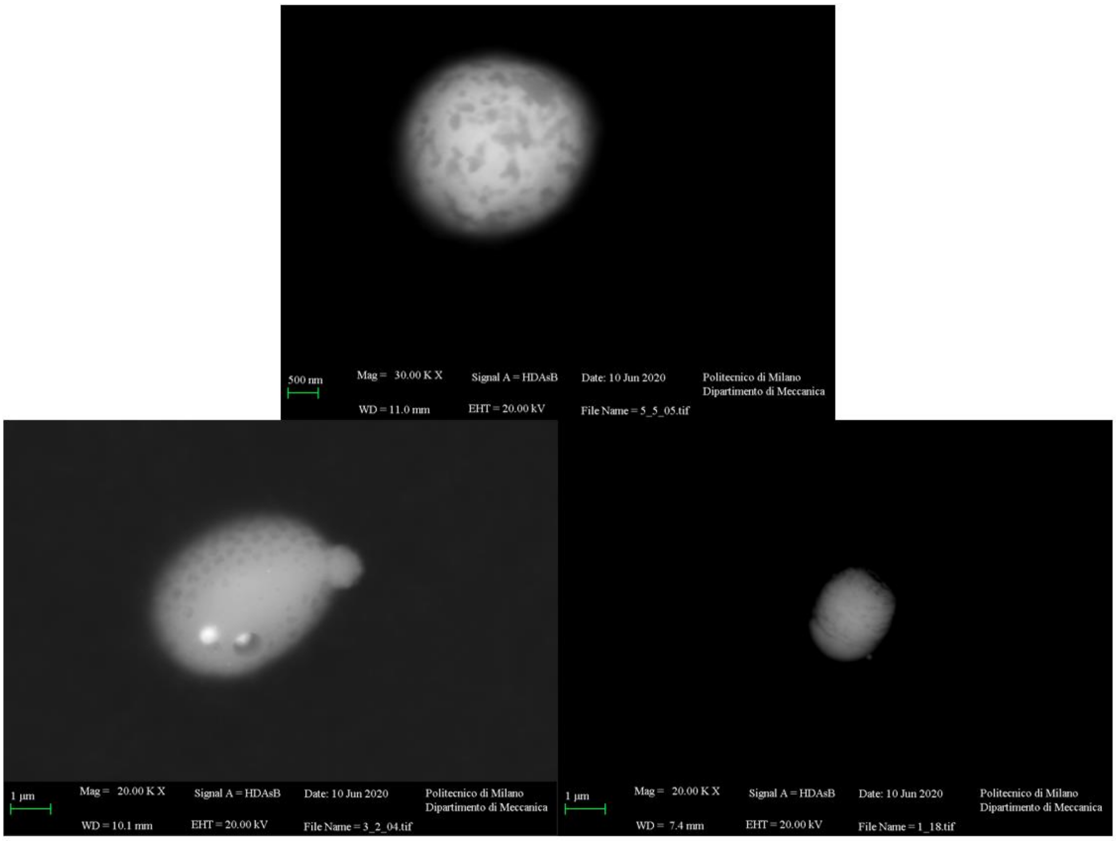


Figure 93: Some strange shapes particles.

Some of them present also some holes in which other particles are stuck, like in the particle in Figure 93 downleft, where the white dots are lead spherules, which is a quite strange phenomenon but confirms the fact that some particles forms and reach the substrate interacting with the surrounding ambient while on the contrary most of them remains undisturbed and maintain the original shape. This thesis is supported also from the strange shape particles that are barely found on some of the collected stubs. For example, in Figure 94 are shown three examples of particles that are clearly fused together. In the top image are showed two fused together particles coming from the polyester while in the downleft and in the downright they come respectively from the cotton and the wool. It is important to notice that in the downleft image the particle on the left is a spherical Cu particle which probably comes from the cartridge case or the bullet jacket, on which it is attached a GSR containing Pb, Ba and Sb. Obviously the fact that some particles interact and collide with each other is an extremely rare phenomenon, which however is not impossible. Moreover, since the possibility that two small micrometric particles collide with each other as a result of the discharge of a firearm is very small, this gives some clue about the number of GSR produced, which is enormous considering that the phenomenon just described can happen.

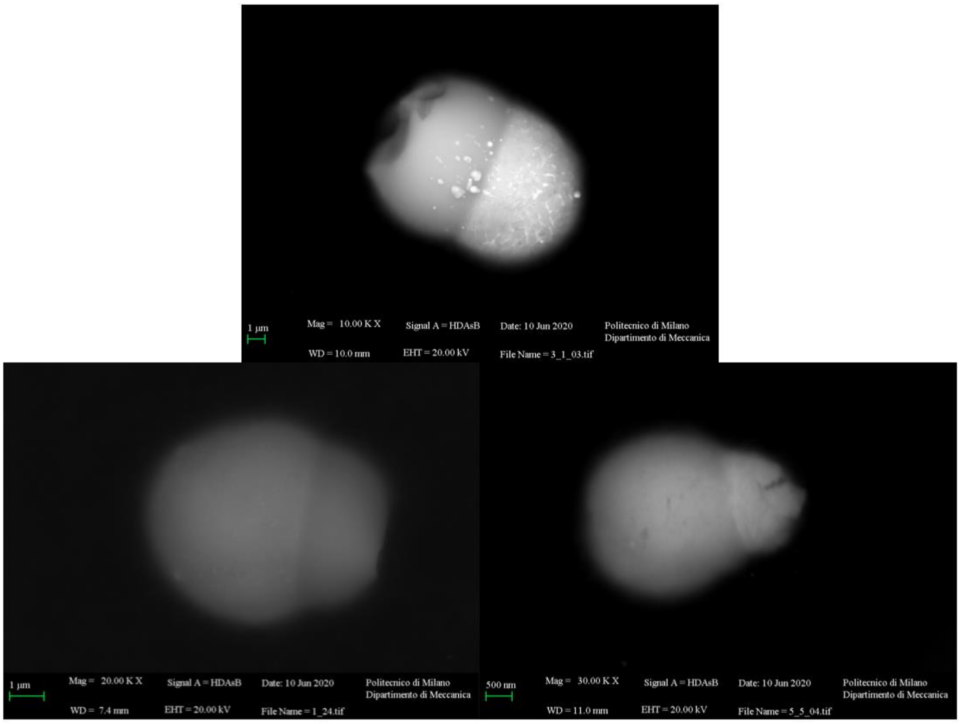


Figure 94: Three examples of fused together particles.

Another very strange shape is found always with the Glock on the wool. As showed in Figure 95, there is a Ba and Sb particle which is like a fragmented shell. It is clearly broken on the outside and is hollow, which is a very rare circumstance but not impossible. This shows also that many other particles, that are not fragmented, could be hollow, but unless encountering a fragmented particle, such in this case, it is not possible with the usual SEM to extract information from the particle’s core, which is possible only with the focused ion beam milling technology. However, also with the latter technology, only some cavities have been shown in the GSR particles, so encountering a completely hollow shell is quite strange and is even barely encountered in literature. In fact, without giving too hasty conclusions regarding hollow GSR particles, a possible source of this shell may come from the type III particles, which have a shell structure and maybe one layer of these particles come off from the core due to fragmentation and appears like the particle in Figure 95; however, no type III is found on the stubs utilized here. Another possibility is the following: since these particles form in an environment of high temperatures, the oxidation is greatly favoured; if the outer oxidized shell breaks and leaves the main metallic core, it could appear at the SEM as the one in Figure 95.

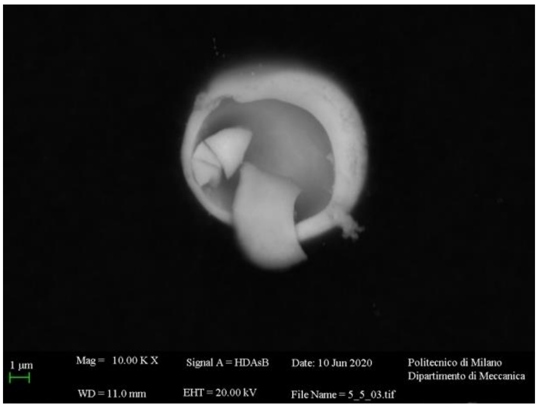


Figure 95: A fragmented hollow particle.

Last but not least, a considerable number of Cu particles are found, which are mostly irregular and of greater dimension than the GSR. The only possible sources of Cu come from the cartridge case or from the bullet jacket, which is eroded by the hot propellant gases or by the rifling of the barrel, and can participate to the particulate matter expelled from the firearm. Most of the times, these are literally pieces of Cu which have an irregular form, as showed in Figure 96.

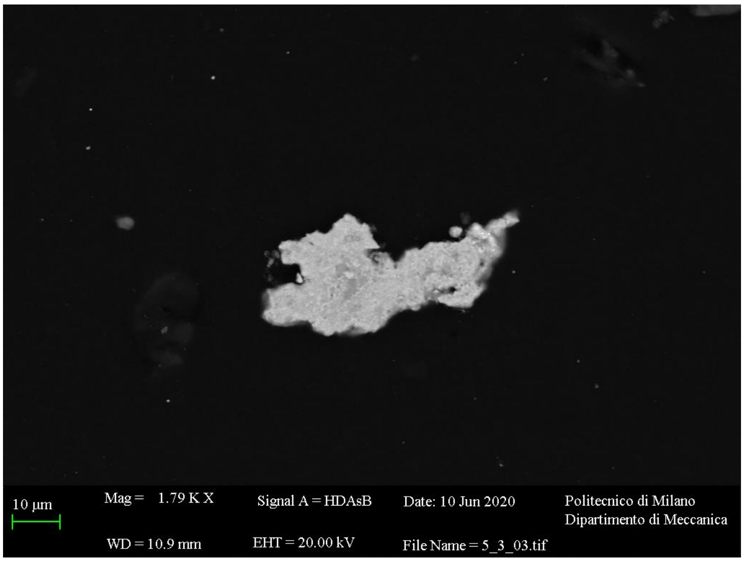


Figure 96: A big Cu particle.

Sometimes, Cu is vaporized and is collected on the stubs as a particle having a sphere like form. Notice that for some unknown reason, Cu particles are often accompanied by Pb. An example is showed in Figure 97, in which the white dots are Pb particles.

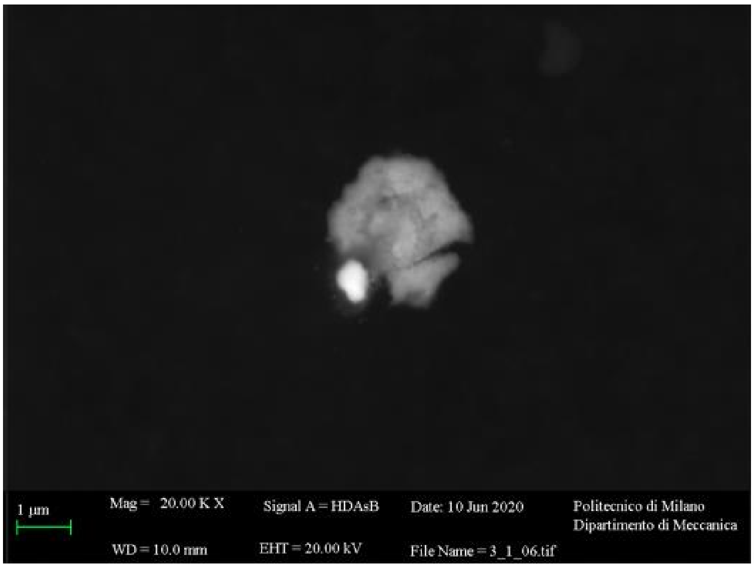


Figure 97: A Cu particle accompanied by a Pb one.

However, none of these Cu particles could be confounded with a GSR due to their shapes. In fact, they always present some crystalline features that makes the analyst able to distinct them with respects to real GSR.

5.2.2 GSR Expelled from the M4 Benelli Using the Fiocchi Ammunition

Regarding the particles expelled from the M4 Benelli using the Fiocchi shotgun ammunition, which contains lead pellets that are not jacketed, on each of the stubs analysed there are a huge number of bright particles. The main strangeness of this results is that in addition to many type I particles are produced also an enormous number of bright particles which are not conductible to any of the types theorized by Basu. In fact, most of the bright particles found are simply spherical and smooth, which dimensions vary a lot, ranging from 1 μm to dozens of μm; on some of them is also possible to see a sort of grain structure and most of them are covered by other smaller spherical particles, as showed in Figure 98; the top particles are taken from the cotton while the bottom ones are taken from the polyester.

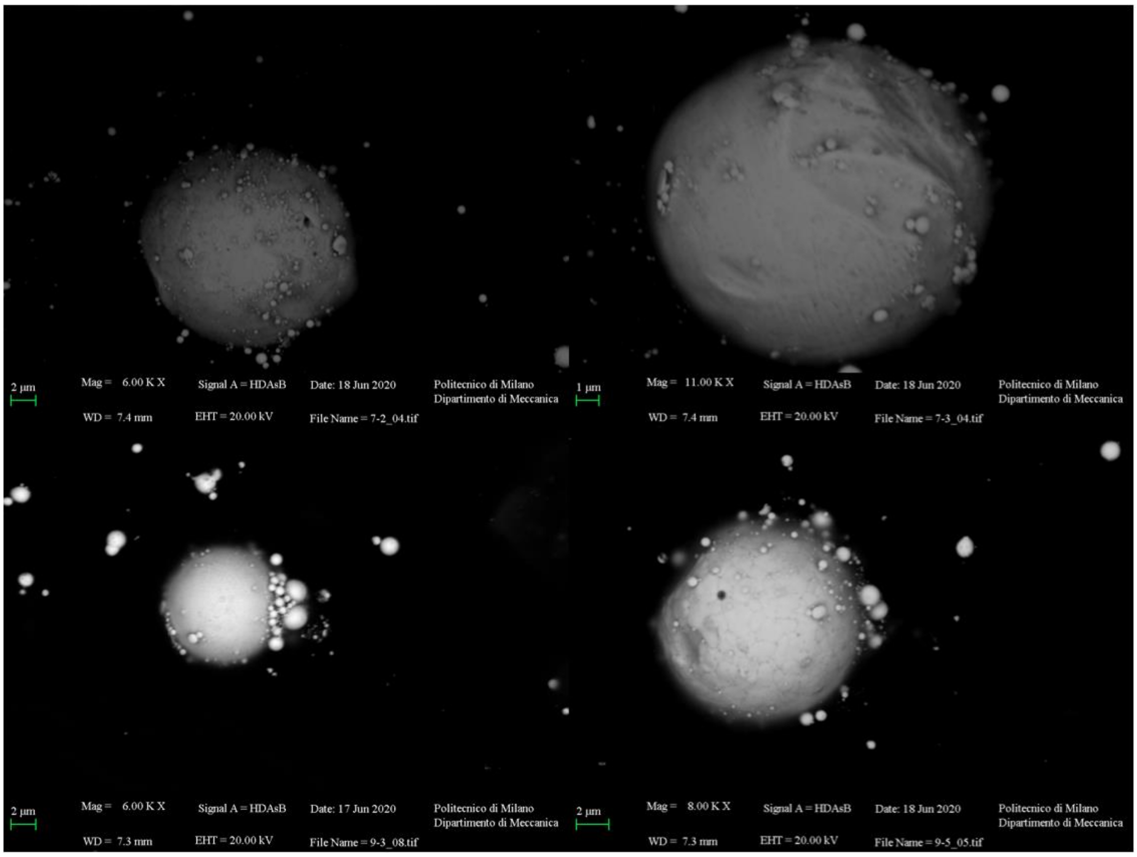


Figure 98: Spherical particles with some smaller particles attached on the surface.

All the small white particles distributed all over the images seen in Figure 98 are simply smaller spherical particles equal to the bigger ones. These small particles sometimes form agglomerates, as showed in Figure 99, probably due to the electrostatic force that is generated between them and also from the fabric itself, especially in the case of the polyester; in fact, smaller particles are more prone to remain attached to the fabrics due to the Van der Waals forces. The agglomerate on the left is collected from the polyester while the right one from the wool. In general, these bright particles are largely present in each of the images taken at 300x magnification and on every stub utilized, so on every fabric used in the experiments performed with the shotgun and the Fiocchi ammunition, so it is possible to say that this specific combination of firearm and ammunition produces a great number of such spherical bright particles; without even a statistical analysis, it is easily possible to be aware of the fact that the Glock does not produce such type of particles.

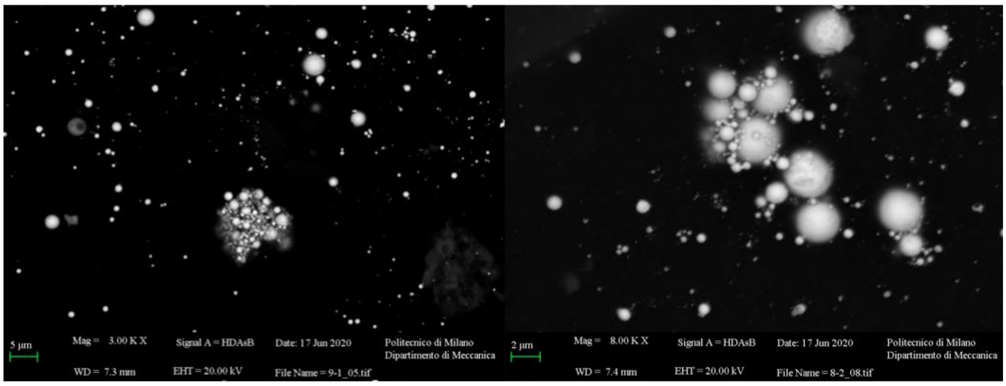


Figure 99: Agglomerates of small spherical particles.

Most of these bright particles are spherical, but also in this case, it is possible that they interact with the surrounding ambient, like the firearm itself or the other particles, modifying their shape becoming elliptical, fragmented, completely irregular with sometimes the presence of holes on the surface, like the examples showed in Figure 100; all these particle are collected from the polyester and the cotton. However, they always have a sphere-like form and no sign of crystallinity.

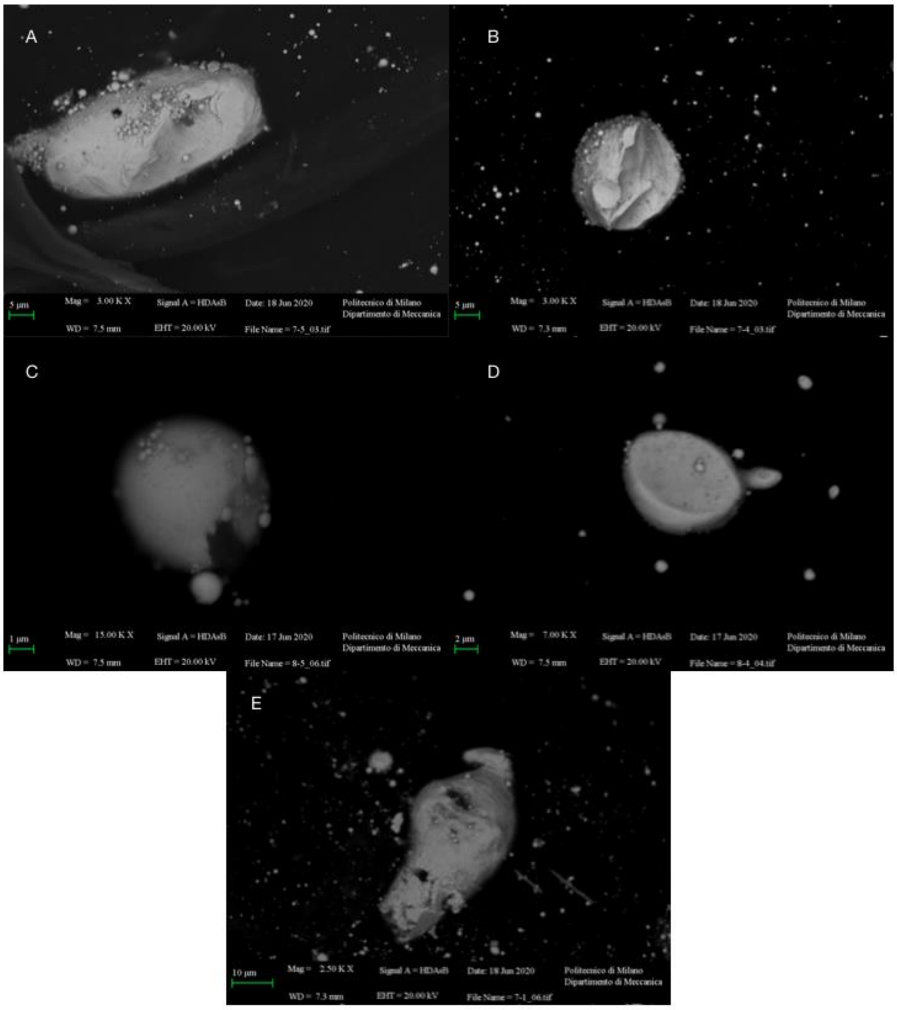


Figure 100: Bright particles that are not spherical: (A) elliptical, (B), (C) fragmented, (D) deformed and (E) completely irregular.

Between these irregular particles, there are some that are clearly derivatives one of the other, as theorized by Kara et al. [23].

As it is possible to see in Figure 101, it seems possible that parts of bigger spheres, probably even before the completion of the solidification process, detach from the main core and forms themselves smaller particles. If the solidification process is concluded before the shape of the detached part of the particles has become a sphere, it is even possible to see a bridge which is probably the last part that was in contact with the main core, resembling the shape of a droplet.

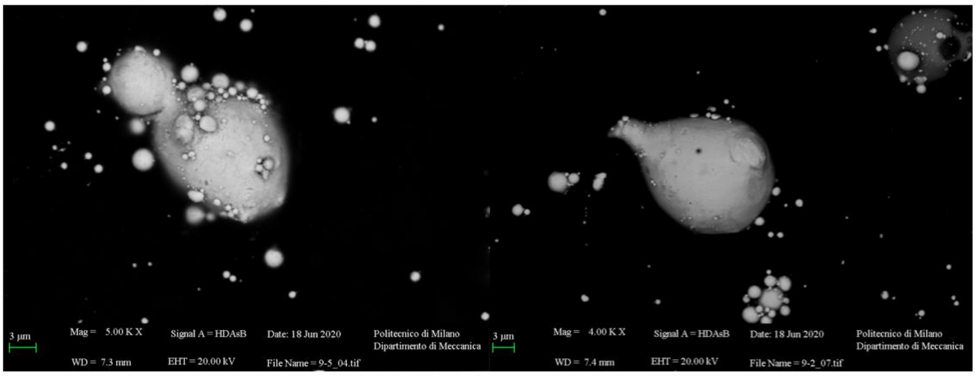


Figure 101: Two examples of particles that derive from a bigger one. In the left image there is a smaller particle that is detaching from the bigger core while in the right image there is a particle that seems a droplet with a broken bridge which probably comes from a bigger core from which this particle has detached; these particles are collected from the polyester.

This makes understand that it is possible that some found particles derives directly from other bigger ones. This reasoning stands when talking about micrometric particles, while when the attention is moved to the nanometric ones, which can hardly be analysed even with this powerful SEM used in these experiments, the reasoning change completely. In fact, what could be pointed out by these analyses is that the micrometric particles are in reality formed by a large number of small nanometric ones that are completely fused and coalesced together. This reasoning is supported both by the literature, since also Melo et al. [24] support the thesis that a cloud of metallic atoms is immediately generated after the shot and then these atoms condensate into metals and metallic oxide crystals due to the reduction of the Gibbs free energy to decrease surface energy leading to nucleation and growth of particles, which then agglomerate around each other forming nanoparticles, which subsequently form the usual GSR particles and is supported also by some strange particles found in this experiments like the one in Figure 102, collected from the cotton.

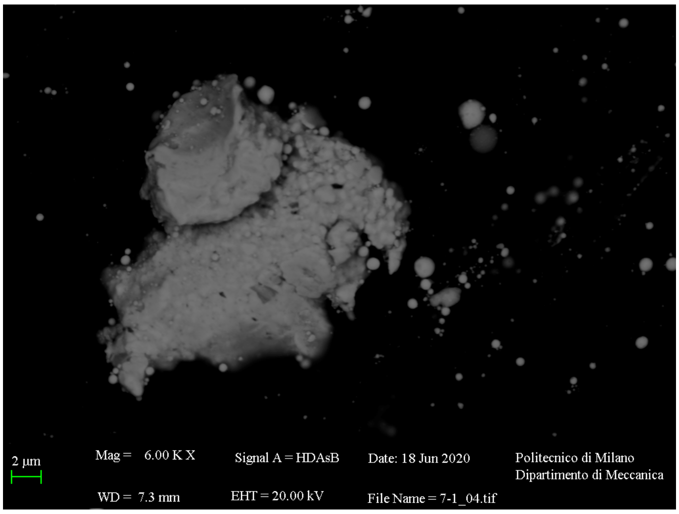


Figure 102: Example of two interacting particles in which it is quite easy to see how the small nanometric particles coalesce and form the bigger one.

In this image, it is possible to see two particles that interact with each other and disturb themselves; what it is important to point out is that in the zone where the two particles are in contact, it is possible to see how the main core is in reality formed by small nanoparticles. Passing from the zone where the particles are in contact to a zone distant from the interaction the surface morphology become more uniform, however it is still possible to see a grain structure which originates from the smaller nanometric particles fused together. The grain structure that is visible only on some particles, like the example in Figure 103, represent in reality the boundaries of the small nanometric particles that are fused together.

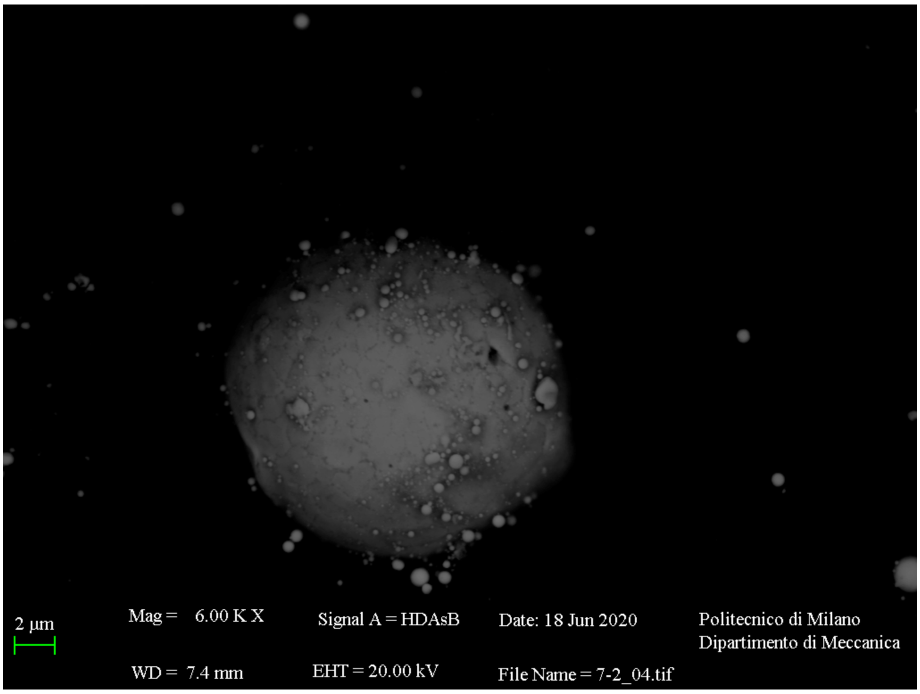


Figure 103: A big GSR particle on which is visible the grain structure, collected from the cotton.

What it is possible to point out from these experiments is that the formation of GSR particles is exactly a condensation phenomenon of a supersaturated phase made by the constituents of the primer mixture and in general from all the heaviest elements that are present in an ammunition, which become gaseous during the deflagration, and then condensate back in the form of spherical droplets; the lighter elements flow away in the atmosphere, this is why they cannot be found in the GSR. However, the first droplets that form are nanometric, and form the bigger particles simply by coalescing between each other; the coalescence is driven by the electrostatic forces that are generated between these small nanoparticles that are exactly the cohesion forces that are generated in any condensation phenomenon, the Van der Walls forces. This cohesion forces explain also why the bigger particles are always surrounded by small particles present on the surface, that are probably attracted by the same forces that attract the other nanoparticles when forming the micrometric ones.

The fact that on some particles this coalescence phenomenon is visible while on others not and they seem perfectly smooth and uniform is probably due to the environmental conditions in which they form, which influence also the solidification process. If the solidification is uniform the droplets coalesce till the grain structure disappear and the particle seems perfectly homogeneous.

This reasoning comes from the observations done in these experiments; for example, the smaller particles are more uniform with respect to the bigger ones, on which is sometimes visible the grain structure, probably because the smaller ones solidify more fast and more uniformly than the bigger ones, and so they have time to completely solidify and fuse together. Moreover, using the Glock, in which the environment of GSR formation is more uniform thanks to the sealing of the bullet which maintain closed the firing chamber, the particles themselves are more uniform and the grain structure is not visible.

On the contrary with the shotgun, in which the firing chamber is not sealed due to the presence of the wads which are not able to completely close the firing chamber, as the seaming of bullet does, the environment of GSR formation is not uniform and there are more particles on which this “grain” structure become visible. Last but not least, another factor that it is able to make uneven the solidification conditions of the GSR particles and to make visible the grain structure is the interaction with other particles. In fact, the small nanometric particles that are forming the bigger one are clearly visible in Figure 102, in which two particles are attached, interact and disturb themselves. In the shotgun with respect to the Glock a large number of particles are produced, which for example may come from the fact that there are bigger quantities of primer mixture and propellant powder, so this phenomenon became more visible. However, this is confirmed also in Figure 94 in which there are particles collected on the stubs utilized in the experiments with the Glock; in this image, there are some examples of particles fused together, therefore interacting with each other, and the “grain” structure become visible. The only other case with the Glock stubs in which it is clearly visible the formation of the bigger particles with the coalescence of the smaller one is showed in Figure 93 downright.

Other than the type of particles analysed till now, the M4 Benelli used with the Fiocchi shotgun ammunition produces also another type of particles, which could be considered the usual type I particles, which consist of a darker core covered by brighter nodules and particles, which are clearly different with respect to the core in terms of chemical composition, which will be analysed in 5.3.2. The core is usually spherical while the number of particles on it and also their dimension is greatly variable, as showed from the examples in Figure 104 and Figure 105; the particles are collected from all the three different types of substrates.

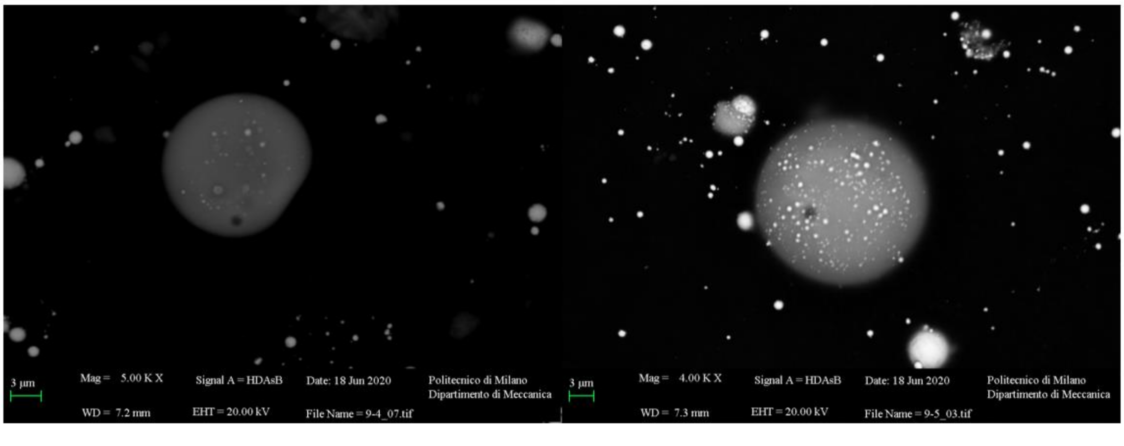


Figure 104: Spherical darker cores with variable number of brighter particles on them.

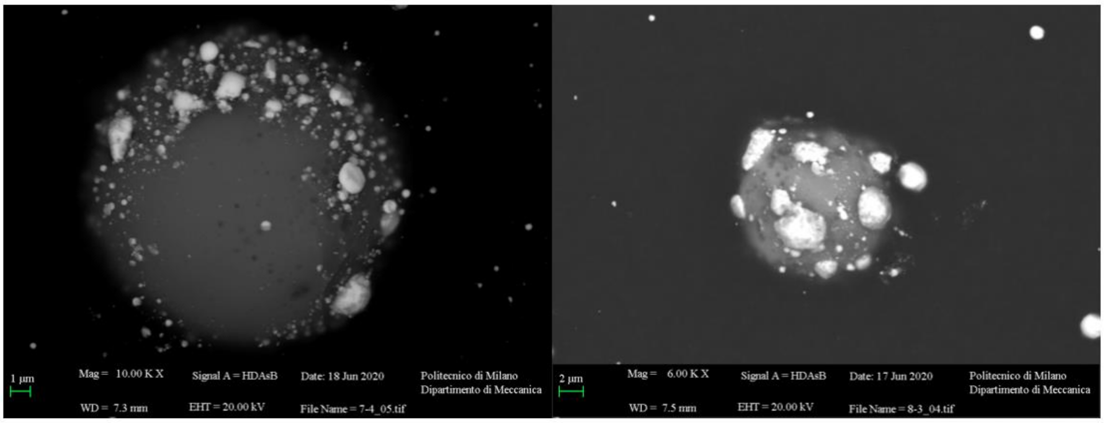


Figure 105: Spherical darker cores with brighter particles on them having variable dimensions.

This particles in Figure 105 resemble the type I particles theorized by Basu, but at the dawn of their formation, meaning that the usual superficial nodules are still perfectly discernible particles, attached to the main core; this reasoning is better explained in 5.3.2. As always, these types of particles present also some variations from the shapes presented in the previous figures, meaning that they are not only spherical but could be also irregular or elliptical, as showed in Figure 106.

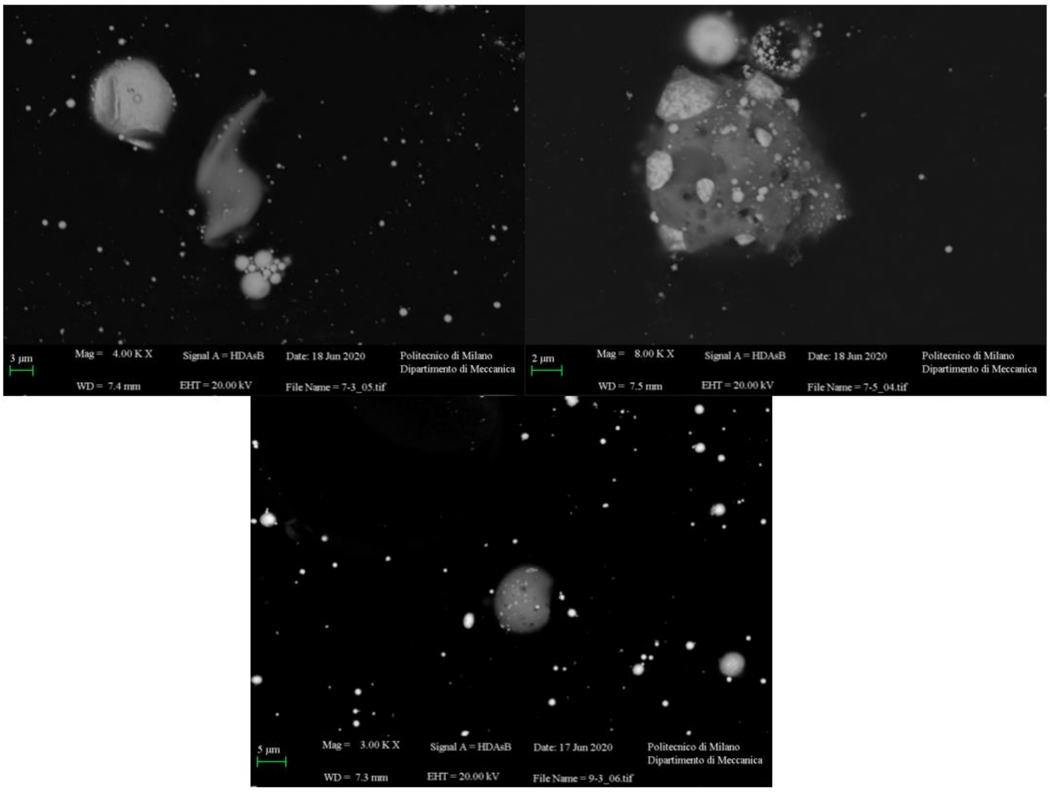


Figure 106: Irregular particles in the top images and an elliptical particle in the bottom one. Pay attention that in the top left image the attention is obviously paid on the darker one.

Some of them present also some cavities which could be empty or filled by some brighter particles, as showed in Figure 107. These examples are helpful since acts as support to the thesis that an inhomogeneous and disturbed solidification due to the interaction between particles can make visible the grain structure explained in the previous section; in fact, the indented particles shows this peculiar superficial structure.

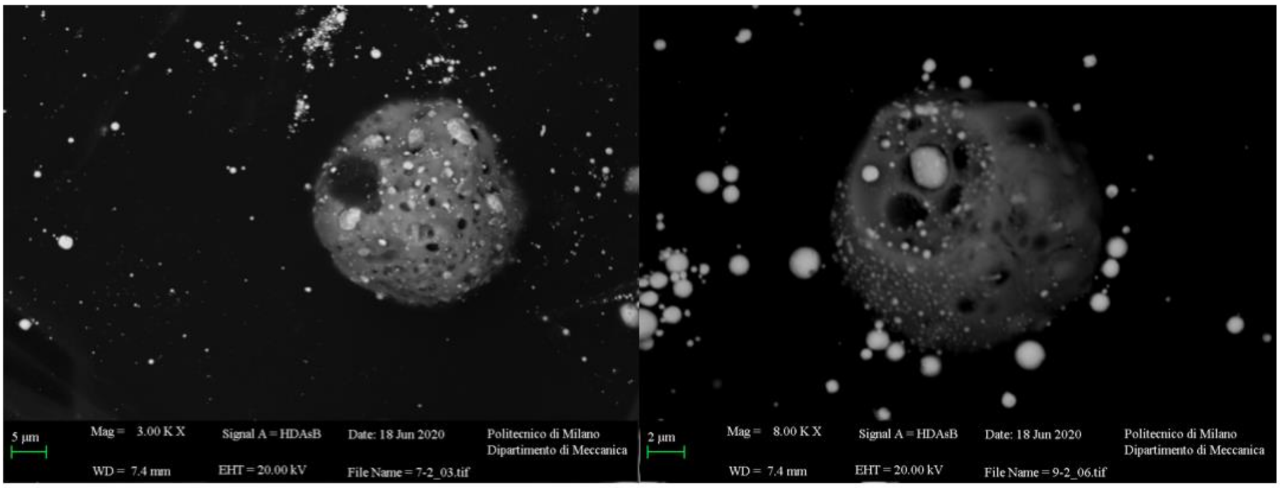


Figure 107: Darker cores on which are indented some brighter particles.

Additionally, also considering these types of darker particles, there are some of them which seems separating into two smaller particles, something similar to the phenomenon that happen also for the brighter ones analysed in the previous section. In in the left image of the Figure 108 is visible a single particle that is separating into two small halves, collected from the polyester, while in the right image, in which there are particles collected from the cotton, nearby the bigger particle, is clearly visible a single elongated one that is almost ending the separation into two smaller spherical halves, confirming once again the possibility that this strange phenomenon happen.

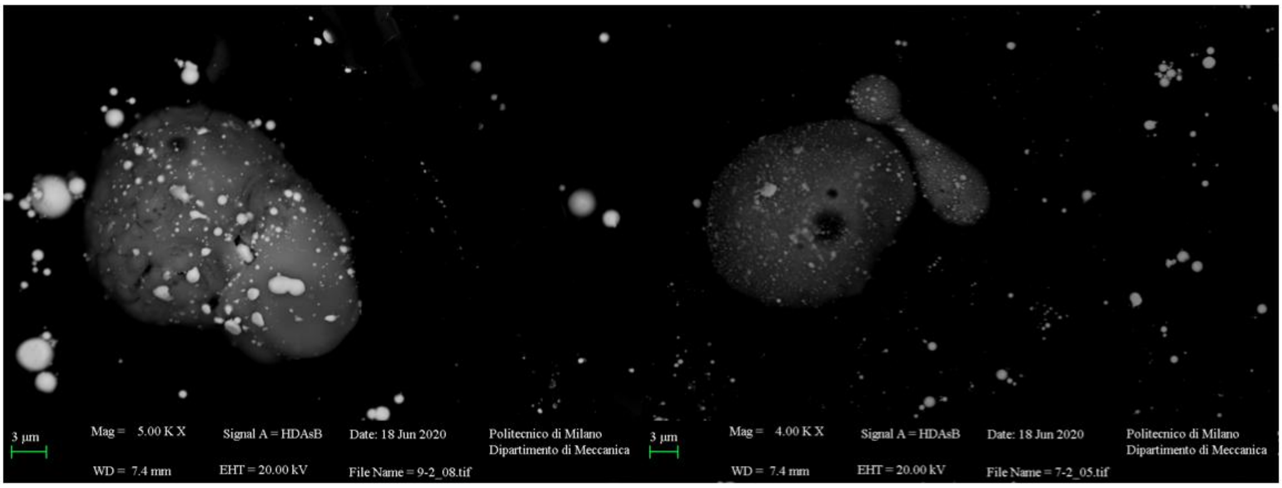


Figure 108: Examples of particles that are separating into two smaller halves.

Notice that in the image on the left in Figure 108 is also visible on the left part of the particle something similar to the grain structure observed on the bright particles, which confirms the fact that all the types of particles are formed via the same phenomenon described before, the condensation from a supersaturated gaseous phase, but on the darker ones this phenomenon is hardly visible. This is probably due to the solidification temperatures which drive this mechanism, since the darker particles contain barium, as will be shown in 5.3.2, which has a solidification temperature higher than Pb and Sb, and so the small nanometric particles have more time to completely fuse together and solidify. This is also confirmed by the fact that barium tend to form bigger and more homogeneous particles with respect to Pb and Sb ones.

The fact that barium is already solid when Pb and Sb are liquid is confirmed not only by the solidification temperatures, which for Ba, Pb and Sb are respectively 860 C°, 327.5 C° and 630 C°, but also from strange shapes of the particles found on the barium core, which sometimes are splashed on it, as showed in Figure 109.

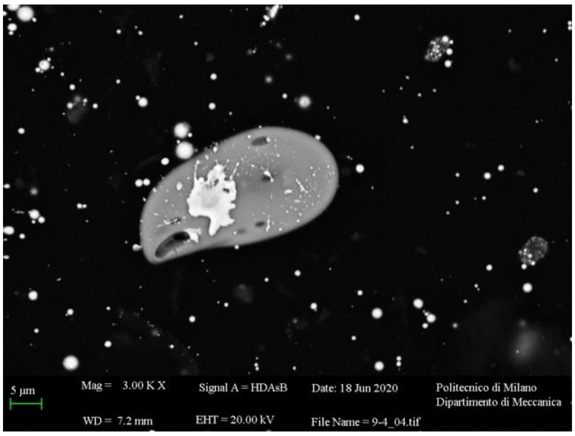


Figure 109: A splashed Pb particle on a core of Ba; the particle is collected from the polyester.

Obviously also in this case, there are some particles that are clearly fragmented, due to the interaction with the surrounding environment and with the other particles. An example is showed in Figure 110, in which it seems that the surface of the particle has been broken but it is still attached to the main core.

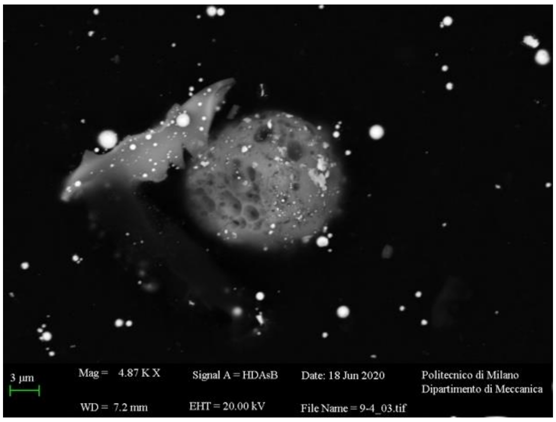


Figure 110: A fragmented particle collected from the polyester.

Last but not least, there is also a particle that shows a strange shape which resemble exactly the one of the particles in Figure 91, confirming that the protuberances that seems grown on the barium core contain barium oxides.

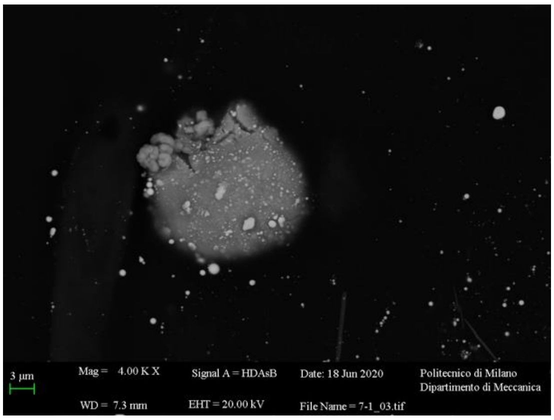


Figure 111: A particle with some barium oxide protuberances.

5.2.3 GSR Expelled from the Desert Eagle

Regarding the morphologies of the particles produced by the discharge of the Desert Eagle, also in this case there are two prevalent morphologies, which can change and vary according to the interaction with the surrounding ambient. However, before looking at the type of morphologies produced, what it is possible to point out directly looking with naked eyes at the images at 300x magnification is that all the particles present are in general smaller than the ones found both in shotgun experiments but also in the Glock ones. In fact, from these experiments it is possible to point out that the number of particles produced depend on the firearm and ammunition used, but the dimension of the particles sampled depends only on the physical activity performed by the sampler or by the substrate on which GSR are deposited. In fact, due to the very high power of the desert eagle shots, the substrate, which is fixed on the steel frame via two clothespins, is wiped out and it is possible that the bigger particles fall off from it and so they are not collected on the stubs. Something similar happens also in the shotgun experiments used with the ammunition containing buckshot, as will be discussed later on, while with the Glock and with the shotgun used with the pellets, the substrates stand still during the shots and also bigger particles can be recovered since they remain attached to the substrate till they are sampled on the SEM's stubs.

However, the first type of particles that come to the eyes when looking at the images at 300x magnification are very small, round and bright particles which are very similar to the majority of bright particles present in the shotgun experiments, however in this case they are largely less present and smaller. Some examples are showed in Figure 112, the particles are collected from the cotton and the polyester.

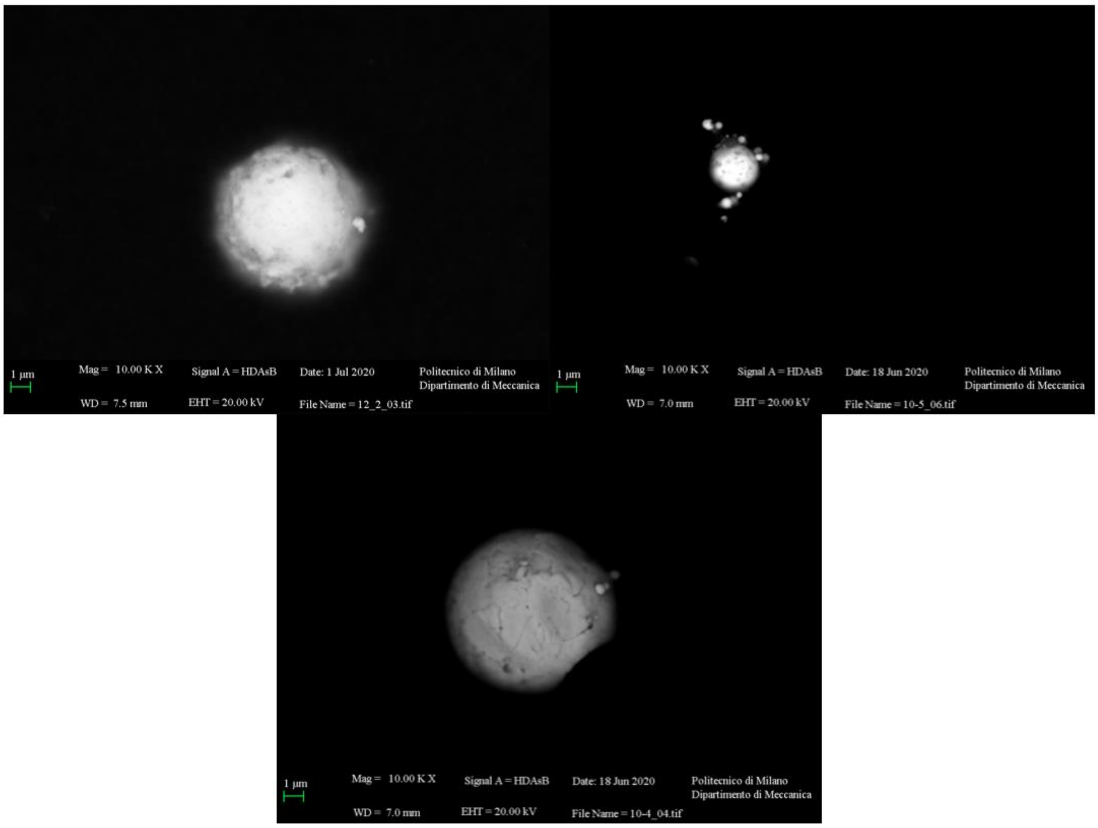


Figure 112: Small bright particles collected from the Desert Eagle experiments.

On some of them, it is also possible to see the previously encountered grain structure. Moreover, they sometimes form agglomerates of small particles, similar at the ones in Figure 112 in the top right image. These bright particles can also appear deformed and irregular, as showed in the examples in Figure 113; the particles are collected from the cotton and from the wool. Moreover, in the downward image in Figure 113, the agglomerate of deformed and irregular particles seem the fragment of a bigger one which maybe it has been disrupted by the sampling action of the stub.

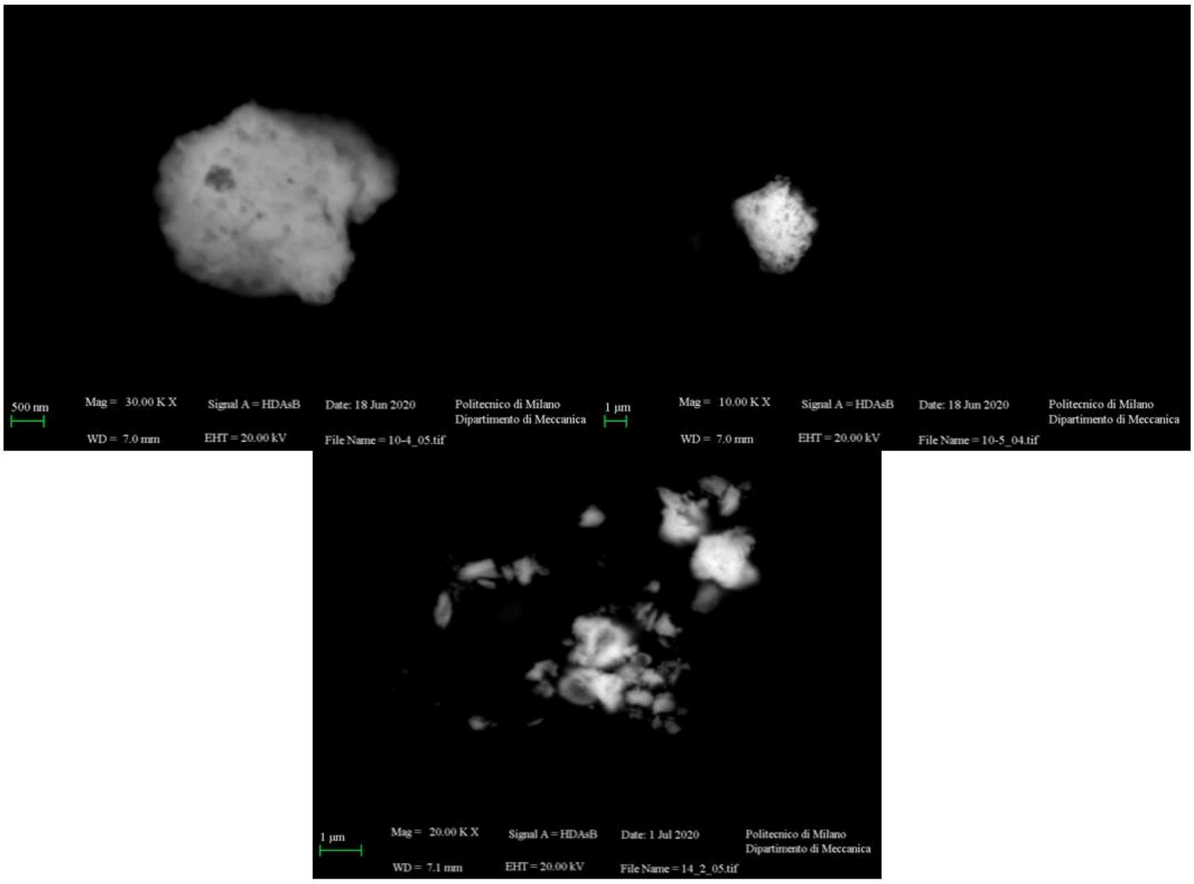


Figure 113: Small bright particles which have an irregular shape.

The other type of particles that are encountered on the stubs appear generally bigger than the latter type, with a darker core and white superficial nodules, and so they can be considered type I particles according to Basu's classification. Again, the dimensions of the superficial nodules and their number could vary a lot. However, what is really strange about these particles with respect to the ones expelled from the Glock or from the shotgun is that the darker core has usually a sponge like structure, full of holes which could be bigger or smaller; it seems that type I particles with an homogeneous core are not produced by the Desert Eagle. This is probably linked to the mechanism of formation of these particles: in the Glock the ambient in which they form is quite small and sealed by the projectile, in the shotgun is bigger and is less sealed due to the presence of the shot cup; here the firing chamber is sealed by the projectile but the ambient has a larger volume than the Glock one, due to the bigger calibre of the ammunition, so probably more air is entrapped in these particles and forms holes and cavities which are clearly visible on the particles. Some examples are showed in Figure 114; the different particles are recovered from all the type of fabric used in the experiments.

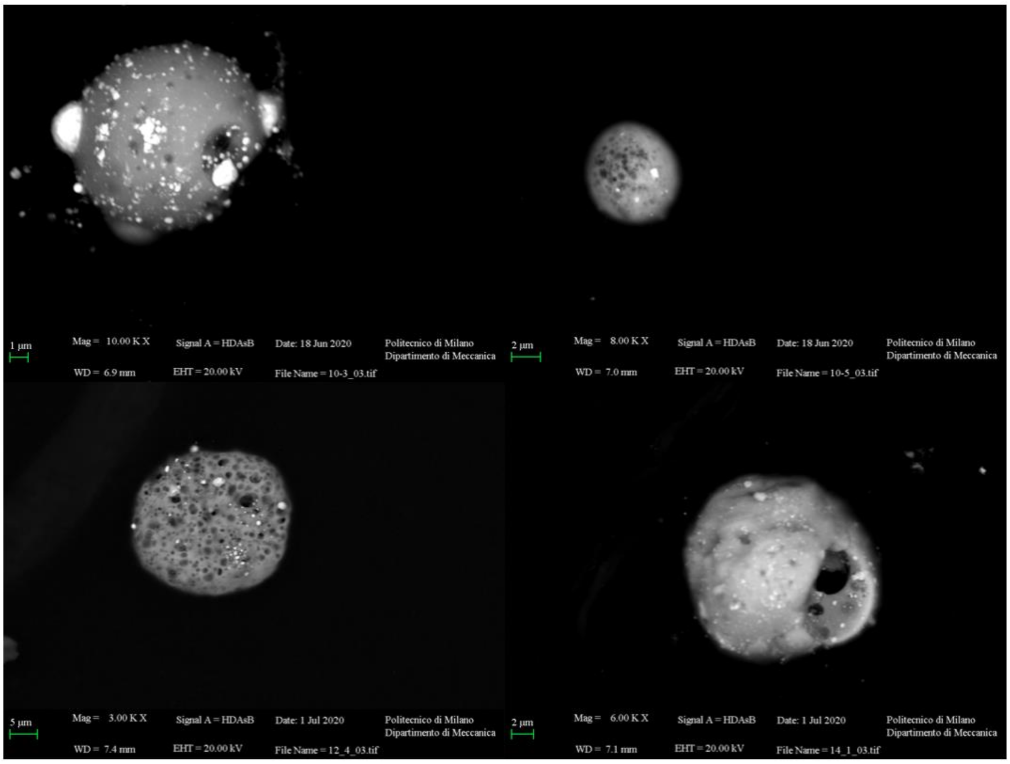


Figure 114: Type I particles with a sponge-like darker core.

It is also possible to encounter some darker cores alone, without nodules or superficial particles, showing that the type I particles do not form in one single passage from the vapor state to the usual type I morphology but firstly the barium core solidify, phenomenon which is explained also from the fact that the solidification temperature of Ba is higher than the one of Pb and Sb, and then the solid or semi-solid Pb-Sb particles impact on it and create the superficial nodules theorized by Basu. Examples of barium cores free from superficial nodules are showed in Figure 115.

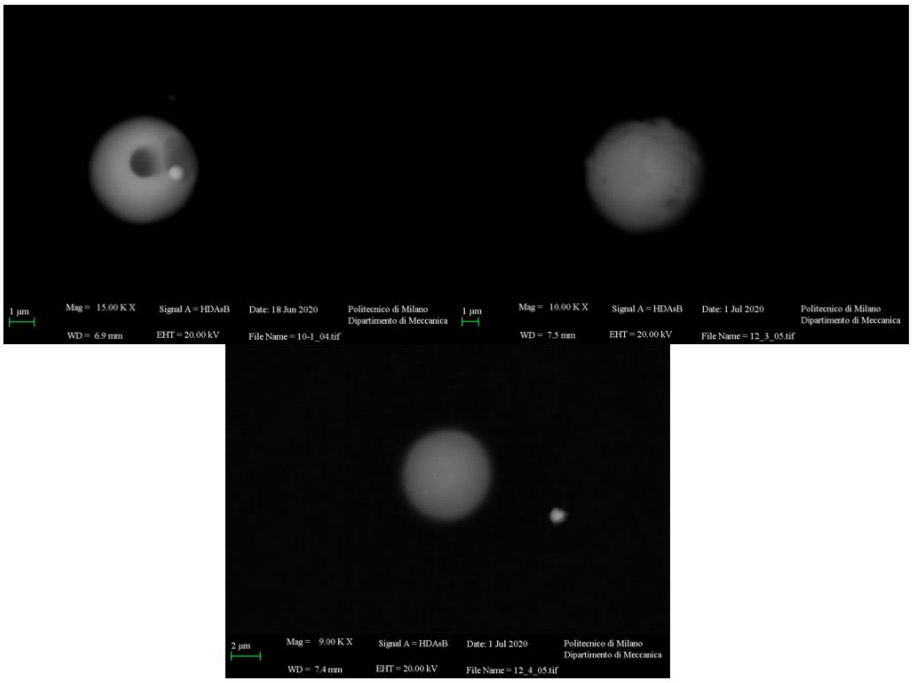


Figure 115: Barium darker cores free from the superficial nodules.

Obviously, also in this case there are type I particles that have an irregular shape. It is worth to notice that in these experiments, the number of irregular GSR particles is not so small as expected, so there is the possibility for the forensic laboratories that are in charge of analysing the GSR to search also for irregular particles, if the sphere like ones results low in number, mainly for two reasons: firstly, the irregular particles remain attached to the substrate or to the skin of the suspect longer than the sphere like ones due to their shape, considering the same size; secondly, as showed in these results, many irregular particles are formed, and are clearly the same ideal GSR particles which are deformed and/or ruptured by the interaction with the surrounding ambient, so discarding these particles only because they are not spherical could reduce a lot the chances of arriving to an unequivocal conclusion.

Obviously, these deformed particles need to be always amorphous and they need to derive from a sphere like shape; moreover, if irregular GSR particles are used in a report for arriving to a conclusion, the chemical analysis should be perfectly concordant with the composition of the searched GSR. Some examples of irregular type I GSR particles are showed in Figure 116; the particles are collected from the cotton, the wool and the polyester, so all the three different type of substrate utilized in the experiments.

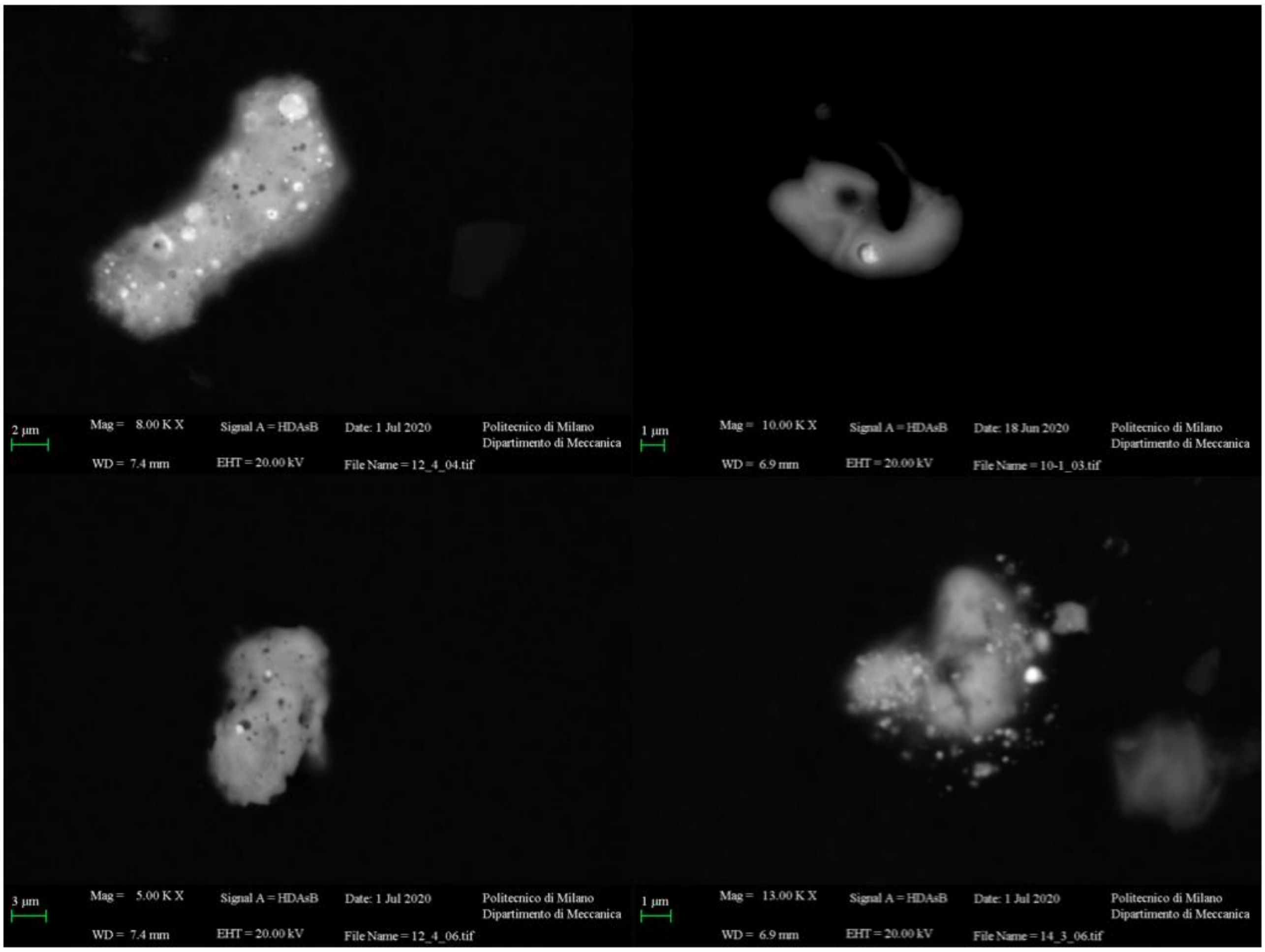


Figure 116: Irregular type I GSR particles.

Another strange morphology that should be reported results from a phenomenon that had never happened before. During the morphological and the chemical analysis of a darker particle made of Ba, on the particle, that appears homogeneous at a first analysis, a crack appeared, which widened more the electron beam remained on it. This phenomenon happens also on a type I particle. The two examples are reported in Figure 117; the particles are collected from the wool and from the polyester.

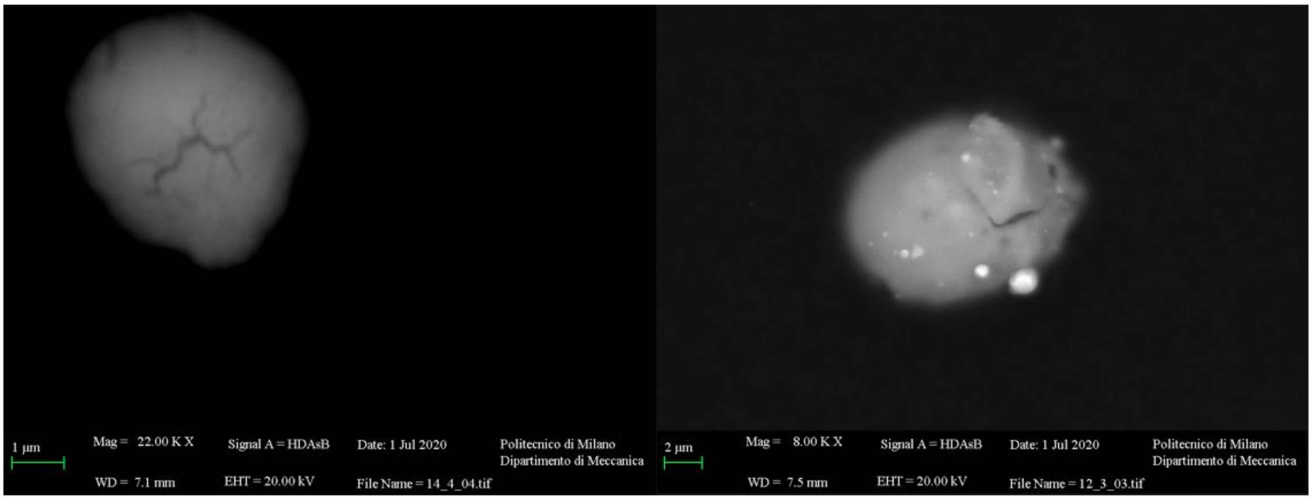


Figure 117: Superficial cracks induced by the interaction with the electron beam of the SEM.

These examples serve to point out that, also if it is a rare circumstance, it is possible that some GSR particles could be modified during the SEM analysis, since it works with a beam of electrons. This happens because the barium particles, and in general all the metallic residues produced by the discharge of a firearm, are oxidized on the superficial layers, so they become more fragile; when hit by the electron beam, the superficial oxidized layer breaks for the induced tensions derived from the heat generated by the interaction with the electrons. Traces of this phenomenon in literature are not reported, but the forensic scientists need to pay attention to it, trying to not modify the particles during the analysis, since it is possible that the superficial layer breaks changing the morphology of them, for examples staying the least possible on the analysed particle. Obviously, this is an extremely rare phenomenon, that out of the several particles analysed in this thesis happens twice, but since it is not impossible, at least the forensic scientists should be aware of this eventuality.

Last but not least, there are some particles which are really helpful to confirm the hypothesis that the GSR particles are formed by a condensation phenomenon and by coalescence of smaller particles into bigger ones. The vapours created after the firearm discharge condense back to a solid state starting from some nanometric GSR particles, which then coalesce together to form the usual micrometric ones. In the examples showed in Figure 118, are clearly visible the nanometric particles which form the bigger one; moreover, this confirms also how the darker particles, which are mostly made by Ba, form exactly following the same phenomenon which has been already explained in 5.2.2 referring to the Pb and Sb particles. Although in general the Ba particles are more homogeneous with respect to the Pb and Sb ones, these examples clearly show that all the GSR are formed following the same phenomenon, the condensation from a supersaturated vapour phase.

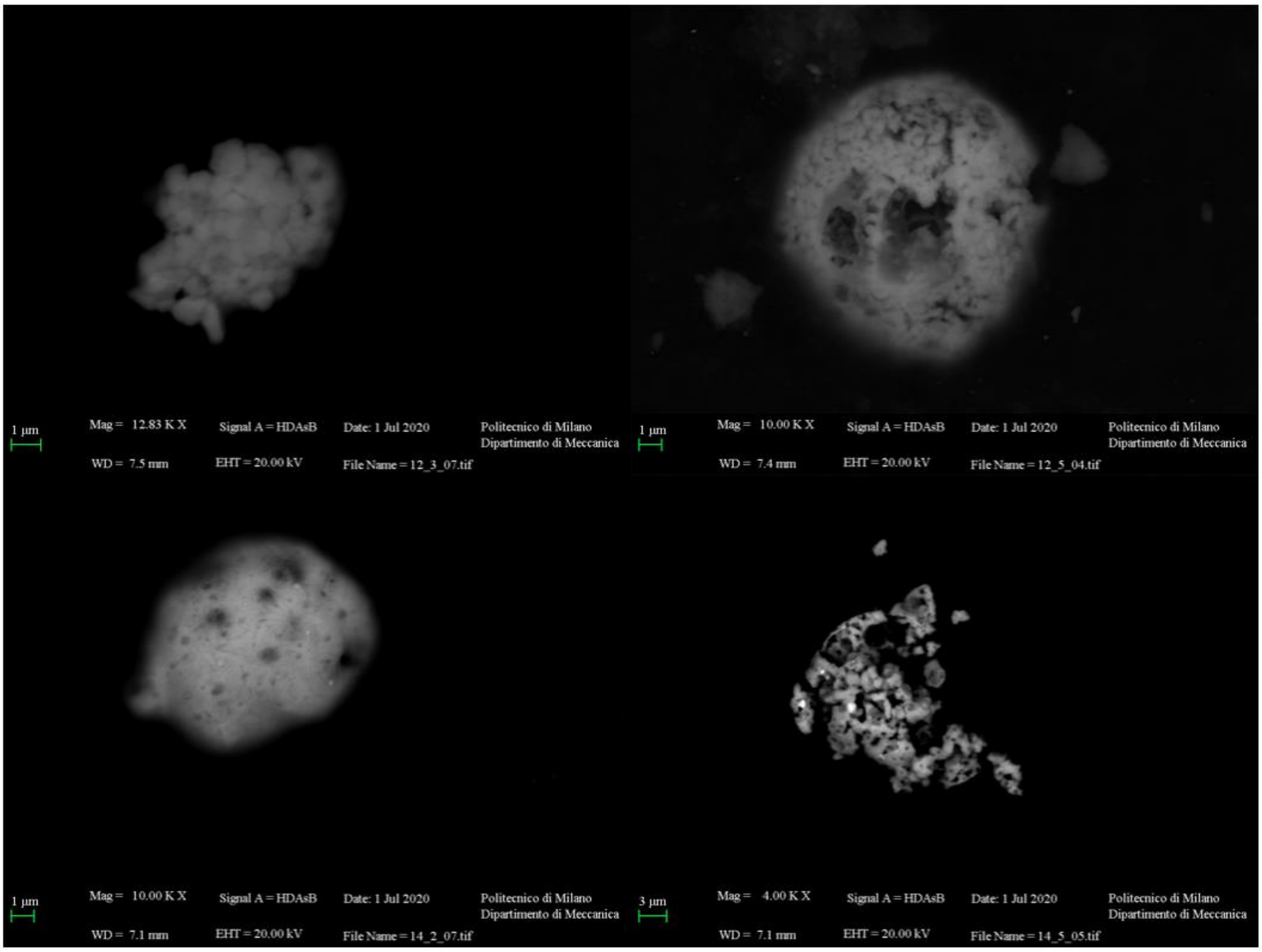


Figure 118: Examples of Ba particles in which are clearly visible the nanometric GSR which form the bigger ones.

5.2.4 GSR Expelled from the M4 Benelli Using the Royal buck Ammunition

With respect to the Fiocchi ammunition, the one used in this set of experiments utilize buckshot instead of pellets. The results analysed on the stubs are really similar between the two cases but the scenario that lies ahead looking at the images at 300x magnification present a smaller number of particles, and in general they are also smaller. A comparison between the same two zones of two different stubs, one utilized with the ammunition containing pellets and one with the ammunition containing buckshot, is showed in Figure 119; notice that both the residues are collected from the polyester.

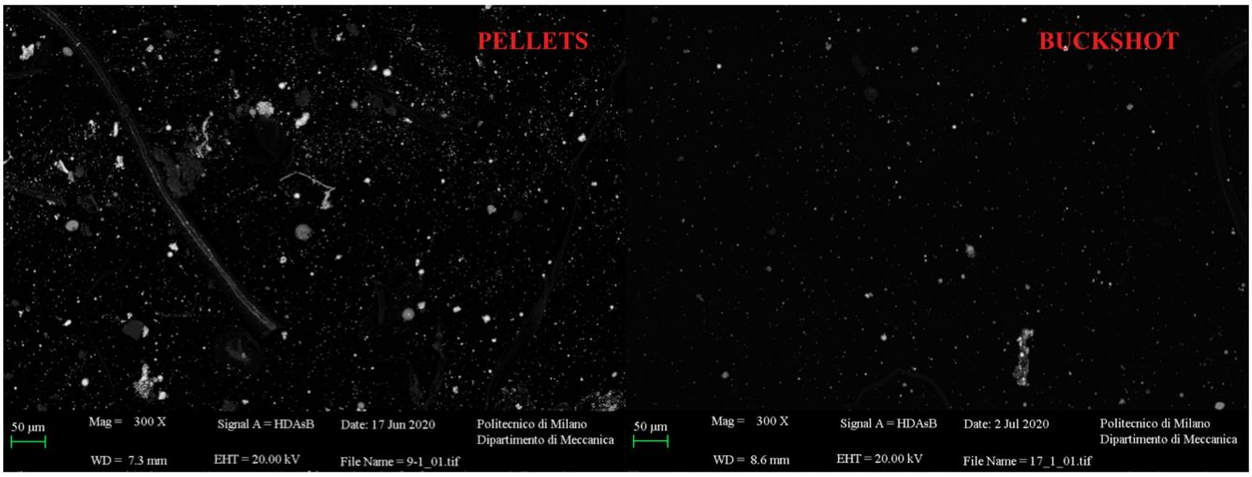


Figure 119: A comparison between same experimental conditions, varying only the type of ammunition used.

This great difference is probably due to two main reasons which are exactly the ones that make also the Desert Eagle results so poor regarding the number of particles collected on the stubs: first of all, with respect to the pellets, the buckshot have an higher power which can move the substrate which on the contrary stays fixed on the frame when performing the shotgun shots using the Fiocchi ammunition. Sometimes the substrate is needed to be recovered some meters away from the position on which it is fixed, this is why many bigger GSR particles flow away during the movement; secondly, it is also possible that in the primer mixture there is a smaller amount of Pb and Sb compared to the Fiocchi ammunition which utilizes pellets, so less small bright particles containing Pb-Sb are produced in this case.

However, neglecting the different number of particles and their different dimensions between the two cases showed in Figure 119 there are again two different type of particles. Regarding the bright ones, they are mostly spherical and usually of small dimension; some examples are showed in Figure 120; the particles are collected from the cotton and from the polyester. What is needed to be pointed out is that some particles are clearly derived from a condensation and solidification process like the one in Figure 120 in the down left image; this to highlight once again that in general, the morphology need forcibly to be amorphous, meaning without sharp edges and no sort of crystallinity, but also irregular particles that are derived from a solidification process or that are clearly deriving from a sphere like shape could be considered GSR. This is why leaving out from the automated analysis which is present on some SEM workstations the irregular particles, searching only for the spheres, could speed up the analysis but it is possible to lose some potential GSR only because of their shape.

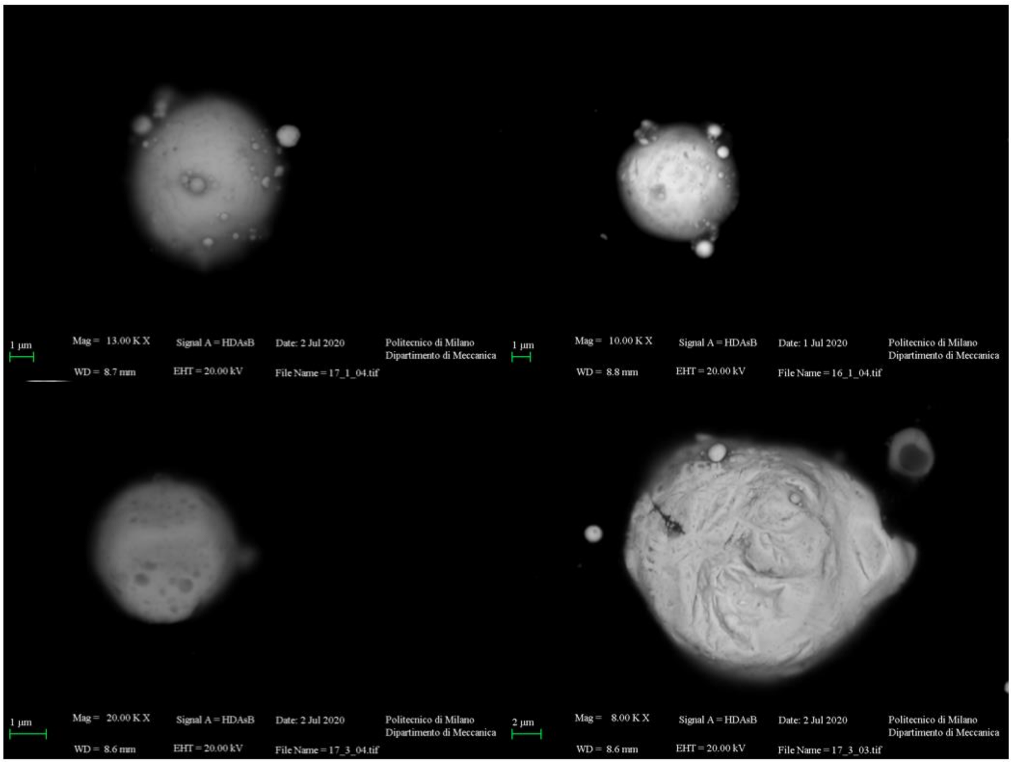


Figure 120: Examples of small bright particles which have a sphere like shape.

Moreover, although it happens only in this case, also this type of particles shows some holes and could resemble a sponge, while in all the other cases, these holes are present only on the darker cores. Additional examples of small bright particles with a sphere like shape that have a sponge like morphology are showed in Figure 121; all the particles are collected from the wool.

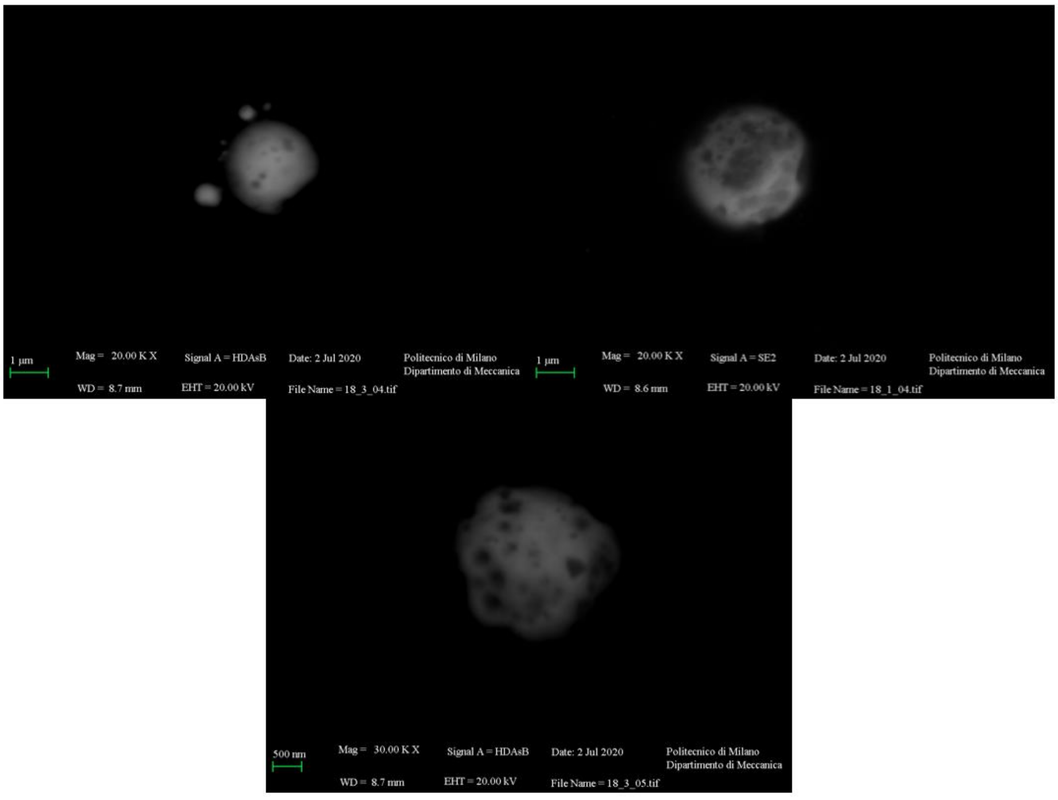


Figure 121: Examples of bright particles with a sponge like morphology.

Notice that these holes could be both due to the air which is entrapped in the particle during the solidification which then goes out when it became solid and also to the penetration of already solidified nanometric particles that pierce the bigger core and create such small round holes. Obviously, also irregular shaped particles are present; some examples are showed in Figure 122; the particles are collected from the cotton, the wool and the polyester.

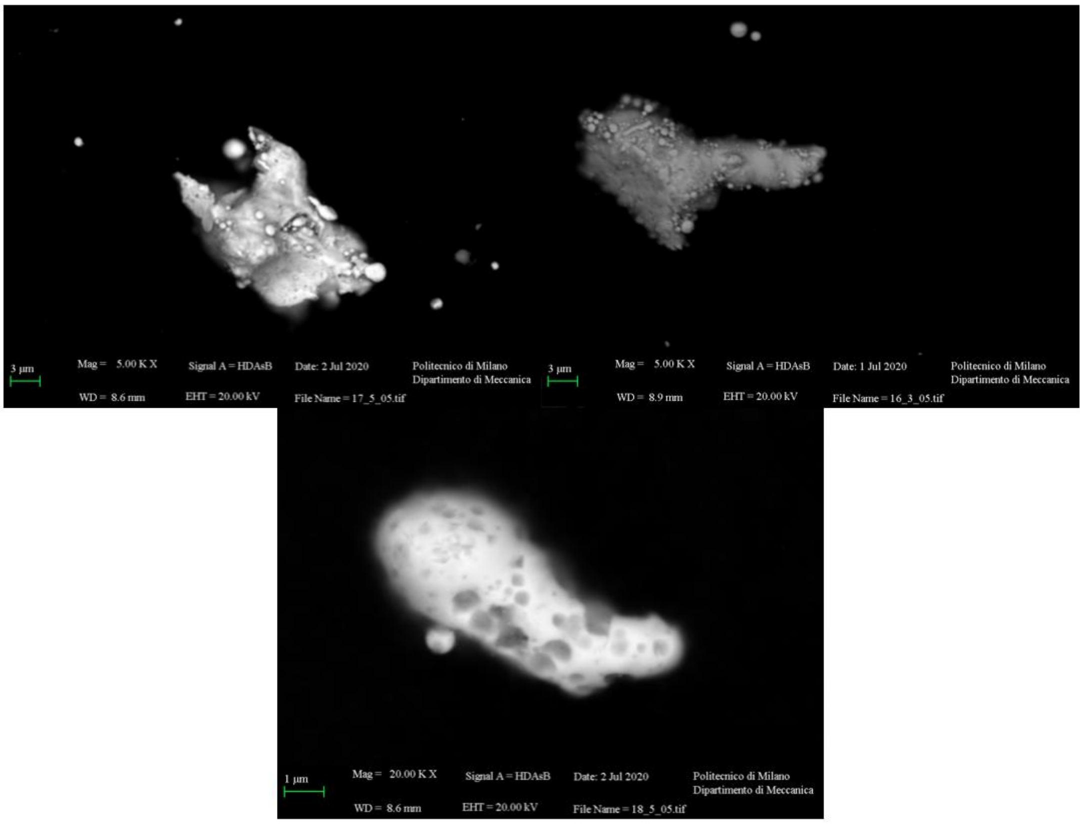


Figure 122: Examples of irregular bright particles.

Notice that on most of the irregular particles are present small nanometric particles, confirming the tendency of the particles to agglomerate due to the electrostatic forces present between them. Other examples of agglomerated particles are showed in Figure 123; notice that these agglomerates could represent the precursor of bigger particles, which didn't have the time to completely solidify and coalesce in a bigger homogeneous particle.

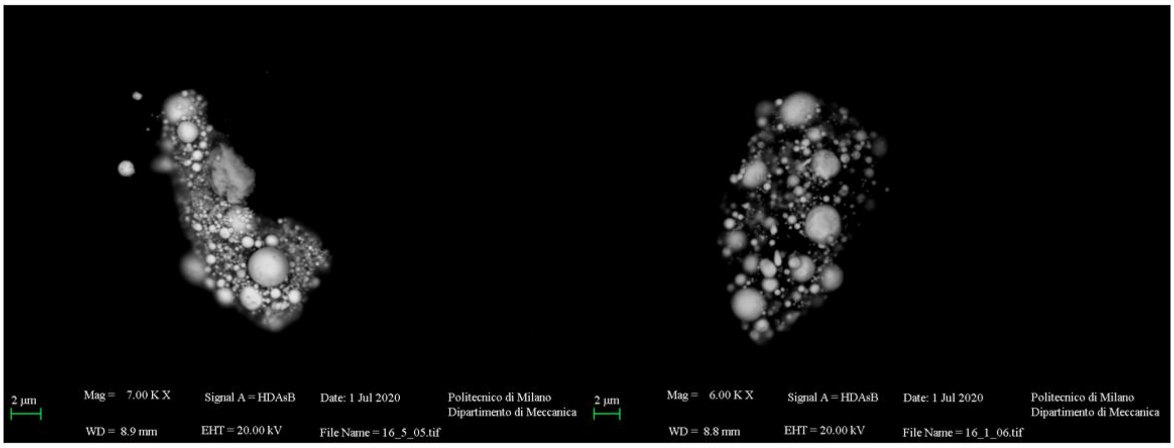


Figure 123: Agglomerates of small bright particles collected from the cotton.

Moreover, also in this case are present some particles that clearly show the previously discussed grain structure like the one in Figure 124; which particle is collected from the cotton.

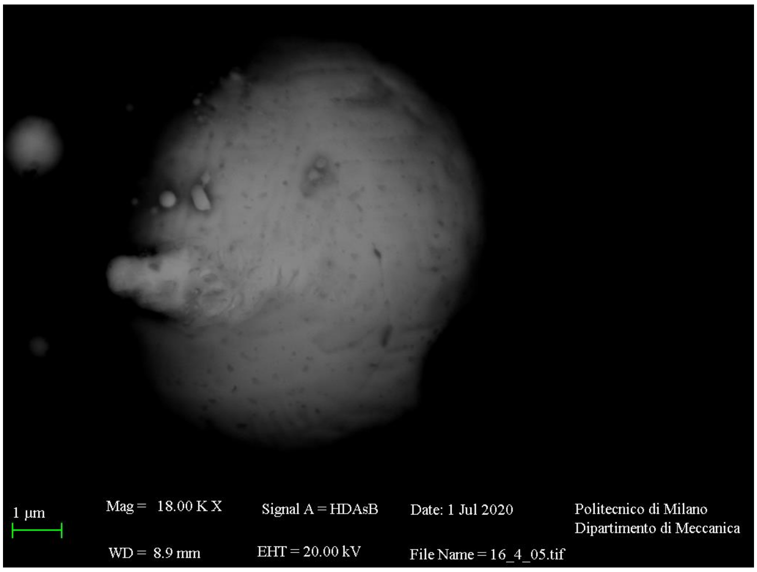


Figure 124: Small bright particle on which is clearly visible the grain structure.

Regarding the darker particles present on the images at 300x magnification, they turned out to be mostly type I particles with a large variability in shapes and in number and dimension of the superficial nodules. As already said, in this case, these type I particles are the majority of the particles found, while in the shotgun experiments using the Fiocchi ammunition, the majority of particles are bright and contain Pb and Sb. Some examples of type I particles found in these set of experiments are showed in Figure 125; the particles are collected from the cotton and the polyester.

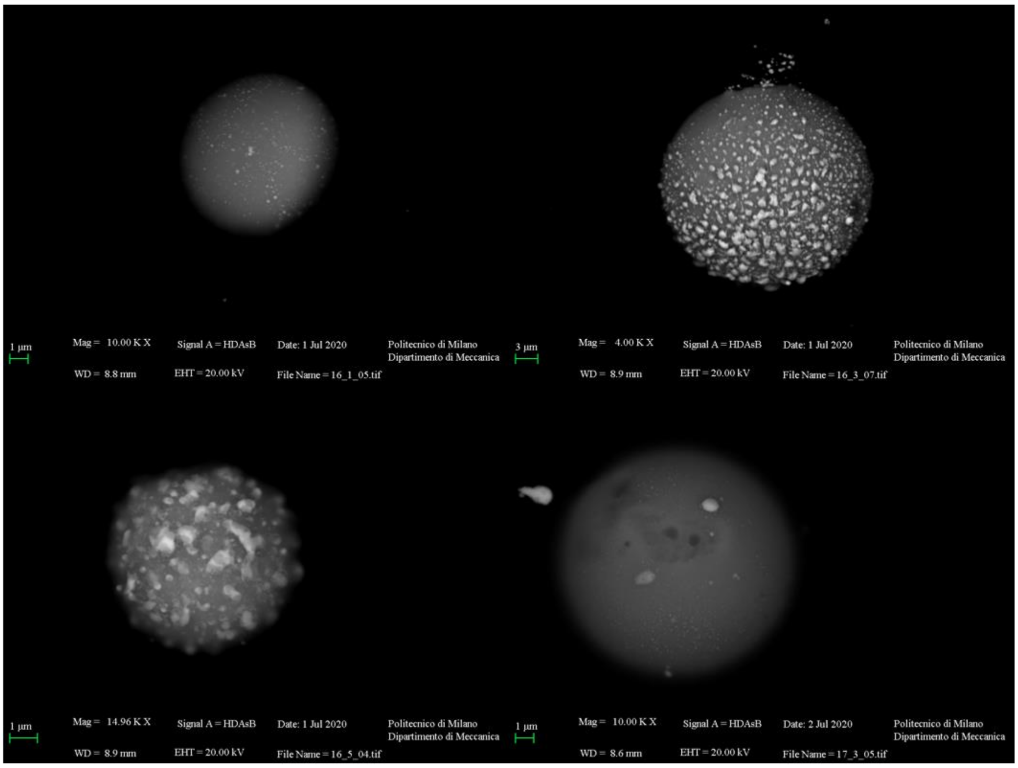


Figure 125: Examples of Type I particles with different number and dimensions of superficial nodules and particles.

Obviously, according to their formation, their interaction with the surrounding environment and the possibility that some air is entrapped in them, they can change their spherical shape assuming an irregular morphology, showing spherical holes and also ruptures on the external oxidized layers. Some examples are showed in Figure 126; the particles are collected from all the different type of substrates utilized in the experiments.

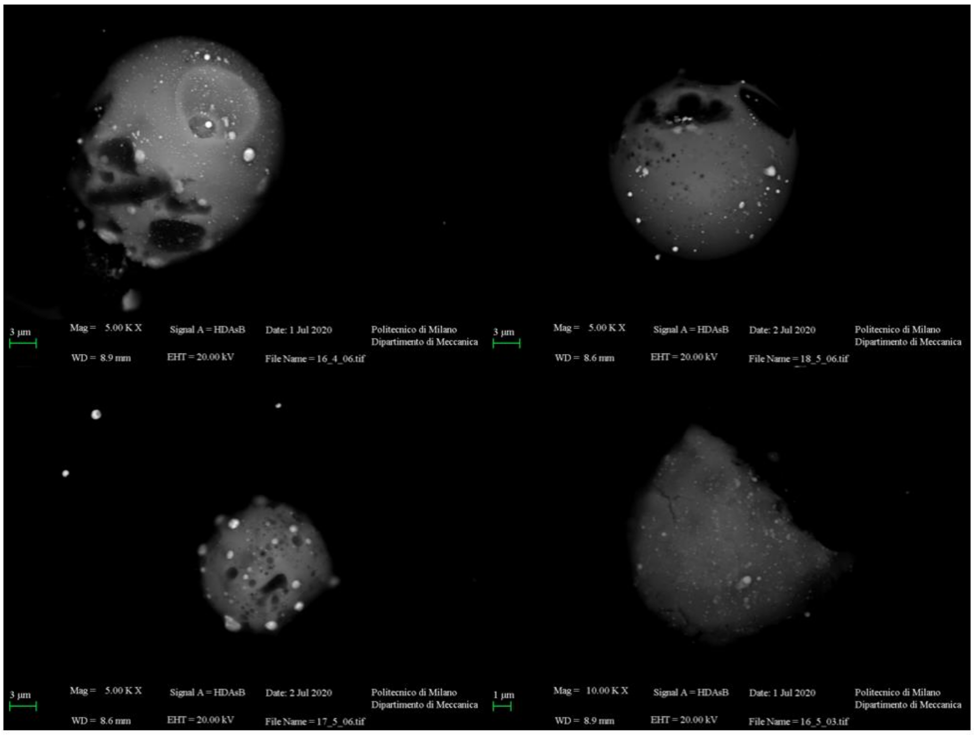


Figure 126: Type I particles that are not spherical but are irregular, holed and cracked.

Other particles are literally sheared and broken, as showed in the examples in Figure 127; the particles are collected from the cotton and the polyester.

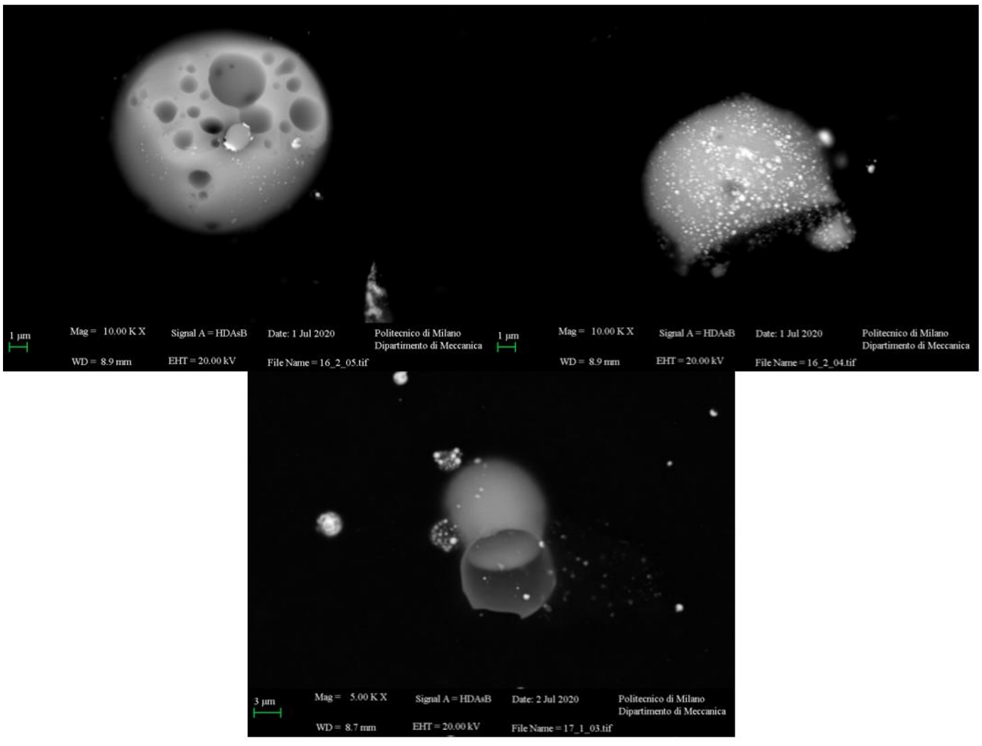


Figure 127: Sheared and broken type I particles.

These particles are very useful because they give the opportunity to analyse also their internal structure, practice that wouldn't be possible if the particles had been intact. In fact, to search and analyse for the internal structure of such small particles, the best technology is without any doubt the focused ion beam milling technology; however, when the particles are sheared or broken, also with the SEM is possible to analyse it. What reveals the internal structure is something similar to the conclusions reached by Niewöhner et al. [22], revealing that some particles present internal cavities and some others on the contrary are solid.

Moreover, also in these results, it is possible to find particles that are clearly derived from the division of a bigger one, confirming once again the hypotheses of Kara et al. [23]. In Figure 128 are showed some examples of this eventuality; the particles are collected from polyester and the wool. In the top left image it is even possible to see the bridge that was the last connection between the particle in the image and the particle from which it separates.

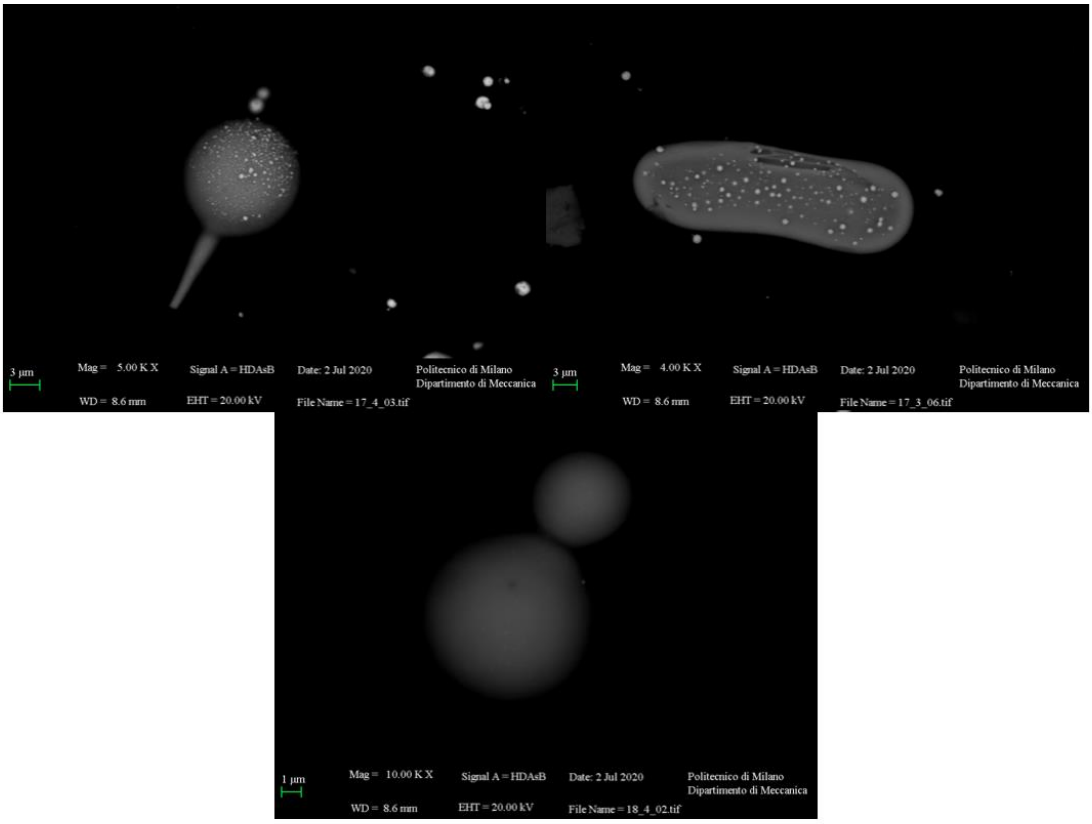


Figure 128: Examples of particles that are clearly derived from the division of a bigger one.

Last but not least, there is a particular type I particle in which are visible on the darker core the small nanoparticles that form it, confirming that all the particles are formed via the same phenomenon, the condensation of small nanometric particles and then the coalescence of them forming the bigger ones. Although seeing the grain structure and the small nanoparticles on these darker cores made of Ba is quite difficult with respect to the bright particles made of Pb and Sb, the example showed in Figure 129 and also in Figure 108 confirm that this mechanism of formation is common to all the type of particles formed, simply it is more visible on some of them with respect to others, bearing in mind that on most of them is not visible at all, since most of the particles seem completely homogeneous.

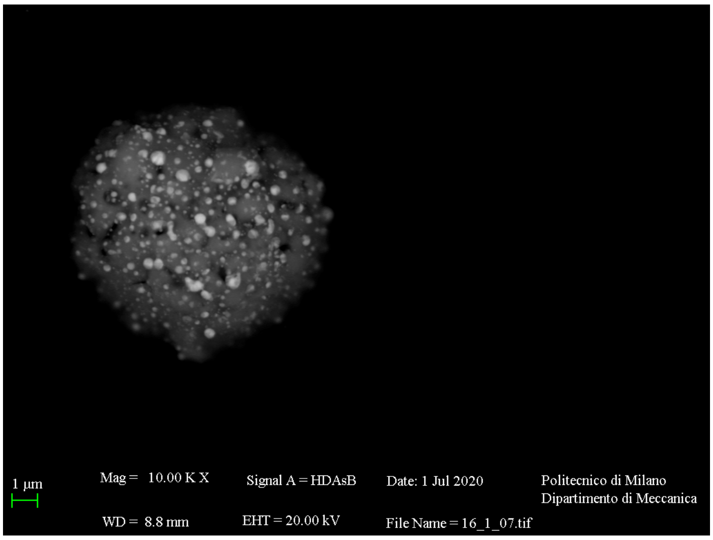


Figure 129: Type I particle in which are visible on the darker core the small nanometric particles that compose it.

5.2.5 Particles which are not GSR

In this chapter are collected some examples of residues which should not be confused with GSR. This is very useful since when these morphologies are found, it is even possible not to chemically analyse them since they will surely not be GSR. In general, GSR should be spherical, or irregular but clearly deriving from a sphere or a condensation phenomenon, without no sort of crystallinity.

For example, the residues showed in Figure 130 have nothing to do with GSR. They are not amorphous and present a crystalline shape, meaning that the borders are sharp. It is also clear how it is not possible that these particles come from a deformed sphere like particle, which is on the contrary quite intuitable from the irregular particles presented in the previous paragraphs. In particular, the residues showed in **Error! Reference source not found.** are made of iron and iron oxides.

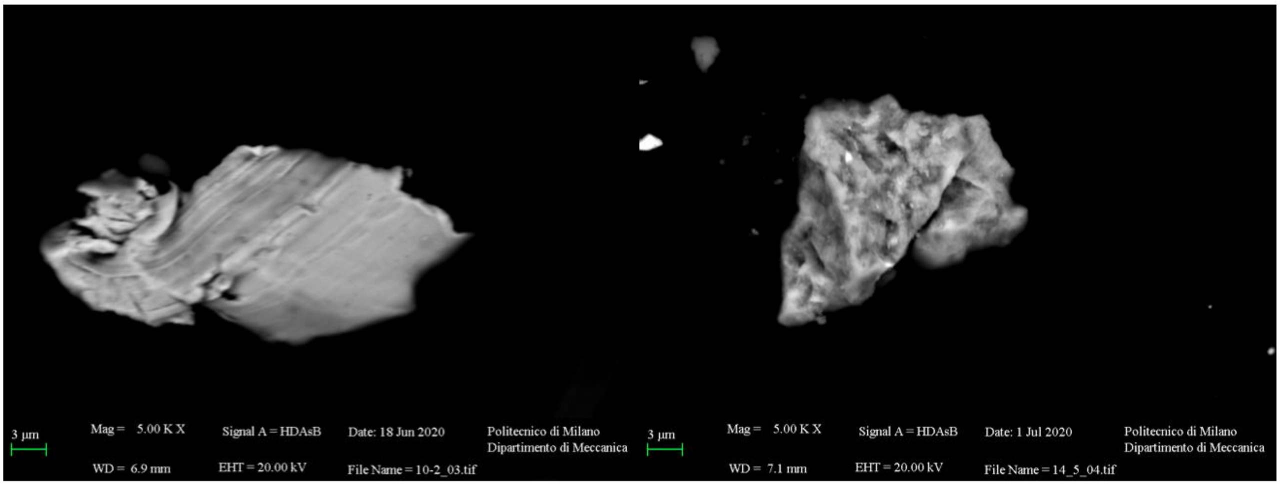


Figure 130: Two iron and iron oxides residues which have nothing to do with the GSR.

Another very useful example to show to the lecturers in not confounding a GSR with a different source simply by looking at the morphology, is showed in Figure 131, in the left image.

This is a Pb residue which could be classified as single element GSR particle if only the chemical analysis had been performed, but by looking at the morphology, it is clearly a residue which present some crystallinity and many sharp edges, so it's not a GSR. Moreover, to be clearer, in the same figure is also showed a Pb particle, which however is considered a GSR. The two particles have the same chemical composition, since they are two Pb particles, but the one on the left is not amorphous and present also a crystalline surface while the one on the right is spherical and clearly deriving from a condensation process. As seen, the crystallinity cannot be confounded with the previously encountered "grain" structure, since the first one has clearly a pattern which is dominated by sharp edges while the latter is formed by smaller nanometric particles which coalesce together to form the overall micrometric GSR particles.

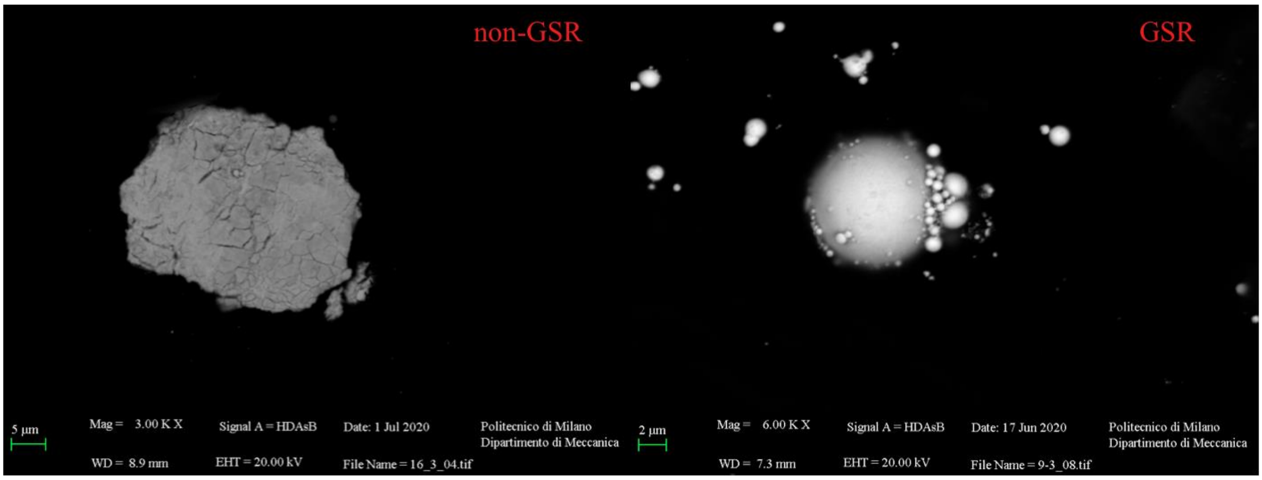


Figure 131: Comparison between two Pb particles; the one on the left is not a GSR while the one on the right is a GSR.

Another example is given by two residues of pure aluminum that are found on the stubs utilized to collect the residues generated from the discharge of the desert eagle. As will be discussed later on, aluminum is present in the Hornady and in the royal buck ammunitions, but in the examples showed in Figure 132, it is clear that they are not GSR, due to their morphology, since they show sharp edges and they seem to be a chip of material which has a different source with respect to the discharge of a firearm and with respect to the spheroidal shapes or the deformed spheres typical of the GSR.

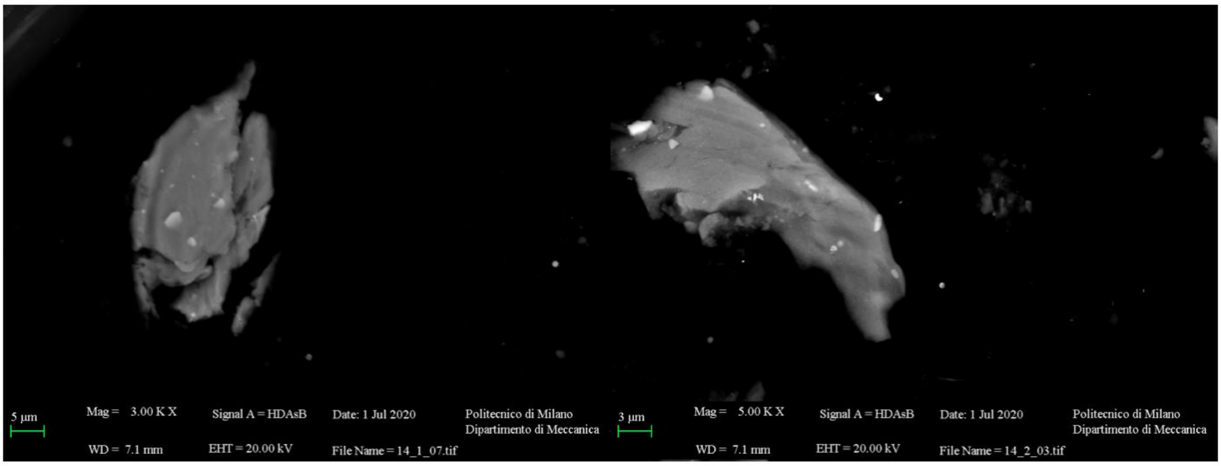


Figure 132: Two aluminum particles that are not GSR.

5.3 Chemical composition of the GSR

In this chapter, the particles expelled from the firearms and ammunitions utilized in the experiments are analysed according to their chemical composition, and their main differences and peculiarities are pointed out.

5.3.1 GSR Expelled from the Glock

Regarding the GSR collected from the stubs utilized to collect the residues expelled from the Glock, what is important to remember is that the lead bullet is completely jacketed, so a very small amount of lead will be found in the residues. In fact, since lead is present only in the priming mixture, this element is mostly present in the type I particles, which are the ones formed directly inside the primer cup during the primer ignition, and the other types of particles present on the contrary a very small amount of lead. The map of the elements extracted from a clear type I particle shows that the core is mostly made of Ba and Sb, while the superficial nodules contain mostly Pb, as showed in Figure 133, in which it is possible to see how in the Ba and Sb maps there are holes exactly on the bright superficial spots in which on the contrary Pb is present. According to Basu's classification, the core contains Ba and the nodules prevalently Pb and Sb while here on the contrary the core contains a homogeneous mixture of Ba and Sb and the nodules only Pb. However, as will be seen in the next paragraphs, this is the only case in which type I particles chemical composition deviates from the Basu's classification.

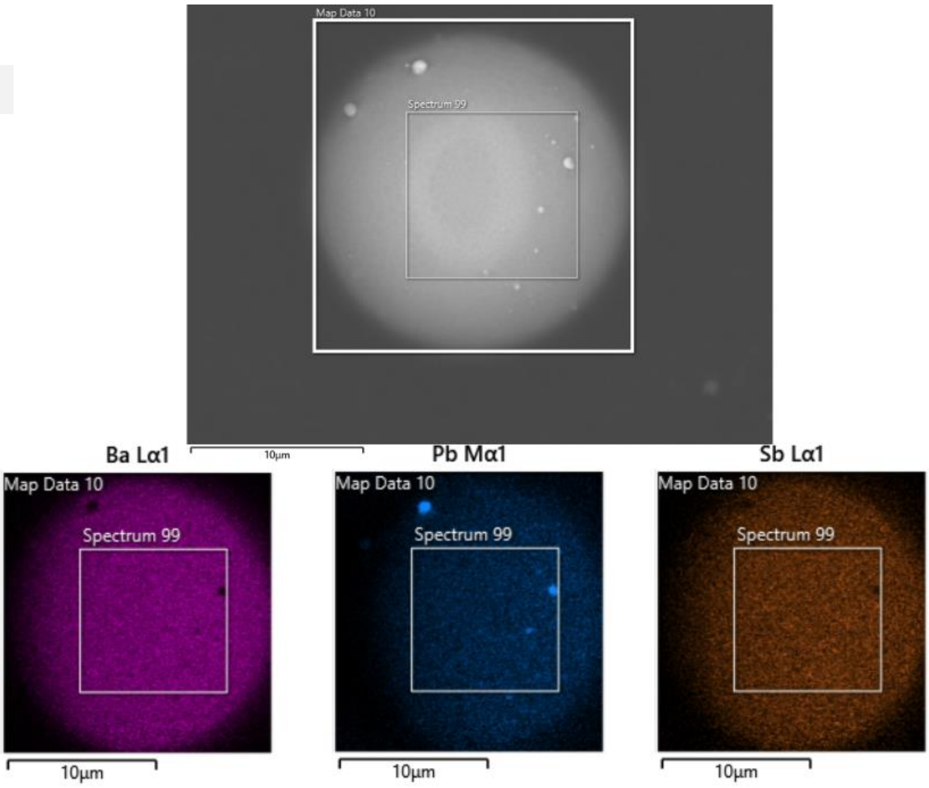


Figure 133: Map of elements extracted from a type I particle collected from the polyester.

As already said, lead is mostly present in the type I particles, while the only Type II particle that is present is mostly made of Sb and Ba. It presents an irregular shape and is completely in accordance with the type II particles as theorized by Basu, since it contains a concurrent and homogeneous mixture of the primer elements, as showed in Figure 134, with less lead present than Ba and Sb.

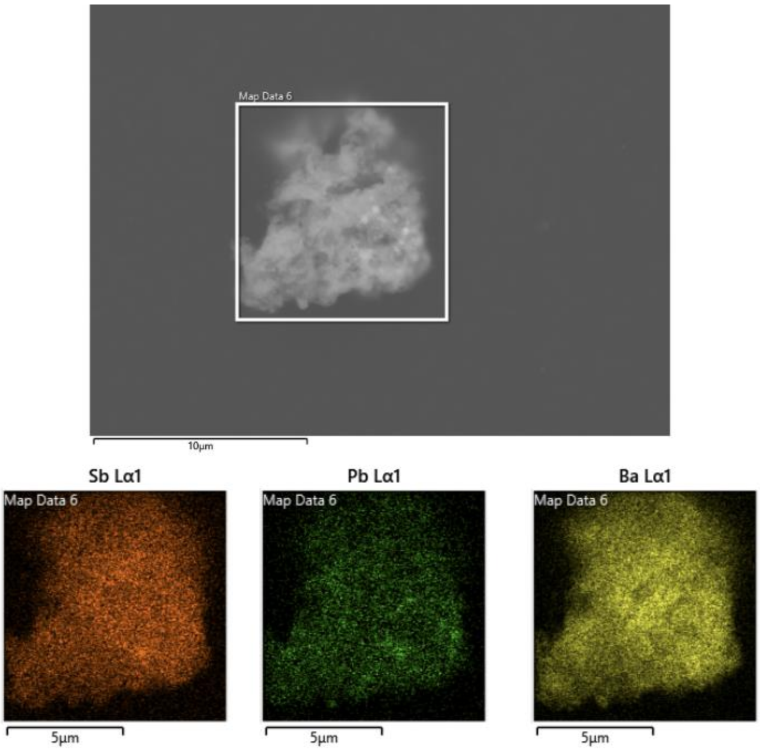


Figure 134: Map of elements extracted from a type II particle collected from the polyester.

What is important to notice is that some type I particles present some protuberances on them. Thanks to these protuberances they become irregular, and so they could be classified as type I particles on which barium oxide protuberances have grown. This hypothesis is supported also form the morphology, since some of these particles nearby the protuberances have some superficial nodules which are the ones of the type I particles. An example of a map of elements of this kind of particles is showed in Figure 135. In this image, also the oxygen map is reported, since it helps to shows how the protuberances are barium oxides.

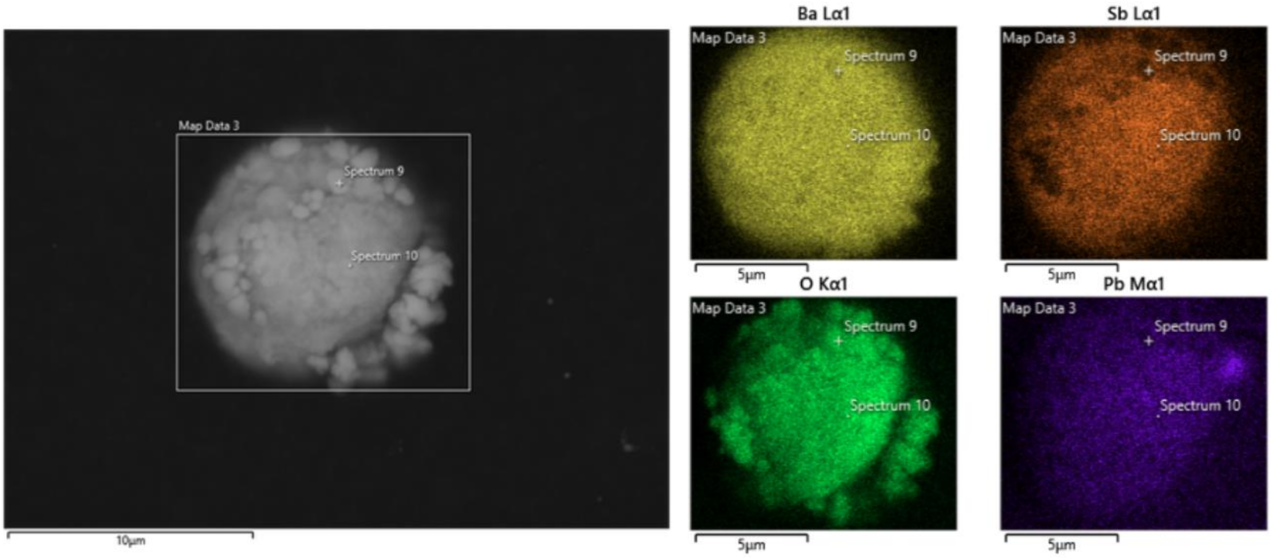


Figure 135: Map of elements extracted from a particle on which there are some protuberances which is collected from the cotton.

This throws new light on the GSR classification system, introducing another type of particle which it is possible that evolves directly from the type I ones.

Last but not least, on one of the stubs on which the GSR expelled from the Glock are sampled, in particular the one used on the polyester, also an elliptical particle containing bismuth is found, which is probably an environmental contaminant, since it may come from the numerous sponges used to soundproof the shooting range, in which some bismuth compounds are used, or it could be a GSR, since Bi could be used in some bullets, although is it is a quite rare practice.

5.3.2 GSR Expelled from the M4 Benelli with the Fiocchi Ammunition

Most of the particles expelled from the shotgun used with the Fiocchi ammunition are bright and contain mostly lead and a small quantity of antimony, with the two elements mixed together homogeneously. An example is showed in Figure 136; Ba is not even detected, and the other particles showed in the image are equal to the one analysed by the microanalysis.

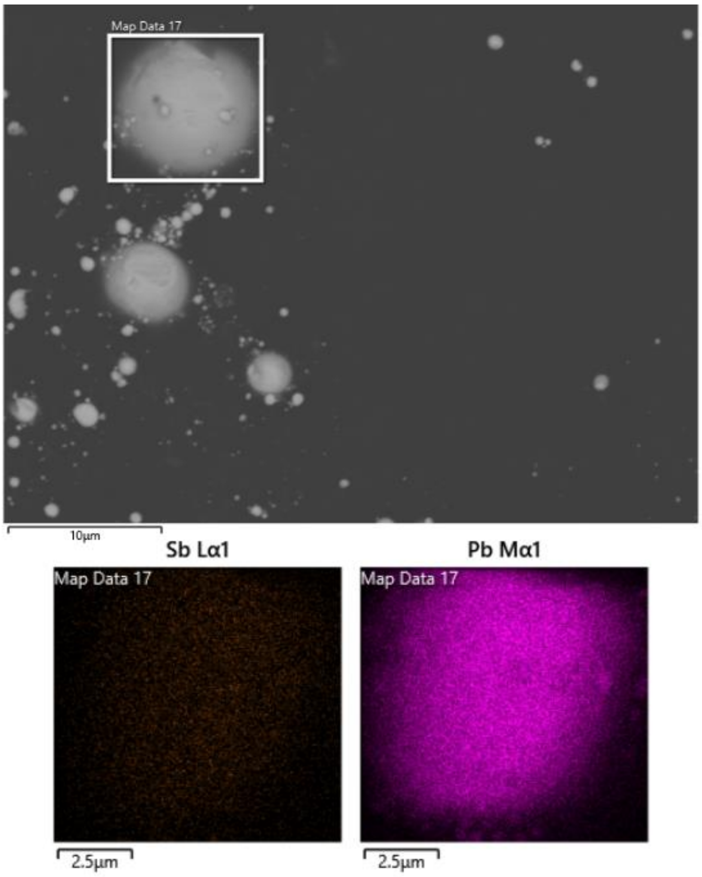


Figure 136: Map of elements of one of the numerous bright Pb and Sb particles.

The fact that most of the particles contain a large quantity of lead is probably due to the fact that the shotgun cartridges utilizes a greater quantity of primer mixture with respect to the handgun cartridges and that it is probably rich in Pb and Sb, which respectively are the initiator and the fuel. It is important to notice that the ammunition manufacturers, in this specific case Fiocchi, do not disclose the information regarding the primer compositions produced. It is only by means of a chemical analysis of the GSR or by firing directly the primer composition picked up by an unspent cartridge and then analysing the oddments that it is possible to understand what is the chemical composition of the primer mixture.

What it is possible to point out from this experiment is that the Fiocchi shotgun ammunitions contain a greater quantity of primer mixture than that in the Fiocchi ammunition used in the Glock, and that it contains a great quantity of Pb and Sb, since there is an enormous amount of lead and antimony particles. Barium is less present with respect to Pb and Sb. Although it is quite intuitive, one can think that the great quantity of lead may come from the unjacketed pellets utilized as bullets in this type of cartridge, but this is not possible, since the pellets are enclosed by a shot cup during the firing of the shotgun, which prevent them from ruining the muzzle of the shotgun. The shot cup falls away exactly when it exits the muzzle, so it protects the unjacketed pellets from the erosion performed by the hot primer and propellant gases, so the excess of lead in the GSR should only come from the primer mixture.

Then, on the images at 300x magnification, there are some particles that are clearly darker than the majority. In order to understand how these particles appear at the backscattered electron image, in Figure 137 is showed an example helpful to better understand the meaning of "brighter" and "darker" particles; in particular, it is represented the bottom left side of the stub used to collect the GSR on the wool.

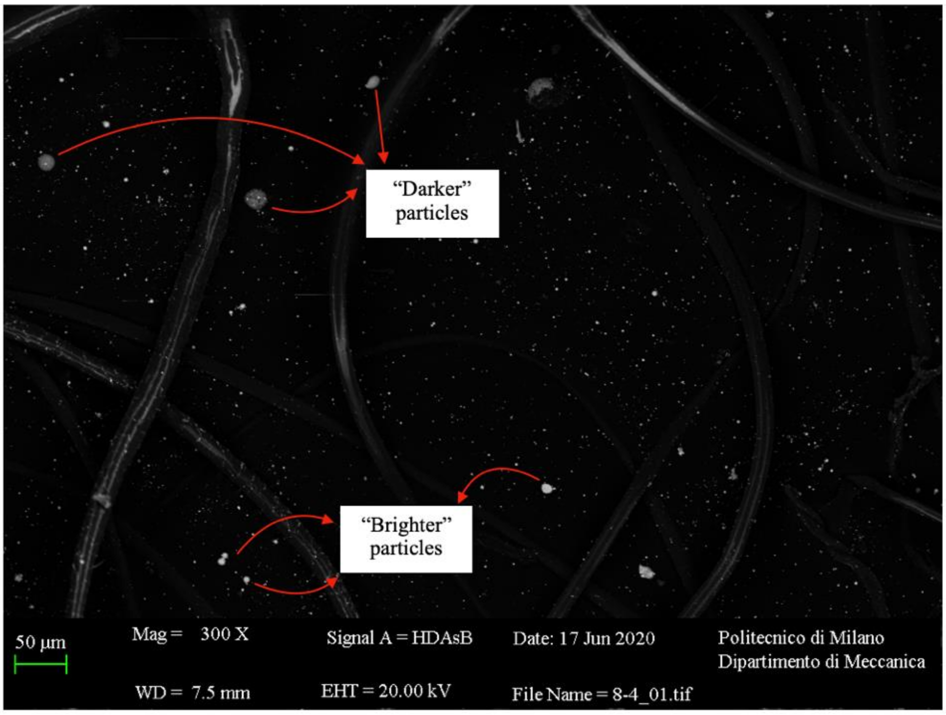


Figure 137: Comparison between darker and brighter particles.

Analysing the darker particles, they present always the same chemical composition. The darker core is made of barium, barium oxide and a small quantity of Al which is probably added to give more power to the shotgun shots while the brighter particles attached on it are the same as the ones analysed in Figure 136, so they predominantly contain Pb and a lower quantity of Sb. These chemical characteristics are well displayed in the map in Figure 138. It is important to notice that the barium core, being formed by pure Ba, is usually oxidized, as it happens easily to this metal when in contact with the ambient air and form crystalline compounds of BaO_2 and BaO.

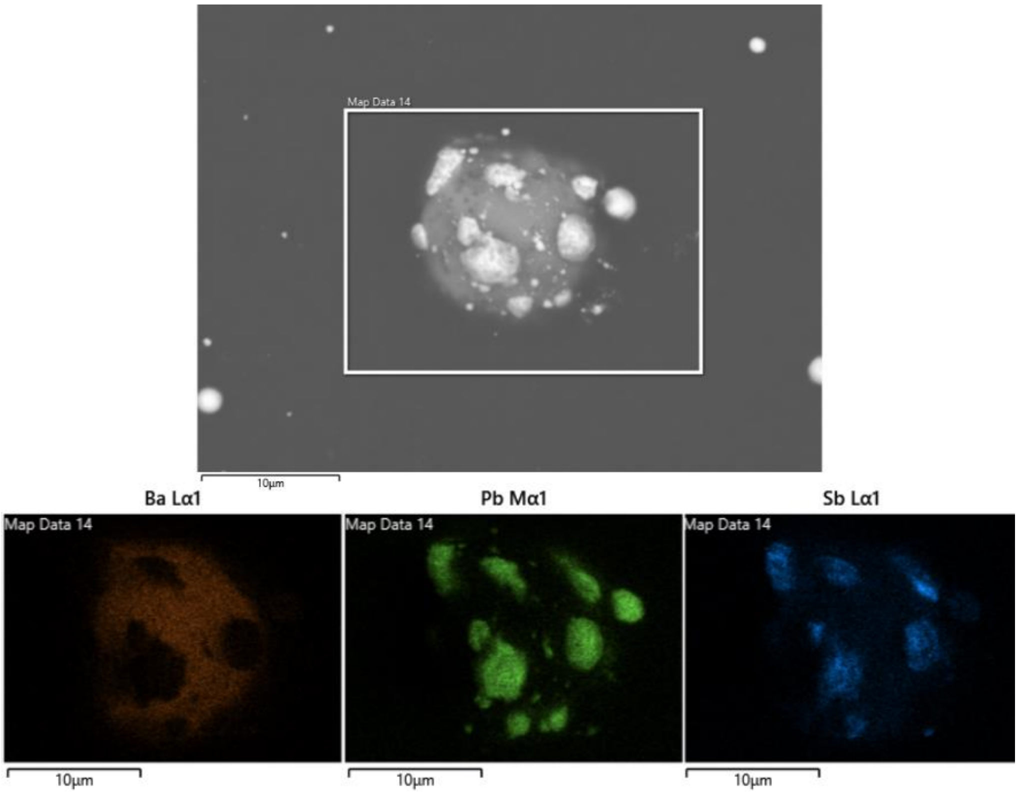


Figure 138: Map of elements of a darker particle, showing the barium core surrounded by the Pb and Sb particles.

What it is important to notice is that the majority of bright particles contain Pb mixed with Sb, but there are also some rare particles that are simply made by Sb alone, as showed in Figure 139, and they are very similar to the Pb and Sb particles.

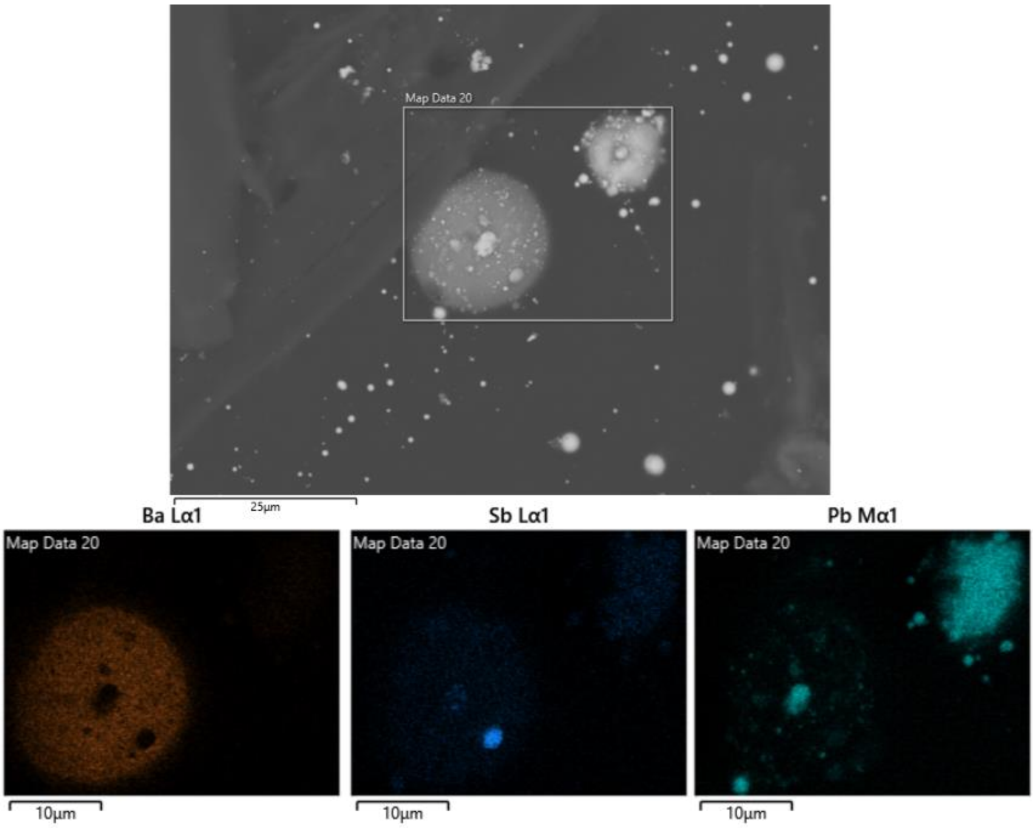


Figure 139: In this map of elements, there is clearly a pure Sb particle on bottom right part of the darker Ba core.

In this image on the dark core there are both a pure Pb particle and a pure Sb particle. However, watching carefully and analyzing the shades of grey, each composition has its own color which stands quite easily with respect to the other, as showed in Figure 140. As confirmed also by literature, for some unknown reason, single Sb particles are very rare, in fact only barely encountered between all the GSR collected, while in the majority of cases Sb is always mixed with Pb.

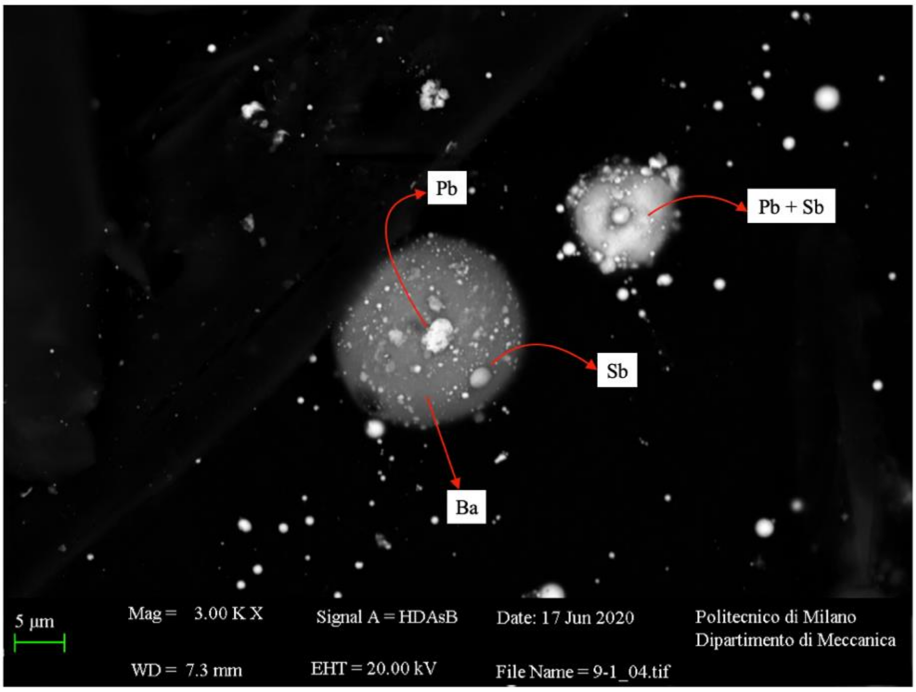


Figure 140: Clear example of a differentiation between different chemical compositions by means of the shades of grey derived from the backscattered electrons image.

This gives an additional clue about the GSR formation in the shotgun with respect to the small calibre handguns and confirms also the fact that the environment of GSR formation in the shotgun is largely less uniform than the one in the small calibre handguns. In the Glock, most of the particles appears as type I particles, but the heavy elements that compose the primer mixture, the classical triplet Pb, Sb and Ba, are mixed together forming a unique particle; this is probably due to the small and uniform environment in which they form, the firing chamber of a handgun, which remains sealed by the projectile till the pressure and temperature reach the proper values to start the motion of the projectile. In a shotgun, the wads and the shot cup containing the bullets start to move when the plastic that closes the upper part of the cartridge case is broken, so the pressures and temperatures reached are even higher than the ones in a handgun due to the higher amount of primer mixture and propellant, but the environment in the firing chamber results less uniform.

This result in the fact that in the shotgun, Pb, Sb and Ba are hardly mixed together. Ba is already solid and pure when it has been hit by the Pb and Sb particles; most of the times, they resemble type I particles, but when they have just been formed, since in theory the superficial Pb and Sb nodules which characterize this type of particle are not distinguishable from the main core. On the contrary in this case, they simply appear as different particles attached or even splashed on the barium core, as showed in Figure 141.

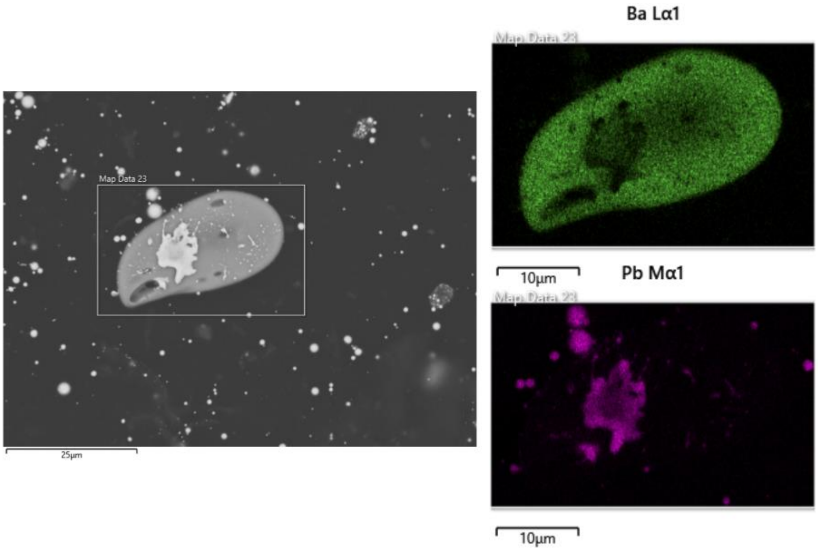


Figure 141: Map of elements of an elliptical barium core with a splashed Pb particle.

Moreover, no type II particle is found, which main peculiarity is to have a uniform and concurrent mixture of Pb, Sb and Ba. The less uniform environment in which the shotgun GSR form, seems to produce particles less mixed together in term of chemical composition; all these circumstances happen also in the other shotgun and Desert Eagle shots, which will be discussed in the next paragraphs.

5.3.3 GSR Expelled from the Desert Eagle

Following the wake of the morphology, utilizing the desert eagle two kind of particles are produced. Regarding the small round particles which appears as the brightest between all the particles present, they contain most of all Pb with a little amount of Sb mixed together. They are very similar to the Pb-Sb particles produced by the discharge of the Fiocchi ammunition with pellets utilized with the shotgun. However, in the shotgun this type of particles is largely the most common between all the particles produced while here on the contrary these particles are the least common with respect to the other type that will be seen in the next paragraphs. The Map of elements of a Pb-Sb particle is showed in Figure 142.

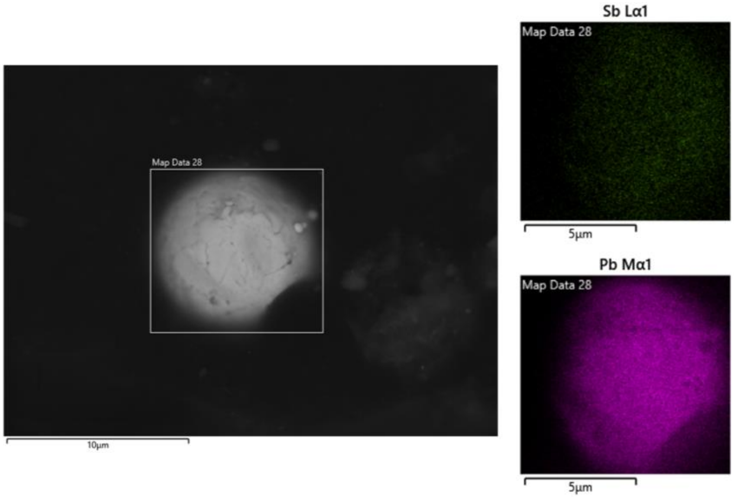


Figure 142: Map of elements of a small round Pb particle with a small amount of Sb.

The second type of particles that are easily found on the stubs are the type I particles, which have a darker core and small bright superficial nodules. An example is showed in Figure 143.

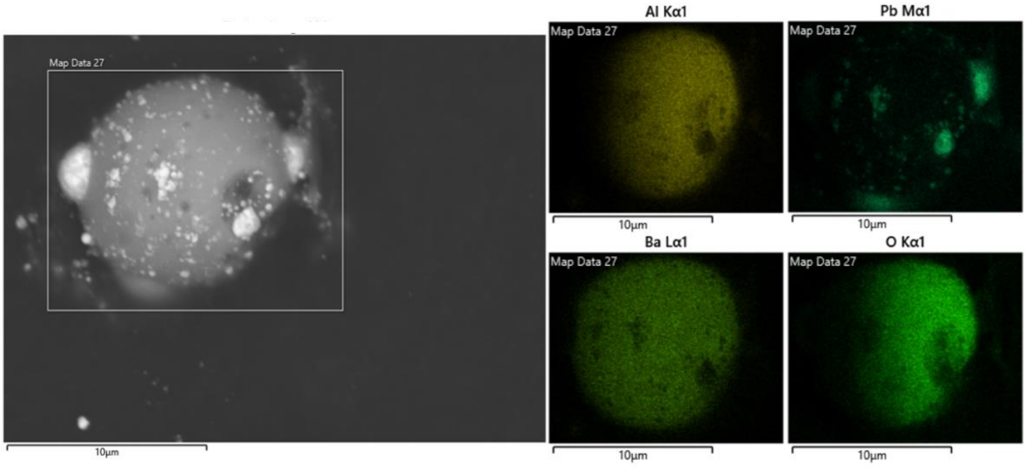


Figure 143: Map of elements of a type I particle with small superficial nodules and particles of Pb and Sb.

The darker core in this case is predominantly made by barium. The core of Ba is usually oxidized in the external layer, so also a considerable amount of oxygen is encountered. Obviously, since these particles form in an environment with high temperature, the oxidation is favoured, but only in the superficial layers. It is exactly this oxidized layer that could eventually be broken when hit by the electron beam as showed in Figure 117. What it is important to notice is that also a in this case, so using the Desert Eagle with the Hornady ammunitions, in the darker core also a great amount of aluminum is mixed with Ba, proving that the primer mixture used in this ammunition contain also Al and not only the classical triplet composed by Pb, Sb and Ba. With respect to the Fiocchi ammunitions for the shotgun, in this case the amount of aluminum is much greater, which is probably used to give more power to efficiently deflagrate the caliber 50 ammunitions which obviously have a bigger bullet with respect to a Glock for example. Regarding Pb and Sb, they are present in the superficial nodules and particles. The strange fact is that the left bright particle, the one encircled in red in Figure 144, is a pure Sb particle while the other particles and nodules contains the usual amount of Pb accompanied by a small quantity of Sb homogeneously mixed together. Single Sb particles are extremely rare, in fact they are barely encountered, and if found, for some unknown reason they usually are never encountered alone but always as superficial particles on the usual type I ones, as it happens here but also in Figure 140, with except to one single case, which will be shown in the next chapter. This is in accordance with the literature, since also B. J. Heard [25] states that pure Sb particles are barely encountered as GSR evidence.

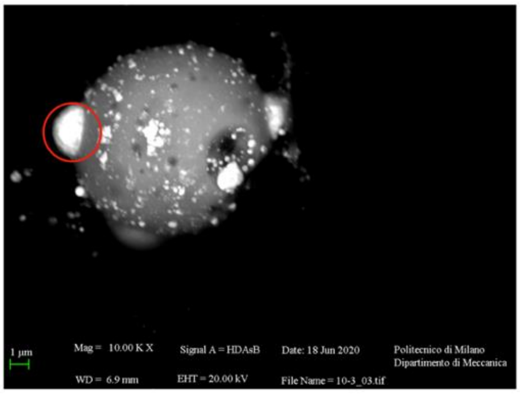


Figure 144: A pure Sb particle on a BaO and Al core.

The confirmation of the fact that the darker particles in this case are made of a barium core surrounded by a barium oxide layer, accompanied with the presence of Al is showed in Figure 145. Notice that being there a hole in the central part of the particle, it is also possible to discern the differences between the external layers and the central core. What it is possible to point out is that barium is obviously present in all the particle while barium oxide and also aluminum are present only in the external layers, since in the map in Figure 145 there is a particle with an hole, and where the hole is present, oxygen and aluminum are not present. However, the SEM technology is not the best one to analyse the internal morphology and chemical composition of the GSR particles; with the SEM is possible to extract some clues on the internal composition and morphology only when the analysed particle is holed, fragmented, or sheared.

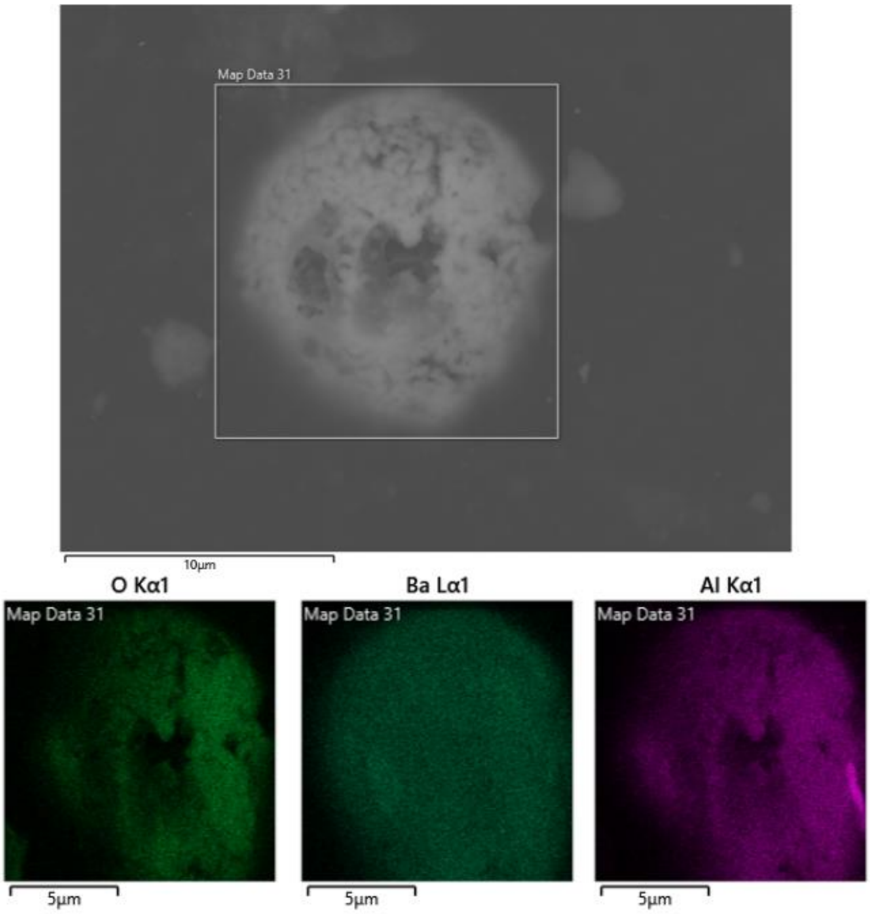


Figure 145: A single BaO and Al particle.

5.3.4 GSR Expelled from the M4 Benelli Using the Royal Buck Ammunition

Regarding the small bright particles, also in this case they mostly contain Pb and a small quantity of Sb, mixed together homogeneously. Since these particles are present also in the discharge products of the Fiocchi ammunitions utilized in the shotgun, in which they are largely more present, it is possible that in this case, a smaller quantity of Pb and Sb is present in the primer mixture.

Considering now the Type I particles largely present in these residues, they are formed by a core of barium, oxidized in the external layers and mixed with a considerable amount of aluminum. These particles are very similar to the one produced by the Desert Eagle; probably the presence of Al in these two ammunitions, the Hornady and the Royal Buck, is needed as already said to give more power respectively to the calibre 50 bullet and to the buckshot which are contained in the two types of ammunitions; on the contrary the pellets present in the Fiocchi ammunition and the calibre 9x21 bullet utilized in the Glock need less power to be effectively discharged, so a lower amount of Al is present in the primer mixture. it is always important to remember that Al is present in the primer mixture and not in the propellant for two main reasons: firstly, all the residues which could be analysed at the SEM are mainly coming from the primer mixture, as largely discussed in the state of the art; secondly, with larger calibre ammunitions which need to discharge larger bullets, the quantity of propellant and primer mixture need to be enhanced. To effectively deflagrate a larger quantity of propellant, also the primer mixture needs to be changed; what it is discovered here is that larger is the bullet to be discharged, larger is the quantity of Al present in the primer mixture, which quantity in general is increased. The map of elements of a type I particle in which is clearly showed the large quantity of Al present in the core is reported in Figure 146.

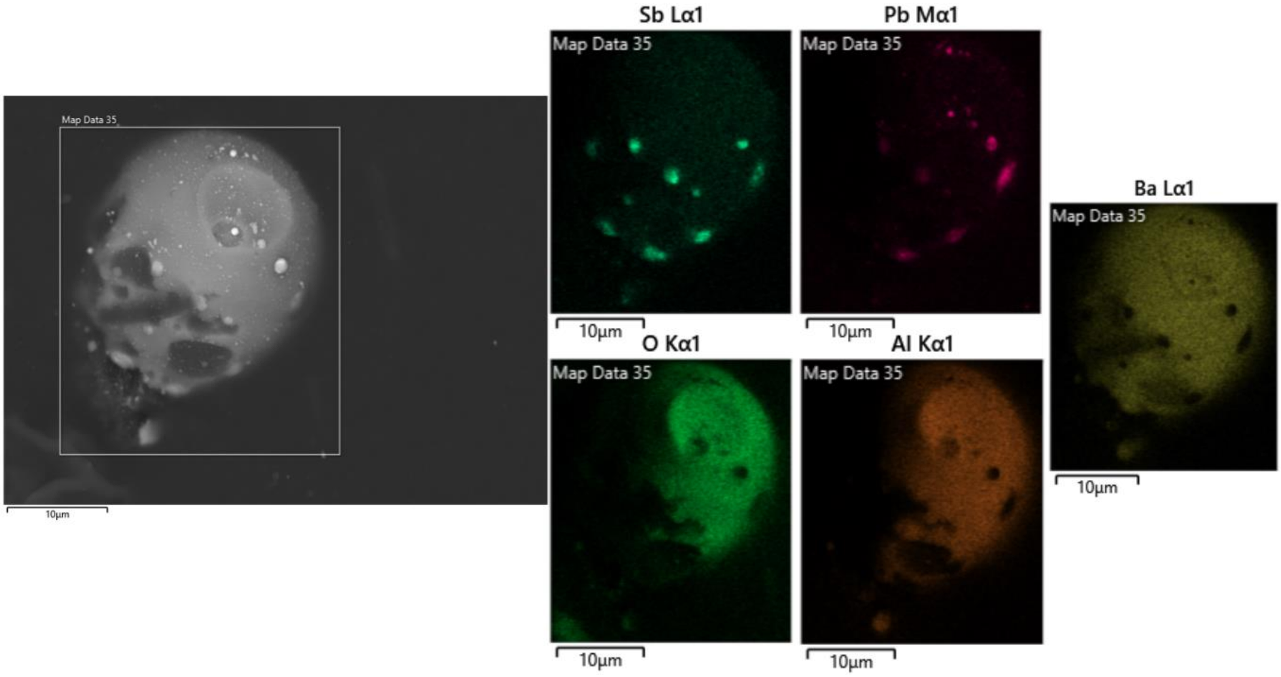


Figure 146: Map of elements of a typical type I particle.

In order to better understand the different quantities of aluminum present in each experimental condition, in Figure 147 are showed four type I particles, collected from the 4 different types of residues produced by the four ammunitions used in these experiments, which are very similar in shape and morphology between each other, but they clearly contain a different quantity of Al.

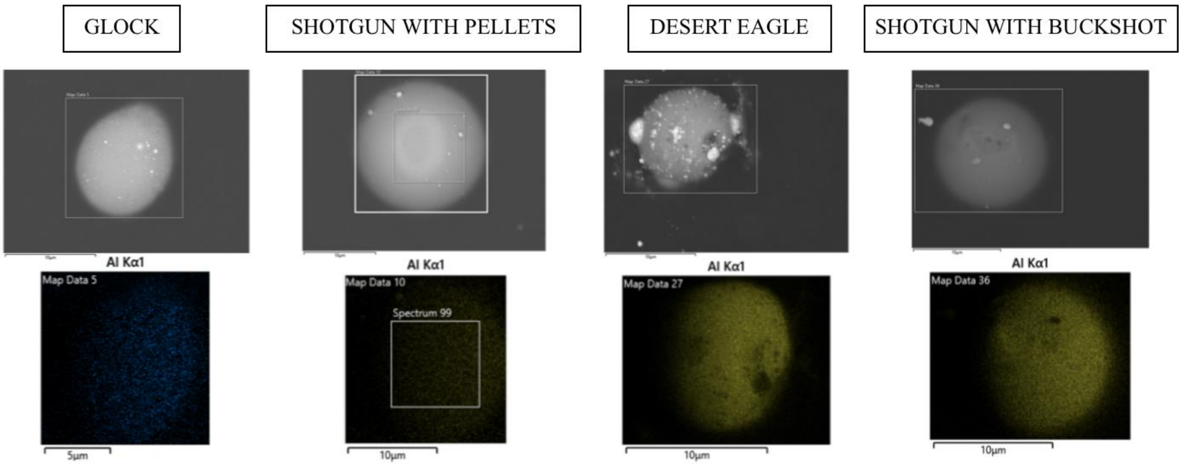


Figure 147: Four different type I particles coming from the four different ammunitions used in the experiments.

Moreover, from Figure 146 it is possible to point out another important aspect. The bright particles present on the surface of the darker core are not all equal between each other. There are some Pb particles in which a small quantity of Sb is present, which are the usual bright particles largely present also in the residues from the Fiocchi ammunition which utilizes pellets, and some others which contain only Sb. Since pure Sb particles are very rare, in fact only a few of them is found in all the other precedent experiments, finding here 4-5 Sb particles on the type I particle is quite strange. It seems that this kind of ammunitions contains a greater amount of Sb and a smaller amount of Pb compared to the other three ammunitions utilized. This reasoning is also supported by the discovery of a pure Sb particle which is found alone, meaning that it is not a nodule or a superficial particle, showed in Figure 148.

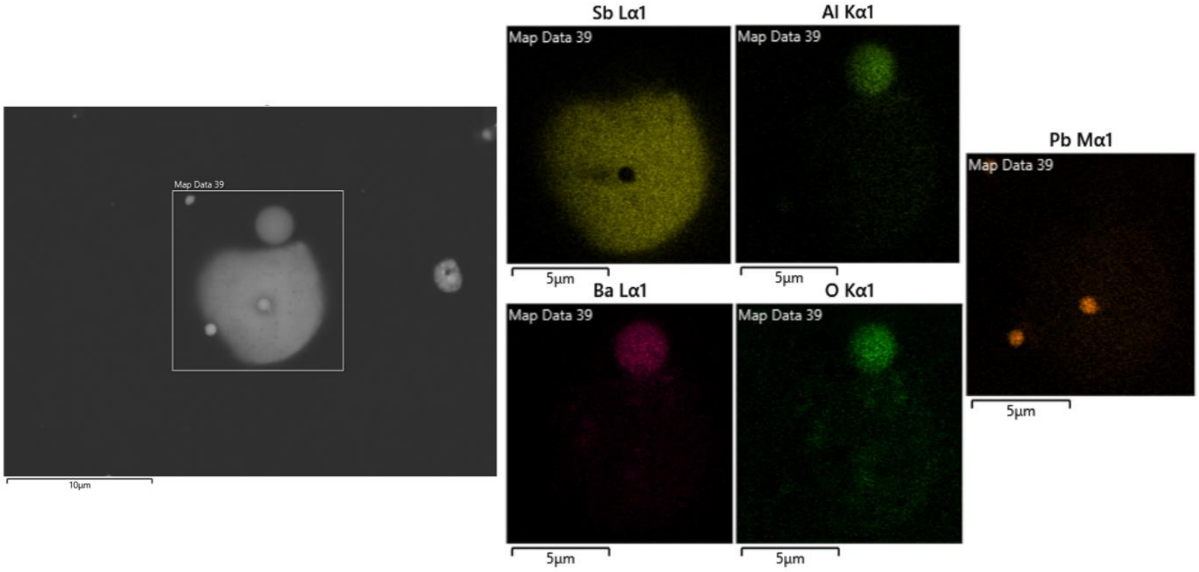


Figure 148: A pure Sb particle accompanied by two Pb and one BaO + Al particles.

Also in this case, it is possible directly at naked eye to discern between chemical phases simply by looking at the different shades of grey of the particles present in the image. There is a pure Sb particle, two smaller Pb particles and a darker one made of BaO and aluminum, as indicated in Figure 149.

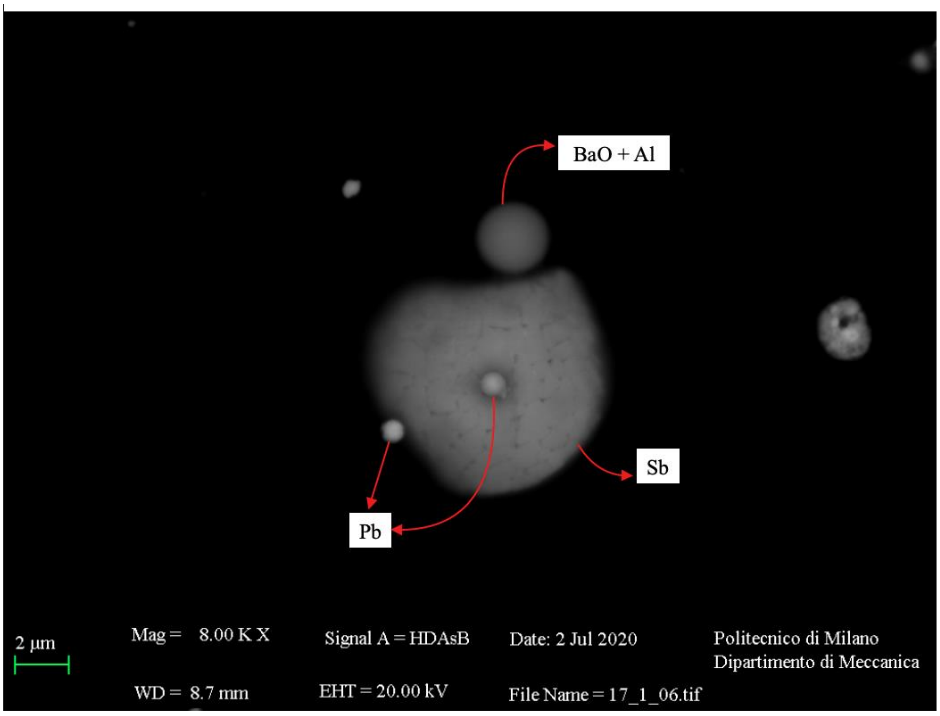


Figure 149: Phase differentiation looking at the shades of grey.

Moreover, on the Sb particle is clearly visible the grain structure, confirming one more time how all the different kind of particles produced are formed via the same mechanism. Since pure Sb particles are not found in the Glock experiments, but are found only when larger calibre ammunitions are fired, this confirms how bigger the calibre of the ammunition, bigger the quantity of Sb present in the primer mixture, since it serves as fuel.

5.4 GSR Persistence

This chapter is entirely dedicated to the persistence of the GSR when the experimental conditions are varied. The idea is to reach a conclusion regarding the GSR persistence and sampling efficiency when different firearms and ammunitions are utilised and when they are recovered with adhesive carbon stubs onto three different type of substrate, on which GSR are ejected.

It is important to point out before describing the inference method utilized, the factors, their levels and the statistical analysis performed needed to reach objective results, that the conclusions that will be exposed at the end of this chapter, are in reality quite intuitable simply by looking at the images at 300x magnification taken with the backscattered electrons of the SEM. In fact, the statistical analysis serves to give a quantitative and objective confirmation of what is already intuitable for example looking at the images in Figure 150; obviously, the same zone of the stubs is compared, the central one.

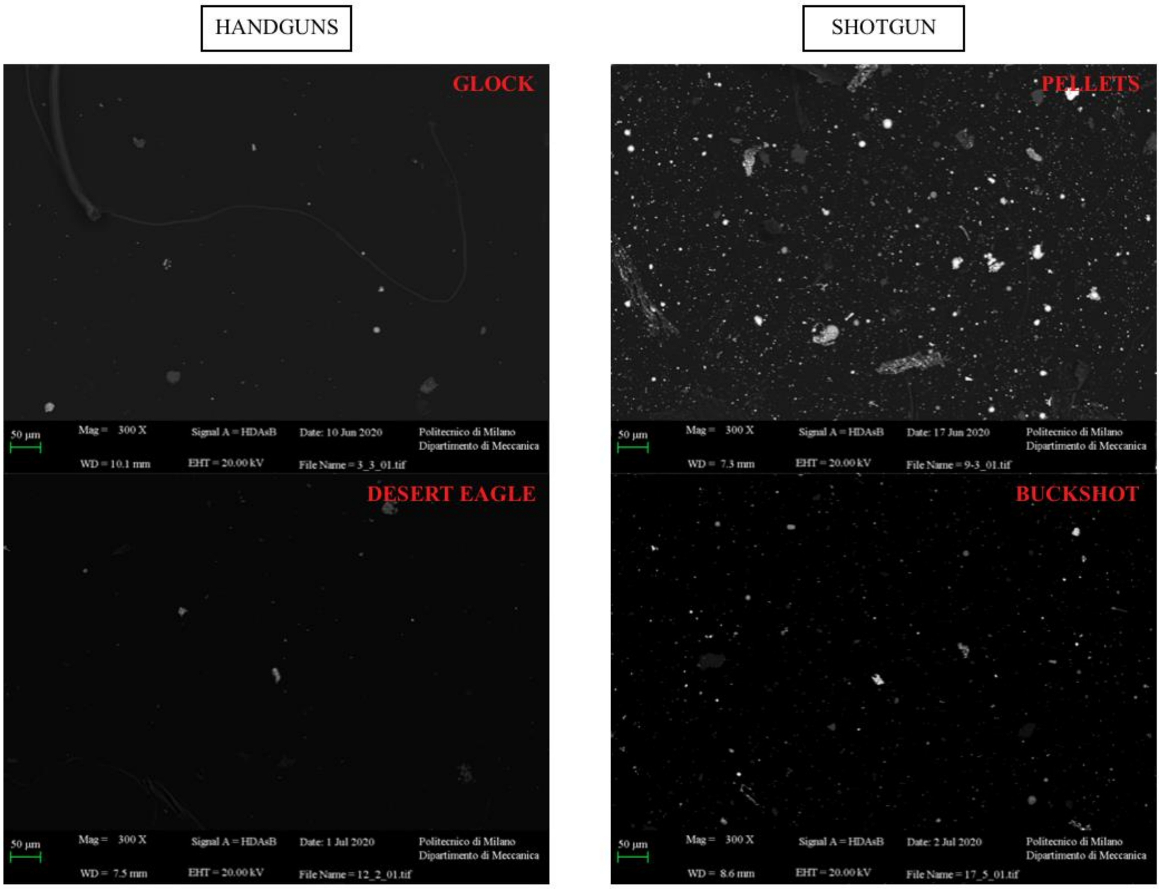


Figure 150: Comparison between experimental conditions; these are four images of the stubs utilized to sample the GSR from the polyester, changing the ammunition, and so the firearm, used.

In fact, even before checking the morphology and the chemical composition of the visible particles in Figure 150, it is quite immediate to point out that the results using the shotguns are enormously different from the results using the handguns. Even at this magnification and even without analysing manually all the bright particles that are visible on this zone of the four different stubs, it is quite immediate to conclude that a large number of particles are expelled from the shotgun with respect to the handguns.

Moreover, always looking at the Figure 150, it is also possible to highlight that probably the residues expelled from the Desert Eagle and the Glock will be comparable while the residues expelled from the shotgun with pellets are largely much more than the ones expelled from the shotgun with buckshot. Obviously not all the visible bright particles will be classified as GSR, however the results are unmistakable and are intuitable directly at naked eye and without the need of a statistical analysis. It is important to bear in mind that these conclusions and also the ones given at the end of the statistical analysis deal with the residues deposited on a target positioned in front of the firearms and after close range shots. This to say that the fact that the shotguns expels much more residues in the frontal direction cannot be used as an information to state that probably much more residues will be found on the hand of a shooter when utilizing a shotgun with respect to a handgun, because the two phenomena are not linked. In fact, the GSR found on the hands come predominantly from the firearms openings around the breech, like the ejection port and the trigger notch in self-loading firearms and from the flash gap between the cylinder and barrel in revolvers and not from the firearm bore. In the shotgun, since there are less openings, it is more difficult for the GSR to reach the hands so in theory they will be less.

Lastly, before introducing the inference method, the same reasoning could be applied also looking at the images at 300x when the type of substrate on which GSR are recovered changes. Considering for example the results utilizing the shotgun with pellets, it is immediately visible how on the sampling efficiency when the GSR are collected from the polyester is enhanced with respect to the wool and the cotton, which are expected to give the same sampling efficiency.

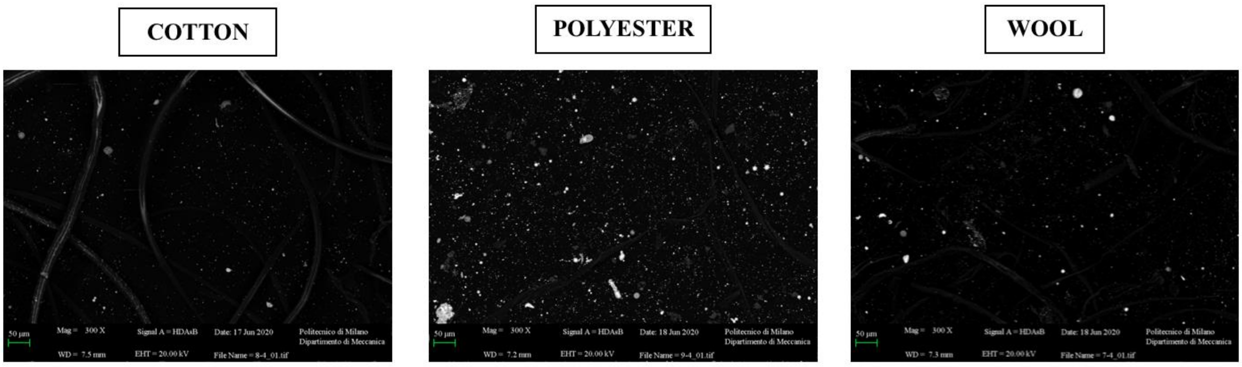


Figure 151: Comparison between different stub images on which GSR are collected from different substrates; obviously all these residues are referred to the same experimental conditions, meaning the shotgun using the ammunition containing pellets.

Notice that in this case are showed the results of the shotgun with pellets because to reach a sort of conclusion about the sampling efficiency on the different substrates directly at naked eye and even before the statistical analysis are needed a lot of residues, and these combination of firearm and ammunition produces many of them, making the conclusion quite evident. In the other three cases, in which a smaller number of residues are produced, it is more difficult to draw a result without a statistical analysis. It seems that more residues are produced, more the polyester shows its capability to collect and maintain the GSR after a close-range frontal shot with respect to the other two substrates utilized in the experiments. However, all these conjectures will be tested via a statistical analysis performed on Minitab.

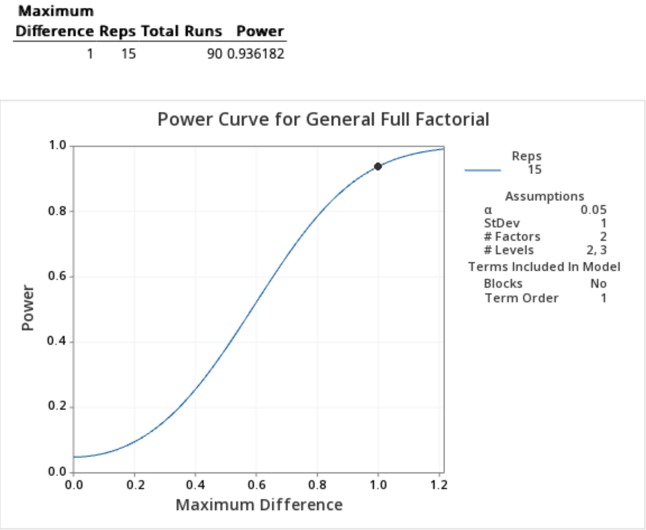
5.4.1 *Inference Method*

In order to reach a quantitative conclusion about the GSR persistence, a two-way ANOVA experiment is performed. As already explained, the response is the number of white pixels present on the images, which is obviously directly correlated with the number of bright particles present on the stub; the factor of the analysis are two and their levels are showed in Table 16.

Table 16: Design of the Experiment.

Response	**Factors**	**Levels of the Factors**
Number of white pixels	Substrates	- Cotton - Wool - Polyester
	Ammunitions	- Fiocchi calibre 9x21 (Glock) - Fiocchi calibre 12 with pellets (Shotgun) - Hornady 50 AE (Desert Eagle) - Royal Buck calibre 12 with buckshot (Shotgun)

Each experimental condition is replicated three times, but since the number of white pixels is obtained five times for each stub, these are used as additional replicates to enhance the power of the ANOVA test, since it is assumed that each of the five zone of the stub on which the images at 300x magnification are taken are statistically equal, due to the homogeneous sampling that was performed immediately after the shoots. So with 15 replicates, the power of the ANOVA test is very high and is able to detect a difference in mean number of white pixels of one standard deviation with a power of about 93.6 %, as showed in Figure 152.



```
Maximum
Difference Reps Total Runs   Power
         1   15         90 0.936182
```

Figure 152: Minitab response which shows how much power the statistical test has in detecting a difference in mean number of white pixels of one standard deviation.

Regarding the data inserted in the ANOVA analysis, thanks to the procedure showed in Figure 83, the number of white pixels for each of the 36 stubs are obtained and are collected in Table 17.

Table 17: Number of white pixels for each zone of the 36 stubs.

Stub	***Number of White Pixels***				
	Zone 1	**Zone 2**	**Zone 3**	**Zone 4**	**Zone 5**
1st	5277	5442	5295	5330	5430
2nd	5678	5465	5123	5456	5343
3rd	5412	5322	5458	5232	5124
4th	5654	5592	5587	5277	5537
5th	5987	5875	6122	5653	5998
6th	5945	6321	6245	5912	5432
7th	5553	5345	5587	5485	5561
8th	5432	5567	5412	5765	5219
9th	5175	5456	5523	5309	5371
10th	8163	9203	9210	7714	7980
11th	7894	8165	8567	8978	7845
12th	7912	8223	9122	7456	8976
13th	8463	9957	8217	7596	7678
14th	8233	9590	7910	8349	8698
15th	8456	9303	8760	7514	7980
16th	16428	20739	18728	17991	16034
17th	19823	16798	18254	19978	16945
18th	17576	18523	18267	19128	18697
19th	6501	5991	6698	5378	5879
20th	6189	6346	5786	5912	6122
21st	5267	5423	5990	5387	5892
22nd	6235	6834	6757	6429	6197
23rd	6546	6124	6456	6987	6754
24th	6243	6903	7012	6765	6718
25th	5860	5578	5547	5230	5761
26th	5897	5543	5682	5981	5993
27th	5815	5914	5541	5612	5871
28th	7122	6792	7202	6586	6761
29th	6541	6985	7135	7992	6723
30th	7998	6345	6754	7658	6994
31st	10346	9534	9987	11124	12420
32nd	11893	12698	10056	10893	9721

33rd	9903	10567	11475	9845	11978
34th	5987	5388	5736	6342	6273
35th	6189	6568	5995	5891	6792
36th	5987	6102	6981	6498	6523

5.4.2 Persistence Results

After having acquired all the number of white pixels, they are inserted in Minitab and the two-way ANOVA test is built.

5.4.2.1 Data Snooping

First of all, it is useful to plot the data acquired in order to understand what is happening even before running the ANOVA. Since both the factors in this analysis are categorical variables, the only useful plot that is performable in order to show all the data acquired is the individual value plot, showed in Figure 153.

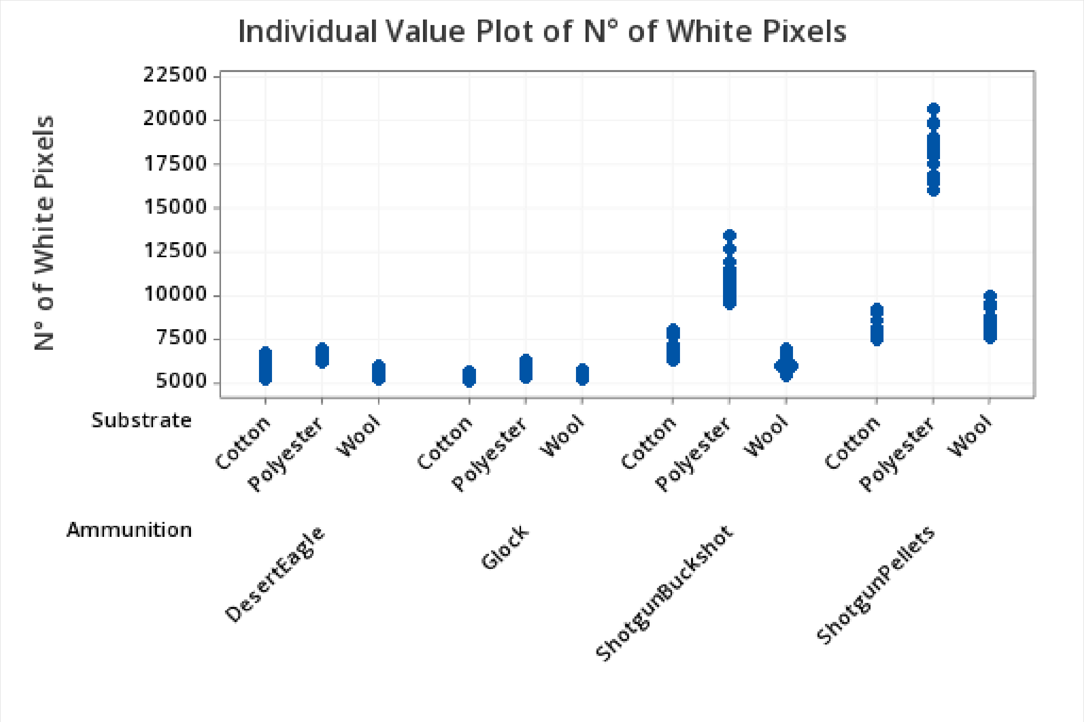


Figure 153: Individual value plot of the number of white pixels against the two factors of the analysis.

From the individual value plot is already possible to point out how the shotgun with pellets seems to produce the highest number of residues while the Glock and the Desert eagle produces a comparable number of residues, which however are lower than the results with both the ammunitions used with the shotgun. Moreover, looking at the substrates, is seems that the polyester is able to collect more residues, whatever type of ammunition is fired. The individual value plot also confirms how more residues are produced, more is visible the higher collection efficiency of the polyester with respect to the other two substrates utilized, the cotton and the wool, which seem to collect a comparable number of residues. Last but not least, the variability throughout all the levels of the factors seems quite constant. Obviously, it is needed the ANOVA analysis to validate all these preliminary considerations.

Another very useful plot, especially in an ANOVA analysis, is the main effect plot, which plots the mean of the number of pixels against the factor of the analysis. This plot is useful since it gives a first indication of the influence of the factors on the response; the main effect plots are showed in Figure 154.

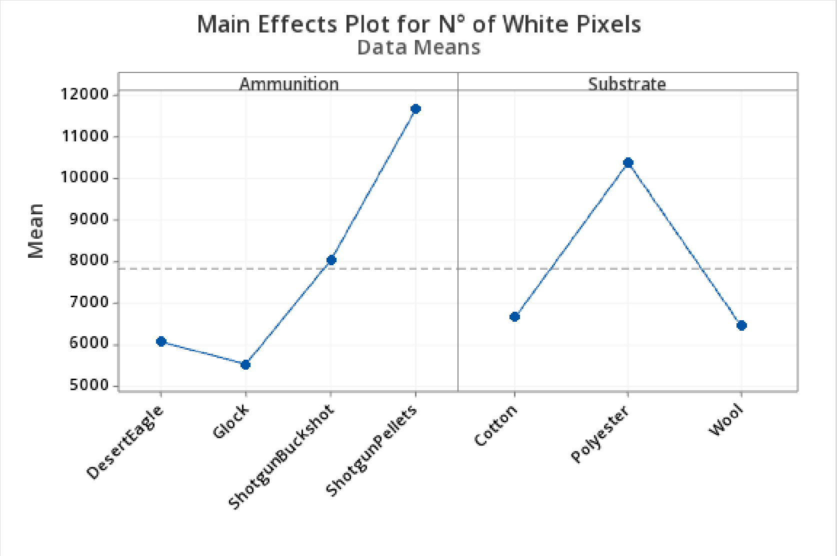


Figure 154: Main effect plots.

The main effect plots confirm the precedent suspects; both the factors seem significant in changing the response. Moreover, the Desert eagle and the Glock together with the polyester and the wool shares approximately the same mean number of white pixels, so probably that they will not be statistically different; however, also in this case, to validate these considerations an ANOVA analysis is needed.

Last but not least, another useful plot in a design like the one analysed here is the interaction plot, to search for possible unknown interactions between the factors of interest. Notice that since are available three replicates for each experimental condition, it is possible to include the interaction factor in the ANOVA analysis to be able to do a statistical test also on the interaction between factors. The interaction plot is showed in Figure 155, indicating the possible presence of an interaction between the type of substrates and the ammunitions utilized, since the lines are not parallel.

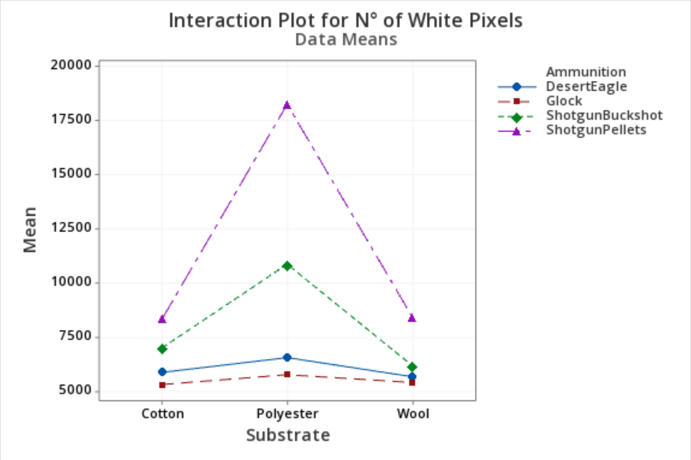


Figure 155: Interaction plot.

5.4.2.2 ANOVA

After having plotted the data, it is possible to run the ANOVA analysis. As already stated, since are available three real replicates of the experiment, it is possible to comprehend in the analysis also the interaction between the substrates and the ammunitions. The ANOVA table is showed in Table 18.

Table 18: ANOVA table considering both the factors and the interaction.

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Ammunition	3	1047050483	349016828	845.92	0.000
Substrate	2	587481718	293740859	711.95	0.000
*Ammunition*Substrate*	6	579936136	96656023	234.27	0.000
Error	168	69314733	412588		
Total	179	2283783069			

From the ANOVA table, the p-values of the factors and the interaction are zero, so they are smaller than the level of significance set at 0.05 %. This means that the ammunition used, the type of substrate and the interaction between them are significant in changing the response, i.e. the number of white pixels, which correspondd to the number of GSR collected on the stubs. Moreover, the R-square of the model is 96.96 %, while the R-square-adjusted, a better indicator with respect to the R-square, is 96.77 %; since it is bigger than 70 %, it is possible to consider appropriate the type of model utilised. However, for checking the correctness of this model is not enough the R-square adjusted but it is needed to check that the hypotheses of the model are respected.

5.4.2.3 Model Adequacy Checking

All the previous considerations are useless if the model assumptions are violated. The latters comprehend the normality of the standardized residuals (SRES), the equality of variance between the SRES and the factors of the model, which is the absence of strange patterns in the plots of the SRES against the fitted values, called FITS, and the factors of the model, the absence of outliers and since also the run-order is available, also the absence of the correlation between the SRES. Regarding the normality of the SRES, they need to belong to a normal standard distribution, so a normality test is conducted. Figure 156 shows the normal probability plot of the SRES; as seen, they don't lie on the red straight line and the p-value of the normality test is lower than the level of significance, which is as always 0.05 %.

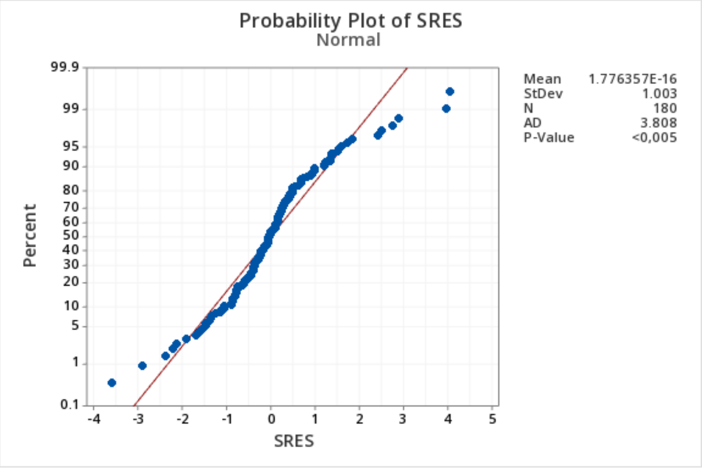


Figure 156: Normal probability plot of the SRES.

This means that the SRES do not belong to a normal distribution, so the ANOVA analysis needs to be reconducted, applying a transformation to the response trying to respect the model assumptions. In Minitab, it’s quite easy to apply a transformation on the response, since it is needed only to open the options of the ANOVA test and to tick the command which will find and apply the optimal transformation, which in this case in $\lambda = -1$, as showed in Table 19. This procedure is called Box-Cox transformation, and since λ is the exponent which is given to the number of white pixels before the analysis is conducted, being equal to -1 means that the same analysis is performed but on the inverse of the number of white pixels.

Table 19: Box-Cox transformation.

Box-Cox transformation	
Rounded λ	-1
Estimated λ	-0.76366

After applying the transformation, it is possible to re-run the ANOVA analysis, which response in showed in Table 20.

Table 20: ANOVA table after the Box-Cox transformation.

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Ammunition	3	0.000000	0.000000	851.53	0.000
Substrate	2	0.000000	0.000000	435.70	0.000
*Ammunition*Substrate*	6	0.000000	0.000000	54.07	0.000
Error	168	0.000000	0.000000		
Total	179	0.000000			

Obviously, since the inverse of the number of white pixels is used as input, the adjusted sum of squares and the adjusted mean squares are zero due to the approximation that Minitab does for the very small numbers. However, also in this case the p-values of the factors and the interaction are smaller than the level of significance, so the conclusions that are drawn with the ANOVA analysis showed in Table 18 stands also here. Moreover, the R-square of this model is 95.71 % while the R-square adjusted in 95.43 %, so also in this case the model could be considered correct. Obviously, also after this transformation, the assumptions of the model need to be checked. Starting again from the normality of the SRES, Figure 157 shows how the p-value of the normality test is largely bigger than 0.05 %, so the SRES could be considered as belonging to a normal standard distribution, in fact they are laying on the red straight line present on the graph.

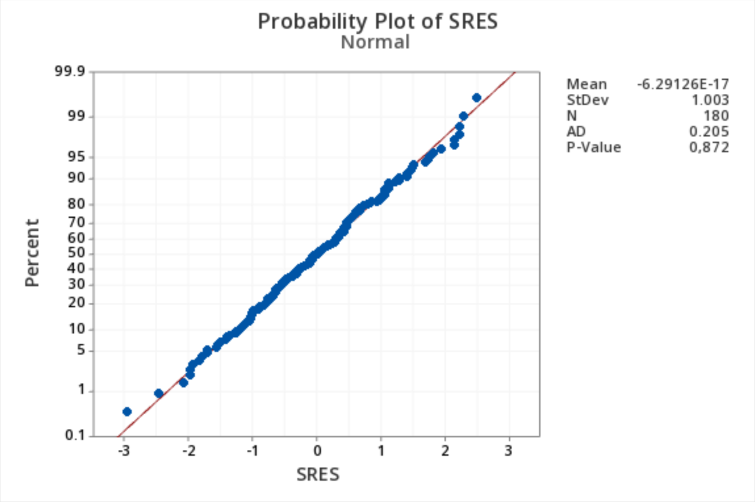


Figure 157: Normal probability plot of the SRES after the Box-Cox transformation.

Another fundamental hypothesis that needs to be checked is the equality of variance throughout all the levels of the factors and of the fitted values. It is possible to check the latter assumption via graphical methods or via a test's p-value, since are present replicates.

The graphical method consists in plotting the standardized residuals against the FITS, and against both the factors of the model. If no pattern and no strange shapes can be recognized in these plots, like a megaphone or a funnel, the variance of the SRES can be considered constant. The scatterplot of the SRES vs the FITS and the individual value plots of the SRES against the two categorical variable which are the substrates and the ammunitions used are showed in Figure 158.

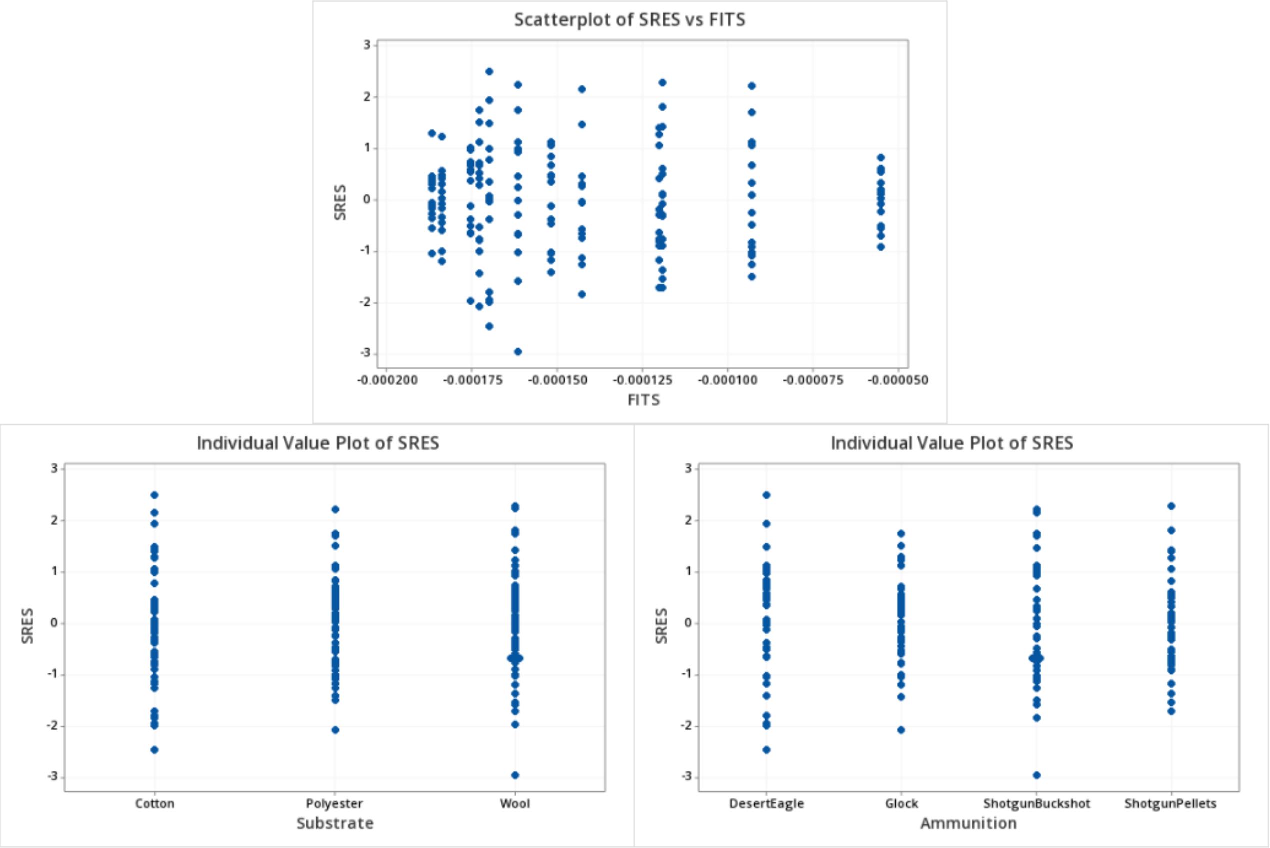
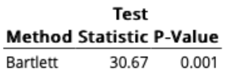


Figure 158: Scatterplot and individual value plots of the SRES vs the FITS, the ammunitions and the substrates.

It is also possible to check that no outliers are present in the SRES, since no one of the SRES exceeds the values ± 3, which is conventionally the limit for considering a certain value which needs to belong to a standard normal gaussian distribution an outlier. Moreover, it seems that the equality of variance of the SRES is verified. In fact, the variance seems constant throughout the FITS and all the levels of the factors. To give objectivity to these considerations, an equality of variance test is conducted. As already written, it is possible to perform this test only due to the fact that replicates of the samples are present, otherwise only graphical methods could be available. Since the normality test on the SRES is passed, it is possible to use the Bartlett test as showed in Figure 159, which however shows that the p-value is smaller than the level of significance, so the equality of variance test is not passed.



Method	Test Statistic	P-Value
Bartlett	30.67	0.001

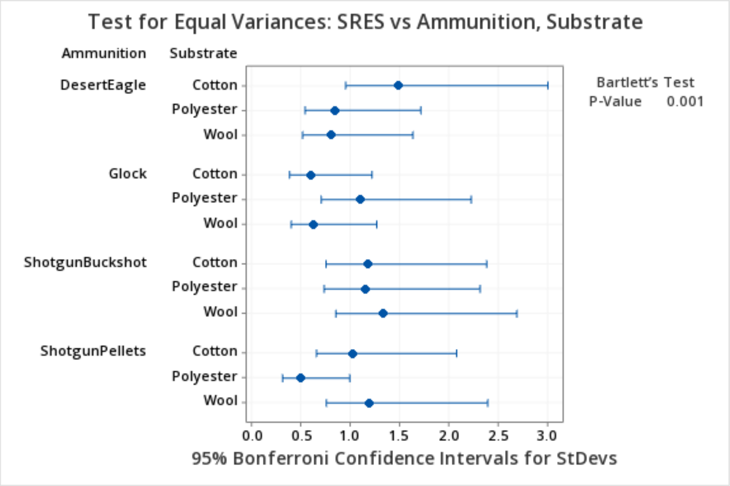


Figure 159: Bartlett equality of variance test.

This is probably due to the fact that in the model, other than the three real replicates, are used also the five fake replicates because of the five images taken for each stub, which are not able to give the real variance that five additional real replicates can give. An example of an experiment in which real replicates can be obtained would have been to shoot fifteen times for each substrate and for each ammunition, having a total of 180 stubs to be analysed. Since for each stub about three hours of analysis are needed both doing the morphological and chemical analysis on the particles, doing an experiment with 15 real replicates would have been impossible. However, a statistical test for the equality of variances is quite difficult to the passed when in the response there are not real replicates, so for making the assumption on the equality of variances verified, it is needed simply that no strange shapes or patterns are present in the graphs in Figure 158, which is what happens here.

Lastly, since also the run-order is known due to the fact that the 36 shots are performed one after the other, it is possible to perform an autocorrelation test on the sorted SRES, which is showed in Figure 160.

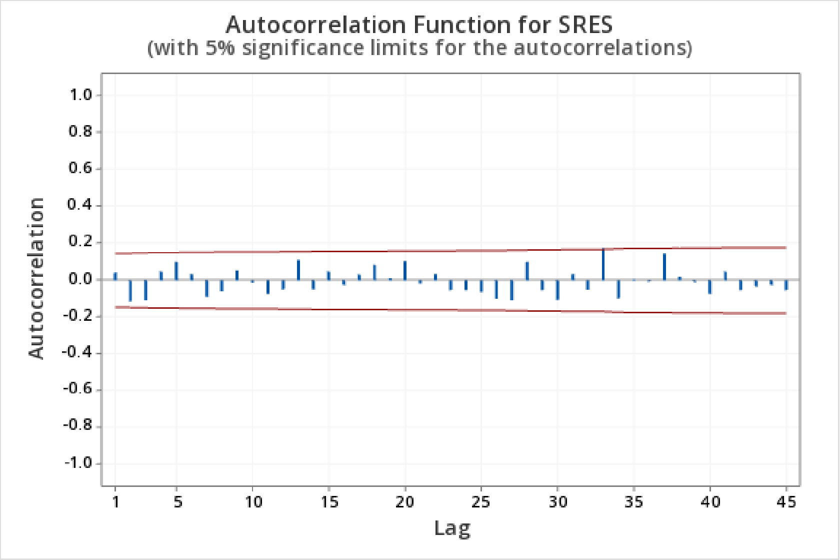


Figure 160: Autocorrelation test on the SRES.

Since there isn’t any blue line that crosses the red ones, it is possible to consider passed the autocorrelation test, so there isn’t any correlation between the sorted SRES.

Now that all the model hypotheses are verified, it is possible to draw conclusions. First of all, type of ammunitions, substrates, and their interaction can be considered significant in changing the persistence and the sampling efficiency of the GSR. The fact that also the interaction is significant is again quite intuitable: since the sampling efficiency of the GSR on the different substrates depends on how much residues the substrate is able to collect, and this capacity is dependent both on the electrostatic force that the substrate is able to exert on the GSR particles and also on how much debris and fibres the substrate releases on the stub during the sampling, if a substrate has an high collection efficiency, and this substrate is coupled with a firearm utilized with an ammunition that produces a great amount of GSR, there will be a great number of residues collected on the related stub with respect to all the other experimental conditions. Obviously, also the contrary stands, since the least number of residues will be found on a substrate which exert a low electrostatic force on the GSR, releases on the adhesive stub a lot of fibres which cover the particles and make more difficult to analyse them at the SEM, coupled with a firearm utilized with an ammunition that generates a low number of GSR when fired.

So obviously the substrate’s GSR retention and persistence is coupled with the capacity of the ammunition to generate the GSR, and this reflects in a p-value of the interaction between the substrates and the ammunitions smaller than 0.05 %. However, if one wants to know which is the substrates which guarantees the highest sampling efficiency and the ammunition which produces the higher number of GSR, the comparisons are needed.

5.4.2.4 Comparisons

Since all the factors and the interaction are significant, three comparisons are performed. First of all, the comparison between the ammunition and the one between the substrates is performed, setting a level of significance equal to the usual 0.05 % and using the Tukey statistical method. The results are showed in Table 21 and Table 22.

Table 21: Comparisons between types of ammunitions.

Ammunition	**N**	**Mean**	**Grouping**			
ShotgunPellets	45	10191.4	A			
ShotgunBuckshot	45	7557.4		B		
DesertEagle	45	6038.0			C	
Glock	45	5525.8				D

Table 22: Comparison between types of substrates.

Substrate	**N**	**Mean**	**Grouping**		
Polyester	60	8470.70	A		
Cotton	60	6457.81		B	
Wool	60	6255.22			C

As expected directly from the beginning, the ammunition, and so the firearm that releases a higher quantity of GSR on a frontal target is the shotgun, both utilizing the pellets and the buckshot, while the handguns produce a comparable number of residues. However, between the pellets and the buckshot, the one that produces more GSR is the ammunition containing pellets, probably due to the already discussed power of the shot, which in the case of buckshot moves the substrate and removes due to physical action some residues that will probably be deposited on the substrate if the latter stand still, as it happens is the ammunition containing pellets and with the Glock.

Regarding the substrates, the one which collects more GSR is without any doubt the polyester, since it exerts the highest electrostatic force on the GSR and releases a lower number of fibres on the adhesive stub. Both the cotton and the wool have an extremely lower GSR retention, which traduces in a lower sampling efficiency, both due to the lower electrostatic forces generated between them and the GSR and because of the fibres which makes very difficult the SEM analyses, greatly present on the stubs with which the sampling operation are performed on the wool.

If one wants to know what is the best combination of factors to collect more GSR via the adhesive stub sampling method, a comparison on the interaction between ammunitions and substrates is needed, and is showed in Table 23, always using the Tukey method. Notice that since the comparison is performed considering both the factors together, the level of significance is set at 0.025%.

Table 23: Comparison between the interaction of the Type of ammunition and the substrates.

Ammunition*Substrate	***N***	***Mean***	***Grouping***								
ShotgunPellets Polyester	15	18170.2	A								
ShotgunBuckshot Polyester	15	10784.7		B							
ShotgunPellets Wool	15	8392.1			C						
ShotgunPellets Cotton	15	8321.4			C						
ShotgunBuckshot Cotton	15	7007.5				D					
DesertEagle Polyester	15	6584.5				D	E				
Glock Wool	15	6190.6					E	F			
DesertEagle Cotton	15	5889.0						F	G		
DesertEagle Wool	15	5794.3							G		
ShotgunBuckshot Wool	15	5708.7							G	H	
Glock Polyester	15	5446.6								H	I
Glock Cotton	15	5355.6									I

As expected, the best combination for obtaining the highest GSR collection efficiency is to collect them on the polyester, after having shoot with a shotgun utilizing an ammunition containing pellets. On the contrary, the worst collection efficiency happens utilizing the Glock and shooting through the cotton; however, the last seven combinations shares a lot of letters between them, so in general it is possible to say that the handguns produce in the fontal direction less residues with respect to the shotgun, so few that also the substrate factor is inhibited, becoming a background factor.

6. Conclusions

In this chapter are collected resumed all the conclusions that are extracted from the experimental work performed, starting from the morphology of the GSR, then passing to their chemical composition and concluding with the statistical analysis between the different fabrics and ammunitions.

Regarding the morphologies of the collected GSR, starting from the ones expelled from the Glock, what it is concluded is that it is possible to find a large variety of shapes; most of all are type I particles but also a single type II particle is found, adopting the classification made by Basu. Moreover, on some of the type I particles it is possible to find some protuberances which give to the particles an irregular shape which are barium oxide protuberances which seem grown on the surface of the particle. Other than these shapes, also some irregular particles are found, showing that the particles are all formed as spheres but then they could be deformed by the surrounding ambient, meaning the propellant, the walls of the cartridge case, the firearm itself, the oxidation of the external layers, and the interaction with other residues which could create very unusual shapes. Additionally, also some hollow shells can be found, which could come from the shell structure of the type III particles, which however are not found in these residues, or from the separation between the oxidized shell of most of the particles from the main core; in fact, the majority of the particles are oxidized on the external layers due to the high temperature of the environment in which they form which favours the oxidation. Lastly, also some non-GSR particles are found, which are mainly Cu which probably come from the cartridge case or from the bullet jacket; also if these particles appears as bright at the backscattered electron image, they have clearly nothing to do with the GSR due to some particulars that are forbidden, i.e. principally is the crystallinity.

Regarding the particles expelled from the shotgun used with the Fiocchi ammunition containing pellets, there are mostly two different kind of particles: small homogeneous bright spheres, which sometimes forms agglomerates o particles due to the electrostatic forces that unites them and obviously also some irregular shapes due to the interaction with the surrounding ambient, and darker cores with superficial nodules, which resemble type I particles. Sometimes, the superficial nodules are literally distinct particles that are attached to the darker core, revealing that the type I particles are in reality formed in two separate steps: firstly, the darker cores form and solidify, secondly, the smaller brighter particles deposits on the surface. This reasoning is also confirmed by Figure 108. Again, also for these darker cores covered by superficial nodules, the morphology is not always spherical, but it is possible to find also some irregular particles. Most importantly, in these particles are found also some examples which show a sort of grain structure on its surface. The finding of this strange surface pattern help to aid some additional information to GSR formation; in fact, there are some examples in which this grain structure is so visible, that it is possible to understand that in reality the grain structure is formed because of the coalescence of smaller nanometric particles that form the bigger ones. Looking at the all population of particles it is possible to conclude that more the solidification and the ambient in which the particles form is homogeneous, less visible is the grain structure.

On the contrary, when there is inhomogeneity in one of the conditions listed before, especially in the case where the inhomogeneity is created because of the interaction between two particles, the grain structure become more visible, sometimes even showing the nanometric particles that form the bigger ones, as showed in the detail in Figure 161.

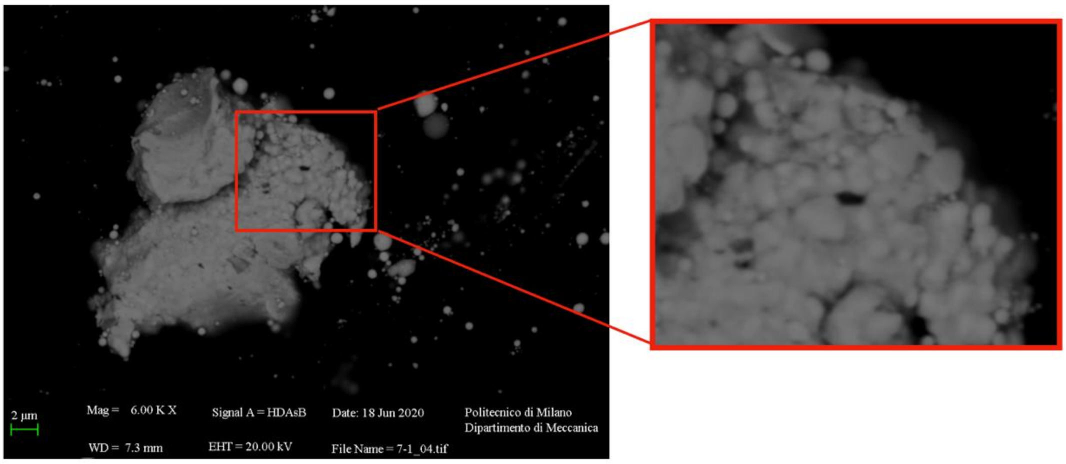


Figure 161: Detail of the small nanoparticles that form the bigger ones.

As already said, the small nanoparticles coalesce into bigger particles due to the electrostatic forces that are created between them, confirmed both by the finding of agglomerates of small particles, and also by the fact that many bigger particles have their surface covered with many small particles which are not fused but seem that they are simply laying on it. The mechanism which drives the formation of the small nanoparticles is the condensation from a supersaturated phase of the vapours formed after the deflagration of the primer mixture which forms small nanoparticles which then the coalesce into the bigger ones forming the usual micrometric particles. Last but not least, in these residues are also found some examples of particles which are clearly derived from the division of a bigger one into two smaller halves which resemble themselves two distinct particles. This phenomenon happens in all the GSR, but evidences of its happening are found only in the shotgun and in the Desert Eagle experiments, but not in the residues expelled utilizing the Glock.

Regarding the Desert Eagle, the particles collected resemble exactly the ones expelled from the shotgun utilizing the Fiocchi ammunition with pellets. They are practically two types, bright homogeneous particles and darker cores covered by bright superficial nodules, which number and dimension could vary a lot; however in general, they are smaller and less than the ones expelled from the shotgun. In both the cases, they are mostly spheres and sometimes they also show an irregular morphology. However, regarding the darker particles, what is really strange and differentiate a lot these particles with all the other ones found in the other experiments is that the darker cores in most of the cases present a sort of sponge-like structure, full of holes and discontinuity. Moreover, it is possible to find some darker cores alone, without superficial nodules. This confirm once again that the type I particles form in two steps: firstly, the darker cores form and solidify, then the superficial nodules deposit on the surface. This is mostly due to the chemical composition, since the darker cores are mostly made of barium, which have a higher solidification temperature than Pb and Sb, which mostly compose the superficial nodules, so it is already solid when the bright nodules impact on it.

Moreover, during the analysis, also a strange phenomenon happens: due to the interaction with the electron beam, the oxidized core of an analysed particles breaks, showing the possibility that the interaction with the SEM's beam could modify the analysed particles. Last but not least, there are also some particles that are really helpful in confirming that the mechanism of formation of the GSR is equal independently of the chemical composition since also some darker cores show the grain structure and the smaller nanometric particles that forms them, as showed in the detail in Figure 162.

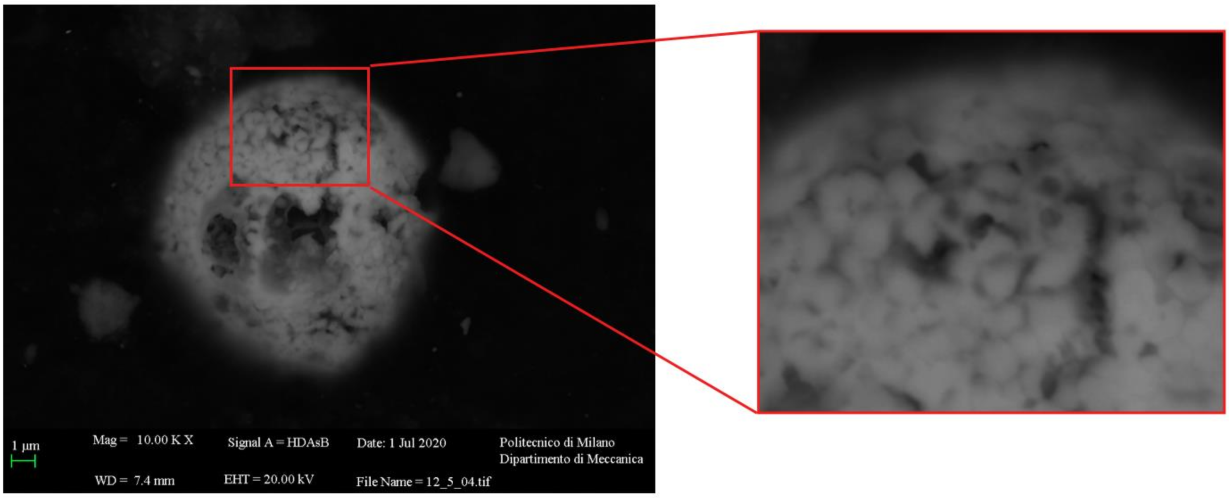


Figure 162: Detail of a darker core on which are visible the small nanoparticles that compose it.

This is important since in the shotgun the grain structure is visible only on the bright Pb and Sb particles; these examples instead show that this is a peculiarity of all the types of GSR, since depends on their mechanism of formation, which is equal for all the GSR, and not on their chemical composition.

Lastly, regarding the residues expelled from the shotgun using the Hornady ammunition containing buckshot, the results are very similar to the ammunition containing pellets, so it is possible to find small bright particles and many type I particles, both could be spherical or irregular; however, there are fewer particles and in general are smaller than the shotgun utilized with the Fiocchi ammunition. The fact that both the Desert Eagle and the buckshot produces fewer and smaller particles makes understand that the great power of both shots which moves the substrate on which GSR are deposited is the main reason why the bigger particles fell off the fabric and are loses. On the contrary the Glock does not even move the substrate so the reason why there is a small number of particles is simply because less residues are produced in that scenario. The most frequent morphology of a GSR particle is as already stated spherical but many examples of irregular particles collected in this case help to point out that also irregular morphologies could be encountered. This is why the irregular particles could not be discarded simply for their shape, but obviously they always need to be amorphous, meaning without no sort of crystallinity and no sharp edges, and usually it is possible to recognize the fact that the irregular particles are deformed spheres due to the interaction with the surrounding ambient or are clearly deriving from a condensation plus a solidification phenomenon. Moreover, some sheared particles are found, revealing their internal structure, and confirming what it has been found in literature, which is that most of the particles are solid but some of them present some internal holes.

Last but not least, some particles that are clearly derived from the division of bigger ones are also found here. Collecting throughout all the experiments every image in which this phenomenon happen, it is possible to reconstruct step by step all the transformation from a bigger particle into two smaller halves, as showed in Figure 163.

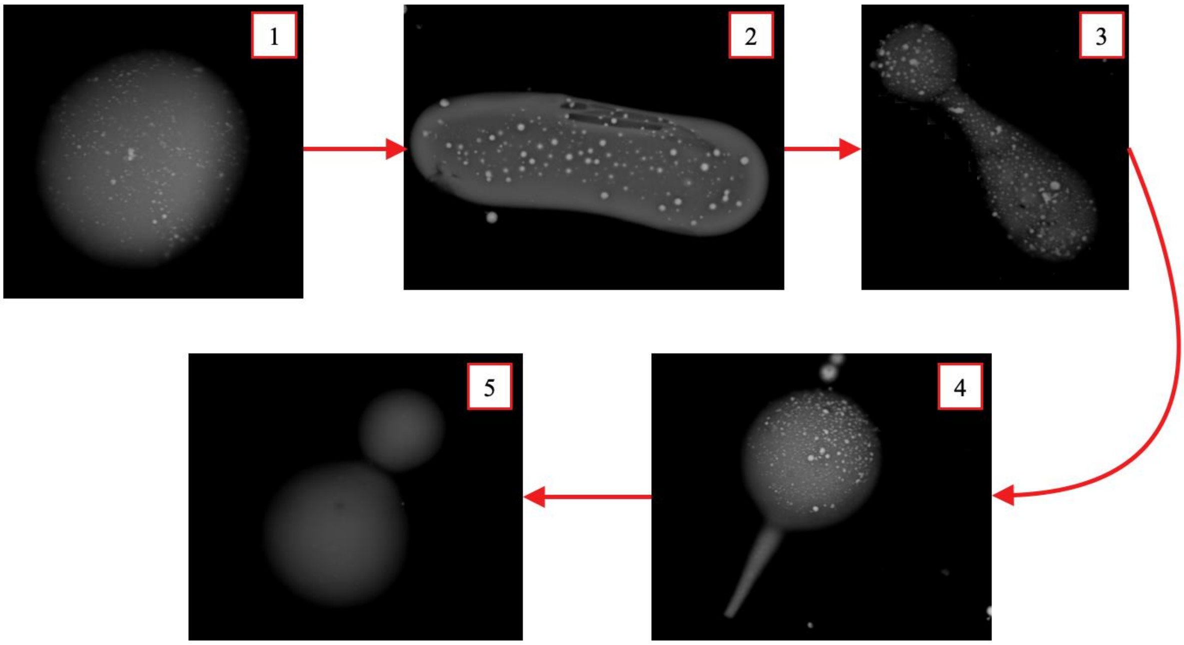


Figure 163: Process of division of a bigger particles into two smaller ones: 1) A spherical particle; 2) a stretched spherical particle which becomes an ellipse; 3) the ellipse is starting the division, the two forming particles are attached by a sort of a bridge; 4) the bridge that connect the particles becomes smaller and smaller; 5) the bridge is broken and the particles are divided.

Notice that also the contrary can happen, simply when two particles collide and fuse together; however, it is a completely different phenomenon with respect to the one showed in Figure 163, since the collision of two particles create a shape which is clearly the fusion of two smaller particles together, and they also could be different, meaning that particles which have a different chemical composition can fuse together. On the contrary, when two particles separate into two smaller ones, if the process is finished, it will be created two homogeneous particles which don't seem to come from a bigger one but have the same chemical composition. Lastly, some particles which are clearly not GSR are found but present some crystalline features which able the analyst to immediately recognize the non-GSR source of such irregular particles.

Regarding the results obtained from the chemical analysis on the particles found, all the type I particles found in these set of experiment reveal a barium core, with an external layer of barium oxides while the nodules are mostly made of Pb with a small quantity of Sb with except of the Glock residues, in which the three elements are mixed together. This reveals the fact that the environment in which the type I particles form matters in changing their chemical composition; in the Glock, the environment in which they form is smaller and more uniform, so the elements are more mixed together, while in the other firearms and ammunitions, due to the bigger calibre, this is not the case, and the type I particles reveals the chemical composition theorized by Basu.

Moreover in the Glock residues and in the shotgun utilized with the Fiocchi ammunition containing pellets the core is made of pure barium with only trace levels of aluminum, while in the shotgun used with buckshot and in the Desert Eagle, probably because of the more power required, a great quantity of aluminum is found in the core, especially in the external layers, mixed with the barium oxides, revealing that to enhance the power of the primer mixture and to correctly deflagrate the propellant, also aluminum is added. The small bright particles reveal to be exactly the nodules of the type I particles which are not attached to the barium cores, and so they are exactly made of Pb and Sb. Only one type II particle as theorized by Basu is found in the Glock residues, and reveal a concurrent mixture of primer elements, which is the characteristic triplet made of Ba, Pb and Sb. No type III particles is found in whatever experimental condition, however this could be due both to the fact that the frequency of occurrence of these type of particles is the smallest one and also to the fact that no automated analysis is performed, so being manual, it is possible that by chance no type III particle and only one type II particle is found. Moreover, the protuberance that seems grown on the barium cores are barium oxides protuberances and could give to the usual type I particles a strange shape. In general the shotgun and the Desert Eagle produce a larger number of Pb and Sb bright particles with respect to the Glock, and this is once again due to the bigger caliber of the ammunitions used, since a greater quantity of primer mixture is present, in which is put a greater amount of Pb and Sb, respectively the initiator and the fuel, being able to correctly deflagrate the major amount of propellant powder. Last but not least, in the residues expelled from the Desert eagle and in the ones expelled from the shotgun used with both the ammunition utilized in the experiments, some pure Sb particles are found. These pure particles are for some unknown reason extremely rare to be encountered between the GSR, so having met them moreover performing a manual analysis, confirms once again how bigger the caliber of the ammunition, bigger the quantity of Sb present in the primer mixture.

Lastly, regarding the persistence and the sampling efficiency of the GSR on different substrate and utilizing different ammunitions, directly at naked eye on the images taken at 300x magnification it is possible to conclude that probably the shotgun utilized with pellets expels much more residues that the shotgun with buckshot, and even less residues are produced with the Glock and with the Desert Eagle, which produces comparable results. Regarding the substrate, the polyester seems to collect more residues that the cotton and the wool. However, these initial considerations are checked via an ANOVA test and the results are that the polyester assures the highest sampling efficiency utilizing the adhesive stubs method and that the shotgun with pellets produces the highest number of GSR. The fact that polyester assures the highest sampling efficiency is probably due to the higher electrostatic forces that such fabric is able to exert on the residues coupled with the fact that no fibres are released on the stubs by the polyester during the sampling, which on the contrary happen when sampling on cotton and wool; in fact such fibers could disturb the SEM analysis and diminish the sampling efficiency. Concluding, the best combination of factors to collect more GSR via the adhesive stub sampling method is to use a shotgun with an ammunition containing pellets and to perform a frontal close range shot against a polyester piece of fabric. In general however, the best fabric to collect GSR expelled from the frontal discharge of a firearm is without any doubt the polyester.

References

[1] F. Saverio Romolo and P. Margot, “Identification of gunshot residue: A critical review,” *Forensic Sci. Int.*, vol. 119, no. 2, pp. 195–211, 2001.

[2] O. Dalby, D. Butler, and J. W. Birkett, “Analysis of gunshot residue and associated materials - A review,” *J. Forensic Sci.*, vol. 55, no. 4, pp. 924–943, 2010.

[3] K. H. Chang, P. T. Jayaprakash, C. H. Yew, and A. F. L. Abdullah, “Gunshot residue analysis and its evidential values: A review,” *Aust. J. Forensic Sci.*, vol. 45, no. 1, pp. 3–23, 2013.

[4] Z. Brożek-Mucha, “Trends in analysis of gunshot residue for forensic purposes,” *Anal. Bioanal. Chem.*, vol. 409, no. 25, pp. 5803–5811, 2017.

[5] James Smyth Wallace, *Chemical analysis of Firearms, Ammunition and Gunshot residue*, vol. 1, no. 3. 2008.

[6] M. Morin and C. Bettin, “I Residui di Sparo,” 2017.

[7] Kast, H. Spreng- u. Zündstoffe, Vieweg & Sohn, Braunschweig, 1921.

[8] A. J. Schwoeble and D. L. Exline, *Current Methods in Forensic Gunshot Residue Analysis*. 2000.

[9] https://rivervalleyarms.com/2015/11/07/slug-country-debates-rifled-barrel-versus-smooth-bore/. Accessed 19th April 2020.

[10] https://www.icollector.com/Winchester-Model-70-bolt-action-rifle-308-cal-22-barrel-black-finish-checkered-wood-stocks_i13668751. Accessed 19th April 2020.

[11] “Handbook on Weaponry,” 1982.

[12] Scientific Working Group for Gunhot Residue, “Guide for Primer Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectrometry,” *Swggsr*, pp. 1–100, 2011.

[13] M. Morin and C. Bettin, “I Residui di Sparo,” 2015.

[14] J. Polovková, M. Šimonič, and I. Szegényi, “Study of gunshot residues from Sintox® ammunition containing marking substances,” *Egypt. J. Forensic Sci.*, vol. 5, no. 4, pp. 174–179, 2015.

[15] B. J. Heard, *Handbook of Firearms and Ballistics: Examining and Interpreting Forensic Evidence: Second Edition*. 2008.

[16] Wolten GM, Nesbitt RS. "On the mechanism of gunshot residue particle formation," J Forensic Sci 1980;25(3):533–45.

[17] Basu S. "Formation of gunshot residues," J Forensic Sci 1982;27(1):72– 91.

[18] B. Burnett, “The Form of Gunshot Residue Is Modified by Target Impact,” *J. Forensic Sci.*, vol. 34, no. 4, p. 12709J, 1989.

[19] J. Lebiedzik and D. L. Johnson, “Rapid Search and Quantitative Analysis of Gunshot Residue Particles in the SEM,” *J. Forensic Sci.*, vol. 45, no. 1, p. 14644J, 2000.

[20] a Markowicz, D. Wegrzynek, E. Chinea-Cano, S. a Bamford, D. H. Torres, and R. P. Alvarez, “Quality management and method Validation in EDXRF analysis,” *X-Ray Spectrom.*, vol. 36, no. 1, pp. 27–34, 2007.

[21] llker Kara, Y. Sarikavak, S. B. Lisesivdin, and M. Kasap, “Evaluation of morphological and chemical differences of gunshot residues in different ammunitions using SEM/EDS technique,” *Environ. Forensics*, vol. 17, no. 1, pp. 68–79, 2016.

[22] L. Niewöhner and H. W. Wenz, “Applications of Focused Ion Beam Systems in Gunshot Residue Investigation,” *J. Forensic Sci.*, vol. 44, no. 1, p. 14419J, 1999.

[23] I. Kara, S. B. Lisesivdin, M. Kasap, E. Er, and U. Uzek, “The Relationship Between the Surface Morphology and Chemical Composition of Gunshot Residue Particles,” *J. Forensic Sci.*, vol. 60, no. 4, pp. 1030–1033, 2015.

[24] L. G. A. Melo, A. Martiny, and A. L. Pinto, “Nano characterization of gunshot residues from Brazilian ammunition,” *Forensic Sci. Int.*, vol. 240, pp. 69–79, 2014.

[25] R. Papers, “18 th INTERPOL International Forensic Science Managers Symposium,” no. December, pp. 1–769, 2016.

[26] R. S. N. G.M. Wolten A.R. Calloway, G.L Loper, P.F. Jones, “Final Report on Particle Analysis for Gunshot Residue Detection,” vol. 77, no. 7915, p. 196, 1977.

[27] Z. Oommen and S. M. Pierce, “Lead-free primer residues: A qualitative characterization of Winchester WinClean^{TM}, Remington/UMC LeadLess^{TM}, Federal BallistiClean^{TM}, and Speer Lawman CleanFire^{TM} handgun ammunition,” *J. Forensic Sci.*, vol. 51, no. 3, pp. 509–519, 2006.

[28] Z. Abrego *et al.*, “A novel method for the identification of inorganic and organic gunshot residue particles of lead-free

ammunitions from the hands of shooters using scanning laser ablation-ICPMS and Raman micro-spectroscopy," *Analyst*, vol. 139, no. 23, pp. 6232–6241, 2014.

[29] Laza D,Nys B,Kinder JD, Kirsch-DeMesmaeker A,Moucheron C (2007) "Development of a quantitative LC-MS/MS method for the analysis of common propellant powder stabilizers in gunshot residue". Journal of Forensic Sciences 52 (4):842–850. doi:10.1111/j.

[30] Moran JW, Bell S. "Skin permeation of organic gunshot residue: implications for sampling and analysis". Anal Chem. 2014;86(12): 6071–9.

[31] R. V. Taudte, C. Roux, L. Blanes, M. Horder, K. P. Kirkbride, and A. Beavis, "The development and comparison of collection techniques for inorganic and organic gunshot residues," *Anal. Bioanal. Chem.*, vol. 408, no. 10, pp. 2567–2576, 2016.

[32] J.S. Wallace e J. McQuillan "Discharge Residues from Cartridge-operated Industrial Tools"del Journal of the Forensic Science Society, vol. 24 (1984).

[33] C. Torre, G. Mattutino, V. Vasino, and C. Robino, "Brake linings: A source of non-GSR particles containing lead, barium, and antimony," *J. Forensic Sci.*, vol. 47, no. 3, pp. 494–504, 2002.

[34] Warlow T.A. (1996), "Firearms, the Law and Forensic Ballistics", CRC, Boca Raton.

[35] Speers SJ, Doolan K, McQuillan J, Wallace JS. "Evaluation of improved methods for the recovery and detection of organic and inorganic cartridge discharge residues". J Chromatogr A 1994;674(1–2):319–27.

[36] P. Bergman, P. Enzel, and E. Springer, "The Detection of Gunshot Residue (GSR) Particles on the Bottom of Discharged Bullets," *J. Forensic Sci.*, vol. 33, no. 4, p. 12518J, 1988.

[37] R. V. Gerard, M. J. McVicar, E. Lindsay, E. D. Randall, and E. Harvey, "The long range deposition of gunshot residue and the mechanism of its transportation," *J. Can. Soc. Forensic Sci.*, vol. 44, no. 3, pp. 97–104, 2011.

[38] R. Gauriot, L. Gunaratnam, R. Moroni, T. Reinikainen, and J. Corander, "Statistical challenges in the quantification of gunshot residue evidence," *J. Forensic Sci.*, vol. 58, no. 5, pp. 1149–1155, 2013.

[39] V. J. M. Di Maio, *Gunshot wounds*, vol. 53, no. 9. 1999.

[40] C. Bettin, "GSR for dummies Guida irriverente ai residui di sparo."

[41] Germani MS. "Evaluation of instrumental parameters for automated scanning electro-microscopy/gunshot residue particle analysis". J Forensic Sci 1991;36(2):331–42.

[42] E. S. Izraeli, T. Tsach, and N. Levin, "Optimizing FEG-SEM combined with an SDD EDX system for automated GSR analysis," *X-Ray Spectrom.*, vol. 43, no. 1, pp. 29–37, 2014.

[43] https://cool.culturalheritage.org/jaic/articles/jaic33-02-008_3.html. Accessed 3rd may 2020.

[44] Romolo FS, Trettene M, Bortolotti F, Schutz F, Tagliaro F. Rapid, "Selective and quantitative determination of nitrite and nitrate ions with capillary electrophoresis: a new screening tool for gunshot residue detection". Forensic Sci Int 2003;136:147.

[45] C. Hofstetter, M. Maitre, A. Beavis, C. P. Roux, C. Weyermann, and A. Gassner, "A study of transfer and prevalence of organic gunshot residues," *Forensic Sci. Int.*, vol. 277, pp. 241–251, 2017.

[46] L. S. Blakey, G. P. Sharples, K. Chana, and J. W. Birkett, "Fate and Behavior of Gunshot Residue—A Review," *J. Forensic Sci.*, vol. 63, no. 1, pp. 9–19, 2018.

[47] Burnett B. "The form of gunshot residue is modified by target impact". J Forensic Sci. 1989;34(4):808–22 [48] Fojtasek L, Kmjec T. "Time periods of GSR particles deposition after discharge - Final results". Forensic Sci Int. 2005;153(2–3):132–135.

[49] D. Merli, A. Brandone, A. Amadasi, C. Cattaneo, and A. Profumo, "The detection of gunshot residues in the nasal mucus of suspected shooters," *Int. J. Legal Med.*, vol. 130, no. 4, pp. 1045–1052, 2016.

[50] L. Fojtášek, J. Vacínová, P. Kolář, and M. Kotrlý, "Distribution of GSR particles in the surroundings of shooting pistol," *Forensic Sci. Int.*, vol. 132, no. 2, pp. 99–105, 2003.

[51] Gerard RV, McVicar MJ, Lindsay E, Randall ED, Harvey E. "The long range deposition of gunshot residue and the mechanism of Its transportation". Can Soc Forensic Sci J 2011;44(3):97–104.

[52] Lepik D, Vasiliev V. “Comparison of injuries caused by the pistols Tokarev, Makarov and Glock 19 at firing distances of 10, 15 and 25 cm”. Forensic Sci Int 2005;151:1–10.

[53] Deinet W, Leszczynski C. “Examinations to determine close-range firing distances using a process control computer”. Forensic Sci Int 1986;31:41–54.

[54] Ditrich H. Distribution of gunshot residues – the influence of weapon type. J Forensic Sci 2012;220:85–90.

[55] T. Jalanti, P. Henchoz, A. Gallusser, and M. S. Bonfanti, “The persistence of gunshot residue on shooters’ hands,” *Sci. Justice*, vol. 39, no. 1, pp. 48–52, 1999.

[56] MacCrehan WA, Patierno ER, Duewer DL, Reardon MR. “Investigating the effect of changing ammunition on the composition of organic additives in gunshot residue (OGSR)”. J Forensic Sci 2001;46(1):57–62.

[57] Lepik D, Vassiljev V. “Comparison of gunshot injuries caused from Tokarev, Makarov and Glock 19 pistols at firing distances of 1, 3 and 5 cm”. J Forensic Leg Med 2010;17(8):412–20.

[58] Nag NK, Sinha P. “A note on assessability of firing distance from gunshot residues”. Forensic Sci Int 1992;56(1):1–17.

[59] Wrobel HA, Millar JJ, Kijek M. “Comparison of properties of adhesive tapes, tabs, and liquids used for the collection of gunshot residue and other trace materials for SEM analysis”. J Forensic Sci 1998;43(1):178– 81.

[60] Degaetano D, Siegel JA, Klomparens KL. “A comparison of 3 techniques developed for sampling and analysis of gunshot residue by scanning electron-microscopy/energy dispersive X-ray analysis (SEM- EDX)”. J Forensic Sci 1992;37(1):281–300.

[61] Zeichner A. “Is there a real danger of concealing gunshot residue (GSR) particles by skin debris using the tape-lift method for sampling GSR from hands?” J Forensic Sci 2001;46(6):1447–55.

[62] Charles S, Lannoy M, Geusens N. “Influence of the type of fabric on the collection efficiency of gunshot residues”. Forensic Sci Int 2013;228 (1):42–6.

[63] Benito S, Abrego Z, Sánchez A, Unceta N, Goicolea MA, Barrio RJ. “Characterization of organic gunshot residues in lead-free ammunition using a new sample collection device for liquid chromatography–quadrupole time-of-flight mass spectrometry”. Forensic Sci Int. 2015;246:79–85.

[64] Mastruko V. “Detection of GSR particles on clothing of suspects”. Forensic Sci Int 2003;136(Suppl. 1):153–4.

[65] Zeichner A, Eldar B, Glattstein B, Koffman A, Tamiri T, Muller D. “Vacuum collection of gunpowder residues from clothing worn by shooting suspects, and their analysis by GC/TEA, IMS, and GC/MS”. J Forensic Sci 2003;48(5):961–72.

[66] Andrasko J, Pettersson S. “A simple method for collection of gunshot residues from clothing”. Sci Justice 1991;31(3):321–30.

[67] Twibell JD, Home JM, Smalldon KW, Higgs DG, Hayes TS. “Assessment of solvents for the recovery of nitroglycerine from the hands using cotton swabs”. J Forensic Sci 1982;27(4):792–800.

[68] Basu S, Ferriss S. “A refined collection technique for rapid search of gunshot residue particles in the SEM”. Scan Electron Microscopy 1980;1:375–84.

[69] J. French and R. Morgan, “An experimental investigation of the indirect transfer and deposition of gunshot residue: Further studies carried out with SEM-EDX analysis,” *Forensic Sci. Int.*, vol. 247, pp. 14–17, 2015.

[70] E. Lindsay, M. J. McVicar, R. V. Gerard, E. D. Randall, and J. Pearson, “Passive exposure and persistence of gunshot residue (GSR) on bystanders to a shooting: Comparison of shooter and bystander exposure to GSR,” *J. Can. Soc. Forensic Sci.*, vol. 44, no. 3, pp. 89–96, 2011.

[71] M. Cook, “Gunshot residue contamination of the hands of police officers following start-of-shift handling of their firearm,” *Forensic Sci. Int.*, vol. 269, pp. 56–62, 2016.

[72] S. Charles and N. Geusens, “A study of the potential risk of gunshot residue transfer from special units of the police to arrested suspects,” *Forensic Sci. Int.*, vol. 216, no. 1–3, pp. 78–81, 2012.

[73] French JC, Morgan R, Davy J. “The secondary transfer of gunshot resi- due: an experimental investigation carried out with SEM-EDX analysis”. X-Ray Spectrom 2014;43(1):56–61.

[74] Kilty JW. “Activity after shooting and its effects on the retention of primer residue”. J Forensic Sci 1975;20(2):219–30.

[75] M. Maitre *et al.*, “A forensic investigation on the persistence of organic gunshot residues,” *Forensic Sci. Int.*, vol. 292, pp.

1–10, 2018.

[76] Lloyd JBF. “Diphenylamine traces in hand swabs and clothing debris: cleanup and liquid chromatography with sequential oxidative and reductive electrochemical detection”. Anal Chem 1987;59(10):1401–4.

[77] Leggett LS, Lott PF. “Gunshot residue analysis via organic stabilizers and nitrocellulose”. Microchem J. 1989;39(1):76–85.

[78] Wolten GM, Nesbitt RS, Calloway AR, Loper GL. “Particle analysis for the detection of gunshot residue. II: occupational and environmental particles”. J Forensic Sci 1979;24(2):423–30.

[79] Z. Brozek-Mucha, “Chemical and physical characterisation of welding fume particles for distinguishing from gunshot residue,” *Forensic Sci. Int.*, vol. 254, pp. 51–58, 2015.

[80] Garofano L, Capra M, Ferrari F, Bizzaro GP, Di Tullio D, Dell’Olio M, et al. “Gunshot residue: further studies on particles of environmental and occupational origin”. Forensic Sci Int 1999;103(1):1–21.

[81] Mosher PV, McVicar MJ, Randall ED, Sild ED. “Gunshot residue— similar particles produced by fireworks”. Can Soc Forensic Sci J 1998;31(3):157–68.

[82] M. Grima, M. Butler, R. Hanson, and A. Mohameden, “Firework displays as sources of particles similar to gunshot residue,” *Sci. Justice*, vol. 52, no. 1, pp. 49–57, 2012.

[83] B. Cardinetti *et al.*, “X-ray mapping technique: A preliminary study in discriminating gunshot residue particles from aggregates of environmental occupational origin,” *Forensic Sci. Int.*, vol. 143, no. 1, pp. 1–19, 2004.