

REVIEW

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# Gunshot residue detection technologies—a review



Priya Shrivastava, V. K. Jain and Suman Nagpal\*

## Abstract

**Background:** Gunshot residue (GSR) is a shred of important trace evidence which helps forensic scientists solve a huge range of incidents related to firearms. The identification of the shooter to bullet identification from a gunshot wound help reconstruct a scene of the crime.

**Main body:** The review of this scientific paper is based on gunshot residue, its composition, and the growing advanced technology which allow us to study about how GSR analysis help to identify and detect residues. Various methods are acquired to identify and analyze organic and inorganic residues present when ammunition is fired. The review highlights the composition of GSR, its collection methods, and analysis part which emphasize on all the methods developed so far. The use of conventional methods including colorimetric and instrumentation-based analysis and advanced technology including electrochemical technique for detecting residues from the last 50 years. Spot tests or chemical tests were performed but they degrade the sample and can sometimes cause hindrance with some other nearby material present at the crime scene. Instrumentation techniques including AAS, ICP-MS, SEM, SEM-EDX, GC, HPLC, etc. are discussed in detail. Mostly advanced electrochemical methods developed are for inorganic gunshot residues (IGSR), but some researchers worked on both residues. Also, the fabricated electrochemical cells are replaced by a single strip-based technique for easy detection. So, to combat these issues, various scientists are moving towards sensor-based methods for rapid and reliable detection. These methods are more user-friendly, sensitive, and cost-effective and provide rapid detection results.

**Conclusions:** This review results in the composition of GSR, its collection methods, and analysis using sophisticated methods that emphasize all the methods developed so far and it also culminates the merits and demerits of all detection methods.

**Keywords:** Firearm, Gunshot residue, Electrochemical method, Detection, Inorganic, Organic, Technology

## Background

Most of the heinous crimes like dacoits, murder, assassination, violence, and police encounters involved the use of a firearm at a frequent rate. Thus, as an evidentiary value, a firearm plays a very crucial/important role in forensically related crime investigation (Aleksander I, 2003). Firearm-related evidence helps to get information about the scene of crime as it gives various answers to the “forensic experts like (1) whether death is because of murder, accident, self-defense, or suicide. (2) Gives a

brief idea about how the crime take place. (3) Distinction can be made whether the original incident took place or not. (4) Give information and estimation of range of firing, direction, and number of firearms used. (5) Helps to determine details about the firearm injury.

This review comprises the components, collection method, and gunshot residue (GSR) analysis at the crime scene, how it is collected and sent to the forensic laboratory and analyzing GSR samples and factors which interfere with the interpretation of the gunshot sample. Important organic and inorganic gunshot residues are discussed which include their formation, distribution, and collection technique with the analytical part. The

\* Correspondence: [snagpal@amity.edu](mailto:snagpal@amity.edu)

Amity Institute of Advanced Research and Studies (Materials & Devices),  
Amity University, Noida, Uttar Pradesh 201303, India

organic component includes various volatile compounds like nitroglycerine, nitro guanine, etc., while the inorganic part includes heavy metals like Pb, Ba, etc. According to the type of residue present at the crime scene, a modified type of collection and analyzing technique can be adopted (Brozek-Mucha, 2007). The areas from where these residues are collected include skin, vehicles (seats and seat backs, doors, windows, dashboards, headliners, interiors, and exteriors), nearby place of the incident, doors, windows, body parts where gunshot wounds are caused, clothing, and any surface in the immediate proximity of a firearm discharge. There are numerous techniques which are used for GSR sample collection and selecting the most appropriate one is important in ensuring maximum collection efficiency. Collection techniques include tape lifting, swabbing, vacuum, and glue lift (Dalby et al., 2010). The collected samples were then extracted in the laboratory for further analysis. The analysis technique applied for detecting GSR includes color test, instrumentation, and electro chemical sensor-based methods. Color spot tests including the paraffin test, dermal nitrate test, Walker's test, and Marshal and Tiwari test were used along with another spot test. But these tests were found to be insufficient for analysis since they will destroy the sample and show interference with other environmental constituents. From the 1960s to the 1970s, these tests have been continuously used in several laboratories, but they are not specific for GSR thus found to be less used nowadays. Thus, the instrument-based technique for organic and inorganic constituents came which replaced the color spot test. Using this technique, bulk elemental analyses have been made possible. The technique is helpful in measuring the total amount of elements present in a sample. First came the neutron activation analysis (NAA) for detecting antimony and barium found in GSR. Then came the atomic absorbance spectroscopy (AAS) which was helpful in making a difference between the person who fired a weapon and the person who did not. It detects Pb, Ba, and Sb even if trace amounts of these metals are present. The technique gives a 90% positive result in GSR detection. Another technique, inductively coupled plasma spectroscopy (ICP), came along with a combination of mass spectrometry. It allows rapid and various element analyses but lacks sensitivity than AAS and NAA. This method has been better when extracted samples were analyzed. Then came the particle analysis technique using scanning electron microscopy-energy dispersive X-ray analysis (SEM/Edx) and found to be a more powerful technique to identify GSR (Germani, 1991; Wolten et al., 1979). The method reveals both the morphology and chemical composition of a gunshot residue. The organic component detail, which originates from the propellant, is helpful in identifying the criminal case several times.

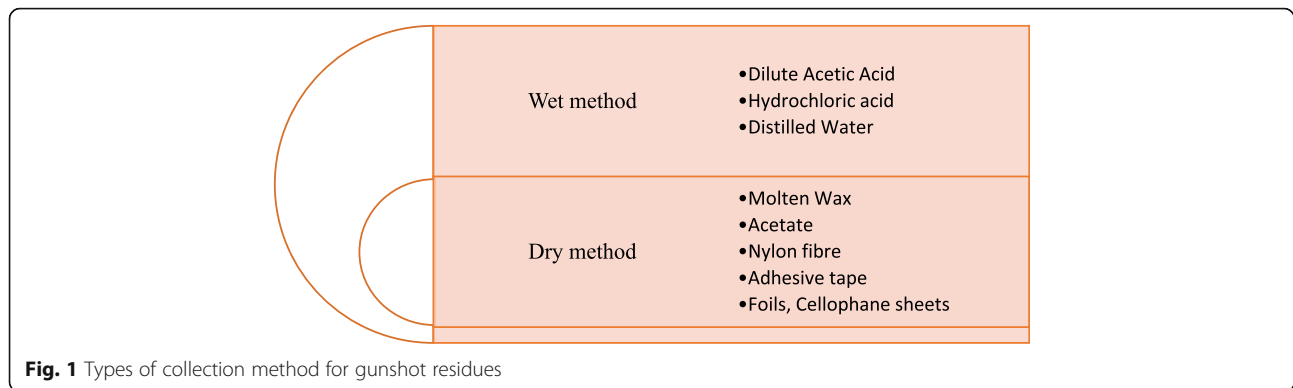
Gas chromatography (GC) was applied for the first time which gives the presence of organic compounds like diphenyl amine (DPA), nitrocellulose (NC), nitroglycerine (NG), ethyl centralite (EC) (Espinoza & Thornton, 1994). GC combined with other spectrometries like gas chromatography-mass spectrometry (GC-MS) and ion mobility spectrometry (IMS) came as a powerful tool for detecting organic constituents. For identifying nitro diphenylamine (NDPA), 2-NDPA, 4-NDPA, EC, and other organic constituents, high-pressure liquid chromatography (HPLC) was performed. Stabilizers collected from swabbing gave positive results in identifying GSR. Fourier transform infrared spectroscopy (FTIR) and Micellar electro kinetic capillary electrophoresis (MECE) helps to detect nitrocellulose and explosive, stabilizers/additives respectively in GSR. Raman spectroscopy based on vibrational frequency can image and characterize particulates present in GSR. The technique has the drawback of not analyzing the component which has metallic constituents in it. All these methods give accurate results but are costly and require highly specialized personnel to handle the instrument in the laboratory. So, to overcome this problem, electrochemical methods came as a promising tool. The method is portable and reliable, has low-cost production, and takes less time in detection in comparison to instruments and color-based tests. Increasing technology leads to advancements in techniques like electrochemical-based sensors. Various electrode-based modules were prepared for easy swabbing of samples.

Numerous works have been done on analysis of gunshot residue using different methods. Our main aim here is to compile all the developed technology for the analysis of GSR. Either from the simple colorimetric method developed since the 1900s to all the heavy instrument-based methods to the simple most reliable electrochemical-based method for both types of residue, the organic and inorganic constituents. Here, a brief view on the type of components and their collection method is also discussed (Fig. 1). The manuscript also covers the merits and demerits of the detection method.

## **Main body**

### **Components of gunshot residues**

Basic components in gunshot include inorganic and organic residues. Most of the organic constituents arise from propellant and lubricant material while inorganic constituents originate from primer, propellant, case, core of the jacket, and ammunition barrel as reported by many scientists (Brozek-Mucha, 2007; Dalby et al., 2010; Brozek-Mucha, 2009). The size of the particle also varies from 0.5 to 10  $\mu\text{m}$  while some reported the size of 100  $\mu\text{m}$  as well (Romulo & Margot, 2001). The constituents of a gunshot escape from the firearm's open part, the



vapor formed materials then get solidified and changes into particulates of varying sizes which help forensic scientists to analyze these particles. In 1250, Roger Bacon is the first one to give information about black powder which is now replaced by smokeless powder. These smokeless powders usually consist of nitroglycerine, nitrocellulose, and some single- and double-base powders. These constituents also contain various lubricants, additives, coolants, inhibitors, plasticizers, etc. (Showable & Edline, 2000). The composition of the inorganic constituent's primer varies from manufacturer to manufacturer. In 1921, the first modern formulation came which contains lead styphnate, barium nitrate, and antimony trisulfate (Harrison & Gilroy, 1959; Basu et al., 1997). The heavy metals present in ammunition cause various harmful problems to the environment and humans too. So, some researchers produce lead-free ammunition (Gunaratnam & Homberg, 1994). Inorganic GSR came from the primer cup, bullet jacket, bullet, barrel, etc (Harris, 1995). while organic compounds were expelled from the propellant and primer part. The major constituents present at the scene of crime (SOC) including organic and inorganic gunshot residues are illustrated in Table 1.

#### Collection method for gunshot residue particle

Gunshot residue can be collected from various areas based on the place and type of crime whether it is a homicidal or suicidal case. The site from where the samples are collected include vehicular sites like seat belts, seats, headlines, inner or outer part of the vehicle, nearby region of the incident, body regions, clothes, target area, and the intermediate part (between target and gun) (Heard, 1997; Jalanti et al., 1999; Murdock, 1984) as shown in Fig. 2. The efficiency of collecting samples greatly affects the analysis of GSR. With time, the particles of GSR start decreasing (Douse & Smith, 1983; Jane et al., 1983; Reiss et al., 2003; Vinokurov et al., 2001; Gialamas et al., 1995). Usually, after firing, the sample starts to

degrade within the first 2 h till 12 h at a high rate, depending on explicit limits. Thus, with each passing hour, there is more and more degradation of evidence as lesser GSR particles are left for accurate analysis leading to difficulty in detection sensitivity. Depending on the residue type present at the SOC whether organic or inorganic, the collection method varies. But the basic type of collection methods is of 2 types as shown in Fig. 1. The dry method includes molten wax, cellulose acetate, nylon fiber, adhesive tapes and foils, and cellophane sheets for gunshot residue particle collection, while wet methods include diluted acetic acid and hydrochloric acid and sometimes distilled water. In collecting the maximum amount of particulate matter present in a gunshot residue sample, the most appropriate method is applied. The details of various methods are given in detail below with basic idea in Table 2.

#### Paraffin method

In this method, a paraffin coat is poured on the victim's hand and left there for a few minutes to entrap the residues. According to Locard's principle, the GSR gets deposited on the paraffin and then further analyzed for the type of residue present.

#### Washing

This method includes the washing of the sample area using acid or sometimes water. Here, the hands of shooters or nearby areas at the scene of crime are washed with dil.  $\text{HNO}_3$  and dil. HCl and then these are collected in a plastic bottle.

#### Tape lift method

A simple technique which uses tape to lift the particles or residues from the region where the crime occurred. This method usually involves adhesive tapes that can easily trap the samples. The tape lifting method was found to be widely used whether it is a fingerprint examination and explosive or gunshot residue analysis. The

**Table 1** Major inorganic (IGSR) and organic (OGSR) particle present in Gunshot Residue encountered at the SOC (scene of crime)

Inorganic constituents	Source	Organic constituents	Source
Lead	Bullet and primer	Nitroglycerine	Primer mix/propellant mix
Barium	Primer	Nitrocellulose	Double-base propellant/primer mix
Antimony	Primer	Diphenylamine (DPA)	Single-base propellant powder
Copper	Jacket of bullet	Ethyl centralite (EC)	Double-base powder/Propellant powder
Iron	Barrel/bullet	Ethyl phthalates	Plasticizers/propellant powder
Chromium	Propellants	Glycerol triacetate	Plasticizers
Nitrates	Inorganic oxide and from propellants	Nitro guanidine	Plasticizers/propellant powder
Nitrites	Propellants	2,4-Dinitrotoluene(DNT)	Flash suppressant/Propellant powder
Zinc	Jacket/Primer cup/Primer mix	2,6-Dinitrotoluene (DNT)	Flash suppressant/propellant powder
Nickel	Nickel coating of shell/case	2,3-Dinitrotoluene(TNT)	Flash suppressant/propellant powder
Sodium nitrate	Primer mix	2,4,6-Trinitrotoluene	Propellant powder/primer mix
Mercury	Primer mix	Akardite II (AK II)	Propellant powder
Potassium	Propellant/primer mix	Methyl centralite (N, N-dimethyl carbanilide)	Propellant powder
Magnesium, aluminum	Primer mix	Cyclonite (RDX)	Propellant powder
Cupro-nickel	Bullet jacket	Pentaerythritol tetra nitrate (PETN)	Propellant powder/primer mix
Zirconium powder	Reducing agent	Benzo nitrile	Combustion byproduct
Tungsten	From bullet	Ethyl centralite	Stabilizer
Tin	Cartridge case	Aniline	Combustion byproduct
Strontium	Oxidizer	Anthracene	Combustion byproduct
Stannic oxide	Oxidizer	Indole	Combustion byproduct
Phosphoric acid	Oxidizer	Naphthalene	Combustion byproduct
Mercury fulminate	Explosive	Nitrobenzene	Explosive
Mercury	Explosive	p-Cresol	Stabilizer
Phosphorus	Cartridge case	Toluene	Combustion byproduct
Manganese/beryllium	Fuel	Picric acid	Explosive
Bronze/brass	Cartridge case	Phytane	Stabilizer

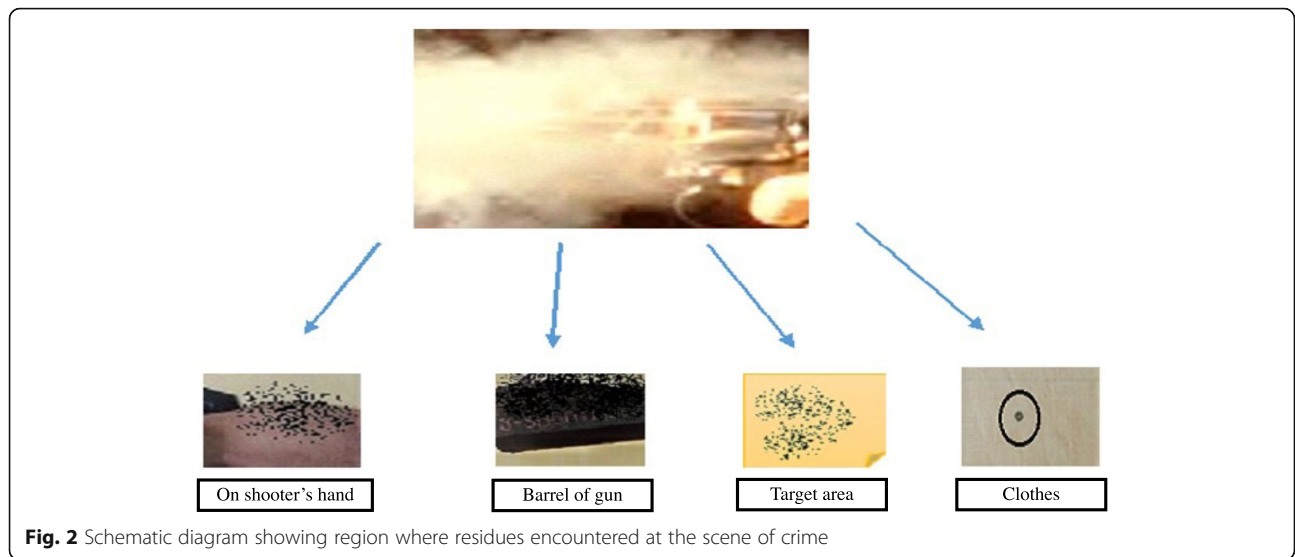
DNT 2, 4-dinitrotoluene, TNT trinitrotoluene, PETN penta erythritol tetra nitrate, AK II akardite II, RDX cyclonite, EC ethyl centralite, DPA diphenylamine

most used technique for collecting inorganic residue from the surface including skin, hair, or some other mediums (Zeichner & Levin, 1993; Shaffer & Yi, 1999; Wrobel et al., 1998). For sampling of gunshot residue, De Gaetano et al. use 3 methods for lifting: (a) tape lift (b) glue lift, and (c) centrifugal concentration technique (De Gaetano et al., 1992). Sild et al. also gave some methods where plasma ash of tape samples proved to be an important technique to reduce organic material, resulting in easy analysis of GSR which were present on the surface of the tape lift (Sild & Pausak, 1979). But Veretto (Veretto, 1990) in 1990 says that only the plasma ash method was inefficient, using oxygen plasma ashing with an electron beam of SEM to destroy the skin epidermis cells. On hair, collection of the GSR was observed as a great

task to carry out. Some say this method is unsuitable for collection, while Zeichner (Zeichner, 2001) reported that this method does not show much variation than swabbing with hair comb and solvent method; thus, the tape lift was found to be an acceptable method.

#### Swabbing

Swabbing means using some adsorbent surface for the collection of samples from the surface. Twi bell et al. (Twibell et al., 1982) used 8 solvents for collecting nitroglycerine from hand samples. From all the solvents, ethanol acts as the best solvent with more stability and recovery was consistent with this solvent. When organic samples were extracted, inorganic samples were extracted also; they are on the swab and



**Fig. 2** Schematic diagram showing region where residues encountered at the scene of crime

then recovered for characterization by SEM/Edx in an organic solvent using membrane filtration of extract as reported. Lloyd and King (Lloyd & King, 1990; Lloyd, 1986) gave a method by which swabs of water extraction along with solid-phase extraction (SPE) act as an effective process for the organic explosive present on cotton swabs using liquid chromatography or GC-MS.

**Glue lift method**

Here, sticky glues were poured over the sample, dried, and then lifted from the surface containing a huge amount of evidence. In comparison with tape lift, this method was found to be more effective as it is less sticky than tape. On analysis, the sample collected from the glue lift contains less interfering particles when SEM

**Table 2** Techniques applied to extract or lift the sample from different areas at the SOC

Method of extraction/lifting	Material used	Extraction region	Merits	Demerits
Paraffin method	Paraffin, wax	Hands	1. Method found to be very effective and easy to perform in less time.	1. The method is bulky and cannot withstand with heavy instrumental method. 2. Another disadvantage is sometime gave false positive test.
Washing method	Acid or water (dil. HNO <sub>3</sub> and HCl)	Hands, nearby materials	1. Advantageous as the quantity of residue came to be high in less time period.	1. Disadvantage of the method is on using acid may cause interference issues while performing detection of the specific inorganic residues.
Tape lift method	Adhesive tape, selotape double-sided	Hands, clothes, and hairs	1. Most commonly used procedure for collecting inorganic residues from skin, hair, and other mediums also. 2. Another advantage is it is more effective than swabbing and the method is cheap, with good collection efficiency, and thus able to perform well in SEM.	1. Major drawback of the method is when collecting sample from clothes other debris materials or fiber may get lifted.
Swabbing method	Cotton ball, filter paper, organic solvent (acetone, ethanol, etc.)	Barrel, hands	1. The solvents used give consistent and stable recovery.	1. Major disadvantage is the interference issues since other compounds or materials may also get dissolved in the solvent.
Glue lift method	Sticky glues	Hands	1. Advantage in using this technique is its less tacky nature than tape lift. 2. Because of less tacky nature it require less dabs on skin surface and thus collect less debris which would be helpful while SEM analysis.	1. Major drawback is its ineffective nature of lifting. 2. The method may not be found effective in analysis of sample on clothes.
Vacuum lift method	Filtered trap attached to vacuum	Clothes	Major advantage of the method is it is helpful in collecting samples from the cloth from the surface as well as depth of the material.	Disadvantage is while collecting sample from the depth which became problematic as it increase the difficulty of interpreting sample analysis, as particle from other shooters may be present.



was performed as reported by Basu et al. (Basu et al., 1997) and thus a better way to lift the sample, while De Gaetano et al. (De Gaetano et al., 1992) say glue is a less effective medium for gunshot residue sample extraction.

#### **Vacuum lift method**

The sample which needs to be collected is vacuumed up and collected onto a filtered trap which is attached to the vacuum. The collected sample is then packed in a clean trace paper and then submitted to the laboratory for further analysis. The vacuum collection of the organic gunshot residue sample using 2 types of filter that is fiberglass and Teflon was developed by Zeichner et al. (Zeichner et al., 2003) in their paper. Tape lifting followed by vacuum lifting was found to be more effective to collect residues. Mastruko (Mastruko, 2003) said that vacuum lifting can be applied above and at the depth of the cloth. Andrasko and Patterson (Andrasko & Peterson, 1991) analyzed that tape lifting was not that much suitable for collection of gunshot residue from clothing as it causes the lift of debris or other fiber materials into the sample extraction and thus vacuum lifting is more suitable than tape lifting as it interferes while performing SEM.

#### **Collection using human mucus**

Noses have hair along with mucus, i.e., liquid and some protein which can trap the particle. When a firearm gets discharged it releases gases which usually settled down on the hair of the nose, so the collection of these particles becomes important. When a person is in the region of the firearm, there comes a problem in its collection method. For airborne residue collection from nasal mucus of humans, a technique was reported by Schwartz et al. (Schwartz & Zona, 1995). He collected the sample by a simple blowing of the nose onto a 5 × 5 piece of substance and it was found that this method contains particles even after 48 h of firing and helps to determine whether the person fired or not.

#### **Gunshot residue particle collected from hairs**

When firing was done, particles settled on hair and help in determining whether the person was present near firing or not. Various methods were developed for collecting gunshot residue from hair like the comb method, swab, and tape lifting according to Zeichner et al. (Zeichner et al., 2003). Mac Creehan et al. (Mac Creehan et al., 2003) reported that when plume from the breach end exit discharge suddenly, it got collected near the front part of the face and head. Twenty-three tests were performed using a wig of human hair out of which 20 tests were found to be positive. Most of the difficulty was encountered in the case of curly hair as combs have very fine teeth. A comparison was made between

residues collected from the inside of the cartridge and from combed samples. From the data, it was concluded that residue collected from the combed method and cartridges showed a good result in comparison with unburned powders.

#### **Analysis technique or evaluation of gunshot residue**

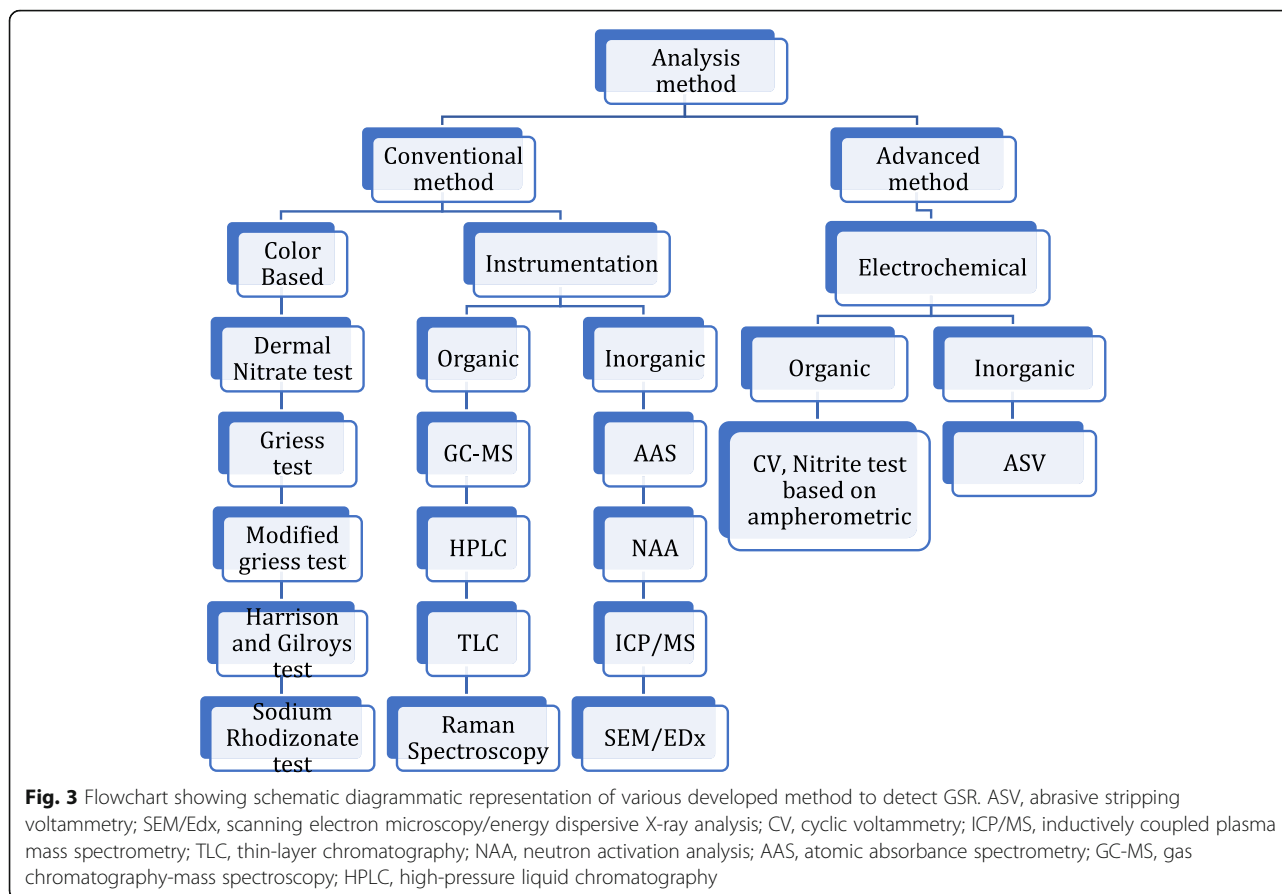
If a firearm is discharged, GSR particle left the firearm and is deposited somewhere else, so to evaluate the particle, various techniques were developed (Matricardi & Kilty, 1977). These techniques gave quantitative as well as qualitative value of components of GSR in micro or Nano quantities. From the very beginning of the 1900's, various color tests were developed for detection of gunshot residue in various laboratories. But these color tests destroy the sample and require more amount of samples with less frequent results. So, with developing technology, various instrumental techniques have taken place of the color test for the analysis of inorganic and organic gunshot residues which are used as a frequent analyzer for these residues. This method also helps to know the distance of firing a weapon. Various types of analysis methods developed so far are shown in Fig. 3. To analyze these residues, the first color test was performed then instrumentation techniques, and to overcome these bulky instrumental techniques, later, the electrochemical methods were adopted which require less trained personnel (Wolten et al, 1977).

#### **Color/spot test for detection of gunshot residue**

These tests can be used to estimate the distance of firing and bullet hole causing the wound and gave frequent results for analyzing GSR. All the developed color tests are illustrated in Table 3 giving a brief idea of all the color tests performed to analyze GSR.

**Dermal nitrate test/paraffin test** Teodoro Gonzalez, in 1933, introduced the dermal nitrate test which involves the use of diphenylamine dissolved in strong H<sub>2</sub>SO<sub>4</sub>. The name of the test itself signifies that it can be applicable to nitrates (Tagliaro et al., 2002). From partially burnt or unburnt propellant particles, these tests gave a deep blue coloration. Some other common materials also gave positive test with paraffin test and thus was not further applied. After this, the Griess test was found to be more suitable.

**Griess test or Walker's test** First described in 1858 by Peter Griess who gave the Griess reagent for the determination of nitrite ion present in solution (Griess, 1858). The test was mainly performed for nitrites present in GSR. Here, bromide paper was treated with 2-naphthylamine 4:8 disulphonic acid (about 5%); then, the treated surface of the bromide paper was placed on the



top and the cloth sample bearing the sample of gunshot placed over it and covered with 20%  $\text{CH}_3\text{COOH}$  and then pressed with a hot electric iron. A dark red color spot indicates the presence of GSR (Walker, 1940).

**Modified Griess test** The test is basically for detecting nitrites present in GSR. Here, the procedure is the same as the Griess test but includes a step where filter paper is sprayed with 2 naphthyl amine sulphanilic and citric acid. A pink color gave the indication of nitrites.

**Harrison and Gilroy's test** Harrison and Gilroy in 1959 gave this method to detect the metallic constituents present in firearm discharge residue (Harrison & Gilroy, 1959). In this test, a swab moistened with dil. HCl was used for collecting GSR from the hands. The swab was dried and then treated with tri-phenylarsonium iodide, then sodium rhodizonate was added. If the color changes to orange, antimony might be there. The second change to red gave an indication of both lead and barium, and on adding dil. HCl, the spot changing to purple indicates lead may be present. No change in color indicates the presence of barium. The test was found to be very useful in identifying the shooter or bullet hole present at scene of crime (SOC). Results that come out cannot be

quantified and some other materials interfere here too. This test gave an unstable color and suddenly changed to another.

**Sodium rhodizonate test** The test is specifically for Pb detection. Here, GSR samples were procured on a cloth piece from hands with 1% HCl. The reagent sodium rhodizonate in the reaction reacts with metallic divalent ions thus forming colored complexes. Depending on the pH, the color varies from blue to violet. The test can be helpful in determining lead in any form whether it is in vapor form, particulate lead, in primer residues, in lead bullet, or shot pellet. Solution colors depend on the pH, as color becomes blue-violet when neutral pH while at pH below 3 shows a very bright red coloration with orange tint for lead metal and barium shows a red-brown color at any pH (Lloyd, 1986; Steinburg et al., 1984; Bartsch et al., 1996). The test further shows positive for Ca and Sb at pH 7, but no change was seen at acidic pH.

**Lunge test** Originally, it was the dermal nitrate test. Here, the reagent consists of diphenyl benzidine and is found to be carcinogenic, so in place of this, diphenylamine has been used. This gives a deep blue color in the presence of nitrites. Here, the reagent was sprayed onto

**Table 3** Color test performed for the detection of GSR

Color test/references	Constituent detected	Color change	Merits	Demerits
Dermal nitrate test (Forensic ballistics, Chemical analysis of gunshot residues (GSR), <a href="#">n.d.</a> )	Nitrates	Blue color spots	1. Major advantage of this test is that it can be applied to all nitro groups' compound analysis.	1. Disadvantage is that it give false positive result in presence of tobacco, leguminous plants, fertilizers etc.
Walker's test/Griess test (Griess, <a href="#">1858</a> )	Nitrites	Red color spots	1. Advantage in using this technique is that it can be helpful in detecting the nitrites in partially burnt and unburnt propellants.	1. Disadvantage is many compounds other than nitrocellulose propellants can give positive reaction e.g. Urine, fertilizer, face powder etc.
Modified Griess test	Nitrites	Pink color	1. Major advantage of this technique is that it can be performed within few minutes and found to be better than dermal nitrate test.	1. It can be applied to detect nitrites only but not for GSR.
Harrison and Gilroy's Test (Harrison & Gilroy, <a href="#">1959</a> )	Pb, Sb, Ba	Sb—orange ring Pb—blue color Ba—red color	1. More successful than dermal nitrate test as it cause less false positive cases. 2. Another advantage is that it can be easily applied to detect GSR samples on hand swabs.	1. Interference with other materials at the SOC can be obtained.
Sodium rhodizonate test (Steinburg et al., <a href="#">1984</a> ; Bartsch et al., <a href="#">1996</a> )	Pb Ba	Blue to violet (pH 7) Bright red color (pH 2.8) Red-brown (any pH)	1. Major advantage of this color test is that it can detect lead and its form in trace level.	1. Major disadvantage with this is it cannot be applied for Ba detection
Lunge test (Forensic ballistics, Chemical analysis of gunshot residues (GSR), <a href="#">n.d.</a> )	Nitrocellulose/ nitrites	Deep blue color	1. Major advantage is it can be performed in few minutes	1. Major disadvantage is it can give positive reaction with other everyday used chemicals. 2. Not further applied for detecting GSR on hand swabs.
Di-thio-oxamide (DTO) test (Forensic ballistics, Chemical analysis of gunshot residues (GSR), <a href="#">n.d.</a> )	Copper, nickel, cobalt	Copper—very dark-green coloration, nickel—pink to violet color, and cobalt—brown color	1. Advantage in using this color test is that it can be applied to detect Cu, Ni and thus helpful in the case of Cupro-nickel-jacketed bullet. 2. Utilized for determining the bullet entry and exit holes in case of fully jacketed gilding metal (Cu/Zn) and cupro-nickel (Cu/Ni) bullets.	1. Drawback with the color test is its applicability to detect nitrites only and not for GSR. 2. Another disadvantage is in presence of blood false negative result can be obtained.
Marshall test (Forensic ballistics, Chemical analysis of gunshot residues (GSR), <a href="#">n.d.</a> )	Nitrites	Purple spots	1. Advantage of the chemical is that it mainly performed to detect the propellant particles in range of firing estimations	1. The test is specific for nitrites and not for GSR
Tewari test (Forensic ballistics, Chemical analysis of gunshot residues (GSR), <a href="#">n.d.</a> )	Nitrites	Yellow spot	1. Advantage of this test is that it is mainly used for determining range of firing estimations by visualization of propellant particles.	1. Performed specifically for nitrites and not for GSR

the cast prepared from the paraffin cast taken from the suspect's hands (Forensic ballistics, Chemical analysis of gunshot residues (GSR), [n.d.](#)).

**Marshall and Tewari test** The method used for detecting propellant particles for estimation of a range of firing cases. Here, the desensitized photographic paper is soaked in 0.5% sulphanic acid for 10 min. Then, after drying the sample, it is then dipped in a solution of N- $\alpha$  naphthyl-ethylenediamine hydrochloride in methanol for 2 min. Again, after drying, the sample is wetted with 20% acetic acid and placed under clothing. The photographic paper is then placed at the top and covered with a dry cloth and given warmth using an iron press for 5

min. A purple color spot gave the presence of nitrites. In the case of the Tewari test, 1 gm of antazoline hydrochloride was dissolved in 50 ml of water, and then, 45 ml of conc. HCL was added until the white precipitate dissolves, then filter paper soaked in acetone was placed over the sample to be tested. It is then air-dried and then deep yellow spots gave the presence of nitrites in the solution (Forensic ballistics, Chemical analysis of gunshot residues (GSR), [n.d.](#)).

**Di-thio-oxamide test** The test was used basically for Cu and Ni which made the bullet jacket in the case of ammunition. Here, the reagent made should be fresh and prepared using 0.2 g of di-thio-oxamide (DTO) in



100 ml ethanol (Forensic ballistics, Chemical analysis of gunshot residues (GSR), *n.d.*). Then, 20 ml of ammonium hydroxide dissolved in 50 ml of distilled water and filter paper moistened with this reagent is pressed onto the hole of the bullet and dropping 3 drops to it gave the indication of Cu by a change in color to gray/greenish color, and for nickel, it will give a blue or violet color.

#### **Instrumentation techniques for IGSR (inorganic) and OGSR (organic) gunshot residue detection**

The details of all the developed instrumentation methods for the detection of organic and inorganic residues present in GSR are elaborated in Table 4.

**Detection of inorganic gunshot residues** Inorganic residues consist of various elements whose detection needs to be done and these elements are bulky in nature. So, the bulk analytical technique is applied which includes NAA, ICP, AAS, and SEM/Edx.

**Neutron activation analysis** First introduced in Denmark by Levi in 1936 (Minc L, 2008). It is based on the principle of optical emission spectroscopy where a sample is placed to emit light by excitation with an electric arc. Each element produces a characteristic spectrum by which it can be identified. The most sensitive, non-destructive, and effective method with a detection sensitivity of about 1 ng only and helps in determination of trace quantities of a broader range of elements (20–30 elements) simultaneously. Mainly Sb and Ba can be identified by the method as examined earlier by various scientists (McFarland & McLain, 1973; Rudzitis & Wahlgren, 1975). It came as the first instrumental technique for the detection of Sb and Ba present in gunshot residue. According to Capannesi et al. (Capannesi & Sedda, 1992), this technique helps to examine the trace elements coming from the jacket of bullet fragments and lead core. In 1975, Kilty proposed some work based on NAA as these gunshot residues transfer from hand to hand and even from hands to clothing and thus determine Ba and Sb in his experiment (Kilty, 1975).

**Flameless atomic absorbance spectroscopy** The first form of AAS was developed by the Australian chemist named Sir Alan Walsh in the 1950s. The most powerful instrument for quantitative determination of trace elements in liquid (Bunsen & Kirchhoff, 1950). This method provides a total metal content of the sample and is independent of its molecular form. It works on the principle that free atoms generated in an atomizer absorbed radiation at a specific frequency. After NAA, a very sensitive and convenient technique for elemental

detection of gunshot residue came. It can detect elements in nanograms and pictograms depending on the principle of where elements absorb the radiation of the same wavelength it emits when excited. First, the AAS-based detection of gunshot particles was reported in 1971. Based on the amount of element or metal constituents, AAS help to reveal the information whether a person fired or not. Results obtained using these techniques gave approximately a 90% case at success. It is a method which is very sensitive for detection of lead metal in GSR samples but gives less result in Ba and Sb amount. To determine Ba and Sb, only atomic absorption spectroscopy is not sufficient while flameless or electrochemical atomizer help to analyze these metals. Some researchers applied fluid nebulizer with flame furnace AAS to improve the detection of tin, in comparison with conventional flame AAS. When compared with conventional AAS, fluid nebulization was found to be more sensitive and with a less detection limit.

**Inductively coupled plasma mass spectrometry analysis** It is an instrument which utilizes coupled plasma to ionize the sample made up of argon gas. The method is applied to detect metallic and non-metallic species in a liquid sample even at a very low concentration. It works on the principle of optical emission spectrometry where plasma energy is given to the sample from the outer region leading to the excitation of atoms; when these atoms come at the lower position, spectrum rays are released, and their photon wavelength can be measured. It is a bulk analysis technique for the analysis of elements present in the primer. The method allows very fast and multi-elemental analysis, but the limit is its sensitivity. It is more advantageous when an extracted sample was analyzed, in the GSR solution.

**Scanning electron microscope X-ray emission** The first scanning electron microscope with very high resolution came in 1937 by Manfred von Ardenne. In SEM, a beam of electrons is bombarded onto a specimen and then the image is formed (von Ardenne, 1937). SEM is a powerful instrument equipped with an X-ray analyzer which emits X-ray providing a morphological feature of the element which needs to be analyzed. The instrument is non-destructive and allows the highest specificity in detection of gunshot residue. The basic principle involved here is scattered electrons which are emitted from the surface of a specimen. In 1968, research for detection of GSR elements was done using SEM/Edx first carried out in England (Ward, 1982). The identification of elements based on morphological features is very important in detecting GSR particles.

The uses of morphological and elemental indicators help to differentiate one ammunition from another and

**Table 4** Combined analysis of organic and inorganic gunshot residues using instrumentation technique

Instrumental technique	Researcher	Constituent detected	LOD	Detection time	Merit	Demerit
<b>Gas chromatography</b>	Toal et al., (2014)	NG, TNT, RDX, PETN	NG—10 ng, TNT—10 ng, RDX—10 ng, PETN—0.5 ng	Less than 20min	1. Major advantage of the technique is when combined with MS, SEM-EDx, TEA, etc. will able to detect organic as well as inorganic residues present in GSR. 2. Another advantage is its capability of detecting compounds of interest in nanogram level.	1. Major drawback of the method is its inability to analyze Nitrocellulose as it not much volatile.
	Roberts et. al (2015)	NG, DNT, DPE	0.34–1.4 mM	Less than 25min		
	(Wu et al., 2001)	4-NDPA, 2-NDPA, 2,4-2NDPA, DPA, N-NDPA	0.05–1 ng	Less than 10min		
	Moran et.al (2014)	DPA, 2-NDPA, 4-NDPA, DMP, EC	–	–		
	Mach et.al (1978)	EC, NG, DPA, DNT,DP	–	–		
<b>High-pressure liquid chromatography</b>	Gassner et.al (2016)	AKII, MC, N-N-DPF, EC, DPA, 2-NDPA, 4-NDPA, N-NDPA	0.005–3.5 ng/ml	Less than 7 min	1. Advantage in using the technique is for analyzing OGSR with various types of detector. 2. Another advantage is its high reproducibility, sensitivity and give stable result.	1. Major drawback of this method is that it can detect organic components with more positive results in spite of inorganic residues.
	Laza et.al (2007)	DPA, AKII, 2-NDPA, EC, MC	In nanogram quantity	Less than 10 min		
	Taudte et. al (2016)	32 organic constituents	0.03–0.2 ng	27 min		
	Xu et. al (2004)	21 nitroaromatics, amines and some Nitric Esters	0.012–1.2 ng	–		
	Maitre et.al (2018)	NDPA, DPA, MC, EC	0.01–5 ppm	Less than 20min		
<b>Capillary electrophoresis</b>	Mac Creehan et.al (1998)	NG, NB, 2,4-DNT, 2,6 DNT, DPA, EC	–	Less than 15 min	1. The advantage of the technique is that it is rapid, with high-resolution separation of complex mixture. 2. Another advantage is when combine with ME than electrically neutral compound can also be separated.	1. Major drawback of the method is its poor detection limit for some compounds.
	Reardon et.al (2001)	NG, DPA, N-NDPA, EC	–	–		
	Northop et.al (2001)	NG, DPA, DNT	–	–		
<b>Thin-layer chromatography</b>	Meng et.al (1994)	EC, NC, NG	–	–	1. Major advantage of using the technique is its ability to detect residues in ppb and ppt levels.	1. Major drawback of this technique is it depends on the volatility and polarity of the molecule to be detected. 2. Only applicable to detect the organic constituents [resent in GSR.
	Leggett et. al (1989)	NC	–	–		
<b>Raman spectroscopy</b>	Lopez et.al (2016)	DPA, NC, N-NDPA, 2-NDPA, 4-NDPA, EC	–	Less than 60 min	1. Main advantage of this technique is its non-destructive nature. 2. Another advantage of the technique is its ability to detect both organic and inorganic residues present in GSR sample.	1. Major drawback of the method is its low sensitivity and cannot be applied for trace constituent's level analysis.
	Khandasammy (2019)	Organic constituents	–	–		
<b>Neutron activation analysis</b>	Chohra et. al (2015)	Pb, Ba, Br, Sb, Sn, Cr, Ti, Fe, Bi, Zn, Na	–	2 h	1. The method helpful for quantitative and qualitative analysis for elemental detection. 2. The method is extremely sensitive and accurate and can detect element in pico- and	1. Major disadvantage of the method is it require access to research nuclear reactor. 2. The instrument require huge amount of sample and require specialized personnel
	Merle et.al (2016)	Ba, Sb	0.005–50.31 µg	12 h		

**Table 4** Combined analysis of organic and inorganic gunshot residues using instrumentation technique (Continued)

Instrumental technique	Researcher	Constituent detected	LOD	Detection time	Merit	Demerit
<b>Atomic absorption spectroscopy</b>	Gibelli et.al (2010)	Sb	0.07–13.89 µg	–	nanogram quantity.	for handling it.
	Ruch et.al (1964)	Ba, Sb	0.05–10 µg, 0.01–0.03 µg	–		
	Pillay et.al (1974)	Ba, Sb, Cu, Au	0.01–1.085 µg	–		
	Yukshel et.al (2016)	Pb, Sb, Ba	35–800 ng per swab	–	1. Major advantage of this technique is the applicability in the detection of Ba <sup>2+</sup> , Pb <sup>2+</sup> , Sb <sup>3+</sup> in nano- and picogram quantity.	1. Major drawback of this technique is its heavy cost and require highly specialized personnel for handling.
	Raver by et.al (1982)	Tin	–	–	2. Another advantage of this technique is that it gives 90% of positive results.	2. Another disadvantage of this method is it require huge amount of sample for detecting the metal constituents
	Koon et. al (1987)	Sb, Ba	–	–		
<b>Inductively coupled plasma spectroscopy</b>	Koon et. al (1988)	Ba, Pb, Sb	0.5–1.4 ng	–	1. The technique is for bulk analysis to detect all the 3 major inorganic residues even in trace levels.	1. Major disadvantage of this technique is that it require more amount of sample for analysis.
	Costa et.al (2016)	Pb, Ba, Sb, Al, Ti, Cr, Mo, Cu, Zn, Sr	0.119–10.9 ng/ml	–	2. Result obtained with this technique is positive in 80–90% of cases	2. The technique is non-destructive, time consuming and require highly specialized personnel for handling the instrument
	Diaz et.al (2012)	Pb, Ba, Sb	0.002–58,928 µg/m <sup>3</sup>	–		
	Lagoo et.al (2010)	–	0.04–2.3 µg	–		
	Halim et. al (2013)	Pb, Ba, Cu	0.098–0.47 µg/ml	–		
	Reardon et al., (2001)	Ba, Cu, Pb, Sb	0.19–1.72 µg	–		
	Krishnan, (1974)	Sb, Ba, Pb	–	–		
<b>Scanning Electron Microscopy (SEM)</b>	Sarkis et.al (2007)	Sb, Ba, Pb	–	–		
	Reiss et al., (2003)	Sb, Ba, Pb	Less than 1 µg/l	–		
	French et al., (2014)	–	0–591 particles	–	1. The method is applied to detect the morphological feature of particle.	1. Major disadvantage of the technique is the cost of instrument and time consuming nature.
	Lindsay et al., (2011)	Pb, Ba, Sb	150–4486 particles	–	2. Along with morphological feature EDx give the elemental analysis too.	2. Another disadvantage is that the cigarette lighter particle are same as GSR in morphology which can cause interference in the study.
	Wrobel et al., (1998)	Al, Si, Ca, S, K, Cl, P, Na	–	–		
	De Gaetano et al., (1992)	Pb, Ba, Sb, Zn, Cu	1–7 particles	60 min		
	Toal et al., (2014)	Ba, Sb, Sn, Zn, Al, W, S	–	–		
	Brozek-Mucha, (2007)	Pb, Ba, Sb, Sn	100–4000 particles	–		
	Brozek-Mucha, (2009)	Pb, Ba, Sb	21–185 particles	–		
	Gerard et al., (2011)	Pb, Ba, Sb	–	–		
	French & Morgan, (2015)	Pb, Ba, Sb	14–443 particles	–		
Brozek-Mucha	Pb, Ba, Sb, Sn	1–70 particles	–			

**Table 4** Combined analysis of organic and inorganic gunshot residues using instrumentation technique (Continued)

Instrumental technique	Researcher	Constituent detected	LOD	Detection time	Merit	Demerit
	Kara (2017)	Pb, Ba, Sb	1603–3911 particles	–		
	Rijnders et al., (2010)	Pb, Ba, Sb, Ti, Zn	5–894 particles	–		
	Brozek-Mucha & Jankowicz, (2001)	Pb, Ba, Sb, Cu	50–7000 particles	–		
	Izzharif et al., (2010)	Pb	–	–		
	Greely & Weber, (2017)	Pb, Ba, Sb, Sn	0–357 particles	–		
	Charles et al., (2013)	Pb, Ba, Sb	3–167 particles	–		
	Schwartz & Zona, (1995)	Pb, Ba, Sb	11–542 particles	–		
	Reyes et al., (2018)	Pb, Ba, Sb	13–756 particles	–		
	Kara (2017)	Pb, Ba, Sb	43–279 particles	–		
	Charles & Geusens, (2012)	Pb, Ba, Sb, Ti, Zn	0–1550 particles	–		
	Gerard et al., (2011)	–	0–36 particles	–		
	Fojtasek & Kmjec, (2005)	Pb, Ba, Sb	0–3020 particles	–		
	Jalanti (1999)	Pb, Ba, Sb	0–187 particles	–		
	Romano (2020)	Pb, Ba, Sb, Zn, Ti, Ca, Cu, K, P, S, Mg	5–40 particles	–		

NDPA nitro diphenylamine, EC ethyl centralite, DPA diphenyl amine, NG nitroglycerine, NC nitrocellulose, RDX cyclonite, DMP dimethyl phthalate, AK II akardite II, MC methyl centralite

to make a difference between firearms used to discharge a round, case, and bullet material was reported by Johnson et al. (Lebiedzki & Johnson, 2000). The residue collected from any region like hair, clothing, and hands showed positive results, thus decreased the danger of accidental sample contamination. In some cases, when inorganic GSR were not there, in that case, organic components are detected. These organic components provide additional information about the sample and sometimes are helpful in making differentiation between the GSR and environmental residues. Some research was also performed using SEM/Edx for the analysis of gunshot residue along with glass fragments from the hands of shooters. This study was performed by Collins et al. (Collins et al., 2003), and according to him, these glass fragments when found along with these inorganic GSR particles, that is, fusion of Pb and Ba, help to discriminate between the two. Hell miss et al. in 1987 equipped an SEM instrument with Auger electron spectroscopy for

the analysis of gunshot residue instead of using EDX (Hellmiss et al., 1987).

**Detection of organic residues in GSR** Detection of inorganic residues was largely practiced in the laboratory, but many scientists start to focus on detection of organic constituents of GSR, which originate from the propellant part of a firearm.

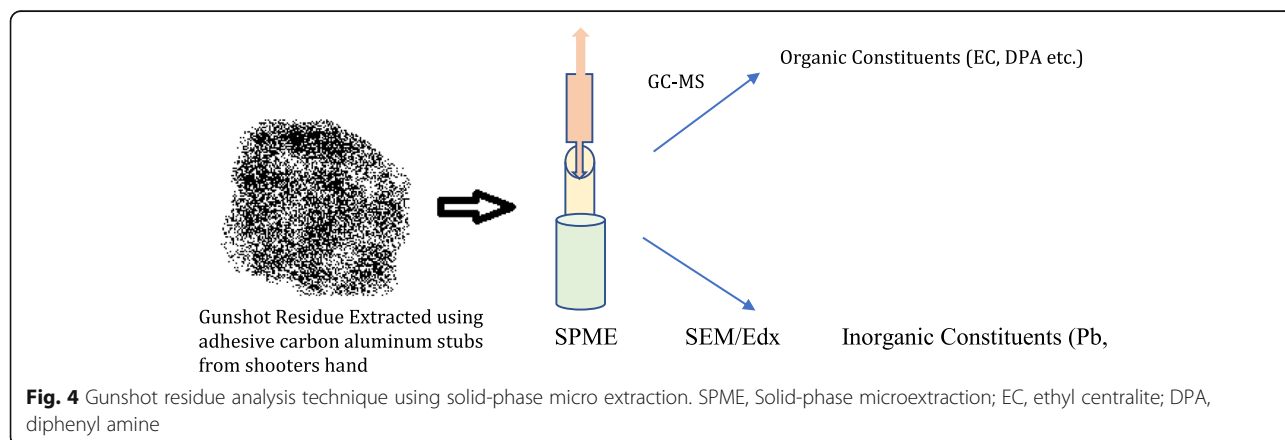
**Gas chromatography-mass spectrometry** The first combination of GC-MS came in 1959 and combining the computer-based mass spectrometer makes it more efficient in 1964 with the help of Robert E. Finnigan (Finnigan, 1964). The technique was applied to separate the mixture depending on the distribution between the stationary and the moving phases. Pyrolysis GC is an advanced form of gas chromatography where solid samples of forensic evidence are pyrolyzed at high temperatures to convert them into gaseous components.

Pyrolysis GC was performed by Newlon et al. (Newlon & Booker, 1979) using only small samples of GSR. Various detectors were combined with GC to carry out the detection of organic residues like thermal energy analysis (TEA), mass spectrometry (MS), electron capture, and flame ionization. Andrasko et al. analyzed organic components in smokeless powder that comes out of the barrel when a firearm is discharged (Andrasko et al., 2003). He combined GC with thermal energy analysis and mass spectrometry to get better results. According to Kirkbride et al., GC-MS was found to be used for the detection of various explosive compounds, from which some are used in gunshot or ammunition (Kirkbride et al., 1998). Dalby et al. analyzed smokeless powder and the capacity of solid-phase micro extraction (SPME) fiber type using gas chromatography-mass spectrometry (Dalby & Birkett, 2010). Joshi et al. evaluated the analysis of around 65 smokeless powder analyses using SPME, GC-MS, GC-micro electron detector, and ion mobility spectrometry (IMS) (Joshi et al., 2011) which further help to determine a list of various components as shown in Fig. 4. Thermal desorption gas chromatography/mass spectrometry was discussed by Stevens et al. (Stevens et al., 2016) in his experiment using ethyl centralite in blank and it is considered as a promising tool for forensic scientists. The advantage of using GC-MS without any sample preparation, pre-concentration, etc. start investigators to investigate this process in continuation. Pigou et al. reported those factors which influence the generation of molecules during the analysis (Pigou et al., 2017).

**High-performance liquid chromatography** First given by Mikhail S. Tswett when he did his study on separation of plant pigments. HPLC is just the opposite of GC where the moving phase is liquid and the stationary phase is solid. Here, the liquid is passed through a

column filled with solid particles (A Chromatographic and Electrophoretic Methods/A High-Performance Liquid Chromatography, n.d.). The liquid carries the sample pass through the column, different components retarded at different times. In HPLC, room temperature is sufficient to carry out the experiment. Amperometry and coulometric detection with mercury and carbon electrodes respectively to analyze NG and DPA using size exclusion chromatography for nitrocellulose were done by Lloyd (Basu & Ferris, 1980). Speers et al. (Speers et al., 1994) evaluated the use of HPLC-PMDE and GCMS for the analysis of organic propellant powder. He combined the technology with SEM/Edx to analyze inorganic residues. Dahl et al. (Dahl et al., 1985) reported the use of HPLC-EC for swabbed stabilizer detection. These stabilizers serve as an identification means of gunshot residue. Some scientists combine both high-performance liquid chromatography with pendant mercury drop electrode detector (HPLC-PMDE) and GC-TEA in combination to get better results, as these combinations lead to a strong or powerful result with more validity. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed by Wu et al. (Wu et al., 2001) for detecting methyl centralite used in GSR as a stabilizer. Even they searched that 25% of MC remain in a sample after 2 h.

Solid-phase extraction (SPE) is a technique which is used to get the concentration and purify the sample. The method developed was found to be good for EC and MC but got poor results for AK II as the recovery level calculated was not good using SPE for AK II. According to Cascio et al., the comparison was made between HPLC and micellar electro kinetic capillary chromatography (MEKC) for the analysis of organic gunshot residue. Using a UV detector in HPLC and MEKC helps to analyze the standard mixture of organic residues present in smokeless powder (Cascio et al., 2004). Mathis et al. (Mathis & McCord, 2003) evaluated the use of reverse-phase liquid chromatography electro-scope ionization





mass spectroscopy for comparing organic additives in smokeless gunpowder (Miryauchi et al, 1998). This method was found to be very useful in analysis of components in smokeless powder found in ammunition. According to the non-target approach, the characterization of both unburnt smokeless powder and organic components was analyzed whether the firearm is of a different caliber, brand, age, etc. These powders were analyzed by LC/atmospheric pressure chemical ionization/time of flight/mass spectrometry in both negative and positive ions. Some scientists applied polytetrafluoroethylene (PTFE) tapes for swabbing organic gunshot residue and then applying it on LC-Qtof-MS (liquid chromatography quadrupole time-of-flight mass spectrometry) for detection of these additives in gunshot residue using MS/MS mode (Benito et al., 2015).

**Capillary electrophoresis** Electrophoresis uses the same criteria of migrating on a stationary phase but differs as it does not use a moving liquid phase. In this technique, an electric potential is placed across the stationary medium/phase. In the capillary electrophoresis method, the analyst moved in the electrolyte solution under the influence of an electric field. The system usually consists of vials, source, electrodes, and detector. Capillary electrophoresis along with mass spectrometry was first used by Richard D. Smith and his colleagues (Krishnan, 1967). Micellar electro kinetic capillary electrophoresis (MECE) is a technique helpful in identification of organic compounds of GSR. This method reduces the cost in comparison with SEM/Edx and separates neutral molecules like stabilizers, explosives, etc. According to Northrop (Northrop, 2001), MECE has the potential to examine organic GSR even those which cannot persist for more than an hour.

**Thin-layer chromatography** The technique of TLC uses the stationary phase as solid and liquid moving phases to separate the constituents of a mixture. Here, a thin layer of silica gel or aluminum oxide is prepared which serves as the stationary phase and the sample to be analyzed may be applied directly onto the plate. The sample starts to rise based on capillary action. This way, the components of the sample are distributed between the stationary solid phase and liquid moving phase. Components with greater affinity to the moving phase travel faster than the components in the stationary phase. Retention value can be calculated using the formula:

$$R_F = \text{Distance travelled by the components} / \text{Distance travelled by moving liquid phase}$$

Peak (Peak, 1980) separated nitrocellulose from nitroglycerine which confirms the presence of flakes of

smokeless powder using the TLC method. Some methods were also developed for determining nitrocellulose in GSR swabs using the FTIR technique by Leggett et al. (Leggett & Lott, 1989). TLC with fluorescence was used by Meng et al. (Meng & Caddy, 1994) to detect EC along with NC and NG present on the shooter's hand.

**Raman spectroscopy** First predicted by Adolf Smekal in 1923 and named after the Indian scientist C.V Raman in 1928 (Smekal & Raman, 1923). The sample analyzed must be pure and colorless and the optical system made of glass or quartz. It consists of a source of light, sample illumination system, wavelength selector, and detector. Doty et al. (Doty et al., 2016; Doty & Lednev, 2018) made a comparison between SEM/Edx with Raman micro-spectroscopic technique where samples are collected through tape lifting. This method helps to identify and analyze various propellant components. A combination of IR with Raman enhances the variation between GSR samples from different origins but does not give effective results on real GSR samples. Bueno et al. (Bueno et al., 2018) studied and detected GSR based on the protocols implied on various particles released from automobile pads and tires. Results obtained gave specifications that the method is independent of Raman microscopes or collection software.

#### **Electrochemical screening of gunshot residue**

The current need for detecting GSR requires high sensitivity and specificity to get reliable results. So, to go beyond these heavy instrumentation techniques to some shorthanded held device which gave result within a few minutes or hour. For detecting the metallic constituents of gunshot residue, the anodic stripping voltammetry (ASV) method starts to implement. For organic constituents, cyclic voltammetry (CV) and square wave voltammetry are reported. From the acid wash, cotton swabbing and lifting using tape and adhesive can be overcome with the use of the abrasive method for gunshot residue particles. In forensic laboratories, SEM and AAS are the first choice but these methods are time consuming and costly and require high-profile personnel. To overcome this, various electrochemical-based sensors are developed and given below in detail. The electrochemical method uses potential, current, and charge measurement to determine the analyte concentration. Also, the activity of analytes can be detected using the electrochemical method. It is both a qualitative and quantitative technique based on electrochemical phenomena occurring within a medium. Even trace amounts of metal components can be analyzed. Various types of electrochemical techniques are there including ion-selective electrodes, coulometry, titrimetric method of analysis, and voltammetry method illustrated in

Table 5. Analysis of GSR using the voltammetry method was very earlier practiced but got much attention over 35–40 years as it is helpful in detecting the constituents very fast to other instrumental methods. The technique was found to be reliable, sensitive, simple to perform, and effective and include portability too. The result obtained is accurate with less cost. The method cannot be applied to barium metal due to its high electrochemical potential.

**Electro analysis detection of inorganic gunshot residue** The most important elements found in gunshot residue containing inorganic components including lead, barium, antimony, and various other metals as shown in Table 1 used above need some advanced detection instead of color- and instrumentation-based techniques. In electrochemical detection, the most important inorganic residue particles detected were Ba, Pb, and Sb. Many researchers worked on these metals, but antimony (Sb) was the least explored element electrochemically detected. Other worked on antimony metal based on the mercury electrode. They observe that the peak of antimony was overlapped by the copper strip peak. In 1948, J. Heyrovsky (Kovaleva et al., 2000) used polarography for Ba detection, but found some limitation since the Ba metal cannot strip at a negative potential, which causes hydrolysis of aqueous solvents. Various inorganic components were studied by anodic stripping voltammetry (ASV) including Cu, Sn, Hg, Bi, Zn, and Ni. Along with several elements, only in one run lead and copper can also be detected with the help of various working electrodes.

Using ASV on graphite electrode, the first attempt of analysis of Pb and Sb was done in 1977, at Queen University, Ontario (Konanur & VanLoon, 1977; Lu et al., 2013). Here, samples were shifted to Nalgene bottles (these bottles prevent contamination), and then,

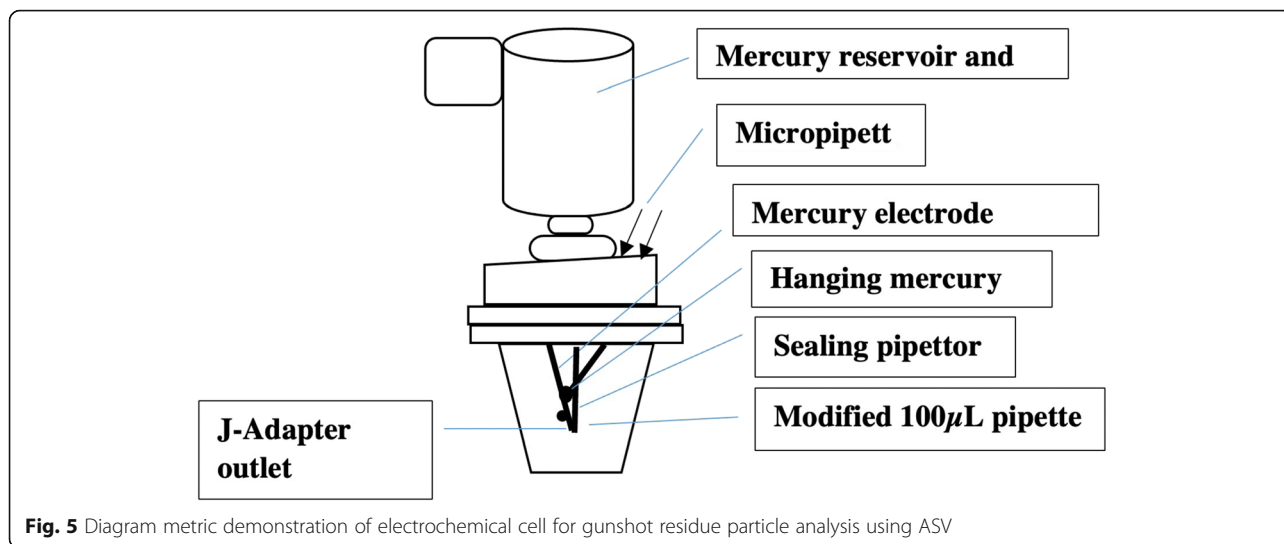
voltammogram was ran using a polarography analyzer in nitric acid and hydrochloric acid. The time of deposition observed was 80–280 s. Detection time was around 2 h for lead (Pb) and antimony (Sb) determination. In 1999, Dewald et al., detected lead and antimony using Hg-film GCE and proceeded to work in 2001 for simultaneous detection of barium and lead. Samples were extracted using cotton-based Q-tips dissolved in acid for 12–16 h and a voltammogram was run in a  $\text{KNO}_3$  hydrazine sulfate solution for 180 s. A single scan detects lead and antimony on an electrode surface. Liu et al., in 1980, carry out the experiment on hanging mercury drop electrode (HMDE) using low-cost polarography for detecting multiple metals made in acetate buffer (Liu et al., 1980a; Liu et al., 1980b). Samples were collected using acid wash for 10 min with a detection limit of 1.26 to 3.74 ng. A new injection-based J-adaptor was made in Brazil in 2005 for Pb constituent detection in GSR as shown in Fig. 5. It is easy to make, install, and operate which works reliably without adjustment or maintenance. LOD for Pb is 20  $\mu\text{g/L}$ . This method was the first method which uses tape lifting along with strip voltammetry (Donato & Gutz, 2005).

In 2011, cathodic adsorptive stripping voltammetry (CadSV) was used with HMDE for gunshot residue analysis for Sb and Pb detection. The LOD for Sb and Pb was  $7 \times 10^{-10}$  M and  $6 \times 10^{-10}$  M respectively. The data was compared with AAS data which uses square wave voltammetry. In 2009, Rodríguez et al. (Rodríguez et al., 2009) did work on Pb using tubular a Bi-film electrode instead of a mercury electrode. Here, Bi was collected on a carbon paste electrode with a deposition time of 60 s. LOD of Pb was detected to be 0.2 mg/L. Thus, Wang's group (Wang & Tian, 1992) uses the sensor strip for over 2 decades. O' Mahoney et al. (Mahoney et al., 2012) use Au-modified carbon screen-printed electrode with novel the "Swipe and Scan" method for

**Table 5** Electrode-based protocol developed to detect gunshot residue

S. no.	Researcher	Electrode used	Method employed/extraction technique		Metal detected	Time
1.	Konnaur et al. (1977)	Hg-film graphite	ASV	Acid Wash	Pb & Sb	> 10 min
2.	Liu et al. (1980a; 1980b)	HDME	ASV	Acid washing	Pb, Sb, Cu, Zn	> 10 min
3.	Briahye et al. (1982)	HDME	ASV	Swabbing	Pb, Sb	8 min
4.	Briner et al. (1985)	Hg-film GCE	ASV	Swabbing	Sb	>10 min
5.	Woo lever et al. (1999)	Hg-film GCE	ASV	Swabbing	Ba, Sb, Pb	6 min
6.	De Donato (2005)	HDME	BIA	Acid/swab/tape	Pb	3 min
7.	Rodríguez et al. (2009)	Bi-film CPE	ASV	Swabbing	Pb	2 min
8.	Eerden et al. (2011)	HDME	CadSV	Tape	Sb, Pb	6 min
9.	Mahony et al. (2012)	Au-modified SPCE	ASV	Swipe	Pb, Cu	2 min
10.	Sales et al. (2012)	Au microelectrode	CV/PCA/ASV	Swabbing	Organic/Inorganic	1 min, 10 min

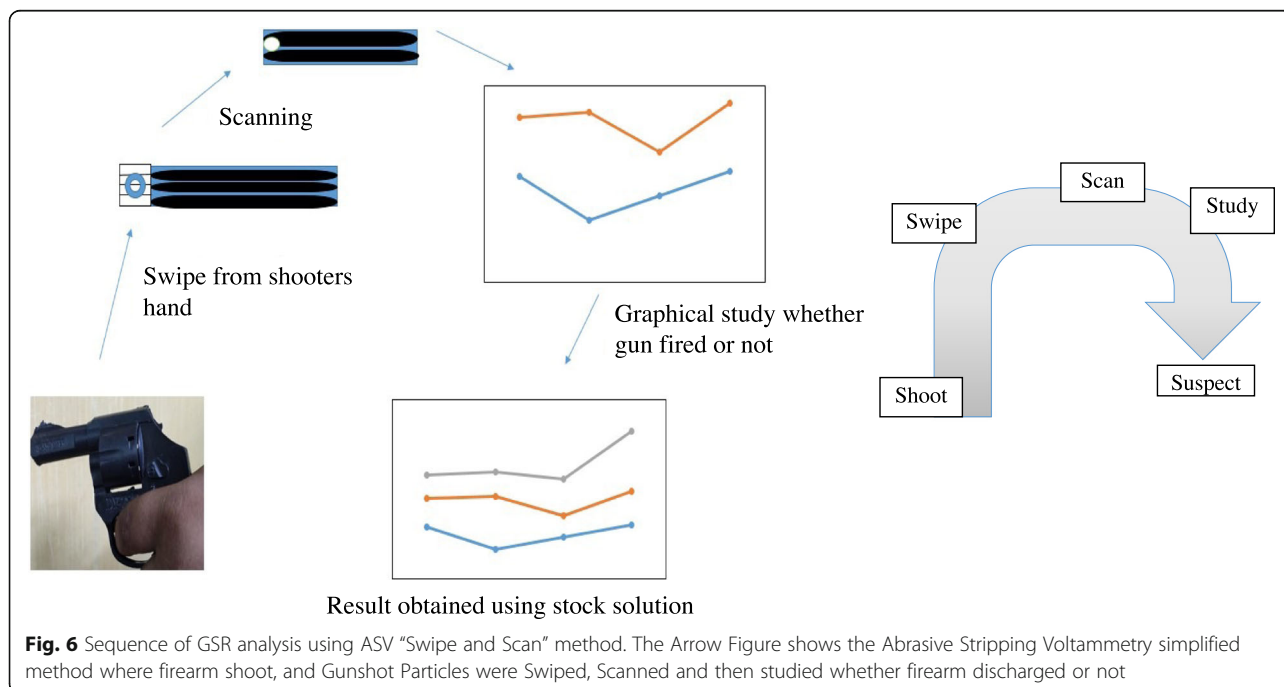
ASV anodic stripping voltammetry, CadSV cathodic adsorptive stripping voltammetry, PCA principal component analysis, HMDE hanging mercury drop electrode, BIA batch injection analysis, GCE glassy carbon electrode, Pb lead, Sb antimony, Cu copper, Zn zinc, Ba barium, Au-modified gold modified, Bi-film bismuth film, CV cyclic voltammetry, Hg-film mercury film



sampling as shown in Fig. 6. These strips were used to detect Pb and Cu which gave results as no contact with GSR, secondary contact, and subsequent firearm discharge. From this method, important inorganic components were analyzed like lead and antimony, but barium was not detected because of negative stripping potential as reported earlier.

**Electro analysis detection of organic residues** There is a huge demand to analyze the organic constituents present in gunshot residue based on electrochemicals. Since various occupational and environmental

contaminants inhibit the instrumental and color analyses, electrochemical detection in gunshot residue needs to be performed. Several researches were carried out in seawater to analyze nitro explosive compounds which consist of several organic species as reported in literature. Thus, organic metals important forensically need to be analyzed and it is outlined here in detail with all known developed protocols for electro analysis detection. So the supplementary norm for analyzing the GSR requisite needs to be taken. Organic constituents like DNT, TNT, RDX, and HMX in analyzing gunshot residue using CV at Hg-film gold electrode or GCE were



used by Kissinger in 1981 (Bratin et al., 1981). Another work was done in 1995 for stabilizer akardite II (AK II), centralite I (CI), and diphenylamine (DPA) by Bergens et al. (Bergens & Danielson, 1995). A CV scan of DPA and ethyl centralite was analyzed. Dahl et al. generated detection of both types of residues by using two different analytical methods (Dahl & Lott, 1987). The method employed was organic detection by HPLC with oxidative electrochemical detection combined with graphite furnace atomic absorption spectrometry (GFAAS) to determine metal constituents Sb, Pb, and Ba. This proves to be helpful in detecting gunshot residues. Further, in 2012, Wang et al. proposed simultaneous detection of both organic and inorganic constituents present in gunshot residue (Donato & Gutz, 2005). This work helps forensic scientists to get reliable work based on CV. Here, cyclic wave voltammetry and square wave voltammetry methods were used to detect the mixture of lead (Pb), antimony (Sb), dinitro toluene (DNT), nitroglycerine (NG), and a mixture of other metals include Zn, Pb, Sb, and DPA. The system generated was even not applicable to real samples but was the first example of a hand-held instrument for both constituents of GSR.

**Amperometry detection of gunshot residue** The amperometry method work on the principle of production of a current when potential is applied between the two electrodes. The basic electrode used in the amperometry sensor is the Clark oxygen electrode which consists of a platinum cathode where oxygen is reduced and silver chloride (AgCl) acts as a reference electrode. In these sensors, current response is used to detect the concentration of analyte (Jian et al., 2018; Lu, 2019).

**Detection of nitrite using amperometry sensor** Nitrite is an inorganic component of gunshot residue generated from primer constituents. Nitrite presence in gunshot was detected using various color tests and instrumental techniques but gave no quantitative determination. So, to overcome this problem, an amperometry sensor was developed to determine nitrite in gunshot residue. The method employed is simple, effective, rapid, and easy to perform. Some cases of firearms include several suspects, so in these cases, fast testing of GSR is applied. In this test, flow injection analysis combined with the electrochemical method was used to detect with less contamination of the sample, great precision value, and better accuracy and less amount of reagent required. The surface area was enhanced by using platinum, palladium, gold, and silver on nano and micro scales. For the detection of nitrite, palladium particles were found to be very suitable as they have good conductive and catalytic nature. The activity of Pd can be enhanced further when they are subjected to carbon material-based

nanoparticles (Promsuwan et al., 2017). The amperometry sensor firstly includes preparation of the Pd-GCMS composite as described by Sirisaeng and his colleagues with some modification (Sirisaeng et al., 2018). After this, electrodes are modified where GCE was polished with alumina slurries. Characterization of prepared GCME was done by CV from + 0.30 to + 0.10V with scan rate of 100 mVs<sup>-1</sup> using phosphate buffer. The developed Pd-GCME was then used to detect GSR. The nitrite from the gunshot was extracted as given by Erol et al.'s method (Erol et al., 2017). The result obtained gave a good linear range of 0.10 μmol/L–4 mmol/L with LOD at 0.030 μm.

## Conclusion

The paper highlights all the methods so far developed for detection of gunshot residue. It includes laboratory testing and on-field methods. Various color tests, instrument-based techniques, and electrochemical techniques developed were interpreted in detail. This review emphasizes mainly on the constituents of gunshot residue detection technology, as gunshot particles play a very important role in detecting crime between the suspect, the incident, and the whole crime. Relevant information can be generated based on the developed method of gunshot residue detection protocol. These developed methods help to correlate the crime whether it is a firearm-related crime or not. The detection of organic and inorganic residues continue till today in most laboratories. Heavy instrumentation to simple handheld electrochemical-based technology is developing at a high rate. With increasing technology, various researchers are combining one technology with other for enhancing the result for easy detection of GSR. Within the inspection of gunshot residue, this paper highlights various detection methods developed till now which need to be inscribed in view to research endeavors. The paper helps the scientist to easily acquire knowledge on developed protocols for GSR detection.

## Abbreviations

GSR: Gunshot residue; IGSR: Inorganic gunshot residues; AAS: Atomic absorbance spectrometry; SEM/Edx: Scanning electron microscopy-energy dispersive X-ray; NAA: Neutron activation analysis; ICP: Inductively coupled plasma spectroscopy; OGSR: Organic gunshot residues; ICP/MS: Inductively coupled plasma mass spectrometry; HPLC: High-pressure liquid chromatography; GC: Chromatography; NG: Nitroglycerine; NC: Nitrocellulose; DPA: Diphenyl amine; EC: Ethyl centralite; IMS: Ion mobility spectrometry; NDPA: Nitro diphenylamine; FTIR: Fourier transform infrared spectroscopy; MECE: Micellar electro kinetic capillary electrophoresis; SOC: Scene of crime; DTO: Di-thio-oxamide; IQL: Instrumental quantification limit; INAA: Instrumental neutron activation analysis; DNT: Dinitro toluene; TEA: Thermal energy analysis; MS: Mass spectrometry; SPME: Solid-phase micro extraction; HPLC-PMDE: High-performance liquid chromatography with pendant mercury drop electrode detector; LC-MS: Liquid chromatography-tandem mass spectrometry; HPLC-API-MS: High-pressure liquid chromatography atomic pressure ionization mass spectrometry; LC-Qtof-MS: Liquid chromatography quadrupole time-of-flight mass spectrometry;



CV: Cyclic voltammetry; ASV: Abrasive stripping voltammetry; TLC: Thin-layer chromatography; LOD: Limit of detection

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#### Authors' contributions

PS is the major contributor in writing this manuscript. While SN and VK read and approved the final manuscript. The author(s) read and approved the final manuscript.

#### Availability of data and materials

All data used in this manuscript have been completely described in this article itself.

#### Declarations

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