

REVIEW

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# A chronological study of gunshot residue (GSR) detection techniques: a narrative review

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## Abstract

**Background** The investigation and reconstruction of firearm-related crimes for the determination of the shooting distance, time since fire, and gunshot residue (GSR) persistence using the analysis of GSR comprising organic and inorganic components are crucial. However, the conventional color tests and allied techniques for GSR analysis are destructive and have limited sensitivity and selectivity.

**Main text** The review gives an elaborate and chronological description of all the methods used to date along with the future aspects of GSR detection techniques. It highlights the significant methods of spectrometry and spectroscopy applied as analytical techniques for the evaluation of GSR. The study is divided into various sections, ranging from the conventional color tests to the current techniques used in GSR analysis. While there is inconsistency and unreliability in these techniques, the current approaches discussed in this study using laser induced breakdown spectroscopy (LIBS), surface enhanced Raman scattering (SERS), ion mobility spectrometry (IMS), and electrochemical sensor-based methods have significant potential for GSR detection. Addressing such limitations will enhance the forensic capabilities of law enforcement and provide an added advantage to forensic laboratories during an investigation. It will also reinforce the use of such spectroscopic data in a criminal investigation. The techniques discussed here have the capability to detect both organic and inorganic components of GSR that has the potential to link GSR particles to the type of ammunition discharged.

**Conclusions** The validity and reliability of these approaches have proved to establish their capability to differentiate between potential false positives known for standard forensic analysis techniques currently used for GSR detection and identification. The paper anticipates a systematic study of the novel methodologies relevant to the current scope of research concerning GSR analysis, when fully developed and implemented in practice will help forensic scientists to detect, identify, and analyze GSR, making it a new and important type of evidence.

**Keywords** GSR, Inorganic compounds, Organic compounds, SEM, LIBS, SERS, IMS, Persistence, Shooting distance estimation, Time since fire, Electrochemical methods

## Background

A complex mixture of burnt, unburnt, and partially burnt organic and inorganic materials is expelled as byproducts through the apertures of a firearm when a firearm is fired. This substance is known as gunshot residue. Before they condense and change into particles of various sizes, these vapor-formed particles can be deposited on the shooter's hands, clothes, face, hair, or the surrounding environment. GSR particles often form spherical shapes because of condensation and range in size from 05 to 50  $\mu\text{m}$ . In situations involving firearms, forensic experts

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examine GSR, which can reveal useful information about the trajectory of the bullet, the area of firing, whether it was a suicide or homicide, and other things that aid in recreating a crime scene. When analyzing the gathered GSR data, several factors such as the loss of GSR owing to secondary or tertiary transfer, the persistence of GSR, and time since fire must be taken into account because they are frequently obtained at different periods after the original firing event (Shrivastava et al., 2021).

The heavy metals present in GSR are also extremely prevalent in the environment because of natural processes and human activities. The presence of these heavy metals might conflate these environmental contaminants with GSR and produce false-positive results. Hence, it is also important to monitor the presence of trace elements and their formation in the environment (Mosher et al., 1998; G M WOLTEN, R S NESBITT, A R CALLOWAY, & G L LOPER., 1979; Shukla et al., 2022). The inorganic GSR markers or heavy metals (Pb, Ba, and Sb) present in the ammunition can have detrimental effects on the environment and living things, which has led to the development of lead-free or non-toxic ammunitions (Mosher et al., 1998).

GSR samples are visually inspected after they arrive at a lab. Despite being cost-effective, visual (colorimetric) testing and traditional procedures lack reliability and specificity because of the vast number of false-positive findings brought on by environmental pollutants (Andreola et al., 2011; Berk, 2009; Grima et al., 2012; Ingo et al., 2004; O'Mahony & Wang, 2013).

#### **Inorganic components of GSR**

The primer mixture lodged at the base of the cartridge case is the primary source of inorganic gunshot remnants. According to several studies, a typical primer is often made up of three complexes: a primary explosive or initiator like lead styphnate ( $C_6H_9N_3O_8Pb$ ), an oxidizer like barium nitrate ( $Ba(NO_3)_2$ ), and fuel-like antimony trisulfide ( $Sb_2S_3$ ). Each manufacturer has a unique formulation of the inorganic components of the primer mixture (Dalby et al., 2010; Fambro et al., 2016; Rowe, 2001).

#### **Organic components of GSR**

The propellant consisting of smokeless powders with various compositions is where the organic components in GSR originate. Single-based smokeless powders are composed of nitrocellulose (NC), double-based smokeless powders are composed of nitrocellulose and nitroglycerin (NG), and triple-based smokeless powders are composed of nitrocellulose, nitroglycerin, and nitroguanidine (NGu). Smokeless powders are preserved and given a longer shelf life by adding various additives, such as stabilizers, plasticizers, flash inhibitors, coolants,

moderants, and surface lubricants, among others. Some of the common volatile organic compounds (VOCs) utilized as additives in smokeless powders include stabilizers like diphenylamine (DPA), methyl centralite (MC), and ethyl centralite (EC), as well as flash suppressors like 2,4-dinitrotoluenes (2,4-DNT) and similar isomers (Schwoeble & Exline, 2000).

#### **Non-toxic or lead-free ammunition**

The development of “non-toxic” or “lead-free” ammunition took place to reduce the hazardous effects of lead exposure in humans and wildlife. This has made it difficult for forensic science professionals to distinguish the IGSR indicators from environmental pollutants. Lead is a highly powerful environmental toxin. Since the IGSR detection depends on the detection of lead, the removal of lead from primers has resulted in an increase in false-positive findings. Therefore, it is crucial to monitor IGSR and OGSR to produce an accurate profile of the ammunition utilized.

Fambro et al. reported on spectroscopic analysis of the non-toxic or lead-free GSR for the identification of the GSR markers present in each composition using LIBS. SEM/EDS was used to assess the extent of preserving the evidence followed by LIBS analysis. The GSR analyzed in this study allowed the detection of Ba, Al, Si, and K, as well as trace levels of Ti, Fe, and S. This study demonstrated that even though a small area on the sample surface is laser ablated, the remaining sample could be preserved for reanalysis after analysis using LIBS. LIBS offered less analysis time compared to SEM/EDS. However, this work includes only analysis and characterization of 9mm lead-free ammunition. Characterization of conventional and lead-free ammunition from various manufacturers and calibers should be a part of future research (Fambro et al., 2016) as such a comparative study can be of great forensic relevance as the primer composition varies from manufacturer to manufacturer and ammunition to ammunition. Such a study would be a valuable database for the forensic community working in the field of firearms and associated components.

Costa et al. used a 0.40 caliber handgun and a 0.38 caliber revolver in a study that combined SEM/EDS, colorimetric testing, and ICP-MS as analysis techniques. The inorganic GSR components created by the non-toxic or clean-range ammunition have undergone a comprehensive examination. The colorimetric tests returned negative results for Pb and Ba. The surface morphological images acquired by SEM/EDS demonstrated dissimilarities from the GSR produced from conventional ammunition whereas ICP-MS gave positive results for Pb, Ba, and Sb having concentrations  $4.20 \mu\text{g L}^{-1}$ ,  $10.9 \mu\text{g L}^{-1}$ , and  $0.119 \mu\text{g L}^{-1}$ , respectively.

Elements including Al, Ti, Cr, Mo, Cu, Zn, and Sr were also identified, from which Al, Zn, Cu, and Sr were identified as novel IGSR markers due to their prevalence (Costa et al., 2016).

A standard methodology for identification and confirmation is needed for most forensic sample examinations. Ion mobility spectrometry (IMS), Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS), ICP-MS, and other approaches have all been used to assess GSR detection (Arndt et al., 2012; Eksinitkun, 2018; López-López & García-Ruiz, 2014; López-López et al., 2013; Roberts et al., 2015). SEM/EDS was the most common method of choice used for GSR analysis in crime scene investigations. This method is not always definite owing to a few limitations. The method has a potential of getting false-positive findings (Dockery et al., 2011) or losing IGSR particles owing to secondary transfer or based on the occupation of the person, because it only analyses inorganic particles found in GSR. Since the non-particulate residues adhere to the skin via intermolecular forces, they are less likely to undergo secondary transfer, making it important to monitor the organic components of GSR (Gassner et al., 2019; Moran & Bell, 2014). However, it has been observed that these tests give false-positive results because they interpret environmental elements. This review paper discusses the analysis of both IGSR and OGSR particles for various studies such as trace analysis, persistence study, shooting distance estimation, and time since the fire of GSR particles using LIBS, SERS, and IMS.

## Main text

### GSR detection techniques

GSR samples are first visually inspected under a microscope after they arrive at a lab. The use of both traditional techniques, such as colorimetric and instrument-based analysis, and cutting-edge technologies, such as electrochemical approach (Harshey et al., 2021), for GSR detection has been emerging since past several years. However, these chemical and spot tests degraded the sample and occasionally interfered with surrounding foreign material that was present at the crime scene, even though they were easy to perform. This review paper aims to discuss a few of the several instrumentation techniques, such as atomic absorption spectroscopy (AAS) (Grant & Peters, 2000), neutron activation analysis (NAA) (Lewis et al., 2005), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) (Ali et al., 2016), Raman spectroscopy (Bueno et al., 2012; Karahacane et al., 2019), ion mobility spectrometry (IMS) (West et al., 2007), and laser-induced breakdown spectroscopy (LIBS) (Goode et al., 2002a), that aids in GSR analysis.

### Color/spot tests

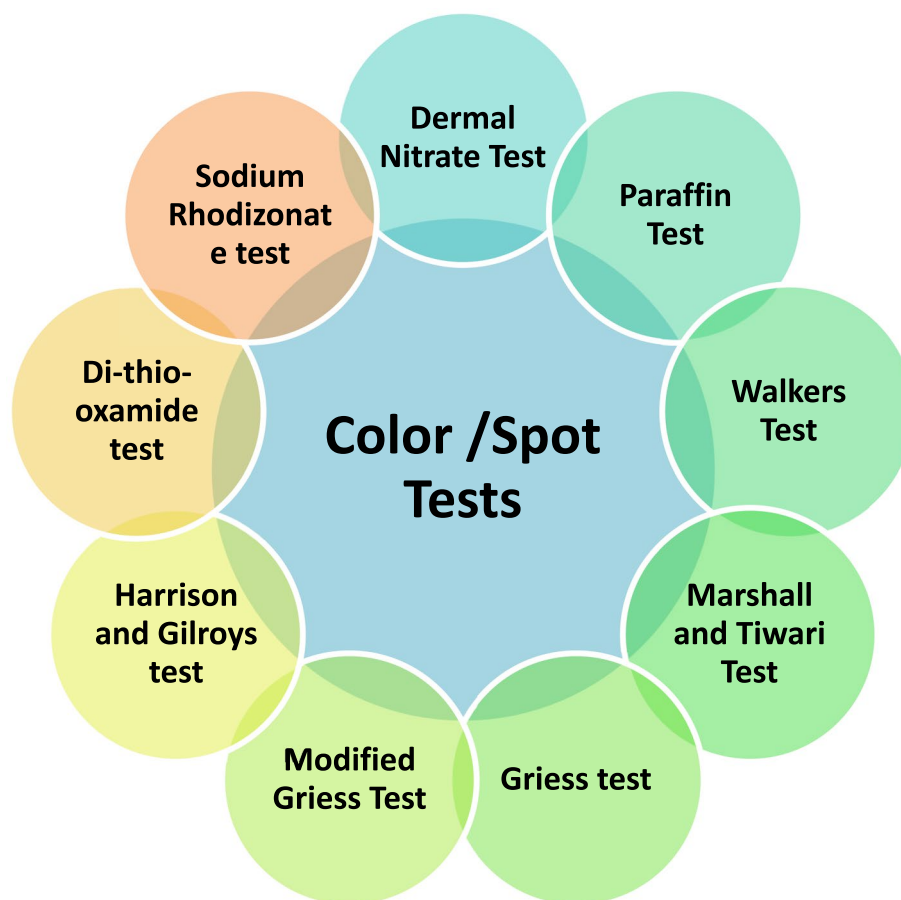
The color/spot tests consisting of the dermal nitrate/paraffin test, Walker's test, Marshal and Tiwari test, modified Griess test, Harrison and Gilroy's test, di-thio-oxamide test sodium rhodizonate test, and another spot test were employed as a preliminary test for GSR in several forensic laboratories since 1900s (Walker & Rodacy, 2002). Figure 1 demonstrates all the color/spot tests employed with GSR detection. However, it has been observed that these tests give false-positive results because they interpret environmental elements incorrectly (Gandy et al., 2018). Aksoy et al. has reported a new method to reduce false positives due to antimony in detection of gunshot residues (Aksoy et al., 2015). Table 1 represents the various color/spot tests and the respective reagents and color changes observed on analyzing GSR showcasing their disadvantages that led to their replacement with instrumental techniques.

Despite being cost-effective, visual (colorimetric) testing and traditional procedures lack reliability and specificity because of the vast number of false-positive findings brought on by environmental pollutants. The color/spot tests were therefore substituted by instrument-based approaches for the assessment of organic and inorganic components. Bulk elemental analysis has been made practicable by instrumental approaches. The method is useful for the qualitative and quantitative analysis of elements in a sample.

### The emergence of instrumental techniques used for the analysis of IGSR components

For the identification of various inorganic metallic components in GSR and allied forensic samples, several approaches were carried out. The neutron activation analysis (NAA) was accepted as a conclusive test in the USA in 1968 (Taylor, 2017; Rudzitis & Wahlgren, 1975). Later came the application of conventional flame atomic absorption spectroscopy (FAAS) started in the early 1970s, with sensitivity for barium and antimony equivalent to that obtained by NAA (Karjala, 1971). This method helped to distinguish between whether a weapon was fired or not fired by a suspect and to detect antimony and barium (Koons et al., 1987) (Newbury, 1980). Even the presence of minute quantities of Pb, Ba, and Sb, can be detected.

In 2003, inductively coupled plasma-mass spectrometry (ICP-MS), a different approach, has been more popular over the past few decades as an instrument with numerous additional analytical advantages for GSR examinations. It enables accurate analytes detection, particularly in trace analysis. With a multi-element capability, accuracy and precision needed for GSR analysis, the analytical detection limits are superior to those



**Fig. 1** A flowchart demonstrating the various color/spot tests employed in GSR analysis

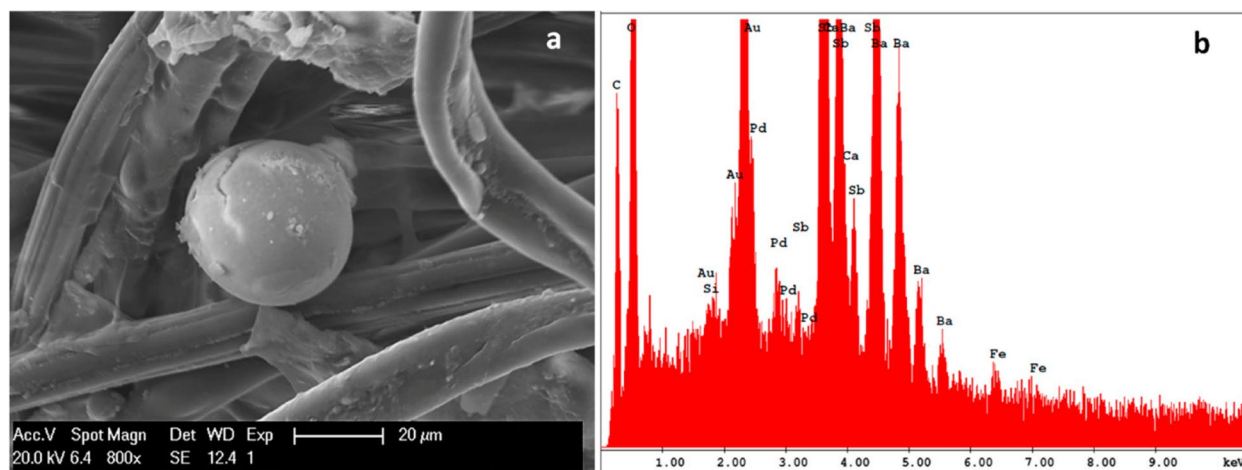
obtained using other approaches. When the extracted samples were analyzed, this approach showed improved performance (Lichtenberg, 1987; Moens & Jakubowski, 1998).

Subsequently in 2000s, the scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) was developed as an analytical method for particle analysis. This technique was later discovered to be a more effective method for identifying GSR. SEM was a popular method for analyzing IGSR because of its ability to correlate surface morphological features and the chemical composition of GSR markers (Vanini et al., 2015). This technique was most often employed in the past to detect IGSR particles which was SEM/EDS as shown in Fig. 2. The term “characteristic particles of GSR” refers to particles that contain the GSR markers (Pb, Ba, and Sb) and possess a spherical shape as determined by SEM/EDS examination (Zuzanna, 2000). Additionally, this method can be utilized to correlate the morphological features and elemental composition of specific particles made up of the heavy metals. The method allows the detection of GSR particles having size ranging from 0.5 to 5  $\mu\text{m}$  (Doña-Fernández et al., 2018).

Since the advent of non-toxic or lead-free ammunition, the method has lost its specificity (Taudte et al., 2014) because the chemical composition of this type of ammunition differs from conventional ammunition due to the replacement of lead in the primer, which produces inorganic components that are different from conventional GSR and is not well detected by the SEM/EDS technique (Charles et al., 2020). In addition, as this technique relies much upon the detection of lead, the removal of it from primers has increased the number of false-positive findings. Therefore, it is essential to develop and implement new techniques that rely on the identification of spectroscopic features arising from OGSR and IGSR components rather than relying on the detection of only specific heavy metals. This ultimately improves the method’s validity (Bueno et al., 2012; Martiny et al., 2008). While there has been a significant advancement in recent years pertaining to the detection limit, specificity, and sensitivity of GSR analysis, there is still much more work that must be accomplished to understand the various environmental factors that affect the persistence and transfer of GSR by using new techniques in place of the traditional ones.

**Table 1** Traditional color based preliminary tests used for the presence of GSR

Sl No.	Color test	Reagents and materials used	Analytes	Color changes observed	Demerits	Literature
1.	Dermal nitrate/paraffin test	Diphenylamine dissolved in strong H <sub>2</sub> SO <sub>4</sub>	Nitrates	Deep blue coloration	It showed positive results for those who were in contact with nitrates or nitrites from other sources like fertilizers, waste water, sewage lines, acid rain etc.	Edwin et al., (Conrad, 1961) and Tagliaro et al., (Tagliaro et al., 2002)
2.	Marshall and Tiwari Test	Desensitized photographic paper Sulphanilic acid N-α naphthyl-ethylenediamine hydrochloride in methanol Acetic acid	Nitrites	Purple color spot	It destroy the sample and show interference with other environmental constituents The test is specific for nitrites and not for GSR	Shrivastava et al., (Shrivastava et al., 2021)
3.	Griess test/Walkers test	Bromide paper treated with 2-naphthylamine disulphonic acid CH <sub>3</sub> COOH	Nitrites	Dark red color	many compounds other than nitrocellulose propellants can give positive reaction eg. Urine	Shrivastava et al., (Shrivastava et al., 2021)
4.	Modified Griess Test	Reagents used for Griess test + 2 naphthyl amine sulphanilic and citric acid	Nitrites	Pink color	It can be applied to detect nitrites only but not for GSR.	Jaluddin et al., (Jaluddin et al., 2021)
5.	Harrison and Gilroy's test	Swab moistened with dil. HCl tri-phenylarsonium iodide and sodium rhodizonate	Antimony Lead & barium Lead Barium	Orange Red Purple No change in color	Interference with other materials at the crime scene can be obtained.	Sharma., (Sharma, 1978)
6.	Di-thio-oxamide test	Di-thio-oxamide (DTO) in ethanol Ammonium hydroxide dissolved in distilled water filter paper	Copper Nickel	Gray/greenish blue or violet color	Is in presence of blood false negative result can be obtained	W. Arendse (Arendse, 2008)
7.	Sodium rhodizonate test	HCl Sodium rhodizonate	Lead (When pH is neutral) Lead (when pH below 3) Barium (at any pH)	Varies from blue to violet. Bright red color with orange tint Reddish brown	It cannot be applied for Ba detection	Jeffrey S Taylor (Taylor, 2017)



**Fig. 2** a SEM image and b energy dispersion X-ray EDX spectra of inorganic gunshot residue found on a swab sample: reprinted from (Argente-García et al., 2019)

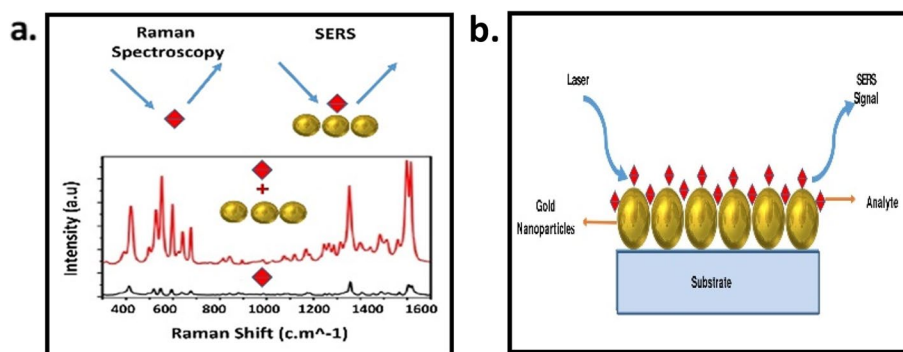
However, the instrumental techniques mentioned above are the conventional methods used for GSR analysis, which enables the detection of only inorganic components of GSR due to which it is necessary to analyze both the inorganic and organic components of GSR, which would increase the result's confidence and reliability. Hence, there is a need for forensic science experts to understand and develop effective analytical techniques to perform IGSR and OGSR analysis (Feeney et al., 2020). Much attention has been given to the upcoming instrumental techniques which have the capability to detect the organic components of GSR or both (IGSR and OGSR), a few of which are discussed in the next section.

#### **Instrumental techniques used for the analysis of OGSR components**

**Raman spectroscopy and surface enhanced Raman spectroscopy** Raman spectroscopy based on vibrational frequency can image and characterize particulates present in GSR. This technique can evaluate a wide range of materials because it is not constrained by its chemical state and does not require sample preparation. The low intensity laser source used in this spectroscopic technique makes it a non-destructive technique. The desired area of analysis on the sample can be achieved by focusing the laser light. The technique has the drawback of not always detecting the component, which has metallic constituents in it. However, this technique has been mostly employed for the detection of OGSR components, but a few researchers have enabled it for the detection of both IGSR and OGSR, the outcomes of which has been reviewed in this section.

A few other downsides of this technique include fluorescence, which can come from contaminants or the specimen as a whole and manifest themselves as lengthy, curved, and severe signals that cover the lower Raman peaks often. Moreover, if the region of interest is small, the laser light may be overly intense and cause heating and burning of the specimen. However, the most effective method must be surface-enhanced Raman scattering (SERS), which involves close contact between the specimen and metallic nano substrates. According to reports, the surface plasmon resonance of the nano substrate analytes can simultaneously extinguish fluorescence while amplifying the Raman signal up to  $10^6$  times (Doty & Lednev, 2018; Langer et al., 2020) as shown in Fig. 3.

Lopez-Lopez et al. have examined gunpowders and macroscopic GSR particles to evaluate the capability of SERS to meet the demand for trace analysis. The same method was used to analyze GSR particles obtained after the discharge of two different caliber ammunition, 0.22mm and 0.38mm onto a target cloth material fixed on a cardboard placed at a firing distance of 1m. The authors for the collection of GSR samples introduced two approaches. The first approach was with aluminum stubs containing adhesive carbon tape pressed against the target cloth and the second approach was by manual picking of GSR particles from the cloth using metallic tweezers. The GSR particles collected using both methods were extracted with ethanol and diluted in a solution containing gold nanoparticles and ultrapure water. The nanoparticles were synthesized by boiling gold chloride trihydrate solution and trisodium citrate dehydrate solution for 30min. A  $\text{CaF}_2$  slide was utilized as a substrate to which one drop of each of the prepared solution was dropped. For DPA, EC standard, and the



**Fig. 3** a A comparison of the spectra obtained from Raman spectroscopy and (b) SERS signal enhancement via surface plasmon resonance

nitrate derivatives, SERS spectra were obtained using gold nanoaggregates with a concentration of  $10^{-6}$  M,  $10^{-6}$  M, and  $10^{-7}$  M respectively indicating a good sensitivity. However, SERS spectra of gunpowders with 2,4-DNT were expected to have additional peaks but weak bands were observed in contrast due to the overlapping of bands from other gunpowder components. While gunpowders with DPA showed intense SERS spectra, the ones with EC gave weak spectra. Although the first approach of sample collection gave better results, the method does not allow reanalysis of the sample by destroying the sample surface (López-López et al., 2016).

Analysis of smokeless gunpowder stabilizers to measure the signal detection limit (SDL), the limit of detection (LOD), and the limit of quantitation (LOQ) was reported by Evan Thayer et al. using SERS. In this work, the authors have extended SERS to portable Raman spectrometers for the analysis of two major gunpowder stabilizers, DPA, and EC, in acetone, acetonitrile, ethanol, and methanol using lasers having wavelengths 785 nm and 1064 nm with laser output 150 mW and 300 mW. This was based on the concept that solution analysis wipes out the non-homogeneous nature in some solid samples. Solutions were prepared by adding gold nanoparticle solution to various concentrations of DPA in acetone or acetonitrile. The sample holder could lodge the samples in any of the mentioned states (solid, liquid, or powder). As 785 nm wavelength with 300 mW laser output gave better resolution, intensity, and lower fluorescence, this combination was utilized throughout the study. This study claims to be the first published report, which involves the application of portable Raman spectroscopy for GSR analysis with and without SERS. While acetone and acetonitrile produced the lowest detection limit for DPA and EC respectively, the addition of gold nanoparticles improved the SDL of all the peaks in both acetone

and acetonitrile supporting their use in GSR detection using SERS (Thayer et al., 2019).

Three commercially available and two fabricated SERS substrates, such as Klarite 312, RAM-SERS-AU, SERSitive and GaN cavities, and GaN pillars respectively, have been used by Liszewska et al. to investigate the possibility of trace analysis of explosive materials such as AN, TNT, and RDX, using a handheld and portable Raman spectrometer. In the method suggested in this study, the samples were dissolved in acetone, this solution is drop cast onto the SERS substrate, dried, and Raman spectra of it were taken. The molecules present in the sample were identified by comparing the obtained spectra with the standard Raman spectral database. The results revealed that among the five, only two substrates (Klarite 312 and GaN pillars) were capable of trace analysis of the studied explosive materials with concentrations ranging from single to hundreds of  $\mu\text{g}/\text{cm}^2$  depending on the sample. Although the portable spectrometer gave a higher resolution, laser power, and wide spectral range than a handheld spectrometer, the quality of the microscopic images was low when compared to a benchtop Raman microscope (Liszewska et al., 2019).

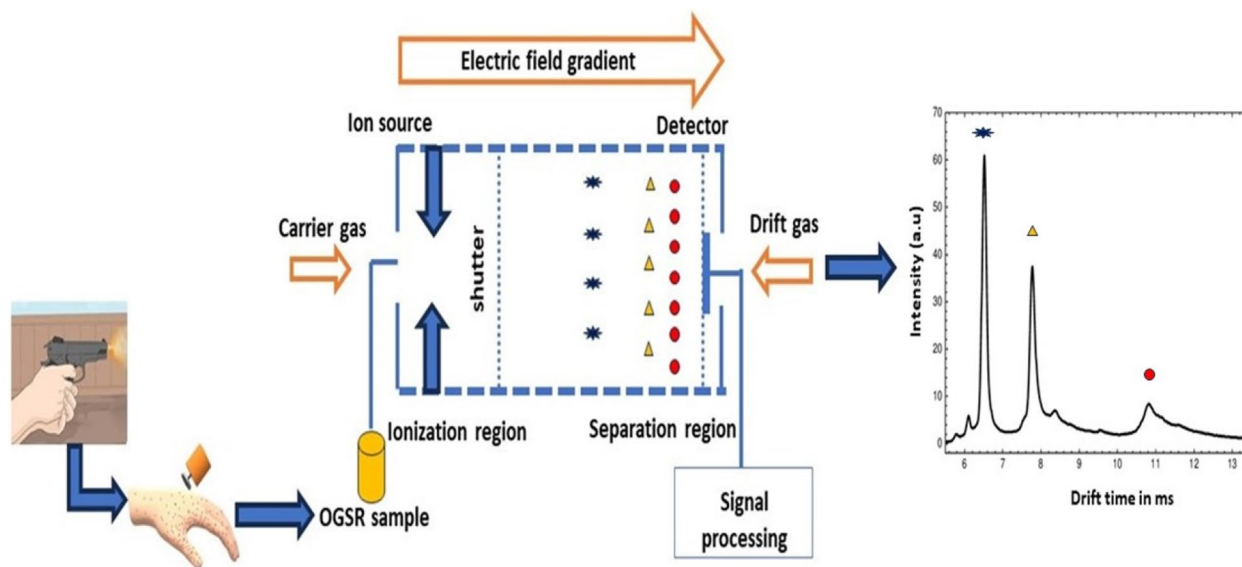
SERS for the identification of three molecules of forensic interest (crystal violet, 2, 4, 6-trinitrotoluene (TNT) and methamphetamine) other than GSR has been reported by Muehlethaler et al. Two different Raman instruments were employed in the study to obtain the SERS spectra. Despite its easy mode of operation, a portable Raman spectrometer for the sample analysis revealed relatively poor sensitivity (LOD value of 0.62 ppm across a scanning range of  $250\text{--}2875\text{ cm}^{-1}$  relative to the benchtop spectrometer having a LOD value of 0.04 ppm in the test solution across a spectral range of  $50\text{--}3400\text{ cm}^{-1}$ ). The spectra obtained under identical laboratory conditions

a few days later also revealed consistent and comparable results. They have demonstrated in their study that the use of SERS has been a reliable and versatile approach for qualitative evaluation and identification of compounds of forensic relevance by attaining a fair rate of signal enhancement. The molecule to be evaluated and how well it binds or interacts with the SERS substrate have a significant impact on both the repeatability and reproducibility of the method. Methamphetamine binds very poorly to the silver colloids, causing significantly larger fluctuation in the data, while crystal violet attaches strongly to silver. TNT has a modest affinity for silver. In spite of having poor binding affinity, compounds like methamphetamine have shown that their measurement is still viable at higher concentrations (Muehlethaler et al., 2016).

A comparative study between a bench-top and a portable Raman spectrometer for the testing of pesticides like maneb and pyrrolidine di thiocarbamate ammonium salt (PDCA) was conducted by Zheng et al. They demonstrated that a portable Raman spectrometer employing a SERS substrate is an effective option for onsite analysis of trace analytes as it allows for both identification and semi-quantification generating reliable and compatible results. It was found that the bench-top Raman displayed roughly ten times greater sensitivity than the hand-held one. The instruments' performance was assessed based on their spectral resolution, signal fluctuation, and sensitivity. Additionally, because the default parameters of a portable Raman device are preset, they cannot be changed to fit various applications making it one of its drawbacks (Zheng et al., 2014).

Using SERS (pSERS Raman technique) and paper spray ionization mass spectrometry (PS-MS method), W. Fedick et al. have employed paper substrate coated with silver nanoparticles for the investigation of forensic specimens other than GSR, such as chemical warfare agent simulants, narcotics, and explosives. Three micrograms of the samples was required for analysis using a paper substrate. The outcomes demonstrated that both approaches permitted analysis on a single low-cost paper substrate without sample pretreatment. Additionally, the inkjet printing on the substrate enables pattern customization in accordance with the sample. The authors contend that the procedure will be more effective if in situ analysis can be done (Fedick et al., 2017). Compared to other approaches, only a small number of researchers have reported the detection of GSR employing a substrate coated with metal nanoparticles. SERS-based GSR analysis is a less-trodden domain.

**Ion mobility spectrometry** IMS is a well-known technique used to detect gunshot residue, various explosives, and chemical warfare agents since the 1960s; its compact size and sensitivity in the ppb range make it a common method. It is an atmospheric pressure method that produces product ions via the reaction of reactant ions with the sample as shown in Fig. 4. These are then separated by an electric field. IMS is a reliable, sensitive, and field-portable method for detecting organic components. In this section, the application of IMS technology in forensically relevant instances, its advantages, and drawbacks has been reviewed based on the literature carried out.



**Fig. 4** Schematic representation of OGSR analysis using ion mobility spectrometry



West et al. have claimed their work to be the first reported study for the detection of gunpowder stabilizers, DPA, and EC using IMS. In this study, the gunpowder from five different cartridges was extracted and examined to assess the positive/negative ions and the nitro/nitroso derivatives arising from DPA and EC. Other compounds that are often present in gunpowder, such as NG, 2, 4-DNT, 2, 6-DNT, and TNT, were also examined. The plasmagrams obtained in the positive ion mode revealed that the EC peak had a higher intensity than the DPA peak. Although the technique successfully identified all derivatives of DPA that were tested, many of the produced ions were incorrectly recognized. While EC and DPA did not create any noticeable anions in the negative ion mode, they did exhibit LOD in the range of around 0.5 to 1 ng and 2ng, respectively. This technique can be utilized to produce the stabilizer profile of smokeless gunpowder's from various ammunitions (West et al., 2007).

Yeager et al. report the presumptive testing of organic components of GSR on hand swabs using IMS. A commonly used wiping substrate, muslin, was used to collect the hand swabs. A handheld and a benchtop model of the IMS instrument was utilized for the study which contained nicotinamide as an internal calibrant and gave comparable results. To detect the presence of background contaminants, laboratory air was also subjected to analysis. The samples significantly degraded when kept at room temperature even though the target analytes, EC, MC, DPA, and dimethyl phthalate (DMT), indicated a holding duration limit of a few days to a few weeks during their stability studies. IMS is a semi-quantitative technique; however, it cannot be used to directly to obtain LOD's of OGSR (Yeager et al., 2015).

M. Joshi et al. employed a portable IMS system and a laboratory-based GC technique to perform a study using 65 samples of smokeless powder. Solid-phase micro extraction (SPME) was performed prior to analysis using IMS. The study was implemented for the on-field detection of several components, including diethyl and dibutyl phthalate, 2, 4-dinitrotoluene (DNT), EC, and MC, as well as DPA. Only two compounds, NG and 2, 4-DNT, were detected in the negative ion mode with the peak for NG predominating. The others were detected in the positive ion mode when the analytes were investigated in both positive and negative ion modes. Of the 65 powders studied, DPA, EC, and MC were found to be present in 96%, 47%, and 8% respectively in the headspace region of the smokeless powders. The results were utilized to develop a library of target chemicals for smokeless powder detection in the vapor phase (Joshi et al., 2011).

In a different study conducted by Joshi et al., the extraction of compounds having odor, characteristic to smokeless powders, has been demonstrated using IMS using five smokeless powders containing both double and single-based powders. All the powders examined were determined to have diphenylamine as a common component. By printing exact quantities of standards onto surfaces and examining them, the response curves were created. These response curves were also used to calculate the absolute detection limits, which for the standards varied from 0.12 to 1.2 ng. It was observed that the amount of diphenylamine and ethyl centralite extracted at the shortest extraction times was greater than the LOD of the compounds. The extraction times ranged from 5 to 40 min. The study demonstrated successful results in the detection of additives like DPA, EC, 2-ethyl 1-hexanol, and 2,4-DNT in smokeless powders using extraction by SPME followed by IMS analysis. It was observed that the mass of ethyl centralite and diphenylamine extracted at the short extraction durations was more than the LOD of the compounds (Joshi et al., 2009).

Moran et al. used IMS to investigate the penetration of OGSR on the skin using polydimethylsiloxane as a model skin membrane (PDMS). EC, DPA, and its nitration products such as n-nitroso diphenylamine (N-NODPA) and 2-nitrodiphenylamine (2-NDPA) were the targeted OGSR compounds in the study. The permeation studies were carried out in Franz diffusion cells (FDCs) and the PDMS membrane was analyzed using IMS which took an analysis time of only 4s. Experimental studies revealed that DPA's skin permeability (Kp) was  $2.6 \times 10^{-2}$  cm/h. The estimated parameters agreed with the mathematical models and showed that the targeted OGSR compounds may permeate the epidermal membrane because of their lipophilic nature. The rate at which the GSR's organic components penetrated through the model skin membranes is consistent with previous studies of the surface of the skin. Additionally, this demonstrated the possibility of IMS for OGSR detection because of its high selectivity and quick detection times, as well as the ability of the PDMS skin model membrane to be employed as a viable replacement for human or animal skin. However, the procedure involved in the extraction of OGSR compounds from the membrane remains time consuming and tedious (Moran & Bell, 2013).

McKenzie et al. accomplished the identification of both elemental and organic components of GSR from skin swabs using electro-spray trapped ion mobility spectrometry coupled to mass spectrometry

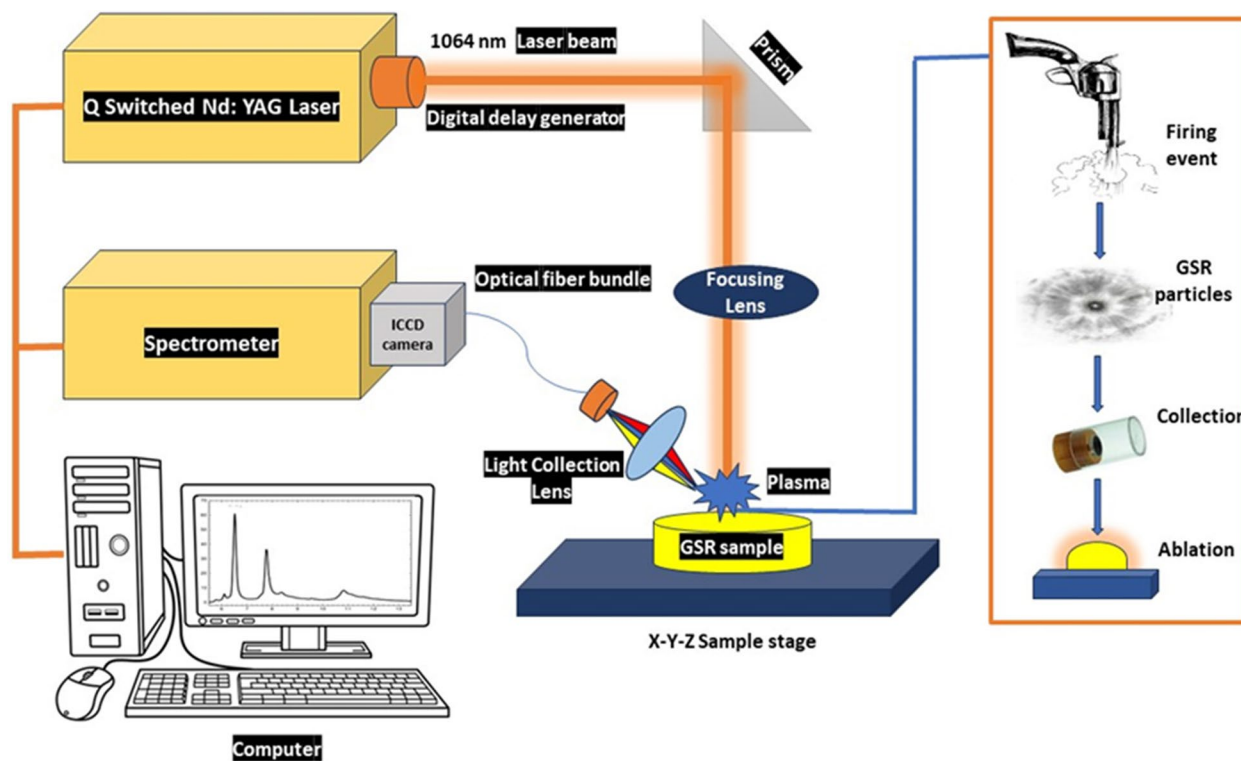
(ESI-TIMS-MS) which is an adaptation of trapped ion mobility spectrometry linked to mass spectrometry. Prior to swabbing, the swabs were moistened with isopropyl alcohol. The method which utilized less than 10µL of the sample allowed simultaneous extraction of OGSR and IGSR components which resulted in the simultaneous detection of DPA, EC, 2, 4-DNT, Ba, Pb, Cu, K, and NO<sub>3</sub>. The instrument operated at both negative and positive ion modes allowing the detection of organometallic components in the positive mode. Depending on the functional groups attached to the molecule under investigation, the organic components were detectable either in a positive or negative mode. The high mass resolution allowed for the precise identification of the compounds based on their mass accuracy and isotopic pattern. The reported study was best in the analytical capability of the method to separate and identify the organic and inorganic compounds from a complex mixture (McKenzie-Coe et al., 2018).

**Combined analysis techniques used for the analysis of IGSR and OGSR components**

*Laser-induced breakdown spectroscopy* LIBS has some benefits over conventional methods of elemental analysis, including fast measurement, adequate detectability,

and the potential for simultaneous non-destructive multi-element analysis. Furthermore, it is a rather easy approach that requires little to no sample preparation. The method uses a pulsed laser that is concentrated on a narrow area of the sample surface as shown in Fig. 5. Moreover, this spectroscopic technique can detect both the organic and inorganic components of GSR (Trejos et al., 2022). This section discusses the various studies carried out demonstrating the potential of LIBS technique to analyze both IGSR and OGSR, which increase the result’s confidence and reliability.

Studies by Goode et al. have shown the LIBS technique’s effectiveness in detecting GSR on shooters’ hands, even in trace levels. In this study, three methods for collecting GSR samples were considered. Samples were collected from the shooter before, during, and after the test fire as well as after the shooter washed their hands with soap and water. The double-sided tape was applied to the shooter’s hands to gather hand samples followed by the immediate evaluation using LIBS produced characteristic emission lines with significant variations. Although the study has indicated the potential of LIBS to be utilized as a screening technique for GSR analysis, it was only indicative for lead and barium. The inability to detect antimony remains as a limitation in the study (Goode et al., 2002b).



**Fig. 5** Schematic diagram of the laser-induced breakdown spectroscopy (LIBS) system

In another study carried out by Goode et al., they have utilized LIBS method to characterize bullets, jackets, and cartridge cases made of lead, copper, and brass respectively, from various manufacturers. The ammunition fragments were identified and correctly differentiated with LIBS combined with a computer-based pattern recognition method. The technique was precise and rapid in that it had the ability to record hundreds of emission spectra in a single day. While the study could well discriminate ammunitions from different manufacturers based on the emission spectra, the variation in the relative amounts of elements composing the bullets, jackets, and cartridge cases were not identified. However, conducting further study using large number of ammunition would allow to test the detection capability of the technique (Goode et al., 2002a).

M. Silva et al. in their work have used a similar approach to sample collection used by Goode et al. in the previous study mentioned above. The method is based on analysis using LIBS along with soft independent modeling of class analogy (SIMCA), a pattern identification software. GSR samples were collected by pressing an adhesive tape against the shooters/non-shooter hands soon after firearm discharge and after having washed the hands with soap and water. A total of 114 samples were utilized in the study. The tapes were analyzed directly under LIBS which also gave characteristic emission lines of barium and lead as reported earlier. The obtained spectral data was correctly categorized as shooters and non-shooters before and after washing their hands, using SIMCA. While the study has shown the capability of this non-destructive method to differentiate between the samples collected from shooters and non-shooters, it was unable to detect antimony. The same approach was utilized by Goode et al. to detect lead and barium using LIBS without utilizing the help of a recognition software (Silva et al., 2009).

Fambro et al. has explored the use of LIBS and SEM/EDX for the characterization of GSR discharged from lead-free ammunition. Two techniques were considered in the study. LIBS to identify the analytical markers present in GSR while SEM/EDX was utilized initially to determine surface morphology and elemental composition of the sample and then to determine the extent of evidence retained or preserved after LIBS analysis. Double-sided adhesive carbon tapes were used to tape lift samples from the shooter's hands and the tape was analyzed. The emission spectra obtained using the LIBS technique identified Ca, Ba, Na, and K. Ba, Al, Si, and K with trace amounts of Ti, Fe, and S were detected by SEM-EDX, from the GSR obtained from lead-free

ammunition assessed in this study. Barium was identified as the main analytical marker in both techniques. Due to its complex nature and heterogeneous distribution of GSR particles, not every laser shot will strike it; hence, only the maximum emission signals were taken into consideration. The study could attain evidence preservation for reanalysis, even after laser ablation. The threshold values were obtained from the statistical data obtained from the blank sample library. However, the analytical marker used to characterize the ammunition primer is only applicable to primers having the same composition. However, this work includes only analysis and characterization of 9mm lead-free ammunition. Further studies should include the characterization of both conventional and lead-free ammunition from various manufacturers with varying calibers and different analytical markers (Fambro et al., 2016).

Lopez et al. in their study have used LIBS imaging for visualizing GSR patterns on the clothing of the victim. White textile fixed on cardboards was used as the target material. The distribution of GSR markers with emission lines showing 283.3 nm for Pb, 455.4 nm for Ba, and 259.8 for Sb on the textile target material, obtained after shooting from different distances, were analyzed. In the study, a LIBS system having two spectrographs, ICCD cameras, and a motorized stage was used since it enabled the detection of GSR markers from conventional ammunition simultaneously because the same laser-induced plasma provides data from two separate wavelength regions. This was used to compensate for the spectral range that was limited to a maximum wavelength of 30 nm. Nine by 19 mm ammunition from different manufacturers were used to conduct the firing on cloth target placed at various distances (30 cm, 50cm, and 150 cm). The particles were manually picked from the target cloth using metallic tweezers and placed on adhesive tape fixed to a microscopic slide. This study also included an approach to detect the degree of evidence preservation after analysis using LIBS as reported in previous literatures, but as the laser shots destroyed the cloth surface, the GSR particles were transferred to an adhesive tape fixed on an aluminum plate by pressing it against the cloth surface. The analysis time was ~2 h and 45 min per sample. While the Pb, Ba, and Sb could be detected from a single laser shot on a single GSR particle is an advantage, the use of two spectrographs to obtain two different wavelength regions makes it complicated and can be considered as one of its limitations (López-López et al., 2017).

Trejos et al. have demonstrated high classification rates for IGSR and OGSR using a combination of LIBS

technique and electrochemical methods. I/OGSR components present in modern ammunition were simultaneously detected using the technique. The authors suggest that the combination of both techniques offered great performance with high sensitivity and less error rates. While 50ng–25 $\mu$ g of Pb, Ba, Sb, Cu, and Al standards were used for method optimization for LIBS, 1–10 ng/ $\mu$ L solutions of Pb, Ba, Sb, Cu, NG, and 2,4- DNT were used in the EC method. The LOD ranged from 0.2 to 200 ng for LIBS and 0.1–1ng/ $\mu$ L for the electrochemical method where the former took <1 min of analysis time for 5 emission lines per target element and the latter could detect and separate the complex mixture containing Pb, Sb, Cu, DNT, and NG not taking more than 3 min per sample. The authors suggest that the method also allows reanalysis of the sample by SEM/EDS used for confirmatory analysis. While the study discussed here represents rapid and simultaneous detection of GSR, it should be noted that the organic constituents of GSR analyzed by the EC method were found to be lost rapidly after being analyzed after a week suggesting the importance of rapid analysis of OGSR. The proposed method if extended to real time analysis would provide a promising fast response (Trejos et al., 2018).

Alicia Dona-Fernandez et al. performed a comparative study using SEM/EDX and a portable LIBS system for GSR element analysis (Sb, Pb, and Ba), obtained from 9mm ammunition and collected using aluminum stubs with graphite adhesive. A portable instrument based on LIBS known as iForenLIBS was developed in this work. Pb, Ba, and Sb could be simultaneously detected using this technique. An appreciable level of sensitivity was obtained for samples with particle number  $\geq 3$  with response time <4 min. The LIBS approach has been cited by the authors as the ideal screening tool for rapid and on-spot identification of gunshot or firearm discharge residue particles. Reanalysis of the samples were performed using SEM/EDX to estimate the degree of evidence preservation after laser ablation. Although the authors have indicated the potential of portable LIBS over SEM/EDX, the necessity that the particle size must exceed 1 $\mu$ m to be detected by LIBS, the inability of LIBS to completely ablate the particles having size greater than 2 $\mu$ m and the requirement of two separate stubs for double sampling using LIBS and SEM/EDX remains as a limitation (Doña-Fernández et al., 2018). Table 2 indicates the various instrumental techniques discussed in the study along with their advantages and disadvantages with respect to GSR analysis.

*Solid-phase microextraction combined with chromatography and scanning electron microscopy* Argente-García

et al. have developed a method for collecting and quantifying organic and inorganic gunshot residues on individuals' hands. This method involves using on-line in-tube solid-phase microextraction (IT-SPME) combined with miniaturized capillary liquid chromatography and scanning electron microscopy with energy dispersion X-ray detection. For organic residues, the best extraction efficiency was achieved using a dry cotton swab followed by vortex-assisted extraction with water. This method preserves inorganic residues. The method had a satisfactory limit of detection for diphenylamine (0.3 ng) and good precision (intra-day relative standard deviation of 9%). The method was tested on samples from shooters' hands, and diphenylamine was detected in 81% of the samples. Inorganic gunshot residues were also analyzed using SEM-EDX with both cotton swab and lift tape kit samplers. Cotton swabs provided better sensitivity for diphenylamine compared to lift tape kits. The presence of both inorganic and organic residues in a sample could be used as evidence in forensic proceedings, eliminating the possibility of environmental or occupational sources when diphenylamine is found together with inorganic residues (Argente-García et al., 2019).

### **Forensic relevance of GSR**

Assessing whether the trace's origin is a weapon discharge and determining what type of activity triggered the transfer are two of the key goals of GSR detection and analysis. It is crucial to distinguish between these two questions because GSR can be conveyed either directly (primary transfer) because of a weapon discharge or indirectly (secondary transfer). Rather than an analytical perspective, a more accurate assessment of GSR from a forensic aspect will result from an increased information gathered from the trace characteristics of GSR particles, its transfer, persistence, and the prevalence in the environment. This section highlights the importance of GSR and its forensic relevance, which has the potential to answer several queries related to a crime reconstruction and investigation of cases involving a firearm.

### **Persistence studies of GSR**

The time frame between a gunfire discharge, hand sampling, and GSR collection depends on a few parameters, including the location of the crime and accessibility to the crime scene. As GSR has a limited persistence (~4h), it may be lost or transferred depending upon the physical activity of the person like washing or rinsing hands, rubbing them against any material, putting them inside the pockets, and shaking hands with someone. Factors affecting the persistence of GSR include contamination, particle size, environmental or atmospheric conditions,

**Table 2** Various instrumental techniques discussed in the study with their advantages and disadvantages

Sl No.	Techniques	Advantages	Limitations	Literatures
1.	<b>SEM/EDS</b>	The method is applied to detect the morphological feature of particle. Along with morphological feature EDX give the elemental analysis too	Cigarette lighter particle are same as GSR in morphology which can cause interference in the study. Not apt for field analysis	Lindsay et al., (Lindsay et al., 2011)
2.	<b>Spectroscopic techniques</b>			
	<b>LIBS</b>	Potential for direct detection LIBS typically samples very small amounts of material (~0.1 µg to 1mg) and is therefore practically non-destructive. Simultaneous multi-elemental analysis.	Increased cost and system complexity. Difficulty in obtaining suitable standards (semi-quantitative) Detection limits are generally not as good as established solution techniques. Poor precision—typically 5–10%, depending on the sample homogeneity, sample matrix, and excitation properties of the laser. Possibility of ocular damage by the high-energy laser pulses.	Silva et al., (Silva et al., 2009)
	<b>SERS</b>	Trace elemental analysis 10 <sup>6</sup> times Signal enhancement than Raman spectroscopy	Destructive technique not allowing additional analyses on the sample. The inherent grain-to-grain inhomogeneity of the gunpowders could be a limiting factor to unequivocally link a GSR macro particle with ammunition	López et al., (López-López et al., 2016)
	<b>Raman spectroscopy</b>	Highly specific like a chemical fingerprint of a material Portable and hand-held spectrometers that enable for data collection and material detection immediately in the field.	Raman signal are inherently weak Portable or hand held instruments have poorer sensitivity that benchtop instruments.	Buzgar et al., (Buzgar et al., 2009)
	<b>IMS</b>	Atmospheric pressure operation No vacuum pumps are required hence simple Overlapping analytes can be separated changing the buffer gas	Not suitable for non-volatile analytes Low proton affinity or ionization potential compounds are hard to detect	Fernandez et al., (Fernández-Maestre, 2012)

and skin conditions. GSR persistence has been studied in recent years using several techniques, a few of which are discussed below. Figure 6 indicates the time-dependent change of the persistence of GSR particles deposited on the barrel of a revolver as reported by (Kara, & Ö. Yalçinkay., 2017).

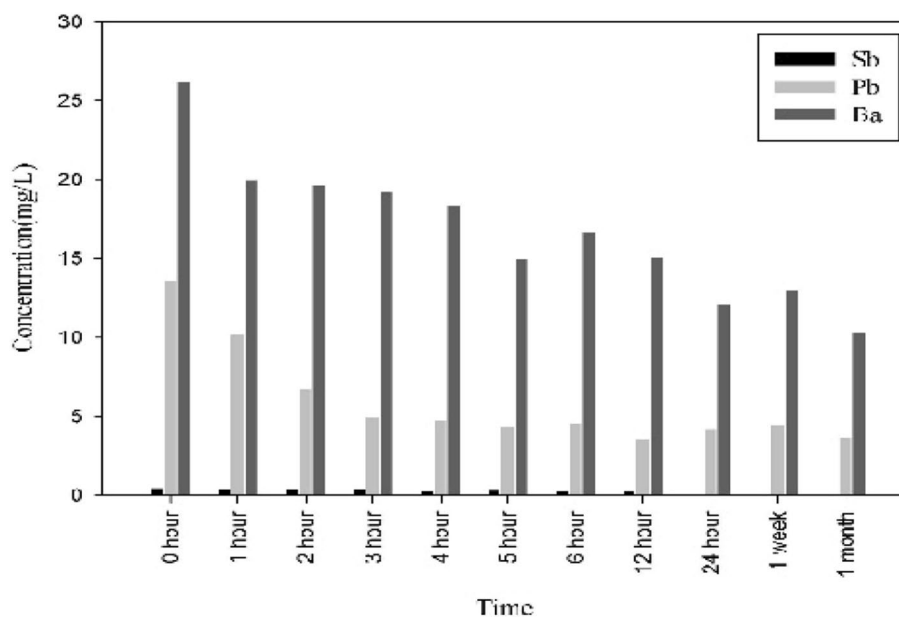
In a study, Jalanti et al. demonstrated that the transmission of these particles causes GSR ratios to differ in various regions of the hands. The OGSR compounds, which are non-particulate residues, are less prone to secondary transfer because of their volatile and lipophilic nature making it adhere to the skin. In contrast, the IGSR particulates are more prone to secondary transfer because they stick to the surface of the suspect's skin or clothing. In their study, sodium rhodizonate chromophoric test and SEM/EDX were used to examine the loss of GSR that was obtained at various time intervals. The investigation revealed that the amount of particles had poor repeatability and fluctuated predictably as a result of GSR loss or transfer (Jalanti et al., 1999).

Transfer and persistence of OGSR was evaluated by Maitre et al., using an ultra-performance liquid chromatography-mass spectrometer (UPLC-MS/MS) method by conducting various shooting events using two different ammunitions. In the study, four OGSR components—EC, MC, DPA, and N-nitrosodiphenylamine (N-nDPA)—were considered to evaluate GSR persistence on the shooter's hands for various time periods. In the trial, GSR persisted for up to 4 hours. Shot-to-shot variation in the

OGSR levels and a drastic drop in the analytes during the first hour after firing were also noted (Maitre et al., 2018).

With DPA as the target analytes, Arndt et al. analyzed the persistence study of OGSR using IMS. Before the samples were introduced to the IMS system, direct thermal desorption was used to examine the swab samples that had been taken from the hands using the solvent swabbing procedure. Although OGSR persistence was shown to remain for around 4 h and was not prone to secondary transfer, using soap and sanitizer on the shooter's hands after shooting a weapon eliminated the organic components from the skin. The background and blank samples did not significantly respond to DPA (Arndt et al., 2012). However, the result of (Kara, & Ö. Yalçinkay., 2017) contradicts this study suggesting that the washing of hands does not sufficiently remove OGSR traces completely.

In a study conducted by Wallace et al., GSR samples were collected at various time intervals after firing. GSR samples from the shooter's hands were collected using carbon tapes secured to aluminum stubs, and they were examined using SEM/EDS. The study examined the persistence of GSR particles over a period of 3 h. The findings revealed a reduction in the amount of GSR particles collected from the shooter's hands after approximately 1 h after the weapon was fired due to the decay of the initial particles over time. To be more precise, approximately 20 min later, there was a significant drop in the level of positive particles spotted on the shooter's hands,



**Fig. 6** Time-dependent change of the persistence of GSR particles: reprinted from (Kara, & Ö. Yalçinkay., 2017)

emphasizing the significance and requirement of sampling a suspect's hands shortly after a shooting incident (Wallace, 2010).

The persistence investigation of GSR particles was carried out by M. Rosenberg and C. Dockery using laboratory LIBS equipment. They have used LIBS for the determination of GSR on the hands of the shooter and have obtained positive results for GSR even after 5.27 days after a firing event. The persistence studies in this report that reveal the presence of GSR even days after may provide a significant indication as to whether the suspect was present during a shooting (Rosenberg & Dockery, 2008).

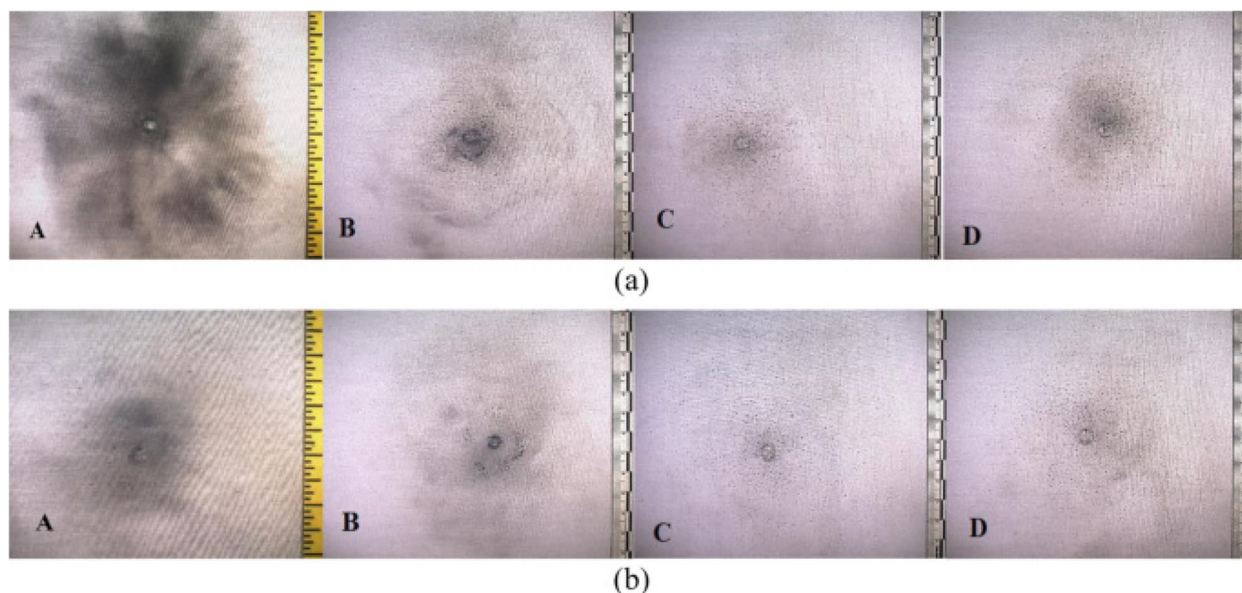
### Shooting distance estimation

Previously, shooting distance estimation from GSR particles was done using color tests, and the results were typically based on visual inspection. However, because these methods have a higher error rate owing to varied interpretations, it is now necessary to adopt advanced techniques that will yield accurate results. Figure 7 demonstrates the pattern distribution of GSR obtained by firing two different ammunitions at different shooting distances as reported by (Zain et al., 2021).

Lopez et al. visualized GSR patterns using LIBS imaging to determine firing distance. After being shot at from various distances, the distribution of GSR markers (Pb, Ba, and Sb) on the textile target material was examined. The study employed a LIBS configuration

that permitted the use of two spectrographs with ICCD cameras and a motorized stage simultaneously. Since the same laser-induced plasma delivers information from two separate wavelength regions, this allowed the simultaneous detection of the GSR markers from conventional ammunition. The method's key benefit is that it enables the measurement of both organic and inorganic components in the laboratory and on the site, improving the simplicity and efficiency of GSR analysis. The approach also permits further verification via SEM/EDS due to its non-destructive nature (López-López et al., 2017).

The estimation of shooting distance using clothing samples fired from various distances was recently introduced by Vander Pyl et al. The obtained LIBS data was used to construct 2D elemental maps. The study was carried out on textile samples with complex patterns and dark colors, which are often challenging for conventional chemical testing to examine. They have developed a modified LIBS approach for GSR detection around bullet holes in their study, even on challenging crime scene substrates. The spatial distribution of the IGSR markers was used to identify the shooting range. Depending on the element, LIBS allowed for the detection of GSR even at low levels ranging from 0.2 to 440ng. When the technique was compared to visual and colorimetric testing, it was discovered that LIBS offered greater sensitivity, selectivity, and accuracy with 100% accurate classification as opposed to color tests, which occasionally misclassified data (Pyl et al., 2019).



**Fig. 7** Pattern distribution of GSR obtained by firing (A, B) 38 inch, and (C, D) 9x19mm ammunition at different shooting distances indicating the effect of shooting distance and the type of ammunition on the pattern distribution: reprinted from (Zain et al., 2021)

In a different study, Vander Pyl et al. used the LIBS approach to measure the gunshot distance from a textile sample stained with human blood as well as to spot bullet holes. A 9-mm handgun was employed for the shooting. When compared to color tests and physical examinations, the approach demonstrated high classification rates. Different target materials like wood, glass, and drywall were used as substrate materials for firing. The target materials were chosen in such a way that it matches a real crime scene scenario. The method not only enabled easy transfer of GSR but also allowed fast mapping of GSR markers owing to its limited sample preparation, little use of chemical reagents, and enhanced sensitivity (Vander Pyl et al., 2020).

Energy dispersive X-ray fluorescence was used by Mishra et al. in their study to examine the dispersion of GSR particles on the trajectory at various shot distances (EDXRF). The acquired data showed a considerable difference in the sulfur, barium, and lead elemental distributions in GSR. However, one crucial aspect of the study was the ability to link GSR dispersion with firing distances (Mishra et al., 2018).

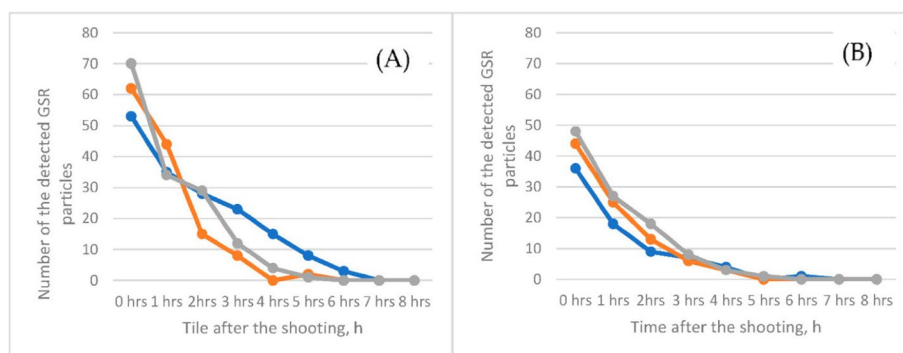
#### Time since fire estimation

The inner walls or surroundings of barrels and cartridge cases are where the heterogeneous combination of GSR that is produced because of firing diverse chemical species sticks the most. Due to various physicochemical processes, such as adsorption on metallic surfaces and diffusion in the air, they gradually lose quantity over time. Gaining any information regarding the residual quantity could be very useful for dating purposes. The scientific verification of whether a weapon was shot or discharged lately would be a vital step in recreating a firing event since it has been extremely difficult for investigators to present a method with scientific validity to estimate the time since fire. Several approaches were

proposed in the past for the same. While some of the traditional approaches are simple (looking for dust or rust on the inner wall of a gun barrel, for example), a few of the modern methods chemically analyze the gaseous and volatile components that constitute the OGSR. Figures 8 and 9 demonstrate the number of particles characteristic of GSR as a function of time after shooting with a higher and a lower caliber ammunition respectively as reported by (Tahirukaj et al., 2022).

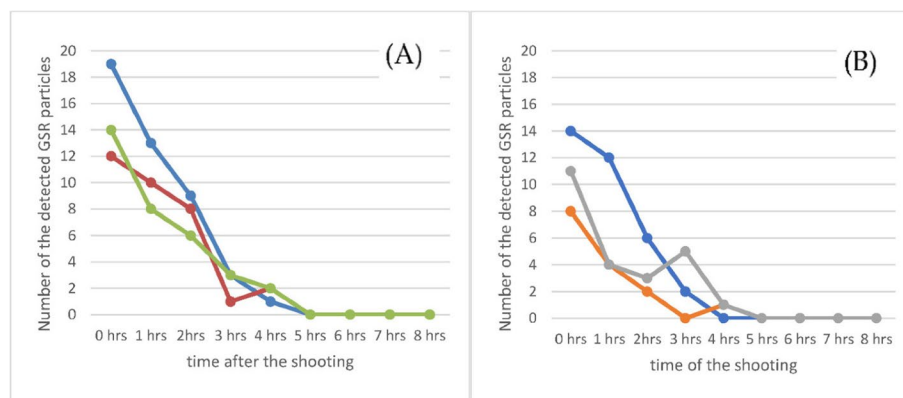
According to a method proposed by Gallidabino et al., the statistical evaluation of the likelihood ratios is used to estimate the amount of time since the fire. The study of the volatile GSR components using SPME and gas chromatography (GC) was utilized. They claim that the analysis of the components present inside the barrels or cartridges at the time of extraction is the only basis for the qualitative and semi-quantitative data obtained through chromatograms from the SPME-GC analyses of the inner atmosphere of the cartridge cases and barrels. Some aging markers, including naphthalene and polycyclic aromatic hydrocarbon, which are often produced by the difference in the burning rates of gunpowder, can be used to estimate the time since a fire (Gallidabino et al., 2013).

The determination of time since fire using the SPME sample approach has been reported by Andrasko et al. In this study, they analyzed the atmosphere inside the cartridge cases looking for the presence of naphthalene or an unknown nitrate compound TEA instead of evaluating the common GSR compounds like biphenylene, DPA, or acenaphthylene. A decrease in the amount of the former was used to estimate the time since fire. The results of the study conducted by Andrasko and Stahling suggest the possibility of analyzing the trapped gases or atmosphere within the barrels of a shotgun, cartridge cases, etc. and determining the time since fire of a fired cartridge. The study also indicated the persistence of



**Fig. 8** Number of particles characteristic of GSR as a function of time after shooting with high-caliber ammunition:  $7.62 \times 39$  mm blue line,  $7.92 \times 57$  mm orange line, and  $7.62 \times 54$  mm gray line carried out during (A) the winter season and (B) the summer season; reprinted from (Tahirukaj et al., 2022)





**Fig. 9** Number of particles characteristic of GSR as a function of time after shooting with low-caliber ammunition:  $7.65 \times 19$  mm blue line,  $9 \times 19$  mm red and orange line, and  $7.65 \times 17$  mm green and gray line, carried out during (A) the winter season and (B) the summer season: reprinted from (Tahirukaj et al., 2022)

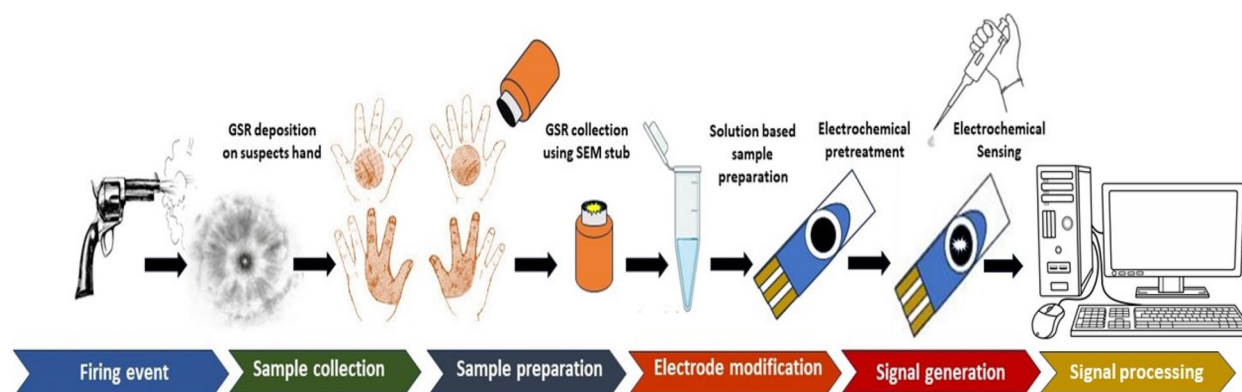
naphthalene and TEA compound to be only a few weeks. For cartridge cases that were left exposed, the components of interest were found to be lost much more rapidly. Additionally, they noted that lengthy barrels were found to contain more volatile organic compounds than short-barreled weapons. However, the technique has not yet been validated and broadly accepted by the American forensic community, yet it aids in the gathering of pertinent data pertaining to shooting incidents (Andrasko & Stähling, 2003).

Weyermann et al. examined organic volatile residues in 9-mm shot cartridges using gas chromatography/mass spectrometry (GC/MS) after SPME to ascertain the time after discharge. The identification of the volatile organic residues was made possible by comparing the detected compounds to reference samples, and the repeatability of the compounds was assessed as a function of time since discharge (Weyermann et al., 2009).

**Challenges faced in GSR analysis** All the techniques mentioned above produce reliable data but are expensive, sometimes time-consuming and demand highly qualified individuals to operate the device. To ensure fair justice rapidly, GSR detection technology innovation is essential. When it comes to cases involving firearms, GSR can offer insightful investigative data. However, the field has faced difficulties with the speed of analysis, the precision of results, and the application to new ammunition types when it comes to established methods of GSR detection. Hence, to safeguard the public and aid investigators in making judgements based on accurate findings, it is imperative to create technologies that can speed up residue testing and boost certainty. It is difficult to develop GSR analysis methods with quantifiable error rates.

**Current scope of research and trends for dual detection of GSR components via novel methodology** The objective of this paper is to review few of the major GSR detection techniques developed so far ranging from the straightforward colorimetric technique developed in the early twentieth century to all the complex instrument-based techniques, to the most straightforward and accurate electrochemical technique for both types of residues, organic, and inorganic components. According to a few researchers, advanced GSR detection approaches could evaluate GSR samples more quickly, more accurately, and with more information than existing laboratory and field-based examinations. Although some researchers worked on both residues, most sophisticated electrochemical methods are used for inorganic gunshot residues (IGSR) analysis. Electrochemical approaches thus emerged as a viable solution to this issue. In comparison to instruments and color-based tests, the method is more portable, more dependable, has lower production costs, and requires less time for detection.

Technology breakthroughs drive improvements in methods like electrochemical-based sensors. Figure 10 represents the electrochemical sensor-based method for the fast screening of gunshot residue. Many studies employing various techniques have been conducted on the analysis of gunshot residue. Moreover, a single strip-based approach is used in place of the manufactured electrochemical cells to make GSR detection simple. As a result, many scientists are turning to sensor-based technologies for quick and accurate detection to overcome these problems. These techniques offer quick results for detection and are more user-friendly, sensitive, and economical. This screening method was discovered to be faster than



**Fig. 10** Electrochemical sensor-based method for the fast screening of gunshot residue

earlier methods, enabling the identification of organic and inorganic residues with 99% accuracy, which is a high level of accuracy for a screening procedure. Furthermore, the methods essentially do not damage the samples, enabling confirmation of the results using additional methods which in turn reduces the backlogs and increases the confidence in the results. This novel dual detection method enables the accurate on field and laboratory detection of both IGSR and OGSR components with analysis times less than 5 to 10 min per sample. Trejos et al. have achieved a notable level of success using this method (Trejos et al., 2022). In their study, they have gathered datasets from a sizable population to serve as the foundation for useful solutions for the forensic community. To estimate the muzzle-to-target distance, 3D chemical maps were created for a variety of target materials. Finally, statistical techniques were utilized to analyze data from our large database and interpret GSR results using probabilistic and artificial intelligence methodologies. Several IGSR and OGSR components are detectable by EC sensors at trace and ultra-trace levels. The proposed approach will be statistically analyzed and validated, allowing measurement of error rates as well as probabilistic definition and identification of components, reinforcing the arguments made in court.

A study reported by Khandasammy et al. highlights the value of OGSR evidence, which can provide crucial insights in criminal investigations. Researchers have been increasingly interested in the analysis of organic components of GSR, which can differentiate between OGSR produced by different ammunition brands and calibers. They employed Raman spectroscopy for molecular information, laser-induced breakdown spectroscopy (LIBS) for elemental analysis, and high-resolution optical microscopy to examine OGSR particle morphology. The study aimed to differentiate OGSR particles from closely related ammunition types of the same caliber and manufacturer,

generated under identical conditions. Advanced chemometric techniques successfully distinguished between the OGSR samples analyzed, demonstrating the potential of this combined approach for specific OGSR identification and characterization, even in cases involving highly similar ammunition types (Khandasammy et al., 2023).

## Conclusions

A significant surge in GSR-focused research has been observed during the past two decades. GSR detection and trace analysis has been one of the most important reasons for the development of these instrumental techniques in the forensic aspect. Overall, this study emphasizes the importance of the numerous traditional and contemporary methods employed in analyzing the organic and inorganic components of GSR. The study also focuses on the forensic relevance of GSR for determining the shooting range, GSR persistence, and time since fire. The challenge of examining a complex sample like GSR was successfully solved by the instruments' combination of selectivity and sensitivity. Additionally, it underlines the significance of GSR and how vital it is in helping to reconstruct a firing event. Although SEM/EDS was formerly the main method for GSR analysis and confirmation, more recent instrumentation methods have emerged. These include LIBS, surface enhanced Raman spectroscopy (SERS), IMS, and electrochemical methods that are available in bench-top and portable variants. Due to their multi-element and on-field analysis capabilities, limited or no sample preparation, capability to do direct analysis on any surface, non-destructive nature, low limit of detection, etc., some of these techniques are frequently employed for GSR analysis.

Discussing the capabilities of various techniques and their role in analyzing the components of GSR leading to diverse interpretations, this review would be a valuable reference for researchers, legal practitioners, and people

working in the field of forensic science as it discusses the current scope of research and trends for dual detection of GSR components via novel methodologies. Utilizing these new technologies, analysis times have been reduced, allowing for a more focused search and the elimination of forensic sample backlogs. Both on-site and mobile lab applications can be implemented using the approaches outlined above. However, the review also discusses the GSR deposition and transfer in simulated indoor shooting ranges. To have a better understanding of the role of GSR in environmental pollution and to assess the various external environmental factors like wind, rainfall, and humidity, affecting GSR, it is necessary to evaluate these aspects in outdoor shooting ranges. Based on the review, the current study aims to provide an overview of the importance of GSR as physical evidence in forensic science. This overview gives an elaborate description of the future aspects of GSR detection techniques. This will help the forensic scientists and researchers choose the most useful approaches to differentiate between different GSR samples. This study provides information on GSR as trace evidence and discusses various spectroscopic and electrochemical techniques employed in GSR analysis to distinguish it to help academicians, researchers, legal practitioners, and forensic soil scientists.

#### Abbreviations

GSR	Gunshot residue
LIBS	Laser induced breakdown spectroscopy
SERS	Surface enhanced Raman scattering
IMS	Ion mobility spectrometry
SEM/EDS	Scanning electron microscopy/energy dispersive X-ray spectroscopy
IGSR	Inorganic gunshot residue
OGSR	Organic gunshot residue
NC	Nitrocellulose
NG	Nitroglycerine
NGu	Nitro guanidine
VOC	Volatile organic compounds
DPA	Diphenylamine
MC	Methyl centralite
EC	Ethyl centralite
DNT	Dinitro toluene
ICP-MS	Inductively coupled plasma mass spectrometry
AAS	Atomic absorption spectroscopy
NAA	Neutron activation analysis
FAAS	Flameless atomic absorption spectrophotometry
SDL	Signal detection limit
LOD	Limit of detection
LOQ	Limit of quantitation
AN	Ammonium nitrate
TNT	Trinitrotoluene
RDX	Royal demolition explosive
SPME	Solid phase micro extraction
ESI-TIMS-MS	Electro-spray trapped ion mobility spectrometry coupled to mass spectrometry
ICCD	Intensified charge coupled device
EDXRF	Energy dispersive X-ray fluorescence
GC/MS	Gas chromatography/mass spectrometry

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#### Authors' contributions

SK carried out an extensive literature survey and was a major contributor in writing the manuscript. PA read and approved the final manuscript

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#### Availability of data and materials

All data generated or analyzed during this study are included in this published article.

#### Declarations

##### Ethics approval and consent to participate

Not applicable as this article does not contain any biological studies with human participants or animals.

##### Consent for publication

All the authors have given consent for publication.

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