Forensic Science International: Synergy 2 (2020) 416–428

Contents lists available at ScienceDirect

Forensic Science International: Synergy

journal homepage: https://www.journals.elsevier.com/forensic-science-international-synergy/

Interpol review of gunshot residue 2016–2019

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ARTICLE INFO

Article history:
Received 6 January 2020
Accepted 16 January 2020
Available online 12 March 2020

Keywords:
GSR
Gunshot residue
Primer residue
Interpol

ABSTRACT

This review paper covers the forensic-relevant literature in gunshot residue analysis from 2016 to 2019 as a part of the 19th Interpol International Forensic Science Managers Symposium. The review papers are also available at the Interpol website at: https://www.interpol.int/content/download/14458/file/Interpol%20Review%20Papers%202019.pdf.

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1. Introduction

This review paper covers advances in scientific methods applied to Gunshot Residues reported since the 17th Interpol Forensic Science Symposium in October 2016.

A literature search was conducted covering articles published in the main analytical and forensic journals in 2016, 2017 and 2018.

During discharge of a firearm, primer and gunpowder residues as well as metal particles from the projectile and the cartridge case are expelled from the muzzle and from other openings of the firearm. These residues are referred as primer residues, firearm discharge residues or gunshot residues (GSR).

Scanning electron microscopy coupled to energy dispersive X-ray microanalysis (SEM/EDS) still is the method of choice for the identification of inorganic GSR (IGSR) on samples. This technique is well suited for the detection of small particles (down to 0.5 μm) containing heavy metals such as Lead, Barium and Antimony originating from primers with a classic composition (e.g. sinoxid primers). Moreover, it allows for the determination of the correlation between the morphology and the chemical composition of individual particles, composed of Lead, Barium and Antimony, considered as characteristic of GSR. However spectrometric techniques such as atomic absorption spectrometry or optical emission spectrometry are still used in some forensic laboratories, because of their high sensitivity, their speed and their ease of use, despite the fact that morphological information of the particles is absent.

The field of GSR was recently reviewed by Brożek-Mucha [1]. After having described and commented the inorganic/organic nature and aspects of GSR, the author examined the recent trends in this field, distinguishing two major strategies to overcome the challenge of the advent of heavy-metal free ammunition. These ammunition produce other types of IGSR that are by nature less well detected by the traditional SEM/EDS technique. The first strategy consists of the use of other elemental techniques such as ion beam analysis or electron backscattered diffraction to characterize more precisely the inorganic nature of the GSR, in terms of trace elements (ion beam analysis), or crystallinity (electron backscattered diffraction) that may be specific to the ballistic origins of the particles. The second strategy is the use of techniques such as liquid chromatography coupled to mass spectrometry, in order to fully characterize the organic fraction of GSR. Although progress has been made during the recent years in terms of sensitivity and limit of detection, research and studies still need to be performed in terms of prevalence, persistence and transfer, in order to gain the favour of the GSR-experts to apply these techniques in their expertise. For instance, since organic GSR (OGSR) analysis is mainly related to bulk chemistry and since current GSR-experts are for most of them working in material analysis departments, in our opinion only a new technique offering substantial benefits in terms of analytical performances will gain the favour of these experts and change their analytical paradigm.

1.1. Inorganic GSR

1.1.1. Fundamentals of GSR formation

Spathis examined by SEM the morphology of GSR particles as a function of the distance from the weapon (up to 1 m) [2]. He observed that although classical spheroidal particles are always

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https://doi.org/10.1016/j.fsisyn.2020.01.011
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present whatever the distance, some additional particles with an irregular morphology may also be observed. Interestingly, by defining different classes of particles as a function of their morphology (from classical spheroidal particles to "splats"), the proportion of particles inside the different classes seems to be distance-dependent. For instance, at distances close to the firearm, particles showing a "molten-looking" appearance are mainly observed. According to the author, this illustrates the fact that the metallic residues were in a liquid state when their flight was disrupted. By analyzing the composition of the particles by SEM/EDS, he also showed a relation between inorganic composition and morphology, this because of the complex chemical environment inside the exhaust plume of the firearm.

Luten et al. examined the influence of time on the local concentration and distribution of airborne GSR particles, this by using impactor technology [3]. The authors showed that the smaller the particle (<1 μm), the longer the time it takes for these particles to fully sediment. Based on the different results obtained with impactor technology, they conducted an additional experimental study: a person wearing a piece of cloth on his shoulders entered in the shooting room 200min after the shooting, walking inside for a period of 2min. The piece of cloth was then stubbed for GSR analysis using SEM/EDS. The results showed that about 300 IGSR particles were found on the sample, illustrating the fact that a high level of contamination can occur, even after a very long period of time (3 h). This time interval is far longer than what was previously reported [4].

While examining with SEM/EDS an usual cluster of 10 μm × 15 μm which was detected on an individual involved in a shooting event for which different types of ammunition were used, Israelsohn-Azulay et al. observed some domains, composed of several building blocks that could have been accumulated to constitute this large particle [5]. According to the authors, the close examination of such type of clusters as a general policy could give some valuable information about the nature of the primer mixes present in the ammunition recently used. This could also give some details about GSR formation, including the mechanism leading to the well-known memory effect of the weapon.

While research has already been performed to determine the characteristics of Lead-based and heavy-metal free GSR, little research has been reported on determining other components of ammunition which may also contribute to GSR. Terry et al. therefore studied the priming cup and the residue that originates from it as this may contribute to IGSR [6]. Five full cartridges and five cartridges containing only the primer cup were fired for each ammunition type available. In the Lead-based primers, in addition to the traditional GSR elements (Lead, Barium and Antimony), elements from the cartridge cases were also observed, particularly Copper and Zinc. Aluminium was also observed in some of the spectra; this element could be indicative of the presence of frictionators in the priming mixture. Conversely, the heavy-metal free primers show a variety of elements which are indicative of their unique mixtures, such as Potassium, Silicon and Titanium. A multivariate statistical approach was used in order to obtain an objective measure of discriminating features within the data set. While the Lead-based primers grouped very close together, this was not the case for the heavy-metal free primers which were spread into various smaller groups, based on the priming compound elements and the cartridge case. As a consequence for heavy-metal free primer ammunition, if an unknown cartridge case is collected from the crime scene, the multivariate statistical approach could help in classifying which type of primer composition was used.

Referring to different case analyses reporting the presence of Selenium in GSR particles, Romolo et al. conducted shooting tests with weapons treated with two different blueing agents (Super Blue® and Aluminum Black®) containing this element [7]. By using SEM/EDS analysis, the authors showed that the shots produced some particles containing Selenium. These blueing agents may therefore be a reasonable source of Selenium observed in GSR particles.

1.1.2. Sampling

Routine sampling prior to SEM/EDS analysis consists of the use of Aluminium stubs of 1.3 cm diameter covered with a double-faced sticky carbon tape, this to stub the hands and the clothing of individuals suspected to be involved in a shooting incident. Some forensic agencies also recommend to sample the faces and/or the hairs, mainly to overcome contamination issues that may occur during interception and arrest by police forces, operations that will mainly affect the hands of the individuals.

Burnett examined the effect of skin debris on GSR sampling and detection [8]. He showed that GSR particles up to 5 μm can be occulted by skin debris. According to the author, performing SEM/EDS analyses at 30 kV allows a higher number of GSR particles to be detected, compared to 20 kV. However, the best method to reveal all the particles consists of the treatment of a bleach digestion prior to analysis, by using a sodium/calcium hypochlorite solution to remove most of the skin debris. These results, obtained by performing analysis with the help of a manual SEM/EDS system, should now be quantitatively confirmed by using an automated SEM/EDS system.

Like for sample collection from faces or hairs, the presence of GSR in samples collected from the nose (nasal mucus or nose hairs) could be a valuable indication of the presence of a suspect in a shooting environment, as these samples pose less problems of interpretation in terms of possible contamination during interception/arrest by police officers. On another note, the acceptable time limit between shooting incident and hand sampling varies, depending on the country and the police institution, 4–6 h being a time limit most often chosen. So when a criminal act occurs, time is crucial, and to extend the useful sampling period of GSR would be of great help to police investigations. It is hoped that sampling nasal mucus or nose hairs to detect GSR would extend the time frame in which testing could be done.

During the period 2016–2018, different techniques have been proposed to sample and analyze the nasal mucus of individuals. Merli et al. examined the possibility to detect GSR in the nasal mucus of suspected shooters by using instrumental neutron activation analysis, focusing on Barium and Antimony [9]. The authors decided not to monitor Lead because of its ubiquitous presence in the environment and because of higher instrumental quantification limits. Compared to control samples, shooters showed a higher amount of Barium and Antimony, elements that could still be detected 12 h after firing. According to these results, the persistence in these sample mode seems to be higher compared to samples collected on hands.

In their study, Aliste and Chávez propose the design of a new procedure for the sampling of possible GSR stored in nasal mucus, through sample analysis by graphite furnace atomic absorption spectrometry [10]. They also seek to establish a comparison of IGSR results obtained in nasal mucus with IGSR results obtained from hands, in order to complement both sampling procedures. Finally, the variation of the IGSR concentration stored in the nasal mucus with time was studied. These obtained values help to quickly identify non-shooters. But it is not possible to differentiate the type of weapon and, furthermore, there is no contamination in the nasal mucus from merely handling weapons. In the study of the variation of the IGSR concentration over time after firing, a linear decrease is not found. In most weapons, except the .22 revolver, the

concentration of the three elements Lead, Barium and Antimony at time zero is at a maximum. The concentration then decreases irregularly with time. It is thought that breathed GSR particles reach internal parts of the nose which cannot be accessed with a cotton swab and that the organism throws out these particles discontinuously with time.

Chávez Reyes et al. report for the first time a new nose hairs sample collection device compatible with SEM/EDS analysis and considered as non-invasive by the shooters involved in the study [11]. Different types of firearms were tested with a collection time varying from 0 to 20 h after firing. According to the authors, it was possible to collect GSR from nose hairs, and this even 20 h after the shooting, revealing a good persistence of GSR in nose hairs, compared to the persistence observed for hands (e.g. less than 6 h).

1.1.3. Heavy-metal free ammunition

Since the early 2000s, the arrival of heavy-metal free ammunition in the market is an attention and this even though the prevalence of such ammunition in casework is still very low, apart perhaps for cases involving police forces.

Costa et al. performed a full characterization of IGSR produced by heavy-metal free ammunition (i.e. clean range ammunition from CBC) using SEM/EDS, colorimetric tests and inductively coupled plasma mass spectrometry [12]. They performed several shots with a 0.40 caliber pistol and a 0.38 caliber revolver. The authors observed no Lead, Barium and Antimony signal with the SEM/EDS, nor the colorimetric test. However inductively coupled plasma mass spectrometry was able to detect small quantities of those elements, illustrating the necessity to still monitor the concentration of Lead in shooters' blood since this element presents a high toxicity. The authors also pointed out Aluminium, Molybdenum, Copper, Zinc and Tin as new markers of IGSR for such type of heavy-metal free ammunition, since these elements were the most abundant species detected.

1.1.4. Non-GSR sources of GSR-like particles

Since the beginning of GSR-forensic casework, concern has been expressed over GSR-like particles originating from a non-ballistic origin, which could lead to false-positive interpretation of the results at the source level. These particles are similar in composition to GSR but do not originate from the use of primers. A number of publications have already described particles produced by detonated fireworks, exploded airbags and used brake pads. Concerning the latter, the latest study was published in 2004 [13]. However, according to new legislation in many countries targeting the reduction of sources of lead coming from the automotive industry, Tucker et al. conducted in 2017 an investigation of the types of particles produced by currently used brake pads [14]. 12 brake pads, but also 22 wheels and the hands of 11 car mechanics were sampled for SEM/EDS investigation. No Lead–Barium–Antimony particles (considered as characteristic of GSR) were found on the samples. Considering the other particles of interest, the most abundant population was found in the Barium–Antimony class (second most abundant after the iron-rich particles). As expected, the occurrence of Lead-rich particles was very low, less than 1% of the total amount of the particles detected. Concerning their morphology, particles from brake pads still appear to be conglomerates of smaller particles, as was described earlier [13].

With the advent of heavy-metal free ammunition, there are some concerns about the ability to distinguish IGSR particles from environmental sources. Hogg et al. [15] examined the power of principal components analysis to make such distinction: the chemical composition of six brands of heavy-metal free ammunition was investigated and compared to that of a rad flare (used as an environmental source). According to the authors, principal components analysis was able to distinguish SEM/EDS spectra of IGSR particles from those of environmental sources, this by focusing on elements such as Aluminium, Potassium, Silicon, Calcium and Strontium.

1.1.5. Prevalence and contamination studies

Lucas et al. [16] examined the prevalence of IGSR in the random population, since this information may be very useful for the interpretation of the results when using the evaluative approach (see next section). The study was conducted in two Australian jurisdictions on a population of about 300 individuals. The authors looked for the presence of Lead/Barium/Antimony particles using SEM/EDS. Among the population examined, only one person (a woman with no declared firearms hobbies nor contacts with weapons) yielded a positive test result: the sample contained three Lead–Barium–Antimony particles, among which two large agglomerates, a morphology to be regarded as a-typical for GSR. The number of two-component particles present in this population was also monitored. Up to 4% of the individuals contained one to five two-component particles. The prevalence of GSR particles reported in this study was consistent with results from similar studies conducted in other countries and published earlier [17,18].

The risk of pollution with GSR particles that migrate from police officers to suspects is regularly evaluated. In 2016, Cook examined the level of IGSR contamination of police officers following start-of-shift handling of their firearm [19]. He observed that most officers were highly contaminated by this operation, with an average of about 60 Lead–Barium–Antimony particles on their hands. However he also showed that washing their hands or using self-drying hand gel removes almost all IGSR particles their hands. As a consequence, performing this action immediately after checking, loading and securing the firearm should prevent most of contamination of suspects by police officers.

Ali et al. examined the presence of IGSR and OGSR on seventy samples collected from Pittsburgh (USA) police stations and vehicles [20]. Only one Lead–Barium–Antimony particle was detected on one interview desk; ethylcentralite was detected at a quantifiable level in only two samples. No correlation was observed between these two samples and the sample containing the IGSR particle. Following these results, the risk of secondary transfer from these facilities to a suspect is considered to be low by the authors.

Reporting a case involving two drivers [21], Burnett conducted a study showing that recreational shooters may transfer many IGSR particles via driver's seats. The case concerns a shooting incident occurring between two vehicles; the question was if the second driver also fired two shots prior to a first shot operated by the first driver. In this case interpretation may not be trivial because of potential contamination pertaining from the undisputed shot. By analysing several samples from the second driver (vehicle, hands, neck and shirt), the author concluded that a shot from the second driver was unlikely to have occurred.

1.1.6. Interpretation of results

During the last three years, a review was published by Maitre et al. [22], specific to interpretation issues. The review discusses the two levels of interpretation – i.e. source level (particles are or are not GSR particles) and activity level (the suspect discharged a firearm or not, the suspect was present in the surroundings of a shooting incident or not) – for IGSR (most of the studies) and OGSR. Studies related to secondary transfers (contamination, pollution) and persistence of GSR are reviewed in the article. The advantage of using the evaluative approach, compared to a more formal approach, is also discussed. According to the authors, the evaluative approach using the Bayesian principle is promising and can for sure

help to fulfil the gap between analytical results discussed at the source level and judicial decisions taken at the offence level.

A second review also dedicated to interpretation issues was recently published by Blakey et al. [23]. This review focuses on IGSR and discusses elements that can influence the deposition, distribution, transfer and persistence of GSR – such as firearm and ammunition type, environmental conditions etc. These elements should be taken into consideration for correct interpretation of data in a forensic context.

Cardinetti et al. proposed in 2006 a statistical evaluation of the detection of GSR on suspects [24]. This proposal was based on the evaluative approach using the Poisson model to calculate the likelihood ratios of probabilities of a suspect involved or not in a shooting. In 2016, Kaplan Damary et al. [25] replaced the Poisson model by the negative binomial model. This model seems to fit the experimental data reported by Cardinetti et al. much better. Applying the negative binomial model and calculating the statistical errors related to this model, Kaplan Damary et al. came to the conclusion that because of the small population of data used, the uncertainty related to the likelihood ratio is very high. So if likelihood ratios can give some valuable information to the court by supporting one hypothesis compared to another, the strength of the evidence must be handled with caution, especially when small population data are used. On the whole, the authors recommend to use large data sets when possible.

Besides working on hypotheses concerning having discharged a firearm or not, having been present in the surroundings of a shooting incident or not, the evaluative approach may also concern hypotheses dealing with the potential link/compatibility between different GSR populations and/or between GSR particles and reference materials (cartridge case, weapon). Based on experimental data published earlier [26] and additional data recently obtained, Bolck and Stamouli used a two-level multinomial model for the calculation of the likelihood ratio in order to have a tool to discriminate between same-ammunition-type GSR compositions and different-ammunition-type compositions [27]. Different variations of the two-level multinomial model were tested, leading to the conclusion that this model can indeed be applied on such experimental data.

Interpretation of GSR data in suspected suicide cases is a difficult task since the victim, who was for sure present in the surroundings of the shooting, may be highly contaminated. On the other hand, the occurrence of false negatives is also quite large. Conducting a follow-up of the study by Molina et al. published earlier [28], Lucas et al. examined the presence of IGSR on the hands of victims of undisputed suicide cases by firearms [29]: 59 cases that occurred in Australia were investigated. About 50% of these cases presented no or very few (less than four) Lead–Barium–Antimony particles, confirming the results of the study conducted by Molina et al., in 2007 (i.e. a high level of false negatives). However, most of the cases presenting such low level of characteristic particles were related to the use of 0.22 calibre rifles (the most popular firearm in Australia), for which the primer of the ammunition usually does not contain Antimony. Not surprisingly, this leads to the production of IGSR particles with no (or very little) Antimony. Taking such particles into account in the statistics, the number of the cases presenting no or very few (less than four) particles of interest falls down to less than 15%. The article presents other interesting statistics, such as the difference of IGSR production as a function of weapon model (i.e. a higher number of GSR particles are produced by revolvers, compared to rifles). Zeichner commented this article, with a discussion about the possible memory effects of the weapon to the contribution of Antimony in IGSR particles [30]. Those interested in this topic may read this letter to the Editor and the author's response [31].

1.1.7. Quality aspects and efficiency

In the domain of IGSR analysis, the reference norm is the ASTM 1588 which was revised in February 2017 [32]. Compared to the previous versions, particles containing Lead, Barium, Tin, Calcium and Silicon are now also considered as characteristic to GSR. This new version also discards the terms "major", "minor" and "trace" that were previously introduced to characterize the peak height of the different elements present in R-ray spectrum of the particles of interest. Finally the SEM/EDS systems should be configured to detect particles down to at least 1 μm, instead of 0.5 μm. Apart from this norm, two guidelines exist: the ENFSI guide (more or less the same in content as the ASTM norm, but not recently revised) [33] and the SWGGSR guide (which is more detailed in terms of result interpretation) [34].

Proficiency tests are conducted every year. They are organised by a commercial provider QuoData (Germany) in collaboration with the ENFSI Expert Working Group "Firearms and GSR" and consist in the detection by SEM/EDS of 150–200 three-element particles (Lead, Barium and Antimony) distributed over six particle size classes (0.5–2 μm). Three of these proficiency tests were conducted during the period of interest (GSR2016, GSR2017 and GSR2018).

Thanks to continuous improvement of SEM/EDS technology used in the domain of IGSR analysis (e.g. automation, new types of EDS detectors, spectral deconvolution algorithms), significant advances have been made to reduce both the analysis time and the time spent during the particle review phase. This optimization is of major interest in terms of cost reduction and efficiency improvement. Mandel et al. proposed a new algorithm based on a binary tree to improve the initial classification step performed during the automatic run [35]. This algorithm was trained on stubs used to sample hands and hairs and gave good results in terms of false positives and false negatives, leading to a reduced time spent to review the particles of interest.

1.1.8. Development of new instrumentations and methods

1.1.8.1. Atomic spectrometry

- Although SEM/EDS will likely remain in the short and medium term the method of choice for crime scene investigations, Heringer and Ranville see reasons to examine alternative approaches [36]. For example, the analysis of the spatial distribution of IGSR, which would require a large number of sample analyses, could give insight into the dynamics of events at a crime scene. Similarly, a temporal study of IGSR on surfaces (skin, textiles, etc.), under various environmental conditions, would provide insight into the persistence of IGSR on evidential materials. The high sensitivity of inductively coupled mass spectrometry makes it a good tool for the analysis of trace metals; moreover, single particle inductively coupled mass spectrometry can identify individual, undigested particles and analyze their composition, giving some information on particle morphology (such as particle size) and number concentration. Although classic characteristic IGSR contains three chemical elements of interest (Lead, Barium and Antimony), quadrupole-based instruments – which are generally used in single particle inductively coupled mass spectrometry – can in principle identify and measure only one element at a time. However, dual element mode analysis (in which the quadrupole is rapidly tuned back and forth between two elements) has been successfully used by the authors to analyze two elements in one IGSR particle. So, although it is not possible to analyze all three elements of a characteristic IGSR particle, particles consistent with IGSR (for which only two of the three elements are present) can be detected. Furthermore, the lack of sample preparation, fast analysis time, automated post processing and the high

number of particles analysed, make this technique a promising technology to investigate further.

- Cid et al. applied subcritical fluid nebulization with online preconcentration in flame furnace atomic absorption spectrometry [37]. According to the authors, this would improve the determination of Tin in IGSR, compared to conventional flame furnace atomic absorption spectrometry. Their results show that the use of subcritical fluid nebulization resulted in important improvements of sensitivity and detection limits by factors of 240 and 325, respectively, when compared to conventional analysis.

- The objective of a study done by Yüksel et al. was to develop and validate a sensitive method using graphite furnace atomic absorption spectrometry, equipped with Zeeman background correction, to determine Antimony, Barium and Lead concentrations in GSR swab samples as a routine forensic chemistry application [38]. The hand swab samples of the shooters were obtained at five different time intervals after firing (0–4 h). Hence, the study was also aimed at investigating the lifetime of GSR on hands. As an end result it can be stated that Antimony, Barium and Lead in GSR still can be detected within the first 3 h after firing and that consequently, in order not to have false-negatives, crime-scene officers should collect the samples from suspects within this period after the shooting incident.

1.1.8.2. Ion beam techniques

- Duarte et al. provide key evidence for the potential of ion beam techniques in the analysis of materials of interest to forensic scientists [39]. In this article, a full characterization of Lead rounded nose, hollow point and heavy-metal free ammunition was carried out with (micro-)particle induced X-ray emission and Rutherford backscattering spectrometry. Relatively large gunshot residue particles stemming from the discharge of these ammunition were analysed as well. The results indicate the presence of Lead in all ammunition, including in the heavy-metal free ammunition. Although in principle this could stem from other parts of the ammunition and cross contamination from the (single) revolver used in the test shootings cannot be ruled out, it must be pointed out that traces of Lead were found in the primer of the heavy-metal free ammunition as well. So, while SEM/EDS suffers from bremsstrahlung background and other techniques like inductively coupled plasma spectrometry can reach even better sensitivity – at the cost of being destructive – ion-based techniques are non-destructive and one single technique is capable of providing truly quantitative analysis and imaging capability of different materials. Therefore, ion-based techniques can provide a full range of analysis services for the forensic community.

1.1.8.3. Laser-induced breakdown spectroscopy

- Since recent studies indicate that laser-induced breakdown spectroscopy has proven successful in characterizing particulate matter and pyrophoric materials, Doña-Fernández et al. performed an extended comparative study of SEM/EDS and portable laser-induced breakdown spectroscopy [40]. By performing a comparison between data collected from shooters and non-shooters, the authors concluded that even when only one single Lead–Barium–Antimony GSR particle was found by SEM/EDS, the laser-induced breakdown spectroscopy system still could detect the presence of GSR, and this after parameter optimization.

- Trejos et al. examined the possibility to use both laser-induced breakdown spectroscopy and electrochemical methods as fast identification of IGSR and OGSR prior to confirmation with SEM/EDS [41]. According to the authors, combining these two techniques offers excellent analytical performances, with very low error rates and high specificity, sensitivity and accuracy, based on measures performed on samples collected from shooters 30min after shooting, and non-shooters. Moreover the selected analytical scheme allows subsequent confirmatory analysis by SEM/EDS, since this scheme preserves most of the surface of the sample (i.e. carbon coated stubs) from degradation.

- Another study explored the use of laser-induced breakdown spectroscopy imaging to visualize GSR patterns through multi-element analysis [42], this for shooting distance estimations (see section C.-a. for more details).

- Fambro et al. reports in Ref. [43] the application of laser-induced breakdown spectroscopy to heavy-metal free GSR analysis by characterizing analogs of heavy-metal free GSR. They started from different material containing simulated primer compositions in order to mimic heavy-metal free primers. A specific calorimeter was used to generate the residues, the latter being then analysed by laser-induced breakdown spectroscopy. The rate of errors was calculated, based on the analysis of samples coming from shooters and non-shooters, and appeared to be promising to differentiate these two categories. According to the authors, this technique could be an effective and rapid screening method prior to confirmation by SEM/EDS. In a follow-up study [44], Fambro et al. characterized GSR originating from three different heavy-metal free ammunition, also using laser-induced breakdown spectroscopy prior to SEM/EDS. The data acquired suggests indeed that laser-induced breakdown spectroscopy may be a suitable method to analyze heavy-metal free GSR and that future research should include efforts to characterize various brands of both classic and heavy-metal free ammunition.

1.1.8.4. Capillary electrophoresis

- A considerable effort has been expended in the past to develop analytical techniques capable of identifying the levels of inorganic anions present. Nitrite and nitrate ions can be used as screening tools for investigating GSR due to the fact that these ions are major inorganic components of GSR. As a high-speed separation method, capillary electrophoresis has been demonstrated to offer promising, effective, and economic approaches for the separation of a large variety of substances, including those encountered in forensic analysis. Although in previous methods alkaline pH separation buffers were used, Erol et al. develop in Ref. [45] a method in acidic pH environment, based upon a new capillary electrophoretic method for simultaneous determination of nitrate, nitrite, and oxalate in vegetables. By employing large volume sample stacking the obtained detectability was superior to previously reported capillary electrophoretic methods with spectroscopic detection. This results in limit of detection values of 0.12 mg/L and 0.11 mg/L for nitrate and nitrite, respectively. The proposed method was successfully applied to authentic GSR samples and results of three GSR

samples and swabs from non-shooter's hands were presented. The proposed method is not only rapid, but also exhibits excellent peak shape and resolution when compared with previously developed capillary electrophoresis methods using alkaline pH separation buffers, although the limit of detection was improved by employing large volume sample stacking.

1.1.9. Luminescent markers and doped ammunition

Since a few years, some research groups are synthesizing and characterizing different fluorescent markers which could subsequently be added to conventional and heavy-metal free ammunition. When a shot is fired with such doped ammunition, the GSR produced may easily be observed under UV radiation, allowing for direct visualisation and this also on the crime scene. Moreover, these fluorescent compounds often contain rare-earth elements, which then can easily be detected by the use of the conventional SEM/EDS technique for unambiguous attribution to the class of IGSR particles. They can indeed be considered as characteristic of GSR, due to the presence in these particles of such very specific elements belonging to the family of the rare-earth elements.

In this respect, Lucena et al. introduced several new luminescent markers, i.e. metal-organic frameworks containing Europium [46,47], Dysprosium [48] or Terbium [47,49] as rare-earth elements. These compounds were synthesized by the authors and characterized by different analytical techniques (photoluminescence spectroscopy among others). The toxicity of the Europium-based compound was also evaluated, showing a low toxicity compared to other luminescent markers recently described. Ammunition containing 10 wt % of markers were then prepared for shooting tests; SEM/EDS analysis was performed to characterize the GSR produced, revealing the presence of particles containing the rare-earth elements (i.e. Europium, Dysprosium or Terbium) as markers.

Lucena et al. also examined the global behavior of two other luminescent markers based on organic complexes containing multiple elements such as Yttrium, Ytterbium and Terbium or Ytterbium and Europium [50]. These compounds were added to gunpowder and shots were fired with them. SEM/EDS analysis revealed the presence of GSR containing the different rare-earth elements.

In another study, Carvalho et al. [51] focused on several metal-organic frameworks containing Europium. Adjusting the composition of the markers, ammunition could easily be encoded and tracked. The authors successfully studied in this work the use of near infrared hyperspectral imaging in detecting macroscopic GSR particles on several forensically-relevant surfaces such as the gun, inside a cartridge case and on a shooter's hand.

The acute toxicity of another Europium-based complex was tested by Destefani et al. [52] and compared to acute toxicity of heavy metals like Lead, Barium and Antimony. Based on experiments performed on mice, the authors concluded on a medium toxicity of the Europium-based complex if compared to the high toxicity of heavy metals: for instance a median lethal dose which was 90 times lower than that obtained with Lead.

Using this type of Europium-based complexes, Arouca et al. set up blind tests to check the efficiency to identify the shooter position, estimate the shooting distance and examine the possibility of secondary and tertiary transfer [53]. According to these tests, the authors concluded that the use of such markers is very effective since the shooter position and the shooting distance were correctly assessed. They also pointed out the possibility to reveal secondary transfers of GSR, for instance when shaking the hands of a shooter.

1.2. Organic GSR

1.2.1. Sampling

In a first study, Gassner and Weyermann compared the efficiency of various sampling materials for the analysis of OGSR, as well as a determination of the matrix effects produced by them [54]. In conclusion, four candidates remained at the end of this evaluation, namely DNA cotton buds, polyester swabs, 3 M tape and PTFE film. The stub-type samplers have preference because of low residue levels they leave on the hand and the long retention time of analytes on their surface in ambient conditions. Sampling devices were then investigated in detail for further quantitation of OGSR by liquid chromatography/mass spectrometry. In conclusion, with a performant QTrap-type mass spectrometer, OGSR can be easily detected just after discharge. Further experiments must be conducted, however, to study the transfer of OGSR and its persistence on different surfaces, as the limits of detection for some OGSR types is already reached after 2 h post-firing (for example on skin).

When implementing OGSR analysis, introducing specific sampling to collect organic GSR can be a step competing with the sampling prior to the conventional analysis of IGSR by SEM/EDS. In a second study, Gassner et al. provide some additional elements of response to questions regarding OGSR sampling and sample storage [55]. In the first part of the study, stubbing was compared to swabbing with alcohol using sequential sampling. The results evidenced a very high variability for both techniques, associated to OGSR production rather than sample collection. Stubbing was considered a better sampling technique, as it left nearly no residues on the hand. Storage conditions were also investigated after sampling using both stubs and swabs. Here again, storage time was dependent on the sampling method with stubs being more stable than swabs at room temperature.

Taudte et al. also examined two protocols for the combined collection of IGSR and OGSR, prior to SEM/EDS and ultrahigh performance liquid chromatography/UV detection analysis [56]: i) swabbing using alcohol wipes, followed by liquid extraction and filtration and ii) stubbing. Also in this study the authors showed that the collection using stubs was significantly more efficient for both IGSR and OGSR present on skin. In another study, Taudte et al. examined the stability of smokeless powder compounds on the same collection devices (i.e. alcohol swabs and GSR stubs) [57]. The highest degree of degradation was found after the first four days. The authors observed that commonly found OGSR analytes such as nitroglycerin, diphenylamine and ethylcentralite showed relatively high overall degradation, which appears to be a serious issue for OGSR analysis. The authors recommend to analyze samples as soon as possible and prior to analysis storage, in a 4 °C refrigerator is a must.

In order to develop field detection tests for GSR, Gandy et al. examined three colour tests selected for their potential sensitivity towards OGSR [58]. The Sodium borohydride test appeared to be a good candidate, demonstrating a high sensitivity and selectivity with standards and mixtures. Additional studies still need to be performed in order to evaluate the potential application to real samples.

1.2.2. Persistence and prevalence studies

OGSR (powder residues as well as additives) have been researched in recent years using a number of different techniques. Although analytical techniques and sampling are relatively well documented, little is known of specific forensic questions such as transfer and persistence of OGSR on hands and clothing of suspects and victims/targets. In the second part of their study [55], Gassner et al. performed shooting experiments to evaluate transfer of OGSR using different ammunition. The variability in quantities detected did not enable the distinction between ammunition based on a single compound. Moreover, when shooting various ammunition with the same firearm, a memory effect was detected which was not alleviated by quick cleaning of the barrel in between ammunition changes. Therefore, the possibility of multiple ammunition

usage should be taken into account if analyzing OGSR with a view to possibly link it to a gunpowder. Finally, various exposed skin surfaces and hair as well as clothing were sampled to evaluate what surfaces would be the best targets for OGSR collection by comparing results just after discharge and 2 h after discharging a pistol. The results indicated that OGSR were more rapidly lost from hands than from clothing. Moreover, it was shown that the face and hair of a suspect might be contaminated through secondary transfer. Thus, OGSR might remain longer on other skin surfaces, hair and clothing than on the hands of a suspect. As a consequence, sampling should not be limited to hands but also include clothing, hair and the face. As the limits of detection were already reached after 2 h for some analytes, it will be necessary to develop a preconcentration technique to evaluate persistence in a thorough study. Obviously, many variables can modify the transfer and persistence of OGSR, including external factors such as cosmetics. Moreover, ammunition and firearm type as well as weather might influence transfer. Finally, activity of the suspect as well as passive processes such as evaporation and skin absorption will impact persistence. This work is therefore but a first step and more studies into this subject will be necessary.

Maitre et al. report in two articles [59,60] regarding the persistence (up to 4 h following discharge) on shooters of three OGSR compounds, i.e. ethylcentralite, diphenylamine and *N*-nitrosodiphenylamine. They used ultra performance liquid chromatography/tandem mass spectrometry as detection and characterization technique. The three compounds were successfully detected in more than 70% of the samples up to 4 h following the discharge, with the largest decrease being observed during the first hour. Not surprisingly, the dominant hand (handling the gun) collects more OGSR than the non-dominant hand. However, and interestingly, the authors showed that the persistence on the non-dominant hand was higher, illustrating the fact that the non-dominant hand, due to limited involvement in regular activities, preserves better OGSR on the surface of the skin. This illustrate the interest to collect on both hands of a suspect and not only on the hand suspected to have handled the gun.

Hofstetter et al. also examined the amount and distribution of OGSR on shooters [61]. This article, reviewing in its introduction the literature of OGSR, also presents a comparison study of the amount of OGSR collected on different location, i.e. hands, faces and clothing of shooters. Although irreproducibility is observed, the authors showed that OGSR can be collected not only on hands, but also on other locations. Even more, and as a global tendency already observed in Ref. [55], the persistence seems to be higher for other locations than hands, probably because the latter are more frequently washed and wiped than other sampling regions. Moreover, the amount of OGSR recovered from clothing is usually larger, when comparing the same area, as skin. According to the authors, a factor explaining this difference could be the moisture present on the skin, acting as a limiting factor for efficient sampling of OGSR. Finally, a prevalence study was performed, showing that a positive sample indicates a very recent (less than a few hours) contact with firearms.

1.2.3. Interpretation of results

Following the same reasoning as proposed for IGSR, Goudsmits et al. proposed for the first time a classification of OGSR compounds as a function of their prevalence and “uniqueness” [62]. For instance, more than 100 compounds have been reported in the literature as being associated to OGSR. However, due to potential other sources, all these compounds cannot be considered as being “characteristic” of OGSR. For example, diphenylamine, a stabilizer present in most ammunition, is also commonly used in the food industry. Among this list, the authors proposed 20 compounds and compound classes that could be of interest for their forensic relevance. These compounds were then split up in three categories as a function of their association with GSR and their application related to other sources.

Dennis et al. analysed more than 700 smokeless reloading powders by pairwise comparison of their physical and chemical characteristics, in order to perform statistical evaluation of likelihood ratio determinations [63]. Gas chromatography/mass spectrometry was used for the chemical analysis. The authors showed that the evidentiary and investigative value of a “same product” versus “different product” assertion was limited, having a low likelihood ratio (less than ten).

Bell and Seitzinger analysed hand swab samples by ion mobility spectrometry and neural networks (for pattern matching of the ion mobility spectra) as a screening test to identify the presence of OGSR [64]. The samples were obtained from 16 known shooters (immediately sampled after shooting) and from a population of 73 individuals claiming not having discharged a firearm within the week before sampling. The authors adopted the evaluative approach using likelihood ratios to express the results, instead of using a threshold value that would lead to a binary selection (shooter vs. not shooter). According to the authors, using this evaluative approach significantly reduces the frequency of false positives and allows for a more informed decision, even in the context of a screening test.

1.2.4. Development of new instrumentations and methods

1.2.4.1. Liquid chromatography/mass spectrometry

- In the majority of the OGSR studies with liquid chromatography/mass spectrometry as detection technique, a targeted approach was used for compound identification, for example using a specific collision-induced dissociation energy or specific multiple reaction monitoring modes that were pre-selected for the target analytes. The development of a non-targeted approach would allow for recognition of all compounds in a powder. This has the potential to offer more informative chemical profiles that may increase discrimination among powders and enhance the ability to associate specific OGSR compounds to the corresponding unburned powder. The work reported by Reese et al. [65] demonstrates such a non-targeted approach for the characterization of both unburned smokeless powders and the OGSR from a variety of ammunition of different brand, caliber, primer composition and age. Powders were analysed by liquid chromatography/atmospheric pressure chemical ionization/time of flight mass spectrometry, in both positive- and negative-ion mode. The resulting chemical profiles were statistically assessed using principal components analysis and hierarchical cluster analysis to evaluate discrimination of unburned powders based on chemical composition as well as to gauge the extent of association of the OGSR compounds to the corresponding unburned powder. Association was most successful for powders that contain akardite II and ethyl centralite as the dominant compounds, but was not realized for powders that contained dibutylphthalate, diphenylamine, or *N*-nitrosodiphenylamine as the dominant compounds. This preliminary work already demonstrates the potential of this technology for smokeless powder characterization. In future work, a wider range of smokeless powders will be investigated and characterization of swabs from shooter’s hands will be undertaken for comparison to the unburned powder.

- Diphenylamine is an important component of a gun propellant, where it is used as a stabilizer that can bond with the degradation products of explosives and slow down the rate of their

decomposition. However, only trace levels of DPA remain on the hands of firearm users; thus, it is hard to identify DPA if the detection method is not sufficiently sensitive. In order to meet the requirements of forensic-type assay of diphenylamine, Mei et al. optimized a method based on high performance liquid chromatography/tandem mass spectrometry [66]. After manually firing a gun, the OGSR in the cartridge case and on the shooter's hand were extracted carefully with a cotton swab soaked with acetone. The authors were able to show the presence of diphenylamine on samples in cartridge cases and on shooter's hands up to 1 h after firing.

1.2.4.2. Gas chromatography/mass spectrometry

- To be of practical use in forensic scenarios, any proposed assay of OGSR should be capable of detecting the residue associated with one to three shots. The thermal desorption gas chromatography system/mass spectrometry system described by Stevens et al. [67] shows promise in this regard, although problems arise due to detection of ethylcentralite in blanks. The adoption of additional qualifier ions across all of the target compounds will therefore be essential. Nonetheless, the advantages of being able to use gas chromatography/mass spectrometry this way (no sample preparation, no pre-concentration, and availability of instrumentation) argues for this type of investigation to be continued.

- In their study of firearms propellants using gas chromatography/mass spectrometry, Pigou et al. studied the factors influencing the formation of certain molecules during the analysis [68]. One of the sources of these artefacts appears to be the soiling of the injection port and liner of the gas chromatograph. The authors could conclude that although the occurrence of artefacts does not affect the ability to identify a particle as a propellant from its chemical profile, caution must be exercised if any quantitative or semi-quantitative comparisons with a source propellant have to be made. Fortunately, contamination of the inlet liner and any artefact formation can be easily monitored by the use of routine quality management procedures in which blanks and standards are interspersed between samples.

1.2.4.3. Other mass spectrometry techniques

- As discussed before, the recent introduction of heavy-metal free ammunition has triggered the screening for OGSR as a way to identify and characterize the chemical evidence. While current analytical efforts are compartmentalized for IGSR and OGSR analysis, recent studies have shown the advantages of using multiple assays and complementary techniques for the characterization of both IGSR and OGSR. Mass spectrometry imaging is rapidly becoming the method of choice for chemical mapping of organic and inorganic compounds from surfaces. Mass spectrometry imaging permits the simultaneous interrogation of surfaces with high sensitivity and without the need for labels or pre-selection of molecules of interest; as in imaging mass spectrometry most if not all inorganic/organic components can be sampled and detected simultaneously. Mass spectrometry imaging's lateral resolution is ultimately defined by the dimensions of the desorption probe (from tens of nm to hundreds of μm). The physical dimensions of the firearm discharge particles and the desirability to preserve the sample demand the use of high spatial resolution probes. The technology must be capable of generating characteristic inorganic and organic ions with little to no need for sample preparation and for the IGSR and OGSR characterization in a single analysis. In their work, Castellanos et al. show for the first time the advantages of using high-spatial resolution mass spectrometry imaging for the analysis of surfaces containing IGSR and OGSR [69]. In particular, secondary electron and secondary atomic/molecular ion maps were obtained from a single analysis with little damage to the physical and chemical surface integrity, thus allowing for a subsequent analysis of the sample. Typical inorganic and organic molecular ions were identified from the skin swabs of shooters after a firearm is discharged. The high spatial resolution mass spectrometry imaging permitted the identification of IGSR and OGSR components based on their spatial distribution using unsupervised principal components analysis. Initial optical inspection of the firearm discharge swabs showed the presence of multiple particulates of varying size. Most of the particles were dispersed and distributed near the surface of the swab material. Closer inspection in the imaging mode permitted the generation of secondary ion and electron maps with sub-μm spatial resolution. When the same field of view was analysed in the spectral mode, a near-micrometric spatial resolution was obtained, while allowing for high mass resolution detection of the secondary ions. The authors recognize that potential challenges may exist in the analysis of GSR from heavy-metal free ammunition containing fewer metals characteristic of IGSR and especially volatile OGSR constituents, but additional studies will enable the identification of characteristic secondary ions for these type of ammunition. Alternatively, further developments of the swab surface chemistry will permit the trapping of volatile OGSR for mass spectrometry imaging/time of flight/secondary ion mass spectrometry analysis. It is anticipated that mass spectrometry imaging will have an increasing role in examining evidence for forensic applications owing to its ability to detect both IGSR as well as OGSR in one single analysis.

- OGSR has been shown to be detectable on skin hours after discharging a firearm. However, there is degradation over time and improved in-situ analysis would greatly benefit the forensic community. In their study, Fedick and Bain used swab touch spray mass spectrometry to search for OGSR on the hands or an article of clothing of the suspected shooter [70]. Swab touch spray utilizes a rayon-tipped swab to collect the analytes of interest by applying the dry swab over the area of interest. The swab is constructed with an aluminium handle, which allows a high voltage lead to be connected directly to the swab to promote ionization when solvent is applied. Swab touch spray has been shown to be an effective method for identifying OGSR from a variety of surfaces including hands, gloves, clothing and spent shell casings. This ambient technique requires no sample preparation, nor lengthy analysis time, and is capable of in-field analysis. Important OGSR compounds were detected after a single discharge of a firearm on both benchtop and portable mass spectrometers. However, the latter test was performed in a laboratory setting and future testing still needs to be performed to identify the capability of these analyses in-situ. The authors finally note that a database of the compounds detectable for different ammunition brands is an important future research direction.

- In a recent study, McKenzie-Coe et al. present a novel workflow for the detection of both elemental and organic constituents of the firearm discharge residue from skin swabs using

electrospray trapped ion mobility spectrometry coupled to mass spectrometry [71]. The small sample size (less than ten μL), high specificity and short analysis time (a few minutes) permits for the detection of both IGSR and OGSR from one sample and in one single analysis.

- As the movement to self-manufacture of firearms with 3D-printing technology grows and as 3D guns themselves become more functional and reliable, it is reasonable to assume that they will be used increasingly in crimes, especially by individuals who may have less access to traditional guns. Incidents involving 3D-printed guns can be expected to grow as the technology improves, costs decline, and as superior gun blueprints are posted on the internet. Direct analysis in real time/mass spectrometry has been used to identify trace particles of explosives in fingerprints and in addition, this technique can provide "fingerprint" mass spectra for the identification of polymers, their additives and other associated materials. However, Direct analysis in real time/mass spectrometry has not been sufficiently applied to GSR and other trace evidence from firearms, in part, because fundamental studies are lacking. In their study, Black et al. fired a gun with barrels made from different polymers and sought to determine whether this technique can be used to readily detect and identify traces of polymer and organic GSR compounds on the bullets, cartridge cases, and in GSR collected from clothing [72]. They have shown that direct analysis in real time/mass spectrometry methods can be used to detect and identify compounds associated with OGSR as well as polymers from 3D-printed guns in trace evidence. Thus, a spectral library of polymers commonly used in 3D-printing can be used for characterizing samples from crime scenes where a 3D-printed gun is suspected of being involved. Moreover, because direct analysis in real time/mass spectrometry can rapidly detect OGSR signature compounds on small evidentiary samples, the technique deserves to be further scrutinized as an alternative approach for OGSR analysis.

- In order to evaluate the benefits of using direct analysis in real time/time of flight mass spectrometry for OGSR detection and characterization, Lennert and Bridge analysed 34 smokeless powders using this technique and compared it to analytical performances using gas chromatography/mass spectrometry [73]. The results show that these two techniques provide comparable data; however direct analysis in real time/time of flight mass spectrometry does offer a shorter analysis time, i.e. 2min compared to 20–30min using gas chromatography/mass spectrometry.

1.2.4.4. Raman spectroscopy

- The use of Raman spectroscopy in forensics was reviewed by Doty et al., in 2016 [74] and 2018 [75]. One section of each review is dedicated to GSR analysis. Compared to SEM/EDS, the authors pointed out Raman micro-spectroscopic scanning, a technique that analyses GSR collected from a surface after tape lifting. Raman spectroscopy allows the identification and analysis of specific components contained in propellant mixtures, enabling the establishment of links between different types of ammunition. Moreover, the combination of Raman spectroscopy and infrared spectroscopy, two complementary methods, increases both specificity and sensitivity and thus enhances the statistical differentiation of GSR samples from different origins. However, a significant number of GSR particles has to be analysed before a link between GSR and a specific ammunition can be claimed, because of the memory effect of the weapon. According to the authors, Raman spectroscopy is a promising technique for the detection of GSR but further research and tests of real samples still need to be performed.

- Bueno et al. performed validation experiments on an analytical scheme combining tape lifting and Raman micro-spectroscopic mapping, in order to collect and detect GSR [76]. This study determined the reproducibility, precision and robustness of this approach. Potential environmental contaminants (i.e. particles generated from automotive brake pads and tires) were also examined. The authors classified data obtained in a previous study, which was designed as a proof of concept, and combined these data with those obtained in the validation experiments of this study using support vector machine discriminant analysis. Results showed that the method is independent of specific Raman microscopes or collection software. Moreover, the particles generated from automotive samples could be successfully differentiated from real GSR using the methodology proposed by the authors.

- López-López et al. discussed the application of surface-enhanced Raman scattering to the analysis of 21 smokeless gun powders and macroscopic GSR obtained after firing two of them [77]. The reproducibility and sensitivity of the method was examined by the authors. They showed that for gun powders most bands observed in the spectra can be attributed to diphenylamine and ethylcentralite, the two most common stabilizers used in smokeless gun powders. Moreover, spectra of macroscopic GSR collected on conventional stubs that are usually used for SEM/EDS analysis were similar to the corresponding gun powders, confirming the feasibility of performing surface-enhanced Raman scattering on such particles. However, the authors pointed out the inherent grain-to-grain inhomogeneity of gun powders as an issue that could limit the linking between ammunition and GSR macro-particles.

1.3. Shooting distance estimation and bullet hole characterization

1.3.1. Methods and instrumentations

The largest part of GSR produced by a shooting is projected on the target (object or victim), provided this target is close enough to the shooter. The diameter and the density of the GSR particles deposition pattern will help to determine the firing distance. This deposition pattern is usually chemically revealed by use of "chromophoric" or colour tests; the most popular colour tests being the Sodium rhodizonate test (detects Lead and Barium) and the modified Griess test (detects nitrites).

Beside the use of colour tests, it is also possible to estimate the shooting distance by using non-chemical techniques. According to a study performed by Ortega-Ojeda et al., classical least squares regression is the adequate data analysis technique for the use of short-wave-infrared images (using radiation in the near infrared region of 1000–1500 nm) of GSR patterns. They used this technique on patterns on white and black cotton targets, shot with 9 mm conventional and heavy-metal free ammunition from a distance of 10 cm [78]. The spectra of the ammunition propellants such as nitrocellulose, diphenylamine, centralite, dinitrotoluene and nitroguanidine show high spectral activity and can be used to identify GSR, irrespective of which type of ammunition was used. The conventional ammunition resulted in the strongest spectral signals, whereas the heavy-metal free ammunition produced smaller GSR patterns on both fabrics. Although the black fabric might have

hampered somewhat, detection of the pattern was still possible.

In order to evaluate the use of multi-spectral imaging for the estimation of shooting distances, clothing targets were shot from seven different distances between 10 and 220 cm using conventional 9 mm ammunition. The resulting patterns were subsequently analysed at 18 different wavelengths within the range of 400–1000 nm [79]. Image processing was performed using principal components analysis on images that were binarized and inverted for better visualisation of the patterns. The wavelengths that provided the largest contrast between the white cotton and the dark GSR particles were 430, 450 and 470 nm. In the end the blue frame at 470 nm was chosen because it corresponds with the blue channel in digital red-green-blue cameras. A mathematical correlation was shown between the pixels and the shooting distance, since an exponential decrease of GSR was observed with distances ranging from 30 to 220 cm. However shorter distances (10–30 cm) could not be assessed, since the diameter of soot particles is smaller than the resolution of the camera. Application in real casework still needs to be tested further, since only lab conditions were used at this stage.

Examining 102 different ammunition types/brands, Hofer et al. have shown that up to 85% of these ammunition contain propellants that could potentially be detected by the infrared luminescence method, which is even applicable after performing a chromophoric test [80]. Four heavy-metal free ammunition were examined and tested in detail. The excitation wavelengths were set at 545–675 nm and the detection wavelength at 725 nm (long pass filter). Two luminescent additives in the powder were identified: urethane derivatives and phthalates. Using the ratio approach, the authors showed that the distribution pattern depends on the shooting distance. Although this method is promising, it cannot be applied to target materials showing a luminescence of their own, nor to ammunition with no luminescence. In order to overcome these issues, Hofer and Wyss added in a second study [81] an extra step prior to infrared luminescence detection in which a chemical reaction with diphenylamine was used. First, a transfer of the nitrocellulose onto a thin layer chromatography plate was performed using an organic solvent. Diphenylamine was then sprayed onto the plate, resulting in a deep blue colour reaction showing the presence of nitrate and nitrite. Ammunition with -partially and non-luminescent propellant powder were tested on white cotton targets. Imaging software was used to determine the distribution of propellant powder particles and particle density vs. shooting distance graphs were successfully drawn.

Hinrichs et al. examined cotton and polyester targets using the backscattered electron detection mode in the SEM [82]. They showed that an estimation of firing distance was possible for distances up to 20 cm because of a linear relation between the approximately exponential decay of GSR coverage and the shooting distance. For this study, backscattered electron micrographs were acquired at different radial distances from the bullet hole. These images were then binarized using adjusted segmentation thresholds, so that the white pixel count per image was attributable to the GSR coverage. The authors also documented the morphology of broken fibre ends of the synthetic fabrics. This can yield additional information on the shooting distance.

A study investigated the use of laser-induced breakdown spectroscopy imaging to visualize GSR patterns through multi-element analysis [42]. The distribution of Lead, Barium and Antimony over the surface of white cotton targets, shot at from three different distances and using three conventional 9 mm ammunition, was measured in laser raster mode. For this purpose the simultaneous use of two spectrographs, covering two different wavelength regions and in combination with a laser emitting at 1064 nm, was needed in order to allow simultaneous detection of elements. The target surface of 13 × 16,5 cm^2 was measured in less than 3 h. As mentioned above, these authors also suggest that laser-induced breakdown spectroscopy could be an interesting tool for heavy-metal free ammunition analysis.

1.3.2. Quality aspects

ENFSI published in 2015 a Best Practice Manual for chemographic methods [83]. It provides a framework of procedures, quality principles, training processes and approaches to the forensic examination in the domain of shooting distance estimation.

FDSD 2015, the new proficiency test for the determination of shooting distances, was implemented and the results were published in 2016 [84]. The artificial samples consisted of a set of 12 reference distances between 2 and 200 cm. Two samples under investigation were placed at 25 and 50 cm. In total 45 laboratories participated in this test. The submitted results were compiled, z scores were calculated and a statistical evaluation was performed. This paper summarizes the results of the study and presents the overall performances of the participating laboratories. For the best allocation to a shooting distance class, the 25 cm and the 50 cm were ranked correctly by 93% of the participants. For the estimated range of the case shot distance, the 25 cm was correctly ranked by 93% of the participants, while only 73% ranked the 50 cm correctly. A tendency toward an underassessment of the larger distance shot was observed.

1.3.3. Case report

Suspected suicide cases are difficult cases to handle for GSR experts, because of a large range of possible results, from a high rate of false negatives (see section A.-f.) to high contamination due to the presence in the surroundings of the shootings. Recently, Brożek-Mucha and Zdeb reported on a controversial suicide case, in which a submachine gun with a sound suppressor was used [85]. Working as a team, involving both forensic chemists and firearms examiners, the authors showed that the shooting distance was at least 30 cm, while the greatest distance that could have been achieved by the victim himself was about 10–13 cm. As a consequence, the results supported the version of homicide rather than suicide. Additional tests were performed and published in a second article [86]. For instance the influence of the use of the silencer on the amount and distribution of GSR on the surface of cotton fabric and fresh porcine skin was examined. It was found that the silencer reduced the amount of solid particles as well as the amount of soot. The same result was obtained when counting the number of GSR particles present in an area of 10 cm diameter around the bullet hole using SEM/EDS. As a consequence, the significantly modified gunshot patterns have an implication on the interpretation of the estimation of the shooting distance.

1.3.4. Bullet hole examination

The rotating bullet will usually produce a wipe ring around the entrance hole. The presence or absence of a wipe ring will therefore help to determine the nature of the bullet hole (entrance or exit).

Previous studies have demonstrated that GSR particles can be found around the entrance hole even at long firing ranges (dozen of meters). Greely and Weber conducted a study to determine if GSR particles are also deposited on targets after having passed through glass windows [87]. According to the tests they conducted, the authors observed significant amount of GSR particles on different samples close to the secondary target holes. According to the authors, this study illustrates the fact that even if the shooter was outside, GSR can also be found on a victim inside; as a consequence caution has to be taken when interpreting results obtained from victims in similar circumstances.

1.4. Time since discharge estimation

In some cases of firearms-related crime the defense does not directly contest the source of the questioned spent cartridge, but rather its relevance, by arguing that it had been fired for legitimate reasons prior to or after the occurrence of the alleged crime. If such allegations are forwarded, estimating the time since discharge might be particularly useful in helping justice with the decision-making process. Estimation of the time since discharge of a weapon or cartridge case is therefore a question that regularly pops up, but is not yet addressed in routine forensic work.

Application of solid phase micro-extraction as a sampling technique to recover and analyze the explosion products was first suggested by Andrasko et al., in 1998, following the encouraging results obtained on shotguns [88]. However, while partial ageing curves could be obtained using this multiple-sampling procedure, the underlying premise relied on the fact that this sampling did not significantly modify the cartridge's internal atmosphere. Subsequent studies proved otherwise for small calibers, making it impossible to compare the obtained partial ageing profiles with reference curves acquired from analogue cartridges sampled immediately after discharge.

In their two-part publication [89,90], Gallidabino et al. studied the comprehensive optimization and validation of a headspace sorptive extraction method to be applied in determining the time since discharge of small-caliber (handgun) ammunition. Using this sampling method, a fast and reliable, semi-quantitative method, capable of extraction and analysis of about 30 target volatile organic GSR compounds from 9 mm Parabellum cartridges, was developed. These target compounds were selected in order to cover the main classes of compounds often present in volatile GSR. The final step was to investigate efficient solutions to comprehensively interpret the GSR profiles in a dating perspective and evaluate the actual potential of providing helpful information on time since discharge in real cases. In this regard, the implementation of multivariate statistical methods was explored instead of current one-compound-at-a-time approaches, in an attempt to implement all sources of information about time since discharge linked to the single compounds into a unique estimation model. In total six regression methods were tested on the data. The accuracy of the obtained outcomes demonstrates potential for estimating the time since discharge in the tested cartridges up to 48 h of ageing or, at least, to differentiate recently fired from older cartridges (e.g. less than 5 h compared to more than 48 h), under known storage conditions. Thus, they rather support the hypothesis that useful information on time since discharge might actually be extracted from analysis of the volatile fraction of GSR, as well as the hypothesis that this type of assessment could be helpful in a casework perspective.

Disclaimer

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Declaration of Competing Interests

The authors declare that they have no conflicts of interest.

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