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Interpol Review of Gunshot Residue 2019 to 2021

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1. Introduction

This review paper covers advances in scientific methods applied to Gunshot Residues reported since the 18th Interpol Forensic Science Symposium in October 2019 [1]. A literature search was conducted covering articles published in the main analytical and forensic journals in 2019, 2020 and 2021. The terms searched in the titles, abstracts and keywords were “GSR”, “gunshot residue”, “shooting distance”, “firing distance” and “muzzle-to-target distance”. A total of 137 articles were identified, of which 101 were selected for inclusion in this review.

When a firearm is discharged, primer and gunpowder residues, as well as metal particles from the projectile and cartridge case, are expelled through the muzzle of the barrel and other openings in the firearm. These residues are called primer residue, firearm discharge residues or gunshot residue (GSR).

Scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM/EDS) is still the method of choice for the identification of inorganic GSR (IGSR) on samples. This technique is well suited to the detection of small particles (down to 0.5 μm) containing heavy metals such as lead, barium and antimony from primers of conventional composition (e.g. sinoxid primers). In addition, it allows the determination of the correlation between the morphology and chemical composition of individual particles. Particles showing a spheroidal morphology and composed of lead, barium and antimony are considered as characteristic of GSR. However, spectrometric techniques such as atomic absorption spectrometry or optical emission spectrometry are still used in some forensic laboratories, due to their high sensitivity, speed and ease of use, despite the fact that morphological information of the particles is in this case not provided.

Vachon and Martinez recently published an article [2] summarising the basics of the GSR field of expertise, addressing in their review aspects mainly of sampling, analytical techniques, interpretation of results and other potential sources of IGSR. This article is a good introduction for those who want to become familiar with this field of expertise. In their conclusions, the authors also discuss the use of this evidence by the judicial actors and the limits of expertise. They insist on the fact that, unlike other evidence, this field of expertise should be more considered as an investigative tool, as indirect or circumstantial evidence, and can at best be used as a piece of a puzzle to help solve a crime.

The field of GSR has also been recently reviewed by Feeney et al. [3]. In addition to focusing on recent developments in the field of GSR, this review is also interesting in that it presents comprehensive tables of organic and inorganic compounds that could contribute to GSR, as well as other tables compiling the main studies contributing to the understanding of GSR formation, collection, instrumental methodologies used and results obtained; the latter table gives a comprehensive overview of the different techniques used in this field. The topics of transfer and persistence, both for organic and inorganic components, are also reviewed. In conclusion, the authors recommend the use of combined methods, either for the IGSR component alone or for both IGSR and organic GSR (OGSR), to cope with the introduction of heavy metal free primers, making it more difficult to operate the commonly used SEM/EDS technique.

The book Emerging Technologies for the Analysis of Forensic Traces published in 2019 devotes a chapter [4] to recent advances in the field of GSR, covering IGSR but also OGSR in a detailed and very complete manner, as well as the estimation of time since discharge. The interest and originality of this book also lies in the fact that for each piece of evidence treated, and therefore also for GSR, a commentary by an end-user is proposed, which makes it possible to anchor these scientific and technical advances to routine and field practice [5]. In this respect, it is interesting to note that there are still some issues to the analysis of OGSR in the context of expertise explaining the still very limited number of laboratories that offer this type of analysis, which is often confined to academic and university research.

In 2019, the ENFSI Firearms/GSR Expert Working group drafted a white paper on the field of firearms and GSR, which was at the end published in the AFTE journal [6]. This white paper reviews emerging trends, innovation and associated barriers to innovation, as well as current needs in both areas. In particular, collaborative efforts between institutes in the areas of training, quality, databases and reporting should be intensified. The steering committee of this ENFSI group commits itself to follow this closely, including an annual review of projects and needs.

It should be noted that the field of GSR and the associated literature were taken as the object of study in a scientometric approach [7]. In the end, all publications containing the words “gunshot” and “residue” in their title, abstract or keywords, published before 2019, were searched.

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A total of 731 publications were identified, with the first article dating back to 1965. This field is experiencing an increase in the number of publications per year, and this increase is greater than in other scientific fields. In recent years, about 40 articles have been published per year, with the main origin being the USA, followed by Italy, Germany and Switzerland. The most cited articles are, not surprisingly, two reviews published in 2001 [8] and 2010 [9]. In terms of topics related to GSR, the authors believe that this scientometric approach may be useful by revealing gaps that need to be filled, particularly with regard to understanding the transfer, persistence and background of GSR.

2. Inorganic GSR

2.1. Fundamentals of GSR formation

The standard practice ASTM E1588-20 [10], which guides SEM/EDS analysis of IGSR, states that these particles "are often spheroid particles, typically between 0.5 μm and 5.0 μm in diameter". In this regard, on the basis of shots fired with different types of ammunition and by sampling the particles from the shooters' hands, Kara classified the particles according to their size (in steps of 1 from 0 to 5 μm, then in steps of 5) and observed that the size followed a Boltzmann distribution [11].

A fraction of these particles (less than 10%) were described in 1982 by Basu as having a peeled orange morphology, i.e. an uniform core rich in barium and antimony, with lead-rich nodules on the surface [12]. At this time, Basu proposed as explanation for this characteristic morphology the capture of lead vapour by a core rich in barium and antimony, this mainly based on the fact that the solidification point of lead was lower than that of the other two elements. By examining the thermodynamics of the barium/antimony alloy, Nunziata and Donghi propose instead that colloidal phenomena involving electrostatic-type interactions are responsible for the formation of these lead nodules [13].

While the morphology of IGSR particles is indeed often spheroidal, other morphologies are observed, such as particles with tails. According to Choban and Starn [14], this type of morphology could be due to incomplete redox reactions during the formation of these particles. To support their hypothesis, an experimental device was set up to measure during a shot the conductivity produced in the powder cloud; and indeed this experimental device showed the production of an electrical pulse at the moment of the shot. According to the authors, the fact that some particles are charged could also explain an aggregate-like morphology; the electrostatic properties of typical materials could in this sense favour the deposition of such type of particle on their surface.

The formation of IGSR is considered to be a very complex phenomenon, involving elements from different origins (ammunition, weapon, previous shots). In the case of the identification of elements absent from the composition of the primer mix, the question of interest is whether these elements originate from the projectile, the weapon, or whether they are linked to a possible memory effect due to previous shots. To this end, Luca et al. examined the internal structure of GSR particles from different ammunition (calibre and brand), using ion beam analysis followed by X-ray mapping [15]. Different types of morphologies and internal compositions could thus be investigated, by cross-sectioning GSR particles using a focused ion beam instrument and by performing X-ray mappings. On the basis of the morphology and distribution of elements within the particles, hypotheses on the sources of the elements present in these particles could be formulated. In this respect, it was shown that elements such as antimony, which are absent from the primer mix of some ammunition (typically .22 calibre), probably originated from the surface of the projectile, rather than from a possible memory effect. Overall, this study demonstrates the added value of studying the sub-surface of GSR particles in order to understand the complex phenomena that govern the formation of GSR.

In the same vein, Burnett et al. studied some 30 firearm gunpowders by SEM/EDS [16] and showed that beside the memory effect of the weapon, these powders could be the origin of the presence of some IGSR particles: surprisingly, particles rich in lead, barium and antimony were identified on the surface of some powders. The presence of these particles, which is reported for the first time, is not clear, but could be due to the manufacturers' desire to increase the ignitability of the powders.

Another study published in 2019 by Romolo et al. confirms that the projectile may be the source of elements present in GSR particles [17]. The study reports several examples of shooting incidents involving long guns (0.22 long rifle and 12 gauge shotgun), where the ammunition did not contain tin; however GSR particles containing tin were still found, especially inside the guns. This is very unusual as tin is mainly used as a foil for the primer cup, but rather limited to 9 mm and 7.65 mm ammunition; apparently the literature has never reported the use of this type of tin-foil for 0.22 and 12 gauge ammunition. The authors showed that in this case, tin came from the projectile, more precisely from its surface which was coated with this element probably to limit bore abrasion during firing. In addition, a memory effect of the weapon could also be demonstrated in one of the example discussed.

On the other hand, another study tends to show that for shotguns, the projectile is not ultimately one of the source of GSR. To this respect, as many shooting incidents in Australia involve the use of shotguns, Hallett et al. examined the influence of projectile composition on the type of GSR produced, as part of the case-by-case approach used to define new classes of IGSR based on available ballistic references. [18]. For this study, pellets containing steel (increasingly common in Australia), bismuth or tungsten were used. The results of this study show that, in the end, the nature of the pellets seems to have very little influence on the composition of the IGSR, as very few (if any) characteristic particles also rich in iron, bismuth or tungsten were collected at the muzzle end of the weapon. This leads the authors of the study to suggest that iron sometimes identified in IGSR particles probably does not come from the projectile, but rather from the firing mechanism inside the weapon.

Also in the context of the detailed examination of the GSR particles, Seyfang et al. were interested in the results of the composition of specific IGSR in relation to the presence in the primer of ground glass, which acts as a frictionator [19]. These particles were examined by conventional SEM/EDS, but also by focused ion beam and time-of-flight-secondary ion mass spectrometry, this to investigate the internal structure of these particles by examining their cross section. The authors were able to show that some particles, qualified as glass-GSR, were essentially composed of elements from the frictionator, partially or even completely covered with a crust of heavy metals coming from the primer. According to the authors, such specific particles offer two types of interesting interpretations at the source level: i) the detailed analysis of the composition of this glass fraction allows to compare and refine a potential link between these particles and possible ballistic references, by carefully examining the concentration of elements typical of this glass fraction; ii) the presence within the same particle of heavy metals potentially coming from a primer and elements typical of glass increases the characteristic or even unique character of this particle; this is all the more interesting for particles that are basically only considered as consistent with GSR because of other possible sources than a shooting incident (typically lead and barium-rich particles, very common for 0.22 calibres): despite the absence of one of the three key elements lead, barium or antimony, their nature as IGSR can be confirmed when these elements are found in association with a glass fraction coming from the frictionator.

Donghi et al. looked at the presence of fluorine in GSR to determine its origin [20]. As a light element, it is not particularly easy to detect by SEM/EDS and its presence is not systematically monitored or even identified. Nevertheless, after a thorough review of particles of interest in cases processed over three years, the authors identified IGSR with fluorine in some cases. By examining the various ballistic references available, the authors were able to determine that fluorine probably comes from fluorine-based protective lubricants used for guns and ammunition components.

Another element that is difficult to detect by SEM/EDS is

molybdenum. Indeed, the strongest line falls in the same region as the lines for sulphur and lead, elements that are abundant in IGSR. The origin of the molybdenum has been assumed to be the gun's barrel, made of steel containing molybdenum [21]. In a recent publication [22], Nunziata et al. examined as a possible source of this element in IGSR molybdenum sulphide, used as a lubricant in weapons. This hypothesis was demonstrated by conducting various shootings and analysing the GSR produced during these tests. The authors tested automatic analysis routines for the detection and correct assignment of this element. They observed that due to the overlap problems, any GSR containing molybdenum is in most cases not correctly classified, and only careful examination by experienced operator allows the correct identification of this element. The authors suggest creating a specific class (sulphur only), in which particles containing molybdenum would be automatically placed.

In addition to the ammunition or weapon as the origin of GSR, an additional potential source of the elements found in such particles may be bone fragments. How then can the origin of calcium and phosphorus in GSR be distinguished, as these elements are present in bone fragments but also in some ammunition ? Brożek-Mucha et al. examined the morphology of the particles and calculated the calcium/phosphorus ratio of such particles [23]. They concluded that the calcium/phosphorus ratio is relatively constant when these elements are coming from bone fragments, whereas this ratio fluctuates greatly if this is not the case. However, when the particles are of the order of μm or less, this ratio is less reliable and it is rather the morphology of the particles that may be a discriminating criterion enabling a hypothesis to be made about their origin.

In [24], Nunziata proposes a theoretical explanation for the findings of Bauer et al. for GSR derived from non-toxic titanium-zinc and gadolinium-doped titanium-zinc primers using SEM/EDS with electron backscatter detector and transmission Kikuchi diffraction. The presence of a titanium-zinc-oxide crystalline spinel phase may be indicative to discriminate GSR titanium-zinc particles from non-GSR particles with the same elemental composition. Moreover, the gadolinium-doped SINTOX FORENSICS primers form a non-crystalline glass phase, inhibiting the formation of a titanium-zinc-oxide spinel structure. Unfortunately, the analysis equipment used in forensic labs is not equipped with the necessary instrumentation for this type of analysis, which furthermore requires a high skill level in order to correctly interpret the data.

2.2. Sampling

Sampling prior to SEM/EDS analysis usually involves the use of 1.3 cm diameter strips of aluminium foil covered with double-sided carbon tape this to stub the hands, face and clothing of persons suspected of being involved in a shooting incident. The advantage of face sampling is that there are in most cases certainly fewer problems of contamination by the police during an arrest than with hands or even clothing.

As with face samples, the presence of GSR in nasal samples (nasal mucus or nose hair) could be a valuable indication of the contact of a suspect with a shooting incident, with also probably less problem of loss due to activities of the shooter after the shooting. To this respect, Aliste et al. analyzed samples taken from the nostrils (using swabs impregnated with EDTA) by scanning laser ablation-inductively coupled plasma-mass spectrometry [25]. The experimental conditions of the analysis technique were optimized to allow analysis of a sample within 40 min.

Another area for sampling GSR could be the ears, which, like the nasal cavities, are relatively well preserved from potential losses due to post-shooting activities. In this regard, Akçan et al. conducted a study comparing SEM/EDS results of IGSR samples taken from different areas, such as hands, face, clothing and ears; and indeed, in the context of expected low persistence, the ears could be a preferred area of interest of sampling [26].

The sodium rhodizonate test is often used in police labs as a presumptive test to determine the presence of GSR on hands and clothing of suspects. Positive results are later to be confirmed with SEM/EDS analysis. There are, however, a large number of variants of the methods of sampling and treatment of samples in use by different police agencies. In 2020 Werner et al. [27] investigated three methods of sampling a shooter's hands for subsequent use of such test, as implemented by the Swiss police. They used filter paper, adhesive foil with photographic paper and finally adhesive foil and polyvinyl alcohol on dry and humidified hands of test shooters to lift particles off. The coloured particles found after treatment were cut out of the supports and analyzed with SEM/EDS. A number of expected results were observed, such as that filter paper support works better in collecting particles on humidified hands than adhesive foils. Also, on humidified hands the spread of the number of particles retained is higher – for all three methods – than on dry hands. In general, it seems that the use of filter paper is advantageous for collection of particles from realistic substrates, although the particles are not glued to the surface and the risk of losing particles in subsequent manipulation is therefore higher. Other disadvantages of using filter paper lifts on the crime scene is that it takes slightly longer than adhesive foil, it requires electricity to dry the paper with a hair dryer and the training of the officer/technician is more involved. Adhesive foils, however, pose extra problems in preparation of samples for SEM/EDS analysis (separation of foil and support, loss of particles, double the number of samples to be analyzed) compared to filter paper. As a conclusion, it can be stated that the filter paper collection method is to be preferred over adhesive foils, although more extensive study is necessary to collect enough statistical evidence. An important advantage of this method, compared to stubbing, is that the location of the particles on the shooter's hand can be documented, which could potentially be of help in interpreting shooting activity in suicide cases.

However, the main disadvantage of this type of sampling technique is usually the relatively long application time, between 15 and 20 min. In a recent study [28], Lux et al. proposed a significantly different protocol, reducing the application time by a factor of two. Different experimental conditions were tested, including the presence of blood on the areas to be sampled. This method was successfully tested on cases of suspected suicide victims.

Husak examined in Ref. [29] whether an alternate light source could help collect gunshot residue on the hands of shooters, this by visualising fluorescent particles. For this study, about 100 police officers were involved in the sampling, firing a Glock 9 mm or a 0.40 calibre with American Eagle ammunition. The most effective alternative light source was found to be 520 nm with an orange filter, with a detection rate of 89%. Infrared light at 850 nm was also explored but did not give immediate results, as an enhancement was required with phot processing software to visualise the particles in black and white, with a detection rate of 67%.

2.3. Heavy metal free ammunition

Since the early 2000s, the arrival on the market of ammunition without heavy metals has attracted attention, although the prevalence of such ammunition in cases is still very low in most countries, except perhaps for cases involving police forces.

However, studies are regularly conducted to accurately characterize the particles produced from this type of ammunition. Romano et al. in a study published in 2020 [30] examined three brands of ammunition, namely Geco SuperClean Technology (primer rich in titanium and zinc), Fiocchi Leadless (primer rich in barium and antimony) and Fiocchi IMI Leadless (primer rich in silicon, aluminum and potassium). Both the morphology and the composition of the IGSR particles were examined, with the particularity that a study of the persistence of this type of particles was also carried out. An interesting point to note is the presence of copper and zinc in all the particles of interest, which makes them conclusive elements for the attribution of the particles as GSR or not.

The authors also showed that the persistence of this type of particle was comparable to that of conventional IGSR rich in lead, barium and antimony.

The challenge with this type of IGSR produced by heavy metal free ammunition is manifold, including less easy automatic detection by SEM/EDS (the average atomic number of this type of particle is inherently lower than that of heavy metal rich particles), as well as the likely difficulty in distinguishing it from particles of environmental origin, as few studies have been conducted on this topic. A common type of free heavy metal ammunition is that with titanium and zinc rich primers. Bender et al. have examined this type of ammunition and the IGSR particles produced, with a focus in this study on automatic classification rules by SEM/EDS [31]. They propose different classes based on the percentages of titanium and zinc (included) and iron (excluded), one of which gets rid of many false positives, thus limiting tedious review work. They complemented the study by examining potential environmental sources of this type of particle, such as waste incineration plants and volcanic ash; the proposed new classification allows such particles to be excluded from the class of interest. The nature and crystal formation of titanium zinc IGSR are also discussed in the article.

2.4. Non-GSR sources of GSR-like particles

Regularly, studies examine the possibility that particles from a non-ballistic origin may have a morphology and composition that could be mistaken for GSR particles. Following on from a study published in 2017 that focused on brake pads as a potential source of such particles [32], Seyfang et al. in a second study examined fireworks, nail guns and matches as potential sources for such particles [33]. Compared to other previously published studies, this study was quite extensive in that the authors sought to obtain an overview of the different types of particles produced, without necessarily limiting the examination to the particles usually searched, i.e. particles whose composition is characteristic of GSR or even consistent with GSR. For fireworks and matches, the authors confirm previous studies, namely a zero risk for an experienced operator to confuse such particles from these origins with those produced during a shooting incident. With regard to nail guns, the authors stated that this type of tool can indeed produce particles that can be mistaken for GSR. For instance this is potentially the case for particles rich in lead and barium, which are abundantly produced by such tool: this can be a problem when shooting incidents involve such lead-barium particles, e.g. those for which a 0.22 calibre is used. One possible way of distinguishing between them is discussed in the study, namely to consider the possible glass fraction, in the continuation of the study described previously in this review [19]. However, according to the authors, this fraction is not necessarily sufficiently discriminating. The only way to differentiate between these particles is to examine the particle population as a whole, and in the case of particles originating from a shooting incident, to highlight those linked to a memory effect of the weapon: next to the lead-barium rich particles, some characteristic particles with antimony should be found, resulting from previous shootings. This type of particles due to a memory effect is very frequent in the case of a GSR nature of the particles, absent in the case of nail guns.

Another potential source of GSR-like particles originating from a non-ballistic origin is exploded airbags. Laflèche and Hearns report a case in which this type of particles was investigated [34]. The case concerns a shooting incident involving a vehicle whose airbags exploded following an accident. A suspect was arrested later that day. The question was whether the particles of interest found on his hands, including particles qualified as characteristics of GSR, could possibly have come from the airbags. The authors therefore took samples from both the outside and inside of the airbags, and finally showed by SEM/EDS analysis that the particles identified on the suspect's hands could not have come from the airbags. The authors insist in their conclusions on adopting when possible a case-by-case approach, with analysis of references (in this case airbags) to identify potential sources of the particles of interest.

2.5. Prevalence, persistence and contamination studies

Data on the prevalence of IGSR are important for interpreting results at the activity level, not only at the source level. As such, an European project involving many forensic institutes aimed to examine the prevalence of IGSR in different groups of interest, namely the general population, car mechanics, arresting police officers and firearm owners. This study was conducted between 2017 and 2018 and was published in 2019 [35]. Statistical processing of the data was then carried out. In the end, it was observed that there was no difference between the general population group and the car mechanics, and that for these type of population, the average probability of observing one particle characteristic of GSR was about 0.4%. In contrast, for the other two groups (arresting police officers and firearm owners), this average was higher, at 25 and 42% respectively.

The prevalence of IGSR in vehicles used by recreational shooters was investigated by Blakey et al., in order to evaluate the risk of secondary transfers associated with this type of activity [36]. Seven vehicles were investigated, with samples taken from 24 areas per vehicle. Overall, IGSR were found in all seven vehicles, with total numbers ranging from approximately 50 to nearly 1000 characteristic of GSR particles. With the exception of the firearm storage area (in the trunks), the most contaminated areas were the seats, probably because of their ability to accumulate particles over time. This study shows once again the need to take into account the risks of contamination of the environment of people who have recreational shooting as a hobby.

While SEM/EDS is the method of choice for the analysis of IGSR, some forensic laboratories still receive swabs for bulk analysis. As a result, prevalence studies must continue to be carried out in order to refine the interpretation of the results. In this respect, Comanescu et al. examined the prevalence of lead, barium and antimony in vehicles, this time not related to a shooter nor a shooting incident, this by graphite furnace atomic absorption analysis [37]. The threshold values for these elements were 0.04 μg for antimony and 0.10 μg for lead and barium, a sample being declared positive if these threshold values were exceeded for all three elements. None of the 50 vehicles examined during the study tested positive for IGSR. However, in the case of vehicles used after shooting, some areas were determined to be positive.

The risk of pollution with GSR particles that migrate from police officers to suspects is also regularly evaluated. Lucas et al. recently proposed a review of this issue [38]. In the same article, the authors report a study comparing the average level of contamination of police officers to a random population. They confirmed that the contamination of police officers is much higher, with approximately 8% of police officers affected by the presence of at least one characteristic of GSR particle on their hands. However, this contamination remains to a certain extent low, with an average of 5 characteristic of GSR particles and a maximum of 12. The conduct of a mock arrest experiment in the context of this study allows the authors to evaluate the maximum risk of a transfer from a police officer to an individual during his arrest at approximately three characteristic of GSR particles. While this transfer is not negligible, it should not be considered a major issue, especially in cases where the suspect is strongly positive.

Also in the context of potential contamination of police facilities, Anders et al. took samples from different locations in and around a police station (furniture, clothing, equipment, vehicles) [39]. Again, a number of samples were positive, but always with a limited number of particles detected, rarely exceeding 3 characteristic of GSR particles.

When a shooter washes his/her hands or, in extreme cases, takes a shower, the persistence of IGSR is assumed to be very low: the probability of finding IGSR is considered to be zero. Faced with this scenario, Rosengarten et al. conducted a study on the presence of IGSR on towels used by shooters after their shower [40]. They showed the possibility of

finding GSR particles (up to a few dozen), some of which were very large (>45 μm). The authors therefore advise that this type of sampling should be preferred when the suspect has taken a shower before being arrested.

In [41] Séguin et al. report on their study of literature on GSR research that is available in a Canadian literature database on '*Transfer Traces on Activity Level*'. Their objective is in the first place to give an overview of what has been studied in 80 years of GSR research (from 1940 to 2020), but also to identify any gaps and needs for new research efforts in order to make GSR investigation better useable in the activity level interpretation of this important trace in gun-related crime. Their conclusion is that, although a large number of studies have already been carried out regarding background levels, transfer and persistence of GSR, still much is unknown regarding the influence of certain conditions like weather and clothing types on these important factors. Especially in a Canadian context, where temperatures can range from −40 °C to +40 °C and clothing is therefore adapted to the season, little is known of transfer and persistence of GSR on winter clothing. Nor has the behavior of the GSR deposition been investigated in these extreme conditions (most studies having been conducted in Europe and the US). Furthermore, most studies focus on GSR produced from a handgun, while in Canada most guns owned by the population and used in gun crime are long weapons. Finally, the authors state that few studies are published relating to case-specific studies of prevalence, persistence and transfer, which is non the less necessary and interesting information for the general and transparent interpretation of the GSR analysis result on the activity level in other similar cases.

2.6. Interpretation of results

When interpreting the results, it is often the number of IGSR particles that will be used to help determine whether or not a suspect has been in contact with a shooting incident: as part of an evaluative approach, it will be stated in the expert report to what extent the results obtained (i.e. the number of GSR particles found on a sample related to a suspect) can be explained by whether or not the suspect was in contact with the shooting incident. This approach was initiated in 2006 by Cardinetti et al. [42] and later completed by Biedermann et al. [43] on the basis of controlled experiments. However, in practice, the use of such experiments for the daily cases is not routinely feasible, as they require too many resources in terms of personnel and analytical equipment to perform these experiments. To overcome this problem, Benzaquen et al. propose in Ref. [44] to use real case data, in this case about 500 suspects, with a mixed approach using different models to estimate the probability of observing a given result (number of characteristic GSR particles found on samples related to a suspect's hands) assuming contact or not with a shooting incident. Among the different results obtained by this approach, the authors could estimate the probability of finding 3 or more GSR particles on the hands of a person who was not in contact with a shooting incident to be about 0.15%. The advantage of this approach is that, ultimately, few resource are needed to collect data from the cases studied.

Court decisions and the interpretation of expert reports in court proceedings are rarely reported and commented on in the literature. This general trend illustrates the gap that can exist between the conclusions of experts and the interpretations that can be made at trial. Shaw reports on a case where a person was convicted of murder based on, among other things, the presence of two characteristic of and two consistent with GSR particles on his jacket [45]. The decision of this trial was revised in 2014, overturning the court's decision. The main argument in favour of revising the decision was that the jury at the time had not been sufficiently alerted to the problem of GSR pollution, for instance when the suspect was arrested. This underlines the importance for the GSR expert to address this type of issue in his/her conclusions, i.e. to discuss the results at the activity level, and not only at the source level as was done in this case.

2.7. Quality aspects and efficiency

In the field of IGSR analysis, the reference standard is the ASTM 1588 standard practice which was revised in September 2020 [10]. Compared to the previous versions, the only notable change is that particles containing lead, barium, tin, calcium and silicon are again no longer considered as characteristic of GSR. Apart from this standard, two guides exist: the ENFSI guide (whose content is more or less identical to that of the ASTM standard, but which has not been revised recently but will be in 2022) [46] and the SWGGSR guide (which is more detailed in terms of interpretation of results) [47].

Proficiency tests are carried out annually. They are organised by a commercial supplier, QuoData (Germany), in collaboration with the ENFSI expert working group "Firearms and GSR" and consist of the detection by SEM/EDS of 150–200 artificial three-element particles (lead, barium and antimony) distributed on a flat surface over six particle size classes (0.5–2 μm). Three of these proficiency tests were performed during the period of interest (GSR2019, GSR2020 and GSR2021). These tests are very interesting for monitoring important parameters and analytical performance of the systems. However, some performances are not examined by these tests, such as the automatic classification of particles, the review performed by the operators, or the interpretation of the results. Charles et al. therefore conducted a round-robin test on a real sample over a two-year period to examine this type of performance [48]. Eleven institutes analyzed this sample with the SEM/EDS systems at their disposal. In the end, a fairly good consensus was observed regarding the classification of particles, since 75% of the particles were classified in the same way by the participating institutes. Some classes are more prone to misclassification than others, notably the barium-antimony class, as the presence or absence of lead traces changes the particle from consistent with to characteristic of GSR (or conversely); and finally the decision to take into account or not the presence of traces of lead depends on local rules which are therefore not standardized within the forensic community.

Also in the context of a quality approach, Menking-Hoggat et al. developed a method for creating artificial samples containing IGSR [49]. This method is based on the deposition on a stub of a microsuspension of an organic solution rich in IGSR. The advantage of this method, apart from the fact that it is carried out under relatively controlled and standardized conditions, is that different types of IGSR can be prepared, namely the typical IGSR rich in lead, barium and antimony, but also other heavy metal free IGSR. The samples were characterized by SEM/EDS of course, but also by ICP-MS and LIBS. The number of particles deposited on the stubs ranged from about 150 to 500.

When acquiring a new SEM/EDS, or simply to better monitor an active SEM/EDS, some parameters need to be checked to ensure that the device is working properly. With this in mind, Ritchie et al. distinguish a set of tests to be considered when (re)commissioning a device or when a malfunction is suspected [50]. These tests concern the SEM (beam energy, probe current, optimal working distance, stage …), the EDS system (energy scale correction, elevation angle, detector alignment, rejection of coincident events, resolution …) or the BSED detector (response time, Z-contrast), each time with didactic information provided in the article on when and why to perform these tests and the practical way to perform them. In addition to these tests, a set of quality checks must be performed on a regular basis, in order to quickly identify any deviation or even failure of the instrument that could have an impact on the quality of the results. These checks are carried out in a few minutes, or even a little longer in the case of a positive GSR sample.

In order to optimise the analytical capabilities of the SEM/EDS, some laboratories have a policy of analysing samples from different suspects, or even different cases, in the same run. It is therefore possible that within the sample chamber, samples with a high number of GSR particles may be present alongside others with a much lower number or even no GSR particles. The question is then to assess the risk of cross-contamination within this chamber. Rosengarten et al. examined this

aspect by conducting several experiments with such configuration [51]. In the end, they conclude that the risk of cross-contamination in the sample chamber can be considered as zero. It should be noted, however, that the risk of contamination before analysis, for instance during sample handling, was not investigated in this study.

2.8. Luminescent markers and doped ammunition

Some police forces, in particular those of Germany and the Netherlands, use specific heavy metal free ammunition, i.e. doped with specific elements for forensic purposes. Such ammunition, namely "ACTION IV Forensis" from RUAG and "PEP II/s" from MEN, contain a rare-earth element as tracer (i.e. gallium or gadolinium) to make the particles produced characteristic of GSR; these ammunition also contain copper to make the projection of GSR onto targets sensitive to a colour test, namely dithiooxamide. These ammunition meet the criteria outlined in the "Technical Guideline for Cartridge 9 mm x 19, pollution reduced" [52]. Donghi et al. now report on a new ammunition developed by FIOCCHI, which according to their analysis, also meets this guideline [53]. While copper is also present in the primer, the rare-earth tracer used this time is samarium, resulting in SmKSiTiCaAl-rich particles. According to the authors, these particles, due to their particular composition, could in future also be considered as characteristic of GSR, since a source other than a shooting incident seems very unlikely.

For several years now, some research groups have been synthesizing and characterizing different fluorescent markers that could then be added to conventional and heavy metal free ammunition. When a shot is fired with such doped ammunition, the GSR produced can easily be observed under UV light, which allows direct visualisation, even at the crime scene. In addition, these fluorescent compounds often contain rare-earth elements, which can then be easily detected by the use of conventional SEM/EDS technique for an unambiguous attribution to IGSR, as discussed above; they can indeed be considered as characteristic of GSR, due to the presence in these particles of very specific elements belonging to the rare-earth family. This field, which is currently undergoing numerous developments and has been the subject of several publications in recent years, was recently reviewed in 2020 by Harshey et al. [54].

To find a useful application in the field of GSR, these compounds must therefore exhibit intense photoluminescence coupled with high thermal stability. In this respect, Silva et al. introduced a new luminescent marker, i.e. a metal-organic framework containing terbium [55] as rare-earth element. This compound was synthesized and characterized by different analytical techniques (photoluminescence spectroscopy among others). Another metal-organic framework containing europium was also synthesized and characterized by the same research team [56]. According to the author, the latter compound has the highest thermal stability among the other compounds of the same family, which is an undeniable quality in the context of its use in ammunition.

In 2013, Charles et al. published a study on the influence of textile type on the efficiency of GSR collection [57]. They found a strong influence of sheddability, i.e. the ability of the textile material to lose fibres, on sampling efficiency; this difference is thought to be related to the saturation rate of the carbon tapes used to sample the garments. Recently, Arouca et al. repeated the protocol of the study published in 2013, but this time using ammunition spiked with luminescent markers to potentially see possible GSR deposits and perform targeted sampling [58]. The samples were examined using a video spectral comparator and sampling was performed using stubs for analysis by SEM/EDS. In this way, according to the authors, it is possible to target the areas of interest to be sampled, thereby delaying saturation of the carbon tape.

An additional dimension to this technology of fluorescent markers is the possibility of using combinations of markers with different concentrations, thus creating unique compositions, i.e. a kind of barcode of ammunition. This technology is already used in the context of banknote staining systems, e.g. in the case of ATM attacks. A specific combination of rare earth elements used as markers in the ink can indeed be used to link a stained banknote to an attack. For the GSR field, Lucena et al. published in 2019 a study [59] reporting the development of ammunition powder formulations enriched with europium, terbium, samarium and/or ytterbium compounds present at different concentrations. Blind tests were then carried out with ammunition having different combinations and concentrations of such elements, in order to see if it was possible to trace the GSR particles back to the ammunition used, this based on SEM/EDS analysis of IGSR particles. These blind tests proved to be successful, as the correct correlations could be established for the eight shots performed. This technique is therefore promising for the future, making it possible to create strong links between GSR particles and ballistic references.

In the same context and following a study published in 2018 [60] that focused on several metal-organic frameworks containing europium with an adjustment of the composition of the markers allowing partial encoding and tracking of the ammunition, Carneiro et al. further developed this approach by also using luminescence and Raman spectroscopy, combined with the use of principal component analysis and partial least squares discriminant analysis tools for a better classification and identification of the markers [61]. Also in the context of being able to differentiate between ammunition containing different markers, the same team examined the possibility of using a video spectral comparator, an instrument much more common in forensic laboratories than spectrofluorometers, to differentiate between two marked ammunition, with ultimately conclusive results using chemometric methods [62].

The toxicity of this type of product (luminescent markers) has already been the subject of several studies, in most cases by assessing their toxicity directly on mice or rats. In this respect, Talhari et al. [63] examined the toxicity of a europium-based compound previously presented as a compound of interest among luminescent markers. Their study concludes that this compound ranks among the least toxic of the compounds studied to date.

On the other hand, these materials, used in a heavy metal free ammunition, produce by-products during firing, the toxicity of which should also be evaluated. In this respect, Arouca et al. analyzed by gas chromatography the derivatives of these products, resulting from the combustion of propellant powders [64]. They identified two potentially toxic and carcinogenic products, namely pyridine and benzene. On the other hand, an estimate by the authors of the concentration of this type of by-product does not suggest that shooters are at risk of being intoxicated. It should be noted that this study also looks at the identification and possible toxicity of the derivatives released by conventional heavy metal free ammunition; in this case toxic derivatives such as benzonitrile and naphthalene have been identified.

3. Organic GSR

3.1. Sampling

In the context of the analysis of the OGSR and its possible future implementation in real cases, it is becoming increasingly clear that the combined collection and analysis of the IGSR and OGSR should be considered. Different strategies exist in this respect: i) the fifty-fifty procedure, which generally consists of using one area of the stub for the IGSR sampling and the other (whose surface may have been modified) for the OGSR sampling, ii) sequential sampling (often with priority given to IGSR sampling), and iii) sequential analysis (also often with priority given to IGSR analysis). Redouté Minzière et al. evaluated these three approaches, using SEM/EDS for IGSR detection and UHPLC-MS/MS for OGSR detection [65]. The samples were taken directly after the shooting. From this study, it appears that of the three approaches examined, sequential analysis seems to be the most promising for the best detection of OGSR compounds. The fact that the samples are carbon coated (for SEM/EDS analysis) is one of the explanations put forward by the authors for a better detection of OGSR: these compounds would be

preserved from degradation by this thin layer of carbon deposited on the samples.

It should be noted that in general active sampling device techniques are used to acquire samples of OGSR from shooters' skin. These samplers (including wet and dry swabs, adhesive tabs and films) have, however, a tendency to result in loss of the analyte under investigation. Zuy et al. test therefore in Ref. [66] a type of passive sampling device in the form of silicone wristbands which are worn by the shooter and therefore adsorb the liberated OGSR compounds. The silicone material can afterwards be extracted in solvent to yield the OGSR analytes of choice. To test the characteristics of this material for OGSR compounds, wristbands were subjected to solutions and mixes of known concentrations of some relevant OGSR components such as (nitro)diphenyl-amine, ethyl centralite and dimethyl phthalate in open and closed vessels, as well as by direct pipetting. After exposure and drying, the OGSR were extracted again using acetonitrile/methanol and analyzed using HPLC-UV/Vis. Tests were conducted with a calorimetric bomb to simulate combustion. Figures of merit were calculated for the analysis of the different compounds, showing a correspondence to results found in literature. The results of combustion simulation are encouraging for ethyl centralite and dimethyl phthalate but not so for (nitro)diphenyl-amine. This suggests the need for further testing using wristbands worn by volunteer shooters.

3.2. Prevalence and contamination studies

As has been done and still continues to be done for IGSR, several studies on prevalence and contamination have recently been conducted at the level of OGSR, in order to enable and facilitate the interpretation of OGSR results in the analysis of real cases.

To estimate the potential pollution, Gassner et al. [67] considered three scenarios: the first involved handling a gun for a short period of time; the second scenario was shaking hands with a person who had very recently fired a gun; the third scenario simulated an arrest by a police officer, similar to what was proposed in another paper [38], except that in this case the police officer was asked to use his firearm prior to the arrest. Three OGSR compounds were targeted and analyzed by UPLC-MS/MS: akardite II, ethylcentralie and *N*-nitrosodiphenylamine. Secondary transfers were observed for all three scenarios, although there were differences: on average the largest transfers were observed for the arrest scenario. The same team shortly afterwards published a similar study, this time focusing on ammunition used in Australia [68]. In this case, two scenarios were examined: the first also simulated an arrest by a police officer, who used his firearm just before; the second scenario examined the potential contamination of OGSR when handling a firearm recently discharged. Three OGSR compounds were targeted and analyzed by UPLC-MS/MS: ethycentralite, diphenylamine and *N*-nitrosodiphenylamine. While transfers were also observed for both scenarios, in this study the transfer was greater in the case of handling the firearm than in the case of the simulated arrest. However, the authors did not observe a substantial excess in OGSR between a shooter and a person who merely handled the firearm. Again, these two studies illustrate the need for caution in interpreting results, ideally with knowledge of the context, in order to refine the interpretation and above all to be aware of the limitations of the expertise.

The prevalence of OGSR was examined by Manganelli et al. in two target populations, namely the general population and police officers [69]. The technique used was also UPLC-MS/MS, with eight OGSR compounds traced. In contrast to similar studies on IGSR, which ultimately showed no (or very little) prevalence of this type of particle in the civilian population, the prevalence of OGSR in this population is considered to be significant with almost 18% of individuals for which at least one target compound was detected on their hands. However, the study showed that the number of individuals affected by two or more compounds decreases significantly, and in these cases the presence of these compounds can, with one exception, be explained by secondary transfers. Logically, the prevalence of OGSR among police officers is greater, with almost 35% of individuals positive for at least one compound. In terms of interpretation in the context of a case, the authors recall the need to detect in a sample more than one target compound in order to establish a potential link with a shooting incident; the authors also advise a case-by-case approach, as advocated in the field of IGSR.

The prevalence of OGSR was also examined in police vehicles by Gassner and Weyermann [70]. 64 vehicles were examined in this study, both front and rear, again using the UPLC-MS/MS technique targeting seven OGSR compounds. In the end, most samples were negative; a few samples had four or more targeted compounds. After careful examination of the positive samples, it appears that the nature of the contamination is secondary transfer, mainly related to the transport of police officers to the shooting ranges. Special attention to this type of transport (e.g. intensive cleaning of vehicles after) would probably significantly reduce the risk of contamination in police vehicles of arrested persons.

4. Development of new instrumentations and methods

4.1. Laser-ablation inductively coupled plasma mass spectrometry and laser-induced breakdown spectroscopy

Ferreira et al. show in Ref. [71] that laser-ablation inductively coupled plasma mass spectrometry in a scanning (imaging) mode can be easily used to distinguish between stub samples acquired from hands of shooters, non-shooters, and fireworks and brake pad contaminated volunteers. To this end, they also demonstrate the use of ternary diagrams in which the concentrations of lead, barium and antimony of the particles found on the hands of the volunteers are depicted. While the particles of non-shooters (blanks) are randomly spread over the diagram (because of the random abundance of these elements in the environment), the samples of the shooters, fireworks and brake pad groups show a distinct grouping in corners of the diagrams. As the scan is very fast (half an hour compared to several hours for SEM/EDS) and as the sample is only slightly damaged by the laser-ablation sampling, the authors state that this method could easily be used as a screening method for a subsequent confirmation by SEM/EDS.

Menking-Hogatt et al. expand their previous experience with laser-induced breakdown spectroscopy in GSR research in Ref. [72] using a 5×5 grid sampling mode. They compare the results obtained in this study with their previous results using a continuous line ablation sampling. The discrete sampling technique offers the advantages of only damaging the sampling stub in a 0.2% area, while the line ablation sampling uses up 0.6% of the stub's area. Furthermore, the stub surface is less damaged by the ablation sampling as the micro-spot sampling requires only two shots per location, while the micro-bulk-line method performs a continuous line scan spectrum using 496 shots of the laser. The stub can therefore easily be used in a subsequent SEM/EDS analysis. The laser-induced breakdown spectroscopy analysis offers chemical information on multiple elements of interest, as well as other (light) elements which may become important with the development and adoption of heavy metal free primers in future. The laser spot can of course not give information on individual particles, as the diameter of the spot is 100 μm, but it was shown to give 99.5% accurate results for detection of GSR markers on the evaluated dataset. The measured samples were produced by sampling of the hands of shooters who had fired five shots with different types of ammunition. As comparison and blanks, stubs with synthetic GSR particles in acetone dispersion and hand samplings from non-shooters were measured. The analysis results were treated using several statistical methods, including Bayesian and neural network models which were shown to be excellent fit for purpose methods for interpretation of the weight of the evidence obtained from these results.

The study published in Ref. [73] is a continuation of the previous study with a combined use of laser-ablation inductively coupled plasma mass spectrometry and laser-induced breakdown spectroscopy. The

samplers are standard coated SEM stubs which are used on the hands of shooters and non-shooters. For method validation, the authors use their previously reported method of producing IGSR particles in acetone dispersion. Using combinations of leaded and lead free ammunition, the authors show the validity of these techniques in obtaining a fast overview of IGSR presence on a SEM stub. These stubs can subsequently still be used for standard SEM/EDS analysis. Laser-ablation inductively coupled plasma mass spectrometry - being a mass spectrometric technique - hereby shows lower limit of detections than laser-induced breakdown spectroscopy (which also suffers from overlapping emission lines of some of the involved elements), but both techniques show some complementarity. Confidence in the result would therefore benefit from both techniques being used on the same samples.

4.2. X-ray analysis

In [74], Madeira et al. describe the use of a combination of X-ray scattering and chemometrics tools to characterize the OGSR components of samples taken from the hands of shooters. X-ray analysis of GSR samples is most often used in conjunction with automated SEM particle search, but here the authors used wavelength-dispersive X-ray fluorescence to analyze the samples. Besides the inorganic element composition, the scattering part of the spectrum also contains information on the organic components which may be present. Although it is since long known that the scattering region of the spectrum contains this information, the use of chemometric methods such as principal component analysis and hierarchical cluster analysis are needed to exploit it. The authors show that using these techniques, it is possible to identify different types of GSR used in shooting experiments with four different ammunition types. Besides shooters, control group samples from car mechanics, gas station attendants, fireworks users and a brake pad were included in the sample groups. Although the technique is shown to work in these controlled conditions, more testing is necessary to certify the effectiveness and applicability in practical forensic conditions (such as detection of a single shot, sampling after several hours etc).

The use of trace analysis techniques in the GSR field dates already from decades ago, but now Ferreira et al. report in Ref. [75] the successful use of total reflection X-ray fluorescence for the detection of important constituent primer elements in hand samples acquired from real shots. Total reflection X-ray fluorescence distinguishes itself from X-ray fluorescence in that sensitivities of ppb (μg/L) range can be attained for elements in solution. A drop of the analyte is hereto brought onto a quartz glass X-ray reflecting sample carrier. The quartz surface is treated before to make it hydrophobic, so that the solution drop doesn't spread out over the entire surface. Using internal standards containing an element that does not belong to the group of elements under investigation (the authors used gadolinium in this instance), the absolute concentrations of the elements of interest can be calculated. The authors were thus able to measure the twelve most relevant inorganic elements of six ammunitions under study down to ppb range. A multivariate statistical treatment of the data allowed them to discriminate the samples into groups according to ammunition type, weapon (pistol, revolver and rifle), blanks and water (environment). With the exception of one ammunition type (.32 cal), the principal component analysis was able to discriminate between samples collected after only one shot experiments and blanks. This is an important finding, as this is a forensically relevant result in for example suspected suicide cases. Unfortunately, as the procedure requires the dissolution of the analyte elements, there is no morphological and particle information and the sample is lost for subsequent investigation.

Sarapura et al. also tested total reflection X-ray fluorescence in a portable setup with the application of IGSR detection on the hands of shooters [76]. In this work, swab samples in nitric acid from the hands of shooters using leaded 9 mm ammunition were studied and compared to blank samples. Several multivariate data treatment techniques including linear discriminant analysis, support vector machines and K-nearest neighbors were used to establish the optimum discrimination. Finally, the decision tree modelling technique proved to yield the best results, with highest accuracy and minimum errors in the classification of the samples.

4.3. Electrochemical analysis

In a review of the use of electrochemical methods for GSR detection, Harshey et al. discuss in Ref. [77] the recent world literature on this subject. As O'Mahony and Wang already published an extensive review of the use of electrochemistry in GSR research in 2013 [78], the authors' review is in fact covering new developments since then. The authors first discuss in depth the basic principles of GSR formation and the use of these traces, noting that due to the global rise in gun crime there is an urgent need for fast, on-site analysis of samples. Electrochemical techniques, adapted to and optimized for GSR detection, can fill this need as the necessary materials and equipment is easily transportable and useable in the field in even the most remote locations. Furthermore, the sampling devices require no special preparations and are essentially non-destructive, so samples can be exploited later in the lab environment using instrumental techniques such as SEM/EDS, laser-induced breakdown spectroscopy or inductively coupled plasma mass spectrometry. Finally, still open issues regarding elemental detection of GSR are discussed such as some selectivity constraints and the advent of heavy metal free ammunition containing predominantly light elements - which are also present in environmental contaminations. They point to other field-deployable technology that is becoming available such as Raman spectroscopy together with chemometrics, wearable micro-sensors and paper-based micro-fluidics as possible avenues for future development in this area.

Also in relation to the development of such analytical techniques for field use, Castro et al. report in Ref. [79] about the development of a new electrode for the simultaneous detection by means of square-wave anodic stripping voltammetry of the ions Pb^{2+} and Sb^{3+} on samples of the hands and clothing of shooters. They have hereto developed a new sampling device/electrode by 3D printing of the sampling/analytical surface in commercially available graphene filament. Strips of this material were treated and stabilized to form the sample collector and working electrode for a (3D printed) analysis cell. This setup was validated and shown to yield a good efficiency, selectivity and reusability for detection of both ions of interest, with these analytical properties being comparable to atomic absorption spectroscopy, a technique only available in a laboratory environment. Using this technology, the police on the crime scene are able to perform a fast screening for lead and antimony on the hands and clothing of suspects.

Continuing on the need for fast screening and in-field testing, Ott et al. present in Ref. [80] an evaluation of the simultaneous analysis of OGSR and IGSR species using electrochemical sensors. To this end, a total of about 400 SEM stub samples were acquired from the hands of shooters and non-shooters (self-declared) as a background. One of the stubs of each hand was washed with acetate buffer and acetonitrile. Aliquots were subsequently analyzed for IGSR and OGSR species respectively using square-wave anodic stripping voltammetry. The analytical properties of the method were validated and were shown to yield excellent limit of detection and repeatability for both IGSR and OGSR species. Although electrochemistry cannot offer morphological information, the combined presence of IGSR and OGSR components in the samples adds to the forensic significance of the results. The SEM stubs can furthermore still be used later on in the lab for a confirming analysis by SEM/EDS. Finally, in order to make an objective interpretation of the measurements possible, several statistical classification techniques were used, among which classic thresholding methods, but also machine learning techniques such as neural networks. These last types of techniques offered superior performance and robustness in avoiding false positives and negatives.

In [81] Promsuwan et al. describe the development and use of a

palladium-covered glassy carbon microsphere electrochemical sensor that can be used to detect nitrites formed after the firing of a gun and deposited on the hands and clothing of the shooter. The sensor was tested in its role of a fast screening method and shows excellent electrocatalytic properties, high sensitivity towards nitrite detection, low limits of detection and a wide linear range. It therefore promises to be also a good sensor for nitrite determination in applications in environmental and food analysis besides its forensic use.

In a review of the technology of glove-based and wearable sensors, Wang and Hubble give in Ref. [82] an introduction to the possibilities that electrochemical printed sensors offer in the fields of forensics, defense and security, medicine and robotics. Particularly the developments made in sensor systems printed onto fingertips of disposable gloves and able to detect GSR, explosives and drugs compounds (including both the drug and the compounds used to "cut" them) are of practical use and interest. With this technology, in-field detection of these substances – in a qualitative manner – becomes practically possible and available to CSI operatives, first responders and border security personnel. By using carbon conductive adhesive tabs as collection surfaces on the fingertip, it is even possible to use a positive sample for subsequent SEM/EDS analysis of GSR particles in the laboratory.

5. Cathodoluminescence

In [83], Donghi et al. describe the use of cathodoluminescence in a SEM for the detection of IGSR particles. In particular, they investigated the use of cathodoluminescence in detecting particles of specific primers that do not contain any heavy metals. A SEM/EDS instrument with standard GSR configuration was hereto extended with a cathodoluminescence detector and a cooled CCD spectrometer to analyze the wavelengths at which the particles emitted. With this system and using the standard GSR particle search and analysis software - adapted to take the cathodoluminescence signal to search for particles instead of the backscattered electron signal - the stubs from the hand samples were scanned. As particles were detected, both their EDS and cathodoluminescence spectroscopic signals were recorded. The cathodoluminescence spectra were deconvoluted using Gaussian peaks to separate the constituting emission lines. Although also classic GSR particles were detected (probably due to a memory effect of the gun), a large number of particles, characteristic of heavy metal free IGSR were recorded. The authors claim that in future these primers will still remain detectable using extended SEM/EDS/cathodoluminescence systems running slightly modified software, and in a combination with OGSR analysis.

5.1. Liquid chromatography mass spectrometry

The use of high performance liquid chromatography mass spectrometry for the detection of OGSR has been under development for a few decades, but this far the applicability in real cases has been hindered by the small amount of the selected trace material - usually diphenylamine or related compounds - present on the hand of the shooter. In their present work [84], Argente-Garcia et al. show a successful enrichment procedure of diphenylamine in cotton swab samples acquired from the hands of shooters down to a level of a few ng. To this end, they use in-tube solid-phase micro-extraction, whereby capillary columns lined with different extractive phases are employed to optimally extract, concentrate and clean-up the sample. In this study the in-tube solid-phase micro-extraction column is coupled directly to a capillary liquid chromatograph which permits a compact and on-line sample clean-up. Finally, the increased sensitivity offered by this setup allows for a simple UV–vis diode array detector instead of a mass spectrometer to be used. In this study, dry cotton swab tips were used as samplers, as was experimentally determined that use of the SEM stub method results in a fourteen times lower yield of the diphenylamine extraction. As a final result, in 81% of the tests diphenylamine was found and quantified from volunteers who had fired a pistol 25 times in a shooting range.

Taudte et al. tested in Ref. [85] the usability of the RapidFire 365 automated solid phase extraction system for the detection of smokeless powder and OGSR compounds in soils and on the hands of shooters. This system operates as a completely automated sample plate handling system (up to 12 plates with a 96 well capacity each) and microfluidic sample preparation robot for the biomedical industry. Up to four solvents can be used to load, wash and extract the samples onto solid phase extraction cartridges (according to the compound type of interest) and subsequently be loaded into a triple quadrupole mass spectrometer for detection of the compounds. The authors tested this system with samples originating from explosives research – using two types of soils spiked with known concentrations of explosives components – and sample swabs obtained from the hands of test shooters after three shots were fired with either a (44 REM) pistol or a (12-gauge SuperX) shotgun. Results after optimization of the method show that the system is very well suited for the analysis of the explosives compounds in soil. On the hands of shooters, however, the method proves to be not sensitive enough to show reliable results. Further work is therefore necessary to increase the sensitivity of the present method for the application in real case work analysis of shooting incidents.

As discussed previously and because of the small number of GSR particles typically being recovered after a shooting incident, the combination of IGSR and OGSR species on the same sample could largely increase the significance of the traces recovered in a police forensic investigation. In order to develop a combined IGSR/OGSR sampling and analysis method, Bonnar et al. tested in Ref. [86] the use of SEM stubs as samplers for OGSR high performance liquid chromatography mass spectrometry analysis, followed by IGSR SEM/EDS study. A test was set up whereby the hands of test shooters, having fired multiple consecutive shots with different caliber firearms, were sampled immediately after the shooting session. To extract the OGSR from the stub without displacing or removing IGSR particles, a drop of acetonitrile was used to carefully rinse the surface. After drying, the stub was analyzed with SEM/EDS using the standard procedure. The acetonitrile extract was analyzed with UHPLC and electrospray ionization source to detect the OGSR species present. The stub surfaces were examined pre- and post-extraction to check for displacement or removal of IGSR and results found that the IGSR were only minimally disturbed by the extraction procedure. Authors conclude therefore that their procedure for dual IGSR/OGSR detection on SEM stubs could be adequate for forensic use. Of course, further testing is necessary to confirm that these encouraging results can be reproduced in real case situations where for example only one shot is fired and considerable time between incident and sampling has elapsed.

Bell and Feeney discuss in Ref. [87] a method that combines the analysis of IGSR and OGSR, sampled onto a single carrier material and in one procedure, namely triple quadrupole mass spectrometry. In order to analyze the combined IGSR and OGSR in one method, crown ether ligands are employed to bring the metal ions into the sample solution. The authors describe the shooting campaigns using pistols and revolvers with 9 mm ammunition, during which hand samples of shooters were acquired prior and just after firing one or two shots. All inorganic species named in the ASTM guide for GSR analysis were detected, except for antimony - an effect which is presently under study. From both IGSR and OGSR quantitative results could be obtained, which, the authors claim, could lead to future quantification and be used in discerning shooters from contaminated by-standers. Since this is not possible with the current SEM/EDS method, this would be a clear advantage of the mass-spectrometric method over the particle analysis in use today. Although the authors don't envisage a take-over of the SEM/EDS technique by triple quadrupole mass spectrometry, they do see a possibility for a synergetic combination of technologies, moreover since triple quadrupole mass spectrometry systems are now readily available in forensic toxicology laboratories.

Feeney et al. describe in Ref. [88] also their experiences with the use of complexing agents to better detect and identify OGSR and IGSR by liquid chromatography mass spectrometry. Although many different analysis techniques have been tried in the last decades to detect IGSR and OGSR, many lack the specificity and/or sensitivity needed to detect the minute amount of trace material deposited during a real shooting incident. The authors have therefore experimented with a number of complexing agents to capture or tag GSR trace particles for subsequent analysis with liquid chromatography and mass spectrometry. As the different traces under study are of a very different physico-chemical nature, tests were carried out using both crown ethers (for lead and barium) and tartaric acid (for antimony). Finally, they decided on a mix of both ligands to bind all three major elements. The procedures to perform the chelation as well as the analytical figures of merit were studied extensively. Also the use of multiple analysis techniques on the washings of SEM stubs in series was tested, showing that it is possible to use one sampling method to be used in various subsequent test scenarios, thereby potentially integrating liquid chromatography mass spectrometry in a general workflow of analysis of GSR.

5.2. Other mass spectrometry techniques

As described above, IGSR detection is widely implemented in routine analysis, the challenge being to integrate OGSR analysis-a promising but still nascent area of analysis - into the analysis process without affecting IGSR analysis. In this respect, Goudsmits et al. examined the possibility of analysing OGSR by solid-phase microextraction gas chromatography mass spectrometry followed by SEM/EDS analysis, this within the same sample [89]. More precisely, the sample, i.e. a conventional stub, is subjected to an solid-phase microextraction step in an oven at 80 °C for 35 min. According to this study, based on samples taken from very recent shooters, this step does not affect the IGSR results in any way. In addition, gas chromatography analyses allow the detection of the main OGSRs of interest, which are ethyl centralite, diphenylamine and 2-nitrodiphenylamine, thus allowing at the end a total chemical profile (IGSR and OGSR) to be established from a single sample.

The association of items recovered on the crime scene with the original source of the traces is of course an important aspect of forensic science. One important problem with GSR traces is that, due to a number of uncontrolled parameters and processes, the composition of the traces changes as a function of, for example, the place where they are sampled (e.g. the hands of a suspect versus the barrel of the gun or the cartridge case). This correlation is particularly difficult to make in the sub-field of OGSR, which therefore necessitates performing reference shots using case ammunition and weapon (which are often not available) to identify the link between the ammunition/weapon and the GSR trace. In the first successful attempt to couple chromatographic data from original smokeless powder with the resulting residue in sillico (this is, in computer software), Gallidabino et al. in Ref. [90] have performed quantitative profile to profile relationship modelling on the powders of 9 different ammunitions and their associated OGSR traces. To this end, samplings of test firings, as well as of the unfired powders, were performed on these ammunitions. These were then characterized using (cold injected) gas chromatography mass spectrometry. The collected profiles obtained were then used in the modelling step, using fourteen different machine learning techniques, with the goal of optimally associating the data from the fired to the unfired powders. Finally, an optimal combination of models was selected which allows for the accurate association of OGSR profiles with the unburned powder profiles and vice versa. The authors furthermore state that this technique may well be implemented in similar problematic areas such arson accelerants, improvised explosive devices, toxicology samples and environmental analysis.

In the chemical analysis of explosives and GSR, ion chromatography coupled with high-resolution mass spectrometry is not widely used. This is mainly due to the fact that ion chromatography is mostly based on an aqueous elution environment, while the sampling of organic residues is based on solvent-rich environments. The combination of both environments obviously gave problems for the extraction of analytes of interest. The new resins used in ion chromatography are, however, more compatible with organic-solvent containing eluents, but have not been tested in the conditions most often used in the forensic environment (i.e. acetonitrile/water). Gallidabino et al. describe in Ref. [91] a method they developed that uses ion chromatography coupled with high-resolution mass spectrometry with an ethanol/water solvent mix to detect OGSR anions from casings and explosives residue from hands and fingermarks of contaminated volunteers. Both targeted and non-targeted principal component analysis was used for the data analysis to investigate the possibilities of this technique in profiling applications. They show that, particularly for the application to GSR type classification, it is possible to discern between GSR ion population arising from three different manufacturers. This result can clearly be of forensic interest in particular cases where munitions from multiple manufacturers are involved.

5.3. Infrared and Raman spectroscopy

Jain and Yadav present in Ref. [92] a review of the use of vibrational spectroscopic techniques (infrared and Raman) which are used in conjunction with chemometric data processing for the identification of GSR traces after criminal incidents. Although they have been available for a long time now, the advent of smaller and portable equipment, which can also be used on the crime scene, has caused for renewed interest in these techniques from forensic scientists. Because these instruments have typically lower sensitivities than their lab benchtop variants, the careful validation of the new equipment is an important task and prerequisite before they can be confidently deployed in the field. Use of chemometric processing and data modelling will be an important and integral part of the way these techniques will be used in future forensic applications.

Another review article on vibrational spectroscopy by Silva et al. [93] discusses the possibilities, trends and challenges of Raman and infrared spectroscopy in forensic science applications. The use of chemometric techniques is explained as well since these are essential in the data analysis in forensics. Further on, the use of these technologies is discussed in more detail in the areas of illicit drugs, GSR and explosives, documents and currency and body fluids. In the GSR field the use and development of Raman and infrared spectroscopy is reported, predominantly for the detection of organic GSR compounds. The authors conclude that developments of vibrational spectroscopy applications in forensics will still continue as there are multiple challenges posed by the forensic samples and their environment such as influence of the carrier substrate of traces and the impurity of traces in real samples. The use of mathematical methods in treating, filtering and classifying of the data will therefore also continue to be a major prerequisite for their adoption by forensic scientists.

The research effort into the detection OGSR is increasing and mostly takes place on the level of the chemical composition of OGSR compounds using mass spectrometric techniques. Khandasammy et al. however, take in Ref. [94] the approach to detect the particulate OGSR using a two-step hyperspectroscopic technique. In a first step, the potential OGSR particles are detected by scanning the sample surface using a 455 nm laser source at a 10X objective magnification. The fluorescence of potential OGSR particles is used to tag them for the second step, which consists of a localized Raman spectrometry analysis at 50X magnification of the individual particles to confirm their ballistic origin. The authors show the feasibility of this technique on samples where individual (visible) OGSR particles were placed on microscope slides, as well as on random samplings of a shot target cloth using adhesive tape on a microscope slide. This last method mimics real samplings of clothing in forensic practice. Authors claim that from these positive tests an adapted instrument could be developed which can detect OGSR particles in a

manner likewise to the SEM/EDS method for IGSR particles which is as specific, but much faster.

On the same topic, Alvarez et al. demonstrate in Ref. [95] how hyperspectral imaging (using infrared microscopy) of a sample of hands of shooters can be used to show the presence of both IGSR and OGSR. The sample can later be used for SEM/EDS analysis as it is acquired on conductive adhesive tape. The hyperspectral imaging in this study operates in the infrared region (4000–650 cm-1) and detects the presence of both organic and inorganic vibrational modes. Prior to imaging, the adhesive samplers were washed with a bleaching solution to remove skin debris and cellular material. The shooting tests consisted of two consecutive firings of firearms, after which the hands of the shooters were sampled with adhesive tape. Three different test ammunition brands were used during the shooting series – spectra of powder from the disassembled cases were characterized with infrared to serve as reference materials for the identification in the hyperspectral images. Authors are able to show the presence of OGSR and IGSR particles on the samples.

Since many of the new heavy metal free ammunition use elements which are common in other technical applications such as paint or fireworks, Raman spectrometry has received increasing interest from GSR experts for the detection of the light elements together with the organic components which may be associated with traces from firing incidents. Especially surface enhanced Raman spectroscopy, which uses nanoparticles of gold, silver or copper to increase the sensitivity, has been of interest to forensic researchers. An added benefit to using Raman spectrometry is that equipment is now available which can be used in the field, enabling GSR detection directly at the crime scene. Thayer et al. show in Ref. [96] that a portable Raman spectrometer is able to measure ethylcentralite and diphenylamine on gold nanoparticles in solutions of methanol, acetonitrile, acetone and ethanol in concentrations down to a limit of quantitation of about 40 mM.

Raman spectrometry has the advantage that it can be used to investigate the nature of OGSR particles without any sample preparation – so long as they can be visualized. Karahacane et al. used in Ref. [97] precisely this technique on the results of shooting experiments on clothing at 20 cm distance with two types of ammunition (Kalashnikov 7.62 mm and 9 mm Makarov). The OGSR particles on these targets are visible in a Raman microscope at 50X magnification, so that spectra can be acquired from individual particles. The particles were furthermore imaged using SEM. On the spectral data several statistical methods were used to facilitate objective discrimination between the two groups of ammunition particles. In particular, a combination of principal component analysis and support vector machines allowed for the efficient discrimination between the two types of ammunition used in this study. The authors conclude that the developed method shows potential in cases where specific particles need to be linked to a particular ammunition type.

6. Shooting distance estimation and bullet hole characterization

6.1. Methods and instrumentations

Most of the GSR produced by a shot is projected onto the target (object or victim), provided the target is close enough to the shooter. The diameter and density of the deposition pattern of the GSR particles will help determine the firing distance. This deposition pattern is usually revealed chemically by the use of colour tests, the most popular colour tests being the sodium rhodizonate test (detects lead and barium) and the modified Griess test (detects nitrites). Other tests exists, such as dithiooxamide for copper and zincon for zinc.

A technical note published in 2019 covers the optimization of the sodium rhodizonate method by three adjustments [98]. Firstly, a heat press has been introduced, replacing the hot clothes iron, which is an improvement in applying more reproducible pressures and temperatures. Secondly, sodium rhodizonate powder was added directly to the buffer solution, which reduces the moisture content of the filter paper. Thirdly, the residue pattern is scanned, instead of being photographed with a digital camera, which results in a better resolution.

Berger et al. tried to maximise the efficiency of the total nitrite pattern visualisation method, an improved version of the modified Griess test [99]. After some modifications, the incubation time for alkaline hydrolysis to release nitrite from unburned propellant powder could be reduced from 1 h to 5 min. Three different adhesive lifters were also tested, and it was found that Duck Brand Peel&Stick clear laminate (contact paper) performed best in withstanding the heat of the press (100 °C) and transferring the residues. In addition, the total nitrite pattern visualisation was adapted in case of blood soaked targets: as the blood makes the transfer of residue difficult due to inadequate adherence, a 2% KOH solution in ethanol was applied directly to the target prior to the transfer of the pattern. Note that total nitrite pattern visualisation does not inhibit the detection of lead residues in a subsequent sodium rhodizonate test.

Chlorindazon DS was tested for the detection of copper as an alternative reagent for dithiooxamide and 2-nitroso-1-naphthol [100], showing a sky blue colour instead of the dark greenish-grey; its sensitivity seems to be better than the two other tests, making it suitable for the detection of heavy metal free primers, solid copper bullets and copper based frangible bullets. In order to avoid any “bleeding effect”, some adjustment were made, e.g. by drastically changing the pH of the environment. Tests have also been carried out for the detection of zinc; it appears that this reagent is sensitive to this element, giving a purple colour.

Since the presence of an elevated lead concentration on the clothing of a shooting victim can be indicative of a close-range shooting, Shrivastava et al. have developed a technology with which Pb^{2+} concentration on the clothing of a victim can be quantitatively measured on the crime scene by untrained personnel [101]. The basis of the technique is the change in light absorbance characteristics of a polyvinyl alcohol-stabilized emulsion of silver nanoparticles that occurs when lead ions are added. Their self-built device performs the absorbance measurement of such an emulsion before and after the addition of an extract of the clothing of the victim, which can be performed at the crime scene. As the handheld device can do this measurement and the calibrated concentration calculations without the help of other equipment or computer, it is possible to carry out this procedure by the police officers called to the scene. The authors claim that the validated and calibrated technique is able to accurately correlate the Pb^{2+} concentration to the shooting distance, and can therefore estimate the shooting distance up to a range of about 1 m.

Quantofix nitrite sheets are heavy filter paper sheets, pre-treated with an azo dye which give a chromophoric reaction with nitrate anions in GSR deposits, to form an intense pink/violet coloured pattern. A technical paper [102] reports on the validation of this sheet as a suitable substitute for the orange reaction on inkjet photo paper obtained with the modified Griess test. To this end a side-by-side comparison was performed between the two media. The targets consisted of 100% cotton textiles, shot at a distance of 25 cm using different weapons. Denim and washed garments were also tested. A 15% acetic acid solution was used, giving a much better result than plain water. It is reported that only oxidizing/reducing substances may interfere with the formation of the coloured reaction, such as e.g. iodine, ascorbic acid, sodium dithionite, amidosulfonic acid and potassium ferrocyanide. It was established that after performing the nitrite test, subsequent testing such as the sodium rhodizonate test (for lead) and dithiooxamide test (for copper) was still possible.

In another study [103], Quantofix sheets were examined to determine whether they could be used on blood-soaked items. To this end, Quantofix was tested on human blood soaked targets before and after treatment with a blood removal agent, i.e. ammonium hydroxide, resulting in a positive reaction for nitrites where blood had been removed and a negative reaction where blood still covered the GSR

pattern.

In [104], an investigation was conducted to compare different swabbing techniques and sampling areas, this to determine for shooting distance estimation the best sampling device and optimal sampling area around a gunshot wound. Inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry were used as quantification techniques. For this purpose, three biological tissues were used: bare pork skin with and without (shaved) bristle, and dried skeletonized bovine ribs, for five shooting distances from contact to 100 cm. Four different sampling media were tested: SEM-EDS graphite tape, Leukosilk® surgical tape, 3 M® transparent tape and cotton swabs moistened with 10% HNO_3. The samples were taken up to 4 cm from bullet hole. In the end, according to the authors the best sampling device was cotton swabs and the optimal sampling area up to 3 cm.

Barrera et al. compared the use of an alternative light source with infrared photography to visualise GSR patterns [105]. Twenty-six dark materials were shot at a distance of 20 cm with a 0.44 revolver. Eight wavelength ranges were tested between 320 and 830 nm, in combination with different colour filters. The best results were obtained with a 440 nm light in combination with an orange filter, turning GSR into fluorescent particles. For about 60% of the textiles, the visibility of the GSR was good. However, wool and polyester seemed less suitable. The infrared photograph shows the powder residue as dark particles on a light background; the visibility of powder residue in the near infrared was only correct on about 38% of the textiles.

Two new methods for estimating the shooting distance were developed by Wongpakdee et al. for distances up to 60 cm, the first method being applicable only to light-coloured fabrics [106]. The first method is to take digital images inside an illuminated box; the images are then inverted into grey intensity values and the values are plotted as a function of shooting distance, resulting in an exponential decay curve. Using the best fitted exponential function, a firing distance estimation curve was obtained for the four fabrics tested (one thick fabric, i.e. 80/20 cotton polyester denim jeans, and three thin fabrics: 100% cotton stretch jersey; 80/20 cotton polyester and 60/40 cotton polyester shirt). The second method is chemically based, using a microfluidic paper-based analytical device for the detection of Pb^{2+} through its reaction with sodium rhodizonate, forming a pink complex. Lead is first extracted from the fabric using a tartaric buffer, which is then applied to the device. The length measurements of these narrow pink bands are then plotted as a function of firing distance, which also resulted in an exponential decay curve. Using the best-fit exponential functions, two firing distance estimation curves were obtained, one for the thick tissue, and one for the three thin tissues.

In addition to the use of colour tests, it is also possible to estimate the shooting distance using non-chemical techniques. Vander Pyl et al. investigated laser-induced breakdown spectroscopy for the determination of shooting distance [107], a technique that by its nature probably offers better sensitivity and selectivity compared to conventional colour tests (sodium rhodizonate test and Griess test). For this purpose, forty-five samples of 100% cotton were shot at known distances (contact to 90 cm) and twenty-eight samples at unknown distances, using a 0.357 Magnum revolver and a 9 mm pistol. According to the authors, laser-induced breakdown spectroscopy resulted in 100% correct classification of shooting distances, compared to about 80% with conventional colour tests. Chemical mapping was obtained, following a 30-min multiple element detection at very low levels, and statistical tools (principal component analysis and multivariate discriminant analysis) were used for shooting distance prediction. A follow-up study published a year later included examination of bloody clothing, impacts on different types of surfaces and the use of a wide range of ammunition [108].

Miranda et al. used the X-ray diffraction technique to predict firing distance, this with the help of a multivariate calibration model obtained after analysing the pre-processed diffractograms [109]. To this end, white cotton cloth was shot at eleven distances between 5 and 300 cm; the targets were then cut to 6 × 6 cm around the bullet holes for X-ray diffraction analysis. The two revolvers used for the shooting gave good prediction models with 3% and 7% error respectively. According to the authors, it should be possible, with this method, to estimate the shooting distance using a revolver similar to the one used in the shooting incident under investigation.

6.2. Quality aspects

The best practice manual for chemographic methods was published by ENFSI in 2015 [110]; there has been no revision since then. It provides a framework of procedures, quality principles, training processes and approaches to the forensic examination in the domain of shooting distance estimation.

In order to verify the influence of the nature of target material on the distribution pattern, six different types of fabrics (cotton, linen, elastane, polyester, silk, viscose) were tested [111]. The surface morphology of the textile structures was examined with optical microscopy and profilometry (for root mean square surface roughness values). Elastane has a very compact structure compared to the highly perforated structure of viscose, allowing less than 5% GSR compared to almost 25% GSR to pass through the fibres. IGSR patterns were visualized using X-ray fluorescence spectroscopy into quantitative distribution maps. The morphology and composition were also examined with SEM-EDS and quantification was done by inductively coupled plasma optical emission spectrometry. Elastane was found to have the best IGSR retention capabilities, followed by linen and cotton; the lower retention was observed on polyester, viscose and silk, which were similar. This study shows that ignoring the nature of target material might cause misinterpretation of distance estimations due to the varying properties of the textile structure that produce different GSR retention capacities. It is therefore recommended to use targets of comparable composition to construct a calibration curve.

A study published in 2020 [112] was designed to determine the impact of wind in determining the distance from the muzzle to the target. To this end, ninety white cotton twill jean targets of were shot at distances of 30–120 cm with a Smith&Wesson 40 calibre. The shorter distance gave a dense dispersion of small diameter particles, while the longer distance produced a small amount of particles with no discernible pattern. The wind speeds tested ranged from 10 to 50 km/h and three different wind directions were also tested: 0° (headwind), 90° (crosswind) and 180° (tailwind). The effect of the wind speed and direction was compared to patterns obtained in the absence of wind, this visually, after a modified Griess test and after a sodium rhodizonate test. When exposed to high wind speeds in the headwind and tailwind directions, the particle patterns at short shooting distances already appear different from those obtained in the absence of wind: the headwind gives less reaction, which makes the distance appear greater than it is, while the tailwind gives more concentrated reaction around the hole, making the distance appear shorter. For this reason it is advisable to extend the range by several cm in windy conditions to report the min/max range of distances.

6.3. Case report

While SEM/EDS is now commonly used in forensic laboratories for IGSR determination, bulk methods such as inductively coupled plasma mass spectrometry remain attractive for special applications. One such application is to help determine whether a decomposing corpse has been the victim of a shot. Indeed, in some cases, the body and clothing are so degraded that it is impossible at first sight to determine whether a shot was fired at the victim. This involves analysing the larvae present in the body to check if abnormal high concentrations of lead, barium and antimony are detected. So far, these analyses have been carried out most of the time in the context of studies. Costa et al. report two examples

where this technique was used in real cases [113]. While in one case the conclusions are unclear, in the second case it was possible to show that, despite the absence of other external evidence, the victim had been shot at close range by a firearm, due to a high concentration of the target elements.

6.4. Bullet hole examination

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

A study published in 2019 was conducted to clarify whether pre-existing (intense) blood staining can prevent bullet wipes from being revealed by the sodium rhodizonate test [114]. Shots (using conventional 9 mm ammunition with sinoxid primer) were fired at a distance of 2 m at three different types of white fabric (light cotton fabric, heavy denim and heavy polyester fabric) which were, prior to firing, stained with varying amounts of pig's blood, resulting in unsaturated, saturated and oversaturated fabrics. The test shots were fired at targets that were still wet and at targets with dried blood. Unsaturated fabrics showed the presence of bullet wipes, as expected. On the oversaturated fabrics, no bullet wipes were found on either the wet or the dried blood samples; however GSR deposits were found at the periphery of the holes; according to the authors, this particular behavior can be caused by back spatter in case of liquid blood, and by backscatter in case of dried blood. For saturated fabrics, when wet, bullet wipes were absent; instead GSR patterns similar to that observed for short-range shots were obtained; this could be explained by the fact that lead compounds from the bullet nose were transferred onto the fluid film and spread like an aerosol. The dried fabric showed clearly visible bullet wipes, and no GSR pattern was present. It can be concluded that the interpretation of sodium rhodizonate test in case of bloodstained fabrics needs to be done with caution, especially in case of (over)saturated fabrics.

6.5. Time since discharge estimation

The domain of time since discharge estimation was for the first time reviewed by Gallidabino and Weyermann in 2020 [115]. While this review covers cases and papers that may be quite old and deal with visual changes and rust formation – thus allowing in some cases a rough estimation of the time since discharge –, recent developments are logically addressed, most notably the use of headspace sorptive extraction coupled with GC/MS. Nevertheless, according to the authors, difficulties remain in the application of this field to real cases. These difficulties are linked to the various factors influencing the initial conditions and the kinetics of ageing, the conservation of evidence before their analysis, as well as to the interpretation of the results. In this respect, a case-by-case approach is recommended by the authors of the review.

During the period of interest 2019–2021, except the review, only one paper was published on this topic. The goal of the study presented in this paper [116] was to assess the time since discharge using a thermal imaging device connected to a smartphone. The author examined with this device the temperature decay of several firearms available in a police station, this after a variable number of shots had been fired. This enabled her to establish temperature decay curves. Blind tests showed that under controlled conditions, when several shots were fired and the time between the shots and the temperature measurement was sufficiently short (less than 20 min), it was possible to estimate the time since discharge with relative a quite good accuracy.

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