Science & Justice 60 (2020) 63–71

Contents lists available at ScienceDirect

Science & Justice

journal homepage: www.elsevier.com/locate/scijus

Comparison of three collection methods for the sodium rhodizonate detection of gunshot residues on hands

Denis Werner[a,*], Anne-Laure Gassner[a], Jorina Marti[a], Stephan Christen[b,*], Philipp Wyss[b], Céline Weyermann[a]

[a] Ecole des Sciences Criminelles, University of Lausanne, Lausanne, Switzerland
[b] Zurich Forensic Science Institute, Zürich, Switzerland

ARTICLE INFO

Keywords:
Firearm discharge residues
Chemographic detection methods
Filter paper
Adhesive foil
Photographic paper
PVAL
Scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX)

ABSTRACT

The aim of this study was to compare three gunshot residue (GSR) collection methods used in conjunction with chemographic detection applied by different regional Swiss police services. The specimens were collected from the hands of a shooter with either filter paper (Filter method) or adhesive foil. The adhesive foil was then either applied against photographic paper during visualisation (AF Photo method) or coated with a layer of polyvinyl alcohol (AF PVAL method). The experiments involved two conditions of the examined hands, i.e. dry and humidified. The residues were revealed using the sodium rhodizonate test (SRT). Preliminary tests assessing the possibility of conducting a confirmatory Scanning Electron Microscopy coupled to Energy Dispersive X-ray spectroscopy (SEM/EDX) analysis after the chemographic test were performed on a number of specimens by cutting positive spots and mounting them on stubs. Obtained results were compared in terms of effectiveness - number of positive spots, time requirements, quality of subsequent SEM-EDX analysis, ease of use and cost.

The Filter method generally yielded a high-quality detection with both dry and humidified hands, as well as a simple, quick and efficient confirmation by SEM/EDX. The AF Photo performed well on dry hands, but not on humidified hands. The AF PVAL method performance was lower compared to the other methods in both examined conditions of the hands. The SEM/EDX analysis showed that the Filter and AF PVAL method provided satisfactory results when a sufficient carbon coating thickness was applied to the cuttings. It was also observed that the thinner the PVAL layer, the better the quality of the spectra and obtained images in SEM/EDX. Furthermore, the surface of the photographic paper did not seem to be conductive, even after the application of a thick layer of carbon.

In conclusion, the Filter method gave the best overall results, but its application required slightly more time and expertise than the two other methods.

1. Introduction

Gunshot residue (GSR), also known as firearm discharge residue, is produced during the discharge of a firearm [1]. The residue exits the muzzle and all other firearm openings, such as the ejector port or the barrel-drum gap [2]. While a part of GSR travels with the bullet and is thus generally detected on the target, the remainder loses its kinetic energy and then settles down on surfaces around the firearm, including on the shooter [3,4]. GSRs are a mixture formed by primer, smokeless powder and lubricant residues as well as metals arising from the projectile, cartridge case and gun barrel [5]. In casework, the forensic examiner's tasks include identifying bullet holes, estimating the firing distance, and evaluating whether an individual has discharged a firearm [5]. For these purposes, various methods can be applied, namely optical, chemographic and instrumental methods [6]. Depending on the context and investigation requirements, these methods can be employed individually or in sequence. As a rule, the examination begins with simple and non-destructive approaches, generally optical methods such as observation under various lighting conditions or using a macroscope/microscope. In a second stage, more efficient and to some extent destructive methods may be needed. Depending on the context, the sequence of applied methods has to be optimised to obtain the greatest amount of relevant information [6,7].

Chemographic methods target GSR using chemical reagents that are specific to an element, thus enabling the visualisation of GSR distribution pattern [7]. They are used to reveal the presence of latent GSR

---

[*] Corresponding authors.
E-mail addresses: denis.werner@unil.ch (D. Werner), stephan.christen@for-zh.ch (S. Christen).

https://doi.org/10.1016/j.scijus.2019.09.004
Received 30 April 2019; Received in revised form 5 August 2019; Accepted 15 September 2019

as well as for shooting distance estimation. Such tests are often used as a screening tool and thus require confirmatory analysis respectively by Scanning Electron Microscopy coupled to Energy Dispersive X-ray spectroscopy (SEM/EDX) or liquid chromatography coupled to mass spectrometry (LC-MS) for inorganic and organic GSR. These methods are specific to one or more chemical elements contained in GSR, but not uniquely present in GSR. Thus, false positive reactions from environmental contaminants may occur. However, the main advantage of these methods compared with instrumental methods is their low cost, easy implementation (partly applicable directly on the crime scene) and short analysis times, leading to frequent use in police services for investigative purposes.

Historically, the first chemical test documented for GSR was the paraffin test, also called the dermal nitrate test, introduced by T. Gonzalez at the Mexico City Police Laboratory [5,8,9]. It consisted of applying molten paraffin to the hand and, after removal, spraying it with diphenylamine in concentrated sulfuric acid to produce a blue reaction product. The paraffin test targeted nitrates and nitrites. However, it was abandoned due to its unreliability [5] as it was found to react with both nitrates and chlorates leading to an unacceptably high rate of false positive results [9]. While nitrates are ubiquitous in the environment, nitrites are less common. This ion, formed by the burning of propellant, is the target of the modified Griess test that results in an orange colour [10]. Both the paraffin and modified Griess tests detect residues from the propellant. However, assays for metallic elements are also available and frequently used in casework. A list of the most common methods is provided in the Best Practice Manual published by ENFSI [7]. One of the most frequently used by police services is the sodium rhodizonate test (SRT), which detects lead and barium. Sodium rhodizonate reacts with divalent metals by forming coloured complexes [11]. Depending on the pH, the resulting colour varies from blue-violet (neutral pH) to scarlet (pH 2.8) for lead, whereas the red-brown colour obtained with barium is independent of the pH [11]. Other bivalent metals such as strontium and copper also react at neutral pH, but produce no coloration at acidic pH. The SRT can be applied directly on the target surface, such as the hands of a presumptive shooter or the clothing of a victim. However, visualisation on dark-coloured fabric can be difficult, leading to the introduction of a transfer step by Bashinksi et al. [12]. A filter paper was soaked in 10% acetic acid and pressed onto the residue pattern, leading to the partial transfer of the residue. The filter paper was then sprayed with sodium rhodizonate, with lead becoming bright pink and barium orange. This procedure is nowadays named Bashinski transfer. A similar indirect procedure was also described by Suchenwirth, who used 1% tartaric acid instead of acetic acid [13]. Nowadays, the indirect procedure is generally applied. However, as highlighted in the ENFSI Best Practice Manual [7], there are at least four variants of this chemical test, differing from each other in transfer and diffusion media. Regarding the transfer medium, various protocols use adhesive foils, filter paper, polyethylene photo paper or cellophane™. The diffusion medium is in all cases acidic, using either acetic or tartaric acid, but an additional layer of polyvinyl alcohol (PVAL) is used in conjunction with the adhesive foil transfer protocol. Yet, there are other variants that are not mentioned in the Best Practice Manual, leading to the aim of the present work.

In Switzerland, some regional police services use pattern visualising methods such as the SRT in addition to SEM/EDX analysis as a rapid screening test for the presence of GSR. In some cases, the distribution of GSR particles on the hands of a suspect or a victim is used to infer the type of activity leading to that specific distribution. At least three variants of the SRT have been reported in Switzerland. However, at present no data allows a direct comparison of their performance. Thus, the aim of this work was to compare the effectiveness of three protocols: one using filter paper, one using adhesive foil (AF) with further GSR transfer onto a photographic paper and the last one using an adhesive foil with the addition of a thin layer of polyvinyl alcohol (PVAL). Experiments were carried out on dry and humidified hands to simulate conditions that can be encountered routinely, such as the presence of blood or perspiration. After visualisation with sodium rhodizonate, the treated samples were scanned and positive reactions optically verified. Then, some positive spots were excised and mounted on a carbon stub for further confirmation by SEM/EDX. Finally, the protocols were compared in terms of the number of positive spots, time requirements, quality of subsequent SEM-EDX analysis, ease of use and cost.

2. Materials and methods

2.1. Shooting experiments

Various factors affecting the formation and the deposition of GSR were standardised to minimise contamination throughout the experiments. In this case, a single person carried out all shooting sessions in an indoor shooting range with the ventilation turned off. The same 9 mm Luger semi-automatic pistol – a Sig Sauer P220 – with Geco Sinoxid® ammunition (124 g, FMJ) from a single batch was used for all experiments. Before every study the firearm was completely dismantled, cleaned and lubricated. Then, five cartridges were discharged to deposit a representative amount of residues in the firearm.

The shooter washed his hands with soap, before blank specimens were collected using the same sampling method applied in the experiment to verify the absence of contamination. Then, the shooter was accompanied in the shooting range by a person not involved in the sampling procedures. Thus, the shooter did not touch anything except the loaded gun to fire it. The gun was held with both hands (always in the same position), the sleeves of the shooter were rolled up to avoid contamination coming from GSR that may be present on the clothes due to previous shooting. One cartridge was fired for each experiment. Ten to fifteen replicate shootings were carried out for each method to characterise the variability of the GSR amount produced during shooting. The sampling methods were applied directly after shooting in a separate laboratory to minimise potential contamination (at time $t \approx 0$).

2.2. Collection methods and visualisation

In a first step, the sampling was carried out on dry hands. Fifteen replicates were performed for each method and each hand was sampled separately. In a second step, these methods were also applied on humidified hands. After the discharge, the operator sprayed a small amount of water (3–5 sprays) onto the shooter's hand. This protocol simulates the humidity potentially caused by dew, rain, sweat, or blood, which can be encountered in real cases. For this second set of experiments, ten replicates per collection method were carried out only for the dominant hand (right), as the majority of positive reactions was observed on this hand during the “dry hand” experiments (see results in Section 3.1).

2.2.1. Method 1 – Filter paper (Filter)

A hardened highly pure filter paper (Albet LabScience Hahnemühle®, model DP 1573 240) was humidified with 8.5% (*w/v*) tartaric acid solution[1] before being firmly pressed against the hand for 1 min. Then, the filter paper was immediately completely dried using a hair dryer, before being sprayed with a sodium rhodizonate solution.[2] The paper was dried again in the same way after this step. If lead or barium was present, the corresponding areas turned pink or red-orange respectively. The protocol of this method is presented in Fig. 1a.

---

[1] 85 g of tartaric acid (Sigma-Aldrich) dissolved in 1000 ml ultrapure water, with 2.5 g of benzoic acid (Sigma-Aldrich).

[2] 0.2 g of rhodizonic acid (Merck) dissolved in 1000 ml ultrapure water.

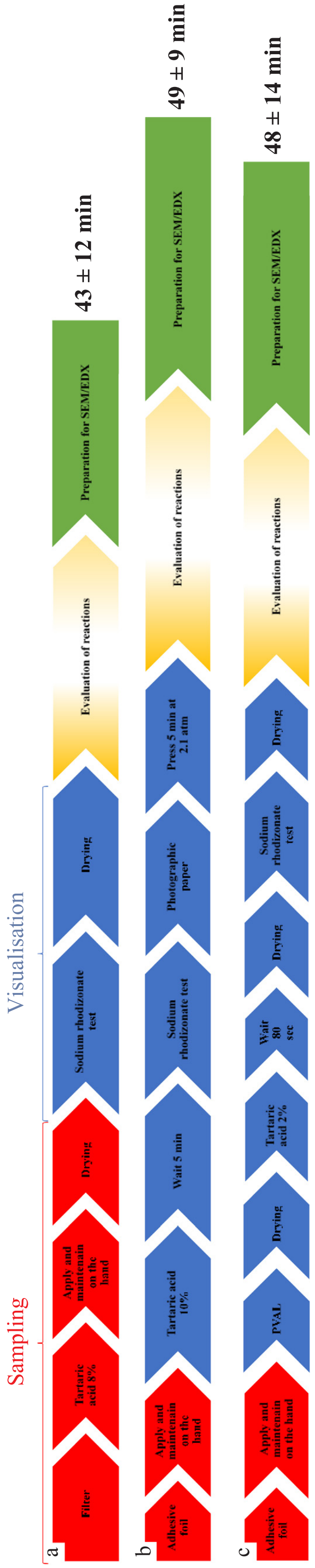

Fig. 1. Protocols of the three collection methods: a) Filter method, b) AF Photo method, c) AF PVAL method. The time required for the preparation of one cutting for SEM/EDX with the AF Photo and AF PVAL methods included the time for the preparation of adhesive foil and paper (separation of two pieces and deposition of each piece on carbon stubs).

2.2.2. *Method 2 – Adhesive foil-photographic paper (AF-Photo)*

This approach used an adhesive foil (HAWE Hugentobler®, model 9400.042) firmly pressed against the hand for the collection of the GSR potentially present. After sampling, the adhesive foil was stuck again onto the substrate paper to simulate sampling on a crime scene. Then, the sticky side was sprayed with a 10% tartaric acid solution.[3] After 5 min, it was sprayed with a sodium rhodizonate solution[2]. Then, a photographic paper (Hewlett Packard®, A4 Premium Plus Glossy Photo Paper with a grammage of 300 g/m^2) was placed onto the sticky side of the adhesive foil and placed for 5 min at 2.1 atm in a Book press (CMC Italia, model MENKAROL MOL5240S) to ensure a better dispersion of the liquids and hence enabling further chemographic reaction with present elements (Fig. 1b).

2.2.3. *Method 3 – Adhesive foil-PVAL (AF-PVAL)*

Method 3 used a different adhesive foil (Netra®, Foilolux® S23) from Method 2, but the sampling protocol was similar: the foil was firmly pressed against the hand and stuck again onto the support paper. Then, the adhesive side of the foil was sprayed with a polyvinyl alcohol layer (PVAL) solution[4] and immediately dried using a hair dryer. Subsequently, it was sprayed with a 2% tartaric acid solution.[5] After 80 s for the reaction to proceed, the adhesive side of the foil was dried again with a hair dryer. In the last step, the foil was sprayed with a sodium rhodizonate solution[2] and dried. It was placed onto the support paper for storage (Fig. 1c).

2.3. *Data digitisation*

The treated samples were scanned with an Epson Expression® 11000XL scanner with a high-resolution of 2400 dpi. The images were analysed with SDP-ColorFinder® (version 4.4.3.19) from Schulz Digitale Projekte, to evaluate the number of positive colorimetric reactions. Automatic mode was used at first to count the number of discrete coloured spots identified. Then one operator confirmed the results of the software in detecting respectively the pink and red-orange spots presumably produced by lead and barium particles, to avoid that an agglomeration of particles was counted as a spot and therefore to consider the spot sizes.

2.4. *Confirmatory SEM/EDX analysis*

Three specimens per method (obtained on dry dominant hands) were selected based on the similar number of positive reactions developed by the sodium rhodizonate and counted by ColorFinder. Every marked spot was excised and mounted on 12 mm carbon stubs from Plano® for automatic SEM/EDX analyses. The adhesive foils and the supports or photographic papers for the AF Photo and AF PVAL methods were separated on two different stubs to allow the analysis of all parts. A suspension of very fine conducting carbon particles (Neubauer Chemikalien®, Leit C nach Göcke Conductive Carbon Cement) was used and applied to edge the cut pieces of paper filters, adhesive foils and photographic papers stuck on the carbon stubs to enhance the conductive layer before actual carbon coating. Then, all stubs were carbon-coated with a Q150T carbon coater from Quorum Technologies® to avoid charging effects, with a layer ranging from 15 nm for the filter and AF PVAL methods to 30 nm and higher for

---

[3] 100 g of tartaric acid (Sigma-Aldrich) dissolved in 1000 ml ultrapure water.

[4] 100 g of solid polyvinyl alcohol (PVAL) (Sigma-Aldrich) mixed with 500 ml ultrapure water and heated at 90 °C until the PVAL was completely dissolved. The temperature was reduced to 50 °C and 665 ml of F25-A ethanol denatured with 5% isopropyl alcohol (Alcosuisse AG) and 3 g of glycerol (Merck) were added.

[5] 25 g of tartaric acid (Sigma-Aldrich) dissolved in 1000 ml ultrapure water, with 2.5 g of benzoic acid (Sigma-Aldrich).

adhesive foil and photographic paper from the AF Photo method. The stubs were analysed by field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FE-SEM/EDX) with a MIRA3 FE-SEM from Tescan® and a XMax EDX from Oxford Instruments. A voltage of 20 kV and a working distance of 12 mm were used for the analysis. The results were analysed with the software INCAGSR (Issue 2.1b SP2, version 5.05) from Oxford Instruments®.

To determine the nature of the elements which caused the "characteristic" spots, the pink and red-orange spots produced by SRT were analysed and classified in one of four categories based on the American Society for Testing and Materials (ASTM) standard ASTM E1588–17 [14]:

- Category 1 for the spots with a PbBaSb composition (particles classified as characteristic of GSR);
- Category 2 for PbBa, PbSb or BaSb compositions (particles classified as consistent with GSR);
- Category 3 for Pb or Ba compositions (particles classified as commonly associated with GSR);
- Category 4 for neither Pb nor Ba particles.

This last category could also contain some particles classified as commonly associated with GSR [14] and which were different from the category 3. If a spot contained more than one particle belonging to different categories, the most specific category was selected. For example, if a particle from category 3 was detected in the same spot as a category 1 particle, the spot was classified as category 1. Every cut (spot) was therefore classified in only one category.

3. Results

3.1. Dry hands

The aim of the first experiment was to compare the three methods in ideal conditions in terms of transferred particles (time $t \approx 0$ after shooting, dry hands). For each method, the procedure was repeated 15 times in order to take into account the high variability in GSR production and transfer. Before and between each experiment, the shooter washed his hands and a blank was collected from each hand using the sampling technique applied in the given set of experiments to check for potential contamination. The blank was considered positive when at least four positive reactions were detected. In such instances, the corresponding sample was removed from the dataset. For this reason, the number of replicates differs slightly between sampling methods.

The numbers of positive reactions on the dominant and non-dominant hands (Fig. 2) were significantly different, with about ten times more positive reactions on the dominant hand. Two factors can explain this difference. First, the construction of the pistol, as the Sig Sauer P220 has its ejector port on the right side. Literature indicates that even though both hands are contaminated when using a semi-automatic pistol, the ejection side is a potential source of higher GSR transfer [15]. The second factor is the position of the shooter's hands on the weapon. Here, the shooter was right-handed and thus held the pistol with his dominant hand on top of the other, partially protecting it from GSR exposure.

A high variability in the number of positive reactions was observed for both hands. The relative standard deviation (RSD) was about 30% for the dominant hand and up to 76% for the non-dominant hand (for the filter paper). Such high variability is commonly observed for GSR primary transfers and can thus only partly be associated with the sampling methods. It was thus essential to carry out enough replicate experiments for a robust comparison of the performance of the three methods. The boxplots for the dominant hand indicate that the Filter and AF Photo methods generally performed better than AF PVAL. As the median and average of each method were relatively close, the sampling methods were also compared two by two using a standard *t*-test (with a 95% confidence interval). The results for the dominant hand indicated that the AF PVAL method performed significantly worse than the Filter and AF Photo methods ($p(T \leq t) = 0.81\%$ and 0.031% respectively). However, the Filter and AF Photo results were not statistically different from each other ($p = 50.9\%$). On the non-dominant hand, no significant difference was observed between the three methods.

These results might be influenced by the performance of two factors: the collection and the visualisation. While it might be expected that the adhesive foil would collect more GSR than filter paper due to its stickiness, the quality of the adhesive itself might influence the results. In this study, the protocols were applied exactly as described in the different police guidelines and no comparison of the adhesives was carried out. In the case of the filter paper, some "stickiness" was obtained by wetting the paper. The second factor is (the effectiveness of) the visualisation. Some sampling materials might impede the reaction with the sodium rhodizonate, hide the particles (e.g. due to an excessively thick PVAL layer) or produce background that is difficult to distinguish from the positive reactions. For the PVAL method, the coloured reactions were especially difficult to identify, as the yellow-orange background of the sodium rhodizonate was strong.

3.2. Humidified hands

The three collection methods were then compared when hands were humidified after shooting. In practice, the hands of a suspect or a victim might be stained with blood, produce perspiration, be exposed to ambient humidity due to dew or rain or be more or less oily depending on the contact frequency with the face. After discharge, the hands were sprayed lightly with water to simulate the aforementioned conditions. For each method, the same procedure was repeated 10 times. The shooter washed his hands before and between each experiment, and a potential contamination from each hand was checked in the same way as dry hands experiments. No contaminated blanks were observed. As expected, this operation had a considerable effect on the results obtained using the three methods, showing medians that were significantly lower than on dry hands (Fig. 3). This decrease was more marked for the AF Photo method with a median very close to that of the AF PVAL method. The standard *t*-test (95%) confirmed a significant difference between the Filter method and the other two methods ($p = 1.98\%$ and 0.45% with AF Photo and AF PVAL, respectively), whereas the AF photo and AF PVAL were not significantly different from each other ($p = 31.49\%$). Such a decrease in positive reactions might be explained by a decreased collection efficiency of the adhesive foils due to loss in stickiness. For the Filter method, the paper can absorb some of the humidity, leading to a lesser influence from humidity for that method. Finally, vaporising water onto the hand can also cause particle losses due to washing away of the GSR. Nevertheless, these results show that tuning experimental conditions is essential to obtain robust conclusions.

3.3. Preliminary SEM/EDX analysis

SEM/EDX was used to determine the nature of the sodium rhodizonate positive reactions on three dry dominant hand samplings per collection method. Each marked spot on the filter, the adhesive foils, the support paper and the photographic paper was cut and mounted on carbon stubs. For each method, an example of sampling, the same stub with cuttings (before the carbon coating) and obtained composition categories of the particles are shown in Figs. 4, 5 and 6 respectively. It must be highlighted that these results are preliminary, the SEM-EDX analysis was not optimised for each sampling method and based on only three replicates.

The number of cuts (n) – positive reactions developed by the sodium rhodizonate and counted by ColorFinder – selected for SEM/EDX analysis was 240, 270 and 176 for the Filter paper, AF Photo and AF PVAL protocols respectively (Fig. 7). For the two AF protocols, the exact

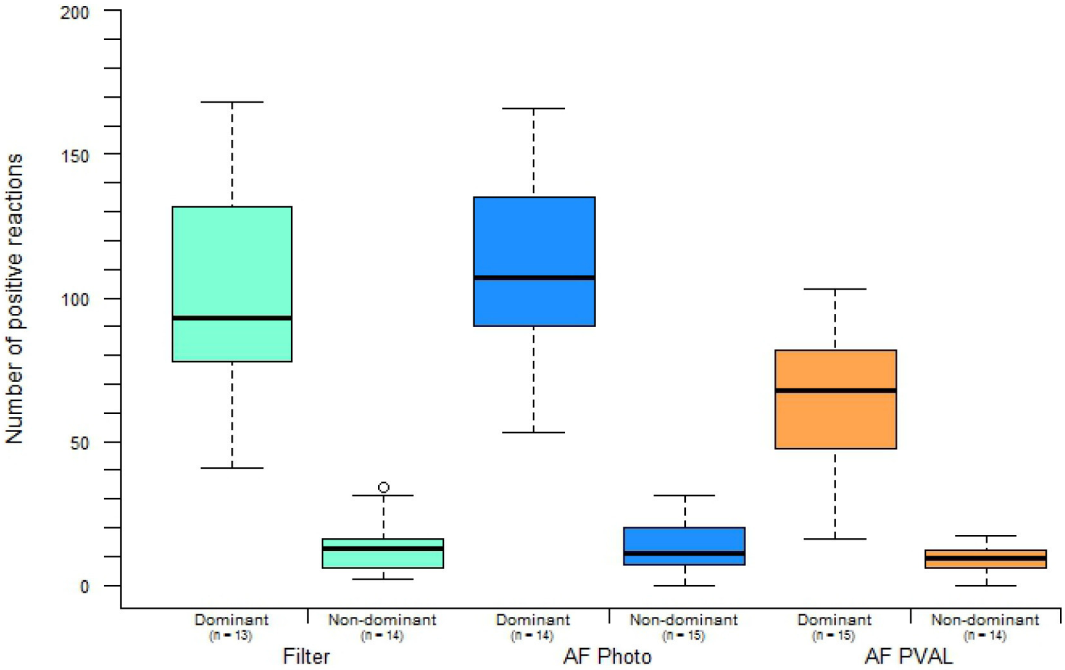

Fig. 2. Number of positive reactions developed by the sodium rhodizonate and counted by ColorFinder on dry hands. "Dominant" and "Non-dominant" are for dominant and non-dominant hand respectively. n indicates the number of replicates.

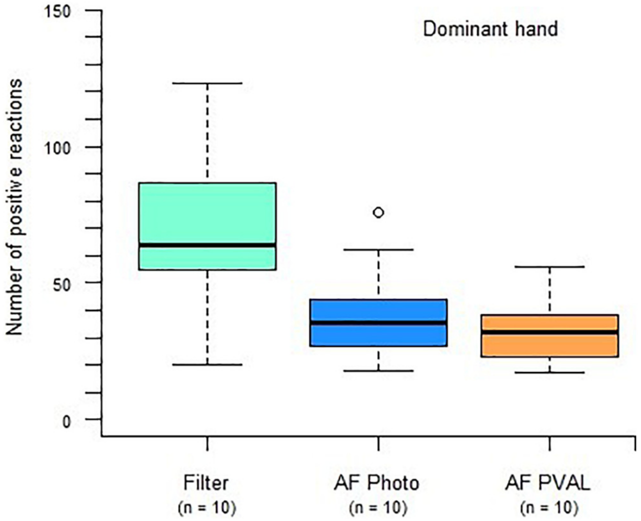

Fig. 3. The number of positive reactions developed by the sodium rhodizonate and counted by ColorFinder on the dominant humidified hand. n indicates the number of replicates.

location of the particles was unknown as the adhesive was separated from the photographic/support paper. Thus, the particle could be attached to either surface. As a consequence, both materials needed to be analysed (a total of m cuts that was the sum of the adhesive and photo/support cuts), leading to a longer analysis time.

The Filter method yielded positive reactions confirmed as lead and/or barium compounds by SEM/EDX for approximately two thirds of the cuts (64.6%[6]), while the AF Photo yielded only 32.3%[6] of positively confirmed cuts. Finally, the AF PVAL method had more than half of the cuttings (53.6%[6]) that were positive of GSR (Fig. 7).

The percentage of cuts with particles classified as characteristic of GSR in comparison with the percentage of cuts with particles classified as consistent with GSR were high for the Filter and AF PVAL methods, especially on the adhesive foil (Fig. 7). For the AF Photo method, in comparison with the number of particles classified as characteristic of GSR, a higher percentage of the cuts with particles were classified in consistent with GSR or commonly associated with GSR categories (11.6 and 18.1% respectively).

The percentage of cuts that comprised neither Pb nor Ba particles (false positive) was higher than expected with all methods (35.4, 67.7 and 46.4%).

The adhesive foils of the AF Photo and AF PVAL methods had to be separated from the photographic or support paper before the SEM/EDX analysis. They had a high ratio of detected GSR, respectively 40.7%[6] and 84.0%[6] of analysed cuts, whereas the photographic and support papers had only about 23–24%[6] of the positive reactions confirmed as GSR compounds.

A higher percentage of cuts with particles were classified as characteristic of GSR for the adhesive foil of the AF PVAL method than for the AF Photo (see Fig. 6, where the number of positive reactions was significantly higher on the adhesive foils). The percentages of cuts with particles classified as characteristic of GSR on the adhesive foil for the AF PVAL (69.7%) and the AF Photo (4.1%) methods were about seven and four times higher than the percentage of cuts with particles classified as characteristics of GSR on the support (10.2%) and photographic (1.1%) papers, respectively. These results could be explained by the protocols of these two methods. The GSR were collected on the adhesive foil, the support papers were only used to protect the sampling before applying the AF PVAL method. The photographic paper was only used to react with the sodium rhodizonate solution (see Sections 2.2.2 and 2.2.3). Given the results of AF PVAL method, it can be recommended to analyse only the adhesive foils in order to save analysis time.

4. Discussion

The comparison of the medians showed that the Filter and AF Photo methods performed better than AF PVAL on dry hands in terms of the number of positive reactions (Table 1). When applying the methods on humidified hands, a lower amount of residue was detected (between 33

---

[6] Sum of the categories 1 to 3.

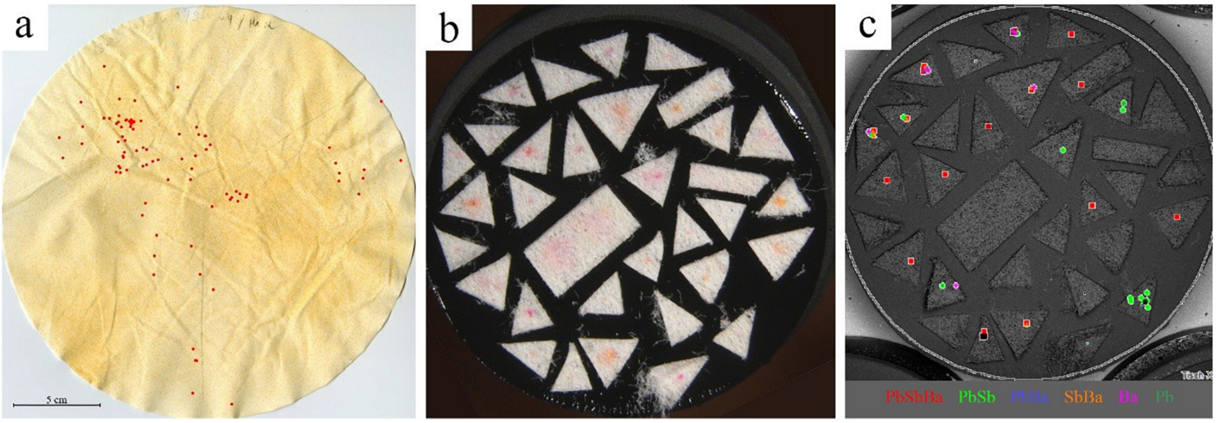

Fig. 4. Examples of results obtained using the Filter method: (a) Sodium rhodizonate reactions highlighted with ColorFinder; (b) Stub with cuttings; (c) Carbon coated stub with targeted components.

and 68% fewer particles than on dry hands). While the Filter method showed a higher variability between replicate experiments, it did yield a significantly higher median than the two other methods on humidified hands (i.e. median of 62 particles against about 30 particles detected). The AF Photo method was considerably less effective than on dry hands (68% decrease), indicating that the method might be less suitable to some casework situations than the Filter method. Due to the loss of adhesive stickiness with humidity, the Filter method is more versatile in practice in humid conditions such as surfaces/skin covered in blood or at an early stage of decomposition [16]. However, even though our results showed that this was not a serious concern, one might argue that the particles are not trapped on the filter paper and may be lost during the manipulation of the specimen. Thus, extra caution must be taken when using the hair dryer, transporting treated filter specimens from the scene to the laboratory and during sodium rhodizonate treatment. The present results also highlight the importance of carrying out experiments under various conditions, because results might be significantly influenced by some experimental parameters.

The total time (without considering SEM-EDX analysis time) required to apply the three methods was similar, the Filter method being the fastest with a difference of 5 min, due to the very simple

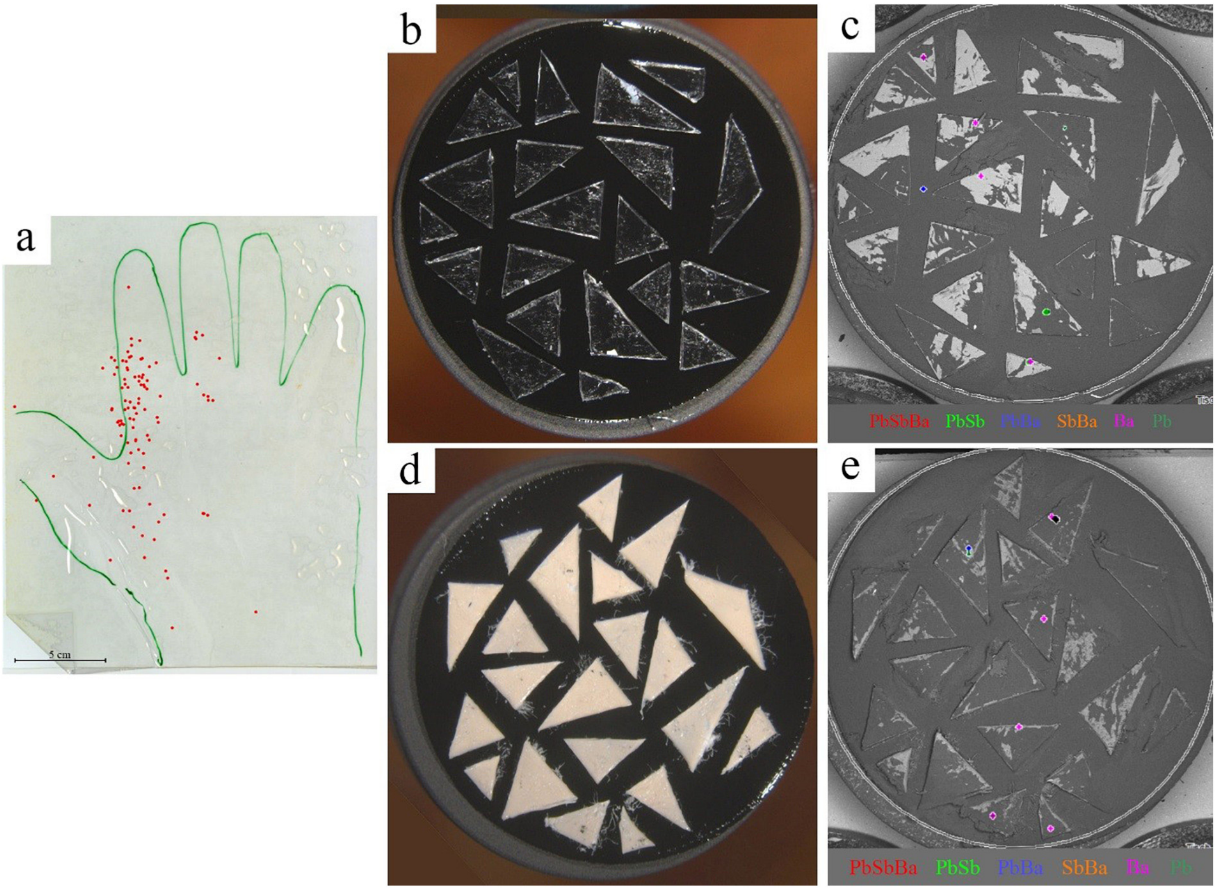

Fig. 5. Examples of sampling with the AF Photo method. Evaluation of sodium rhodizonate solution reactions with ColorFinder (a); stub with cuttings of adhesive foil (b) and photographic paper (d); carbon coated stub with targeted components on cuttings of adhesive foil (c) and photographic paper (e).

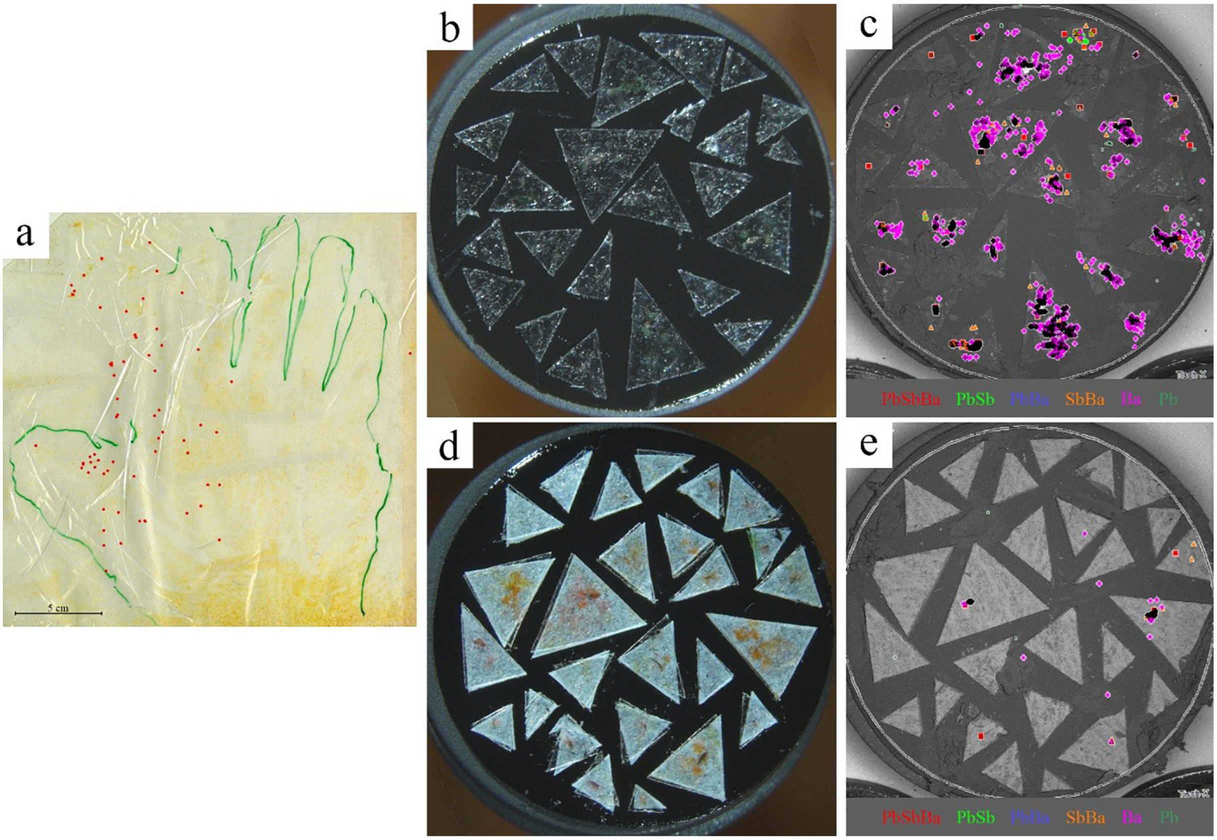

Fig. 6. Examples of sampling with the AF PVAL method. Evaluation of sodium rhodizonate solution reactions with ColorFinder (a); stub with cuttings of adhesive foil (b) and support paper (d); carbon coated stub with targeted components on cuttings of adhesive foil (c) and support paper (e).

visualisation step in the laboratory (Fig. 1). However, when considering the sampling step alone, both methods using adhesive foils were ca. 3 min quicker than the Filter method. Between the two adhesive methods, the AF Photo method collection time was slightly faster due to the type of adhesive foil used. Indeed, being more rigid, it was easier to manipulate and unstick when the adhesive was accidentally stuck to itself. In terms of sampling steps, the Filter method required wetting the paper with tartaric acid before applying it to the hand and then drying it. Moreover, care must be taken not to move the paper during sampling as the particles might become displaced leading to an imprecise particle distribution. Then, electricity is required to dry the filter paper with a hair dryer or another warm air source. In conclusion, application of the Filter paper method on the crime scene needs more expertise from the person responsible for collection and awareness that an electric source has to be present to dry the filter papers.

The collection step is important because the person carrying out the sampling might be an untrained police officer or crime scene investigator acting on the site. Thus, during the investigation of a crime scene, the amount of work required by GSR sampling might be substantial in relation to a number of other required tasks. When specimens are collected in a forensic laboratory, the sampling time and complexity are less of an issue. It must be highlighted that in this work, the method

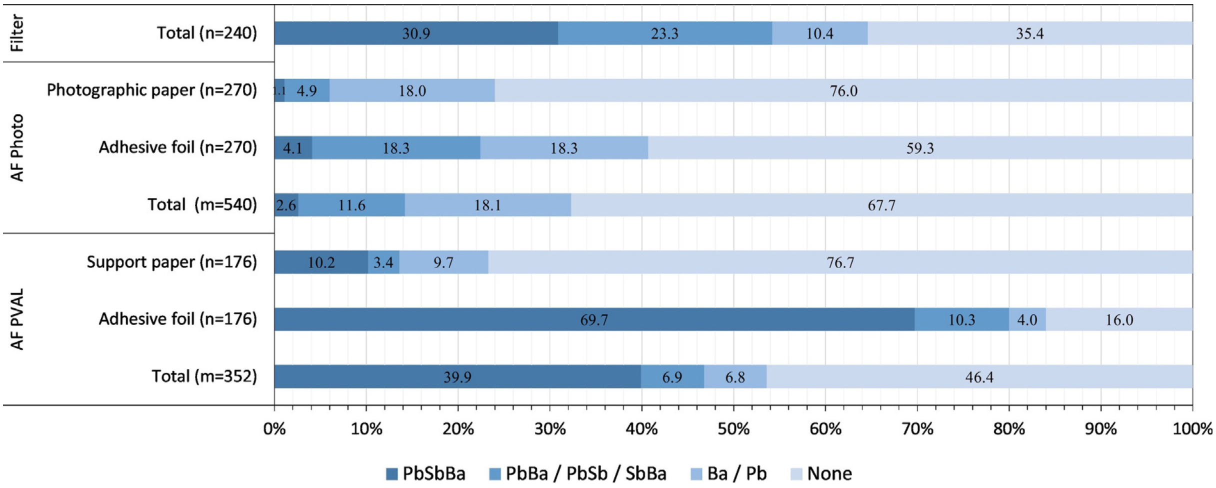

Fig. 7. Percentages of cuts (n) of adhesive foils, photographic or support papers classified according to the four categories. The total number (m) is equal to the sum of cut numbers of adhesive foils and support / photographic papers for the AF Photo and AF PVAL methods.

Table 1
Subjective evaluation of the methods with regard to effectiveness, duration SEM-EDX specimen preparation, SEM-EDX analysis and cost criteria. (+) positive, (○) neutral and (−) negative.

	Filter	AF Photo	AF PVAL
Results on dry hands	+	+	○
Results on humidified hands	+	○	○
Total time (w/o SEM/EDX analysis)	43 ± 12 min	49 ± 9 min	48 ± 14 min
Sampling time	5 ± 1 min	2 ± 1 min	2 ± 1 min
Sampling procedure	−	+	+
SEM-EDX specimen preparation	+	−	−
SEM/EDX results	+	−	+
Cost	○	−	○

duration did not include the SEM/EDX analysis time. For a SEM analyst, the choice between the methods might also be driven by the number of specimens to analyse. Indeed, both methods using adhesives produced two specimens per cutting, one for the adhesive and one for the photographic paper or PVAL respectively, as the particles were distributed on both surfaces. Thus, the SEM analysis time was doubled for these methods. This might be an issue when the SEM/EDX instrument is used continuously. Another option might be to analyse for example only the adhesive. However, the analyst must be aware that some particles might be missing due to incomplete specimen analysis.

Regarding the specimen preparation for SEM/EDX confirmation, both adhesive foil methods required cutting the specimen and then separating the adhesive foil from the photographic paper or the support paper respectively. While the adhesive foil covered by PVAL was relatively easy to separate from the support paper, the stickiness was an issue when isolating the adhesive foil from the photographic paper, those being very difficult to separate from each other. The glue tended to stick to the scalpel used for cutting, leading to potential damage of the particles when force had to be applied to separate the two layers, and to particles potentially being moved and hidden by a thick layer of glue or even to losses due to complete removal of the particles from the support. For the Filter paper method, particles may also be lost during using hair dryer or cutting as they are not stuck to the paper. Thus, careful manipulation is recommended during specimen collection and preparation.

Regarding the SEM/EDX analysis itself, both Filter and AF PVAL methods provided satisfactory results when a sufficient thickness of carbon coating was applied to the cuttings before analysis. It was also observed that the thickness of the PVAL layer had an influence on the quality of the SEM/EDX experiments [16]. The thinner the layer, the better was the quality of the images and spectra obtained. Thus, it is advised to apply a very thin layer of PVAL, because this layer might also hide particles when too thick. For the photographic paper, even though a relatively thick layer of carbon coating was applied, charging effects prevented the acquisition of good quality images and spectra. It seems that the surface was not conductive enough in spite of the application of a thicker layer of carbon compared to the other two methods. The low vacuum mode may be better suited for the analysis of the photographic paper and additional experiments are required to optimise SEM-EDX analysis for this material. It would also be interesting to analyse the surfaces that did not present a positive coloured spot using the SEM/EDX in order to consider the false negative rates of the SRT. Indeed, the SRT detection limits for lead and barium are 0.1 and 0.25 µg respectively [11].

The relatively high false positive rates (i.e., between 35 and 68% of SRT spots not confirmed using SEM-EDX) might evaluated through several explanations. For AF Photo and AF PVAL methods, the particles were located on either the adhesive foil or the photographic / support paper, while the coloured spots would be visible on both. This explanation might explain the AF PVAL method false positive rate (46.4%), but would only partially explain by the particularly high AF Photo method positive rate (67.7%). A second explanation might be that particles were not detected by the SEM/EDX analysis due to interferences from the substrates. SEM/EDX manual analysis might be an option to improve the number of positive reactions confirmed as GSR compounds. A third cause especially for the Filter paper method might be the potential loss of particles during the preparation of specimens (cuttings and placing on carbon stubs), because they are not firmly attached to the paper. The last possibility is that other compounds reacted with the SRT such as copper, mercury, cadmium, zinc, strontium or tin [6].

The cost was in this study a secondary criterion as all three methods were relatively inexpensive and a more effective method would be preferred despite its slightly higher price. Indeed, the cost difference between methods was negligible, as the only expensive material was the photographic paper (about 4 CHF per A4 sheet [16]).

In summary, the Filter paper method was the most versatile method, providing the best results in dry and humid conditions. However, its disadvantage is a more complex and longer specimen collection that might be a hindrance for some crime scene applications. Depending on the case conditions and the necessity of SEM-EDX result confirmation, the AF Photo method might equally represent an interesting alternative. It would be interesting to carry out further studies in order to evaluate the best compromise between crime scene implementation and expected results. Experiments involving various backgrounds (e.g. bloody surfaces, textile items) should also be further investigated, as the background collected using an adhesive is stronger than using a filter paper, potentially leading to other types of interferences.

5. Conclusions

This research project evaluated the performance of three GSR collection methods to be used in conjunction with the SRT. These methods, which are commonly used by Swiss police services for the detection of GSR and its distribution, were compared in terms of the number of positive reactions on dry and humidified hands, time requirements, ease of use and possibilities of subsequent SEM-EDX analysis and cost. All in all, the Filter method showed the best results with both dry and humidified hands as well as a simple, quick and efficient confirmation by SEM/EDX. Both Filter and AF Photo methods performed better than AF PVAL on dry hands. However, when applying the methods to humidified hands, the efficiency of the Filter method was much higher than when using the other methods, despite a higher variability. The Filter method showed therefore the most effective and robust performance for collecting GSR on the hands.

The SEM/EDX analysis demonstrated that it is possible to verify the GSR particles after the chemographic procedures on all surfaces. However, the Filter and AF PVAL methods presented a high percentage of cuts with particles classified as characteristics of GSR (category 1) when a sufficient thickness of carbon coating was applied to the cuttings. It was also observed that the thinner the PVAL layer, the better was the quality of the images and spectra obtained. Furthermore, it seems that the surface of the photographic paper was not conductive even after the application of a thick layer of carbon and therefore few particles classified as characteristics of GSR (category 1) were detected. More experiments are required to optimise subsequent SEM-EDX analysis using the AF Photo method.

In conclusion, the Filter method showed the best results, but its sampling required slightly more time than the two other methods, and its application requires more expertise than for the other two methods and required more expertise from the person in charge of the collection. However, the specimen preparation for the SEM/EDX analysis of this method was 5 min faster for one cut. The possibility to combine one of these sampling methods with the combined use of stubs must be evaluated (sequencing of sampling methods), taking into account influence factors such as the time between the event and the sampling, the person's activity or the type of ammunition.

Finally, these chemographic methods allow both the detection and visualisation of distribution of GSR on the hands, as well as a subsequent confirmation by SEM/EDX. Indeed, this research opens new perspectives on the best approach to adopt to obtain rapid investigative information about the potential presence of GSR on the hands of a suspect and may provide information for discriminating hypotheses regarding the activities having led to GSR particles on the hands. For example, the distribution of GSR on the hands might be used to distinguish between a shooter and a non-shooter (people present during the shooting or just holding the weapon). These methods might also prove helpful with the interpretation of suicide or secondary transfer cases where the amount of GSR is not necessarily significant [17].

Declaration of Competing Interest

None.

Acknowledgements

The authors would like to acknowledge Mr. Urs Nachbur, from the police services of Canton of Basel-Landschaft in Switzerland, and Mr. Stefan Meichtry from the police services of Canton of Bern in Switzerland, for providing their protocols and training to reproduce them and Dr. Amanda Frick from Ecole des Sciences Criminelles of the University of Lausanne for revising early drafts of the article.

References

[1] A. Zeichner, Firearm discharge residue: analysis of, Wiley Encyclopedia of Forensic Science, John Wiley & Sons L, 2009.
[2] H. Ditrich, Distribution of gunshot residues - the influence of weapon type, Forensic Sci. Int. 220 (2012) 85–90.
[3] A. Zeichner, Recent developments in methods of chemical analysis in investigations of firearm-related events, Anal. Bioanal. Chem. 376 (2003) 1178–1191.
[4] A.J. Schwoeble, D.L. Exline, Current Methods in Forensic Gunshot Residue Analysis, CRC Press, Boca Raton, 2000.
[5] H.H. Meng, B. Caddy, Gunshot residue analysis - a review, J. Forensic Sci. 42 (1997) 553–570.
[6] A. Gallusser, Traces d'armes à feu: expertise des armes et éléments de munitions dans l'investigation criminelle, 2 ed, Presses Polytechniques et Universitaires Romandes, Lausanne, 2014.
[7] ENFSI, Best Practice Manual for Chemographic Methods in Gunshot Residue Analysis, (2015).
[8] F.S. Romolo, P. Margot, Identification of gunshot residue: a critical review, Forensic Sci. Int. 119 (2001) 195–211.
[9] J.I. Thornton, The chemistry of death by gunshot, Anal. Chim. Acta 288 (1994) 71–81.
[10] J.H. Dillon, The modified Griess test: a chemically specific chromophoric test for nitrite compounds in gunshot residues, AFTE J. 22 (1990) 243–250.
[11] F. Feigl, H.A. Suter, Analytical use of sodium rhodizonate, Ind. Eng. Chem. 14 (1942) 840–842.
[12] J.S. Bashinski, J.E. Davis, C. Young, Detection of lead in gunshot residues on targets using the sodium rhodizonate test, AFTE J. 6 (1974) 5–6.
[13] H. Suchenwirth, Ein einfaches spezifisches Abdruckverfahren zum Erfassen und Beurteilen von Schmauchbildern, Arch. Kriminol. 150 (1972) 152–159.
[14] ASTM, Standard practice for gunshot residue analysis by scanning electron microscopy/energy dispersive X-ray spectrometry, (2017), pp. 1–5.
[15] L.S. Blakey, G.P. Sharples, K. Chana, J.W. Birkett, Fate and behavior of gunshot residue-a review, J. Forensic Sci. 63 (2018) 9–19.
[16] S. Christen, M. Lory, U. Neuwald, P. Wyss, Schmauchspurensicherungsmethoden im Vergleich. Vor- und Nachteile der Filterpapier- und Folienmethode, InFOR: Forensisches Inst. Zürich 21 (2018) 1–2.
[17] A.L. Gassner, M. Manganelli, D. Werner, D. Rhumorbarbe, M. Maitre, A. Beavis, et al., Secondary transfer of organic gunshot residues: empirical data to assist the evaluation of three scenarios, Sci. Justice 59 (2019) 58–66.