An evaluation of the secondary transfer of organic gunshot residues

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Abstract

The present study aimed at providing data to assess the secondary transfer of organic gunshot residues (OGSR). Three scenarios were evaluated in controlled conditions, namely displacing a firearm from point A to point B, a simple handshake and an arrest involving handcuffing on the ground. Specimens were collected from the firearm, the hands of the shooter and the non-shooter undergoing the secondary transfer in order to compare the amounts detected.

Secondary transfer was observed for the three scenarios, but to a different extent. It was found that displacing a firearm resulted in secondary transfer in less than 50% of the experiments. The firearm also had an influence, as contrary to the pistol, no secondary OGSR were detected using the revolver. Shaking the hand of the shooter also transferred OGSR to the non-shooter's hand. In that case, the amount of OGSR was generally higher on the shooter than on the non-shooter. Finally, the largest secondary transfer was observed after the arrest with handcuffing with positive results in all cases using the pistol. In that scenario, the amounts on the shooter and the non-shooter were in the same range.

This study highlights that the secondary transfer must be taken into account in the interpretation of OGSR. Indeed, an individual's hands might be contaminated by handling a firearm or having physical contact with a shooter.

Keywords

Firearms; LC-MSMS; firearm discharge residues; stubs

1. Introduction

Chemical analysis of gunshot residues (GSR), also called firearm discharge residues is a specific field of firearm examination that aims at establishing the circumstances of an event involving a firearm discharge. For example, GSR analysis is used to estimate the shooting distance, identify bullet entry/exit points, or associate a suspect to a firearm discharge. GSR is the mixture of vapours and particulate material produced and expelled during the discharge process. Depending on the chemical composition, it can be classified as inorganic (IGSR) when originating from primer, projectile, cartridge, or firearm; and organic (OGSR) when originating from propellant and lubricant [1, 2]. In forensic science laboratories, the analysis of IGSR is routinely performed by Scanning Electron Microscopy coupled to Energy Dispersive X-ray spectroscopy (SEM-EDX) [3]. However, the introduction of heavy metal-free ammunition producing less characteristic particles, as well as the potential environmental and occupational sources have complicated the task of the forensic analyst. So two research trends can be observed: the first one consists in gaining new insight into the evolving composition of inorganic particles and the second in developing a complementary examination based on organic residue [4]. The second approach has the advantage of enlarging the range of target traces. Thus, information based on the analysis of both IGSR and OGSR might significantly strengthen the evidential value of GSR and overcome issues related to false positives and negatives [5].

Propellants are made of explosives and various additives such as stabilizers, plasticisers or flash inhibitors that endow the gunpowder with specific properties [1, 5, 6]. Many analytical techniques have been applied to the detection of these compounds [5-7]. While no consensus has been reached about the most appropriate technique in routine work, a number of results were obtained using liquid chromatography (LC) or LC coupled to mass spectrometry (LC-MS) [8-14]. Although this technique is destructive due to specimens liquid extraction, its high selectivity and sensitivity enable the detection of some compounds down to the femtogram level with the best instruments. The analysis of IGSR is well characterised through several guidelines edited by the American Society for Testing and Materials (ASTM E1588-17 [15]) and other forensic science working groups (SWGGSR [16]). They provide information on the morphology and chemical composition of typical IGSR particles. Three particle categories were created to refer to their relevance, namely “characteristic”, “consistent with” GSR and “commonly associated with” GSR. By analogy, it is expected that some OGSR compounds are more relevant than others. Two criteria are important when determining the relevance of target analytes. Firstly, the compound must be present in most gunpowders and therefore frequently encountered in OGSR. The compounds that represent a significant percentage of the gunpowder are more likely to be detected after discharge than those present at a trace level. The second criteria is specificity. Ideally, the compounds should be restricted to propellants manufacture and have no potential alternative sources. For example, dibutyl phthalate is an ubiquitous compound and thus not a good candidate. There are currently no guidelines for OGSR, but some attempts to classify these compounds have been made. Based on literature, a list of 136 compounds considered to be associated with OGSR was created by Goudsmits et al. [7] and further reduced to 20 compounds divided into three categories according to their relevance with respect to criteria of low environmental prevalence and strong association with ammunition [17]. According to their study, the stabilizers ethylcentralite (EC) and methylcentralite (MC), and the explosives nitroglycerin and nitroguanidine might be the best candidates. However, the detection of one "characteristic" compound is not sufficient. Similarly to IGSR with particles composed of lead, barium and antimony, a set of compounds has a higher evidential value. Indeed, it is less likely to detect a combination of OGSR compounds that are from an environmental source than from a firearm discharge.

The distinction between OGSR compounds from a discharge or from environment is of interest if discussing the source of the trace [18]. However, in the context of a trial, the court might be more interested in knowing if the suspect was involved in the discharge in question, discussing hypotheses at the activity level. Here, the question of interest might be to determine to what extent the results discriminate between two competing propositions of interest, for instance "the person of interest (POI) has discharged a firearm" versus "an unknown person has discharged a firearm" [19]. To be able to assess GSR results in the context of such a pair of propositions, data estimating the prevalence of OGSR in various populations, in public places and in specific places such as police stations are required. Another question of interest for the interpretation of OGSR is the secondary transfer. Indeed, GSR can also be transferred via a contact with a shooter, a by-stander or an object that was present during the initial firearm discharge (primary transfer). It might be interesting to be able to distinguish between primary and secondary transfer because a POI might explain the presence of GSR on their hands by a contamination, possibly via secondary transfer. That type of contamination might occur in a police environment, for example during an arrest, transportation in a police vehicle or into the police facilities. In the literature, the question of secondary transfer is rarely considered, but it is essential to evaluate its probability of occurrence by performing different simulations with controlled parameters. Regarding IGSR analysis, Charles and Geusens showed that secondary transfer from police officers to a POI during an arrest is not negligible [20]. Brozek-Mucha detected IGSR after several situations, such as a handshake with a shooter and handling a gun immediately after its discharge [21]. French and colleagues simulated a handshake and transferring a firearm to a third party and concluded that relatively large numbers of particles can be transferred if the simulation takes place just after discharge [22]. They repeated their experiments with a chain of two handshakes and found that IGSR could also undergo a tertiary transfer [23]. All of the aforementioned studied concluded that a secondary transfer must be considered as a possible explanation for IGSR detection. For OGSR, a single study investigated the secondary transfer in controlled conditions [24]. The simulation consisted in shaking the hand of a shooter just after three cartridges were discharged. The specimens were collected by swabbing the hands of the POI and analysed by IMS. None of the three individuals tested positive for

OGSR, whereas the swabs of the three shooters contained OGSR. In another study, four volunteers were handcuffed and transported in a police vehicle and none of them was positive for OGSR [25]. IGSR particles and OGSR have completely different physical properties and due to their lipophilicity, OGSR are seemingly less prone to secondary transfer [26]. The limited number of replicates in the two aforementioned studies combined with the fact that two different analytical techniques were used (with different sensitivity) is insufficient to draw conclusions regarding the question of secondary transfer.

Many parameters might influence secondary transfer. Figure 1 summarises the various steps and associated parameters that take place from OGSR production (discharge, time t = 0) to specimen collection. Transfer is characterized by three parameters: the source, the recipient and the environment. Here, the source of primary transfer is the discharge (production of OGSR vapour and burnt particles). The amount and type of OGSR transferred will be dependent on the ammunition (composition, combustion efficiency) and firearm (type, contamination, lubricant) used. The number of shots might also influence the transfer. While it is hypothesised that more shots will mean a higher amount of OGSR, the important pressure and displacement of air during the discharge might also to some extent push OGSR away from the hands of the shooter or the firearm. The recipients are numerous: the shooter, the victim/target, a bystander, the firearm or any surface in the vicinity. The properties of each surface involved will play a significant role (e.g. smooth against rough surfaces, skin properties, presence or absence of hair). For the shooter (as well as his clothes) and the firearm used, the way the weapon is held will probably be an important factor. For the potential victim or target, as well as for any by-stander, the transfer will be dependent of the position and distance to the firearm. Finally, the environment will have an influence, such as the location in which the shooting occurred (indoors/outdoors) and the position of eventual furniture or weather conditions.

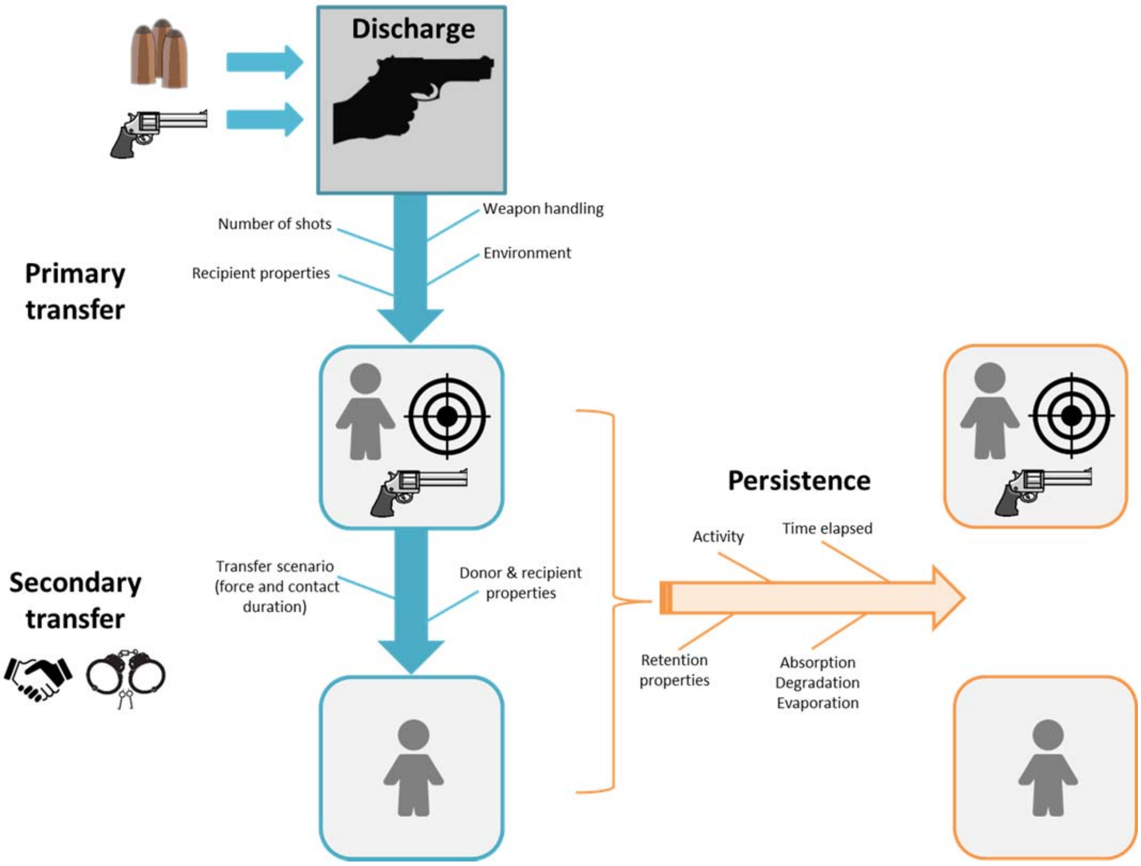


Figure 1: Scheme of the parameters influencing the amount of residue from OGSR formation to specimen collection

After primary transfer (time t > 0), OGSR will be lost due to the activity of the shooter or through physical processes such as evaporation, absorption or degradation. The loss will normally be much higher for people and objects that are moving, than for furniture or immobilised victims. If the shooting happened outside, the weather (temperature, wind or humidity) will also play an important role in the persistence and loss processes. Secondary transfer can occur just after shooting. It can also happen at any time after the discharge (t > 0), as long as OGSR stemming from the primary transfer are still present on the surfaces in contact. Then again, secondarily transferred OGSR might be lost over time through different activities or environmental conditions before specimen collection. Finally, the collection efficiency as well as the analytical protocol used to acquire the data might slightly modify the amount detected. Thus, complex interactions are involved in the different processes of transfer and persistence mechanisms of OGSR and it is important to gain as much knowledge as possible about these processes.

The present research aims to partly fill the gap by providing new data assessing the secondary transfer of OGSR. Three scenarios were performed in controlled conditions shortly after shooting (time t ~ 0), namely displacing a firearm from point A to point B, a simple handshake and an arrest involving handcuffing on the ground. Twelve replicates were obtained for each simulation. Specimens were collected from the firearm, the hands of the shooter and the non-shooter undergoing the secondary transfer in order to compare the amounts detected. The analysis was then performed using LC-MS/MS.

2. Materials and methods

2.1 Experimental protocols

Shooting sessions were conducted in an indoor shooting range located in a specific building section with the ventilation turned off. Extraction and analysis of the specimens were performed in a separate laboratory in another section to minimise potential contamination. Two different 9 mm Luger handguns were used: a semi-automatic pistol Sig Sauer P226 (see SI) and a revolver Smith & Wesson model 940 (see SI). Geco Sinoxid® ammunition was utilised for the experiments (124 gr, FMJ, batch 51 B L024). Additionally, Thun Pist Pat 41 ammunition (124 gr, TMJ, batch 399-12T) was tested for comparison in some cases. The firearms were completely dismantled, cleaned and lubricated before the study and after a change in ammunition. After cleaning, ten cartridges were discharged to normalize the amount of residues.

Various steps were taken to minimize contaminations. Table surfaces and the outer parts of the handguns were cleaned using a piece of paper wetted with ethanol at the beginning of the experiment and after every OGSR collection. This was done to avoid accumulation of OGSR and have a similar background for all the replicates. The shooter washed his hands with soap before entering the shooting range and was not allowed to touch anything before loading and firing. Blank samples from his hands before discharge were collected. The shooter held the gun with both hands and fired three cartridges. OGSR collection took then place outside the shooting range. After collection, he washed his hands before starting the procedure again.

Three simulations were carried out. They are described in the following sections (Table 1). To ensure a certain level of repeatability in the execution of the simulations, the same person played the role of the shooter in all scenarios and for all replicates. Twelve people volunteered to take part to the study. Except for the shooter, the volunteers involved in the study were not exposed to GSR in their daily life. Before starting the simulation, the volunteers washed their hands and their hands of were stubbed to detect potential contamination. In simulation 1, a blank sample of the firearm hand grip and trigger was also taken to verify their cleanliness. To maximize the probability of secondary transfer and thus detection, simulations were performed just after firing.

Table 1: Summary of the experiments carried out. Three cartridges were shot for each replicate

AMMUNITION	FIREARM	SCENARIO STUDIED	# OF REPLICATES
GECO	Sig Sauer P226	1, 2 & 3	n = 12 per scenario
	Smith & Wesson Model 940	1, 2 & 3	

THUN	Sig Sauer P226	1 & 3

2.1.1 OGSR collection

Specimens were collected using carbon stubs from Plano (Wetzlar, Germany), consisting of an adhesive carbon tab 12 mm in diameter placed on an aluminium stub 12.5 mm in diameter. This assembly was inserted in a plastic vial with a screwed cap. Following recommendations from Zeichner et al [27], the stubs were dabbed about 100 times on the skin. A single stub was used to dab both hands. Specimen collection was first performed on the thumb-index region and then on the back and palm. In the arrest simulation, wrists were also dabbed to account for the larger contact surface between both participants.

2.1.2 Simulated scenario 1: firearm displacement

The aim of the first simulation was to evaluate if a person not exposed to GSR can be contaminated when carrying a handgun from point A to point B (approximately 9 meters). After blank collection, the shooter loaded the handgun with three cartridges, discharged them and put down the gun on a table protected by a paper outside the shooting range. Then, the volunteer came to take the gun by its handgrip and put it down on another clean table within the same room (about 8-10 seconds). This scenario aimed at reproducing a situation where the shooter holds a gun out to an accomplice or a situation where a person comes after the discharge and touches the firearm.

2.1.3 Simulated scenario 2: handshake

The second simulation consisted in a simple handshake between a shooter and a person free from GSR. The shooter was right-handed and shook hands using his right hand only. As for the previous simulations, the scenario started with blank collection. Then, the shooter went inside the shooting range to load and discharge three cartridges. Immediately after, he came out of the shooting range and shook hands with the volunteer (about 1-2 seconds). Finally, specimens from the hands of both participants were taken.

2.1.4 Simulated scenario 3: arrest

The third simulation investigated the secondary transfer during the arrest of a person not exposed to GSR. The arrest procedure is illustrated in Supporting Information (SI). The scenario started with blank collection from both shooter and non-shooter. The shooter played the role of a police officer. He was equipped with a belt holding the handcuffs and a holster. The handcuffs were cleaned before starting the simulation to avoid accumulation of OGSR and ensure a similar background level for all replicates. As in simulation 1, the shooter loaded the handgun and discharged three cartridges. Then, he placed the gun back in the holster and came out of the shooting range to proceed with the handcuffing of the volunteer on the floor. Afterwards, he helped the volunteer back on their feet and removed the handcuffs immediately. OGSR collection took place just after handcuffs removal.

2.2 Specimen preparation and analysis

2.2.1 Chemicals

Acetonitrile, methanol, formic acid (FA) and water were of ULC–MS grade (Sigma-Aldrich, Buchs, Switzerland). The study targeted eight OGSR compounds: diphenylamine (DPA) from Fluka (Buchs, Switzerland); ethylcentralite (EC), *N*-nitrosodiphenylamine (*N*-nDPA), 4-nitrodiphenylamine (4-nDPA), akardite II (AK II) and *N*,*N*-diphenylformamide (*N*,*N*-DPF) from Sigma–Aldrich (Buchs, Switzerland); 2-nitrodiphenylamine (2-nDPA) from Alfa Aesar (Karlsruhe, Germany); methylcentralite (MC) from MP Biomedicals (Illkirch, France). Standard solutions at 1 mg/mL were prepared in MeOH and stored at 4°C.

2.2.2 Extraction protocol

For OGSR extraction, the carbon adhesive was removed from the stub with carefully cleaned tweezers and transferred to a 20 mL scintillation vial containing 1 mL MeOH. Then, the vials were ultrasonicated during 15 minutes at room temperature to solubilize OGSR. Finally, the resulting solution was filtered through a 0.2 μm Chromafil PTFE syringe filter (Macherey-Nagel, Düren, Germany) to remove carbon particles. In order to monitor laboratory contaminations during OGSR extraction, methanol blanks were prepared, one before starting an extraction session and one after preparation of a sequence of specimens. Likewise, a blank carbon tab was extracted to check for potential contamination of the stub batch.

To analyse gunpowders, a cartridge of each gunpowder was opened using a slide hammer. A 1 mg/mL extract was prepared using the aforementioned protocol.

2.2.3 Instrumentation

The specimens were analysed using an Agilent Infinity 1290 ultra-high performance liquid chromatography (UHPLC) from Agilent Technologies. The instrument was equipped with a binary pump enabling a maximum delivery flow rate of 5 mL/min, an autosampler, and a thermostatically controlled column compartment. Separation was performed using a C18 Kinetex core-shell column from Phenomenex (2.1 mm × 100 mm, 2.6 μm). A SecurityGuard ULTRA cartridge with C18 selectivity was used to protect the analytical column. The UHPLC system was coupled to a triple quadrupole mass spectrometer (5500 QTrap) from AB Sciex. Electrospray ionization was operated in positive mode. The $[M+H]^+$ of the target compounds were defined as the precursor ions, and quantification was obtained from the SRM measurements.. The source parameters were as follows: the desolvation temperature was set to 500°C, the nebulizer gas to 60 psig, the turbo gas to 50 psig and the curtain gas to 25 psig. The IonSpray voltage was adjusted to 5500 V. Data acquisition, treatment and instrument control were monitored using Analyst software. Detailed LC method, MS/MS parameters and limits of detection can be found in SI. Semi-quantitative data were obtained from a calibration curve (11 levels, 2 replicates) measured for each sequence of experiments.

3. Results and discussion

3.1 Gunpowder composition

The two ammunitions were qualitatively analysed to determine the main compounds. One cartridge was dismantled for each gunpowder. Results are summarized in Table 2.

Table 2: Composition of the ammunition. M is for major compound, m for minor and t for traces. n.d. means not detected

Ammunition	AK II	*N,N*-DPF	EC	MC	DPA	*N*-nDPA	2-nDPA	4-nDPA
Geco	M	m	M	n.d.	M	m	m	m
Military	n.d.	m	M	t	M	M	m	m

From a quantitative point of view (estimated from the peak areas, see chromatograms in SI), some compounds are present in large amounts in both ammunition, such as DPA and EC. *N*,*N*-DPF is present at very low concentrations and MC is only present in trace amounts in the military ammunition. AK II was found only in Geco ammunition and slight differences were observed for the quantity of DPA derivatives. These derivatives' presence is broadly dependent on the age of the gunpowder as DPA acts as a nitrate scavenger and may vary if a batch is stored over a certain period of time [28].

3.2 Firearm displacement (scenario 1)

The first scenario involved a shooter discharging three cartridges and leaving the handgun on a clean table. Then, an individual previously unexposed to GSR took the gun and moved it to another table within the same room.

Various blanks were collected to control the presence of OGSR. No OGSR were detected in these blanks, except for one person that was highly contaminated with OGSR. Consequently, the specimen taken after manipulating the firearm for that person was removed from the dataset and as a consequence there are 11 replicates instead of 12 for the experiment using the pistol and Thun ammunition. Blanks from the firearm and the shooter were also collected before the experiment. These blanks were not expected to be negative in all cases. Indeed, the firearms were only cleaned externally with an ethanol wipe and due to the shape and texture of the handgrip, only a full immersion in a solvent would enable complete removal of residues. OGSR were frequently detected in pistol blanks, whereas the handgrip of the revolver was clean with only two positives close to the LOD in 36 specimens (see figure in SI). However, as the stub is rigid, there was no contact with the valleys of the textured handgrip and the actual level of contamination of that part of the grip could not be assessed [29]. When a person holds a firearm, the skin can stretch and be in contact with the valleys. Thus, the amount that can be transferred cannot be extrapolated from the firearm specimens. For the shooter, some of the blanks were positive to OGSR (see figure in SI), even after hand washing. However, as the 12 replicates were acquired in a row, the clothes and hair of the shooter were contaminated and residues were probably transferred to his hands for example from his sleeves. In real cases, the shooter and the firearm might not be free from residues. Primary transfer is not a repeatable process and there was no build-up in OGSR amounts during a series of experiments. In these conditions, positive blanks for the shooter and the firearm were considered normal and acceptable.

Results for the non-shooter after displacing the firearm are illustrated in Figure 2. Only the three most frequently detected compounds are shown (see SI for all compounds). DPA, 4-nDPA and *N*,*N*-DPF were never detected.

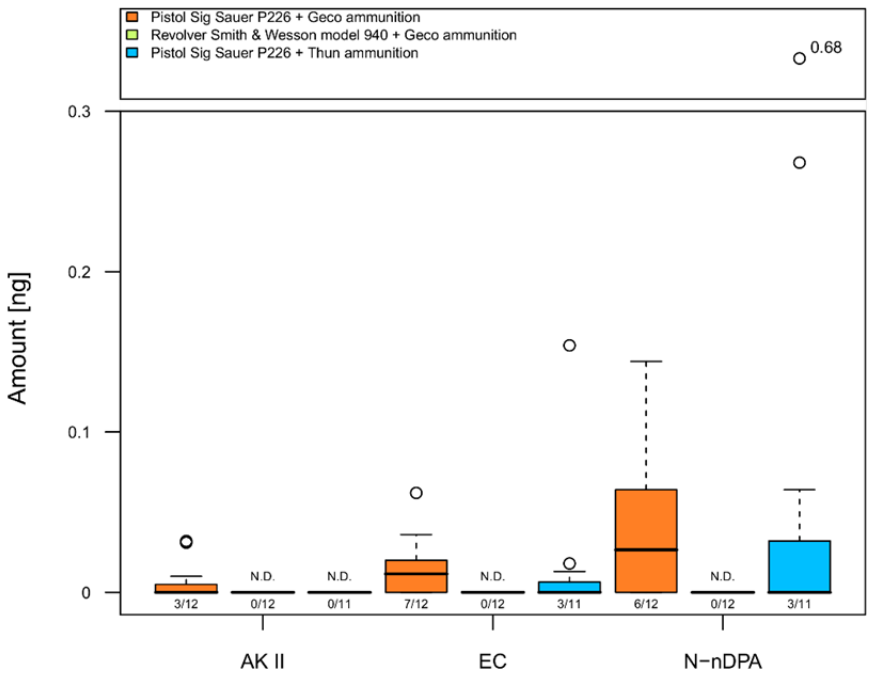


Figure 2: Amount of OGSR detected on the hands of a non-shooter after displacing a firearm (n = 12 or n = 11 because of the contaminated volunteer). The firearm was previously discharged three times. N.D. is for not detected. The numbers under the boxplots represent the number of positive results over the number of replicates.

No OGSR were detected with the revolver experiments. With the pistol, amounts less than one ng were detected. In terms of compounds, the same molecules were found in residues and in gunpowder. Major compounds, such as AK II and EC were often detected, while minor compounds such as *N*,*N*-DPF, 2-nDPA and 4-nDPA were less often detected. DPA was never detected even though it was a major component of the gunpowder. However, this might be explained by the low sensitivity of the mass spectrometer toward that compound with a LOD 20 higher than for DPA derivatives. EC and *N*-nDPA were the most frequently detected compounds with a maximum of 58.3% positive results for the combination Sig Sauer P226-Geco ammunition. Thus, it seems that displacing a firearm does not induce massive secondary transfer. Nevertheless, one must take into account the decontamination of the outer parts of the firearms. In reality, such cleaning process is not carried out and larger amounts might be expected in practice.

Comparison of the present results with a primary transfer study involving the same firearm and ammunition showed that the amounts observed for secondary transfer were about 100 times lower than for primary transfer (medians > 10 ng for the right hand) [30]. However, that study focused on OGSR detection on hands after shooting and the amount of OGSR on the firearm itself was not reported. The handgrip is less exposed than the hands during discharge and lower amounts might be transferred on that surface. The difference between pistol and revolver might also be due to the handgrip's size that is shorter for the revolver, presumably leading to a lower primary transfer. Moreover, the texture of the handgrip and its material certainly has an influence. Furthermore, that revolver is a double action only model with a fully enclosed hammer leading to less GSR propagation at the back than a conventional revolver. Finally, the present scenario evaluated touching a firearm only. One might obtain more secondary transfer with a lengthy manipulation of the firearm, such as removing the magazine or opening the breech. Other parameters such as the number of discharges and the storage conditions of the weapon since discharge (e.g. outside, inside, elapsed time and activity) might influence the results. In conclusion, it is possible for a person not present during a shooting to get OGSR-contaminated by handling a firearm on the crime scene.

3.3 Handshake (scenario 2)

The second scenario consisted in a handshake between a shooter and a non-shooter. Similarly to the previous simulation, the shooter discharged three cartridges, went out of the shooting range and immediately shook the hand of the non-shooter.

No OGSR were detected in the non-shooter blanks, except for one person who was positive only for EC (0.011 ng). However, the specimen taken after the handshake for that person was negative. For the shooter (see SI), some blanks showed the presence of low amounts of OGSR (up to three ng), even after hand washing. As the 12 replicates were acquired on the same day, the clothes and hair of the shooter were contaminated and residues probably re-transferred to his hands. Nevertheless, as there was no build-up in the quantities detected in the volunteers' specimen and due to the low repeatability of primary transfer, it was deemed normal and unavoidable.

Like for the previous scenario, the most frequently detected compounds were AK II, EC and *N*-nDPA. Results for the non-shooter after shaking the shooter's hand are presented in Figure 3a (see SI for all compounds). Except for *N*,*N*-DPF, all the compounds were detected at least once. As a whole, results were lower than ten ng. Pertaining to the amounts of compounds, there is no significant difference between all firearm-ammunition combinations. By looking at the number of positive replicates, it can be observed that there are more positives with the Sig Sauer-Geco, followed by the Sig Sauer-Thun. An aberration was also identified. AK II was detected in specimens collected using the Thun ammunition. Yet, that molecule is not a component of that gunpowder. Further investigation showed that the molecule was not present in the shooter's blanks, but was detected in the shooter's after discharge-specimens. As a consequence, the compound was transferred during the shots. This might be explained by a memory effect of the weapon to a previously used ammunition even though it was cleaned before the ammunition change [31]. Another explanation might be a contamination of the outside of the weapon. Because AK II was a major compound of Geco ammunition, it seems that in the present case, the cleaning and the normalisation with ten discharges before starting the simulation were not sufficient to get rid of all traces of the previous ammunition.

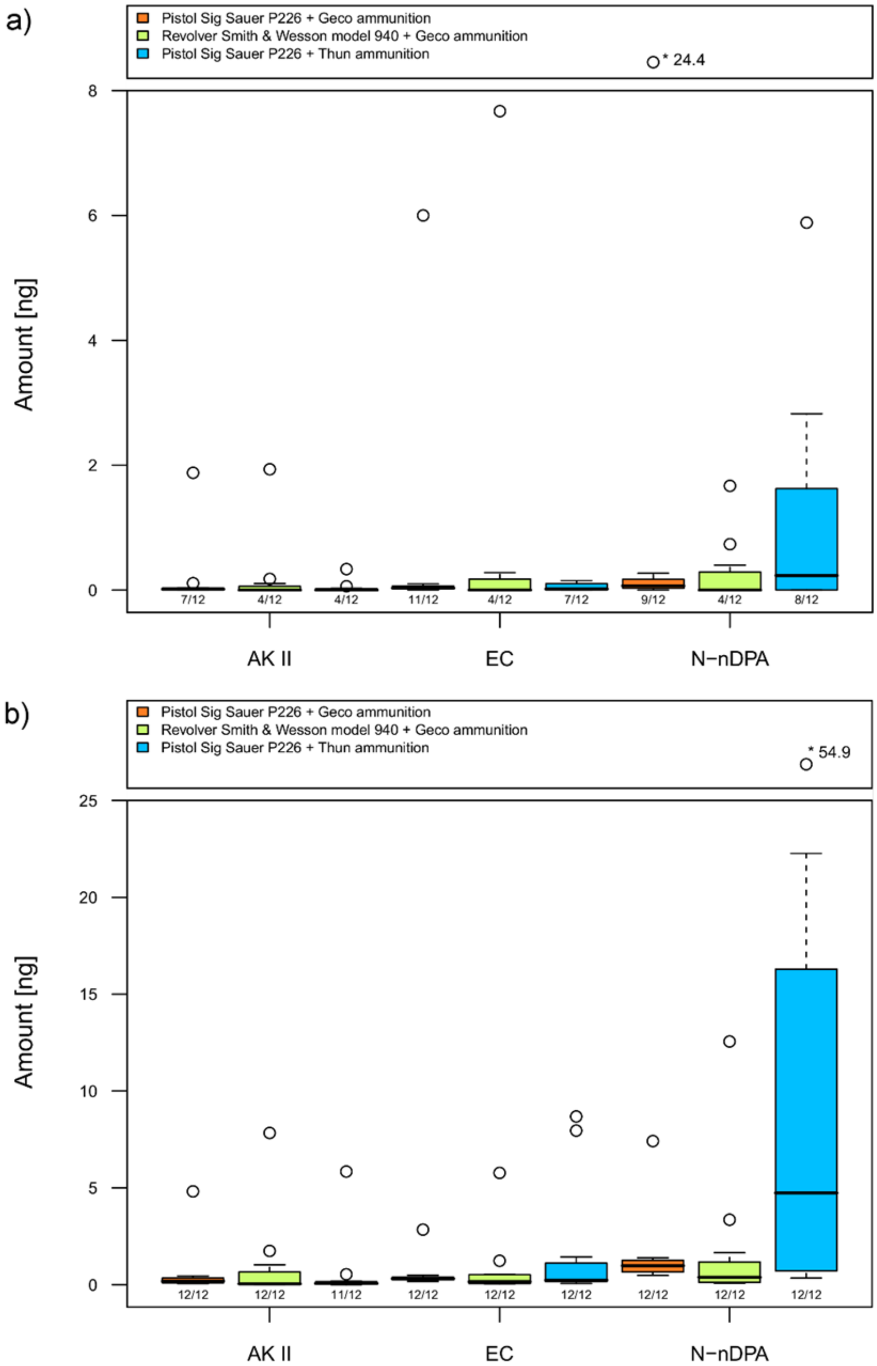


Figure 3: a) Amount of OGSR detected on the hands of a non-shooter after shaking the hand of a shooter (n = 12). b) Amount of OGSR detected on the hands of the shooter after shaking the hand of a non-shooter (n = 12). The firearm was

previously discharged three times. The numbers under the boxplots represent the number of positive results over the number of replicates. The asterisk indicates an extrapolated value (outside of calibration range).

It is interesting to compare the results of the non-shooter to those of the shooter (see Figure 3b). It can be seen that the y-axis scale is wider in the second case. Amounts detected are five to ten times higher than for the non-shooter. A simple calculation was made to roughly estimate the proportion of secondary transfer. Assuming a 100% collection efficiency, the amount of *N*-nDPA collected from the suspect was divided by the total *N*-nDPA amount collected on both shooter and non-shooter. Results showed average values of 16.2, 20.9 and 9.2% of secondary transfer for the combinations Sig Sauer-Geco, S&W-Geco and Sig Sauer-Thun respectively. However, this percentage was highly variable, as values ranged from 0 to 94.6%. Thus, in most of our handshake experiments, there was more OGSR on the shooter than on the non-shooter, but the opposite can also occur. In summary, secondary transfer can be observed during a handshake, even though it is limited, as OGSR are generally left in significant quantities on the shooter's hands. The activity leading to secondary transfer seems to play an important role and will be discussed in the next section.

3.4 Arrest (scenario 3)

The third scenario simulated the arrest of a non-shooter by a shooter just after discharging a firearm. First, the shooter discharged three cartridges. Then he came out of the shooting range to arrest a non-shooter suspect by handcuffing him on the ground. Finally, the shooter helped the suspect getting back on his feet and removed the handcuffs. The specimens were collected immediately after the simulation.

Five of the non-shooter blanks were lightly contaminated (values close to LOD). Among the samples collected after these blanks, three were removed from the dataset because it was not possible to distinguish between contamination and secondary transfer. The last two samples were considered, as values significantly higher than LOD were obtained. Like in the previous simulations, some shooter blanks were positive to OGSR (see SI), even after hand washing.

Results for the non-shooter after being handcuffed on the ground are presented in Figure 4a. Only the three most frequently compounds detected, AK II, EC and *N*-nDPA are presented. All the compounds present in the gunpowder were detected at least once (see SI for all compounds). Most of the results are below ten ng. With regard to the amounts detected, there is no significant difference between pistol and revolver. While revolvers are normally expected to produce more residues than pistols due to the type of ammunition used (higher amount of gunpowder) [32], the number of positive replicates is much higher for the pistol for which all the replicates were found positive for the three compounds (see Fig 4a). Only about 59% of them were positive for the revolver (average of the three compounds). As the same ammunition was used with both firearms, that difference is due to a different firearm construction. With that revolver, primary transfer to the shooter's hands is thus less than with the pistol and more variable as extreme outliers were observed on the shooter's hands. One replicate from the revolver series (indicated by the asterisks in Fig 4a) resulted in extremely high OGSR amounts, at a level similar to what could be expected in a primary transfer. Such exceptional result might be explained by the transfer of an unburnt or partially burnt particle of gunpowder. Due to its potential large size, such a particle would normally be rapidly lost during activity of the suspect and its observation here is only due to the specimen collection taking place just after secondary transfer.

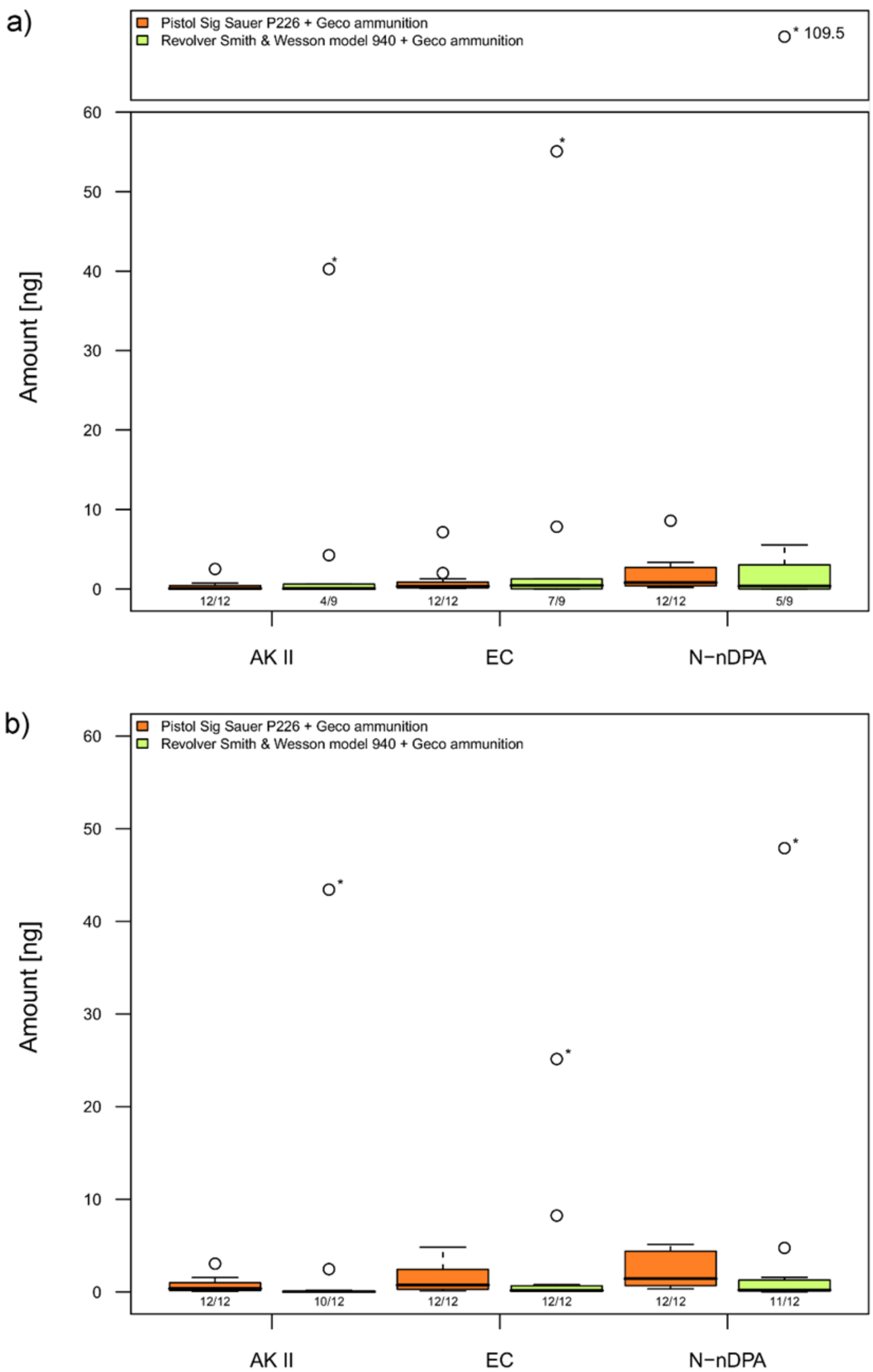


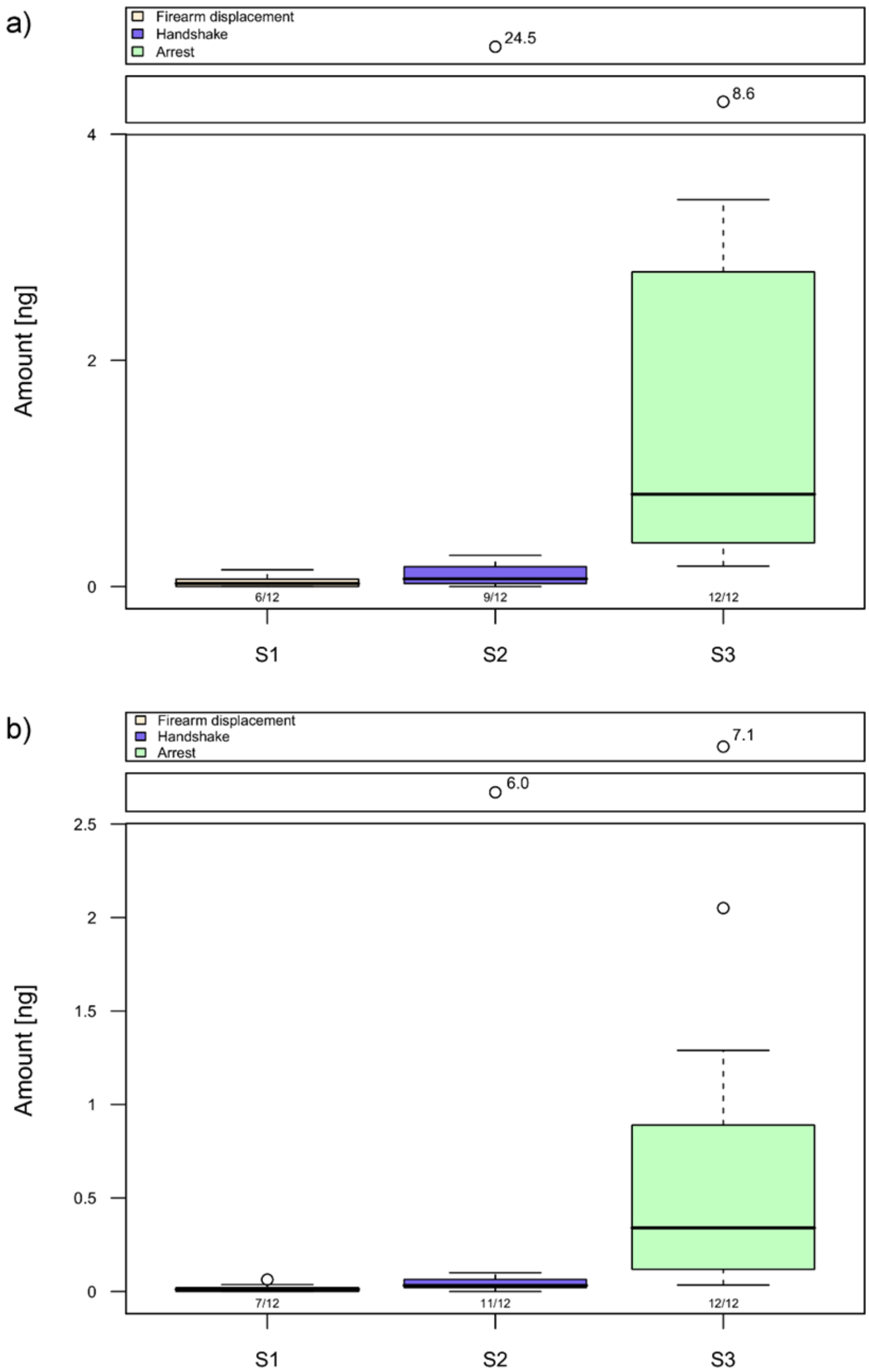
Figure 4: a) Amount of OGSR detected on the hands of a non-shooter after being handcuffed on the ground by a shooter (n = 12 or indicated). b) Amount of OGSR detected on the hands of the shooter after handcuffing a non-shooter on the ground (n

= 12). The firearm was previously discharged three times. The numbers under the boxplots represent the number of positive results over the number of replicates. The asterisk indicates an extrapolated value (outside of calibration range).

Data collected after the arrest simulation for the shooter (see Figure 4b) can be compared to those of the non-shooter. It can be seen that the values are in the same range as for the non-shooter with the majority of results below 10 ng. As a whole, the values for the shooter were slightly higher than for the non-shooter. The calculation made for the previous scenario was applied. Averages of 41.9 and 52.2 % were obtained for pistol and revolver respectively (*N*-nDPA). The highest value was 96.1%, showing that it is possible to detect more residue on the non-shooter than on the shooter. At the opposite end of the scale, the lowest value was zero, showing that secondary transfer is not guaranteed by the presence of residue on the shooter, but that other parameters are also at play. It must be noted that the present simulation involved a fully cooperative suspect. In reality, if force has to be used during the arrest, a higher degree of secondary transfer might be observed.

3.5 Comparison of the scenarios and discussion

The results of the three simulations were compared to see what activity resulted in the highest secondary transfer (see Figure 5). It can be observed that the arrest with handcuffing on the ground transferred the highest amounts. The results for the experiments using the revolver were similar, except for the firearm displacement with no OGSR detection at all. Such observations are easily explained by the conditions of the investigated activities, *i.e.* the surface area involved, the force (pressure) and duration of the contact between the source of secondary transfer and the non-shooter. Indeed, a handshake involves only contact between hands for a few seconds and mainly through palm contact, whereas the arrest involved contact with hands and arms of a longer duration. In addition to the palms, the back of the non-shooter's hands was also in contact with the shooter during the arrest. A firmer pressure was also used in the arrest case and the shooter helped the non-shooter getting up afterwards, extending the contact duration. In the firearm displacement scenario, the low amounts might be explained by the same parameters. The surface area (palms in contact with handgrip), force and duration were lower than for the arrest. However, other factors that play a major role are the amount of OGSR primarily transferred and the handgrip material. The hands of the shooter surrounded the handgrip during the discharge and presumably received most of the residues. In the present scenario, the weapon was held with both hands during shooting. As a consequence, the same experiment holding the firearm with only one hand might possibly result in more OGSR on the grip and thus more secondary transfer through handling the weapon.


a)
Firearm displacement
Handshake
Arrest
24.5
8.6
Amount [ng]
4
2
0
6/12
9/12
12/12
S1
S2
S3
b)
Firearm displacement
Handshake
Arrest
7.1
6.0
Amount [ng]
2.5
2
1.5
1
0.5
0
7/12
11/12
12/12
S1
S2
S3

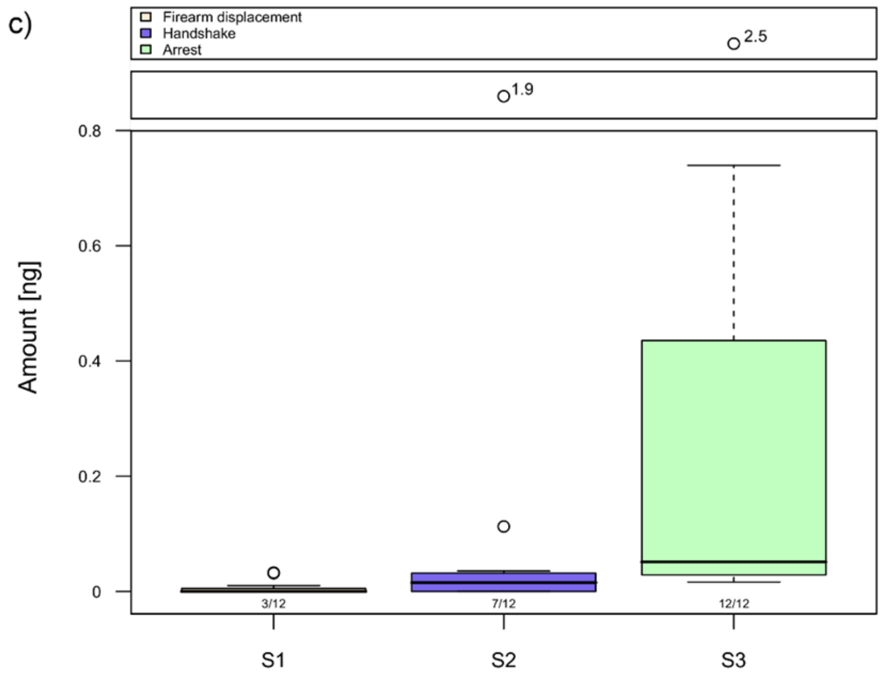


Figure 4: Amount of a) N-nDPA, b) EC and c) AK II detected on the hands of a non-shooter after displacing a pistol (S1), shaking the hand of a shooter (S2) and being handcuffed on the ground (S3). The pistol Sig Sauer P226 was previously discharged three times using Geco ammunition. The numbers under the boxplots represent the number of positive results over the number of replicates.

Only one study was found in the OGSR literature for comparison purpose. For the handshake scenario, our results are in contradiction with those from Arndt et al [24] who concluded to an absence of OGSR secondary transfer. In their study, a handshake following three shots with a Glock Model 19 (9 mm Luger) was investigated. The experiment was repeated three times. Even though the scenario and the time after collection are the same, parameters such as the firearm, ammunition have been shown to produce very different OGSR amounts. Moreover, the sampling material, swabs versus stubs, as well as the analytical technique, IMS vs LC-MS might influence the results. Indeed, IMS is less sensitive than LC-MS. In another article from the same research group, the LOD for DPA and EC were evaluated at 50 and 1 ng respectively [33], while with LC-MS, LOD of 0.5 and 0.01 ng can be attained. The value of 1 ng was only exceeded once for EC in our study. Thus, the difference in sensitivity could explain the contradictory results.

As already mentioned in the introduction, several studies with regard to the secondary transfer of IGSR were published. The secondary transfer during firearm exchange was investigated in two studies [21, 22]. Both concluded to a significant secondary transfer in such a scenario. Two research groups that considered the handshake scenario indicated that IGSR particles can undergo secondary transfer [21, 22] and even tertiary transfer during handshakes [23]. Finally, an arrest scenario by special force police units was examined by Charles and Geusens [20]. Two contamination levels were considered depending on the equipment of the police officers. The scenario involved laying down the suspect, handcuffing and frisking him. They concluded that secondary transfer cannot be neglected during arrests. Obviously, data for IGSR and OGSR cannot be compared due to their different physical and chemical nature. However, it is interesting to observe the same trend for both GSR types regarding their propensity for secondary transfer.

In our study, no (or minimal) persistence steps were involved because secondary transfer experiment and specimen collection took place directly after discharge (time t ~ 0). The results might be different if some time had elapsed between the shots and the transfer experiments. Persistence studies showed that the amount of OGSR decreases rapidly [24, 31, 34]. Thus, if the simulations had taken place for example one hour after the discharge, a secondary transfer would be less likely to occur and to be detected due to significantly lower amounts on the shooter. That would depend on the time elapsed and the activity of the shooter. The same reasoning applies to the non-shooter, as specimen collection might occur some time after secondary transfer. In real cases, the POI is rarely arrested just after shooting and he might be stubbed at the police station after being transferred in a police vehicle (that may also be contaminated). Then, the amount of residue would be much lower due to losses related to activity. The present experiments were not only performed in controlled conditions but also represent extreme cases. While in reality, the POI will rarely be apprehended directly after the police officer shot, one has to keep in mind that police officers apprehending a POI might be a source of contamination even if they did not shoot during the arrest. Indeed, police officers often handle their weapon and practice shooting.

Thus, more studies are required to evaluate the risks of secondary transfer during an arrest by a police officer and transportation in a potentially contaminated vehicle. Prevalence studies in police populations and police stations would also provide an indication on the risks of POI contamination. Such results would provide a baseline to compare to experimental studies. If the prevalence is very low, then risks of contamination would be low. Otherwise, it would be advisable to establish guidelines to minimise the risks, such as avoiding any contact with a POI if a firearm was discharged or collecting specimens from the POI before transportation.

4. Conclusions

The aim of the present study was to investigate the secondary transfer of OGSR. Three scenarios were evaluated, namely a firearm displacement from point A to point B, a handshake and a fake arrest with handcuffing on the ground. Experiments were carried out in controlled conditions immediately after shooting.

Secondary transfer occurred for the three scenarios, but to a different extent. It was found that displacing a firearm resulted in the lowest secondary transfer. On a whole, secondary transfer was observed in less than 50% of the experiments. The firearm also had an influence, as contrary to the pistol, no OGSR were detected using the revolver. Shaking the hand of the shooter also transferred

OGSR to the non-shooter's hand. In that case, the amount of OGSR was generally higher on the shooter than on the non-shooter. Finally, the highest secondary transfer was observed after the arrest with handcuffing. For N-nDPA and EC, OGSR were transferred for all experiments using the pistol, whereas the frequency of occurrence was slightly lower with the revolver. In that case, the amounts on the shooter and the non-shooter were in the same range.

This study highlights that the secondary transfer must be taken into account in the interpretation of OGSR analyses. An individual's hands might be contaminated by handling a firearm or having physical contact with a shooter. Moreover, while the present study showed that a POI might be contaminated during an arrest, it must be emphasized that transportation in a police vehicle or being held at a police station may also result in contaminations.

Currently, it is impossible to fully evaluate the risks and more studies are required. First, prevalence studies in police populations and police stations would provide a baseline of the OGSR detected in these environments. Then, secondary transfer experiments would provide some insight into the transfer mechanisms depending on the scenarios studied. All these data combined with data regarding initial transfer and subsequent persistence will form a basis on which OGSR analysis needs to be interpreted in casework.

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