A forensic investigation on the persistence of organic gunshot residues

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Abstract

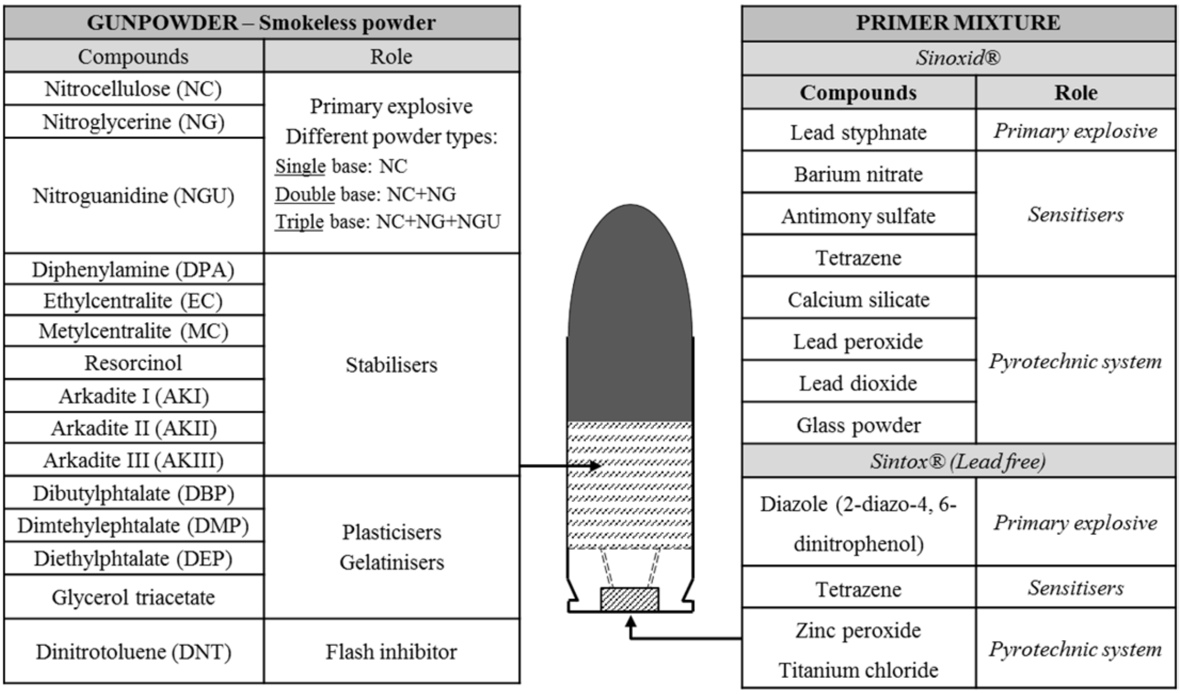
Gunshot residues (GSR) are a potential form of evidence in firearm-related events. In most forensic laboratories, GSR analyses focus on the detection and characterisation of the inorganic components (IGSR) which are mainly particles composed of lead, barium and antimony originating from the primer. The increasing prevalence of heavy metal-free ammunition challenges the current protocols used for IGSR analyses. To provide complementary evidence to IGSR particles, the current study concentrated on the organic components (OGSR) arising from the combustion of the gunpowder. The study focused on four compounds well-known as being part of OGSR: ethylcentralite (EC), methylcentralite (MC), diphenylamine (DPA), N-nitrosodiphenylamine (N-nDPA). This study assessed the retention of these OGSR traces on the shooter's hands. The persistence was studied through several intervals ranging from immediately after discharge to four hours and two ammunition calibres were chosen: the .40 S&W calibre, used by the NSW Police Force, and the .357 Magnum, which is frequently encountered in Australian casework. This study successfully detect the compounds of interest up to four hours after discharge. The trends displayed a large decrease in the amount detected during the first hour. A large variability was also observed due to numerous factor involved in the production, deposition and collection of OGSR. The overall project aim was to provide appropriate information regarding OGSR persistence, which can be suitable to be integrated into the interpretation framework of OGSR as recommended by the recent ENFSI Guideline for Evaluative Reporting in Forensic Science.

Keywords: Firearm discharge residues, OGSR, interpretation, .40 S&W, .357 Magnum, UPLC-MSMS

1. Introduction

In 1982 Hagel and Redecker patented a new primer mixture for the manufacture of ammunitions called Sintox®, produced by Dynamit Nobel AG [1]. This then new primer formula – known as lead-free or heavy-metal free primer (Figure 1) – was originally designed to minimise airborne heavy metal such as lead, barium and antimony to avoid health and environmental issues, especially in firing ranges and during hunting seasons. In the primer of these ammunitions, the primary explosive, lead styphnate, is replaced by 2-diazo-4,6-dinitrphenol (diazole) [2].

The introduction of lead-free ammunition is presenting a challenge for GSR analysis by forensic science laboratories. The usual GSR characterisation, based on the presence of spherical particles of lead, barium and antimony [3-7], is no longer suitable due to the lack of heavy metals (Figure 1). Consequently, several studies [8-14] attempted to identify GSR through their organic components (OGSR) which mainly arise from the composition of the gunpowder, as displayed in Figure 1.



GUNPOWDER – Smokeless powder	
Compounds	Role
Nitrocellulose (NC)	Primary explosive Different powder types: Single base: NC Double base: NC+NG Triple base: NC+NG+NGU
Nitroglycerine (NG)	
Nitroguanidine (NGU)	
Diphenylamine (DPA)	Stabilisers
Ethylcentralite (EC)	
Metylcentralite (MC)	
Resorcinol	
Arkadite I (AKI)	
Arkadite II (AKII)	
Arkadite III (AKIII)	
Dibutylphtalate (DBP)	Plasticisers Gelatinisers
Dimtehylephtalate (DMP)	
Diethylphtalate (DEP)	
Glycerol triacetate	
Dinitrotoluene (DNT)	Flash inhibitor

PRIMER MIXTURE	
Sinoxid®	
Compounds	**Role**
Lead styphnate	*Primary explosive*
Barium nitrate	*Sensitisers*
Antimony sulfate	
Tetrazene	
Calcium silicate	*Pyrotechnic system*
Lead peroxide	
Lead dioxide	
Glass powder	
Sintox® (Lead free)	
Diazole (2-diazo-4, 6-dinitrophenol)	*Primary explosive*
Tetrazene	*Sensitisers*
Zinc peroxide Titanium chloride	*Pyrotechnic system*

Figure 1. Composition of firearm ammunition – Gunpowder residues are known as organic GSR (OGSR) [8, 9, 15-17] and the primer mixture residues are categorised as inorganic GSR (IGSR) [15-17].

Additionally, the analysis of OGSR can be beneficial as the amount of gunpowder present in an ammunition cartridge is significantly larger than the amount of primer mixture. This can lead to a potential greater amount of residues arising from the propellants when compared to the primer mixture.

Single and double base powders are the most common propellants used in the manufacture of modern ammunition. The triple base mixture is less common on the market because it is primarily used in large calibres, rockets and military weapons [18]. Additives such as stabilisers, plasticisers and flash inhibitors are also present to improve the powder workability and stability, and to control the burning rate [8, 19]. Compounds such as methylcentralite (MC) and ethylcentralite (EC) are restricted to the production of gunpowder and consequently are considered the most characteristic of propellant powder. Their detection is, hence, important as their presence increases the probative value of associating the source of the samples to a firearm discharge rather than an unknown and legitimate source of contamination [10, 20]. Diphenylamine (DPA) is also considered characteristic of GSR when associated to its nitrated-derivatives such as N-nitrosodiphenylamine (N-nDPA), 2-nitrodiphenylamine (2-nDPA) or 4-nitrodiphenylamine (4-nDPA) [9].

Several analytical techniques have been successfully utilised for the detection of OGSR such as gas chromatography (GC) [21-23], micellar electrokinetic capillary electrophoresis (MECE) [11, 24-26], Raman spectroscopy [18, 27, 28], desorption electrospray ionisation–mass spectrometry (DESI–MS) [20, 29, 30] and liquid chromatography tandem mass spectrometry (LC-MSMS) [31-33]. However, the analytical aim relates to only one dimension of the task of the forensic scientist. The central purpose relates to the information given by the expert about OGSR traces to the investigative and judicial stakeholders involved in the investigation process [34]. It requires forensic scientists to have a better understanding of OGSR traces in an activity context beyond the simple question of analytical detection [34].

Indeed developing knowledge about the persistence of such traces is crucial when considering OGSR analysis as routine analysis for casework. In an investigative perspective, having such research informs on the utility of collecting GSR samples knowing that the case occurred a certain point in time. This is necessary for forensic laboratories when planning the analysis strategy for cases under investigation. Additionally, an understanding of persistence is also significant in an interpretative perspective when questions regarding the accordance of the recovered traces with the sequence of the events are raised.

This project aimed to provide additional information regarding OGSR traces. The question of interest concerned the possibilities to detect OGSR compounds from samples arising from the hands of the shooter after a certain amount of time is elapsed between the firearm discharge and the samples collection. The persistence factor is crucial when considering the detection and interpretation of OGSR in routine analysis.

2. Material and method

2.1 OGSR standards

Ethylcentralite (EC), methylcentralite (MC), diphenyamine (DPA) and N-nitrosodiphenylamine (N-nDPA), presented in Table 1, were chosen as the compounds of interest based on current literature [19]. They are the ones of most relevant and common compounds present in gunpowder and therefore the most likely to be detected in OGSR samples.

Table 1. Compounds of interest

Compounds	Provider	Concentration	Solvent
EC	Novachem Pty Ltd	100 µg/mL	Methanol Acetonitrile (1:1)
MC		100 µg/mL	Methanol Acetonitrile (1:1)
DPA		1000 µg/mL	Methanol
N-nDPA		1000 µg/mL	Methanol
d10-DPA (IS)	C.D.N Isotopes Inc.	Solid	-

D10-DPA was chosen as the internal standard for its similar ionisation and fragmentation response to the analytes of interest. It was also reported as a suitable internal standard in research conducted by Ali et al. [35]. Stock solution of internal standard, d10-DPA, was prepared at a concentration 1000 µg/mL in methanol:acetonitrile (1:1) v/v. These standards were used for identification of compounds and analytical method validation purposes. Additionally, a five point standard curve (0.01 ppm to 1 ppm) was prepared and analysed with every run of samples for quality control purposes.

2.2 Sample collection

Recent research in the field of OGSR suggests that the recovery rate of the organic residues is significantly higher when collected by mean of carbon-coated adhesive stubs when compared to alcoholic swabs [33, 36]. The collection of OGSR traces was carried out with SEM-EDX stubs (Ted Pella Inc, USA), which are commonly used for GSR sampling [37]. The thumb-forefinger, part of the palm and back of the hand as well as the wrist were sampled as presented in Figure 2. The area of sample collection was chosen based on the exposition of this area to the GSR plume when a firearm is discharged. The back of the hand is often more in contact to the plume of gas expelling from the ejection port/cylinder gap than other area. Additionally, as the hand firmly grips the firearm there is a high chance of primary transfer of OGSR onto the palm and the web area through the way the shooter handle the weapon [38, 39]. Residues from both hands of the shooter were each collected separately. The collected samples were packaged by sealing with the cover and placed in their respective boxes. Sampled were stored at 4ºC until extraction. The extraction process was performed within 24 hours of collection to avoid degradation of the compounds [40].

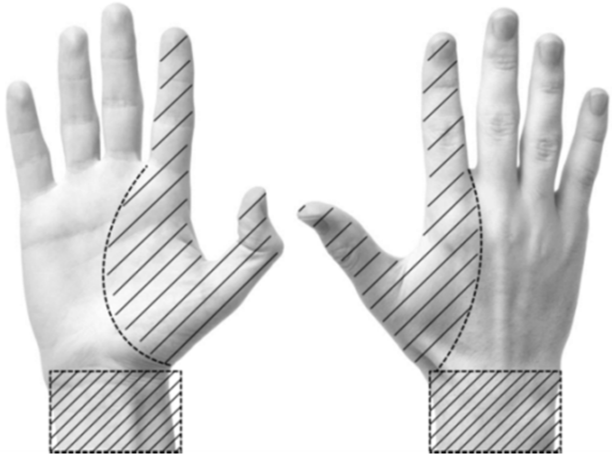


Figure 2. The shaded parts represent the areas of interest sampled on the hands of the shooter for GSR collection.

2.3 Persistence: Shooting experiment procedure

In order to study the persistence influencing the detection of OGSR, authorised personnel at the NSW Police Force based in Sydney (Sydney, Australia) performed the firearm discharges for this study in an indoor shooting range.

Two calibres and firearms were selected based on the occurrence in NSW casework. The first firearm used was a Glock 22® calibre .40 S&W, chosen due to its use as the service calibre and weapon of the NSW Police Force. The second firearm was a .357 Magnum (.357 Mag) S&W Revolver model 686 (4” barrel). The ammunitions used for the .40 S&W was lead-free primers: Winchester WinClean® (180Gr. Brass Enclosed Base) and the .357 Mag was traditional primers: PPU Ammunition® (158 Gr. Semi-Jacketed Hollow point). The revolver ammunitions (.357 Mag) contained traditional lead primers, however, the ammunitions used when discharging the Glock 22® (.40 S&W) were lead-free primer (WinClean®). These particular ammunition were selected to emphasise the importance of the detection of the organic residues as a complementary source of information to IGSR. As lead-free primers do not produce the traditionally analysed characteristic Pb-Ba-Sb IGSR particles, it is therefore fundamental to improve the analysis of GSR by providing an appropriate method to provide complementary information to the inorganic SEM-EDX analysis with the analysis of the organic residues that are mainly resulting from the combustion of the gunpowder.

The shooting process is presented in Figure 3. This required the shooter to decontaminate their hands before blanks were taken. Following three discharges of the firearm, the shooter continued with their daily activities (with the only restriction to not wash their hands) for the studied time intervals (immediately after discharge (T0) and 30 minutes (T0.5h), 1 hours (T1h), 2 hours (T2h) and 4 hours (T4h) after discharge. The samples were collected with stubs after the respective time had elapsed. The stubs were dabbed on the shooter's hands until it has lost all stickiness. The experiment was repeated in quintuplicate for each time point (in triplicate for T4h) and both firearm-ammunition combinations.

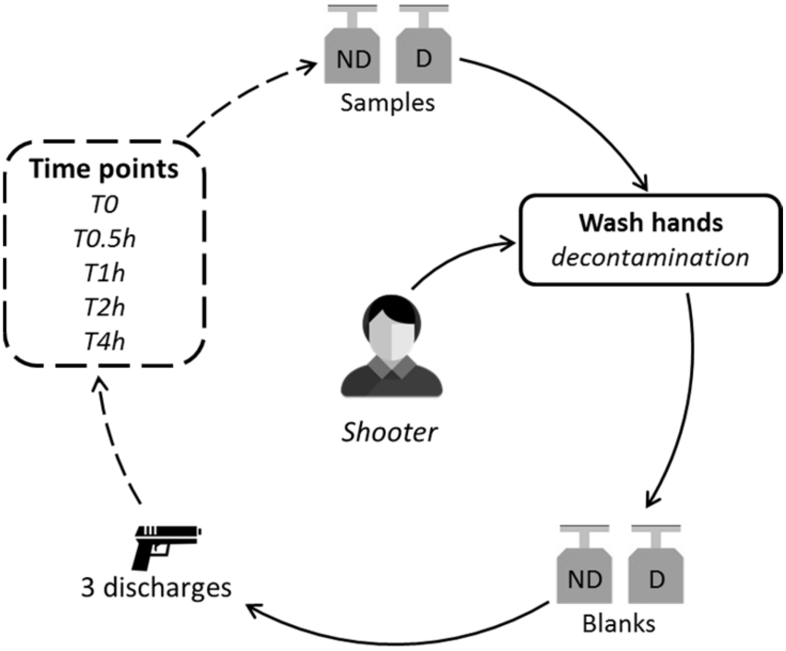


Figure 3. The sampling procedure during shooting experiments. D = dominant hand, ND = Non-dominant hand. A set of blanks are taken after the hands wash to avoid contaminations in the results.

2.4 Analytical method

2.4.1 Samples extraction

The extraction protocol described by Taudte et al. [36] was used. Briefly, residues of interest were extracted from the stubs in acetone, filtered, before the solvent was evaporated under nitrogen. Finally, the samples were reconstituted in methanol and acetonitrile (1:1, v/v) and the internal standard is added with a final concentration of 20 ppm.

2.4.2 UPLC analysis

The chromatographic separation was performed on a Waters UPLC ACQUITY® system. An Agilent ZORBAX RRHD Eclipse XDB 80Å C18, 3.0 x 100 mm, 1.8 µm was used coupled to a ZORBAX Eclipse XDB 80Å C18, 3.0 x 5 mm, 1.8 µm UHPLC guard. The mobile phases used were methanol (Hypergrad Lichrosolv®, Merck KGaA) with 1% (v/v) formic acid and ultrapure Milli-Q® Water (18.2 MΩcm, Q-POD®, Merck KGaA) with 0.1% (v/v) formic acid using the gradient method described in Table 2, which includes a 4.6% increase of methanol per minute [31]. The column temperature was thermostatically maintained at 43 °C and an injection volume of 2 µL was used throughout. The curve represents the rate of change in the gradient.

Table 2. UPLC Gradient conditions [31].

Time (min)	**Flow rate (mL/min)**	Mobile phases		**Curve**
		Water *+ 0.1% v/v formic acid (%)*	**Methanol** *+ 0.1% v/v formic acid (%)*	
0.00	0.8	70 %	30 %	6
12.00	0.8	14.8 %	85.2 %	6
15.00	0.8	70 %	30 %	6
17.00	0.8	70 %	30 %	6

2.4.3 MSMS analysis

Detection of OGSR and explosives is commonly conducted using QqQ instrumentation [9, 31-33, 35]. The desolvation temperature was set at 250 °C. The detection was performed using Multi-Reaction-Monitoring (MRM) from 0 to 12 minutes) as described in Table 3, with electrospray ionisation (ESI) source set at 140 °C.

Table 3. QqQ MRM transitions.

Compounds	Precursor ion [m/z]	Product ions [m/z]	Cone Voltage	Capillary Voltage	ESI Polarity
NnDPA	199	66 169	26	24 12	+
MC	241	106 134	32	26 16	+
DPA	170	65 93	42	32 30	+
D10-DPA (IS)	180	71 98	42	42 28	+
EC	269	120 148	28	24 14	+

2.4.4 Analytical method validation

Validation of the method was conducted using the International Conference on Harmonisation (ICH) guidelines [41] in order to ensure the reliability of the results. Several parameters were investigated including the specificity, linearity, accuracy, precision and robustness. The validation was performed over two days to assess the repeatability of the results. It involved the injection of seven points calibration curve (0.01 ppm to 5 ppm) and three quality controls (QC, 0.05 ppm, 0.5 ppm and 5 ppm). The robustness was assessed by deliberately changing the chromatographic method. Three parameters were assessed: the column temperature (+/-1 ºC), the solvent composition (+/-5 % methanol) and the flow rate (+/-0.05 mL/min). The relative retention times (RRt) were calculated for assessing the reliability of the method.

2.5 Data extraction and normalisation

The detected peaks were integrated by mean of Waters software (QuanLynx®). The presence of precursors to both product ion transitions was a required condition in an abundance above the limits of detection (LOD) for considering the compounds as present. All peak integrations were manually checked before being exported for further processing in MS Excel®. The data collected for each compound was normalised to the IS and each associated blank was subtracted to remove any possible contamination. Finally, the ratios are pre-processed with the square root [42, 43] as shown in equation 1.

Eq. (1)

$$\text{Normalised Peak Area}_{\text{analyte}} = \sqrt{\frac{(\text{Peak Area analyte}_{\text{sample}}) - (\text{Peak Area analyte}_{\text{blank}})}{\text{Peak Area}_{\text{Internal Standard}}}}$$

3. Results and discussion

The study of the persistence is essential in order to improve the knowledge and understanding of OGSR traces. It enables to provide meaningful information to the different stakeholders involved in the investigation process. Firstly, to the investigators and forensic laboratories which needs to prioritise samples analysis. The persistence study provides information on the likelihood of getting positive results after a certain time elapsed between the shooting event and the collection time. Secondly, it provides information to the forensic experts whom need to interpret OGSR analysis results in light of the case circumstances.

3.1 Analytical method validation

The method used underwent a full validation to ensure it was fit for purpose for the targeted analytes. It was achieved by assessing a set of parameters following the ICH harmonised guideline [41]. The validation results are presented in Table 4, the method was found to be fit for purpose. A quantification of the results was not performed, as the initial amount present into each fired cartridge was usually unknown. Moreover, many factors affect the combustion of the gunpowder as well as the deposition and collection process of the residues. These parameters being highly variable, unpredictable and usually unknown in casework make a quantification of the results uninformative.

Table 4. Results summary of the analytical method validation

	Parameters	**Samples**	**Results**
Specificity	*Selectivity*	Separated standards	Interference < 19 %
Linearity	*Calibration curve*	7pts: 0.01 to 5 ppm	$R^2 > 0.995$
		Limit of detection (LOD)	NnDPA: 5.64×10-03 ppm
			MC: 1.75×10-04 ppm
			DPA: 2.09×10-03 ppm
			EC: 3.82×10-04 ppm
Accuracy/ precision (level I)	*Repeatability – Calibration curve and QCs*	QC1: 0.05 ppm	> 92 % accuracy
		QC2: 0.5 ppm	> 91 % accuracy
		QC3: 5 ppm	> 90 % accuracy
Robustness	*Column temperature +/- 1 °C*	QC2: 0.5 ppm	97 % < RRt < 101 %

	Solvent composition +/- 5 % methanol	
	Flow rate +/- 0.05 ml/min	
Precision (level II)	*Repeated over 2 days*	% RSD < 15 %

3.2 Persistence of OGSR evidence

All the targeted compounds were considered as "detected" when the abundance was found above the limit of detection (LOD) presented in Table 4. The three compounds were all successfully detected up to 4h after discharge for the both semi-automatic pistol (.40 S&W) and the revolver (.357 Mag). It is consequently noteworthy to report that the percentage of positive samples is of 72% for the .40 S&W and 89% for the .357 Mag after 4hrs (Figure 4). The number of positive samples is defined as the number of samples in which the three compounds of interest were detected simultaneously out of the total number of samples analysed.

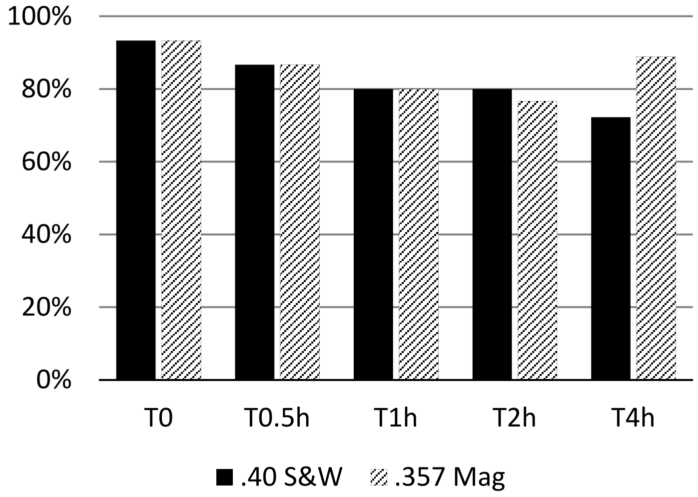


Figure 4. Overall percentage of samples considered positive to the three compounds of interest.

Figure 5 and 6 present the results of the normalised peak area (eq. (1)) of the targeted compounds for each of the ammunition calibres investigated at each time point (T0-T4h). MC was not detected in any of the samples collected, therefore the number of compounds successfully detected were DPA, N-nDPA and EC. This is not surprising given the manufacture of gunpowder typically includes MC or EC, rarely both in combination as MC is usually used as an EC substituent in the manufacture of certain gunpowders.

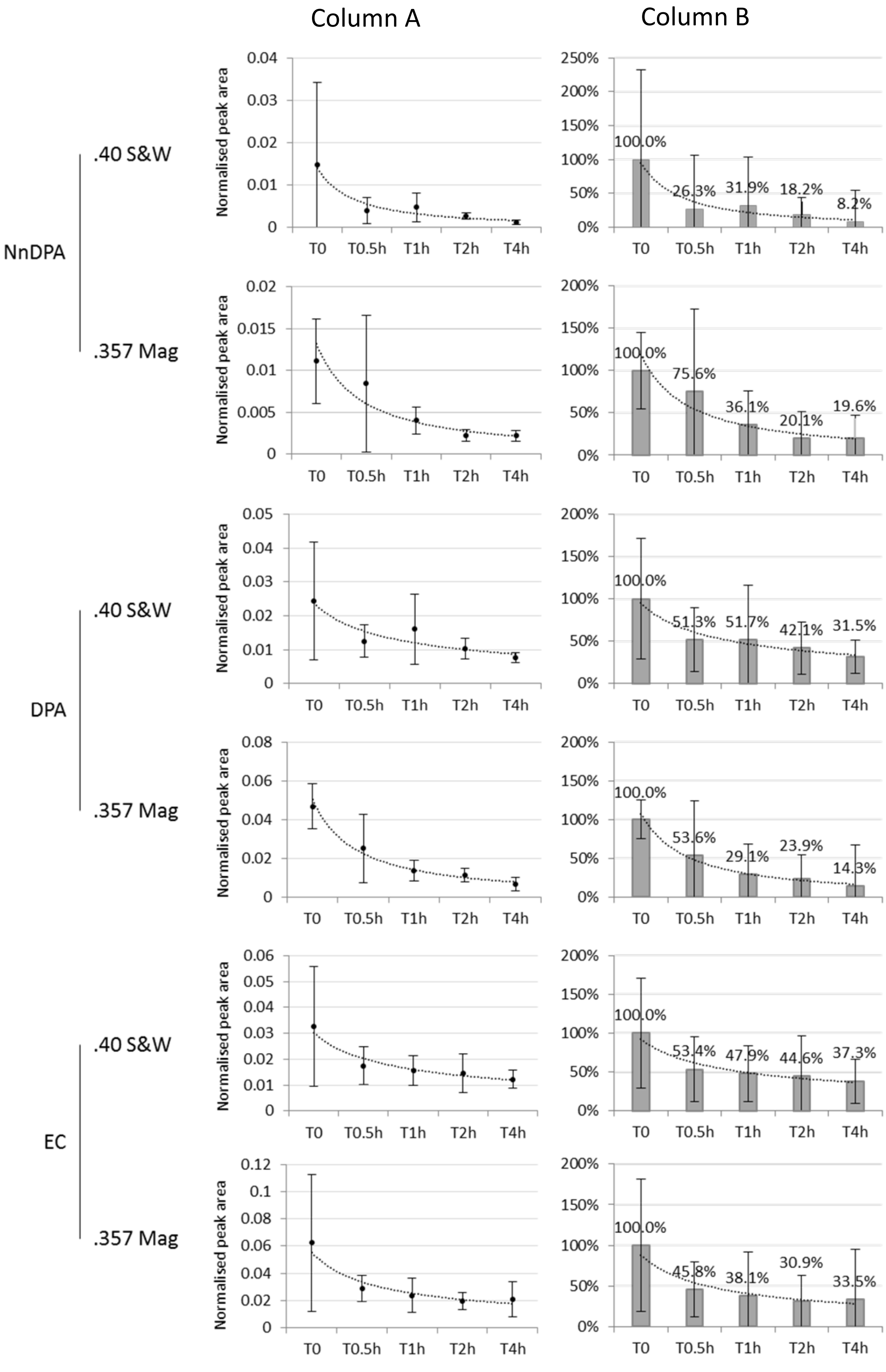


Figure 5. Column A: Average normalised peak area (eq.1) of each targeted compound, the error bars represent the Standard deviation. Column B: percentage when each time point is normalised to T0.

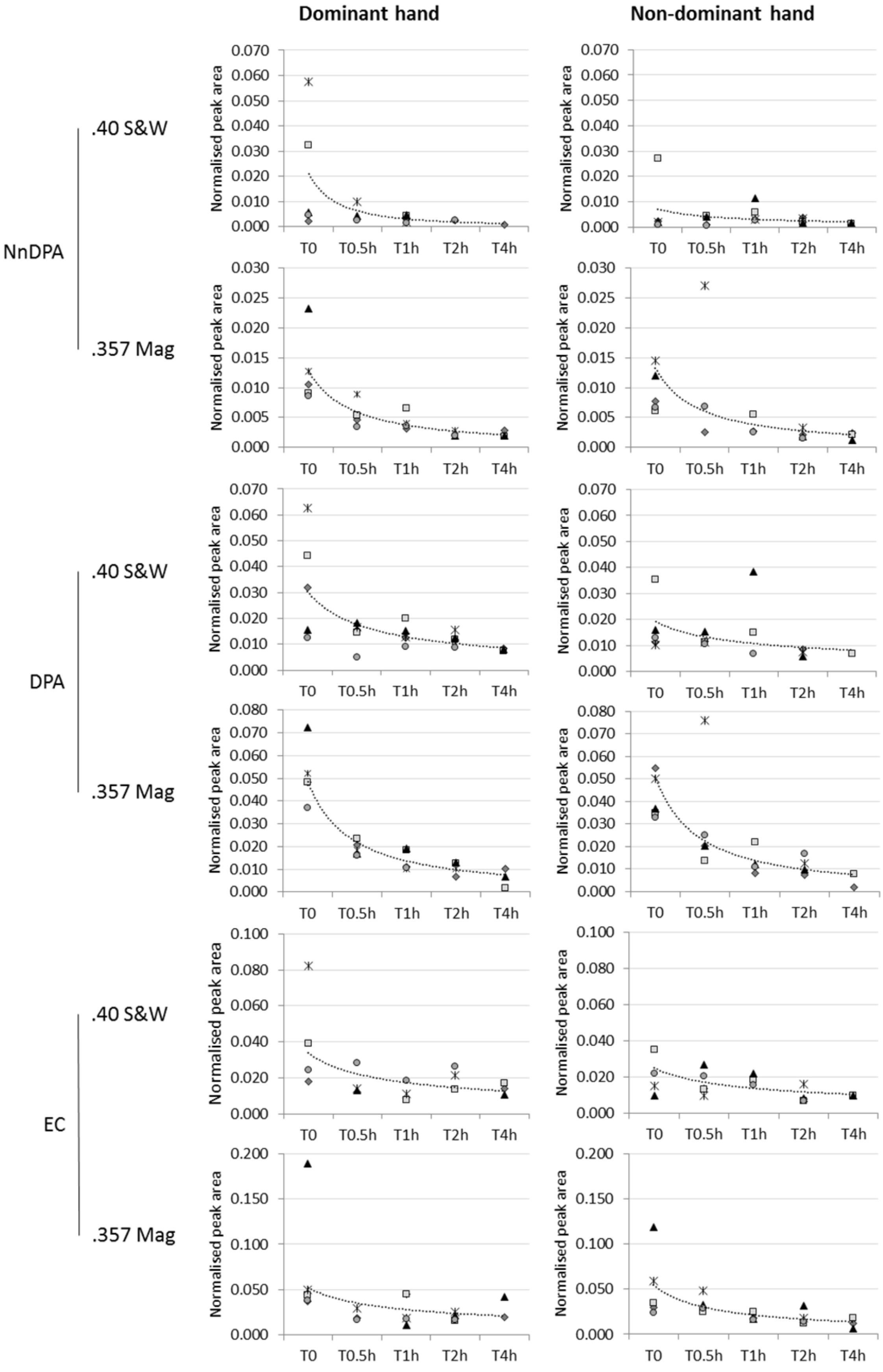


Figure 6. Normalised peak area of each targeted compound. Each data point represents a replicate of the experiment (n=5 for T0, 0.5h, 1h, 2h and n=3 for 4h).

Figure 5 represents a global visualisation of the trends over time for both calibres. The results presented include the combined amount detected on both dominant and non-dominant hand of the shooter. The left set of graphs represents the average amount detected on the hands of the shooters. The right set of graphs represent a relative percentage of the amount detected once normalised to T0. A consistent trend was observed with a large decrease in the amount of each compound detected after the first hour since discharge. It was observed that after the first hour, an average of 34.0% of NnDPA, 40.4% of DPA and 43.0% of EC were still detectable. After four hours, an average of 13.9% of NnDPA, 22.9% of DPA and 35.4% of EC were still detectable (Figure 5 column B).

Figure 6 plots each replicate collected detailing the results of each shooting experiment at the studied time points. It is essential to emphasise the limitations, as this was a controlled experiment, where the shooter did not wash their hands for the given time periods to provide results for a best-case scenario. Previous research indicates that that hand washing and wiping has a drastic effect on the amount of GSR remaining on the surface of the hands [44, 45]. Arndt et al. (2012) observed that the activity of washing hands completely removed all traces of DPA on the hands of the shooter [7].

The aim of the study was to assess the effect of activities on the retention of OGSR traces on the hands of the shooter. In this particular case the activities undertaken after the firearm discharges involved police and office works (without hands washing and without any additional contact with firearms). The observed decrease of the amount detected was consequently highly dependent to the kind of activities undertaken. As such, the more intense the activity the greater potential for the loss of residues. In addition to the activity effect, a previous study conducted by Moran et al. (2014) hypothesised that the evaporation as well as the absorption of the organic compounds by the skin is also a significant parameter in the retention and recovery of OGSR [46]. Additionally, it has been previously emphasised that the lipophilic aspect of the organic residues may increase their retention to the surface of the skin when compared to the inorganic particles that may be more easily lost or removed [7, 46]. However, the general trends observed in Figure 5 were consistence with the studies performed on the inorganic component of GSR where the highest decrease in the amount detected is occurs during the first two hours after the firearm discharge [47, 48]. Brozek-Mucha recorded a 96% decrease of the amount of particles during the first 30 minutes after discharge [48]. However, it is important to note that most studies on the persistence of IGSR do not provide enough information to proceed to a more reliable comparison with that of

OGSR. Nevertheless, the results of this study show that the decrease of OGSR over time seems less significant than the loss of IGSR mentioned in the current literature with an average amount detected, across the targeted compounds, of 43.83% for .40 S&W and 34.43% for the .357 Mag after one hour (Figure 5). These results support the suggestion that the lipophilicity of OGSR is a key factor in the persistence of OGSR on the shooter skin.

When comparing different types of firearms, it is commonly reported that the amount of GSR detected is greater with a revolver than a semi-automatic pistol [49]. The results from this study report that the amount detected from the .357 Mag are in the same range as that of the .40 S&W calibre fired with a semi-automatic Glock 22® (Figure 6). These results are interesting as it is commonly assumed that the amount of GSR detected is greater with a revolver than a semi-automatic pistol due to the difference in the construction and mechanism of the weapons [49]. Revolvers have a more rudimentary construction that presents larger gaps for the GSR plume to expel (e.g. cylinder, firing pin, and trigger).

3.2.1 Variability of OGSR

A large variation in the amount detected was observed in Figure 5 as illustrated by the errors bars (standard deviation) and predominantly visible at T0. When observing the details of each replicate presented in Figure 6, it was apparent that the result of the large variation was a discharge-to-discharge variability. As each time point studied represents a separated discharge process (Figure 3), this suggests that the variability observed at T0 is the consequence of primary transfer. The factors influencing the variability of the primary transfer are numerous along the firing process. Primary transfer can occur before the firearm discharge through a contamination of the grip, which is due to previous discharges of the weapon. During the firing process, the combustion of the gunpowder may vary from shot to shot as the composition of the gunpowder may vary slightly from cartridge to cartridge (e.g. due to different storage conditions or a heterogeneous gunpowder manufacturing process) which causes the production of variable amounts of OGSR. Lastly, after the firing process, different environmental conditions (e.g. airflow) also greatly affect the dispersion of GSR plume, and the conditions of the shooter, such as his skin, hairiness and the clothing, greatly influence deposition of OGSR traces. These factors conceivably add-up making the primary transfer highly variable and mostly unpredictable as observe on Figure 5 and illustrated on Figure 6 with the large scattering of the replicates at T0. Consequently, for every time point longer than T0, the original amount deposited on the shooter hands is unknown and cannot be extrapolated to other time points. For instance, a high amount of DPA is detected on the non-dominant hand at T0.5h for the .357 Mag ammunition. This reflects the primary transfer variability with a potentially high amount deposited on the hands of the shooter at the time of discharge for this particular sample. A similar observation was seen in the .40 S&W calibre on the non-dominant hand at T1h.

Other human factors must be taken into account when observing data that includes uncontrolled activities such as daily work. The first one is considering the dominant hand, which is the preferred hand when undertaking activities such as grabbing object, opening a door and many others. The different involvement of the two hands in such activities may highly influence the degree of retention of OGSR traces with a rapid decrease observed on the dominant than compared to the non-dominant. Conversely, the non-dominant hand, due to its lower implication in such activities, may preserve the traces on the surface of the skin such as OGSR for longer. Secondly, another factors concern the possible cross-contamination of the hands during the time of the experiment as the two hands may enter in contact with each other spreading the traces over their surface. When compared to the inorganic component of GSR, it appears that high variability is also observed. Jalanti et al. reported a poor reproducibility in the counts in particles and suggested that the particle retention was not dependent of their chemical composition [47].

3.2.2 Future considerations

As a final point, this study provides valuable information to forensic science practitioners and legal parties. As mentioned by the ENFSI guidelines[50], to achieve a proper and meaningful interpretation of traces such as OGSR, it is essential to integrate the results into the context and the chronology of the case under investigation. The interpretation of forensic evidence at the activity level of the hierarchy of propositions requires taking into account factors such as the persistence and the secondary transfer [50], which relate to activities undertaken affecting OGSR traces properties. The focus of this research was to evaluate the effect of activities on the retention of OGSR on the hands of a shooter as POI are rarely apprehended immediately at the scene of crime. This study provides several information regarding the source level through the successful identification of the three compounds being detected in OGSR samples and more importantly about the activity level by observing the trends of the amount detected at different time points. It was observed that OGSR could be detected up to four hours after the firearm discharge with trends showing a large decrease during the first hour after the discharge. This information can therefore be used in order to strategically plan analysis according to the context of the casework [39]. Additionally, it can be worthwhile to include such information into the interpretation process to consider the chronology between the event under investigation, the kind of activities undertaken and the time of sampling. The inclusion of the persistence data into an appropriate interpretative framework will be attempted and discussed in a future paper, which will relate to the Bayesian interpretation of OGSR evidence in forensic investigation.

4. Conclusion

The aim of this study was to investigate the persistence of OGSR up to four hours after discharge. The UPLC-MSMS method was validated and found to be fit for purpose for the detection of three compounds associated to OGSR: DPA, N-nDPA and EC.

The three compounds of interest were successfully detected in more than 70% of the samples four hours after the discharge. This study showed the largest decrease of the OGSR amount during the first hour. The observed trends are similar to that of inorganic particles, however, it appears that the decrease is less brutal, supporting the hypothesis that the retention of the organic residues might be caused by the lipophilic aspect of the compounds of interest.

Additionally, as observed in previous studies on the retention of inorganic particles, a high variability in the OGSR amount detected from shot to shot was observed. These observations were due to numerous factors involved in the formation, dispersion and deposition of the residues. Nevertheless, the trends observed suggest that OGSR is a useful and meaningful source of information as a complement to the inorganic particles analysed by SEM-EDX. Finally, this study provides a better knowledge on the behaviour of OGSR traces, which can be used to improve the interpretation of organic gunshot residues evidence.

5. Ethics

UTS Human Research Ethics Committee (HREC) approved the presented research (application number 2015000480).

6. Acknowledgment

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