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Should inorganic or organic gunshot residues be analysed first?

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ABSTRACT

Gunshot residues (GSR) collected during the investigation of firearm-related incidents can provide useful information for the reconstruction of the events. Two main types of GSR traces can be targeted by forensic scientists, the inorganic (IGSR) and the organic GSR (OGSR). Up to now, forensic laboratories have mainly focused on the detection of inorganic particles on the hands and clothes of a person of interest using carbon stubs analysed by scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM/EDS). Several approaches have been proposed to also analyse the organic compounds since they might bring additional information for the investigation. However, implementing such approaches might disrupt the detection of IGSR (and vice versa depending on the applied sequence of analysis). In this work, two sequences were compared for the combined detection of both types of residues. One carbon stub was used for collection, and the analysis was performed either by targeting the IGSR or the OGSR first. The aim was to evaluate which one allows maximum recovery of both types of GSR while minimising losses that might occur at different stages of the analysis process. SEM/EDS was used for the detection of IGSR particles while an ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS) was used for the analysis of OGSR compounds. Extracting OGSR first required the implementation of an extraction protocol that did not interfere with the IGSR particles present on the stub. Both sequences allowed good recovery of the inorganic particles since no significant difference was observed in the detected concentrations. However, OGSR concentrations were lower after IGSR analysis than before for two compounds (ethyl and methylcentralite). Thus, it is advised to extract rapidly the OGSR before or after IGSR analysis to avoid losses during the storage and analysis processes. The data also indicated that there was a low correlation between IGSR and OGSR highlighting the potential of a combined detection and analysis of both types of GSR.

1. Introduction

During or immediately after the discharge of a firearm, residues (e.g., particles, elements, and compounds) known as gunshot residues (GSR) are generated and transferred on all surfaces near the firearm and the target [1,2]. Two main types of GSR are produced and reported in the literature: the inorganic and organic GSR (I and OGSR). IGSR are metallic particles formed after the vaporisation and condensation of inorganic elements mainly found in the primer mixture while OGSR are organic compounds that originate from the incomplete ignition, vaporisation, and condensation of the propellant powder [1,3–5]. To date, forensic laboratories primarily analyse IGSR using scanning electron microscopy coupled to energy dispersive X-ray spectrometry (SEM/EDS) [6–9]. This highly sensitive and specific technique allows the detection of inorganic particles on a specimen and provides information on their elemental compositions and morphology [10,11]. Recent studies suggest that OGSR could bring additional information in the investigation of shooting events, particularly when heavy-metal-free ammunition was used [12–14]. OGSR can also contribute to the estimation of the distance or time of shooting [15–17]. Standard practice has been recently proposed for the analysis of OGSR using liquid chromatography coupled to mass spectrometry (LC-MS) or gas chromatography coupled to mass spectrometry (GC-MS) [18,19]. LC-MS presents lower LOD values and was successfully implemented in some forensic laboratories [20,21]. However, the implementation of OGSR analysis in practice still requires the development of an efficient protocol for the combined analysis of I and OGSR allowing a maximum recovery with a minimal loss of both types of residues. The best option would be the simultaneous collection and analysis of I and OGSR with one analytical instrument [22–25]. While this option is particularly interesting, to date, no method showed sufficiently

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Table 1
Summary of the specimens collected to compare the different analysis sequences (*OGSR only* and *IGSR first*) and the two OGSR extraction protocols (reference and new).

Sequence name	Number of specimens		Total	IGSR analysis (Carbon deposition and SEM/EDS)	OGSR analysis (UHPLC-MS/MS)	
	Right hand	Left hand			Order of analysis	Extraction method
IGSR first	12	12	**24**	First	Second	Reference (350 µL for 15 min)
OGSR first	12	12	**24**	Second	First	New (120 µL for 30–35 sec)
OGSR only	12	12	**24**	–	Only	Reference (350 µL for 15 min)
Total	**36**	**36**	**72**	**48**	**48 references 24 news**	

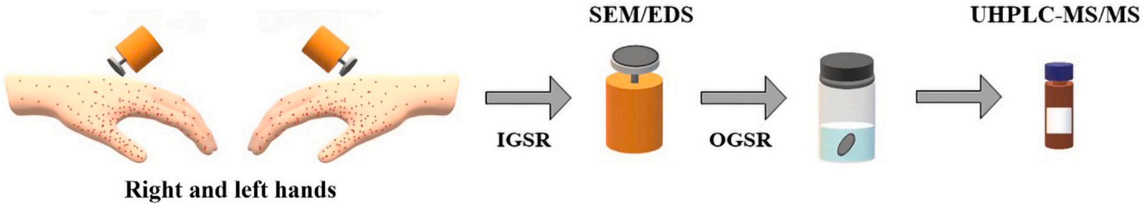

Fig. 1. Schematic representation of the sequence analysing the *IGSR first*. After GSR collection on both hands, a carbon layer was deposited on the adhesive, and IGSR were analysed using SEM/EDS. Then, OGSR were extracted and analysed using UHPLC-MS/MS.

low LOD values for both types of GSR [22,24]. Another option is to collect two separate specimens or to divide the collected specimen into two for the parallel extraction and analysis of IGSR and OGSR using different methods [26–29]. The main disadvantage of this approach is that part of the GSR is necessarily lost, as only the dedicated specimen is analysed for either I or OGSR. A third option is to collect GSR with one device and then analyse both GSR types in sequence with two different instruments [30–36]. The risk of this last approach is that the first analysis may induce a loss of the subsequently analysed GSR type. Losses can occur at different stages of the IGSR or OGSR analysis. The specimen preparation, the exposure to a vacuum environment (carbon coating or SEM/EDS) and the OGSR extraction method are examples of steps that can induce losses of IGSR and/or OGSR. Several promising approaches were proposed in the literature for this sequential analysis [21,31,35]. Thus, the purpose of this research was to evaluate which analysis sequence induced the least loss: IGSR first or OGSR first. IGSR were analysed using a standardised SEM/EDS protocol [37] while OGSR were analysed using ultra-high performance liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). Two OGSR extraction protocols were also compared as the extraction of OGSR from the adhesive stub can hamper further IGSR analysis. Finally, the correlation between IGSR and OGSR results has been studied to evaluate the potential added value of OGSR in practice.

2. Material and methods

2.1. Shooting sessions and specimens collection

Shooting sessions were conducted in an indoor shooting range. For all the tests, a semi-automatic 9 mm Parabellum Sig Sauer P226 was used with Geco Sinoxid® ammunition (batch no. 41 NM 069). Before starting the experiments, the firearm was completely dismantled, cleaned, and lubricated with WD-40®. Then, ten consecutive discharges were performed to minimize memory effects.

During the experiments, the ventilation was turned off and between each shot, the external parts of the firearms and the magazine were cleaned with methanol to reduce the risk of GSR accumulation and contamination. A total of 36 shots were carried out and between each shot, the volunteer washed his hands with soap. The firearm was held with both hands and the right index finger pulled the trigger. Specimens were collected directly after one shot (within 5 min) on both hands with two stubs (one for each hand). The aluminium stubs, inserted in a plastic holder with a large cap, were mounted with double-sided carbon adhesives (Plano, Germany). Each stub was dabbed between 100 and 150 times on each hand respectively (palm and back of the hand including the fingers). No blanks were collected as the risk of contamination was considered minimal (i.e., high concentrations were expected directly after the discharge) [38,39]. After GSR collection, the specimens were stored at − 24 °C until analysis using SEM/EDS or UHPLC-MS/MS.

2.2. Sequences for the analysis of IGSR and OGSR

Two sequences for the analysis of IGSR and OGSR were tested and compared. In total, 72 specimens were collected 36 from the right hand and 36 from the left hand. 24 specimens were analysed for IGSR first, 24 for OGSR first and 24 for OGSR only (as a reference) (**see** Table 1).

2.2.1. IGSR first

For this sequence the IGSR were analysed first using SEM/EDS (Fig. 1). After sampling on both hands, a layer of carbon was deposited on the stubs' adhesives to avoid charging effects and limit the evaporation of volatile OGSR [1]. The stubs remained for 24–30 h in the SEM/EDS. OGSR compounds were then extracted and analysed with a UHPLC-MS/MS. The carbon adhesive was removed from the aluminium stub with cleaned tweezers and deposited in a 15 mL vial. The extraction was performed by adding 350 µL of methanol (grade ULC-MS from Biosolve, France) and by placing the vial for 15 min in an ultrasonic bath at room temperature. Preliminary tests indicated that a volume of 350 µL was the minimal amount in which the adhesive could be entirely immersed for extraction. Extracts were filtered through a 0.2 µm Chromafil PTFE syringe filter (Macherey-Nagel, Germany) and transferred into a vial of 2 mL with an insert of 250 µL. The vials were stored in the freezer at − 24 °C until analysis.

2.2.2. OGSR first

To extract the OGSR first, without removing the IGSR particles, another extraction method needed to be used [35]. Rather than placing the carbon adhesive in the solvent, 120 µL of methanol was deposited on the carbon adhesive (Fig. 2). Preliminary tests showed this volume to be the maximal quantity that could be placed on the stub without spilling over the edge. To ensure that the solvent was well distributed on the adhesive, slight twisting movements of the stub were performed. After 30–35 sonds, the extract was recovered by pipetting from the edge and by transferring it into a 250 µL insert in a 2 mL vial. A shorter extraction time was needed for this protocol to avoid evaporation of the extraction solvent. The vials were stored

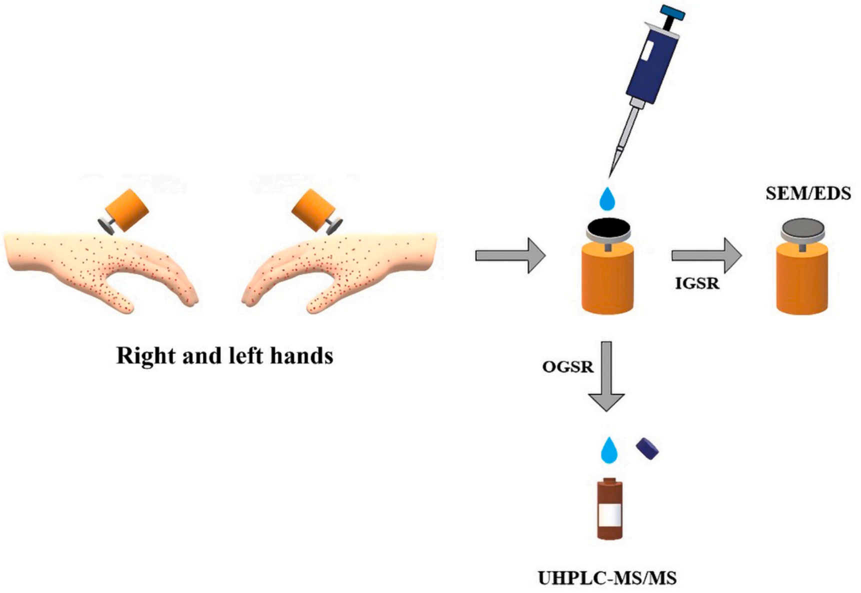

Fig. 2. Schematic representation of the sequence analysing the *OGSR first*. After GSR collection on both hands, OGSR were extracted and analysed using UHPLC-MS/MS. A carbon layer was then deposited on the adhesive and IGSR were analysed using SEM/EDS.

in the freezer at − 24 °C until UHPLC-MS/MS analysis. Particular attention was taken at all stages of the extraction process, to avoid any contact between the adhesive and the pipette tip to ensure no displacement of inorganic particles. After the OGSR extraction, a layer of carbon was deposited on the adhesives and the inorganic particles were detected using the SEM/EDS.

2.2.3. OGSR only

For both sequences, two different OGSR extraction protocols were applied. The reference protocol required the immersion of the adhesive in an organic solvent as described above (Section 2.2.1). This protocol is commonly reported in the literature as having good recovery rates for the OGSR compounds (above 90%) [36,40,41]. However, another option is required to extract the OGSR first, without altering the stub for subsequent IGSR analysis. This "new" protocol was recently proposed to avoid interference with the subsequent IGSR analysis by the deposition of a smaller volume of organic solvent on the adhesive as described above (Section 2.2.2) [35]. To evaluate the efficiency of this "new" OGSR extraction protocol, obtained results were compared with the "reference" method (see OGSR only in Table 1).

2.3. GSR analysis

2.3.1. IGSR analysis

A Carbon coater *108carbon/A* from Cressington Scientific Instruments was used to deposit a carbon layer on the adhesives. A vacuum pressure of at least 0.1 mbar and a current between 100 and 150 A were applied. The analysis was carried out using a Σigma SEM/EDS with GEMINI technology® from Zeiss equipped with a 60 mm^2 X-Max detector from Oxford Instruments. A working distance of 8.5 mm and an accelerating voltage of 20 kV were used. Particles were searched according to the classification of inorganic particles in the standard protocols for the IGSR analysis with the SEM/EDS (such as the ASTM, OSAC, ENFSI, and SWGGSR guidelines) (Table 2) [37,42–44].

Due to the high concentrations of IGSR expected shortly after the discharge, stubs were analysed for a defined period (4 h per stub). For 43 out of 48 specimens, the entire surface was scanned corresponding to an area of approximately 78.0 mm^2 (the diameter of the carbon adhesive was on average d = 10.5 mm ± 1 mm). For the 5 remaining specimens, more than half of the stub was analysed with areas ranging from 40 to 70 mm^2. Thus, the results were reported as concentrations, the number of particles per analysed surface in mm^2 (rather than absolute numbers). Manual confirmation of the elemental composition and morphology of the detected particles was not carried out due to time restraints. It was considered less crucial from a research perspective.

2.3.2. OGSR analysis

Eight organic compounds were targeted in this research as they are commonly found in ammunition and detected after the discharge of a firearm [13,34,45,46] (Table 4**):** Nitroglycerin (NG), diphenylamine (DPA), *N*-nitrosodiphenylamine (*N*-nDPA), akardite II (AK-II), ethylcentralite (EC), 2-nitrodiphenylamine (2-nDPA), 4-nitrodiphenylamine (4-nDPA), and methylcentralite (MC). Stock solutions containing 100 µg/mL of each standard in methanol or acetonitrile were purchased from NEOCHEMA (Germany). Calibration standards from 0.1 to 5 ng/mL for the MC, 4-nDPA, and 2-nDPA, from 100 to 16000 ng/mL for the NG, and from 0.5 to 100 ng/mL for the AK-II, N-nDPA, DPA and EC (10 levels in duplicate), were prepared for the quantification of the specimen concentration.

Detection of the targeted organic compounds was performed using a UHPLC-MS/MS instrument from AB Sciex. An ExionLC™ AD system (UHPLC capabilities) was used for chromatographic separation. This instrument was equipped with a Kinetex Core-Shell C18 LC column (2.6 µm x 2.1 mm × 100 mm) from Phenomenex, maintained at 40 °C during the analyses. Table 3 summarises the parameters of the positive and negative ionisation mode methods. Solvents (acetonitrile, methanol, and water) and formic acid were ULC-MS grade and were purchased from Biosolve (France).

The QTRAP 6500 + mass spectrometer operated in multiple reaction monitoring (MRM). Table 4 summarises the MS/MS parameters of each organic compound. In positive mode, an electrospray Turbo V Ionization Source probe was used to ionise MC, AK-II, EC, N-nDPA, DPA, 2-nDPA, and 4-nDPA. A voltage of 5500 V, a desolvation temperature of 500 °C, a curtain gas of 25 psig, and a turbo gas of 50 psig were used. In negative mode, the only targeted compound was NG. This compound is known to be unstable and according to previous tests, a softer ionisation was more adequate for its detection [47,48]. Thus, an atmospheric pressure chemical ionization

Table 2
Classification of the inorganic particles according to the ASTM E1588–20 guidelines [37].

Classification	Elemental Compositions	
	Sinoxid-type primer	Lead-free / Non-toxic primer
Characteristic particles	PbSbBa	GdTiZn, GaCuSn
Consistent particles	PbBaCaSi, BaCaSi, BaSb, PbSb, BaAl, PbBa	TiZn, Sr
Commonly associated particles	Particles with one of the following compositions: Pb, Sb or Ba	–

Table 3
UHPLC parameters.

Ionisation	*Positive mode*			*Negative mode*		
Flow rate	0.25 mL/min			0.40 mL/min		
Injection volume	5 µL			5 µL		
Gradient method	**Time [min]**	**Mobile phases**		**Time [min]**	**Mobile phases**	
		Water + 0.1% v/v formic acid [%]	**Acetonitrile + 0.1% v/v formic acid [%]**		**Water**	**Methanol**
	0	65	35	0	80	20
	0.5	65	35	1	80	20
	6	20	80	6	50	50
	7	0	100	8	50	50
	7.5	0	100	9	0	100
	8.1	65	35	10	0	100
	10	65	35	10.5	80	20
	–	–	–	14	80	20

(APCI) probe was used with a source temperature of 137.5 °C, a curtain gas of 30 psig, and an ion source gas of 36 psig.

Furthermore, blank stubs were stored in the laminar flow hood and the laboratory for 72 h before the specimen preparation to detect contamination in the laboratory environment [49,50]. A stub was also placed in the flow hood during OGSR specimen extraction to identify contamination that may occur. Carbon adhesives were additionally analysed to determine whether inorganic elements or organic compounds were present in the sampling material. DPA, EC, and MC were detected in the carbon adhesives, but always below the limits of quantitation **(see LOQ values in** Table 4**)**.

2.4. Data analysis

Median as well as relative standard deviation (RSD) were calculated to compare the IGSR results of the two analysis sequences and OGSR extraction methods. Boxplots were built to illustrate the distribution of the results. Statistical analysis was also performed to determine whether there was a significant difference between the obtained results. Since the majority of the data did not follow a normal distribution, a nonparametric test, the Mann-Whitney U test, was applied (a two-tailed hypothesis with a significance level of 0.05). Furthermore, to establish whether there was a correlation between IGSR and OGSR results, a Pearson correlation coefficient matrix was built. The data were transformed by the square root to reduce the influence of some variables exposing high concentrations (values in the same order of magnitude).

3. Results and discussion

3.1. IGSR results

The blanks and the carbon adhesives did not contain any of the targeted inorganic elements **(see in** Table 2**)**. The concentrations of characteristic particles were compared between the two sequences**.** On the right hand, higher median concentrations were obtained with the *IGSR first* sequence with a median of ~37 particles/mm^2 compared to a median of ~18 particles/mm^2 obtained with the *OGSR first* sequence. However, the results were very variable for both approaches with RSDs of 108% and 74%, respectively **(**Fig. 3**)**, and the observed difference was not statistically significant **(see** Table 5**)**. Similarly, results for the left hand were not significantly different

Table 4
Target OGSR compounds and MS/MS parameters.

Compound	Parent ion [*m/z*]	Declustering potential [V]	LOQ [ng/mL]	Product ion [*m/z*]	Collision energy [V]	Collision Cell Exit Potential [V]	Ionization mode
Nitroglycerin (NG)	227	-5	2	107.8	-7	-10	APCI-
	$[M]^-$			62	-9	-7	
Diphenylamine (DPA)	170.1	51	0.1	93	25	10	ESI+
	$[M + H]^+$			92.1	31	10	
***N*-nitrosodiphenylamine (*N*-nDPA)**	199.0	21	0.02	66	29	8	ESI+
	$[M + H]^+$			169	15	20	
Akardite II (AK-II)	227	61	0.04	170	33	20	ESI+
	$[M + H]^+$			91	23	10	
Ethylcentralite (EC)	269.1	40	0.04	148	29	16	ESI+
	$[M + H]^+$			120	19	10	
2-nitrodiphenylamine (2-nDPA)	215.0	91	0.02	180	19	20	ESI+
	$[M + H]^+$			198	23	20	
4-nitrodiphenylamine (4-nDPA)	215.0	191	0.1	198	43	20	ESI+
	$[M + H]^+$			167	21	18	
Methylcentralite (MC)	241.1	31	0.02	134	19	14	ESI+
	$[M + H]^+$			62	-9	-7	

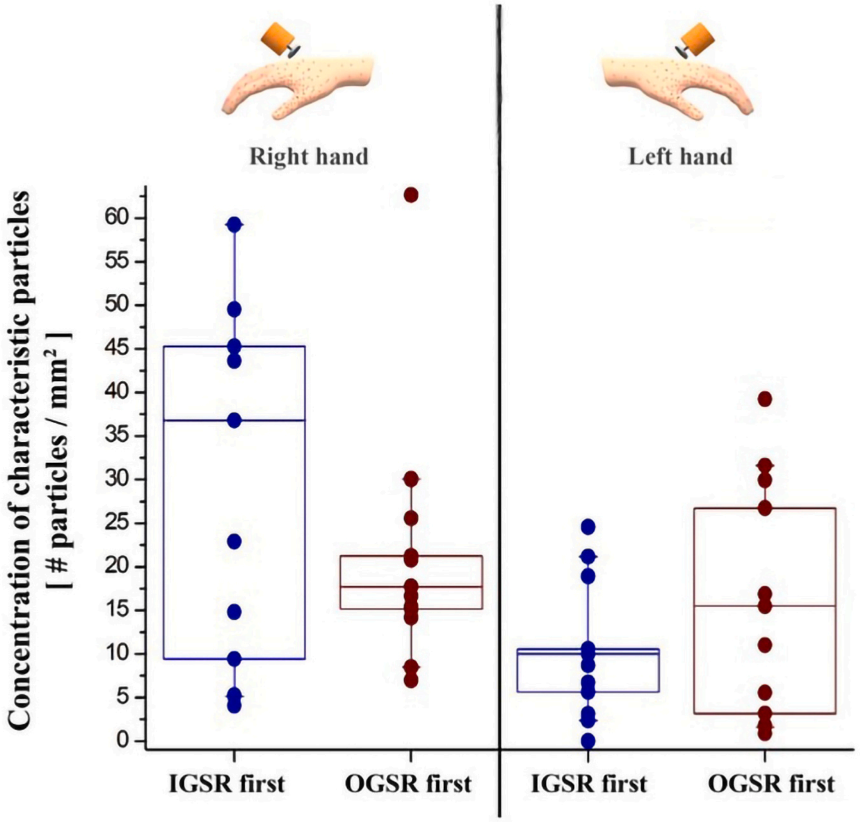

Fig. 3. Boxplots representing the concentrations of characteristic particles per mm^2 detected on the stub collected from the right and left hands of a shooter immediately after a single shot (n = 12 / sequence / hand).

with medians of ~11 (RSD of 76%) and ~16 (RSD of 88%) particles/mm^2 for the *IGSR first* and the *OGSR first* sequences, respectively (Fig. 3 **and** Table 6). Based on these results and the statistical comparison (i.e., Mann-Whitney U test), it can be concluded that there was no significant loss of characteristic IGSR particles during the extraction of OGSR (i.e., OGSR *first* sequence) compared to the IGSR *first* sequence.

The concentrations of consistent particles were also compared between the two sequences. In both cases, particles having the elemental composition of BaSiCa and BaSb showed the highest concentrations while PbBa particles showed the lowest concentrations (Figs. 4 and 5). As for the characteristic particles, very high RSD values were obtained (Tables 5 and 6**).** Statistical comparison indicated a significant difference between the two sequences only for the BaAl particles detected on the left hand (p-value < 0,05), showing a slightly higher median concentration with the *OGSR first* sequence compared to the *IGSR first* (with median values of 3 vs. 2 particles /mm^2). This observation can be explained by the very high variation of the results, illustrating that more replicate would be useful for such statistical comparison. A misclassification of the composition of the particles could also explain the results as no manual confirmation was performed increasing the possibility of an error in the elemental composition of the consistent particles. Indeed, if a loss occurred it should be observed for the OGSR *first* rather than the IGSR *first* sequence. Therefore, for consistent particles, results indicated that the two sequences allowed similar recoveries of particles at least shortly after the discharge, and within the important variability induced by "case-specific" difference from discharge to discharge [14].

Finally, the concentrations of commonly associated with GSR particles were also compared between the two sequences **(see** Tables 5 and 6**, and** SI – Figs. 1 and 2). No significant differences were observed

Table 5
Summary of the median, RSD and statistical analysis of IGSR particles recovered on the right hand of a shooter after a single shot.

Right hand							
Combined method		IGSR first		OGSR first		Comparison of both approaches	
Class of particles	Composition	Median [# particles/mm^2]	*RSD [%]*	Median [# particles/mm2]	*RSD [%]*	Mann-Whitney U test	
						p-value	Significant difference
Characteristic	PbSbBa	36.79	108	17.72	74	0.62	**No**
Consistent	BaSiCa	9.78	89	12.57	58	0.19	**No**
	BaSb	9.90	116	14.66	71	0.26	**No**
	PbSb	3.80	75	1.86	63	0.19	**No**
	BaAl	2.02	111	3.25	81	0.17	**No**
	PbBa	2.52	104	0.98	38	0.08	**No**
Commonly associated with GSR	Pb	2.39	42	2.17	110	0.93	**No**
	Sb	1.01	144	1.09	62	0.40	**No**
	Ba	0.16	166	0.24	92	0.75	**No**

Table 6
Summary of the median, RSD and statistical analysis of IGSR particles recovered on the left hand of a shooter after a single shot.

Left hand							
Combined method		IGSR first		OGSR first		Comparison of both approaches	
Class of particles	Composition	Median [# particles/mm^2]	*RSD [%]*	Median [# particles/mm2]	*RSD [%]*	Mann-Whitney U test	
						p-value	Significant difference
Characteristic	PbSbBa	10.57	76	15.51	88	0.51	**No**
Consistent	BaSiCa	6.58	117	14.62	57	0.09	**No**
	BaSb	6.20	116	8.67	154	0.62	**No**
	PbSb	3.13	74	1.05	76	0.07	**No**
	BaAl	1.77	121	3.10	27	0.02	**Yes**
	PbBa	0.88	82	0.71	43	0.51	**No**
Commonly associated with GSR	Pb	2.00	73	2.02	51	0.12	**No**
	Sb	0.94	112	1.80	93	0.41	**No**
	Ba	0.05	133	0.17	81	0.17	**No**

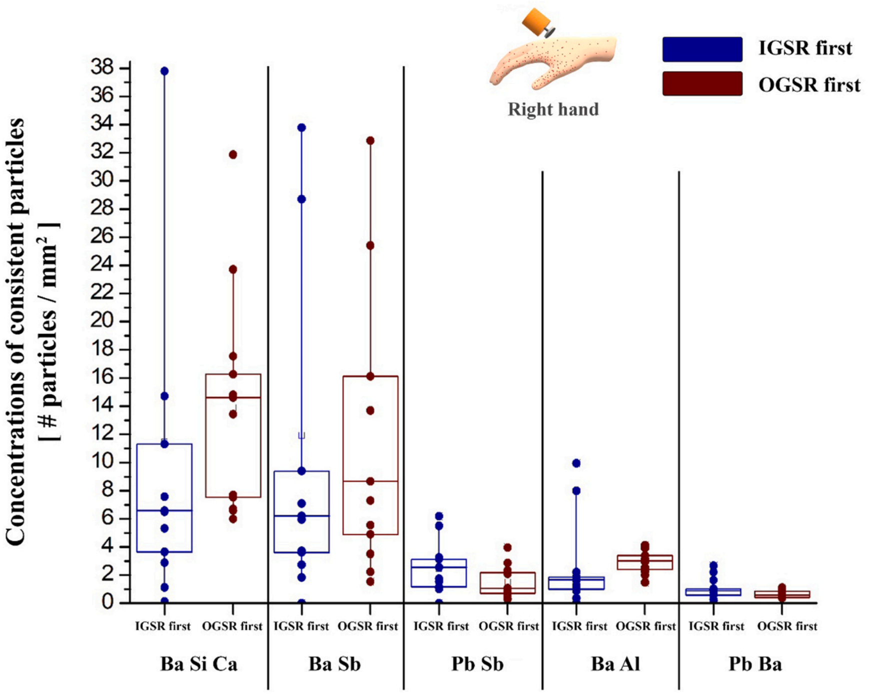

Fig. 4. Boxplots representing the concentrations of consistent particles per mm^2 detected on the stub collected from the right hand of a shooter immediately after a single shot (n = 12 / sequence).

between the two sequences. Additionally, no significant differences were observed between the right and left hand for the characteristic, consistent, and commonly associated with GSR particles.

The comparison of IGSR results between the two sequences was conducted to determine whether the OGSR extraction by placing solvent on the carbon adhesive with a pipette led to losses of inorganic particles. While this step was considered critical since it could impact the IGSR particles found on the stub (i.e., may remove some of the IGSR particles collected), our results indicated no significant differences between the characteristics, consistent or commonly associated with GSR particles detected with both sequences. To further evaluate if the extraction provoked a displacement of IGSR particles, the location of the three classes of inorganic particles on the stub was studied for all specimens. 23 out of 24 specimens for which OGSR were extracted first (OGSR *first* sequence) showed a random distribution of IGSR (Fig. 6). The same random distribution was observed for the 24 stubs analysed first with SEM-EDS before OGSR extraction (*IGSR first* sequence).

However, for one specimen a clustering of IGSR particles was observed on the stub surface and might be due to a displacement of inorganic particles during the OGSR extraction. The concentration of characteristic particles for this stub collected on the right hand was 18, while the median value was ~18 (Table 5). Thus, special care must be taken during the OGSR extraction to avoid disruptive movements and contact between the adhesive and the pipette tip. Further experiments should be conducted to confirm that displacement was/could be induced by the OGSR extraction. Furthermore, it was observed that old carbon adhesives may lift after the OGSR extraction due to the loss of adhesiveness with time (e.g., for relatively old stubs[1]), thus hampering subsequent SEM-EDS analysis. Thus, care must be taken to use relatively recent carbon adhesive stored adequately (e.g., less than 6 months old).

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[1] These observations were shared by several forensic laboratories during a recent discussion about problems encountered with older adhesive stubs. It was suggested that stubs should not be stored too long at a higher temperature, such as in a car in the summer, as this might accelerate the ageing process. Further tests should be conducted to determine how and how long can stubs be stored.

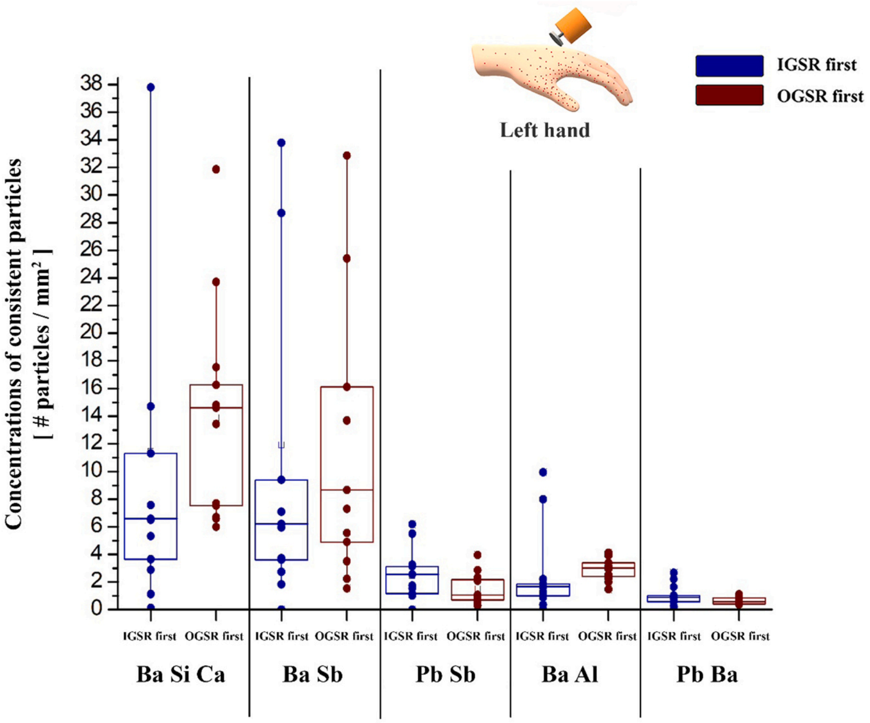

Fig. 5. Boxplots representing the concentrations of consistent particles detected per mm^2 detected on the stub collected from the left hand of a shooter immediately after a single shot (n = 12 / sequence).

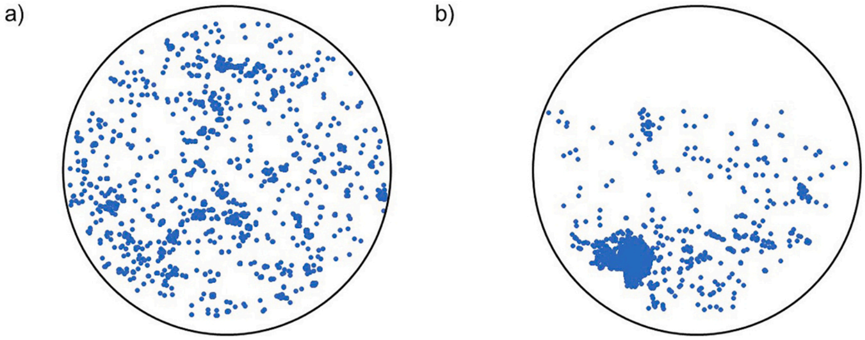

Fig. 6. Illustrations representing the distribution of all selected classes of IGSR particles on the analysed surface after OGSR extraction (specimens collected on the right hand): (a) The particles were randomly distributed on the stub, and b) The particles were concentrated on a spot on the left and bottom of the stub indicating a potential displacement of the IGSR particles during the OGSR extraction process. In both cases, the entire surface of the adhesive was scanned.

3.2. OGSR results

3.2.1. Comparison of two OGSR extraction methods

Two methods were tested for the extraction of OGSR. The extraction efficiency was expected to be higher with the “reference” protocol requiring the immersion of the carbon adhesive for a few minutes in a vial than with the “new” protocol involving the deposition of a small volume of solvent with a pipette on the adhesive for a few seconds [35,36,41]. However, OGSR can only be analysed first if no (or minimal) alteration of the IGSR particles results from the extraction step *(see Section 3.1 . above)*. Thus, while both extraction methods can be implemented for the IGSR *first* sequence, only the second extraction method requiring a smaller volume and a shorter extraction time can be implemented for the OGSR *first* sequence. The two extraction methods were compared to determine if extraction efficiency was similar or if one approach allowed a better recovery of the OGSR compounds. Since the final volume was different between the two extraction methods (350 vs 120 µL), the recovered quantities were also compared. Concentrations and recovered quantities were reported since the final volume was different between the two extraction methods (350 vs 120 µL). The concentrations reflect the value detected by the UHPLC-MS/MS instrument for the injected volume (extrapolated from the calibration curves), while the recovered quantities express the total amount of OGSR that was extracted on the stub.

In both cases, the organic compound with the highest concentrations/quantities was NG (Fig. 7). NG constitutes a large proportion of the ammunition since it is one of the primary explosives used in ammunition [29,46,51]. Detected concentrations were not significantly different between the two protocols (Tables 7 and 8 - left). However, recovered quantities were significantly higher for the “reference” compared to the “new” extraction method (see Tables 7 and 8 - right). Comparable observations were made for 4-nDPA, *N*-nDPA, 2-nDPA, DPA, AK-II, MC, and EC (Tables 7 and 8, Figs. 8 and 9, and SI - Figs. 3 to 7), with similar concentration values between the extraction methods but significantly higher quantities for some compounds when using the reference extraction method **(see** Tables 7 and 8): 4-nDPA and DPA quantities were significantly higher on

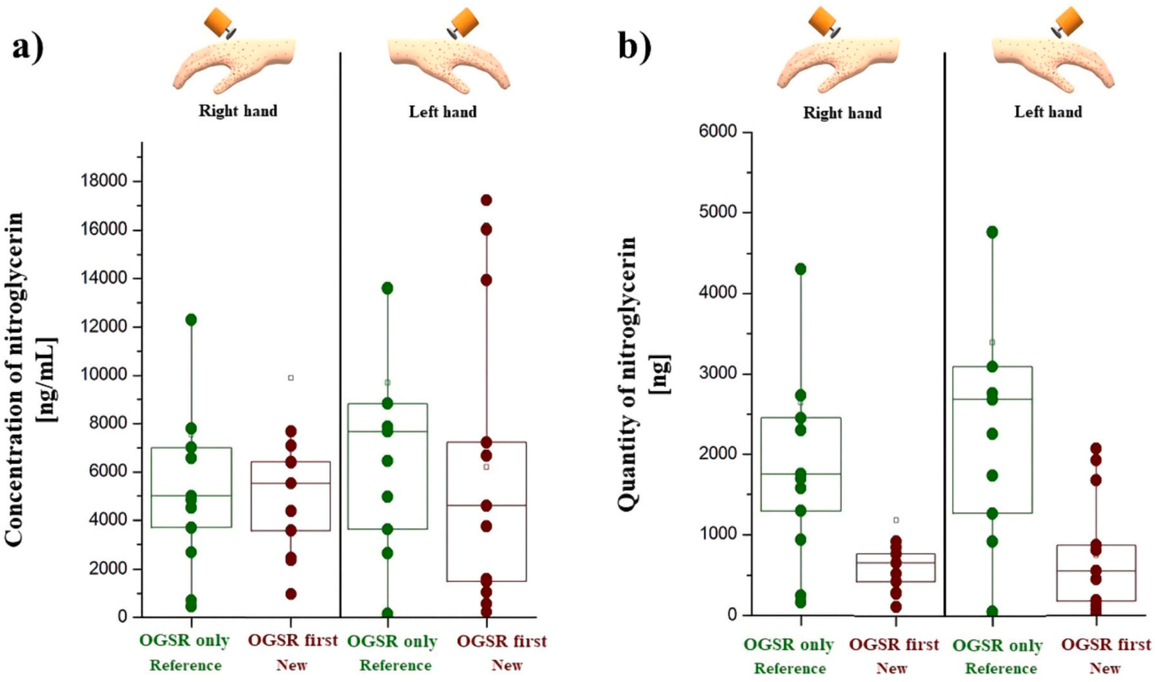

Fig. 7. Boxplots representing the concentrations of nitroglycerin (NG) detected from the sampling of both hands of a shooter immediately after a single shot (n = 12 / OGSR extraction method / hand). (a) The detected concentrations b) the recovered quantities.

Table 7
Summary of the median concentration, RSD, and statistical comparison of OGSR compounds recovered on the right hand of a shooter after a single shot using two different extraction methods: "Reference" (adhesive extracted in 350 μL of methanol for 15 min) and "New" (120 μl deposited on the adhesive 30 s).

Right Hand												
	Detected concentrations						Recovered quantities					
OGSR extraction	OGSR only (Reference)		OGSR first (New)		Comparison between both extraction methods		OGSR only (Reference)		OGSR first (New)		Comparison between both extraction methods	
Compounds	Median [ng/mL]	*RSD [%]*	Median [ng/mL]	*RSD [%]*	Mann-Whitney U test		Median [ng/mL]	*RSD [%]*	Median [ng/mL]	*RSD [%]*	Mann-Whitney U test	
					p-value	Significant difference					p-value	Significant difference
NG	5008.00	122	5534.00	187	0.79	**No**	1752.80	122	664.08	187	0.02	**Yes**
DPA	67.58	86	73.71	121	0.98	**No**	23.65	86	8.81	121	0.02	**Yes**
***N*-nDPA**	45.71	96	27.63	184	0.51	**No**	16.00	96	3.31	184	0.02	**Yes**
AK-II	19.08	216	36.76	148	0.16	**No**	6.68	216	4.41	148	0.70	**No**
EC	10.45	101	13.70	181	0.19	**No**	3.66	101	1.64	181	0.09	**No**
2-nDPA	1.66	106	2.34	201	0.28	**No**	0.58	106	0.28	201	0.06	**No**
4-nDPA	1.23	82	1.57	147	0.44	**No**	0.43	82	0.19	147	0.05	**Yes**
MC	0.14	53	0.31	59	0.07	**No**	0.05	43	0.04	59	0.02	**Yes**

Table 8
Summary of the median concentration, RSD and statistical comparison of OGSR compounds recovered on the left hand of a shooter after a single shot using two different extraction methods: "Reference" (adhesive extracted in 350 μL of methanol for 15 min) and "New" (120 μl deposited on the adhesive 30 s).

Left Hand												
	Detected concentrations						Recovered quantities					
OGSR extraction	OGSR only (Reference)		OGSR first (New)		Comparison between both extraction methods		OGSR only (Reference)		OGSR first (New)		Comparison between both extraction methods	
Compounds	Median [ng/mL]	RSD [%]	Median [ng/mL]	RSD [%]	Mann-Whitney U test		Median [ng/mL]	RSD [%]	Median [ng/mL]	RSD [%]	Mann-Whitney U test	
					p-value	Significant difference					p-value	Significant difference
NG	7676.00	129	4611.00	100	0.62	**No**	2686.60	129	553.32	100	0.02	**Yes**
DPA	86.07	90	66.16	94	0.28	**No**	30.13	90	7.94	94	0.01	**Yes**
***N*-nDPA**	45.41	115	24.35	112	0.70	**No**	15.89	115	2.92	112	0.06	**No**
AK-II	22.40	151	28.45	109	0.28	**No**	7.84	151	3.41	109	0.79	**No**
EC	13.58	148	11.46	108	0.70	**No**	4.75	148	1.38	108	0.01	**Yes**
2-nDPA	3.03	108	1.38	135	0.37	**No**	1.06	108	0.17	135	0.01	**Yes**
4-nDPA	1.35	108	1.22	132	0.45	**No**	0.47	108	0.15	132	0.02	**Yes**
MC	0.13	143	0.16	164	0.24	**No**	0.04	143	0.02	164	0.20	**No**

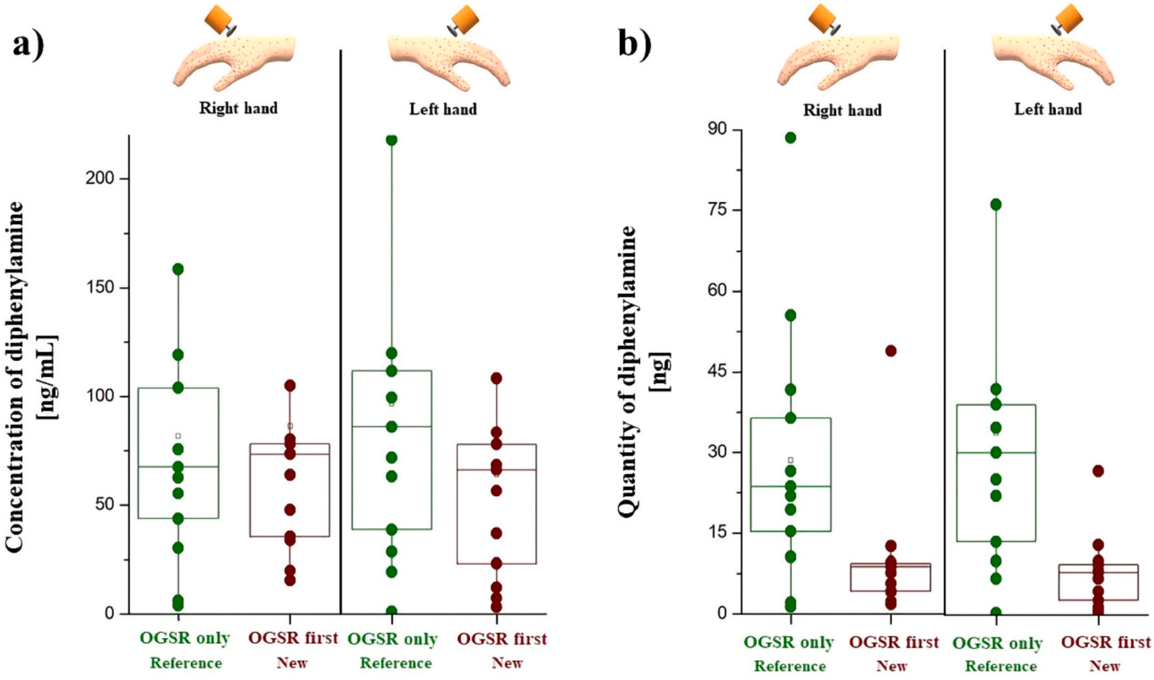

Fig. 8. Boxplots representing the concentrations of diphenylamine (DPA) detected from the sampling of both hands of a shooter immediately after a single shot (n = 12 / OGSR extraction method / hand). (a) The detected concentrations b) the recovered quantities.

both hands, while MC, EC, N-nDPA and 2-nDPA were significantly higher only on one of the two hands. All obtained p-value indicating a significant difference was relatively close to the threshold ($0.01 < \text{p-value} < 0.05$). No significant difference was observed in the amount of AK-II.

Thus, the quantities recovered using the “reference” method were slightly better for some OGSR compounds meaning that the extraction was more efficient with this protocol for these organic compounds. However, both extraction methods resulted in comparable concentrations for all compounds. This is mainly due to the different extraction volumes used in the two methods (with a difference of almost a factor 3). As specimen concentration through evaporation may result in a loss of some organic compounds (i.e., the most volatile), the lowest the extraction volume is, and the highest is the final concentration. Thus, the efficacy for both protocols was comparable because extracting with 350 µL led to better but more

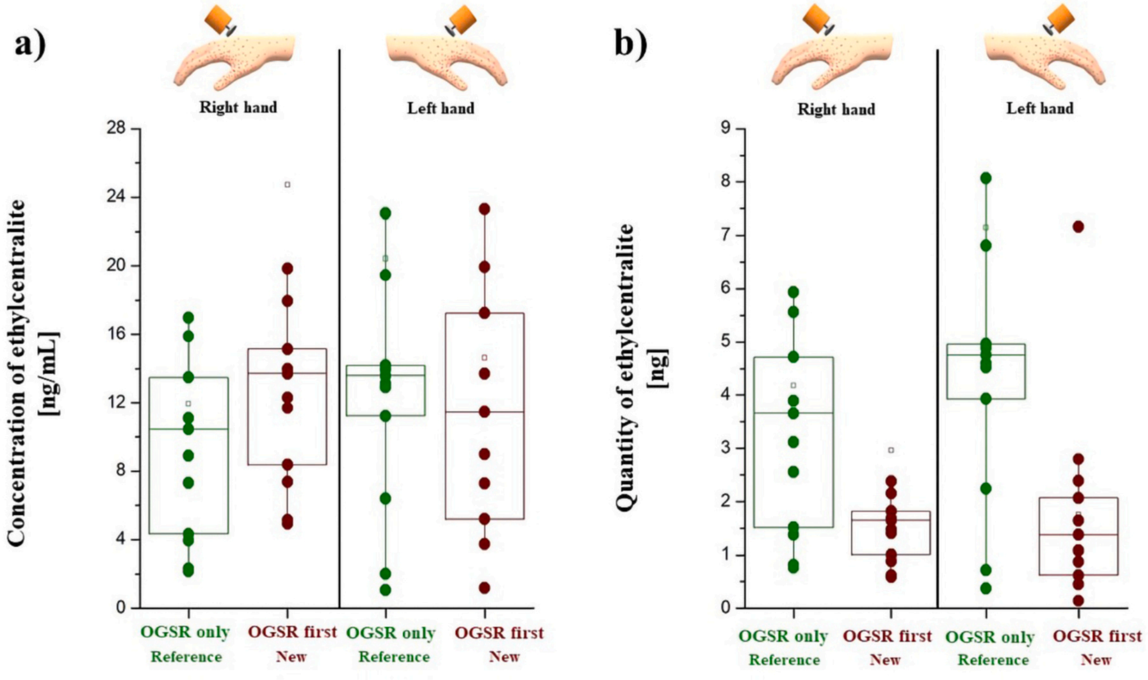

Fig. 9. Boxplots representing the concentrations of ethylcentralite (EC) detected from the sampling of both hands of a shooter immediately after a single shot (n = 12 / OGSR extraction method / hand). (a) The detected concentrations b) the recovered quantities.

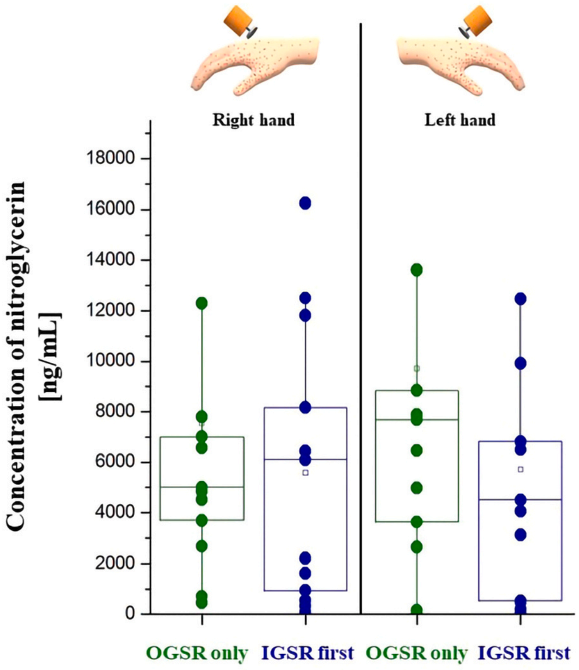

Fig. 10. Boxplots representing the concentrations of nitroglycerin (NG) detected from the sampling of both hands of a shooter immediately after a single shot (n = 12 / sequence / hand).

diluted recoveries, while the lower extraction volumes (120 µL) led to lower amounts but more concentrated specimens (resulting in the same median concentrations for both protocols). It might be interesting to further optimise the "new" OGSR extraction method (e.g., by testing longer extraction time). It has to be noted that the "new" method has the advantage to be efficient with minimal extraction time and steps, thus lowering the risks of contamination and interference for the subsequent IGSR analysis. The stub may also be stored for further (mainly IGSR) analysis.

3.2.2. *Impact of the IGSR analysis on the OGSR recovery*

To evaluate the effect of the carbon deposition and SEM/EDS analysis on OGSR recovery, concentrations obtained before and after IGSR analysis were compared.[2] For all the specimens and similarly to IGSR results, high variability was observed from one shot to another (as indicated by the high RSD values). While this variability was expected as firearm discharge is known to be a highly variable event [38,52,53], the calculated RSDs were higher for OGSR than IGSR concentrations (see Tables 5 and 6 compared to Tables 7 and 8): a mean RSD value of 126% (max = 201%) vs 86% (max = 166%) was obtained for OGSR compared to IGSR concentrations, respectively.

No significant differences between the right and left hand were observed for any of the targeted OGSR compounds, and for most organic compounds, no significant differences in the recovered concentrations were observed between the two analysis sequences (Fig. 10, Tables 9 and 10, and SI – Figs. 8 to 12). However, for MC (on both hands) and EC (only on the right hand), significantly higher concentrations were obtained for the OGSR first protocol, with p-values of 0,02 (Fig. 11, and Tables 8 and 9). MC always showed the lowest concentrations in all specimens and might thus be more impacted by the vacuum environment of the carbon coater and the SEM/EDS instruments.

Table 9
Summary of the median concentration, RSD and statistical comparison of OGSR compounds recovered before and after IGSR analysis on the right hand of a shooter after a single shot.

Right Hand						
Specimens	OGSR only (Reference)		IGSR first (Reference)		Comparison	
Compounds	Median [ng/mL]	RSD [%]	Median [ng/mL]	RSD [%]	Mann-Whitney U test	
					p-value	Significant difference
NG	5008.00	122	6095.00	100	0.62	**No**
DPA	67.58	86	58.67	119	0.26	**No**
***N*-nDPA**	45.71	96	40.76	111	0.40	**No**
AK-II	19.08	216	9.59	188	0.47	**No**
EC	10.45	101	11.40	228	0.62	**No**
2-nDPA	1.66	106	1.67	118	0.51	**No**
4-nDPA	1.23	82	0.78	120	0.21	**No**
MC	0.14	53	0.30	130	0.02	**Yes**

Table 10
Summary of the median concentration, RSD and statistical comparison of OGSR compounds recovered before and after IGSR analysis on the left hand of a shooter after a single shot.

Left Hand						
Specimens	OGSR only (Reference)		IGSR first (Reference)		Comparison	
Compounds	Median [ng/mL]	RSD [%]	Median [ng/mL]	RSD [%]	Mann-Whitney U test	
					p-value	Significant difference
NG	7676.00	129	4501.00	105	0.43	**No**
DPA	86.07	90	67.41	105	0.28	**No**
***N*-nDPA**	45.41	115	34.27	97	0.89	**No**
AK-II	22.40	151	5.77	203	0.21	**No**
EC	13.58	148	8.60	94	0.02	**Yes**
2-nDPA	3.03	108	2.08	93	0.34	**No**
4-nDPA	1.35	108	1.54	92	0.49	**No**
MC	0.13	143	0.05	93	0.02	**Yes**

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[2] While two different OGSR extractions methods were used, the obtained concentrations were not significantly different and could be compared (see Tables 7 and 8 – left).

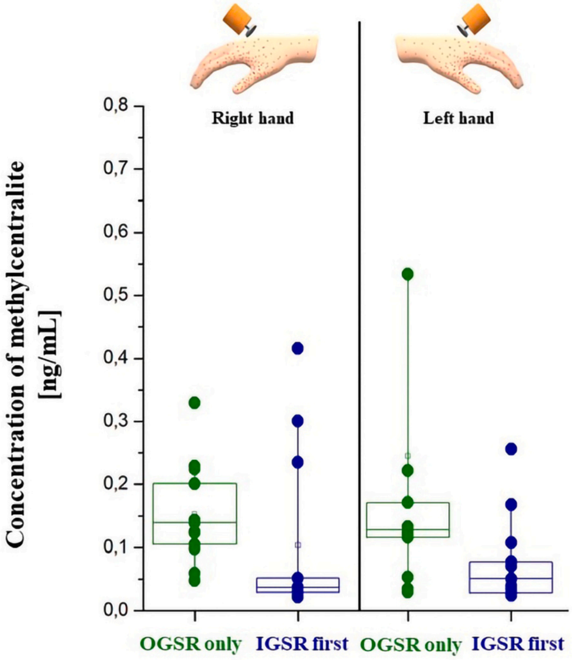

Fig. 11. Boxplots representing the concentrations of methylcentralite (MC) detected from the sampling of both hands of a shooter immediately after a single shot (n = 12 / sequence / hand).

These results indicate that the recovery of some OGSR compounds may be influenced by the IGSR analysis. While DPA and its derivatives are reported in the literature as the most volatile OGSR compounds [41,54], there were apparently not significant impact by the IGSR analysis in this study. Only EC and MC were slightly impacted (p-value = 0,02). Yeager et al. (2015) reported that although less volatile, EC and MC could be degraded [54].

In this research, some parameters were controlled to avoid major losses of OGSR compounds. The time in the vacuum environment of the carbon coater and the SEM/EDS was kept to a minimum (t < 30 h). Moreover, the storage conditions between sampling and analysis were optimised (storage in the freezer at – 20 °C before/after transporting them to/from the SEM/EDS laboratory). However, in practice, it is sometimes difficult to control these parameters. The uncontrolled storage conditions (e.g., some police services tend to collect specimens from several cases before bringing them to the laboratory for practical reasons) and longer analysis times may impact significantly the recovery of OGSR. Thus, the implementation of the IGSR *first* sequence in actual cases would require further testing and/or optimisation of the specimen storage and analysis conditions to ensure minimal OGSR loss.

3.3. Correlation between IGSR and OGSR

To evaluate if the OGSR analysis provides additional information, it is important to determine if and to what extent IGSR and OGSR are correlated. A heatmap of the Pearson correlation coefficient matrix was built with all the combined data collected in this work, to illustrate the values of the correlations obtained for the pair-wise comparison of all GSR variables using (Fig. 12). Heatmaps were also generated separately for the *IGSR first* and *OGSR first* sequences, and results showed a comparable pattern. A low correlation was observed between OGSR and IGSR results. This may be explained by the fact that different mechanisms are involved in the formation and deposition of the different types of residues, and also in the persistence shortly after the discharge (t ~ 0). The heatmap also shows that some OGSR compounds (DPA, 2-nDPA, *N*-nDPA, and NG) were highly correlated (correlation coefficient above 0.90). Inorganic particles were in general less correlated as the highest correlation value was 0.76 (for Ba and BaAl). However, for inorganic particles, results should be taken with caution as no manual confirmation of the elemental composition was performed. These low correlations between IGSR particles and OGSR compounds support the

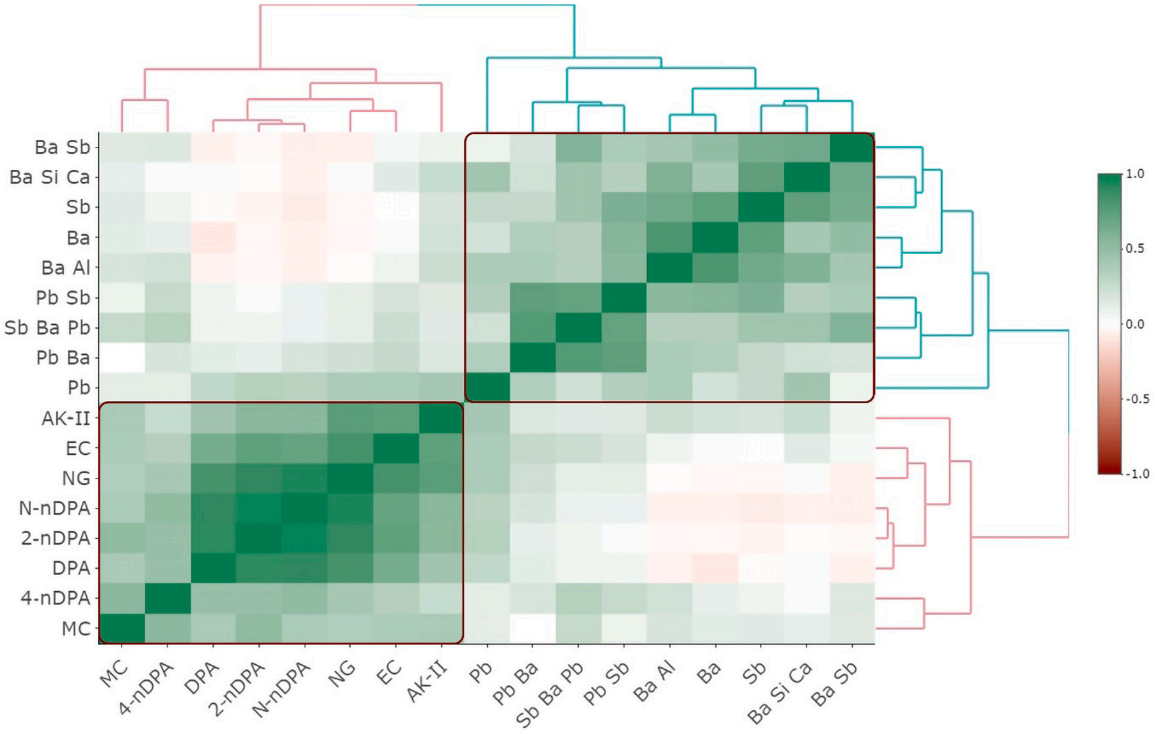

Fig. 12. Heatmap representing the correlation between inorganic particles and organic compounds detected on the hands of a shooter immediately after a single shot (representing the combined data from 48 specimens, 24 per sequence and hand coming from 24 discharge).

hypothesis that OGSR analysis could bring useful complementary information for the reconstruction of shooting events.

4. Conclusions

The purpose of this work was to evaluate if inorganic (I) or organic (O) GSR should be analysed first in a combined analysis sequence that maximises the recovery of both types of GSR. Data from specimens collected shortly after the discharge of a firearm (t ~ 0) indicated that both sequences allowed a comparable recovery of inorganic particles since no significant difference was observed between the results. On the other hand, a slight loss of two OGSR compounds (methylcentralite and ethylcentralite) was observed when IGSR were analysed first. In general, OGSR concentrations were more variable than IGSR ones with mean RSD values of 126% against 86%, respectively.

Analysing the OGSR first required a “new” extraction procedure (i.e., deposition of the solvent on the stub with a pipette rather than immersing the adhesive in solvent). This “new” extraction may disrupt the inorganic particles on the carbon adhesive through the movement of the pipette and solvent during the extraction. A cluster of IGSR particles was observed in one specimen out of 24 and, thus, more research is needed to assess whether this cluster was due to the displacement of IGSR particles during the extraction of OGSR. While the recovered quantities using this “new” protocol were slightly lower for some compounds, no significant differences were observed for the obtained concentrations. This “new” extraction method has the advantage to be more efficient in terms of time (i.e., a gain of ~14 min), solvent amount (i.e., reduced by almost a factor of 3), and preparation steps (i.e., no filtration). If applied correctly (i.e., by avoiding touching the adhesive with the pipette), it is also non-destructive for IGSR as the stub can then be preserved after the IGSR analysis for a potential further IGSR analysis (i.e., counter-expertise). On the other hand, analysing IGSR first has the advantage to maintain actual procedures in forensic laboratories (and avoid any risk of loss however small). However, some OGSR compounds could be lost under the vacuum of the SEM/EDS.

Thus, If forensic laboratories want to implement OGSR analysis in complement to the current IGSR analysis, it is advised to extract rapidly the OGSR before or after proceeding with the IGSR analysis. According to the chosen sequence, it is advised to minimise the time under the vacuum of the SEM/EDS if OGSR are analysed after the IGSR analysis. While further studies are needed to optimise OGSR storage and extraction procedures (if possible, on more realistic samples collected later after the discharge), the potential added value of OGSR in practice was confirmed by the low correlations observed between the two types of residues. This added value has to be further evaluated as a combined GSR analysis requires two relatively expensive and complex instruments.

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CRediT authorship contribution statement

Virginie Redouté Minzière: Conceptualisation, Data curation, Data treatment, Writing – original draft, **Olivier Robyr:** Conceptualisation, Writing – review & editing, workplan, **Céline Weyermann:** Funding acquisition, Conceptualisation, Project administration, Writing – original draft.

Declaration of Competing Interest

None.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.forsciint.2023.111600.

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