

Organic gunshot residues: observations about sampling and transfer mechanisms

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Abstract

This work aimed at studying the sampling, storage, transfer and persistence of organic gunshot residue (OGSR), mainly stabilizers, using liquid chromatography hyphenated to mass spectrometry. Collection using swabs and stubs was compared through sequential sampling in terms of amount of residues left on the hand of a shooter. While stubs collected nearly all residues, swabs left about 50% of the residues on the hands. Moreover, the study of storage conditions after sampling showed that stubs were more stable than swabs and could be held at room temperature without significant compound loss up to two weeks. Then, shooting experiments were performed to evaluate transfer of OGSR. It was not possible to differentiate different brands of ammunition based on a single compound concentration. Moreover, a memory effect was identified when different ammunition was shot using the same firearm. Finally, various exposed skin surfaces and hair as well as clothing were sampled to estimate what surfaces might be the best targets for OGSR sampling by comparing results just after discharge and two hours after discharging a pistol. The results indicated that OGSR were more rapidly lost from hands than from clothing. Moreover, it was shown that the face and hair of a suspect might be contaminated through secondary transfer. Thus, OGSR might remain longer on other skin surfaces, hair and clothing than on the hands of a suspect. As a consequence, sampling should also include clothing, hair and face.

Keywords

Firearm discharge residue; sample collection; swab; stub; LC-MS; persistence

33 1. Introduction

34 Sensitive and robust analytical techniques are essential to face an increasing number of incidents
35 related to firearms, for example to link an individual to an incident or to estimate the firing distance.
36 Gunshot residues (GSR) originate from the primer, propellant, lubricants and metals present in the
37 bullet, cartridge and firearm [1, 2]. A distinction is drawn between inorganic (IGSR) and organic
38 gunshot residues (OGSR) [3]. While in practice the analysis of IGSR using Scanning Electron
39 Microscopy Energy-dispersive X-ray spectroscopy (SEM-EDX) is well established in forensic
40 laboratories, complementary information could be obtained from OGSR. Indeed, the introduction of
41 heavy metal-free or “non-toxic” ammunition on the market presents an additional challenge.
42 Furthermore, the composition of the particles produced by this type of ammunition can also be
43 generated by alternative sources [4]. Therefore, the development of a sensitive and robust method able
44 to detect OGSR without compromising the analysis of IGSR by SEM-EDX is of great interest.

45 The main contribution to OGSR is from propellants that are made up of explosive compounds, as well
46 as a number of additives such as stabilizers, plasticizers or flash inhibitors that confer specific
47 properties to the powder [3]. Based on their explosive content, gunpowders can be single base
48 containing only nitrocellulose (NC), double base containing NC together with nitroglycerine (NG) or
49 triple base containing NC, NG and nitroguanidine [1]. A wide array of analytical techniques were
50 applied to the analysis of OGSR, each with advantages and drawbacks. Nevertheless, no general
51 agreement has been reached on the best technique and research carries on all fronts. Among potential
52 instrumentation, ion mobility spectrometry (IMS) seems promising, because it is a very rapid field
53 technique [5-7]. However, even with considerably improved sensitivity, further confirmatory analysis
54 is required. The past few years have seen the advent of spectroscopic techniques such as Raman [8-12]
55 and Fourier transformed infrared spectroscopy [13, 14] for the analysis of gunpowders and OGSR.
56 However, these instruments do not permit formal compound identification. Furthermore, no
57 quantitative data were obtained and applicability in practice was not demonstrated yet. Mass
58 spectrometry (MS), more particularly desorption electrospray ionization [15, 16] provides fast
59 identification, though matrix effects are a considerable issue and strongly impact sensitivity when no
60 previous separation is performed. Gas chromatography (GC) was found to be highly selective and
61 various detector types were evaluated, namely thermal energy detection (TEA) [17-19], flame
62 ionization detection (FID) [20, 21], nitrogen phosphorous detector (NPD) [22] and MS [6, 17, 19, 23,
63 24]. However, thermolabile compounds such as NG and *N*-nitrosodiphenylamine are degraded by the
64 high temperatures used in GC, even if detection of NG remains possible due to the high concentrations
65 found in gunpowders and OGSR. Capillary electrophoresis [25-30] was also assessed, but as a result
66 of the low volumes injected and small capillary diameter, it appears not to be sensitive enough to be
67 implemented in casework. Finally, liquid chromatography (LC) [31-37] is more suitable for

68 thermolabile analytes, and provided adequate separations. Its coupling with MS detection has largely
69 improved sensitivity, enabling detection of OGSR just after discharge without preconcentration.

70 To date, irrespective of the instrumentation used, most of the studies focused on the development of a
71 method that was applied to the detection of OGSR sampled just after discharge from the shooter's
72 hand or from a target made of cloth or paper. Regarding sampling, some data is available in recent
73 publications that compared sampling materials [34, 36, 37]. All results indicated a preference towards
74 stubs. Techniques applied to OGSR collection were summarized in a recent review [38]. If analytical
75 techniques and sampling are relatively well documented, little is known of specific forensic questions
76 such as transfer and persistence. As expected, the amount transferred on a target depends on the
77 shooting distance [19]. The amount of GSR escaping in the firearm vicinity is a function of the
78 weapon type, revolvers producing normally more residues than pistols [39]. Arndt *et al.* did not
79 observe OGSR secondary transfer, suggesting different interaction mechanisms with skin in
80 comparison to IGSR [5]. Pertaining to persistence, early studies by Lloyd showed that it was possible
81 to detect NG up to 2.5 hours after discharge of several rounds of ammunition, either from the hand
82 [40] or from a garment [41]. In another study, he stated that NG was detected up to seven hours on
83 hands, face and throat, and even up to five days on clothing [42]. King reported average NG values of
84 9 ng and 42 ng for swabbing of hands and vacuuming of clothing in casework between April 1991-
85 April 1992 [43]. Northrop did not observe OGSR on the hand of a shooter one hour after shooting
86 three rounds [26]. In 2003, Zeichner *et al.* detected NG on clothing six hours after firing one round
87 [17]. More recently studies from Bell *et al.* indicated that diphenylamine (DPA) might persist on skin
88 around four hours [5]. They also evidenced absorption of OGSR compounds by the skin due to their
89 lipophilic properties [6]. The authors predicted that with the actual limits of quantification of LC-MS,
90 OGSR detection might be possible for nearly 24 hours after a firing event and that the ideal target
91 analytes for recovery from the skin were ethylcentralite (EC), 2- and 4-nitrodiphenylamine.

92 So far, data was mainly obtained from hand samples. However, some studies also investigated other
93 surfaces and successfully detected NG in the hair of the shooter using either a modified comb or tape-
94 lifting [18, 29]. NG, DPA and EC [32] as well as NG and dinitrotoluenes [17] were also found on
95 clothing sampled by vacuum. Another question of interest relates to the stability of OGSR after
96 sampling, and a study from Yeager *et al.* using swabs indicated a limited storage time from a few days
97 to a few weeks depending on the storage temperature (room temperature and fridge/freezer,
98 respectively) [7]. Finally, the issue of cross-contamination linked to the use of different ammunition in
99 the same firearm might arise, phenomenon sometimes also called memory effect [44]. This
100 phenomenon was already observed for IGSR with particles having mixed composition [45]. In the
101 field of OGSR, Andrasko indicated no contamination from propellant flakes from previous shootings
102 when analyzing OGSR particles recovered on clothing used as target [20]. On the contrary, Northrop

103 observed carryover when using different ammunition [26]. As a consequence, additional research is
104 necessary to get more insight into the issues mentioned above.

105 This study intends to provide some elements of response to questions regarding OGSR sampling,
106 sample storage, transfer and persistence of OGSR. Using LC-MS in positive electrospray ionization
107 (ESI) mode, nine major stabilizers found in OGSR were targeted. This choice was based on the larger
108 number of relevant compounds detected in positive mode, as only nitroglycerine and dinitrotoluenes
109 are analysed in ESI negative. The study was divided in four parts. In the first section, stubs were
110 compared to swabs in terms of collection efficiency using sequential sampling. Zeichner and Levin
111 proposed this approach to evaluate the efficiency of sampling by evaluating what is left after sampling
112 by sampling the surface a second time using another technique [46]. In the second part of the study,
113 storage after sampling was investigated for both stubs and swabs to determine optimal holding
114 conditions. In the third section, shooting experiments were performed to evaluate transfer of OGSR
115 using different ammunition fired by the same firearm. Finally, various exposed skin surfaces and hair
116 as well as clothing were sampled to estimate what surfaces might be the best targets for OGSR
117 potential detection by comparing results just after, as well as two hours after discharging a pistol.

118

119 **2. Material and Methods**

120 *2.1 Chemicals*

121 LC-MS grade water containing 0.1 % formic acid, methanol, formic acid, and acetonitrile were
122 purchased from Sigma-Aldrich (Buchs, Switzerland). Diphenylamine was from Fluka (Buchs,
123 Switzerland). Ethylcentralite, *N*-nitrosodiphenylamine, 4-nitrodiphenylamine, akardite II, 1,3-
124 diphenylurea and *N,N*-diphenylformamide were obtained from Sigma-Aldrich (Buchs, Switzerland).
125 2-nitrodiphenylamine was from Alfa Aesar (Karlsruhe, Germany). Methylcentralite was purchased
126 from MP Biomedicals (Illkirch, France).

127 *2.2 Instrumentation*

128 The experiments were carried out using an Agilent Infinity 1290 ultra-high performance liquid
129 chromatography (UHPLC) from Agilent Technologies. The instrument was equipped with a binary
130 pump enabling a maximum delivery flow rate of 5 mL/min, an autosampler, and a column
131 compartment thermostated at 40°C. Separation was performed using a Kinetex core-shell column from
132 Phenomenex (2.6 µm, 2.1 mm × 100 mm), with a C18 stationary phase. A SecurityGuard ULTRA
133 cartridge with C18 selectivity was used to protect the analytical column. The UHPLC system was
134 hyphenated to a triple quadrupole mass spectrometer (5500 QTrap) from ABSciex. Electrospray
135 ionization was operated in positive mode. The $[M+H]^+$ of the target compounds were defined as the
136 precursor ions, and quantification was obtained from the SRM measurements. MS/MS parameters are

137 given in Table 1. The source parameters were as follows: the desolvation temperature was set to
 138 500°C, the nebulizer gas to 60 psig, the turbo gas to 50 psig and the curtain gas to 25 psig. The
 139 IonSpray voltage was adjusted to 5500 V. Data acquisition, treatment and instrument control were
 140 monitored using Analyst software.

141

142 **Table 1:** Target compounds and MS/MS parameters

Compound	Parent ion [m/z]	Product ions [m/z]	Declustering potential [V]	Collision energy [V]
Akardite II (AK II)	227.1	170.1 91.9	120	27 36
1,3-diphenylurea (1,3-DPU)	213	94 77	100	25 48
Methylcentralite (MC)	241.2	134.1 105.9	125	24 36
N,N-diphenylformamide (N,N-DPF)	198.1	92 65	130	30 54
Ethylcentralite (EC)	269.2	147.9 120	120	20 33
2-nitrodiphenylamine (2-nDPA)	215.1	197 180.1	80	14 23
4-nitrodiphenylamine (4-nDPA)	215.1	197.8 167.1	60	18 47
Diphenylamine (DPA)	170.1	93 66	200	32 58
N-nitrosodiphenylamine (N-nitrosoDPA)	199.1	169 66	60	15 30

143 The organic mobile phase consisted of acetonitrile containing 0.1% of formic acid. Water with 0.1%
 144 formic acid was used as aqueous phase. The following gradient method was used: 35% B (from 0 to
 145 0.5 min), 35–80% B (in 5.5 min), and 80-100% B (in 1 min). The injection volume was 5 µL and the
 146 mobile phase flow rate was set to 0.25 mL/min.

147 A calibration curve was measured for each sequence of experiments to account for instrument
 148 response variation from sequence to sequence. Moreover, to avoid any bias linked to that issue and
 149 allow comparison, sample series for sequential sampling and stability were acquired during a single
 150 sequence.

151 2.3 Shooting experiments

152 Shooting sessions were conducted in an indoor shooting range located in a specific building sector
 153 with the ventilation turned off. Extraction and analysis of the samples was performed in a separate
 154 laboratory in another sector to avoid any contamination of the samples. A semi-automatic 9 mm
 155 Parabellum Sig Sauer P226 was used for all experiments. 9 mm Luger cartridges, all containing heavy

156 metals, were from Geco (batches 62 QS and 54 G K096), Fiocchi, PMP and RUAG Ammotec (Swiss
157 military ammunition). The shooter was asked to wash his hands before entering the shooting range and
158 was not allowed to touch any surface except for the firearm at the time of firing. Another person was
159 in charge of loading the gun. Then, the shooter was asked to hold the gun with both hands and fire one
160 cartridge. He was then sampled outside the shooting range. After sampling, he washed his hands
161 carefully again before starting the procedure once more. The firearm was not cleaned between shots.
162 In this study, shooters were three women, aged between 27 and 40, having mid-long hair and not using
163 hand cream or hair gel.

164 2.4 Sampling of OGSR

165 Two sampling methods were compared in the study: swabs and stubs. ESD polyester swabs were from
166 ITW Texwipe (Netherlands). Uncoated aluminium stubs were from Plano (Germany). This collection
167 device consisted of a metal stub 12.5 mm in diameter inserted in a plastic vial with a screwed cap.
168 Carbon tape is commonly used for IGSR collection, but in this study double sided tape 665 from 3M
169 (USA) was used instead. Hand sampling by swabbing was carried out by moistening the swabs with
170 ethanol and scrubbing the right hand surface (back of the hand and surface between thumb and index
171 finger) repeatedly. With the stubs, 50 dabbings were applied to the same part of hand as for swabs and
172 200 dabbing for sampling hair and clothing following recommendations from Zeichner *et al.* [46]. To
173 avoid any bias when comparing swabs and stubs, the surface area sampled from the hand was the same
174 with both techniques. After sampling, both swabs and stubs (the adhesive was removed from the stub)
175 were transferred to a 1.5 mL vial, extracted using 1 mL MeOH, ultrasonicated during 15 minutes at
176 ambient temperature and finally centrifuged.

177 For the sequential sampling, the procedure was the same as described above with an additional
178 sampling step using a second collection material different from that of the first sampling. Thus, either
179 a swab-stub or a stub-swab sequence was applied. After employing both sampling methods, the
180 shooter washed his hands carefully before repeating the same procedure again.

181 For spent cartridge analysis, 500 μ L of MeOH was poured in the cartridge and the liquid was pipetted
182 a few times to homogenise the solution. It was then decanted in a vial and 500 μ L of MeOH were
183 further added to reach the same volume as for swab/stub samples. Finally, it was ultrasonicated and
184 centrifuged following the same protocol as for swabs and stubs.

185 2.4 Stability studies

186 In order to gain knowledge regarding the storage conditions and degradation of OGSR collected onto
187 swabs and stubs, two stability studies were carried out. The first considered spiked samples and the
188 second used samples obtained from shooting sessions. Spiked samples have the advantage of sample

189 standardisation, providing improved repeatability. Nevertheless, spiking a target analyte mixture onto
190 a sampling material does not take into account relative proportions between particulate and vapour
191 deposits of OGSR. It was still considered useful to provide a first estimation of compound losses over
192 time due to evaporation and/or degradation. It was then necessary to evaluate the storage of real
193 samples, even if the variability induced by the firearm discharge cannot be controlled.

194 The spiking experiments were only performed on swabs, because spiking liquid onto a stub is too
195 different from the real sampling process (*i.e.* dry physical process). A mix of the nine compounds
196 reported in Table 1 was prepared at a concentration of:

- 197 - 100 ppb for AK II, EC, MC and 1,3-DPU
- 198 - 200 ppb for 2-nDPA, 4-nDPA, *N*-nitrosoDPA and *N,N*-DPF
- 199 - 5000 ppb for DPA

200 Ten μL of solution was spiked onto the swab and left to dry for five minutes before cutting the handle,
201 placing the polyester part of the swab inside a 1.5 mL screw vial and closing it tightly. Three
202 conditions, namely ambient temperature (20 °C), fridge (4 °C) and freezer (-20 °C) were evaluated to
203 check for potential influence of the temperature on evaporation/degradation of the compounds. Five
204 samples were prepared for each condition at day 0, 1, 3, 7, 10 and 15. All samples were then extracted
205 as described in section 2.3 and analysed in the same LC-MS sequence.

206 For the stability experiments with samples acquired during shooting sessions, both swabs and stubs
207 were evaluated. Eight samples per time point were taken from the right hand of the shooter to account
208 for the higher variability compared to spiking experiments. A semi-automatic 9 mm Parabellum Sig
209 Sauer P226 and 9 mm Luger cartridges from the same batch of Geco ammunition were used. Samples
210 were collected at day 0, 7 and 14 for swabs, and day 0, 9 and 16 for stubs. All samples were then
211 extracted as described in section 2.3 and analysed in the same LC-MS sequence.

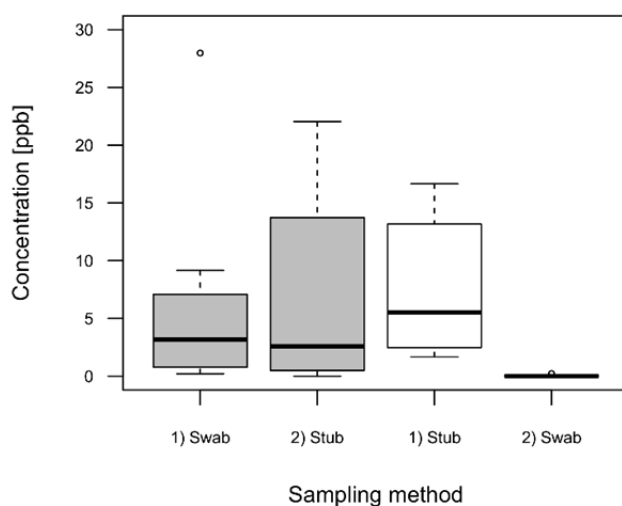
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213 **3. Results and Discussion**

214 *3.1 Collection efficiency of swabs versus tape-stubs: sequential sampling*

215 As mentioned in the introduction, various studies compared the efficiency of sampling materials for
216 IGSR and OGSR resulting in materials being ranked according to their collection efficiency.
217 Nevertheless, in the case of OGSR, the experiments only estimated the amount of compounds
218 collected and not the remaining residue on the hands after sampling. As the quantity of OGSR
219 produced during discharge is highly variable, it is not possible to determine the absolute recovery.
220 Indeed, the total amount deposited on any surface is unknown and not reproducible. However, by
221 estimating how much is left after sampling using another material/method might give some insight

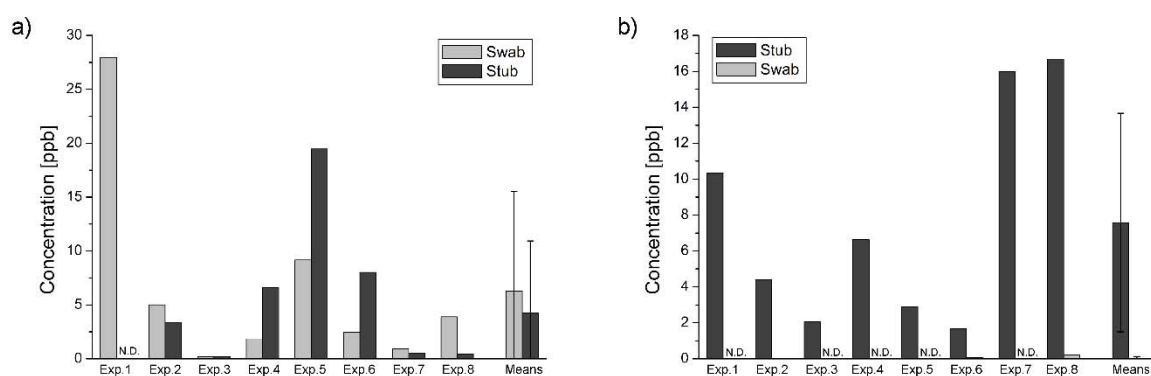
222 into the collection efficiency mechanism. In 1993, Zeichner and Levin used sequential sampling to
223 compare swabbing with stubbing for IGSR sampling from hair and showed that both methods were
224 comparable [46]. Here, after a first sampling using either a polyester swab or a tape stub, a second
225 sampling was carried out using the other method to see how much OGSR could still be collected. The
226 results obtained for EC are presented in Figure 1. Detailed information for other molecules can be
227 found in the Supplementary Information (AK II, DPA, *N*-nitrosoDPA, 2-nDPA and 4-nDPA).



228
229 **Figure 1:** Boxplots illustrating the concentration of EC recovered from the right hand of the shooter after one pistol discharge
230 ($n = 8$). In grey (left), the sampling sequence is swab and then stub. In white (right), stubbing was used before swabbing.
231 Geco gunpowder was used. Concentration values in ppb are equivalent to amounts in ng.

232
233 From Figure 1, it is obvious that when swabbing is performed just after firing, recovery is probably
234 not higher than 50%, as the stub applied to the hand during the second sampling was able to collect
235 about the same amount of EC. However, when tape-stubbing was performed first, the swabs were
236 unable to collect such a high amount of OGSR during the second sampling, as only trace amounts
237 were detected. Results are only shown here for EC, but values obtained for the other compounds
238 detected showed the same trend. While data relative to the physical state in which OGSR are deposited
239 is still missing, it is suspected that part of OGSR is deposited as vapour and part as particles.
240 Therefore, a specific sampling method might be more adapted to one physical state. As swabbing uses
241 a solvent, it is probably better suited to sample vapour deposits because the amount of solvent might
242 not be sufficient to dissolve particles completely. When swabbing is performed, it is possible that the
243 swab moves particles on the hand and does not capture them. That would explain why such a big
244 amount of OGSR can still be sampled with the stub afterwards. In this regard, the stub would be more
245 efficient to collect particles similarly to IGSR particles. The amount collected by the swab after
246 stubbing was very low. This might indicate that the amount of OGSR deposited as vapour is relatively
247 low or that the adhesive collected skin flakes which could have absorbed vapour deposits [46].

248 It is also not clear why the total amount recovered from the hand using the sequence swab-stub is
 249 higher than the sequence stub-swab (mean 13.2 ppb vs 7.6 ppb and median 9.4 ppb vs 5.5 ppb).
 250 Indeed, the median of the first sampling is more or less the same for both swabs and stubs, whereas the
 251 medians for the second sampling are significantly different. While it might be explained by the high
 252 variability in OGSR production and deposition as illustrated in Figure 2, there is no obvious
 253 explanation for this difference.



254
 255 **Figure 2:** Bar plot illustrating the variation in EC amount recovered from the right hand of the shooter (n = 8). On the left,
 256 the sampling sequence is swab and then stub. On the right, stubbing was used before swabbing. Geco gunpowder was used.
 257 Exp. is for experiment and N.D. for not detected. Concentration values in ppb are equivalent to amounts in ng.

258
 259 One could wonder if stubbing might hinder subsequent sampling with a swab. However, an alternative
 260 explanation would be that total recovery depends on three experimental parameters: collection
 261 efficiency, MeOH extraction efficiency and matrix effects. For each sampling method, each step might
 262 be different and thus influences total recovery. Consequently, one must be cautious when comparing
 263 average values, as the effects observed are not solely due to collection. However, it is clear that when
 264 swabbing is performed first, the amount recovered by stubs later is sometimes lower and sometimes
 265 higher than what was collected by the swab, indicating that collection efficiency is lower for swabs
 266 than stubs, as the amount collected by swabs after stubbing is always lower when using the stub first.

267 In the course of a shooting session, the amount recovered during the first sampling varied
 268 considerably. Depending on the molecule, the lowest relative standard deviations were about 50% and
 269 reached up to 150%. For example, the first experiment in the sequence swab-stub produced an
 270 extraordinarily intense peak with a concentration superior to 25 ppb, statistically considered as an
 271 outlier (Grubbs' test at 95%, $G = 2.346 > G_{crit} = 2.126$) when constructing the boxplots of Figure 1.
 272 The rest of the sequence lead to values lower than 10 ppb. In the stub-swab sequence, no outlier was
 273 identified, but the means of the EC concentrations for the whole sequence, illustrated in Figure 2,
 274 confirm the high variability of OGSR deposition. It was relatively common during a shooting session

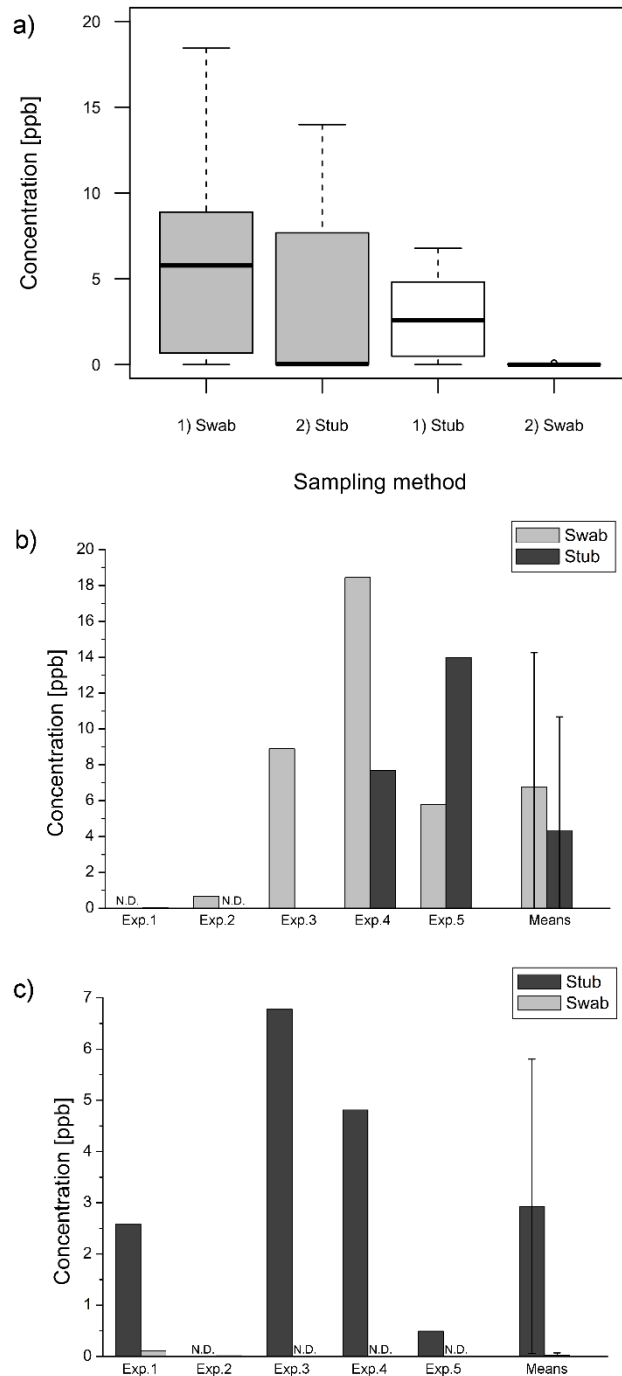
275 to observe a large particle on the hands, but its production was completely random. Another way to
276 look at these results is by calculating the following sampling ratio (SR):

277
$$SR [\%] = [EC]_{\text{sampling1}} * 100 / ([EC]_{\text{sampling1}} + [EC]_{\text{sampling2}}) \quad (\text{Eq. 1})$$

278 The values for the sequence swab-stub ranged between 1 and 100% (mean 49% and median 46%),
279 whereas the reverse sequence provided values between 95 and 100% (mean 99% and median 100%).
280 This shows that about 50% of OGSR was recovered when swabbing, whereas nearly 100% was
281 recovered with stubs. These results also highlight the fact that robust statistics should be used when
282 dealing with OGSR data. Means are strongly affected by extraordinary values, while medians are less
283 influenced.

284

285 Geco gunpowder produced a lot of residues compared to other tested gunpowders. A number of
286 particles were visible to the naked eye on the hand, inorganic and organic confounded. The
287 experiments were thus repeated with a gunpowder from Fiocchi producing less residues to confirm the
288 results (Figure 3).



289

290 **Figure 3:** a) Boxplots illustrating the concentration of EC recovered from the right hand of the shooter after one pistol
 291 discharge (n = 5). In grey, the sampling sequence is swab and then stub. In white, stubbing was used before swabbing. b) Bar
 292 plot illustrating the variation in EC amount recovered from the right hand of the shooter (n = 5) using the sampling sequence
 293 swab-stub. c) Same as b) but using the sequence stub-swab. Exp. stands for experiment and N.D. for not detected.
 294 Concentration values in ppb are equivalent to amounts in ng. Fiocchi gunpowder was used.

295

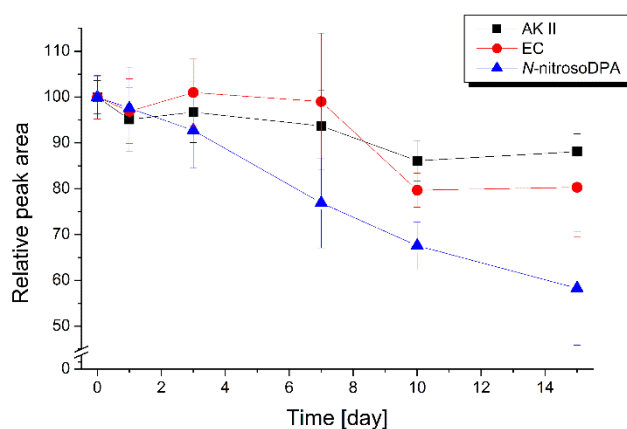
296 The same trend was observed for Fiocchi gunpowder, even if the amount of OGSR collected with the
 297 stub was lower than for Geco gunpowder. The results obtained for AK II are shown in Supporting

298 Information as these were the only target compounds detected in this gunpowder (Table 2). These
299 results confirm that stubs might indeed be better suited to collect OGSR. This sampling method did
300 not leave residues on the hand and would moreover be far easier to apply to sampling on clothes and
301 hair. It is also a well-established method for the routine sampling of IGSR within forensic laboratories
302 and police services.

303

304 3.2 Stability studies

305 When samples are collected, it is not always possible to analyse them immediately. Thus, the optimal
306 storage conditions have to be determined in order to avoid compromising the sample. A recent study
307 from Bell *et al.* showed that OGSR compounds evaporate relatively quickly [7]. In this work, an
308 exploratory study was first carried out with swabs spiked with a mix of target analytes. Three
309 conditions, namely ambient temperature (20 °C), fridge (4 °C) and freezer (-20 °C) were evaluated to
310 check for potential influence of the temperature on evaporation/degradation of the compounds. Then,
311 with regard to the results obtained in the previous section and the potential physical state in which
312 OGSR are predominantly collected, stability of the target molecules was studied for both polyester
313 swabs and tape stubs.



314

315 **Figure 4:** Analyte concentration losses for swabs spiked with a solution of target analyte mix at ambient temperature over a
316 two week period (n = 5).

317 As illustrated in Figure 4 for samples stored at ambient temperature, the extent of analyte loss on
318 spiked swabs depends on the family of compounds. DPA-related analytes decrease was more marked
319 than for the other molecules. For *N*-nitrosoDPA, the loss reached more than 40% after 15 days,
320 whereas for AK II, this value was limited to about 10%. These results are in accordance with those
321 obtained by Yeager *et al.* [7] in the sense that a trend towards lower values was observed. However,
322 the extent of the loss was lower than reported in their study, indicating losses superior to 50% for

323 DPA, EC and MC over nine days. At lower temperatures (fridge and freezer), no significant decrease
324 was detected in our samples after 15 days (Table 2).

325

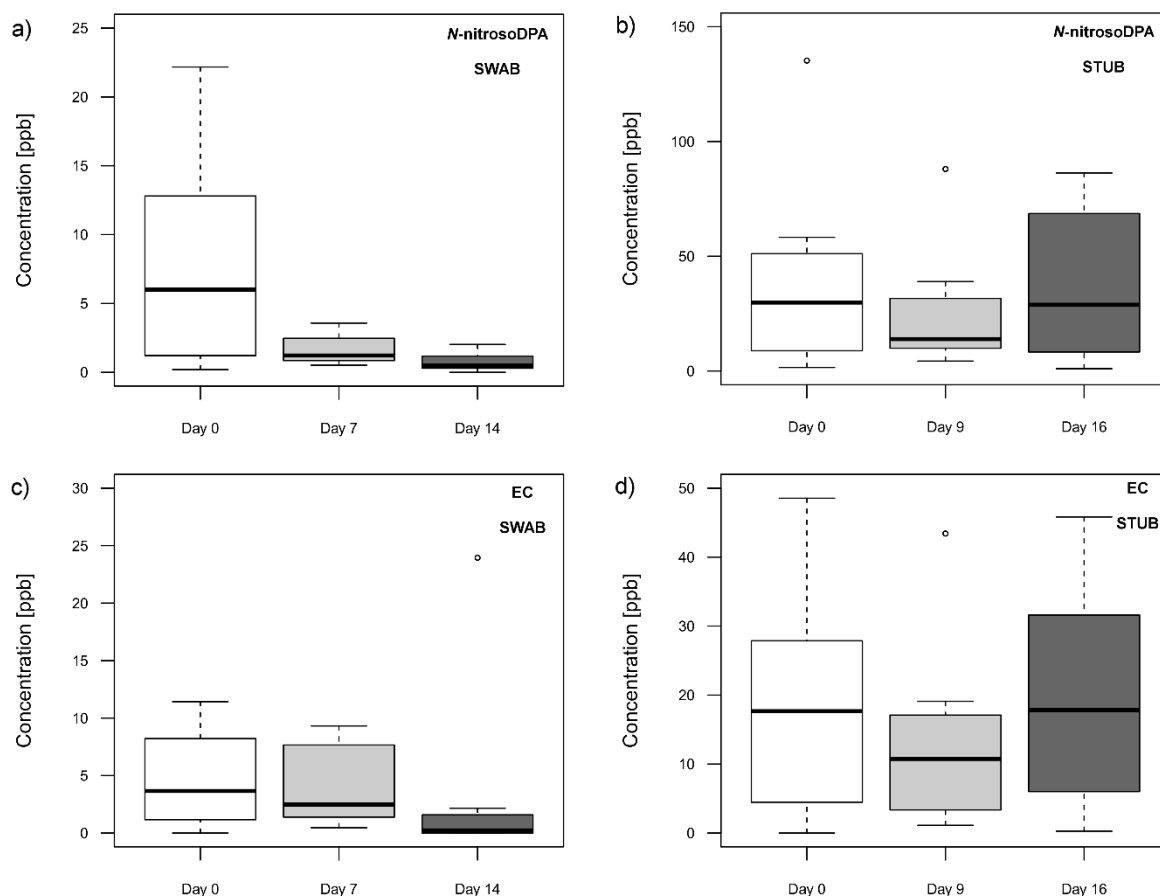
326 **Table 2:** Analyte concentration losses for swabs spiked with a solution of target analyte mix: ratio of the peak area at 15 day
327 to the peak area at time zero for the three temperatures studied.

Temperature	AK II	EC	<i>N</i> -nitrosoDPA	1,3-DPU	MC	<i>N,N</i> -DPF	2-nDPA	4-nDPA	DPA
Ambient (20 °C)	88.2%	80.3%	58.3%	102.0%	68.3%	67.7%	66.8%	66.8%	63.6%
Fridge (4 °C)	98.2%	97.9%	97.2%	102.9%	94.9%	106.2%	100.5%	99.7%	108.8%
Freezer (-20 °C)	95.0%	101.2%	99.6%	100.1%	94.9%	105.5%	103.5%	99.8%	108.2%

328

329 Indeed, at -20 °C and 4 °C, the ratios between peak areas at day 15 and day zero were mostly superior
330 to 95% with RSD around 5%, so the decrease was not significant. Values larger than 100% are due to
331 measurement variation. Thus, storage in a fridge is recommended for that type of samples. Yeager et
332 al. observed a decrease in concentration even when the sample was stored in a freezer. However, the
333 concentration at which the study was carried out was not the same (lower in the present case in order
334 to be close to amounts that might be encountered in casework). Moreover, in the present work, swabs
335 were stored in the vial where the extraction further took place, whereas in Yeager's study the samples
336 were stored in a Petri dish. The different protocols might thus significantly influence the results.

337 A series of shooting experiments was then performed in order to evaluate the stability of real samples
338 containing a biological matrix susceptible to degrade the compounds of interest. Both swabs and stubs
339 were evaluated to check for potential differences. Eight samples were collected from the right hand of
340 the shooter and the samples were stored at room temperature and analysed in the same analytical
341 sequence (Figure 5, Table 3).



342
 343 **Figure 5:** Stability of samples collected from the right hand of a shooter from swabs (left column) and stubs (right column).
 344 Data are presented for *N*-nitrosoDPA and EC and were obtained using Geco ammunition (n = 8). Samples were stored at
 345 room temperature. Concentration values in ppb are equivalent to amounts in ng.

346
 347 **Table 3:** p-values calculated for *N*-nitrosoDPA and EC for data from Figure 5. w/o stands for without.

	<i>N</i> -nitrosoDPA swab	<i>N</i> -nitrosoDPA stub	EC swab	EC stub
p-value (all points)	0.0098	0.7013	0.9118	0.6898
p-value (w/o outliers)	-	0.2957	0.0338	0.3084

348
 349 A different trend can be observed for both sampling methods. Indeed, after two weeks, there is a
 350 significant decrease in concentration for both *N*-nitrosoDPA and EC in swabs (if not considering the
 351 outlier), whereas the concentrations are similar for stubs. Similar results were obtained with the other
 352 molecules. The decrease seems to happen faster for *N*-nitrosoDPA than EC, in accordance to what was
 353 observed for spiked samples (Figure 4). It is not clear why there is a difference in stability. However,
 354 the physical state of the OGSR might explain these results. During swabbing, OGSR are probably
 355 dissolved by the solvent and are more prone to evaporation than particles. Studies from Bell *et al.*
 356 showed that evaporation is a relatively fast process for some compounds such as DPA and losses occur
 357 in a matter of hours [6]. If stubs collect mainly particles, these seem less affected by degradation than

358 what is collected by swabs. In conclusion, storage time should be chosen according to the sampling
 359 method. Stubs seem to have a better stability than swabs, at least one week longer. However, as a
 360 precaution, all samples shall be stored in the fridge and be analysed relatively rapidly after collection.

361

362 3.3 Transfer of OGSR on the right hand of the shooter using different ammunition

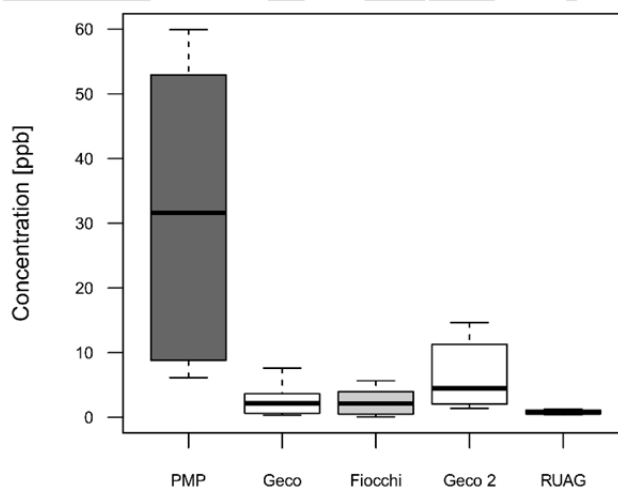
363 In order to study the influence of the chemical composition of a gunpowder on detected OGSR, five
 364 different gunpowders were used in shooting sessions. Table 4 presents the main target compounds
 365 detected in the gunpowders.

366 **Table 4:** Target analytes detected in gunpowders used in shooting sessions. Presence is indicated in grey.

	AK II	EC	DPA	N-nitrosoDPA	2-nDPA	4-nDPA
PMP		x				
Geco (batch 62 QS)	x	x	x	x	x	x
Fiocchi	x	x				
Geco 2 (batch 54 G K096)	x	x	x	x	x	x
RUAG Ammotec		x	x	x	x	x

367

368 A series of five discharges were carried out for each ammunition type, except for the most recent batch
 369 of Geco ammunition (Geco 2, n = 8) (Figure 6).



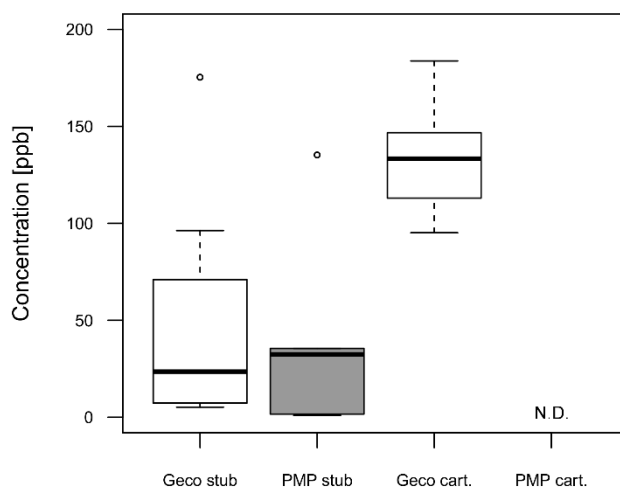
370

371 **Figure 6:** Boxplots illustrating the concentration of EC recovered from the right hand of the shooter after one pistol discharge
 372 for five types of ammunition (n = 5 except for Geco 2 for which n = 8). Concentration values in ppb are equivalent to
 373 amounts in ng.

374

375 For EC, the amounts of OGSR detected for each ammunition were similar, except for PMP. However,
 376 the concentration of EC in this gunpowder was much higher than for the other gunpowders. Due to the
 377 high variability in OGSR production and recovery, it seems difficult to distinguish OGSR from

378 different gunpowders based on the concentration of a specific compound. However, the presence of a
379 specific compound can be a good indication for qualitative comparison with ammunition that might be
380 discovered at a suspect's place for example. Exceptions can arise as results obtained for OGSR
381 produced by PMP ammunition were not consistent with the composition of the gunpowder. Indeed,
382 AK II, DPA, *N*-nitrosoDPA, 2-nDPA and 4-nDPA were detected, whereas these compounds were
383 absent from the gunpowder. Discharges of PMP ammunition were performed after shooting of a series
384 of Geco cartridges. The pistol was not cleaned in-between (Figure 7).

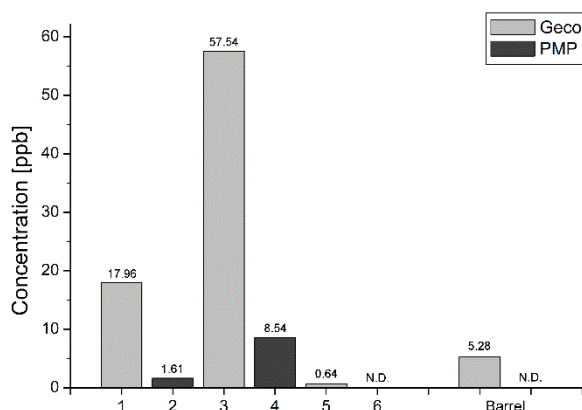


385
386 **Figure 7:** Boxplots illustrating the concentration of DPA recovered from the right hand of the shooter after one pistol
387 discharge when eight cartridges of Geco ammunition were discharged followed by the discharge of five cartridges of PMP
388 ammunition. The spent cartridges were also analysed for comparison. Concentration values in ppb are equivalent to amounts
389 in ng.

390
391 From Figure 7, it is obvious that the DPA recovered from the hand of the shooter did not originate
392 from the PMP ammunition, as this molecule was detected neither in the spent cartridge nor in the
393 gunpowder (Table 4). However, this molecule was a major component of Geco gunpowder. This
394 demonstrates that a memory effect between shots cannot be excluded as already observed by Northrop
395 [26].

396 To estimate if this interaction came from particles present in the barrel, the latter was scrubbed with a
397 cotton bud to remove particles and soot before another experiment was carried out alternating Geco
398 and PMP ammunition (Figure 8).

399



400

401 **Figure 8:** Bar chart illustrating the concentration of DPA recovered from the right hand of the shooter after one pistol
 402 discharge when alternating discharge of Geco and PMP ammunition (n = 3). Horizontal numbers on the axis indicate the
 403 discharge number. A sample from the end of the barrel was also analysed for comparison after shots 1 and 2. Concentration
 404 values in ppb are equivalent to amounts in ng.

405 By cleaning the barrel in-between discharges, the extent of memory effect was reduced, but did not
 406 completely disappear. A thorough cleaning by completely dismounting the firearm might be the only
 407 way to get rid of this interaction. However, in real cases, the suspect might not be very fussy about
 408 firearm cleaning and potential memory effect must be taken into account when interpreting OGSR
 409 evidence. Following these observations, proper identification of the ammunition batch used in a case
 410 might be impossible if maintenance of the firearm is not carried out on a regular basis and different
 411 types of ammunition are regularly used.

412

413 3.4 Sampling of other exposed skin surfaces, hair and clothing

414 To date, most studies used samples collected from the hands of the shooter or from a target. As
 415 evidenced by the analysis of IGSR, large particles are rapidly lost from the hands due to activity such
 416 as hand washing, lessening the chances to later recover GSR. Moreover, as previously mentioned,
 417 evaporation and skin permeation of OGSR will also affect recovery. As a consequence, other exposed
 418 surfaces that are less frequently washed, such as face and hair are potentially interesting targets. Some
 419 crime scene units already have protocols for IGSR collection from eyebrows and hairline. Clothing is
 420 also of great interest, as the fibres might better retain particles than skin. A few experiments were
 421 carried out to see where OGSR can be detected at time zero and two hours after discharging three
 422 rounds of ammunition. The shooter was wearing a long-sleeve sweater made of cotton and polyester.
 423 Sampling was performed on the sleeves up to the elbow and on the part of hair closest to the forehead.
 424 For the time interval between discharge and sampling, the shooter was working on her computer. She
 425 was allowed to walk inside the building and touch her face/hair, but not to wash her hands. Tables 5
 426 and 6 show detected compounds.

427

428 **Table 5:** Molecules detected just after discharge of three rounds of Geco ammunition (n = 1). Presence is indicated in grey.
 429 The LOD for each compound is also indicated.

	AK II	EC	DPA	N-nitrosoDPA	2-nDPA	4-nDPA
LOD [ng/mL]	0.01	0.005	0.5	0.02	0.02	0.02
right hand	x	x	x	x	x	x
left hand	x	x	x	x	x	x
right sleeve	x	x	x	x	x	x
left sleeve	x	x	x	x	x	x
right eyebrow + forehead		x		x		
left eyebrow + forehead	x	x			x	x
hair	x	x		x		

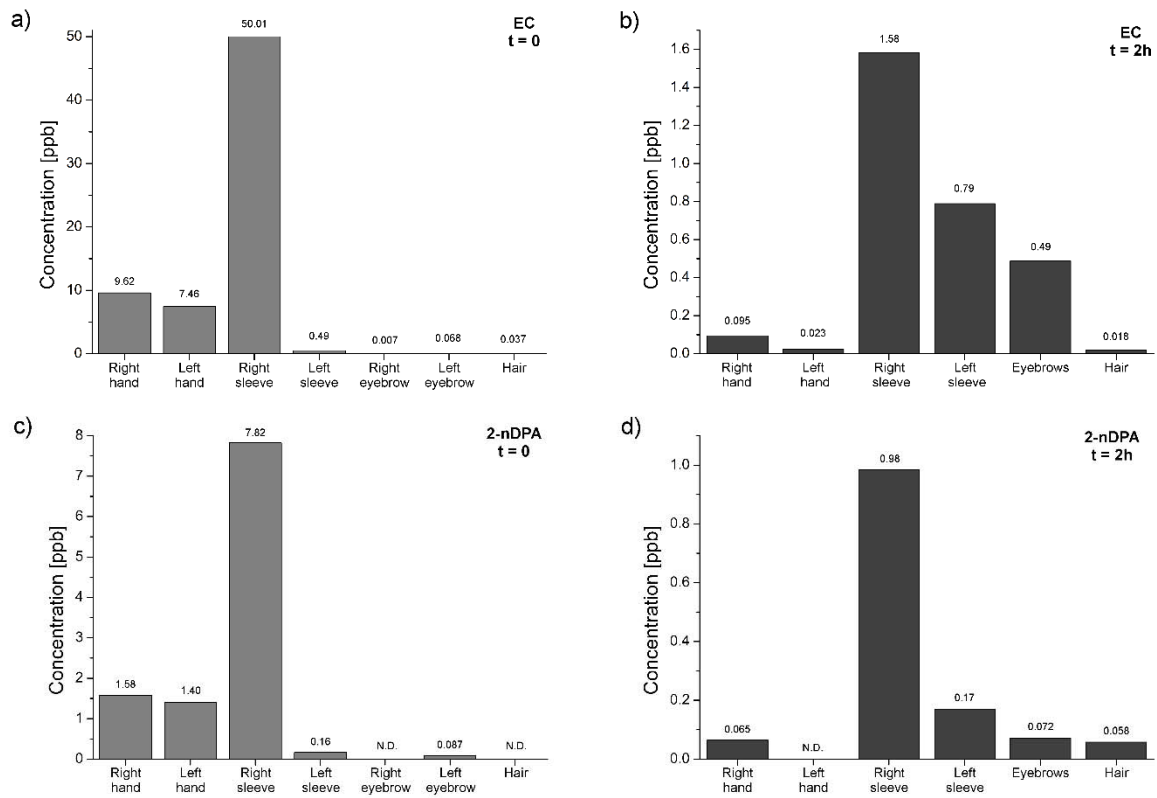
430

431 **Table 6:** Molecules detected two hours after discharge of three rounds of Geco ammunition (n = 1). Presence is indicated in
 432 grey.

	AK II	EC	DPA	N-nitrosoDPA	2-nDPA	4-nDPA
right hand	x	x	x	x	x	
left hand		x		x		
right sleeve	x	x	x	x	x	x
left sleeve	x	x	x	x	x	x
eyebrows + forehead	x	x	x	x	x	
hair	x	x		x	x	

433

434 Just after discharge, all main compounds of the gunpowder were detected on both hands and pullover
 435 sleeves. In hair and on the face, fewer compounds were detected. Two hours after discharge, all the
 436 compounds were detected on the sleeves only. However, more compounds were detected on the face
 437 than just after discharge. Figure 9 presents the concentrations recovered from the different exposed
 438 skin surfaces, hair and clothing for EC and 2-nDPA.



439

440 **Figure 9:** Concentrations of EC and 2-nDPA detected on various exposed skin surfaces, hair and clothing just after (left
 441 column) and two hours after (right column) discharge of three rounds of Geco ammunition (n = 1). Concentration values in
 442 ppb are equivalent to amounts in ng.

443

444 At both time zero and two hours, the highest amount of EC and 2-nDPA was recovered from the right
 445 sleeve of the shooter's sweater. Regarding the distribution of concentrations, it can be seen that the
 446 concentration on hands strongly dropped, by a factor of 100 for EC and superior to 20 for 2-nDPA. As
 447 a comparison, the ratio is only 31 and 8 for the right sleeve. Hands were not washed during these
 448 experiments. Thus, results would be worse if hands were washed carefully. It is probable that no more
 449 OGR would be detected. The quantities detected on the eyebrows and hair were relatively low, but
 450 their concentration did not decrease much after two hours. This indicates that transfer might actually
 451 occur after discharge when the shooter touches his face and hair with hands contaminated with OGSR.
 452 More data on OGSR transfer is required to determine which surface might be the one to receive most
 453 OGSR and what minimal and maximal amounts can be expected. However, from these data, it is clear
 454 that OGSR are more rapidly lost from hands than from clothing. Thus, due to longer persistence, there
 455 might be more chances to detect OGSR on clothing than on hands. Nonetheless, one must keep in
 456 mind that the evidential value associated to OGSR detection also depends on the location where these
 457 were discovered. Thus, GSR on clothing is less meaningful for linking a suspect to a discharge than
 458 GSR detected on hands, face or hair. Hence, it is essential to sample all relevant surfaces and not only
 459 clothing.

460 **4. Conclusions**

461 This study intended to provide some information regarding OGSR sampling, sample storage, transfer
462 and persistence. In the first part stubbing was compared to swabbing using sequential sampling. The
463 results evidenced a very high variability for both techniques, associated to OGSR production rather
464 than sample collection. When swabbing was performed before stubbing, the swab collected only about
465 50% of the total amount recovered, whereas this value was close to 100% for the reverse sequence.
466 Stubbing was thus considered a better sampling technique as it left nearly no residues on the hand. In
467 the second part of the study, storage conditions were investigated after sampling using both stubs and
468 swabs. Here again, storage time was dependent on the sampling method. Stubs were more stable than
469 swabs and could be held at room temperature without significant compound loss for two weeks. For
470 longer storage times, it might be advisable to keep samples in the fridge.

471 Shooting experiments were then performed to evaluate transfer of OGSR using different ammunition.
472 The variability in quantities detected did not enable the distinction between ammunition based on a
473 single compound. Moreover, when shooting various ammunition with the same firearm, a memory
474 effect was detected. In the present case, DPA-related compounds were detected in hand samples even
475 if these compounds were absent from the gunpowder. A quick cleaning of the barrel using a cotton
476 bud was not sufficient to remove all traces from the previous shot and the possibility of multiple
477 ammunition usage should be taken into account if analyzing OGSR with a view to possibly link it to a
478 gunpowder. Finally, various exposed skin surfaces and hair as well as clothing were sampled to
479 evaluate what surfaces would be the best targets for OGSR collection by comparing results just after
480 discharge and two hours after discharging a pistol. The results indicated that OGSR were more rapidly
481 lost from hands than from clothing. Moreover, it was shown that the face and hair of a suspect might
482 be contaminated through secondary transfer. Thus, OGSR might remain longer on other skin surfaces,
483 hair and clothing than on the hands of a suspect. As a consequence, sampling should not be limited to
484 hands and also include clothing, hair and face. Also, OGSR concentrations detected after two hours
485 were relatively low compared to what can be detected just after discharge. As the limits of detection
486 were already reached after two hours for some molecules, it will be necessary to develop a
487 preconcentration technique to evaluate persistence in a thorough study.

488 Obviously, many variables can modify the transfer and persistence of OGSR. Factors such as gender,
489 skin type (pH, humidity, sweating, and so on), pilosity, age or hair type/length can possibly affect the
490 detection of OGSR. External factors such as cosmetics might also play a role. Moreover, ammunition
491 and firearm type as well as weather might influence transfer. Finally, activity of the suspect as well as
492 passive processes such as evaporation and skin absorption will impact persistence. This work is
493 therefore a first step into the wide panel of factors interacting during transfer and persistence of
494 OGSR. More studies will be necessary to acquire more knowledge about these phenomena.

495

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497

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501

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