



Bullet contribution to inorganic residue on targets

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ABSTRACT

Identifying the composition and the physical characteristics of the bullet that generated a specific hole in the victim's clothes or skin may be crucial in shooting incident reconstructions. In forensics, chemographic tests are routinely conducted to visualize lead, copper, or nitrite deposits around entrance holes with the aim of confirming a projectile impact or estimating the shooting distance. A quantitative chemical analysis of the particles collected from the periphery of an entrance hole is required for identifying the type of passing bullet. In real cases, such analysis would be affected by the possible cross-contributions of both inorganic residue from the discharged ammunition primer and metallic fragments from previous rounds projected from the gun barrel. The actual contribution of the sole bullet to the composition of the inorganic residue deposited on target is then hardly distinguishable. In the present study, the deposits left by three different copper/zinc jacketed bullets on targets were analysed by inductively coupled plasma optical emission spectrometry and by X-ray fluorescence spectrometry. To reduce any possible source of contamination, a heavy metal free primer mixture and a brand new pistol were used. Elements of interest were quantified varying the shooting distances with the aim of identifying different bullet contributions to the inorganic residue on targets.

Introduction

Identifying which bullet generated a specific hole in victim's clothes or skin may be crucial in shooting incident reconstructions. Different firearms and ammunitions could be indeed discharged on the crime scene and bullets could fully pass through the target and get lost. Determining the nature of the projectile that caused a wound could give information on the ammunition used and, consequently, on shooter identity. In forensics, chemographic tests are routinely conducted to visualize both inorganic and organic deposits around suspect entrance holes [1,2]. The sodium rhodizonate test, the dithiooxamide test, and the modified Griess test are used to induce chemical colouring of lead, copper and nitrites respectively. The resulting patterns are mostly used for confirming a projectile impact or for estimating the shooting distance [3]. Presumptive tests may indeed lead to ammunition identification in particular cases, as for the dimethylglyoxime reagent [4] when uncommon nickel-coated bullets are fired. A quantitative chemical analysis of particles around the entrance hole would be the ideal solution to identify the nature of the passing projectile. In real cases such analysis

would be affected by two sources of cross-contamination, potentially responsible for hiding the actual bullet contribution to the residue population on target. A first contamination would be due to inorganic gunshot residue (GSR or, more precisely, pGSR) from the ammunition primer mixture. When SINOXID [5] primers are discharged, pGSR particles will have a lead-based chemical composition [6] and targets will be supplied with lead even if total metal case bullets are fired [3]. Metallic fragments from previous rounds, deposited in the gun barrel [7] and projected together with the last bullet, would be a second source of contamination. This phenomenon is known as "memory effect" in firearms [8] and it is also responsible for producing GSR of unusual composition [9]. The actual contribution of the sole bullet to the inorganic residue deposited on target is hardly distinguishable and consequently mostly unknown.

Recently, concerns [10] about wildlife poisoning by lead pellets and possible health-related problems caused by the recurring use of lead ammunitions at indoor ranges led to an increased popularity of non-toxic alternatives to lead-based bullets and primers. Gunshot residue from heavy metal free (HMF) primers are often composed of K, Si,

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Al, and Ca [11–13], elements that cannot be taken for the ones originating from bullets.

As a matter of fact, ammunition identification from the analysis of residue collected on target is a forensic theme widely explored in recent years. In 2001, Brozek-Mucha and Jankowicz [14] tried to achieve a group identification of the discharged ammunitions on the base of SEM-EDS analysis of GSR collected on shooters' hands. Years later, a quantitative technique as ion beam analysis was used by Christopher et al. [15] to group within a canonical discriminant function graph three individual makes of cartridge from a single manufacturer. In both these studies, primer residues only were used for ammunition identification, regardless the nature of the fired projectiles. The analysis of organic gunshot residue (OGSR) by Raman spectroscopy [16,17] was also suggested for ammunition discrimination. OGSR allowed the identification of the discharged cartridges when their propellant powders were different. Udey et al. [18] firstly achieved a differentiation of passing bullets on pig skin by using inductively coupled plasma mass spectrometry (ICP-MS). The amount of copper and lead in fresh and in moderately decomposed tissue specimens allowed a differentiation of the projectiles in terms of jacketed or non-jacketed bullets only. In 2018, Eksinikun [19] quantified by ICP-MS lead, antimony and barium collected from bullet holes on wood and metal targets. The reported quantity of lead was systematically higher on targets hit by Jacketed Hollow Point (JHP) bullets than on targets hit by Lead Round Nose (LRN) bullets. No explanation was given for this unusual result that could be due to the release of lead deposits from previous LRN bullets in the same barrel.

In the present study, the deposits left on targets by three different jacketed bullets were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF) spectrometry. Use of HMF primed ammunition in a brand new pistol opened the possibility to recognize, by quantitative analyses, different bullet contributions to the inorganic residue on targets. A quantification of elements originating from the primer mixture and from the bullets was performed on cotton targets shot from different distances. Analyses were also extended to the residue that passed through the cotton texture towards an underlying sheet of filter paper. Such experimental setup mimics a shooting incident involving a human body where the garment with the bullet's hole deteriorated or became somehow unavailable for the analysis.

Materials and methods

Firearm, ammunition & targets

The firearm used for the shooting tests was a Pietro Beretta 92FS, calibre 9×19 mm, self-reloading pistol. The gun was brand new and it had not discharged any cartridge but the mandatory proof house test rounds. In most European countries all guns, for security reasons, at the end of their production cycle, are indeed tested by discharging two SINOXID primed cartridges, whose residues are impossible to completely remove [7].

For this study, 9×19 mm (9 mm Parabellum) ammunitions by Fiocchi Munizioni S.p.a. were used. All the cartridges were loaded with Fiocchi ZetaPi ("Zero-Pollution") [20] heavy metal free primer mixture. According to the material safety datasheet [21], this explosive mixture is mainly composed of potassium nitrate (3 ÷ 5% w/w), diazodinitrophenol (2 ÷ 3% w/w), and other organic explosives (tetrazene, penthrite). The ZetaPi primer mixture also contains chemically inert aluminosilicate glass (see Supporting Information file Figure S1), used as friction agent in the explosive mixture.

Three different types of bullets were selected for the shooting sessions, as illustrated in Table 1.

Targets were $30 \text{ cm} \times 30 \text{ cm}$ untreated white cotton squares. The cotton fabric was $180 \mu\text{m}$ thick, with a density of 150 g/m^2 . Each cotton square was put upon a Whatman® Grade 42 ashless filter paper sheet

Table 1
description of the three types of bullet selected for the shooting tests.

Bullet ID	Bullet characteristics	Bullet description
SJSP	Semi-jacket soft point 6.5 g (100 grains)	A Sn core is encased in a tombac (CuZn10) shell leaving a single opening on the bullet-tip that exposes the core.
TMC	Total metal case 8.0 g (124 grains)	A Pb:Sb core is entirely encased in a brass (CuZn30) shell.
FMJ	Full metal jacket 8.0 g (124 grains)	A brass (CuZn30) jacket is swaged over a Pb:Sb core, leaving a single opening on the base that exposes the core

and pinned down on a cardboard support. Each target was hit once and transferred to a separated plastic envelope. Negative control specimens (field blanks) were collected by exposing 2 targets in the shooting range, 1 meter behind the shooter.

Shooting sequence

Before collecting the targets, the gun barrel was conditioned by discharging ten HMF primed cartridges with SJSP bullets. Five barrel-to-target distances (5 cm, 20 cm, 40 cm, 80 cm, and 100 cm) were selected for the test firings. For each distance, seven different target replicas were shot, for a total of thirty-five rounds discharged for each bullet type. Five further ZetaPi primed blank cartridges (i.e. without any bullet) were discharged before changing the bullet type. The shooting sequence was the following: SJSP-cartridges, then TMC-cartridges, and finally FMJ-cartridges. The shooting history of the chosen firearm is summarized in Table 2.

Elements of interest

Gunshot residues from Fiocchi ZetaPi primer mixture are mainly OSiKAlCa [20] particles. K, Si, Al and Ca were then chosen for the analyses as HMF primer elements. Sb and Ba, constituting with Pb the characteristics residues from SINOXID primers, were added to the list of elements of interest to evaluate any possible firearm memory effect due to the proof house test rounds. Projectile cores were potential sources of Sn (SJSP bullets) and Pb (FMJ bullets), while Cu and Zn could originate both from bullet jackets and from primer cups. Pb, Sn, Cu and Zn concentrations on targets were similarly investigated.

Table 2
a brief summary of the shooting history of the chosen firearm.

Session ID	Rounds	Primer type	Bullet type	Comments
Proof house test rounds	2	SINOXID (Lead-based)	Unknown	Possible bullet types: FMJ or TMC
Barrel conditioning #0	10	Fiocchi ZetaPi (HMF)	SJSP	Initial barrel conditioning
Session #1	35	Fiocchi ZetaPi (HMF)	SJSP	Targets collected for the analyses
Barrel conditioning #1	5	Fiocchi ZetaPi (HMF)	Blank (no bullet)	Session ending barrel conditioning
Session #2	35	Fiocchi ZetaPi (HMF)	TMC	Targets collected for the analyses Bullets core not exposed
Barrel conditioning #2	5	Fiocchi ZetaPi (HMF)	Blank (no bullet)	Session ending barrel conditioning
Session #3	35	Fiocchi ZetaPi (HMF)	FMJ	Targets collected for the analyses

X-Ray Fluorescence

XRF analyses were conducted using an Ametek-Spectro MIDEK II LD spectrometer, equipped with a molybdenum anode (30W, accelerating voltage up to 48 kV) and a 30 mm² Silicon Drift Detector. In the long distance (LD) configuration, samples are set at a working distance of 20 mm and the MIDEK II spectrometer detects elements having atomic number $Z \geq 18$, providing fully quantitative results for $Z \geq 22$. The X-ray beam width on the sample can be selected using a square collimator. All the analyses were performed in air choosing a spot size of 1,2 mm. For collecting each X-ray fluorescence map, a square area of 125 mm × 125 mm centred in the bullet hole was digitalized into a 104 pixel × 104 pixel matrix. The dwell time (single-point acquisition time) was set to 18 seconds, for a specimen total running time of about 60 h.

ICP-OES

The elemental analysis was conducted by a Thermo Scientific iCAP 7000 duo series ICP-OES instrument, equipped with a quartz torch and a Charge Injection Device detector. The software used was a Qtegra Reichsmarkver. 2.9.2944. Experimental conditions are described in the Supporting Information file (see Table S1 and S2). Calibration curves were drawn by using multi-element standards by Sigma Aldrich, choosing the concentrations of 1 mg/L, 5 mg/L, 10 mg/L for K, Si, Ca, Ba, Sb, Pb, Cu and of 200 µg/L, 500 µg/L, 1000 µg/L for Al, Sn, Zn. All the working solutions were prepared diluting a 1000 mg/L standard for each element, all of them but Si acidified with 0.5% HNO₃. From each calibration curve, the limit of quantification (LOQ, expressed in µg/cm³) is calculated as $LOQ = 10\sigma/S$, where S is the slope of the calibration curve and σ is the standard deviation of the data regression line. As already reported [22], method quantification limit (MQL, expressed in µg/cm²) was calculated for each element from the corresponding LOQ as follows: considering a 7 cm × 7 cm (49 cm²) square target treated with 25 cm³ of water/nitric acid mixture, $MQL (\mu\text{g}/\text{cm}^2) = LOQ (\mu\text{g}/\text{cm}^3) \times 25 (\text{cm}^3) / 49 (\text{cm}^2)$.

Specimen preparation

No specimen preparation was required for performing the XRF maps and 30 cm × 30 cm targets were analyzed as collected. For ICP-OES analyses only, the following procedure was adopted. For each target, four 7 cm × 7 cm squares (see Figure S2 in the Supporting Information file), sharing a vertex in the bullet hole, were cut out from the cotton fabric and from the underneath filter paper. The field blanks were cut similarly. It is noteworthy to recall [22] that more than 50% in weight of the inorganic residue settles in a circle of radius 1 cm centred in the bullet hole and contributions from distances greater than 6 cm are usually negligible. Following an established method [23], each 7 cm × 7 cm specimen was put in a polypropylene 50 cm³ Falcon centrifuge tube and elements extracted with 10 cm³ of 10% w/w nitric acid (diluted from ultrapure grade 70.0% HNO₃ by Sigma Aldrich) at room temperature (20°C) for 24 h. The centrifuge tube was then sonicated for 20 minutes at 80°C and the solution diluted by adding 15 cm³ of double distilled water. After specimen removal, the solution was filtered using 0.22 µm nylon syringe filter and analyzed by ICP-OES.

Data presentation

For each set of replicated specimens, mean values $\langle v \rangle$ and standard deviations δ of the ICP-OES data were calculated for all atoms of interest. Element concentrations for each set of replicas were presented in the form $\langle v \rangle \pm \delta$, expressed in µg/cm² units, and plotted as points (or histogram rectangles) with error bars. Two limit cases required specific data assessments. If an element concentration for a certain replica in the set resulted below the corresponding MQL, its value was set equal to zero and excluded from the statistical calculus. In case the calculated

value $\langle v \rangle - \delta$ resulted below the MQL, the element concentration for the set of replicas was briefly indicated as “< MQL”. “< MQL” was also used if more than one-half of the replicas were below MQL, due to the lack of a reliable statistics. Differently, if an element concentration for a certain replica in the set resulted below the corresponding field blank threshold, the measured value was however considered for the determination of $\langle v \rangle$ and δ . In case the calculated value $\langle v \rangle - \delta$ resulted below the field blank threshold, the element concentration for the set of replicas was briefly indicated as “< Blank”.

Specimen data were used to draw ternary graphs for bullet identification. Each point (x, y, z) in a ternary graph is represented by a set of three coordinates having just two degrees of freedom, as the normalization constraint $x+y+z=1$ applies. The three chosen variables were the relative concentrations of elements Pb, Sn and Cu.

Results

Primer mixture elements: K, Si, Al, Ca

ICP-OES results for elements originating from the ZetaPi primer mixture, collected on targets shot from a distance of 5 cm, are reported in Table 3.

The concentration values of K and Si, detected on cotton targets shot from different distances, are shown in Fig. 1. The corresponding XRF maps of potassium on targets are plotted in Fig. 2.

Memory effect elements: Sb, Ba

Antimony concentration was below the corresponding MQL (0.003 µg/cm²) for all bullet types and shooting distances, both on the cotton targets and on the filter paper sheets. Barium was detected above its MQL (0.005 µg/cm²) for cotton targets shot from a distance of 5 cm only, as shown in Fig. 3.

Bullet elements: Pb, Sn, Cu, Zn

ICP-OES results for elements originating from bullet cores and jackets, collected on targets shot from a distance of 5 cm, are reported in Table 4.

On cotton targets shot from a distance of 5 cm, lead concentration was above its field blank threshold for all bullet types. Lead was also detected on targets shot from 20 cm and 40 cm using FMJ bullets only. In Fig. 4, ICP-OES results for lead are shown. The corresponding XRF maps of lead on targets are reported in Fig. 5.

On cotton targets shot from a distance of 5 cm, tin concentration was above the corresponding MQL for all bullet types. Tin was also detected on targets shot from 20 cm using SJSP bullets only. In Fig. 6, ICP-OES results for tin are shown. Tin concentration on all targets was too low to get reliable XRF maps.

On cotton targets, copper and zinc were detected above their field

Table 3

K, Si, Al and Ca concentrations on cotton targets and on corresponding filter paper supports shot from a distance of 5 cm. Values are expressed in µg/cm² units.

	[K]	[Si]	[Al]	[Ca]
MQL	0.043	0.004	0.020	0.015
COTTON TARGETS				
Field blanks	0.36	2.05	0.07	4.55
SJSP	3±1	2.3±0.3	0.22±0.09	5.3±0.4
TMC	1.5±0.2	2.5±0.3	0.18±0.02	5.3±0.2
FMJ	2.2±0.3	2.4±0.2	0.24±0.03	5.2±0.3
FILTER PAPER SUPPORTS				
Field blanks	0.15	0.07	0.025	4.20
SJSP	0.38±0.04	< Blank	< Blank	< Blank
TMC	0.34±0.06	< Blank	< Blank	< Blank
FMJ	0.40±0.04	< Blank	< Blank	< Blank

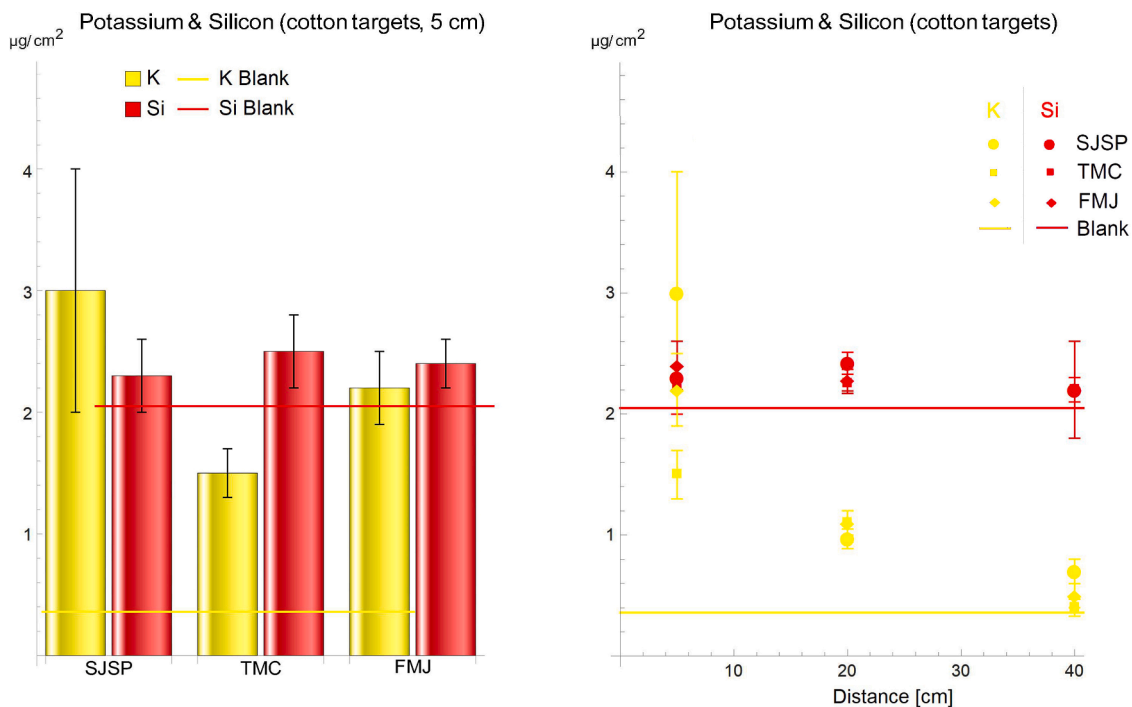


Fig. 1. K and Si concentrations on cotton targets shot from 5 cm using different bullets (left chart) and their decay up to 40 cm (right chart). For longer distances values fall below the reported field blank thresholds.

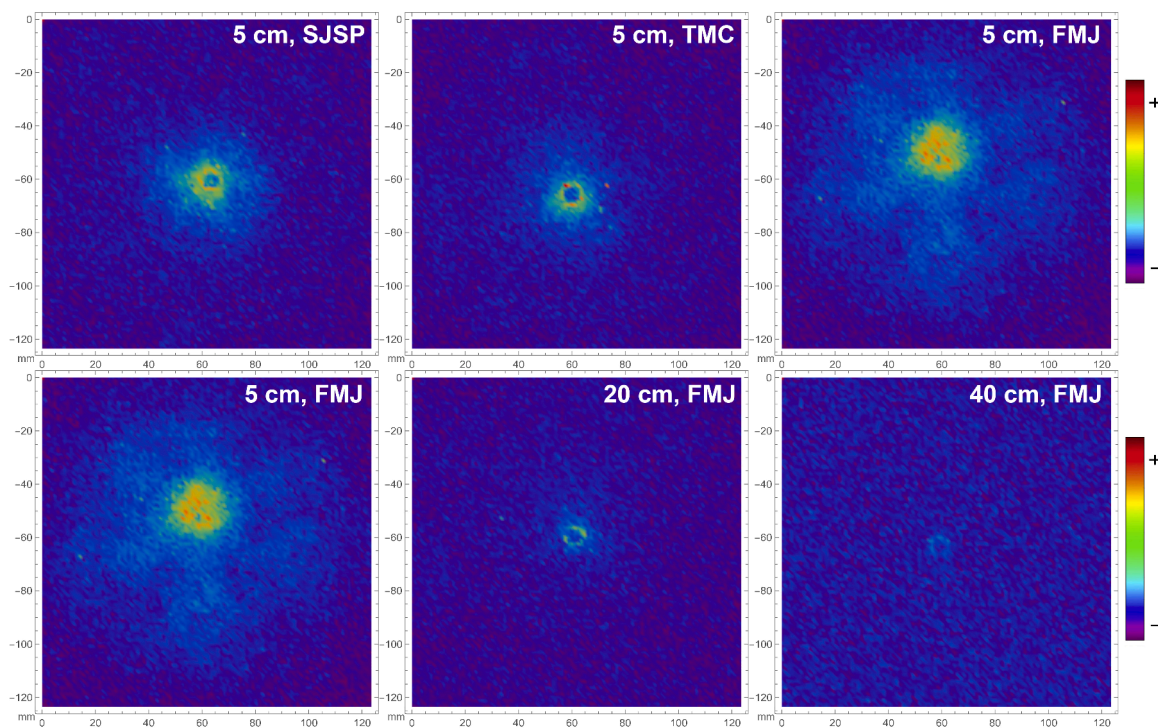


Fig. 2. K distribution patterns on cotton targets shot from 5 cm using different bullets (upper line) and up to 40 cm (lower line) using FMJ bullets only.

blank thresholds for all bullet types up to a shooting distance of 40 cm. In Fig. 7, ICP-OES results for copper and zinc are shown. The corresponding XRF maps of copper on targets are reported in Figs. 8 and 9.

Relative concentrations of Pb, Sn and Cu were visualized using ternary graphs, as shown in Fig. 10.

Discussion

On primer mixture elements

A statistical research [24], conducted in 2013 on 1500 GSR particles taken from 10 ZetaPi primed spent cartridge cases, showed that K was the main peak in the spectrum in 546 out of 1500 residues (36.4%), Si in

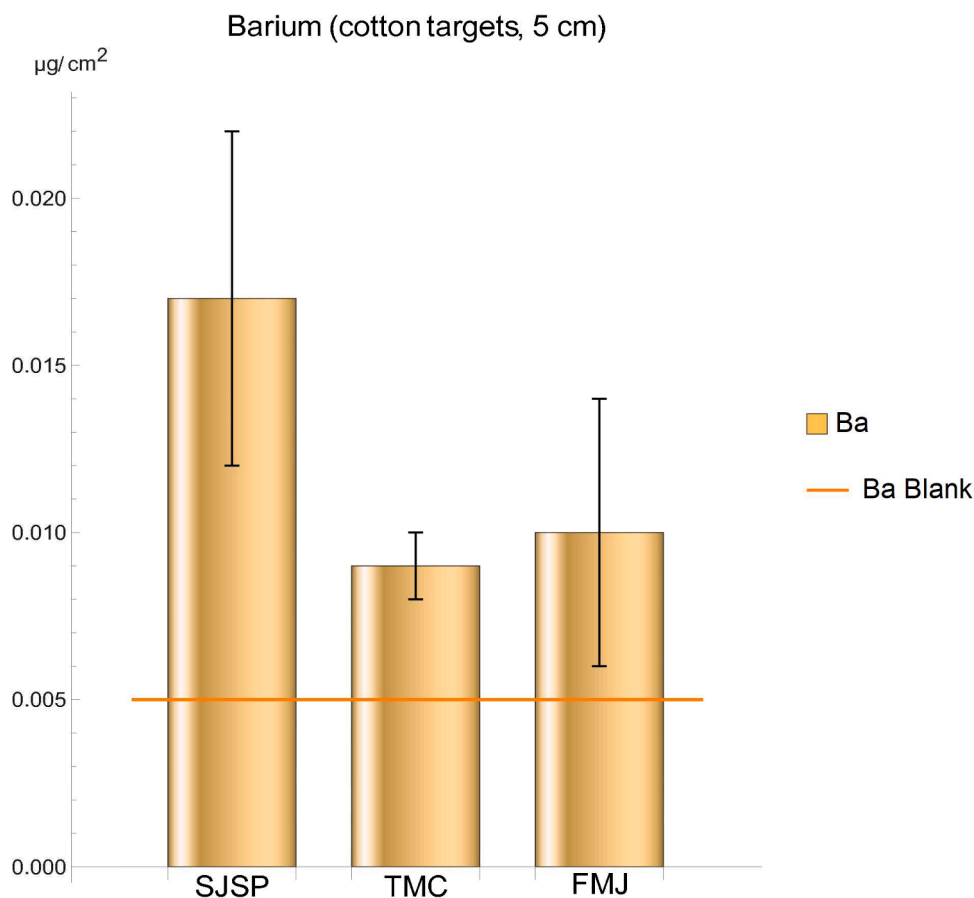


Fig. 3. Ba concentrations on cotton targets shot from a distance of 5 cm.

Table 4

Pb, Sn, Cu and Zn concentrations on cotton targets and on corresponding filter paper supports shot from a distance of 5 cm. Values are expressed in $\mu\text{g}/\text{cm}^2$ units.

	[Pb]	[Sn]	[Cu]	[Zn]
MQL	0.003	0.005	0.003	0.001
COTTON TARGETS				
Field blanks	0.007	< MQL	0.139	0.026
SJSP	0.02±0.01	0.10±0.04	0.6±0.2	0.2±0.1
TMC	0.010±0.003	0.018±0.003	1.0±0.1	0.22±0.04
FMJ	3±1	0.017±0.004	1.0±0.2	0.43±0.09
FILTER PAPER SUPPORTS				
Field blanks	< MQL	< MQL	0.023	0.014
SJSP	< MQL	0.024±0.006	0.12±0.04	0.05±0.02
TMC	0.004±0.001	0.012±0.002	0.15±0.03	0.07±0.02
FMJ	0.18±0.06	0.013±0.003	0.20±0.04	0.09±0.04

474 residues (31.6%), Al in 267 residues (17.8%) and Ca in the remaining 213 residues (14.2%). The presence on targets of K, Si, Al and Ca, originating from the ZetaPi primer mixture, was confirmed by the ICP-OES analyses. According to the ICP-OES data, once the background (field blank) contribution was removed, potassium resulted the most abundant among the primer elements collected on targets, corroborating the results of the cited statistical research. Calcium followed potassium as the second most abundant element on targets. This result may appear incoherent with previous researches, as calcium is usually found as a minor element [20] in residues from Fiochi ZetaPi primer mixture. It should be considered that calcium, together with potassium itself, is also used as an additive for propellant powders [25] and its abundance on targets may indeed not originate from primer residues only. Even if these elements are widely diffused in the environment, their distributions

around the bullet holes, as shown in the XRF maps, confirmed a firearm-related origin (see Fig. 2 for potassium). For the two shorter shooting distances (5 cm and 20 cm), primer elements distributed around the entrance hole as a symmetric cloud of micrometric or sub-micrometric particles. The total amount of primer residue on target decreased with increasing the range of fire and, for longer shooting distances (≥ 40 cm), primer elements were visible in the bullet wipe only. There were no evidences of a possible correlation between primer element concentrations and fired bullet types.

On elements within the barrel

Memory effect in the selected firearm, due to the two SINOXID primed rounds previously discharged by the Italian proof house, was barely detectable. After discharging the first 10 HMF primed ammunitions (*Barrel conditioning #0*), barium was found in quantities just above its MQL for the cotton targets shot from 5 cm only, while antimony concentration was below its MQL in all the specimens.

Lead concentration on cotton targets shot from 5 cm decreased (-58%) passing from SJSP bullets (*Session #1*) to TMC bullets (*Session #2*). The effect of discharging a sequence of HMF ammunition whose bullets had no exposed lead was to reduce the amount of lead within the barrel and its consequent deposition on targets. On the contrary, few FMJ bullets (*Session #3*) were enough to boost lead presence inside the barrel and lead concentration on targets rapidly increased of more than two orders of magnitude. The XRF maps (see Fig. 5) clearly illustrate this behaviour. No lead signal was visible in the maps referring to cotton targets shot from 5 cm using both SJSP and TMC bullets, while the characteristic pattern of vaporized lead was predominant when FMJ bullets were fired. The lead pattern faded as soon as the shooting distance increased. On cotton targets shot from 20 cm and from 40 cm using

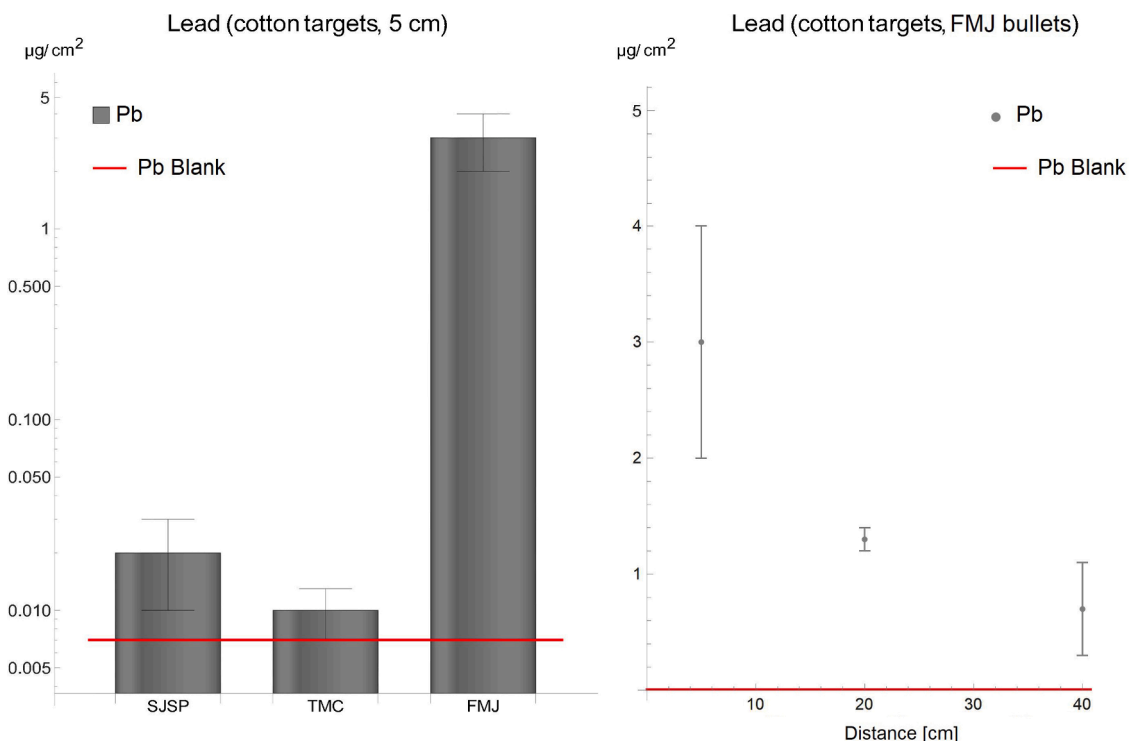


Fig. 4. Pb concentration on cotton targets shot from 5 cm using different bullets (left chart, in logarithmic scale) and its decay up to 40 cm (right chart) using FMJ bullets. For longer distances values fall below the reported field blank threshold.

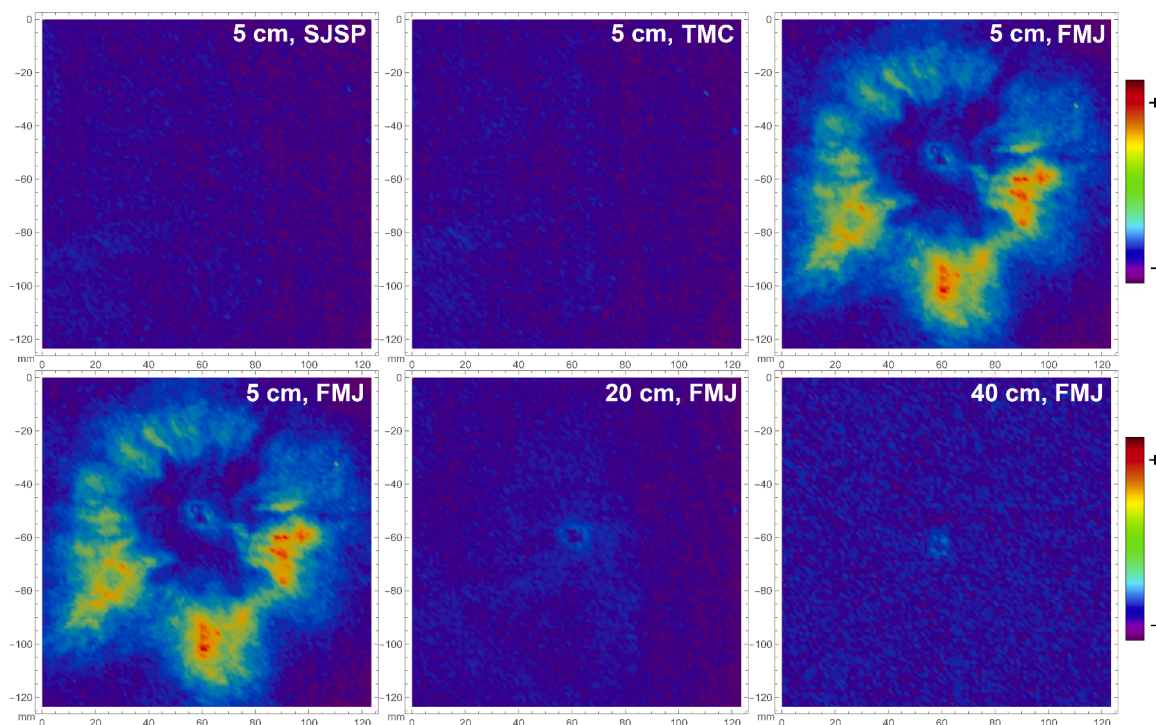


Fig. 5. Pb distribution patterns on cotton targets shot from 5 cm using different bullets (upper line) and up to 40 cm (lower line) using FMJ bullets only.

FMJ bullets, lead became barely visible in the bullet wipes only. The lack of lead in the primer mixture is held accountable for the rapid disappearing of the Pb signal [3], even at shooting distances where the XRF technique is still supposed to visualize detailed lead patterns.

The use of jacketed bullets enriched barrel residue population in copper and zinc, and both their concentrations on targets showed an

increasing trend passing from Session #1 to Session #2 and finally to Session #3. Copper and zinc deposited around entrance holes as scattered distributions of brass fragments, small pieces of swarf torn off from bullet jackets by the barrel rifling. Intense copper spots were indeed clearly visible in XRF maps from the cotton targets shot from 40 cm also (see Fig. 9). Copper and zinc were found in higher percentages than lead

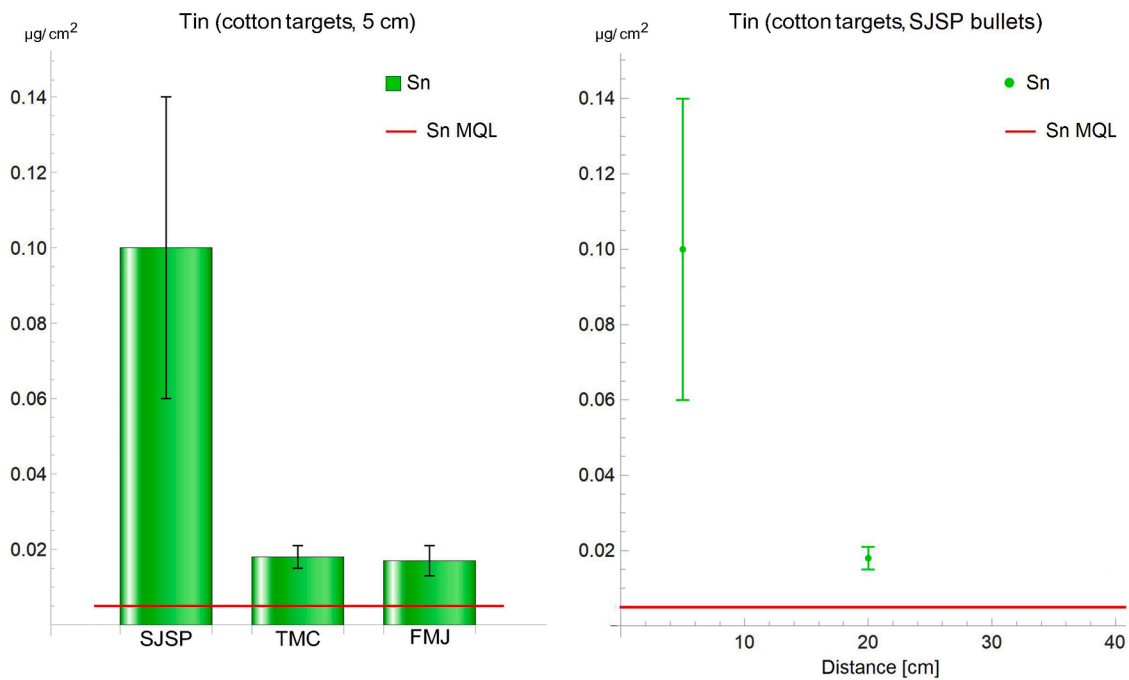


Fig. 6. Sn concentration on cotton targets shot from 5 cm using different bullets (left chart) and its decay up to 20 cm (right chart) using SJSP bullets. For longer distances values fall below the reported field blank threshold.

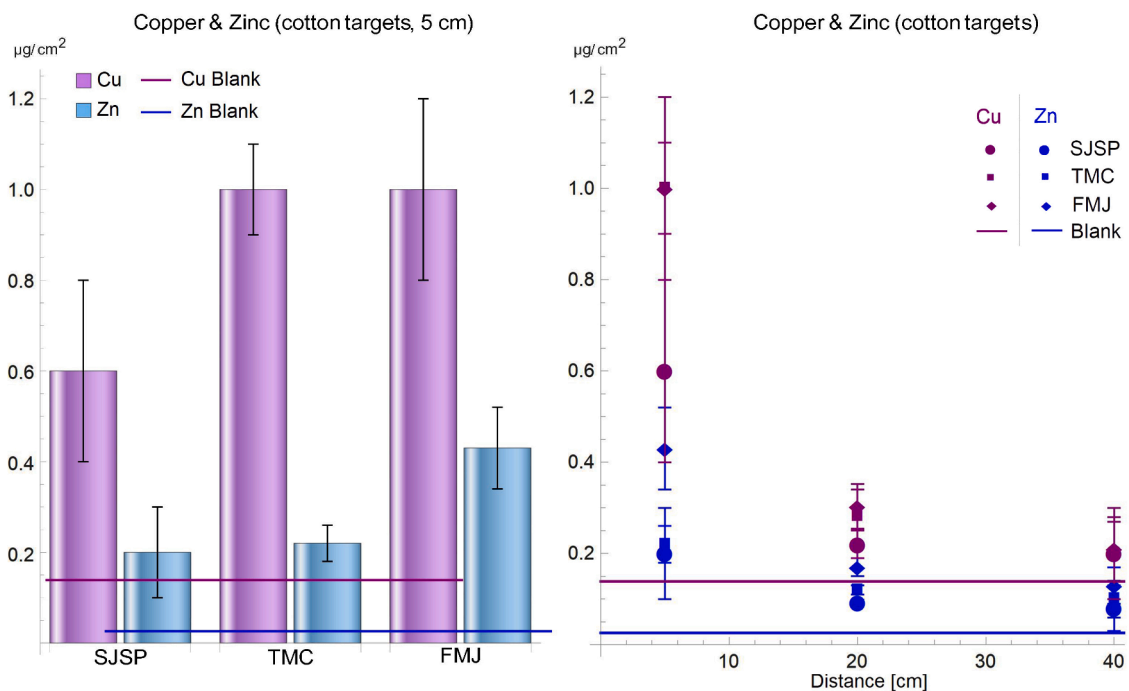


Fig. 7. Cu and Zn concentrations on cotton targets shot from 5 cm using different bullets (left chart) and their decay up to 40 cm (right chart).

on the filter papers behind the cotton targets (see Table 4). For the target shot from a distance of 5 cm using FMJ bullets, the amount of copper and zinc measured on the underlying filter paper sheet was about the 20% (19% and 22% respectively) of the mass detected on the cotton fabric. For lead, this value was the 6% only. The momentum of the copper/zinc fragments is supposed to be higher than the momentum of the smaller lead vaporized particles and it is held responsible for the deeper penetration of the pieces of brass swarf through the cotton targets.

On bullet identification

Ternary graphs were used for bullet identification. The relative concentrations of Pb, Sn and Cu were plotted within equilateral triangle charts (see Fig. 10).

For data collected on cotton targets shot from a distance of 5 cm, all specimens of the same bullet type grouped together in a limited area of the chart. For the shortest shooting distance, the mean values of the three selected elements were above their MQL or blank thresholds for all

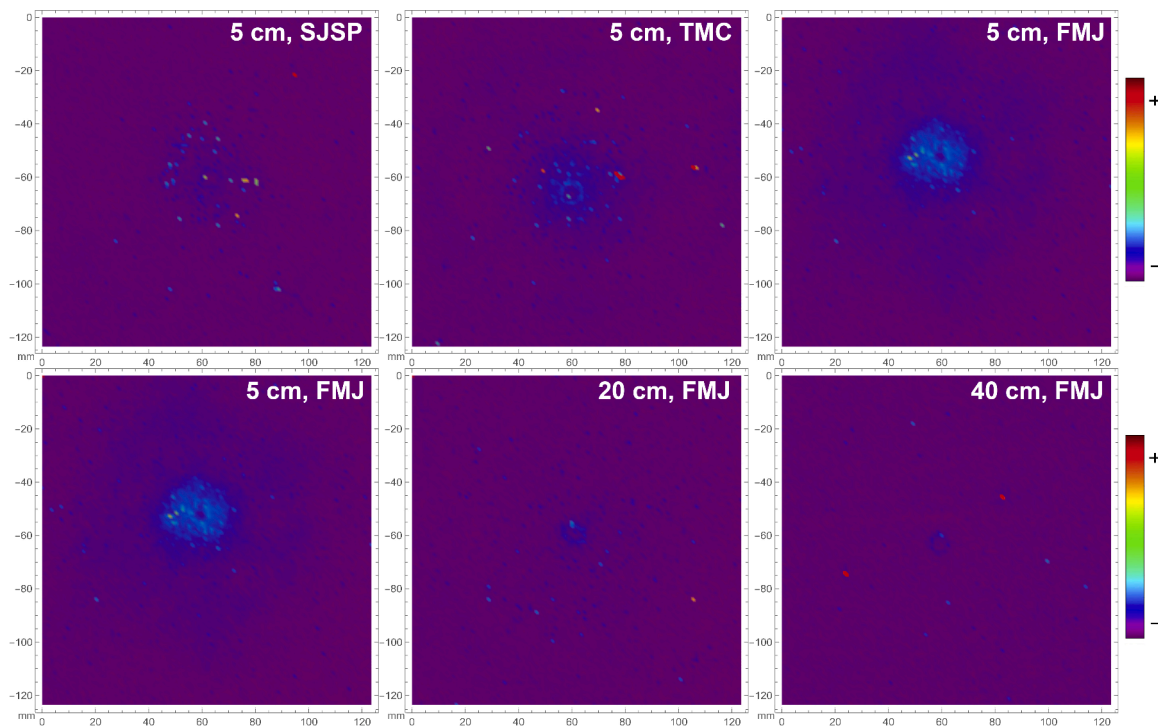


Fig. 8. Cu distribution patterns on cotton targets shot from 5 cm using different bullets (upper line) and up to 40 cm (lower line) using FMJ bullets only.

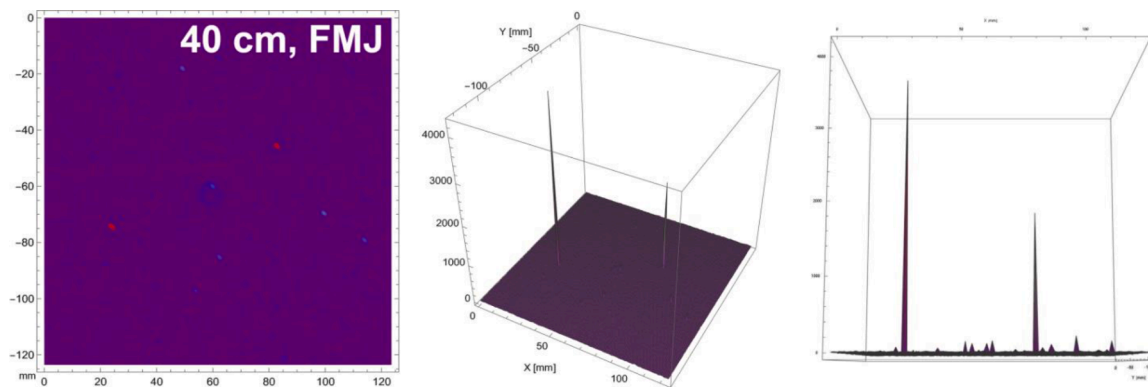


Fig. 9. Scattered distribution of the Cu signal on cotton target shot from a distance of 40 cm (left chart). Cu spots are clearly visible using 3D representations (middle and right charts).

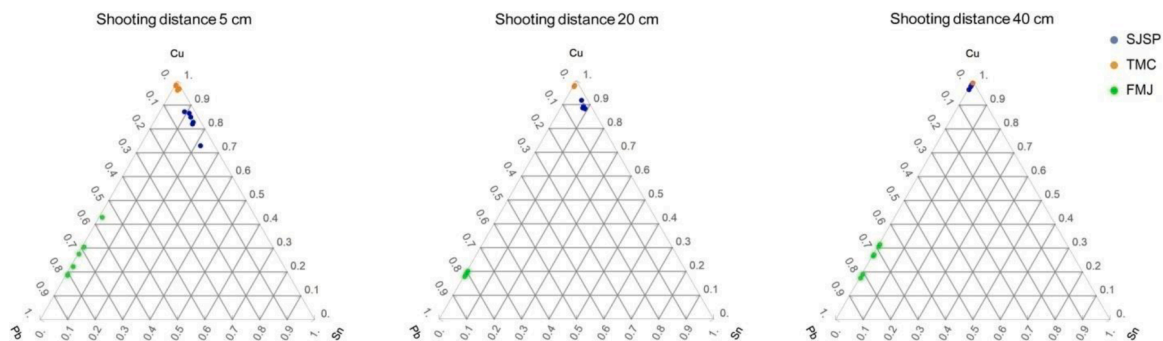


Fig. 10. Pb, Sn and Cu relative concentrations on cotton targets shot from a distance of 5 cm (left chart), 20 cm (middle chart), and 40 cm (right chart) using different bullets.

bullet types. High values for the relative concentration of Pb drove the FMJ markers in the lower-left part of the diagram. High relative concentration of Sn forced the SJSP markers in the upper-right part of the chart. Low values for the relative concentrations of both Pb and Sn in the TMC specimens implied high relative concentration for Cu and TMC markers grouped in the upper vertex of the triangle.

For data collected on cotton targets shot from a distance of 20 cm, Pb concentration was below its blank threshold for all SJSP and TMC specimens while Sn concentration below its MQL (and consequently set to zero) for all FMJ and TMC specimens. High values for the relative concentration of Pb grouped the FMJ markers in the lower part of the diagram, on the left side of the triangle. High relative concentration of Sn pushed the SJSP markers closer to the upper vertex, where the TMC markers were.

For data collected on cotton targets shot from a distance of 40 cm, Pb concentration was below its blank threshold for the SJSP specimens and below its MQL for the TMC specimens while Sn concentration was below its MQL for all specimens. The FMJ markers grouped on the left side of the triangle, in the lower part of the diagram, due to the high Pb concentration values. Due to the missing contribution of the relative concentrations of both Pb and Sn, the SJSP markers and the TMC markers overlapped in proximity of the upper vertex.

Forensic implications

The use of HMF primed ammunition in a brand new gun, together with a selection in the fired bullets, created a sort of ideal situation, not commonly encountered in real cases. The presented data have nevertheless some forensic implications in real cases.

First of all, it has been demonstrated that the threshold shooting distance, under which the most diffuse forensic technique are effective, depends on the firearm history. Usually, when lead is only found in the bullet wipe of an entrance hole, a shooting distance above 50 cm – 100 cm is speculated. In our experiments no lead deposition pattern was found on targets hit from 20 cm even if FMJ bullets, having exposed lead at the base, were fired.

Furthermore, it was proven that traces of the tip of a SJSP can be detected by ICP-OES on targets. Bullet soft-tips are usually made of lead, and lead presence on targets cannot be distinguished from SINOXID primer residue. When lead-free core bullets are used, soft-tip traces around the entrance holes can be used for projectile discrimination, at least for the shooting distances of 5 cm and 20 cm.

Finally, the limits of a high sensitive technique as ICP for forensic residue detection were pointed out. In previous researches, detectable quantities of lead, barium and antimony were found on the periphery of bullet entrance holes up to shooting distances of 2.5 meters and 1.5 meters, by ICP-MS [19] and ICP-OES [26] respectively. These values can be easily misinterpreted as the maximum distances for which the ICP technique can be used for firing range estimation purposes. In the present paper, although the test firings were performed with barrel-to-target distances up to 100 cm, ICP-OES data for most elements resulted below their MQL or field blank thresholds in specimens shot from the two longer distances of 80 cm and 100 cm. The tests performed at these two distances contributed to the whole shooting history of the firearm, so they were mentioned in the text. Although the upper barrel-to-target distance detection limit depends strongly on the chosen gun and on the ammunition [27], for shooting distances greater than 60 cm most of the relevant elements indeed accumulate in the bullet wipe only, as easily seen by XRF [28–30]. In our ICP-OES analyses, the elemental concentrations were calculated for a wider area, 7 cm × 7 cm, and meaningful data were collected for most elements up to a shooting distance of 40 cm. That was strictly true for the primer elements, as shown in the paper for K and Si, and this result is considered of potential forensic interest, too.

Conclusions

The use of HMF primed ammunition in a brand new pistol allowed distinguishing the amount of inorganic residue on targets originating from the bullets from that from the primer mixture. Element contributions were quantified by ICP-OES and visualized using XRF maps. Lead from the base of FMJ bullets and copper/zinc fragments from jacketed bullets were not the only sources of metallic residue on targets. A single opening on the tip of SJSP bullets, exposing the inner plain tin core, was enough to enrich in tin the inorganic residue on targets. The chosen shooting sequence (SJSP bullets first, then TMC and FMJ bullets) played indeed a role in reducing the presence of some elements within the barrel. Bullet type identification by residue analysis was possible using ternary charts as long as detectable amounts of Pb, Sn, and Cu were found on targets.

CRedit author statement

Daniele Merli: Conceptualization, Methodology, Supervision, Writing - Original Draft; **Cristiano Di Trocchio:** Investigation, Formal analysis, Writing - Original Draft; **Andrea Capucciati:** Investigation, Formal analysis; **Silvia Fabbris:** Investigation, Formal analysis; **Antonella Profumo:** Project administration; **Lucia Cucca:** Investigation; **Matteo Donghi:** Conceptualization, Investigation, Writing - Review & Editing, Visualization.

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Declaration of Competing Interest

The authors report no declarations of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.talo.2021.100067](https://doi.org/10.1016/j.talo.2021.100067).

References

- [1] B. Glattstein, A. Vinokurov, N. Levin, A. Zeichner, Improved method for shooting distance estimation. Part 1. Bullet holes in clothing items, *J. Forensic Sci.* 45 (4) (2000) 801–806.
- [2] N. Geusens, B. Nys, S. Charles, Implementation and optimization of the sodium-rhodizonate method for chemographic shooting distance estimation, *J. Forensic Sci.* 64 (2019) 1169–1172, <https://doi.org/10.1111/1556-4029.13984>.
- [3] B.J. Heard, Range of firing estimations and bullet hole examinations. *Handbook of Firearms and Ballistics: Examining and Interpreting Forensic Evidence*, second edition, Wiley Blackwell, Chichester – UK, 2008, pp. 211–239.
- [4] M.G. Haag, L.C. Haag, Some useful reagents and their application. *Shooting incident reconstruction*, second edition, Academic Press, San Diego–CA, USA, 2011, pp. 67–86.
- [5] U. Brede, R. Hagel, K.H. Redecker, W. Weuter, Primer compositions in the course of time: from black powder and SINOXID to SINTOX compositions and SINCO booster, *Propellants Explos. Pyrotech.* 21 (1996) 113–117, <https://doi.org/10.1002/prop.19960210302>.
- [6] ASTM E1588-20 standard practice for gunshot residue analysis by scanning electron microscopy/energy dispersive X-ray spectrometry, *Book of Standards Volume 14.02*, ASTM International, West Conshohocken, 2020, <https://doi.org/10.1520/E1588-20>.
- [7] A. Khanmy, A. Gallusser, Influence of weapon cleaning on the gunshot residues from heavy metal free ammunition, in: B. Jacob, W. Bonte (Eds.), *Advances in*

Forensic Sciences: Proceedings of the 13th Meeting of the International Association of Forensic Sciences, Düsseldorf, August 22nd to 28th 1993, Vol. 3, Verlag dr. Köster, Berlin, 1995, pp. 60–65.

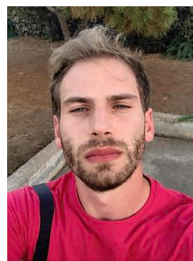
- [8] S. Charles, B. Nys, N. Geuens, Primer composition and memory effect of weapons—some trends from a systematic approach in casework, *Forensic Sci. Int.* 212 (1–3) (2011) 22–26, <https://doi.org/10.1016/j.forsciint.2011.05.001>.
- [9] A. Zeichner, N. Levin, E. Springer, Gunshot residue particles formed by using different types of ammunition in the same firearm, *J. Forensic Sci.* 36 (4) (1991) 1020–1026.
- [10] O. Black, S.Cole Smith, C. Roper, Advances and limitations in the determination and assessment of gunshot residue in the environment, *Ecotoxicol. Environ. Saf.* 208 (2021), 111689, <https://doi.org/10.1016/j.ecoenv.2020.111689>.
- [11] Z. Oommen, S.M. Pierce, Lead-Free Primer Residues: A Qualitative Characterization of Winchester WinClean, Remington/UMC LeadLess, Federal BallisticClean, and Speer Lawman CleanFire Handgun Ammunition, *J. Forensic Sci.* 51 (3) (2006) 509–519, <https://doi.org/10.1111/j.1556-4029.2006.00107.x>.
- [12] S.R. Hogg, B.C. Hunter, R. Waddell Smith, Elemental characterization and discrimination of nontoxic ammunition using scanning electron microscopy with energy dispersive X-ray analysis and principal components analysis, *J. Forensic Sci.* 61 (2016) 35–42, <https://doi.org/10.1111/1556-4029.12881>.
- [13] M. Donghi, K. Mason, F.S. Romolo, Detecting gunshot residue from seller & ballot nontox heavy metal-free primer by in situ cathodoluminescence, *J. Forensic Sci.* 64 (2019) 1658–1667, <https://doi.org/10.1111/1556-4029.14110>.
- [14] Z. Brozek-Mucha, A. Jankowicz, Evaluation of the possibility of differentiation between various types of ammunition by means of GSR examination with SEM–EDX method, *Forensic Sci. Int.* 123 (1) (2001) 39–47, [https://doi.org/10.1016/S0379-0738\(01\)00518-7](https://doi.org/10.1016/S0379-0738(01)00518-7).
- [15] M.E. Christopher, J.W. Warmenhooven, F.S. Romolo, M. Donghi, R.P. Webb, C. Jeynes, N.I. Ward, K.J. Kirkby, M.J. Bailey, A new quantitative method for gunshot residue analysis by ion beam analysis, *Analyst* 138 (16) (2013) 4649–4655, <https://doi.org/10.1039/C3AN00597F>.
- [16] M. López-López, J.J. Delgado, C. García-Ruiz, Ammunition identification by means of the organic analysis of gunshot residues using raman spectroscopy, *Anal. Chem.* 84 (8) (2012) 3581–3585, <https://doi.org/10.1021/ac203237w>.
- [17] D.S. Karahacane, A. Dahmani, K. Khimeche, Raman spectroscopy analysis and chemometric study of organic gunshot residues originating from two types of ammunition, *Forensic Sci. Int.* 301 (2019) 129–136, <https://doi.org/10.1016/j.forsciint.2019.05.022>.
- [18] R.N. Udey, B.C. Hunter, R.W. Smith, Differentiation of bullet type based on the analysis of gunshot residue using inductively coupled plasma mass spectrometry, *J. Forensic Sci.* 56 (5) (2011) 1268–1276, <https://doi.org/10.1111/j.1556-4029.2011.01836.x>.
- [19] G. Eksinitkun, The collection and identification of gunshot residues to distinguishing 4 types of bullets by ICP-MS, *J. Phys.: Conf. Ser.* 1144 (2018), 012118, <https://doi.org/10.1088/1742-6596/1144/1/012118>.
- [20] S. Romano, F. De-Giorgio, C. D’Onofrio, L. Gravina, S. Abate, F.S. Romolo, Characterisation of gunshot residues from non-toxic ammunition and their persistence on the shooter’s hand, *Int. J. Legal Med.* 134 (2020) 1083–1094, <https://doi.org/10.1007/s00414-020-02261-9>.
- [21] Article Informative Card ZetaPi Small Pistol Primer. Available online at: https://ffocchi.com/pub/static/frontend/bs_mazia/bs_mazia2/it_IT/media/catalogs/innes-co-small-pistol-zetapi-small-pistol-zp-primer.pdf (accessed 31 May 2021).
- [22] S. Fabbris, A. Profumo, G. Alberini, S. Bonomi, C. Milanese, M. Donghi, A. Amadasi, M. Patrini, L. Cucca, D. Merli, Interaction of gunshot residues (GSR) with natural and synthetic textiles having different structural features, *Talanta Open* 2 (2020), 100017, <https://doi.org/10.1016/j.talo.2020.100017>.
- [23] J.C.D. Freitas, J.E.S. Sarkis, O.N. Neto, S.B. Viebig, Identification of gunshot residues in fabric targets using sector field inductively coupled plasma mass spectrometry technique and ternary graphs, *J. Forensic Sci.* 57 (2) (2012) 503–508, <https://doi.org/10.1111/j.1556-4029.2011.01956.x>.
- [24] N. Sponticcia, Identificazione di un metodo statistico per la descrizione della popolazione di residui dello sparo da inneschi innovativi, Master Thesis in Mathematics, Università di Bologna, 2014, p. 34. https://amslaurea.unibo.it/6933/1/sponticcia_noemi_tesi.pdf.
- [25] R. Bender, D. Neimke, L. Niewöhner, M. Barth, M. Ebert, Discrimination of SINTOX® GSR against environmental particles and its automated investigation by SEM/EDS, *Forensic Chem.* 24 (2021), 100338, <https://doi.org/10.1016/j.forc.2021.100338>.
- [26] E. Turillazzi, G.P. Di Peri, A. Nieddu, Bello S, Monaci F, M. Neri, C. Pomara, R. Rabozzi, I. Riezzo, V. Fineschi, Analytical and quantitative concentration of gunshot residues (Pb, Sb, Ba) to estimate entrance hole and shooting-distance using confocal laser microscopy and inductively coupled plasma atomic emission spectrometer analysis: an experimental study, *Forensic Sci. Int.* 231 (1–3) (2013) 142–149, <https://doi.org/10.1016/j.forsciint.2013.04.006>.
- [27] R. Hofer, S. Graf, S. Christen, The use of unburned propellant powder for shooting-distance determination. Part I: infrared luminescence, *Forensic Sci. Int.* 273 (2017) 10–19, <https://doi.org/10.1016/j.forsciint.2017.01.019>.
- [28] A. Berendes, D. Neimke, R. Schumacher, M. Barth, A versatile technique for the investigation of gunshot residue patterns on fabrics and other surfaces: m-XRF, *J. Forensic Sci.* 51 (2006) 1085–1090, <https://doi.org/10.1111/j.1556-4029.2006.00225.x>.
- [29] edited by R. Schumacher, M. Barth, D. Neimke, L. Niewöhner, Investigation of gunshot residue patterns using milli-XRF-techniques: first experiences in casework, in: M.T. Postek, D.E. Newbury, S.F. Platek, D.C. Joy (Eds.), *Proceedings of SPIE 7729, Scanning Microscopy 2010, 2010, 772917*, <https://doi.org/10.1117/12.853852>, edited by.
- [30] S. Latzel, D. Neimke, R. Schumacher, M. Barth, L. Niewöhner, Shooting distance determination by m-XRF—Examples on spectra interpretation and range estimation, *Forensic Sci. Int.* 223 (1–3) (2012) 273–278, <https://doi.org/10.1016/j.forsciint.2012.10.001>.



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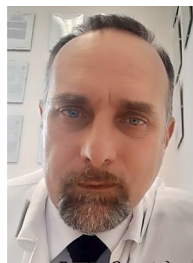
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