Electronic Supplementary Material (ESI) for Analyst.

Analysis of primer gunshot residue particles by Laser Induced Breakdown Spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Supplementary material for the article titled:

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S1. Elemental Heat Maps of Blank Carbon Adhesive GSR Collection Stubs

For fast visualization for interpreting the presence or absence of an element in a single micro-area, heat maps were creating using the SNR ratios of elemental profiles for each ablation spot. Heat maps for leaded and non-leaded *p*GSR standards can be seen in the main manuscripts as Figure 4 and Figure 5. Blank stubs were also analyzed for comparison to known GSR samples. Figure S1 below shows heat maps created from elemental intensities obtained during LA-ICP-MS analysis. Scales were matched to those of leaded and non-leaded heat maps, for each respective element. The blank heat maps show lower concentrations, represented as white colored spots, compared to heats maps created from known microparticle standards. All 25 spots were below the signal-to-noise threshold of 3, indicating the absence of monitored elements (i.e. ^{138}Ba, ^{208}Pb, ^{121}Sb, ^{49}Ti, ^{64}Zn). The heat maps provide a quick screening of any elements that may be present in the stub background prior to deposition of *p*GSR standards or collection from known shooters. No false positive results recorded from blank samples provides further confidence that future detection of IGSR elements on shooter samples indicates the presence of GSR particles.

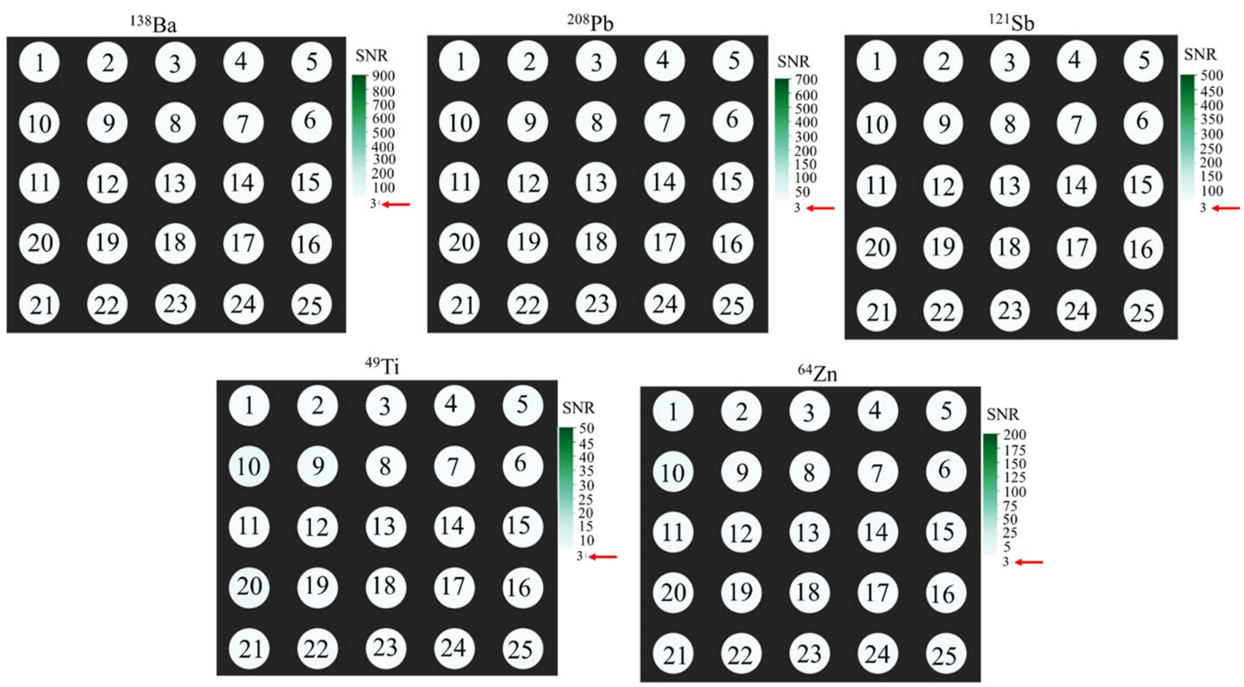

Figure S1. Heat maps created using LA-ICP-MS integrated area for blank sample for Ba, Pb, Sb, Ti and Zn). The threshold of SNR of 3 is pointed out with an arrow and is represented here with the whitest shade in the scale. In this example, none of the spots were below the threshold. In this example, all ablated regions were below threshold (SNR ≥3).

S2. Assessment of LA-ICP-MS analysis for the classification of authentic background and shooter samples

S2.1. Analysis of 60 individual background hand samples

Hand samples were collected from sixty individuals who were considered “low-risk” for containing IGSR-like particles due to their occupations and non-recent use of a firearm. Occupations such as mechanics, police officers, and electricians, as well as anyone who had discharged a firearm less than 24 hours prior to collection, were avoided during sampling. The sixty individual samples are summarized below in Table S1. A background sample was considered a false positive 2 or more IGSR elements (e.g Pb, Ba, Sb) were detected in a single ablation spot. Four false positive samples were detected in the background population collected for this study. However, only one spot in the 25 spot ablation pattern showed presence of IGSR elements, for each of the contaminated individuals. The rest of the population (56 individuals) we pristine background samples with no detection of IGSR elements of interest.

Background hand samples were used to provide critical threshold amounts of elements in the general population. The critical thresholds were calculated as the mean of the 60 background samples plus 3 times the standard deviation. When applied to authentic shooter samples, if elements appeared above the critical threshold determined by the background hands samples, they were considered present. Conversely, if the elements in the authentic shooter samples appeared below the critical threshold, they were considered absent. The final critical thresholds calculated from the 60 hand samples were: 12.3 ^{208}Pb, 24.8 ^{138}Ba, 12.5 ^{121}Sb, 109.1, ^{209}Bi, 154.7 ^{63}Cu, 96.2 ^{64}Zn, and 266.0 ^{49}Ti.

Table S1. *Summary table of background hand sample classifications (N/A= not applicable as none of the target elements are anticipated in true negative backgrounds)*

Sample	IGSR Elements Expected	IGSR Elements Detected	Classification
Indiv_01	N/A	---	Negative
Indiv_02	N/A	---	Negative
Indiv_03	N/A	---	Negative
Indiv_04	N/A	---	Negative
Indiv_05	N/A	---	Negative
Indiv_06	N/A	Sb, Ba (1 spot)	False Positive
Indiv_07	N/A	---	Negative
Indiv_0	N/A	---	Negative

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Indiv_09	N/A	Pb, Ba, Sb (1 spot)	False Positive
Indiv_10	N/A	Pb, Sb (1 spot)	False Positive
Indiv_11	N/A	---	Negative
Indiv_12	N/A	---	Negative
Indiv_13	N/A	---	Negative
Indiv_14	N/A	---	Negative
Indiv_15	N/A	---	Negative
Indiv_16	N/A	---	Negative
Indiv_17	N/A	---	Negative
Indiv_18	N/A	---	Negative
Indiv_19	N/A	---	Negative
Indiv_20	N/A	Ba, Pb (1 spot)	False Positive
Indiv_21	N/A	---	Negative
Indiv_22	N/A	---	Negative
Indiv_23	N/A	---	Negative
Indiv_24	N/A	---	Negative
Indiv_25	N/A	---	Negative
Indiv_26	N/A	---	Negative
Indiv_27	N/A	---	Negative
Indiv_28	N/A	---	Negative
Indiv_29	N/A	---	Negative
Indiv_30	N/A	---	Negative
Indiv_31	N/A	---	Negative
Indiv_32	N/A	---	Negative
Indiv_33	N/A	---	Negative
Indiv_3	N/A	---	Negative

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Indiv_35	N/A	---	Negative
Indiv_36	N/A	---	Negative
Indiv_37	N/A	---	Negative
Indiv_38	N/A	---	Negative
Indiv_39	N/A	---	Negative
Indiv_40	N/A	---	Negative
Indiv_41	N/A	---	Negative
Indiv_42	N/A	---	Negative
Indiv_43	N/A	---	Negative
Indiv_44	N/A	---	Negative
Indiv_45	N/A	---	Negative
Indiv_46	N/A	---	Negative
Indiv_47	N/A	---	Negative
Indiv_48	N/A	---	Negative
Indiv_49	N/A	---	Negative
Indiv_50	N/A	---	Negative
Indiv_51	N/A	---	Negative
Indiv_52	N/A	---	Negative
Indiv_53	N/A	---	Negative
Indiv_54	N/A	---	Negative
Indiv_55	N/A	---	Negative
Indiv_56	N/A	---	Negative
Indiv_57	N/A	---	Negative
Indiv_58	N/A	---	Negative
Indiv_59	N/A	---	Negative
Indiv_6	N/A	---	Negative

0			

S2.2. Analysis of 37 individual authentic shooter samples using standard ammunition

Authentic shooter hand samples were collected from individuals immediately discharging 5 rounds of standard ammunition from either a pistol or revolver firearm. Four stubs were collected from each individual (left hand back, left hand palm, right hand back, right hand palm). Out of the four stubs, the one determined to have highest intensities of IGSR elements by LIBS was chosen to be analyzed by LA-ICP-MS. All of the standard ammunition used in this study contained the elements lead, barium, and antimony as major IGSR markers. Sample data was assessed using the previous determined critical thresholds of 12.3 ^{208}Pb, 24.8 ^{138}Ba, 12.5 ^{121}Sb, 109.1. Much like background hand samples, an ablation spot was considered positive if 2 or more elements of interest were present above the critical threshold and negative if one or no elements were detected above thresholds. A summary of all 37 individual samples can be seen below in Table S2.

All 37 individuals tested positive for IGSR elements of interest, and were categorized as characteristic classifications according to the ASTM 1588-20 guidelines for GSR analysis by SEM-EDS[1]. However, in a previous characterization study performed by our group, one standard ammunition manufactured by TulAmmo did not contain the major IGSR element of Ba. Therefore, TulAmmo (TUL) samples that detected Ba, along with Sb and Pb were considered to have memory effect from the firearm. The presence of barium arose from memory effect and shooting range carry over that is described in-depth in Section 3.4.2 of the main manuscript. Still, only 3 of 37 individuals were effected by memory of the firearm, leading to performance rates of 91.8% true positives and 8.2% true negatives, therefore providing evidence that LA-ICP-MS analysis is a useful tool in the screening of GSR hand samples collected from suspected shooters.

Table S2. Summary table of standard shooter hand sample classifications by LA-ICP-MS

Sample	Ammunition	Firearm	Standard IGSR Elements Expected in Primer	IGSR Elements Detected	Classification	Number of Spots with Memory Effect Detected (X/25)
Indiv_01	REM	9mm Pistol	Pb, Ba, Sb	Pb, Ba, Sb	Positive (characteristic)	0
Indiv_02				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_03				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_04				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_05				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_06				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_07				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_08				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_09		9mm Revolver		Pb, Ba, Sb	Positive (characteristic)	0
Indiv_10				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_11				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_12				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_13				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_14	WIN	9mm Pistol	Pb, Ba, Sb	Pb, Ba, Sb	Positive (characteristic)	0
Indiv_15				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_16				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_17				Pb, Ba, Sb	Positive (characteristic)	0

Indiv_18				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_19				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_20				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_21				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_22	Blazer	9mm Pistol	Pb, Ba, Sb	Pb, Ba, Sb	Positive (characteristic)	0
Indiv_23				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_24				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_25				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_26				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_27	SAB	9mm Pistol	Pb, Ba, Sb	Pb, Ba, Sb	Positive (characteristic)	0
Indiv_28				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_29				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_30	TUL	9mm Pistol	Pb, Sb	Pb, Ba, Sb	Positive (memory effect)	25
Indiv_31				Pb, Ba, Sb	Positive (memory effect)	25
Indiv_32				Pb, Ba, Sb	Positive (memory effect)	25
Indiv_33	FED	.357 Revolver	Pb, Ba, Sb	Pb, Ba, Sb	Positive (characteristic)	0
Indiv_34				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_35				Pb, Ba, Sb	Positive (characteristic)	0
Indiv_3				Pb, Ba, Sb	Positive	0

6					(characteristic)	
Indiv_37				Pb, Ba, Sb	Positive (characteristic)	0

S3. References

1. ASTM International, *E1588-20: Standard Practice for Gunshot Residue Analysis by Scannin Electron Micropscopy/Energy Dispersive Z-Ray Spectrometry,* West Conshohocken, 2020.