Electronic Supplementary Information (ESI)

A novel method for unequivocal identification of inorganic and organic gunshot residue particles of lead-free ammunitions in the hands of shooters using Scanning Laser Ablation- ICPMS and Raman micro-spectroscopy

*.Zuriñe Abrego [a], Nagore Grijalba [a], Nora Unceta [a], Maite Maguregui [a], Alicia Sanchez [a], Alberto Fernández-Isla [b], M. Aranzazu Goicolea [a], Ramón J. Barrio, [a] **

[a] Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country, UPV/EHU, Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain

[b] Scientific Police Laboratory, Ertzaintza, Department of the Interior, Basque Government, Erandio, Spain

* Corresponding author.

E-mail address: r.barrio@ehu.es

FAX: +34 945014351

Ammunition	Bullet	Primer	Composition
Fiocchi 9 mm Luger ZP: **F1**	Sn bullet jacketed with Cu	Heavy-metal free	Diazodinitrophenol, tetracene, PETN, nitrocellulose, aluminium silicate, Cu, Zn, Zr
Fiocchi 9 mm Luger Gas Check: **F2**	Pb bullet, jacketed with Teflon®/PTFE	Lead-free	Diazodinitrophenol, tetracene, PETN, nitrocellulose, $Ba(NO_3)_2$, Sb_2S_3, Al, Cu, Zn
Fiocchi 9 mm Luger 9x19 Leadless: **F3**	Cu bullet	Lead-free	Diazodinitrophenol, tetracene, PETN, nitrocellulose, $Ba(NO_3)_2$, Sb_2S_3, Al, Cu, Zn
Remington/UMC Leadless TM 9 mm Luger: **R1**	Pb bullet, jacketed with Cu	Lead-free	Diazodinitrophenol, 2,4-dinitrotoluene, tetracene, nitrocellulose, nitroglycerin, dibutyl phthalate, diphenylamine, Cu, Zn, Pb, Ba, Sb, As, Ni, graphite
Sellier&Bellot 9 mm Luger FMJ: **SB1**	Pb bullet jacketed with Cu	Lead-containing primer	Nitrocellulose, nitroglycerine, dibutyl phthalate, diphenylamine, dinitrotoluene, trinitroresorcinate, tetracene, PETN, Pb, Cu, Zn, Fe, Sb, As, Ni, Ba, S, B, K, graphite

Table S-1. Inorganic and organic composition of the ammunitions [1-4]

(1) Remington-Arms, Material Safety Data Sheet: Centerfire rifle, pistol & revolver loaded round (lead-less); Remington-Arms Company: Madison, NC, USA, **2001**.

(2) Fiocchi-Munizioni, Scheda di Sicurezza Prodotto: Inneschi boxer "ZETAPI" per cartucce a fuoco centrale; Fiocchi Munizioni S.P.A. **2006**.

(3) Fiocchi-Munizioni, Scheda di Sicurezza Prodotto: Leadless boxer primers for centerfire ammunitions; Fiocchi Munizioni S.P.A. **2007**.

(4) Sellier-Bellot, Safety data sheet: Center-fore cartridges; Sellier & Bellot, **2009**.

Ammunition	F1			F2			F3			R1		
Elemental profile of particles found	Shots *(n = 3)*			Shots *(n = 3)*			Shots *(n = 3)*			Shots *(n = 3)*		
	1	3	6	1	3	6	1	3	6	1	3	6
Pb-Sb-Ba	3±2	4±1	5±2	7±5	6±3	13±5	1±1	5±3	8±6	4±3	11±2	11±7
Sb-Ba	2±1	3±3	8±3	3±3	4±1	4±2	2±2	4±3	7±2	1±1	3±2	2±2
Sb-Pb	1±1	1±1	1±1	2±2	1±1	2±2	2±2	-	3±3	1±1	-	2±1
Pb-Ba	1±1	1±1	-	-	1±1	1±1	-	-	1±1	1±1	-	2±1
Pb	3±3	3±3	3±2	2±2	2±2	4±3	2±1	2±2	5±5	1±1	1±1	1±1
Ba	3±3	2±1	2±2	2±1	1±1	3±1	1±1	3±3	5±2	3±3	1±1	3±2
Sb	5±3	4±3	5±4	1±1	1±1	1±1	1±1	3±2	2±2	2±2	1±1	3±1
Zr	2±1	1±1	7±3	2±1	1±1	4±2	1±1	2±2	4±3	1±0	2±2	3±2
Cu	3±2	2±1	3±2	3±2	3±1	3±3	4±1	3±3	5±4	4±1	4±1	6±6
Al	2±2	1±1	3±1	6±1	4±2	8±1	3±1	3±3	5±1	2±1	1±0	6±2
Ni	3±3	0±0	1±1	-	-	-	-	-	-	-	-	3±3
Ti	1±0	2±1	12±7	2±1	3±1	13±6	2±1	2±2	9±9	2±2	2±1	12±11
Sr	-	-	-	-	-	-	1±1	1±1	2±2	1±1	1±0	4±4
Sn	-	-	2±2	-	1±1	2±2	-	-	-	-	-	-
Al-Ti	-	-	3±2	-	1±1	2±2	-	-	-	1±1	1±1	2±2
Cu-Zn	-	2±1	2±1	3±2	3±2	5±5	2±1	1±1	1±1	4±3	4±1	1±1
Sr-Zr	-	3±1	1±1	1±1	3±2	4±3	1±1	4±3	1±1	-	-	-
Cu-Zn-Sn	-	-	-	-	-	-	-	-	-	-	3±3	-
Al-Sr-Zr	-	2±0	1±1	-	-	-	1±1	1±1	1±1		-	-

Table S-2. Elemental profile and number of particles found by LA-ICP-MS analysis after 1, 3 and 6 shots from the five ammunitions investigated. Uncertainty given as 95% confidence intervals.

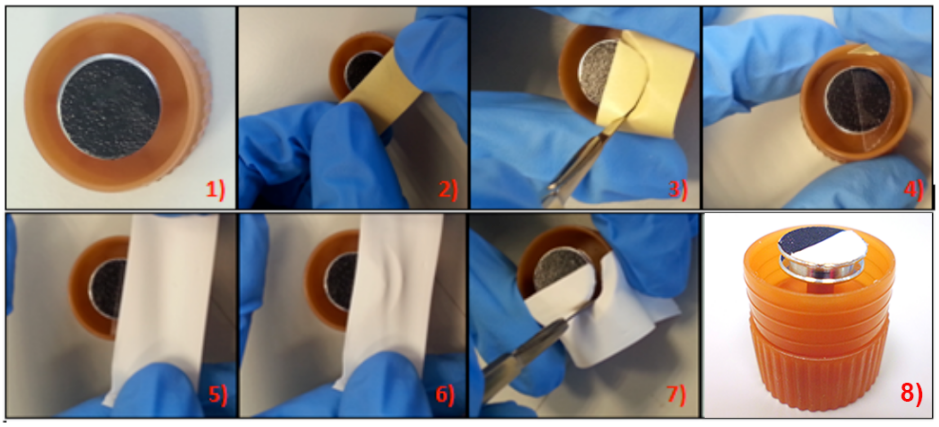

Figure S-1. Home modified tape lift manufacture

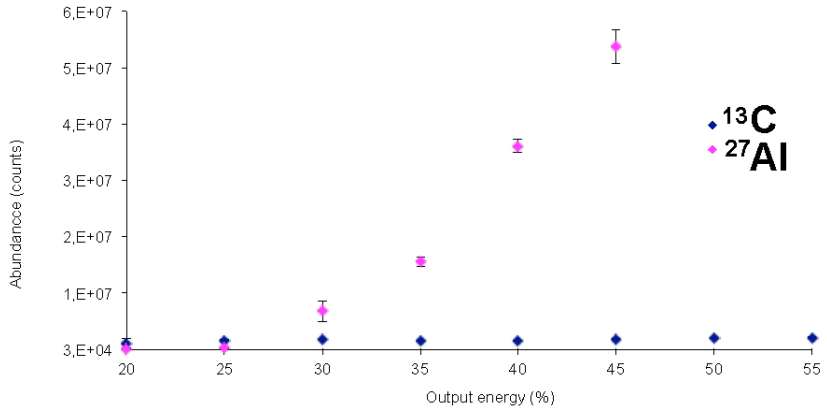

Figure S-2. Influence of the laser output energy on the ^{27}Al and ^{13}C signals.

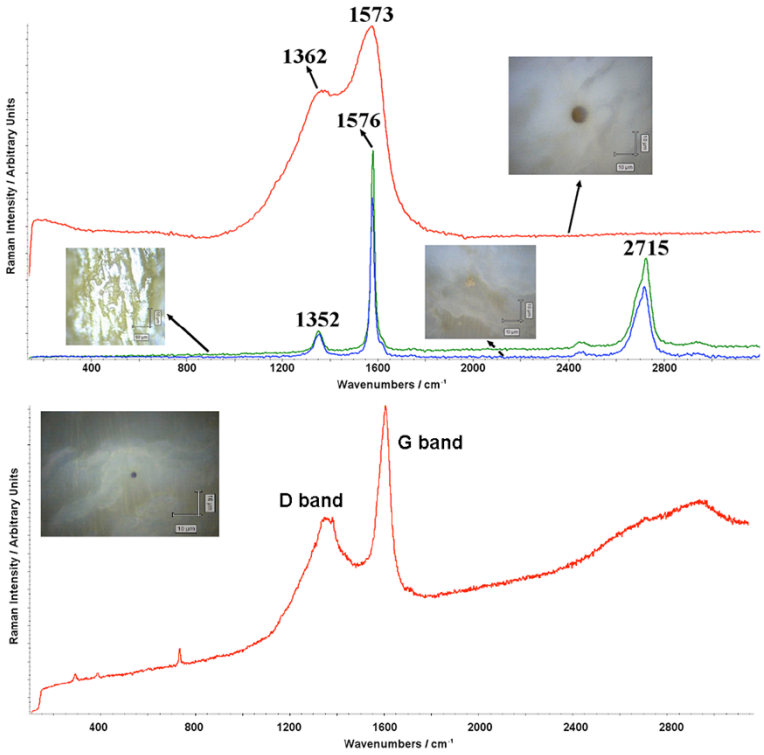

Figure S-3. A) Raman spectrum of F1 ammunition graphite covering (green), Raman spectrum of a non-spherical particle of unburnt graphite from the covering of the ammunition (blue) and Raman spectrum of amorphous carbon coming from the blackened spherical particle (red). On the left, a microscopic detail of the graphite covering (20x objective lens), in the middle a microscopic detail of the unburnt graphite particle (100x objective lens) and on the top-right a microscopic detail of the blackened spherical particle (100x objective lens). B) Raman spectrum of a 2 μm spherical black particle (see a microscopic detail under 100x objective lens) showing the bands of carbon.

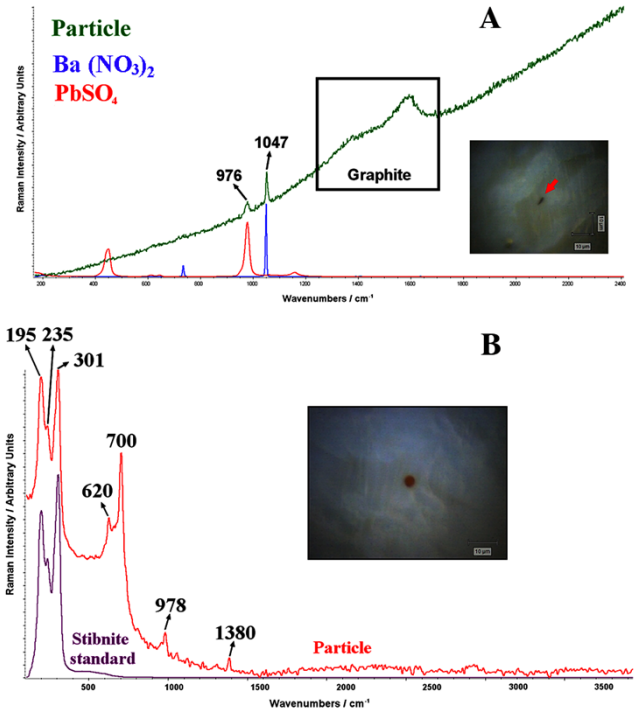

Figure S-4 A) Raman spectrum of a representative R1 GSR particle (green) (see a microscopic detail of the particle under 100x objective lens) and Raman spectra of nitrobarite (blue) and $PbSO_4$ (red) standards. B) Raman spectrum of a representative F2 GSR particle (see a microscopic detail of the particle under 100x objective lens) and Raman spectra of stibnite standards.

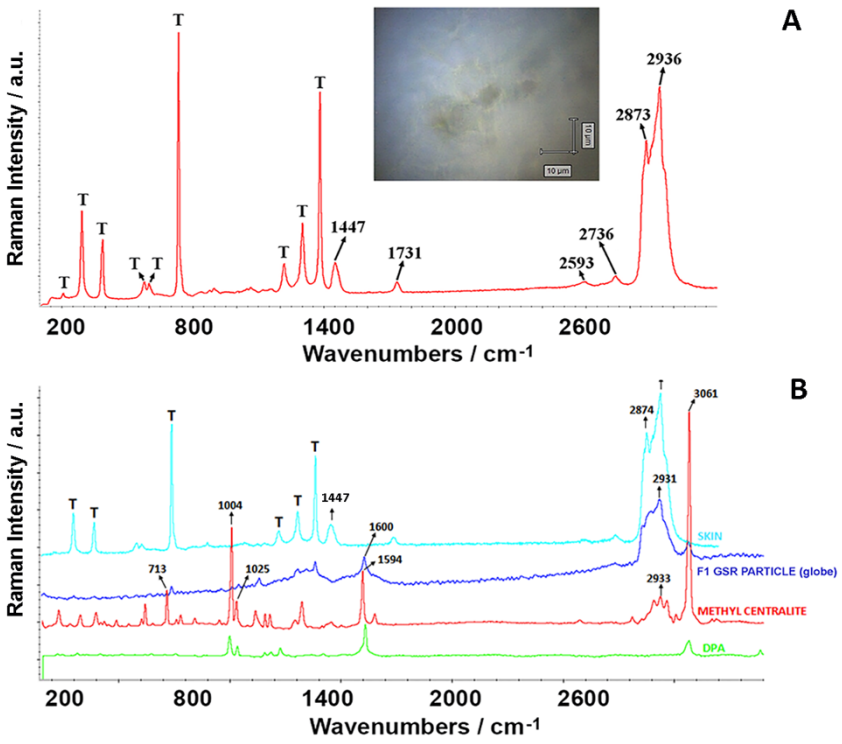

Figure S-5. Raman spectrum of brownish spots (see a microscopic detail using the 100x objective lens) on the PTFE sampling support (bands assigned to PTFE are labeled using a T).

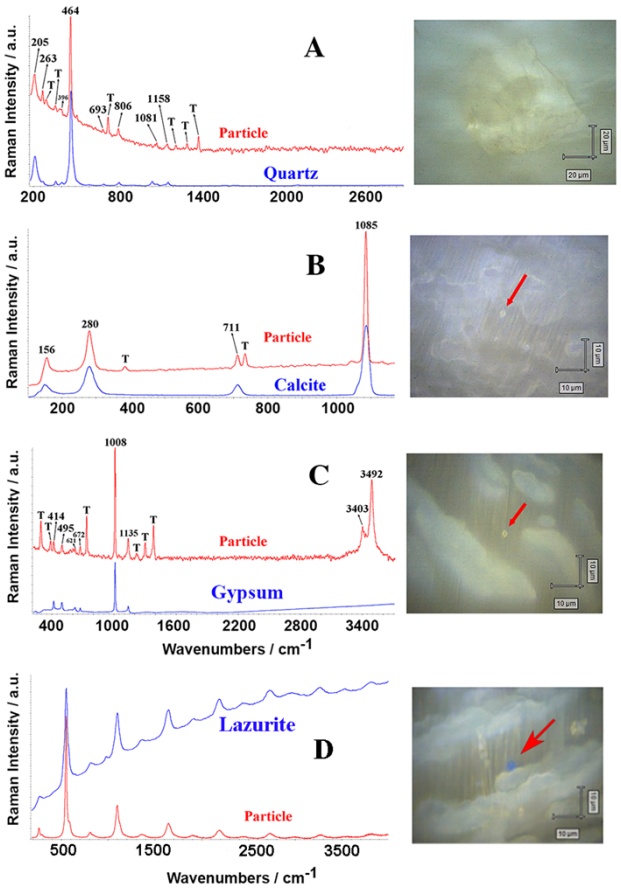

Figure S-6. A) Raman spectrum of a F3 GSR particle in red (see a microscopic detail under the 50x objective lens)) and a Raman spectrum of a quartz standard in blue. B) Raman spectrum of a F2 GSR particle in red (see a microscopic detail under the 100x objective lens) and a Raman spectrum of a calcite standard in blue. C) Raman spectrum of a F1 GSR particle in red (see a microscopic detail under 100x objective lens) and a Raman spectrum of a gypsum standard in blue (bands assigned to Teflon are labeled using a T).