Supplemental Information

A Feasibility Study of Direct Analysis in Real Time-Mass Spectrometry for Screening Organic Gunshot Residues from Various Substrates

Supplemental Information

1. Shooter's Hand Samples Results

Tables S1 and **S2** provide detailed information on the results obtained from the DART-MS analysis of the shooter's hand samples per compound. These results were used to determine whether a sample was classified as characteristic of OGSR (colored green in the table's criteria column, at least two *Category I* compounds present), consistent with OGSR (yellow, at least one *Category I* and one *Category II*), commonly associated with OGSR (orange, at least one *Category I* or *Category II* compound present), or was negative for OGSR (red, no compounds detected). For information regarding compound-specific classification criteria (i.e., *Category I or II*), please refer to **Table 4** within the main text. Samples with compounds listed as not detected (ND) had either the compounds outside of the mass range or below the relative intensity limit, and these results are presented in white background cells in **Tables S1 and S2**. In **Tables S1 and S2**, the results for detected compounds that met the mass range criteria (± 0.005 Da) and the minimum relative intensity criteria (>3%) are presented in cells colored in green. The results for each detected compound include the exact mass and the relative intensity percent (RI).

Table S1 illustrates that out of the 50 samples examined, 15 had residues characteristic of OGSR, 8 consistent with OGSR, and 8 commonly associated with OGSR, for a total of 31 of the samples having at least one OGSR compound (62%). The remaining 19 samples were negative for OGSR screening. Fiocchi and Winchester provided the most positive results from the ammunition tested in this set.

Table S2 presents the results for the second set, consisting of Winchester ammunition of various calibers. In this set, the samples were only monitored in positive mode due to uncontrolled circumstances of malfunctioning of the negative mode at that time, therefore affecting the capability of reporting results *characteristic of OGSR*. However, there was an increase in the positive results, with 15 out of 30 samples classified as consistent with OGSR, and 12 additional samples commonly associated with OGSR, for a total of 27 samples with at least one OGSR

compound (90%). In this second set, samples exposed to ammunition with higher caliber produced higher positive rates.

Table S1. Results from the first 50 shooter's hand samples analyzed by DART-MS (set 1). The table lists the sample number, respective manufacturer, and compounds analyzed in positive and negative modes.

Authentic Hand Samples - DART-MS, Subset 1																	
		Positive Mode									Negative Mode						
Sample No.	Manufacturer	[AKII]	AKII RI	[MC]	MC RI	[EC]	EC RI	[DPA]	DPA RI	[2-,4-NDPA]	2-,4-NDPA RI	[NG]	NG RI	[2,4-DNT]	2,4-DNT RI	[2-,4-NDPA]	2-,4-NDPA RI	Criteria
1	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
2	Blazer	ND	N/A	ND	N/A	269.16251	97.0	ND	N/A	ND	N/A	288.99393	61.8	ND	N/A	ND	N/A	Characteristic
3	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
4	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
5	Blazer	227.11896	17.2	ND	N/A	ND	N/A	170.09911	5.6	ND	N/A	288.99460	69.0	ND	N/A	ND	N/A	Consistent
6	Blazer	227.12070	29.1	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99509	25.2	ND	N/A	ND	N/A	Consistent
7	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
8	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
9	Blazer	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
10	Blazer	227.12274	21.9	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99396	15.0	ND	N/A	ND	N/A	Consistent
11	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99310	5.9	ND	N/A	ND	N/A	Commonly Associated
12	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
13	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
14	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
15	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99146	46.2	ND	N/A	ND	N/A	Commonly Associated
16	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
17	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
18	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
19	Federal	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
20	Federal	227.12198	20.1	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99170	40.1	ND	N/A	ND	N/A	Consistent
21	Fiocchi	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
22	Fiocchi	ND	N/A	ND	N/A	269.16428	7.4	ND	N/A	ND	N/A	288.99313	5.2	ND	N/A	ND	N/A	Characteristic
23	Fiocchi	ND	N/A	ND	N/A	269.16125	76.7	170.09769	8.7	ND	N/A	288.99152	89.5	ND	N/A	ND	N/A	Characteristic
24	Fiocchi	ND	N/A	ND	N/A	269.16974	5.6	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated
25	Fiocchi	ND	N/A	ND	N/A	269.16116	21.3	ND	N/A	ND	N/A	288.99094	100.0	ND	N/A	ND	N/A	Characteristic
26	Fiocchi	ND	N/A	ND	N/A	269.16147	36.0	ND	N/A	ND	N/A	288.99118	29.5	ND	N/A	ND	N/A	Characteristic
27	Fiocchi	ND	N/A	ND	N/A	269.16339	23.2	ND	N/A	ND	N/A	288.99136	14.5	181.02693	8.7	ND	N/A	Characteristic
28	Fiocchi	ND	N/A	ND	N/A	269.16174	41.3	ND	N/A	ND	N/A	288.99164	100.0	181.02603	7.3	ND	N/A	Characteristic
29	Fiocchi	ND	N/A	ND	N/A	269.16312	100.0	170.09608	20.0	ND	N/A	288.99121	22.5	181.02646	9.9	ND	N/A	Characteristic
30	Fiocchi	ND	N/A	ND	N/A	269.16202	15.0	ND	N/A	ND	N/A	288.99323	6.1	ND	N/A	ND	N/A	Characteristic
31	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
32	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99130	10.3	ND	N/A	ND	N/A	Commonly Associated
33	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
34	Remington	ND	N/A	ND	N/A	269.16336	100.0	ND	N/A	ND	N/A	288.99084	100.0	ND	N/A	ND	N/A	Characteristic
35	Remington	ND	N/A	ND	N/A	269.16495	100.0	ND	N/A	ND	N/A	288.99106	100.0	ND	N/A	ND	N/A	Characteristic
36	Remington	ND	N/A	ND	N/A	269.16345	47.2	ND	N/A	ND	N/A	288.99045	100.0	181.02596	5.4	ND	N/A	Characteristic
37	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
38	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
39	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99094	36.6	181.02515	10.9	ND	N/A	Consistent
40	Remington	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99152	4.8	ND	N/A	ND	N/A	Commonly Associated
41	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	181.02829	7.3	ND	N/A	Commonly Associated
42	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
43	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99249	9.3	ND	N/A	ND	N/A	Commonly Associated
44	Winchester	227.11890	70.0	ND	N/A	269.16931	10.4	170.09979	10.5	ND	N/A	288.99139	28.1	ND	N/A	ND	N/A	Characteristic
45	Winchester	227.12108	26.6	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99109	100.0	181.02263	4.4	ND	N/A	Consistent
46	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99130	29.2	181.02876	9.9	ND	N/A	Consistent
47	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	288.99133	39.0	181.02682	10.8	ND	N/A	Consistent
48	Winchester	227.11940	79.1	ND	N/A	269.16882	12.1	170.10046	12.9	ND	N/A	288.99133	100.0	ND	N/A	ND	N/A	Characteristic
49	Winchester	227.11951	100.0	ND	N/A	269.16656	13.1	170.09882	18.8	ND	N/A	288.99081	100.0	ND	N/A	ND	N/A	Characteristic
50	Winchester	227.12062	28.4	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated

Table S2. Results from the second set of 30 shooter's hand samples analyzed by DART-MS. This table follows the same layout as **Table S1**. In this study, it is important to note that the samples were only monitored in positive mode.

Authentic Hand Samples - DART-MS, Subset 2												
		Positive Mode										
No.	Manufactu	[AKII]	AKII RI	[MC]	MC RI	[EC]	EC RI	[DPA]	DPA RI	[2-,4-NDPA]	2-,4-NDPA RI	Criteria
	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
	Winchester	ND	N/A	ND	N/A	269.16540	8.8	ND	N/A	ND	N/A	Commonly Associated
	Winchester	227.12048	22.9	ND	N/A	269.16820	3.8	170.09800	4.5	ND	N/A	Consistent
	Winchester	227.12265	6.7	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated
	Winchester	227.11998	11.5	ND	N/A	ND	N/A	170.09680	3.3	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
	Winchester	227.11993	9.3	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated
	Winchester	227.12053	3.4	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated
	Winchester	227.12042	3.7	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Commonly Associated
	Winchester	227.11855	17.1	ND	N/A	ND	N/A	170.09590	4.6	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	269.16610	4.0	170.09660	3.6	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16670	7.5	170.09650	10.5	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	ND	N/A	170.09640	5.6	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	269.16680	8.2	170.09620	15.9	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	ND	N/A	170.09620	5.8	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	269.16600	13.7	170.09700	18.2	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16600	9.9	170.09630	15.3	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	ND	N/A	ND	N/A	ND	N/A	Negative
	Winchester	227.11986	16.5	ND	N/A	269.16550	17.0	170.09610	31.2	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16540		170.09610	3.2	ND	N/A	Consistent
	Winchester	227.12125	11.4	ND	N/A	269.16530	6.5	170.09700	17.7	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16580	17.3	170.09630	27.1	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16700	5.7	170.09660	19.8	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16570	3.6	170.09600	19.3	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	ND	N/A	170.09550	3.9	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	269.16590	3.7	170.09620	12.9	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	ND	N/A	170.09590	7.6	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	ND	N/A	170.09610	11.9	ND	N/A	Commonly Associated
	Winchester	ND	N/A	ND	N/A	269.16730	3.3	170.09670	17.0	ND	N/A	Consistent
	Winchester	ND	N/A	ND	N/A	269.16590	7.7	170.09680	11.5	ND	N/A	Consistent

Tables S3 and **S4** provide detailed information on the results obtained from the LC-MS/MS analysis of the shooter's hand samples. These results were used to determine whether a sample was considered positive or negative for OGSR using the same categories described above for DART-MS, except that the "commonly associated with OGSR" result is not applicable for a confirmatory method. The method's LODs are listed for each compound at the bottom of the table. Compounds listed as ND produced a predicted concentration result below the method's LOD and are presented in cells with white background. Compounds colored on a green background list the estimated concentration in ppb. Here, it becomes evident that some of the compounds detected by LC-MS/MS were present in the hand samples at concentrations below the DART-MS method's LOD, providing a better understanding of the screening results presented in Tables S1 and S2. Notably, one disadvantage of the LC-MS/MS configuration used in this study is that it only detects the compounds in positive mode, therefore, NG and 2,4-DNT were only monitored by DART-MS. In the first set, only 27 of the 50 samples monitored by LC-MS/MS were positive for OGSR (54%), which is somehow atypical of positive rates observed in previous studies with larger population datasets. **Table S4** shows that when evaluating a second dataset with other ammunition types, the positive rates drastically increased to 97%, all of which were classified as *characteristic of OGSR*. These results corroborate the findings of the DART-MS screening and indicate that the success rates on hand residues are dependent on the ammunition used in the shooting event. Importantly, all the DART-MS presumptive "positive" results were further corroborated by LC-MS/MS confirmatory method, indicating the utility of DART-MS for screening purposes.

Table S3. Results from the first 50 shooter's hand samples analyzed by LC-MS/MS for set 1.

Authentic Hand Samples- LC-MS/MS, Subset 1								
ample No.	Manufacturer	[AKII]	[MC]	[EC]	[DPA]	[2-NDPA]	[4-NDPA]	Criteria
1	Blazer	ND	ND	ND	ND	ND	ND	Negative
2	Blazer	ND	ND	62.8	5.6	ND	ND	Consistent
3	Blazer	ND	ND	ND	3.9	ND	ND	Negative
4	Blazer	ND	ND	ND	ND	ND	ND	Negative
5	Blazer	8.8	ND	ND	22.9	ND	ND	Consistent
6	Blazer	7.4	ND	ND	20.6	ND	ND	Consistent
7	Blazer	ND	ND	ND	ND	ND	ND	Negative
8	Blazer	ND	ND	ND	3.9	ND	ND	Negative
9	Blazer	ND	ND	ND	ND	ND	ND	Negative
10	Blazer	5.8	ND	ND	12.6	ND	ND	Consistent
11	Federal	ND	ND	ND	7.4	ND	ND	Negative
12	Federal	ND	ND	ND	ND	ND	ND	Negative
13	Federal	ND	ND	ND	5.5	ND	ND	Negative
14	Federal	ND	ND	ND	ND	ND	ND	Negative
15	Federal	1.1	ND	ND	9.2	ND	ND	Consistent
16	Federal	ND	ND	ND	ND	ND	ND	Negative
17	Federal	ND	ND	ND	ND	ND	ND	Negative
18	Federal	ND	ND	ND	ND	ND	ND	Negative
19	Federal	ND	ND	ND	ND	ND	ND	Negative
20	Federal	4.3	ND	ND	16.6	ND	ND	Consistent
21	Fiocchi	ND	ND	ND	4.2	ND	ND	Negative
22	Fiocchi	ND	ND	10.5	12.9	ND	ND	Consistent
23	Fiocchi	ND	ND	128	139	4.8	7.4	Characteristic
24	Fiocchi	ND	ND	ND	5.0	ND	ND	Negative
25	Fiocchi	ND	ND	65.4	53.6	ND	4.5	Characteristic
26	Fiocchi	ND	ND	54.2	51.2	ND	3.9	Characteristic
27	Fiocchi	ND	ND	40.3	32.0	ND	3.4	Characteristic
28	Fiocchi	ND	ND	70.6	75.4	ND	4.2	Characteristic
29	Fiocchi	ND	ND	361	426	9.4	10.6	Characteristic
30	Fiocchi	ND	ND	31.6	33.8	ND	3.7	Characteristic
31	Remington	ND	ND	ND	4.9	ND	ND	Negative
32	Remington	ND	ND	20.1	19.1	ND	ND	Consistent
33	Remington	ND	ND	21.9	20.7	ND	ND	Consistent
34	Remington	ND	ND	272	7.7	ND	ND	Consistent
35	Remington	ND	ND	355	7.2	ND	ND	Consistent
36	Remington	ND	ND	208.9	4.4	ND	ND	Consistent
37	Remington	ND	ND	3.1	ND	ND	1.9	Negative
38	Remington	ND	ND	ND	ND	ND	1.9	Negative
39	Remington	ND	ND	10.0	3.9	ND	ND	Consistent
40	Remington	ND	ND	3.7	ND	ND	ND	Negative
41	Winchester	ND	ND	ND	ND	ND	ND	Negative
42	Winchester	ND	ND	ND	ND	ND	ND	Negative
43	Winchester	102	ND	18.3	269	5.9	7.3	Characteristic
44	Winchester	12.2	ND	3.1	29.1	ND	3.1	Characteristic
45	Winchester	ND	ND	ND	3.6	ND	ND	Negative
46	Winchester	ND	ND	5.9	6.6	ND	ND	Characteristic
47	Winchester	86.5	ND	14.3	226	5.0	6.1	Characteristic
48	Winchester	2.6	ND	ND	13.4	ND	ND	Consistent
49	Winchester	114	ND	20.1	319	5.5	7.8	Characteristic
50	Winchester	32.6	ND	4.1	78.4	ND	3.7	Characteristic
LOD (ppb)		0.3	0.3	1.0	3.4	2.7	3.0	

Table S4. Results from the second set of 30 shooter's hand samples. This table follows the same layout as **Table S3.**

Authentic Hand Samples- LC-MS/MS, Subset 2								
Sample No.	Manufacturer	[AKII]	[MC]	[EC]	[DPA]	[2-NDPA]	[4-NDPA]	Criteria
1	Winchester 9mm	ND	ND	4.5	ND	ND	ND	Negative
2	Winchester 9mm	16.5	ND	38.4	36.6	5.6	ND	Characteristic
3	Winchester 9mm	101	ND	14.5	91.5	5.3	ND	Characteristic
4	Winchester 9mm	40.1	ND	5.9	32.5	3.5	ND	Characteristic
5	Winchester 9mm	248	ND	27.3	255	12.1	6.4	Characteristic
6	Winchester 9mm	58.2	ND	9.6	44.0	4.3	ND	Characteristic
7	Winchester 9mm	118	ND	16.2	91.8	6.7	ND	Characteristic
8	Winchester 9mm	42.4	ND	1.8	35.5	3.3	ND	Characteristic
9	Winchester 9mm	76.1	ND	6.0	47.2	4.6	ND	Characteristic
10	Winchester 9mm	330	ND	38.9	315	17.5	9.8	Characteristic
11	Winchester .40	ND	ND	35.5	107	10.5	11.6	Characteristic
12	Winchester .40	ND	ND	29.0	181	19.4	21.1	Characteristic
13	Winchester .40	ND	ND	28.2	191	20.2	25.1	Characteristic
14	Winchester .40	ND	ND	18.9	149	12.6	12.9	Characteristic
15	Winchester .40	ND	ND	38.5	238	25.0	31.8	Characteristic
16	Winchester .40	1.3	ND	79.4	564	44.1	48.0	Characteristic
17	Winchester .40	ND	ND	49.1	279	25.0	33.0	Characteristic
18	Winchester .40	ND	ND	41.8	257	22.4	22.8	Characteristic
19	Winchester .40	110	ND	140	905	71.7	76.3	Characteristic
20	Winchester .40	1.7	ND	68.7	527	35.2	31.0	Characteristic
21	Winchester .40 Defense	79.1	ND	76.1	770	79.6	75.0	Characteristic
22	Winchester .40 Defense	ND	ND	49.3	447	41.1	43.6	Characteristic
23	Winchester .40 Defense	ND	ND	24.4	268	23.8	22.3	Characteristic
24	Winchester .40 Defense	ND	ND	19.6	316	37.8	33.4	Characteristic
25	Winchester .40 Defense	ND	ND	28.1	324	35.2	41.1	Characteristic
26	Winchester .40 Defense	ND	ND	22.0	357	43.4	40.1	Characteristic
27	Winchester .40 Defense	ND	ND	34.4	653	66.7	58.4	Characteristic
28	Winchester .40 Defense	ND	ND	18.9	279	33.0	38.1	Characteristic
29	Winchester .40 Defense	3.0	ND	59.1	970	86.2	65.0	Characteristic
30	Winchester .40 Defense	ND	ND	42.4	265	31.7	34.5	Characteristic
LOD (ppb)		0.3	0.3	1.0	3.4	2.7	3.0	