Final Report

Viable, Affordable, and Meaningful Integration of Organic and Inorganic Analysis of Firearms Discharge Residue

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Overview and Project Purpose

The proposal stated the goals of the project as *"to develop protocols that integrate GSR and OGSR in ways that can easily be implemented by forensic laboratories exploiting existing resources, instrumentation, and expertise. The project is built on literature studies and a significant body of past work in our research group. Successful completion will provide novel, practical, and affordable method for analyzing the full complement of firearms discharge residue. Orthogonal analytical methods and data will increase the utility and reliability of the evidence. "*

Initially we evaluated the use of thermal desorption of swabs (wipes) characterized using a specialized inlet (TSP, Agilent Technologies) coupled to GC to characterize the organic constituents of FDR. Results were mixed and the data showed that this methodology held little promise for the analysis of organic gunshot residue analysis. This paper was published in *Forensic Chemistry* in 2017.

The second methodology was the use of LC/MS for the characterization of organic and inorganic residues of FDR. The novelty of this work is the utilization of a "microbulk" extraction of the sample followed by the addition of complexing agents and ligands. The resulting metal complexes can be characterized using electrospray mass spectrometry (ESI/MS) and can also be separated chromatographically. This line of inquiry has been much more successful and was the focus of the last two years of the

project. This report emphasizes the work done recently and is meant as a summary document to complement the progress reports and deliverables already submitted.

Project Design, Methods, and Data Analysis

The project design and methodology was typical of analytical method research and development. Preliminary feasibility studies using knowns and controls (i.e., samples obtained from discharged cartridge cases). Once the general conditions for the method were established, an iterative period of method design, testing, optimization, and analysis followed. Once the parameters were nearly finalized, testing using authentic samples was undertaken at our Ballistics Research Facility under an approved IRB protocol. The iterative phases associated with the two methods were the most time- and labor-intensive phases. Data analysis was integrated at each stage, as was appropriate method validation procedures to establish figures of merit related to accuracy and precision.

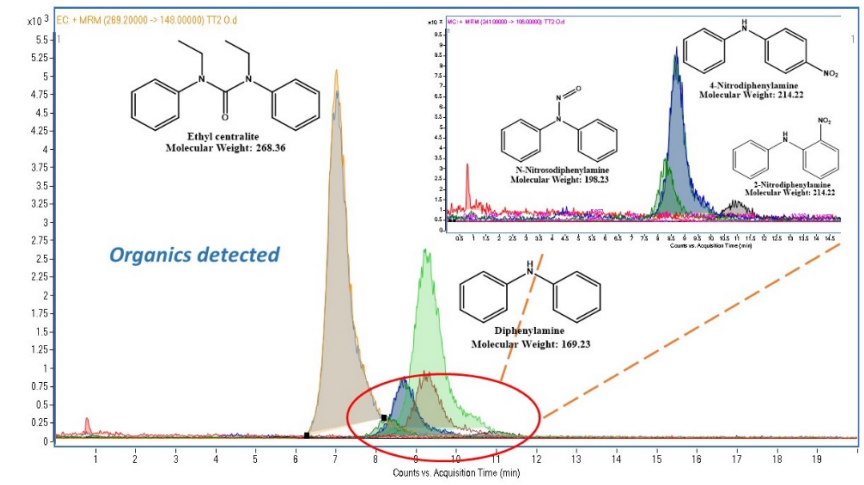
Results and Findings

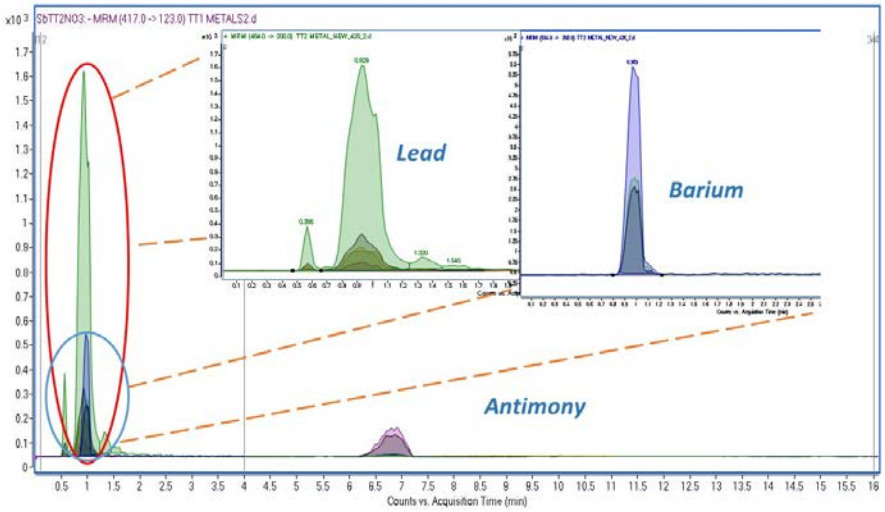
Using the LC/MS method, we demonstrated that it is possible to reproducibly detect IGSR and OGSR components from a single sample collected after the discharge of a single shot. The results of the shooting study were recently published in *Forensic Science International* (submitted with this report).

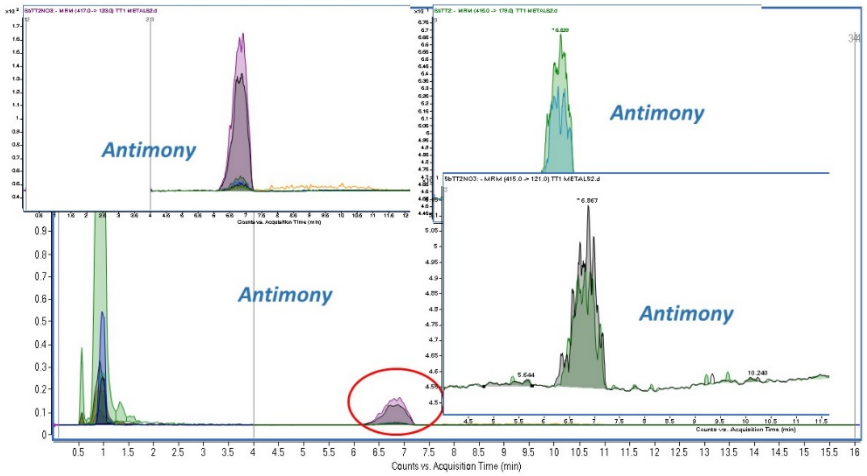
Table 1. Results of integrated IGSR/OGSR shooting study

		# in which detected at >LOD (n=9)						
Firearm	*# of shots*	Ba	Pb	Fe	DPA	EC	MC	NNDPA
9 mm semiautomatic pistol	*One*	7	9	7	0	9	9	8
	Two	9	9	6	0	9	9	7
	Three	6	9	3	0	9	9	9
.38 revolver	*One*	7	9	9	0	9	2	4
	Two	8	9	9	0	9	5	3
	Three	6	8	7	9	9	3	2

Since this submission, we have adjusted the extraction method such that antimony is detected as a complex with tartaric acid. A chromatographic method has been developed that allows for detection of the IGSR and OGSR compounds with separate injections on the same column, an Agilent Poroshell 120 PFP (2.7 µm x 2.1 µm x 50 mm) coupled with a Hamilton guard column, a PRP-X100 (2.1x50mm). The PFP is a relatively new perfluorobenzene phase that has shown the ability to separate many ionics and compounds amenable to reverse phase. The PRP phase is an a weak anion exchanger that increased the retention time of the tartaric acid complexes. Example chromatograms from authentic 3-shot trials (9mm) are shown below.







The following table summarizes the conditions in use at the time of completion of the work:

Table 2. Chromatographic conditions

Setting	IGSR	OGSR
Aqueous solvent	H_2O w/ 0.1% formic acid	H_2O w/ 0.1% formic acid
Organic solvent	ACN w/ 0.1% formic acid	ACN w/ 0.1% formic acid
Gradient	50A/50 to 100A/0B	80A/20B to 0A/100B
Flow rate	0.25 mL/min to 0.6 mL/min	0.3 mL/min to 0.6 mL/min
Injection volume	20 µL	3 µL
Column temperature	30°C	30°C

Table 3. Ion source conditions

Setting	IGSR	OGSR
ESI needle voltage	4500+ / 2500-	4500+ / 2500-
Gas Temp	350C	350 C
Gas flow	10 L/min	10 L/min
Nebulizer	20 psi	20 psi
Sheath gas flow	11L/min	11 L/min
Sheath gas Temp	400 °C	400 °C

Table 4: Detectable target analytes

OGSR	MRMs	IGSR	MRMs	Isotope
Diphenylamine	170->93 170->65	Ba	**CE*** 464 ->200 463 ->199 462 ->198 461 ->197	138 137 136 135
n-Nitrosodiphenylamine	199->169 199->168	Cu	**TT****249 -> 187 TT251 -> 189 CE 390 ->63 CE 392 ->65	63 65 63 65
Ethyl centralite	269->120 269->148	Zn	TT407 -> 250 64 409 -> 252 66 410 -> 253 67 411 -> 254 68	64 66 67 68

Methyl centralite	241->134 241->106	Fe	CE 383 ->56 382 ->57 380 ->54	56 57 54
2,4-Dinitrotoluene	181->113 181->105 181->69	Ca	CE352-> 40 353-> 41 354-> 42 356-> 44	40 41 42 44
2-Nitrodiphenylamine	215->180 215->167	Sr	CE414 -> 105 88 413-> 104 87 412-> 103 86	88 87 86
4-Nitrodiphenylamine	215->198 215->180	Sb	TT415->267 179 121 417->269 181 123	121 123
		Pb	CE534->270 208 533->269 207 532->268 206	208 207 206

*CE: Crown ether complex
**TT: Tartaric acid complex

Products delivered to date:

Publications:

Stevens B, Bell S, Adams K, Initial evaluation of inlet thermal desorption GC-MS analysis for organic gunshot residue collected from the hands of known shooters, For. Chem. 2 (21) (**2016**) 55-62.

Single shot, single sample, single instrument detection of IGSR and OGSR using LC/MS/MS, For. Sci. Int. 299 (**2019**), 215-222.

Presentations:

Feeney W, Bell S, Exhaustive characterization of firearm discharge residue using mass spectral imaging and time-of flight secondary ion mass spectrometry, Abstr. Pap. Am. Chem. Soc. 254 (2017)

Brooks S, Feeney W, Bell S, Application of host-guest complexation and tandem mass spectrometry to the characterization of elemental constituents of firearms discharge residue, Abstr. Pap. Am. Chem. Soc. 254 (2017)

Two updates presented at the AAFS meetings at the NIJ Research symposium, 2017 and 2019; also presented at Pittcon, 2019

Dissertations:

Comprehensive Modernization of Firearms Discharge Residue Analysis; Advanced Analytical Techniques, Complexing Agents, and Tandem Mass Spectrometry. PhD Dissertation, 2017, ProQuest Dissertations Publishing, 10268170.

Products pending:

One more manuscript will be produced from this grant. A shooting study is being conducted this summer that will use multiple shooters and ammunition types with

the samples being characterized using the LC/MS methodology described above. The study will include stubs half covered with the polymeric material and half with SEM carbon tape. This will allow for samples to be characterized by LC/MS and SEM from the same shooting event. The ability of the LC/MS method to discriminate between shooters and by-standers will be evaluated as well. The doctoral student overseeing this work will be writing his dissertation within 18 months which will also acknowledge this grant as providing support.

Implications for Criminal Justice Policy and Practice in the United States

This methodology could contribute to a revitalization of FDR analysis within the justice system. The instrumentation utilized is commonly available in forensic laboratories and is routinely used for toxicological assays. The loss of morphological information in the partial digestion methodology is offset by the ability to detect orthogonal data from the inorganic and organic constituents of FDR. Thus, the methodology is nearly ready to be deployed as a supplement to the existing SEM methodology.

A significant advantage of this methodology is that it is based on a common analytical instrument system available in forensic labs. As such, it can evolve with improvements in instrumentation. It could become a routine assay comparable to post-mortem drug analysis and will only improve as instrumentation does.