Interpol Review of Gunshot Residue Analysis 2016 – 2019
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ASCLD Forensic Research Committee
Future Forensics Subcommittee

Gunshot Residue Analysis 2016-2019 (Summarized by Ed Sisco)

Inorganic GSR (IGSR)

- The study of IGSR formation continues to be an area of active research. Recent work has shown that IGSR morphology may be able to determine distance, due to solidification of molten GSR particles in flight [2], and that IGSR can remain suspended in air for up to 200 min after firing [3].
- Several studies had looked into IGSR sampling approaches that would lower the probably of GSR particulate being present from interception or arrest. Nasal sampling was shown to be one viable approach with the sampling of mucus [9] or nose hairs [11] allowing for detection of GSR up to 20 hours after firing.
- Due to the prevalence of heavy-metal free IGSR, a proposed list of elements for monitoring has been developed and include Al, Mo, Cu, Zn, and Sn [12].
- In terms of IGSR prevalence and contamination, up to 4 % of individuals in a random population have been found to have two-component particles on their person [16].
- A number of studies have been completed looking to establish statistical models for the evaluation of GSR evidence though there are noted issues in sample sizes for many studies, which need to be considered.
- The use of a two-level multinomial model was demonstrated for the discrimination of ammunition type, which may prove helpful in identifying whether or not a suspect fired a particular weapon [27].
- ASTM 1588 was updated in Feb 2017 and updated the types of particles that are characteristic to GSR, removal or terminology describing peak heights of elements and altering the size particles SEM/EDS needs to detect to 1 µm.
- Several new analytical methods have been investigated for the IGSR analysis:
    - Single particle inductively coupled plasmas mass spectrometry (ICP-MS) has been shown to provide both elemental information and size information with minimal sample preparation and a fast analysis time. The technique, however, is limited in the number of elements it can scan for at one time (when a single quadrupole MS is used) and is destructive [36].
    - Ion beam techniques, such as X-ray emission spectroscopy, provide non-destructive, quantitative analyses with the ability to also image.
    - Several studies have highlighted the use of laser induced breakdown spectroscopy (LIBS) for detection of IGSR, with some proposing that LIBS be used as a screening tool with SEM/EDS confirmation.

        - Trejos *et. al* combined LIBS w/ electrochemical techniques for identification of IGSR and OGSR in an approach that allows for subsequent SEM/EDS analyses if necessary [41].
    - Capillary electrophoresis (CE) offers a promising approach for the analysis of anions that can be used a screening tool [45].

<u>Organic GSR (OGSR)</u>

- A number of studies have been completed investigating different sampling and storage approaches for OGSR. Much of the research is focused on traditional GSR stubs and alcoholic wipes. Degradation of OGSR components post-collection is still an area of concern, warranting more research.
- There is a push to also better understand the persistence of OGSR after a shooting event. Fairly little is known regarding presence and persistence of OGSR on suspects or victims' hands or clothing though recent studies have highlighted that greater losses are observed from hands than clothing and OGSR can be detected on a shooter's hair and face.
- Goudsmits *et. al* [62] provided an approach for classification for OGSR culls the list of 100+ reported compounds down to 20, split into three different categories, based on the individual compounds' prevalence and uniqueness.
- Analytical approaches have been demonstrated for the analysis of OGSR include:
    - Liquid chromatography mass spectrometry (LC-MS) has been demonstrated in both targeted (more common) and non-targeted modes, though non-targeted mode provides the ability to see nearly all compounds in OGSR
    - Gas chromatography mass spectrometry (GC-MS) has also been demonstrated for detection of a wide range of OGSR compounds.
        - Stevens et al [67] has demonstrated the use of thermal desorption (TD)-GC-MS as a potential tool for OGSR with no sample prep or pre-concentration
    - Mass spectrometry imaging, specifically secondary ion mass spectrometry (SIMS), was used for simultaneous IGSR and OGSR analyses [69].
    - Ambient ionization mass spectrometry (AI-MS) approaches are showing promise for OGSR analysis and benefit from lack of sample preparation and rapid analysis times. Demonstrations utilizing swab touch spray MS [70] and direct analysis in real time mass spectrometry (DART-MS) [72] have been shown.
        - The DART-MS study also highlighted the need for additional research into the analysis of 3D-printed guns. Polymer signatures obtained from 3D-printed guns could provide additional evidentiary information.
    - Raman spectroscopy, typically using micro-Raman scanning can be used for OGSR analysis and can be complimented with FTIR spectroscopy. The use of surface enhanced Raman spectroscopy (SERS) has also been demonstrated [77]

<u>Shooting Distance Estimation and Bullet Hole Characterization</u>

- A few references have demonstrated novel approaches to visualization of GSR patterns that can supplement and/or replace the traditional color tests which use sodium rhodizonate test to react with Pb and Ba and a modified Griess test to react with NO_3^-). These approaches include: short-wave-infrared imaging (demonstrated on both traditional and heavy-metal free ammunition) [78], multispectral imaging, SEM with backscatter detection, and LIBS.

- ENFSI has a published best practices manual for traditional chemographic methods.
- A study was conducting to demonstrate that GSR can be found on victims through even when the bullet passes through glass [87].
- A method, leveraging volatile OGSR compounds, was developed to estimate the time since discharge. The authors were able to determine whether or not the cartridge was recently fired (within the last 48 hours) [89,90]

Selected References of Interest

[12] R.A. Costa, L.C. Motta, C.A. Destefani, R.R.T. Rodrigues, K.S. do Espírito Santo, G.M.F.V. Aquije, *et al.* **Gunshot residues (GSR) analysis of clean range ammunition using SEM/EDX, colorimetric test and ICP-MS: a comparative approach between the analytical techniques** Microchem. J., 129 (2016), pp. 339-347

[16] N. Lucas, H. Brown, M. Cook, K. Redman, T. Condon, H. Wrobel, *et al.* **A study into the distribution of gunshot residue particles in the random population** Forensic Sci. Int., 262 (2016), pp. 150-155

[27] A. Bolck, A. Stamouli **Likelihood Ratios for categorical evidence; Comparison of LR models applied to gunshot residue data** Law Probab. Risk, 16 (2–3) (2017), pp. 71-90

[41] T. Trejos, C. Vander Pyl, K. Menking-Hoggatt, A.L. Alvarado, L.E. Arroyo **Fast identification of inorganic and organic gunshot residues by LIBS and electrochemical methods** Forensic Chem., 8 (2018), pp. 146-156

[62] E. Goudsmits, G.P. Sharples, J.W. Birkett **Preliminary classification of characteristic organic gunshot residue compounds** Sci. Justice, 56 (6) (2016), pp. 421-425

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

[89] M. Gallidabino, F.S. Romolo, C. Weyermann **Time since discharge of 9mm cartridges by headspace analysis, part 1: comprehensive optimisation and validation of a headspace sorptive extraction (HSSE) method** Forensic Sci. Int., 272 (2017), pp. 159-170

[90] M. Gallidabino, F.S. Romolo, C. Weyermann **Time since discharge of 9mm cartridges by headspace analysis, part 2: ageing study and estimation of the time since discharge using multivariate regression** Forensic Sci. Int., 272 (2017), pp. 171-183