DETECTION AND INTERPRETATION OF ORGANIC GUNSHOT RESIDUES

Matthieu Maitre

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text. This research is supported by an Australian Government Research Training Program and by a Premier's Research and Industry Fund grant provided by the South Australian Government Department of Further Education, Employment, Science and Technology.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Matthieu Maitre

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Abbreviations

.357 Magnum	.357 Mag
.40 Smith & Wesson	.40 S&W
Automatic colt pistol	ACP
American Society for Testing and Material	ASTM
Bayesian network	BN
Diphenylamine	DPA
Diphenyl-d10-amine	d10-DPA
Dimethyl phthalate	DMP
Electrospray Ionisation	ESI
Ethylcentralite	EC
European Network of Forensic Science Institutes	ENFSI
Gunshot residues	GSR
Ion-Mobility Spectrometry	IMS
Inorganic gunshot residues	IGSR
Internal standard	IS
International conference on harmonisation	ICH
Likelihood ratio	LR
Limit of detection	LOD
Mass spectrometer	MS
Methylcentralite	MC
Multi reaction monitoring	MRM
New South Wales	NSW
New South Wales Police Force	NSWPF
N-nitrosodiphenyamine	*N*-nDPA
Organic gunshot residues	OGSR
Principal component analysis	PCA
Principal component	PC
Probability density function	PDF
Part per billion	ppb

Part per million	ppm
Person of interest	POI
Quality control	QC
Relative retention time	RRt
Relative Standard Deviation	RSD
Retention time	Rt
Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy	SEM-EDX
Total ion chromatogram	TIC
Triple quadrupoles tandem mass spectrometer	QqQ-MS
Ultra performance liquid chromatography	UPLC

Abstract

The traces produced when a firearm is discharged, called gunshot residues and abbreviated GSR, can provide important information in cases when questions regarding the association of a person of interest (POI) with the event are raised. In most forensic laboratories, routine GSR analyses focus on the detection and characterisation of the inorganic components (abbreviated IGSR), which are mainly particles containing mixtures of lead, barium and antimony, originating from the ammunition primer. The increasing prevalence of heavy metal-free ammunition challenges the current protocols used for IGSR analysis. To provide complementary information to IGSR particles, the current project concentrated on the organic components (abbreviated OGSR), which are arising from the combustion of the ammunition propellant powder.

The overall aim of this project was to develop additional knowledge about OGSR in order to assess the possibilities of using these organic traces to provide a complementary to the IGSR and as a complementary tool in cases where heavy-metal free ammunition might be suspected. The project aimed at evaluating the relevancy of OGSR by assessing the persistence and secondary transfer, which are two crucial parameters when approaching forensic traces. This project focused on the detection of four compounds well-known as being part of OGSR: ethylcentralite (EC), methylcentralite (MC), diphenylamine (DPA), *N*-nitrosodiphenylamine (*N*-nDPA). The specimens were liquid-extracted and analysed by UPLC-QqQ-MS, which was validated using the "International Conference on Harmonisation of technical requirements for registration of pharmaceuticals for human use guidelines" (ICH guidelines). Two studies were carried out during this project.

Throughout the project, it was observed that the research studies highlighted a successful detection of three of the four compounds of interest in specimens arising from the firearm discharges.

The first part of the project tackled the study of the persistence of OGSR traces on a shooter's hands. The overall study aim was to provide additional information regarding OGSR retention, which can be integrated into an appropriate interpretation framework as recommended by the recent guidelines for "Evaluative Reporting in Forensic Science" of the European Network of Forensic Science Institutes (ENFSI). The persistence was studied through several intervals ranging from immediately after discharge to four hours, and two ammunition calibres were chosen: .40 S&W, used by the NSW Police Force; and .357 Magnum, which is frequently encountered in Australian casework. This study successfully detected three compounds of interest up to four hours after discharge. The trends displayed a large decrease in the amount detected during the first hour. A large variability was also observed due to numerous factors involved in the production, deposition, collection and analysis of OGSR.

The second part of the project concerned the study of the secondary transfer of OGSR. Similar to the situation with IGSR, OGSR compounds originally deposited on the shooter during the firing process may further be transferred onto another individual or surface. Hence, the aim of this study was to provide additional information regarding the risk of a secondary transfer of OGSR. Two scenarios were investigated, the first one related to the arrest process and the possibilities of a secondary transfer arising between a shooter onto a non-shooter (e.g. between a police officer and a POI). The second scenario concerned the transfer of OGSR onto the non-shooter after handling a firearm for few minutes without discharging it. One calibre was investigated, the .40 S&W calibre, used by the

NSW Police Force. A secondary transfer was observed in all cases for the two scenarios investigated, for three compounds of interest (EC, DPA and *N*-nDPA). The firearm handling scenario resulted in a larger secondary transfer to that of the arrest scenario. Overall, the amounts of OGSR detected on the non-shooter were generally lower than that detected on the shooter and controls after the arrest scenario. The results of this study provide complementary knowledge about OGSR, which can be further used to improve the current practice and the interpretation of OGSR evidence. In particular, it highlights that the secondary transfer proposition must be considered during the interpretation of forensic findings, especially when small amounts of OGSR target compounds are detected.

However, with advances in technology, the forensic challenges presented by OGSR, are moving from the analytical domain to the interpretation of the analytical results. As emphasised by the recent ENFSI guidelines, an interpretative framework, based on the application of Bayesian reasoning has to be developed for the appropriate assessment of evidence in regards to activity-related questions. This approach allows an evaluation of the evidence that is more closely aligned to judicial and investigative aims.

Therefore, the last aim of the project was to encapsulate the results obtained in the persistence and secondary transfer of OGSR into an appropriate interpretation framework with a concrete application of the Bayesian theorem for the assessment of OGSR evidence. This study showed that likelihood ratios (LR) could be calculated for each compound of interest. It was found that the magnitude of the LR obtained were consistent across the different targeted OGSR compounds, with a magnitude ranging from "moderate" to "strong" support of one of the propositions under investigation.

Finally, the application of the LR approach to assess OGSR traces highlighted that normal probability density functions were the most suitable method to assess OGSR. It was found that LR could be calculated for the three compounds of interest. It was also found that all LR were not supporting the propositions at the same level, which was found to be intrinsically linked to the degree of overlap of the different population distributions. However, the LR approach was found to be applicable to the interpretation of OGSR traces by being able to provide meaningful and relevant information because of its ability to support a proposition rather its alternative.