

**Improving Forensic Casework
Analysis and Interpretation
of
Gunshot Residue (GSR)
Evidence**

by

Stephanie Hales

A thesis
submitted for the degree of
Doctor of Philosophy

University of Technology, Sydney

2011

CERTIFICATE OF AUTHORSHIP / ORIGINALITY

I certify that 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.

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.

Signature of Candidate

Production Note:
Signature removed prior to publication.

Dedicated to the memory of

Robin Keeley

Without his efforts in the field of forensic gunshot residue evidence
and his contributions to scanning electron microscopy
this work would not have been possible.

Acknowledgements

When something takes up so much of your life there are a lot of people to thank. I truly appreciate the contribution of each and every one of them.

I thank my wonderful husband Paul who has supported me in so many ways through this journey. I thank my beautiful children, Ethan and Sophie, who I adore, for putting up with Mummy always being busy with 'PhD work'.

I thank my Mum and Dad and my sister Gerry for being my constant encouragement and motivation. I thank Carolynne and John for wanting a daughter-in-law they could call 'Dr' and doing everything they could to help.

I thank my supervisors, Professor Claude Roux, Professor Chris Lennard and Associate Professor Michael Dawson for their guidance and inspiration.

I thank the New South Wales Police Force (NSWPF) and Dr Tony Raymond for mentoring me and supporting me through providing study time for this research. I also thank the NSWPF Forensic Ballistics Investigation Section for providing ammunition samples.

I thank the Australian Federal Police (AFP) and Professor James Robertson for providing funding for the project as well as chemical standards, ammunition and access to AFP facilities. I also thank Dave Royds, Paul McFawn and Eric Davies for assistance with various areas of the research.

I thank Dr Ric Wuhler and Professor Matthew Phillips for making me welcome in the University of Technology, Sydney (UTS) Centre of Expertise Microstructural Analysis and for their assistance and technical support with the scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX) work.

I thank Jim Keegan and Dr Harry Rose for their assistance with the liquid chromatography tandem mass spectrometry research.

I thank Dr Sarah Benson for her assistance with the initial surveys, sampling and instrumentation for the gunshot residue background study research.

I thank Liz Chan, Dr Sonia Taflaga, Kate McCann and Joanna Maniago for their assistance with the ion mobility spectrometry research. I also thank Liz for helping me set-up the Forensic Microanalysis Laboratory and for being my 'fix-it' person and general sounding board.

I thank Professor Christophe Champod and Dr Simon Walsh for their assistance with the Bayesian statistical modelling.

I thank Glyn Smith and Ivan Sarvas of Forensic Science South Australia, Bernie Lynch of the Chemistry Centre Western Australia and Peter Ross and Harald Wrobel of the Victorian Police Forensic Science Centre for opening their laboratories and imparting their gunshot residue wisdom to me.

I thank the Sydney University Australian Centre for Microscopy and Microanalysis staff for their SEM/EDX technical assistance.

I thank all of the survey participants from around Australia. I thank the volunteer participants in the general population study and the NSWPF participants in the general duties, tactical response, crime scene and firearms examiner studies.

I thank Australian Defence Industries (now Thales Australia) for teaching me about the ammunition manufacturing process and providing component samples and analytical methods.

I thank Charlie Midkiff and Max Houck for providing literature and ideas at the inception of the research.

I also thank the original UTS Forensic Science Research Group; Karen Scott, Dr Susan Bennett, Steven Armitage and Dr Juuso Huttunen; for keeping me sane in those early days.

Table of Contents

List of Figures	xii
List of Tables	xv
List of Abbreviations	xvii
List of Conference Presentations	xx
Abstract	xxii
Chapter 1: Introduction	1
1.1 <i>What is Gunshot Residue?</i>	2
1.2 <i>Evidential Value of GSR</i>	3
1.3 <i>The Chemistry of GSR</i>	4
1.3.1 <i>Primer</i>	4
1.3.2 <i>Propellant</i>	5
1.3.3 <i>Projectile</i>	7
1.3.4 <i>Cartridge Case</i>	8
1.4 <i>Formation of GSR</i>	8
1.5 <i>Deposition of GSR</i>	8
1.6 <i>Transfer of GSR</i>	10
1.7 <i>Collection of GSR</i>	10
1.7.1 <i>GSR Collection Kits</i>	13
1.8 <i>Analysis of GSR</i>	13
1.8.1 <i>Chemical Tests</i>	13
1.8.2 <i>Bulk Elemental Analysis</i>	14
1.8.3 <i>Scanning Electron Microscopy/Energy Dispersive X-ray Analysis</i>	15
1.8.4 <i>New Ammunition Types</i>	19
1.8.5 <i>Inorganic Analysis for Detection of GSR from New Ammunition Types</i>	19
1.8.6 <i>Organic Analysis – The Future of GSR Analysis?</i>	20
1.8.6.1 <i>Thin Layer Chromatography (TLC)</i>	22
1.8.6.2 <i>Gas Chromatography (GC)</i>	22
1.8.6.3 <i>High Performance Liquid Chromatography (HPLC)</i>	23
1.8.6.4 <i>Micellar Electrokinetic Capillary Electrophoresis (MECE)</i>	24
1.8.6.5 <i>Fourier Transform Infrared Spectrometry (FTIR)</i>	24
1.8.6.6 <i>Differential Thermal Analysis (DTA)</i>	25
Chapter 2: The Interpretation of GSR Evidence	26
2.1 <i>Composition</i>	26
2.2 <i>GSR Interpretation Issues</i>	29
2.3 <i>Deposition, Transfer and Persistence of GSR</i>	32
2.4 <i>False Negatives</i>	33
2.5 <i>False Positives</i>	34
2.6 <i>Potential for Contamination of a Suspect During Arrest</i>	36
2.7 <i>Contamination of a Firearm with GSR from Previous Firings</i>	40
2.8 <i>Interpretation Issues Regarding Organic GSR</i>	40
2.9 <i>Bayesian Approach to Interpretation</i>	41

Chapter 3: General Aims: Improvement of GSR Analysis and Interpretation Techniques	43
3.1 Screening for GSR Components Using Ion Mobility Spectrometry (IMS).....	43
3.2 Physical and Chemical Characteristics of Lead and Heavy Metal Free Ammunition.....	44
3.3 Analysis of Organic GSR Components by Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS) ...	44
3.4 GSR Background Study of the NSW Police Force.....	45
3.5 AFP Laboratory GSR Contamination Study	45
3.6 Bayesian Framework for GSR Evidence Interpretation.....	45
Chapter 4: Screening for GSR Components Using IMS	46
4.1 Instrumentation	47
4.2 General Operation	48
4.2.1 Sample Collection.....	48
4.2.2 Analysis	48
4.2.3 Mode of Ionisation.....	51
4.2.3.1 Explosives Mode / Negative Ion Mode	51
4.2.3.2 Drugs Mode / Positive Ion Mode	52
4.2.4 Detection Algorithm.....	52
4.2.5 Verification	52
4.2.6 Data.....	52
4.3 Materials and Method	53
4.3.1 Standards	53
4.3.2 Ammunition and Firearms	53
4.3.3 Test Firings.....	53
4.3.4 Sample Collection.....	53
4.3.5 Experiments Using Existing IONSCAN Settings.....	54
4.3.6 Programming in New Substances	55
4.3.7 Casework Trials	57
4.3.8 Re-examination of Test Firing Data.....	57
4.4 Results	57
4.4.1 Experiments Using Existing IONSCAN Settings.....	57
4.4.1.1 .40 Calibre Glock	57
4.4.1.2 .38 Calibre Revolver.....	58
4.4.1.3 Summary of Results of Experiments Using Existing IONSCAN Settings	59
4.4.2 Programming in New Substances	60
4.4.3 Casework Trials	61
4.4.3.1 Case #1	61
4.4.3.2 Case #2	61
4.4.3.3 Case #3	64
4.4.4 Re-examination of Test Firing Data.....	64
4.5 Discussion	66
4.6 Conclusions	69
Chapter 5: Physical and Chemical Characteristics of Lead and Heavy Metal Free Ammunition	70
5.1 Investigation of Available Background Technical Information	71
5.1.1 Literature	71
5.1.2 Manufacturers' Information	75
5.1.2.1 Winchester Ammunition	76

5.1.2.2 Delta Frangible Ammunition (DFA).....	77
5.1.2.3 CCI (Blount) Ammunition	77
5.1.2.4 PMC Ammunition	79
5.1.3 Material Safety Data Sheets (MSDS)	79
5.1.4 Industry Enquiries	80
5.2 <i>Materials and Method</i>	83
5.2.1 Heavy Metal Free Ammunition Samples	83
5.2.2 Examination of Physical Characteristics.....	83
5.2.3 Controlled Test Firings	84
5.2.4 Sample Collection	85
5.2.5 Sample Preparation	85
5.2.6 Chemical Analysis.....	85
5.2.7 Compilation of a Database	87
5.3 <i>Results</i>	87
5.3.1 Investigation of Available Background Technical Information	87
5.3.2 Examination of Physical Characteristics.....	87
5.3.3 Chemical Analysis.....	95
5.3.4 Database	101
5.4 <i>Discussion</i>	103
5.5 <i>Conclusions</i>	107
Chapter 6: Analysis of Organic GSR Components and Explosives by LC-MS/MS	108
6.1 <i>Industry Enquiries</i>	110
6.2 <i>Instrumentation</i>	110
6.2.1 Ionisation Source	111
6.2.2 Mass Spectrometer	111
6.3 <i>Materials and Method</i>	113
6.3.1 General Approach.....	113
6.3.2 Organic Explosive and Ammunition Component Standards.....	114
6.3.3 Solvents.....	114
6.3.4 Mass Spectrometry	116
6.3.4.1 Direct Infusion MS Operating Conditions.....	116
6.3.4.2 Experiment 1: IonSpray vs. APCI Ionisation Source.....	116
6.3.4.3 Experiment 2: Positive vs. Negative Ionisation	116
6.3.4.4 Experiment 3: Optimisation of MS and MS/MS Operating Parameters	117
<i>MS Mode</i>	118
<i>MS/MS Mode</i>	118
6.3.4.5 Experiment 4: Effect of Probe Temperature	119
6.3.4.6 Experiment 5: Effect of Mobile Phase / pH	119
<i>Negative Ionisation</i>	119
<i>Positive Ionisation</i>	120
6.3.4.7 Experiment 6: Effect of Discharge Needle Current (NC).....	120
<i>Negative Ionisation</i>	120
<i>Positive Ionisation</i>	121
6.3.4.8 Experiment 7: Effect of MS Scan (Q1) Parameters.....	121
<i>Negative Ionisation</i>	121

<i>Positive Ionisation</i>	121
6.3.4.9 Acquisition of MS and MS/MS Data for Compounds.....	122
6.3.4.10 Experiment 8: Distinguishing DNT Isomers	122
6.3.4.11 Detection Limits	122
6.3.4.12 Analysis of Mixed Standards	123
6.3.5 Liquid Chromatography Separations	124
6.3.5.1 Negative Ion Compounds.....	124
<i>Experiment 9: Effect of Mobile Phase</i>	125
<i>Experiment 10: Effect of Column Oven Temperature</i>	126
<i>Experiment 11: Effect of Changing MS Parameters Throughout Separation</i>	126
<i>Acquisition of Optimised Standard LC-MS/MS Data</i>	127
6.3.5.2 Positive Ion Compounds	127
6.3.6 Evaluation.....	128
6.4 Results	128
6.4.1 Mass Spectrometry	128
6.4.1.1 Experiment 1: IonSpray vs. APCI Ionisation Source	128
6.4.1.2 Experiment 2: Positive vs. Negative Ionisation	128
6.4.1.3 Experiment 3: Optimisation of MS and MS/MS Operating Parameters	129
6.4.1.4 Experiment 4: Effect of Probe Temperature	130
6.4.1.5 Experiment 5: Effect of Mobile Phase / pH	130
<i>Negative Ionisation</i>	130
<i>Positive Ionisation</i>	131
6.4.1.6 Experiment 6: Effect of Discharge Needle Current (NC).....	131
<i>Negative Ionisation</i>	131
<i>Positive Ionisation</i>	131
6.4.1.7 Experiment 7: Effect of MS Scan (Q1) Parameters.....	131
<i>Negative Ionisation</i>	131
<i>Positive Ionisation</i>	133
6.4.1.8 Acquisition of MS and MS/MS Data for Compounds.....	133
6.4.1.9 Experiment 8: Distinguishing DNT Isomers	133
6.4.1.10 Detection Limits	134
6.4.1.11 Analysis of Mixed Standards	134
6.4.2 Liquid Chromatography Separations	134
6.4.2.1 Negative Ion Compounds.....	134
<i>Experiment 9: Effect of Mobile Phase</i>	134
<i>Experiment 10: Effect of Column Oven Temperature</i>	135
<i>Experiment 11: Effect of Changing MS Parameters Throughout the Separation</i>	136
<i>Acquisition of Optimised Standard LC-MS/MS Data</i>	136
6.4.2.2 Positive Ion Compounds	138
6.4.3 Evaluation.....	139
6.5 Discussion	140
6.5.1 The Current Research.....	141
6.5.1.1 MS/MS Component.....	141
6.5.1.2 LC Component.....	143
6.5.1.3 Some Compound Specific Issues.....	144

6.5.2 Comparison to Other Organic Explosive Analysis Techniques	146
6.5.3 A Holistic Approach.....	147
6.5.4 Further Work.....	148
6.6 Conclusions	150
Chapter 7: GSR Background Study of the NSW Police Force	152
7.1 Initial Surveys	153
7.2 Materials and Method	153
7.2.1 General Approach.....	153
7.2.2 Sample Collection.....	154
7.2.2.1 Questionnaires.....	154
7.2.2.2 Kits	154
7.2.2.3 General.....	155
7.2.2.4 Controls	157
7.2.2.5 Specific Categories	158
General Population	158
General Duties Police Officers	158
State Protection Group Officers	158
Crime Scene Investigators	160
Forensic Firearms Examiners	161
7.2.2.6 Summary	161
7.2.3 Sample Preparation	162
7.2.4 Scanning Electron Microscopy / Energy Dispersive X-ray Analysis	163
7.2.4.1 Backscattered Electron Detector	164
7.2.4.2 BSE and Magnification Calibration	164
7.2.4.3 EDX Calibration	165
7.2.4.4 Software	165
7.2.4.5 General Operation	165
7.2.4.6 Classification.....	165
7.2.4.7 Automated Particle Search Parameters	166
7.2.4.8 Particle Review / Interpretation.....	168
7.2.4.9 Positive GSR Standard	172
7.2.4.10 Blank / Negative Standard.....	173
7.2.5 Data Treatment.....	173
7.2.6 Data Processing	174
7.3 Results	175
7.3.1 General Population	175
7.3.2 General Duties Police Officers	176
7.3.3 State Protection Group Officers	176
7.3.4 Crime Scene Investigators	180
7.3.5 Forensic Firearms Examiners	182
7.3.6 Processed Data	183
7.4 Discussion	188
7.5 Conclusions	194
Chapter 8: Contamination Prevention Procedures and Their Effect on Laboratory Background Levels of GSR	196

8.1 Contamination Prevention Procedures	196
8.1.1 Physical Separation of Functions / Personnel	197
8.1.2 Cleaning Procedures	200
8.1.3 Personnel Procedures.....	200
8.2 Materials and Method	200
8.2.1 Sample Collection.....	200
8.2.2 Sample Preparation	202
8.2.3 Analysis	203
8.2.4 Data Processing	203
8.3 Results	205
8.3.1 Original Laboratory Areas	205
8.3.2 Newer Laboratory Areas	205
8.3.3 Processed Data	207
8.4 Discussion	210
8.5 Conclusions	213
Chapter 9: A Bayesian Statistical Framework for GSR Evidence Interpretation	214
9.1 Value of GSR as Forensic Evidence	214
9.2 Current Methods of Interpretation.....	214
9.3 Bayes Theorem	215
9.4 Bayesian Approach for Interpretation	216
9.5 Bayesian Networks	218
9.6 Materials and Method	223
9.6.1 Formulation of the Bayesian Network.....	223
9.7 Results	223
9.7.1 Series of Events in a Shooting Investigation.....	223
9.7.2 Factors to be Considered in Relation to GSR Evidence Interpretation.....	225
9.7.3 Nodes for Bayesian Network.....	226
9.7.4 A Bayesian Network for GSR Evidence Interpretation.....	227
9.7.4.1 Issues at Hand – Red Group.....	229
9.7.4.2 Case Information from the Investigation – Blue Group	229
9.7.4.3 Core Technical Information Outside the General Knowledge of the Investigators / Parties – Pink Group	230
9.7.4.4 Results Observed on the Samples – Yellow Group.....	230
9.7.4.5 Nodes Calculated Based on the Various Inputs – Green Group	230
9.7.4.6 Use of the BN	231
9.7.5 Current Data Available.....	231
9.7.6 Case Example – Homicide.....	233
9.8 Discussion	235
9.9 Conclusions	238
Chapter 10: Improvements to Forensic Casework Analysis and Interpretation of GSR Evidence	240
10.1 Improvements to Analysis.....	240
10.2 Improvements to Interpretation	248
10.3 Overall Improvements.....	254
10.4 Future Directions.....	255
Appendix I: IONSCAN Negative Ion Instrument Control Parameters/Detection Algorithm – Test-firings.....	257

<i>Appendix II: IONSCAN Positive Ion Instrument Control Parameters/Detection Algorithm – Test-firings.....</i>	<i>260</i>
<i>Appendix III: IONSCAN Negative Ion Instrument Control Parameters – Programming In</i>	<i>263</i>
<i>Appendix IV: IONSCAN Positive Ion Instrument Control Parameters – Programming In</i>	<i>264</i>
<i>Appendix V: Plasmagrams for Substances Programmed Into the IONSCAN.....</i>	<i>265</i>
<i>Appendix VI: IONSCAN Negative Ion Final Detection Algorithm.....</i>	<i>271</i>
<i>Appendix VII: IONSCAN Positive Ion Final Detection Algorithm.....</i>	<i>274</i>
<i>Appendix VIII: Lead and Heavy Metal Free Ammunition Database</i>	<i>276</i>
<i>Appendix IX: LC-MS/MS Operation</i>	<i>287</i>
<i>Appendix X: Optimisation of MS and MS/MS Operating Parameters</i>	<i>293</i>
<i>Appendix XI: Final Optimised LC-MS/MS State Files</i>	<i>300</i>
<i>Appendix XII: MS and MS/MS Data for Compounds.....</i>	<i>303</i>
<i>Appendix XIII: General Duties Police Survey.....</i>	<i>337</i>
<i>Appendix XIV: Crime Scene Investigator Survey</i>	<i>355</i>
<i>Appendix XV: State and Territory Protocol for GSR Sample Collection Survey</i>	<i>376</i>
<i>Appendix XVI: Australian Forensic Laboratory Survey</i>	<i>389</i>
<i>Appendix XVII: GSR Sampling Questionnaire – General Population</i>	<i>421</i>
<i>Appendix XVIII: GSR Sampling Questionnaire – NSW Police Force</i>	<i>425</i>
<i>Appendix XIX: SEM/EDX Instrumentation Identification and Detailed Experimental Procedure.....</i>	<i>430</i>
<i>Appendix XX: NSWPF FML Contamination Prevention and Monitoring Procedures</i>	<i>440</i>
<i>References</i>	<i>445</i>

List of Figures

Figure 1-1: Main components of a revolver (NSWPF 1998)	2
Figure 1-2: Typical ammunition cartridge (DiMaio 1987)	3
Figure 1-3: Primer mechanism (DiMaio 1987)	4
Figure 1-4: Structures of some organic ammunition and explosive compounds.....	7
Figure 1-5: Common distribution of gunshot residue on hands (DiMaio 1987).....	10
Figure 1-6: Gunshot residue particle (Varetto 1990).....	17
Figure 2-1: EDX spectrum of a typical three-component GSR particle	27
Figure 2-2: Police officer handcuffing a suspect.....	37
Figure 4-1: Barringer GC-IONSCAN 400B	47
Figure 4-2: Collection swabs.....	48
Figure 4-3: Schematic of an IMS unit (Barringer 2000).....	49
Figure 4-4: Swabbing for GSR.....	54
Figure 4-5: Plasmagram – NG alarm from GSR from test firing a .40 calibre Glock with ammunition containing double base propellant (sample collected from the shooter’s hands after five consecutive shots were fired).....	58
Figure 4-6: Plasmagram – Negative ion dimethylphthalate peaks	61
Figure 4-7: Example of an IONSCAN alarm for PETN in a shooting investigation (Case #2).....	62
Figure 4-8: Example of a negative ion plasmagram relating to a sample from a shooting investigation (Case #3) demonstrating additional 3,4-DNT peak	63
Figure 4-9: Example of a negative ion plasmagram from test firings using the .40 calibre Glock demonstrating additional peaks of interest	65
Figure 4-10: Example of a negative ion plasmagram from test firings using the .38 calibre revolver demonstrating additional 3,4-DNT peak	65
Figure 5-1: Structure of DDNP (diazodinitrophenol)	75
Figure 5-2: CCI Blazer’s signature aluminium alloy cartridge case	88
Figure 5-3: DFA proprietary nylon, tungsten and copper composite bullet.....	89
Figure 5-4: Overall cartridge and headstamp of .38 Special + P Lapua Lead-free Primer ammunition	90
Figure 5-5: Overall cartridge and headstamp of 9mm Luger PMC Green Non Toxic ammunition	91
Figure 5-6: Micrographs of propellant from (top) .38 Special + P Lapua Lead-free Primer and (bottom) 9mm Luger Winchester Ranger Reduced Hazard Non-Toxic ammunitions	93
Figure 5-7: Morphology / spectrum of a typical SbBaSCuZn particle from Sample 10 (at 5647x magnification).....	96
Figure 5-8: Morphology / spectrum of a typical KSCuZn particle from Sample 9 (at 3765x magnification).....	97
Figure 5-9: Morphology / spectrum of a typical Sr particle from Sample 2 (at 2824x magnification).....	98
Figure 5-10: Morphology / spectrum of a typical WK particle from Sample 1 (at 3765x magnification).....	99
Figure 5-11: Spectrum of a PbSbBaAl particle from 9mm Luger Speer Lawman Clean-Fire ‘LF’ ammunition.....	100
Figure 5-12: Spectrum of a composite PbSbBaSr particle from Sample 3.....	100
Figure 5-13: Spectrum of a composite PbSbBaWK particle from Sample 1.....	101
Figure 5-14: Database entry relating to .38 Special + P CCI Blazer Clean-Fire ammunition.....	102
Figure 6-1: Schematic of LC-MS/MS instrument	111
Figure 6-2: Schematic of the LC interface and the triple quadrupole mass spectrometer (PE Sciex 2000).....	112
Figure 6-3: Schematic of MS/MS voltages (PE Sciex 2000).....	117
Figure 6-4: Structure of nitrobenzene.....	129
Figure 6-5: LC separation a. Negative ion trace b. UV trace.....	137
Figure 7-1: Sampling hands for GSR	156

Figure 7-2: GSR classification scheme used for the SEM/EDX analyses	166
Figure 7-3: Example of the SEM/EDX run parameters used for the GSR analyses	168
Figure 7-4: Example of a SEM/EDX summary of results page	169
Figure 7-5: Example of a SEM/EDX results particle list	170
Figure 7-6: Example of a report page from the SEM/EDX analyses	171
Figure 7-7: Example of a PLANO 'all stub particles' map	172
Figure 8-1: Floor plan of areas sampled in the original AFP laboratory	198
Figure 8-2: Floor plan of areas sampled in the newer AFP laboratory	199
Figure 9-1: Types of connections in Bayesian networks (a) serial; (b) diverging and; (c) converging (Aitken and Taroni 2004)	219
Figure 9-2: BN for fibre evidence (Aitken and Taroni 2004).....	220
Figure 9-3: BN for GSR evidence (Biedermann et al. 2009).....	221
Figure 9-4: Proposed Bayesian GSR network.....	228
Figure 10-1: Flowchart depicting the proposed overall protocol for the sampling and analysis of GSR evidence...	247
Figure 10-2: NSW Police Force Forensic Microanalysis Laboratory design.....	251
Figure V-1: Plasmagram – Negative ion diethylphthalate peak	265
Figure V-2: Plasmagram – Negative ion N-nitrosodiphenylamine peaks	265
Figure V-3: Plasmagram – Negative ion carbazole peaks	266
Figure V-4: Plasmagram – Negative ion 2-amino-4,6-dinitrotoluene peaks	266
Figure V-5: Plasmagram – Negative ion 4-amino-2,6-dinitrotoluene peaks	267
Figure V-6: Plasmagram – Negative ion 3,4-dinitrotoluene peak	267
Figure V-7: Plasmagram – Positive ion methyl centralite peak	268
Figure V-8: Plasmagram – Positive ion ethyl centralite peak	268
Figure V-9: Plasmagram – Positive ion diphenylamine peak	269
Figure V-10: Plasmagram – Positive ion N-nitrosodiphenylamine peaks	269
Figure V-11: Plasmagram – Positive ion carbazole peaks.....	270
Figure IX-1: Ionisation by IonSpray (PE Sciex 2000).....	288
Figure IX-2: Ionisation by APCI (PE Sciex 1996)	289
Figure IX-3: Schematic of the LC interface and the triple quadrupole mass spectrometer (PE Sciex 2000).....	291
Figure X-1: MRM experiment process (PE Sciex 2000)	297
Figure XII-1: Negative ion mass spectrum of 2,4-DNT	303
Figure XII-2: Negative ion mass spectrum of HMX.....	304
Figure XII-3: Negative ion mass spectrum of RDX	304
Figure XII-4: Negative ion MS/MS of 2,4-DNT.....	305
Figure XII-5: Negative ion MS/MS of HMX	306
Figure XII-6: Negative ion MS/MS of RDX.....	306
Figure XII-7: Negative ion mass spectrum of TNT	307
Figure XII-8: Negative ion mass spectrum of PETN	308
Figure XII-9: Negative ion mass spectrum of NGU.....	308
Figure XII-10: Negative ion MS/MS of TNT	309
Figure XII-11: Negative ion MS/MS of PETN.....	309
Figure XII-12: Negative ion MS/MS of NGU	310
Figure XII-13: Negative ion mass spectrum of Resorcinol	311
Figure XII-14: Negative ion mass spectrum of m-Cresol	311
Figure XII-15: Negative ion mass spectrum of Carbazole.....	312

Figure XII-16: Negative ion MS/MS of Resorcinol	312
Figure XII-17: Negative ion MS/MS of m-Cresol.....	313
Figure XII-18: Negative ion MS/MS of Carbazole	313
Figure XII-19: Negative ion mass spectrum of DPA	314
Figure XII-20: Negative ion mass spectrum of 4-NDPA.....	314
Figure XII-21: Negative ion MS/MS of DPA.....	315
Figure XII-22: Negative ion MS/MS of 4-NDPA	315
Figure XII-23: Negative ion mass spectrum of 2,6-DNT	316
Figure XII-24: Negative ion mass spectrum of NG	316
Figure XII-25: Negative ion MS/MS of 2,6-DNT.....	317
Figure XII-26: Negative ion MS/MS of NG.....	317
Figure XII-27: Negative ion mass spectrum of 1,3,5-TNB (from LC method)	318
Figure XII-28: Negative ion mass spectrum of 1,3-DNB (from LC method).....	318
Figure XII-29: Negative ion mass spectrum of 2-A-4,6-DNT (from LC method)	318
Figure XII-30: Negative ion mass spectrum of 4-A-2,6-DNT (from LC method)	319
Figure XII-31: Negative ion mass spectrum of NT.....	319
Figure XII-32: Positive ion mass spectrum of DPA.....	320
Figure XII-33: Positive ion mass spectrum of 4-NDPA	321
Figure XII-34: Positive ion mass spectrum of N-NDPA.....	321
Figure XII-35: Positive ion MS/MS of DPA	322
Figure XII-36: Positive ion MS/MS of 4-NDPA.....	322
Figure XII-37: Positive ion MS/MS of N-NDPA	323
Figure XII-38: Positive ion mass spectrum of MC.....	324
Figure XII-39: Positive ion mass spectrum of EC	324
Figure XII-40: Positive ion MS/MS of MC	325
Figure XII-41: Positive ion MS/MS of EC.....	325
Figure XII-42: Positive ion mass spectrum of DMP	326
Figure XII-43: Positive ion mass spectrum of DEP	327
Figure XII-44: Positive ion mass spectrum of DBP	327
Figure XII-45: Positive ion MS/MS of DMP.....	328
Figure XII-46: Positive ion MS/MS of DEP	328
Figure XII-47: Positive ion MS/MS of DBP	329
Figure XII-48: Positive ion mass spectrum of RDX.....	330
Figure XII-49: Positive ion mass spectrum of NGU	330
Figure XII-50: Positive ion MS/MS of RDX	331
Figure XII-51: Positive ion MS/MS of NGU.....	331
Figure XII-52: Negative ion mass spectrum of Tetryl.....	332
Figure XII-53: Positive ion mass spectrum of NG	332
Figure XII-54: Negative ion MS/MS of Tetryl	333
Figure XII-55: Positive ion MS/MS of NG	334
Figure XII-56: Negative ion mass spectrum of 2,3-DNT	335
Figure XII-57: Negative ion MS/MS of 2,3-DNT.....	335
Figure XII-58: Negative ion mass spectrum of 3,4-DNT	336
Figure XII-59: Negative ion MS/MS of 3,4-DNT.....	336

List of Tables

Table 2-1: Frequency of different compositions of FCCs encountered in NSWPF casework.....	31
Table 4-1: Summary of results of test firing experiments using existing IONSCAN settings	59
Table 4-2: Effective mode of ionisation determined for each target compound	60
Table 4-3: Results of IONSCAN and SEM/EDX analyses for Case #2.....	63
Table 4-4: Results of IONSCAN and SEM/EDX analyses for Case #3.....	64
Table 5-1: Summary of results from the lead and heavy metal free ammunition study by Oommen and Pierce (2006)	73
Table 5-2: Summary of chemical information from available MSDSs	80
Table 5-3: Summary of results from the lead and heavy metal free ammunition study by Josef Lebiedzik (2003)....	81
Table 5-4: Results of the lead and heavy metal free ammunition study at the Munich Forensic Laboratory, Germany (Leuftl 2003)	82
Table 5-5: Lead and heavy metal free ammunition samples obtained for this study.....	84
Table 5-6: SEM/EDX conditions used for the analysis of residue samples.....	86
Table 5-7: Summary of physical characteristics for the ammunitions examined.....	92
Table 5-8: Summary of propellant characteristics for the ammunitions examined.....	94
Table 5-9: Results of SEM/EDX analyses of the primer residues from the ammunitions examined.....	95
Table 6-1: Organic explosive and ammunition component standards obtained and employed in this study	115
Table 6-2: Mobile phases evaluated	120
Table 6-3: MS Scan parameters used for the optimisation studies	121
Table 6-4: MRM experiment transitions for mixed standards analyses	124
Table 6-5: Mobile phases used in the LC experiments	125
Table 6-6: Effective mode of ionisation determined for each target compound	129
Table 6-7: Effect of probe temperature on ionisation	130
Table 6-8: Effect of mobile phase on negative ionisation.....	130
Table 6-9: Effect of mobile phase on positive ionisation	131
Table 6-10: Effect of discharge needle current (NC) on negative ionisation.....	132
Table 6-11: Effect of discharge needle current (NC) on positive ionisation	132
Table 6-12: Effect of MS Scan parameters on negative ionisation.....	133
Table 6-13: Effect of MS Scan parameters on positive ionisation	133
Table 6-14: Effect of mobile phase on negative ion LC separation and run time.....	135
Table 6-15: Effect of column oven temperature on LC separation and run time.....	136
Table 6-16: LC-MS/MS negative ion data.....	138
Table 6-17: MS/MS positive ion data.....	139
Table 7-1: Summary of samples collected in this study	162
Table 7-2: SEM/EDX operating conditions used in this study for the GSR analyses	167
Table 7-3: GSR background study on hands of 20 members of the general population.....	175
Table 7-4: Background levels of particles on hands of 2 general duties police officers	176
Table 7-5: GSR background study on hands of 19 SPG tactical response officers	177
Table 7-6: Background levels of particles on SPG TOU firearms, operations truck and ammunition magazine control room	179
Table 7-7: GSR background study on hands of 14 crime scene investigators.....	180
Table 7-8: GSR background levels on hands of a CSI after annual firearms training and the following day during their normal shift.....	182

Table 7-9: Background levels of particles on hands of 3 forensic firearms examiners.....	183
Table 7-10: Frequency of subjects from each sampling group having >0 of given particle types on their hands	184
Table 7-11: Frequency of a member of the general population having a given number of a given particle type on their hands	185
Table 7-12: Frequency of a Crime Scene Investigator having a given number of a given particle type on their hands	185
Table 7-13: Frequency of a State Protection Group officer having a given number of a given particle type on their hands	186
Table 7-14: Frequency of a Forensic Ballistics Investigator having a given number of a given particle type on their hands	187
Table 8-1: Samples collected from the AFP Forensic Services original laboratory.....	201
Table 8-2: Samples collected from the AFP Forensic Services newer laboratory.....	202
Table 8-3: Background levels of GSR in the AFP original laboratory	206
Table 8-4: Frequency of an AFP newer and older laboratory surface having >0 of a given particle type present ...	207
Table 8-5: Frequency of an AFP older laboratory surface (minus the Firearms area) having >0 of a given particle type present.....	208
Table 8-6: Frequency of an AFP older and newer laboratory surface (minus the Firearms area and floor surfaces) having >0 of a given particle type present.....	209
Table 8-7: Frequency of an FML surface having >0 of a given particle type present.....	210
Table 9-1: Summary of data currently available.....	232

List of Abbreviations

AAS – atomic absorption spectrometry
ABS – Australian Bureau of Statistics
ADI – Australian Defence Industries
2-A-4,6-DNT – 2-amino-4,6-dinitrotoluene
4-A-2,6-DNT – 4-amino-2,6-dinitrotoluene
2-ADPA – 2-amino-diphenylamine
4-ADPA – 4-amino-diphenylamine
AFP – Australian Federal Police
Al – aluminium
APCI – atmospheric pressure chemical ionisation
API – Atmospheric Pressure Ionisation
ASV – anodic stripping voltammetry
Ba – barium
BC – butyl centralite
BN – Bayesian network
BSE – back scattered electron
Ca – calcium
CAD – collision activated dissociation
CCI – Cascade Cartridge Industries
CE – capillary electrophoresis
CF – Clean-fire
CSI – crime scene investigator
CSSB – Crime Scene Services Branch
Cu – copper
DAL – Division of Analytical Laboratories
DBP – dibutylphthalate
DDNP, diazo – 2-diazo-4,6-dinitrophenol
DEP – diethylphthalate
DFA – Delta Frangible Ammunition
DMP – dimethylphthalate
DNA – deoxyribonucleic acid
DNB – 1,3-dinitrobenzene
2,4-DNDPA – 2,4-dinitrodiphenylamine
DNT – dinitrotoluene
DPA – diphenylamine
DTA – differential thermal analysis
EC – ethyl centralite
EDX – energy dispersive x-ray analysis
FA – firearm activity
FBIS – Forensic Ballistics Investigation Section
FCC – fired cartridge case
FDR – firearms discharge residue
FIA – flow injection analysis
FMJ – full metal jacket
FML – Forensic Microanalysis Laboratory
FSG – Forensic Services Group
FSSA – Forensic Science South Australia

FTIR – Fourier transform infrared
FWHM – full width half maximum
GC – gas chromatography
GCMS – gas chromatography mass spectrometry
1,2-GDN – 1,2-glycerol dinitrate
1,3-GDN – 1,3-glycerol dinitrate
GSR – gunshot residue
HEPA – high efficiency particle arrestors
HMF – heavy metal free
HMX – octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC – high performance liquid chromatography
HPLC-MS – high performance liquid chromatography mass spectrometry
ICP-AES – inductively coupled plasma - atomic emission spectrometry
IMS – ion mobility spectrometry
K – potassium
LC – liquid chromatography
LC-MS/MS – liquid chromatography tandem mass spectrometry
LF – lead free
LHS – left hand side
LR – likelihood ratio
MC – methyl centralite
m-cresol – 1-hydroxy-3-methylbenzene
MRM – multiple reaction monitoring
MS – mass spectrometry
MSDS – material safety data sheets
Na – sodium
NA – not applicable
NAA – neutron activation analysis
NATA – National Association of Testing Authorities
NB – nitrobenzene
NC – nitrocellulose
2-NDPA – 2-nitrodiphenylamine
4-NDPA – 4-nitrodiphenylamine
NG – nitroglycerine
NGU – nitroguanidine
NIFS – National Institute of Forensic Sciences
N-NDPA – N-nitrosodiphenylamine
NSW – New South Wales
NSWPF – New South Wales Police Force
NT – nitrotoluene
Pb – lead
PDA – photo diode array
PE – Perkin-Elmer
PETN – pentaerythritol tetranitrate
PMDE – pendant mercury drop electrode
QA – quality assurance
RDX – 1,3,5-trinitro-1,3,5-triazacyclohexane
RHS – right hand side
ROI – region of interest
RWS – Dynamit-Nobel

S – sulphur
Sb – antimony
SE – secondary electron
SEM – scanning electron microscopy
SEM/EDX – scanning electron microscopy/energy dispersive X-ray analysis
Si – silicon
SIM – selected ion monitoring
SMANZFL – Senior Managers of Australian and New Zealand Forensic Laboratories
Sn – tin
SOPs – standard operating procedures
SPC – Sydney Police Centre
SPG – State Protection Group
Sr – strontium
Tetracene – 1-(5-tetrazolyl)-4-guanyltetrazene hydrate
Tetryl – 2,4,6-N-tetranitro-N-methylaniline
Ti – titanium
TIC – total ion chromatogram
TLC – thin layer chromatography
TMJ – total metal jacket
TNB – 1,3,5-trinitrobenzene
TNT – 2,4,6-trinitrotoluene
TOU – Tactical Operations Unit
Triacetin – glyceryl triacetate
UHP – ultra high purity
US – United States
USA – United States of America
UTS – University of Technology, Sydney
VPFSC – Victorian Police Forensic Science Centre
W – tungsten
XRD – X-ray diffraction
XRF – X-ray fluorescence
z – stage height
Z – atomic number
Zn – zinc

**List of Conference
Presentations**

Characteristics of Lead / Heavy Metal –Free Ammunition

*Stephanie Hales, BSc; Claude Roux, PhD; Michael Dawson, PhD;
Chris Lennard, PhD; Eric Davies*

Presented at the 18th International Symposium on the Forensic Sciences,
Fremantle WA, Australia, April 2006 (National ANZFSS Scholarship winner)

A Bayesian Model for GSR Evidence Interpretation

*Stephanie Hales, BSc; Claude Roux, PhD; Simon Walsh, PhD; Chris Lennard,
PhD*

Presented at the 18th International Symposium on the Forensic Sciences,
Fremantle WA, Australia, April 2006 (National ANZFSS Scholarship winner)

**Contamination Prevention Procedures and Their Effect on
Laboratory Background Levels of GSR**

Stephanie Hales, BSc; Chris Lennard, PhD; Claude Roux, PhD

Presented at the 17th International Symposium on the Forensic Sciences,
Wellington, New Zealand, March 2004

**Use of Ion Mobility Spectrometry (IMS) for Detection of GSR in
Shooting Investigations**

*Stephanie Hales, BSc; Elizabeth Chan, BSc; Sonia Casamento, BSc;
Kate McCann, BSc; Joanna Maniago, BSc*

Presented at the 17th International Symposium on the Forensic Sciences,
Wellington, New Zealand, March 2004

**Use of the Environmental Scanning Electron Microscope for the
Analysis of Gunshot Residue**

*Joanna Maniago, BSc; Claude Roux, PhD; Stephanie Hales, BSc;
Matthew Phillips, PhD; Richard Wuhler, PhD*

Presented at the 18th Australian Conference on Microscopy and Microanalysis,
Geelong VIC, Australia, February 2004

Presented at the 17th International Symposium on the Forensic Sciences,
Wellington, New Zealand, March 2004

Presented at the Microscopy and Microanalysis Conference,
Savannah, USA, August 2004

Gunshot Residue (GSR) Evidence Interpretation Issues

*Stephanie Bull, BSc; Sarah Benson, BSc; Claude Roux, PhD; Chris Lennard,
PhD*

Presented at the 16th International Symposium on the Forensic Sciences,
Canberra ACT, Australia, May 2002 (National ANZFSS Scholarship winner)

Propellant & Explosives Analysis by LC/MS/MS

Stephanie Bull, BSc; Claude Roux, PhD; Michael Dawson, PhD; Chris Lennard, PhD

Presented at the 16th International Symposium on the Forensic Sciences, Canberra ACT, Australia, May 2002 (National ANZFSS Scholarship winner)

Presented at the INTERPOL Symposium, Lyon, France, October 2001

Barringer GC-Ionscan: A Field Instrument for Clan Lab Investigations

Karen Scott, BSc; Greg Cook; Stephanie Bull, BSc; Priscilla Barsenbach, BSc

Presented at the 16th International Symposium on the Forensic Sciences, Canberra ACT, Australia, May 2002 (National ANZFSS Scholarship winner)

Presented at Clandestine Laboratory Investigating Chemists 2001

– A Technical Training Seminar, Monterey, California, USA, September 2001

Application of Analytical Chemistry to Forensic Science Problems – an Overview of Method Development and Validation

Claude Roux, PhD; Stephanie Bull, BSc; et al

Presented at Pittcon 2001, New Orleans, LA, USA, March 2001

Investigation Into the Possibility for Secondary Transfer of Gunshot Residue to a Suspect During an Arrest

Stephanie Bull, BSc; Sarah Benson, BSc; Claude Roux, PhD; Chris Lennard, PhD

Presented at the CrimTrac 15th International Symposium on the Forensic Sciences, Gold Coast QLD, Australia, March 2000
(NIFS/SMANZFL Younger Practitioner Award)

Organic Propellant and Explosives Analysis by LC/MS/MS – Preliminary Results

Stephanie Bull, BSc; Claude Roux, PhD; Michael Dawson, PhD; Chris Lennard, PhD

Presented at the CrimTrac 15th International Symposium on the Forensic Sciences, Gold Coast QLD, Australia, March 2000
(NIFS/SMANZFL Younger Practitioner Award)

Presented at the International Association of Forensic Sciences 15th Triennial Meeting, LA, California, USA, August 1999

Abstract

There are two main challenges to gunshot residue (GSR) evidence.

The first concerns analysis. The lack of screening techniques complicates sampling and analysis of large areas or numbers of exhibits. Also, lead or heavy metal free ammunitions present limitations to the technique for confirmatory detection of residues – scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX).

A screening technique was developed to detect GSR components from all ammunition types. Ion mobility spectrometry (IMS) was proven to allow sensitive and effective screening before proceeding to confirmatory analysis.

Lead and heavy metal free ammunitions were examined and a technique developed for detecting components in the organic portion of the residue. Liquid chromatography tandem mass spectrometry (LC-MS/MS) was extremely effective, detecting twenty seven components. The technique is sensitive (to around 1 ppb), selective, rapid and cost effective. The combination of IMS, SEM/EDX and LC-MS/MS, with visual, physical and microscopic examination, is proposed as a complete protocol for GSR analysis from all ammunition types.

The second challenge involves interpretation. Factors that lead to positive and negative findings must be considered and the weight of evidence assessed. Both background data and application of an interpretive framework have been inadequate.

Background levels of GSR in the NSW general population and NSW Police Force were studied and the chances of random presence on a suspect and of contamination during arrest and sampling process determined.

Nil GSR was detected on hands of the NSW general population or the sample of general duties police officers. A moderate probability was demonstrated for low levels of GSR on hands of crime scene investigators. GSR was detected on hands of all forensic firearms examiners tested, however their role limits access to suspects and items

sampled for GSR, limiting the chance of contamination. Significantly, one high risk area for contamination was identified, the tactical response officers.

Background levels of GSR in the Australian Federal Police laboratories were compared before and after implementing contamination controls. The configuration of the original laboratory along with the lack of controls lead to GSR being detected on almost every sample. The newer laboratory was extremely clean, only one GSR particle being detected, demonstrating the importance of effective contamination controls during sample collection and analysis.

A statistical interpretive framework was developed. The model utilises Bayesian networks to consider existing data relating to transfer and persistence, and new data from this research, providing more objective assessment and allowing broader application of the Bayesian framework.