

UNCLASSIFIED

The Use of Advanced Analytical Techniques to Enable Batch and Source Matching of Homemade Explosives

A thesis submitted for fulfilment of the degree of Doctor of Philosophy

Paul Matthew McCurry

Bachelor of Technology (Forensic and Analytical Chemistry)
Bachelor of Science (Honours)



Flinders University of South Australia
Faculty of Science and Engineering
School of Chemical and Physical Sciences

Centre of Expertise in Energetic Materials (CEEM)

February 2015

UNCLASSIFIED

Contents

CONTENTS	I
FIGURES	VIII
TABLES.....	XII
ABBREVIATIONS.....	XV
SUMMARY	XIX
DECLARATION	XXI
ACKNOWLEDGMENTS	XXII
PUBLICATIONS	XXIII
1. INTRODUCTION	1
1.1 Intelligence	2
1.2 Explosives.....	3
1.2.1 Primary Explosives	3
1.2.2 Secondary Explosives	4
1.3 Types and Uses of Explosives	4
1.3.1 Military	4
1.3.2 Commercial.....	4
1.3.3 Homemade Explosives.....	5
1.3.3.1 Fuel-Oxidiser Mixtures.....	5
1.3.3.2 Unitary Explosives.....	5
1.3.3.3 Peroxides	6
1.3.3.4 Organic-based.....	6
1.4 Ammonium Nitrate	6
1.4.1 Industrial Accidents.....	6
1.4.2 Terrorism and Insurgency	7
1.4.3 Regulation of Ammonium Nitrate	7
1.4.3.1 Australia	7
1.4.3.2 Internationally	8
1.5 Ammonium Nitrate Manufacturing Process	8
1.5.1 Overview	9
1.5.1.1 Ammonia Synthesis.....	10
1.5.1.2 Nitric Acid Synthesis	11
1.5.1.3 Ammonium Nitrate Synthesis.....	12
1.6 Calcium Ammonium Nitrate Manufacturing Process.....	13
1.6.1 Production of Calcium Ammonium Nitrate	13
1.6.2 Source Materials for CAN Fertiliser Production	14
1.6.2.1 Ammonia.....	14
1.6.2.2 Nitric Acid.....	14
1.6.2.3 Rock Phosphate	14

1.6.2.4	Carbon Dioxide	14
1.6.2.5	Other Raw Materials.....	15
1.6.3	The Odda Process.....	15
1.6.3.1	Digestion of Phosphate Rock.....	15
1.6.3.2	Crystallisation and Filtration of Calcium Nitrate Tetrahydrate.....	16
1.6.3.3	Production of Calcium Ammonium Nitrate	16
1.7	Prilling and Granulation.....	17
1.7.1	Prilling	17
1.7.2	Granulation by Rotating Drum.....	18
1.7.3	Modern Pugmill Granulation Process.....	19
1.8	Alternative CAN Manufacturing.....	20
1.9	Additives and Anti-Caking Agents.....	20
1.9.1	Inert Additives and Dusts.....	21
1.9.2	Organic Surfactants and Other Surface Active Agents.....	22
1.9.2.1	Non-ionic surfactant	22
1.9.2.2	Cationic surfactants	22
1.9.2.3	Anionic surfactants	22
1.10	Homemade Ammonium Nitrate	23
1.10.1	Precursors.....	23
1.10.2	Synthesis.....	23
1.10.3	Purification of Commercial Ammonium Nitrate	24
1.11	AN-Based Homemade Explosives	25
1.11.1	Addition of Aluminium	25
1.12	Current Analysis Methods.....	26
1.12.1	The Application of Intelligence to Forensic Investigations.....	28
1.13	Isotope Ratio Mass Spectrometry	31
1.13.1	Instrumentation.....	33
1.13.1.1	Quantitative High Temperature Conversion.....	34
1.13.1.2	Quantitative High Temperature Combustion.....	34
1.13.2	Common Forensic Uses of IRMS	35
1.13.2.1	Drug Analysis.....	35
1.13.2.2	Poisons.....	35
1.13.2.3	Food Authenticity	35
1.13.2.4	Other Materials of Forensic Interest	35
1.13.2.5	Explosives.....	35
1.14	Inductively Coupled Plasma - Mass Spectroscopy.....	38
1.14.1	Limitations of Inductively Coupled Plasma - Mass Spectroscopy for Analysis	40
1.14.2	Elemental Analysis as a Forensic Tool	41
1.14.2.1	Explosives and Gunshot Residue	41
1.14.2.2	Determining Food Origin.....	42
1.14.2.3	Illicit Drugs.....	42
1.14.2.4	Elemental Analysis of Homemade Explosive Precursor Materials	42
2.	INITIAL INVESTIGATION INTO THE FORENSIC PROFILING OF AMMONIUM NITRATE AND CALCIUM AMMONIUM NITRATE.....	45
2.1	Isotope Ratio Mass Spectrometry	45
2.1.1	Instrumentation.....	45
2.1.2	Nitrogen Isotope Analysis	45
2.1.3	Carbon Isotope Analysis	45
2.1.4	Samples of Interest.....	46

2.1.5	Detectable Variations in Ammonium Nitrate	47
2.1.5.1	Manufacturing Process	48
2.1.5.2	Source Materials	48
2.1.6	Nitrogen Isotope Analysis Results for All AN and CAN Samples	49
2.1.7	Carbon Isotope Analysis Results for All AN and CAN Samples	51
2.1.8	Carbon and Nitrogen Isotope Results for Selected CAN Samples	53
2.1.9	Carbon and Nitrogen Isotope Results for AN Samples	55
2.2	Inductively Coupled Plasma - Mass Spectrometry of AN and CAN	57
2.2.1	Experimental	57
2.2.1.1	Instrumentation	57
2.2.1.2	Sampling and Contamination	58
2.2.1.3	Reagents and Labware	59
2.2.2	Results and Discussion	61
2.2.2.1	Method Development and Validation	61
2.2.2.2	Preparation of Calibration Standards	61
2.2.2.3	Internal Standard	63
2.2.2.4	Optimisation of Integration Times	63
2.2.2.5	Construction of Calibration Plots	64
2.2.2.6	Estimation of Limits of Detection and Quantification for Elements of Interest	66
2.2.2.7	Preparation of Test Samples	67
2.2.2.8	Method Detection Limit (MDL) and Working Ranges of Elements of Interest	67
2.2.2.9	Spike Recovery	69
2.2.2.10	Measurement Uncertainty Calculations	70
2.2.2.11	Sample Preparation	72
2.2.3	Authentic Sample Analysis and Quality Control	73
2.2.3.1	Calibration	73
2.2.3.2	Quality Controls	73
2.2.3.3	Reference Material	74
2.2.3.4	Influence of Sample Collection and Preparation	76
2.2.3.5	Interpretation and Presentation of ICP-MS Data	77
2.2.4	ICP-MS of AN	78
2.2.5	ICP-MS of CAN	80
2.3	Conclusions	81
3.	BULK IRMS AND ICP-MS ANALYSIS OF CAN-BASED HME	83
3.1	Introduction	83
3.2	Isotope Ratio Mass Spectrometry of CAN-based Explosives	83
3.2.1	Objective	83
3.2.2	Instrumentation	84
3.2.3	Nitrogen Isotope Analysis	84
3.2.4	Carbon Isotope Analysis	84
3.2.5	Carbon and Nitrogen Isotope Analysis Results for CAN-based HME Samples	84
3.3	ICP-MS Analysis of CAN-based HME	88
3.4	The Purification of CAN-based Fertilisers	91
3.4.1	Materials	92
3.4.1.1	Experiments involving the small-scale “cooks” utilised the following materials	92

3.4.1.2	Experiments involving the large-scale “cooks” utilised the following materials	92
3.4.2	Experimental.....	92
3.4.2.1	Small-scale (Triplicate “cook” for each time period)	92
3.4.2.2	Large-scale (Two “cooks” completed)	95
3.4.3	Analytical Methods.....	96
3.4.3.1	Isotope Ratio Mass Spectrometry	96
3.4.3.2	Inductively Coupled Plasma Mass Spectrometry	96
3.4.4	Small-scale Results.....	96
3.4.4.1	Isotope Ratio Mass Spectrometry	96
3.4.4.2	Potential Mechanisms for Purification/Degradation of CAN.....	98
3.4.5	Thermal Analysis of the CAN/Water Cooking Process.....	99
3.4.5.1	Decomposition of Ammonium Nitrate.....	99
3.4.5.2	Simultaneous Thermal Analysis - Infrared Spectroscopy	100
3.4.6	Large-scale Results.....	102
3.4.6.1	Isotope Ratio Mass Spectrometry	102
3.4.6.2	Inductively Couple Plasma - Mass Spectrometry	103
3.5	Problems Associated with Bulk Analysis of CAN-based HME	108
3.5.1	IRMS.....	108
3.5.2	ICP-MS.....	108
3.6	Investigation into Identified Problems	108
3.6.1	Identified Weaknesses and Potential Problems with Bulk Nitrogen Isotope Analysis of Ammonium Nitrate	108
3.6.2	Limitations to Trace Metal Analysis Due to Contamination	110
3.6.2.1	Contamination Considerations: Human Factors	111
3.6.2.2	Contamination Considerations: Environmental Factors	112
3.7	Conclusions	115
4.	NITROGEN ISOTOPE ANALYSIS OF NITRATE SPECIES ISOLATED FROM AMMONIUM NITRATE AND CALCIUM AMMONIUM NITRATE.....	118
4.1	Potential Use for Separation of Ammonium Nitrate	118
4.2	Previous Work in the Separation of Ammonium Nitrate for Isotopic Analysis	118
4.2.1	Isotopic Analysis of Nitrates	118
4.2.1.1	Nitrate Fertilisers.....	118
4.2.1.2	Other Nitrate Sources	121
4.2.2	Isotopic Analysis of Ammonium Ions	122
4.3	Ion Exchange for the Separation of Ammonium and Nitrate	122
4.4	Experimental.....	123
4.4.1	Samples.....	123
4.4.2	Synthesis of Homemade AN Samples	124
4.4.3	Purification of AN from Cold Packs.....	125
4.4.4	Preparation of Representative AN-based HMEs.....	125
4.4.5	Isotope Ratio Mass Spectrometry (IRMS).....	126
4.4.6	Fourier Transform Infrared Spectroscopy (FT-IR)	126
4.4.7	Flow Injection Analysis (FIA).....	126
4.5	Preliminary Studies.....	127
4.6	Final Separation Method Test and Validation.....	129
4.7	Application of Nitrate Separation to AN and CAN Samples	131
4.7.1	Samples.....	131
4.7.2	Ammonium Nitrate Samples	132

4.7.3	Calcium Ammonium Nitrate and Processed Ammonium Nitrate Samples.....	133
4.7.4	$\delta^{15}\text{N}$ Analysis of Homemade Ammonium Nitrate Samples	135
4.8	Application of Nitrate Separation to AN-based HME Samples.....	138
4.8.1	Aluminium Powder Coating Agent Study.....	141
4.8.2	Using a Combination of $\delta^{15}\text{N}$ Values to Discriminate Between AN-based HME Samples	144
4.9	Using $\delta^{15}\text{N}_{\text{Nitrate}}$ and $\delta^{13}\text{C}_{\text{Carbonate}}$ to Improve Clustering.....	145
4.9.1	Sample Preparation.....	146
4.9.2	IRMS Analysis	147
4.9.3	Conclusion.....	148
5.	ANALYSIS OF SUGARS	151
5.1	Historical Used of Sugars as a Fuel in Homemade Explosives.....	151
5.2	Use of Sugar in Home Made Explosives on Current ADF Operations	151
5.3	Types of Sugar.....	151
5.4	Sugar Production by the C_3 , C_4 and CAM Metabolic Pathways.....	152
5.4.1	C_3 Metabolic Pathway	152
5.4.2	C_4 Metabolic Pathway	153
5.4.3	CAM Metabolic Pathway	154
5.5	Commercial Production of Sugars.....	154
5.6	IRMS Analysis of Sugars	155
5.7	Analysis of Sugar by ICP-MS	156
5.8	Analysis of Sugars by Gas Chromatography/Mass Spectrometry	157
5.9	Analysis of Sugars by High Performance Liquid Chromatography.....	158
5.10	Aim.....	158
5.11	Experimental.....	158
5.11.1	Samples.....	158
5.11.2	Isotope Ratio Mass Spectrometry	160
5.11.3	High Performance Liquid Chromatography (HPLC).....	160
5.11.3.1	Sugar Calibration	161
5.11.3.2	Sugar Sample Preparation	162
5.11.3.3	CAN/Sugar Sample Preparation.....	162
5.12	Results.....	163
5.12.1	IRMS Results.....	163
5.12.2	Percentage of Sugar and its effect on the $\delta^{13}\text{C}$ of CAN/Sugar mixtures.....	164
5.12.3	Separation of Sugar from CAN/Sugar	168
5.12.4	Problems with the Isotopic Analysis of Bulk Samples	169
5.12.5	Inductivity Couples Plasma Mass Spectrometry.....	171
5.12.6	High Performance Liquid Chromatography.....	171
5.13	Conclusion.....	175
6.	ANALYSIS OF PLASTIC PARTICULATES RECOVERED FROM HME SAMPLES.....	177
6.1	Analysis Types.....	177
6.1.1.1	Visual Analysis.....	177
6.1.1.2	Physical Analysis	178
6.1.1.3	Chemical Analysis.....	178
6.2	Analysis of Authentic Samples.....	178
6.3	Glitter.....	180

6.3.1	Glitter Production	180
6.3.2	Characterisation of Glitter.....	180
6.4	Materials and Methods.....	181
6.4.1	Samples.....	181
6.4.2	Instrumentation, Techniques and Sample Preparation	182
6.4.2.1	Visual Microscopy.....	182
6.4.2.2	Scanning Electron Microscopy/Energy Dispersion X-ray	182
6.4.2.3	Infrared	183
6.4.2.4	Pyrolysis Gas Chromatography/Mass Spectrometry.....	183
6.4.2.5	IRMS.....	184
6.4.2.6	ICP-MS.....	184
6.5	Results and Discussion.....	185
6.5.1	Glitter Analysis.....	185
6.5.1.1	Visual Microscopy.....	185
6.5.1.2	Scanning Electron Microscopy/Energy Dispersion X-ray	186
6.5.1.3	Infrared	187
6.5.1.4	Pyrolysis Gas Chromatography/Mass Spectrometry.....	189
6.5.1.5	IRMS.....	189
6.5.1.6	ICP-MS.....	191
6.6	Statistical Analysis	192
6.7	Conclusions	194
7.	CHEMICAL EXPLOITATION OF ORGANIC-BASED HME	197
7.1	Objective	197
7.1.1	Instrumentation.....	197
7.1.2	Nitrogen Isotope Analysis	197
7.1.3	Carbon Isotope Analysis	198
7.2	Results.....	198
7.3	Conclusions	206
8.	CONCLUSIONS AND RECOMMENDATIONS.....	208
9.	REFERENCE LIST	213

Summary

This thesis describes the application of advanced analytical techniques: namely isotope ratio mass spectrometry (IRMS) and inductively coupled plasma mass spectrometry (ICP-MS) to the analysis of a variety of ammonium nitrate (AN) based homemade explosives.

AN has been widely used in the preparation of homemade explosives (HME) due its relative stability and ease of acquisition. The aim of this research was to develop methods that enable the identification of batch-to-batch matches between samples and to determine the origin of source materials used in such mixtures.

The work described in Chapter 2 indicated that the IRMS technique has the potential to discriminate samples of AN-based explosives due to the variations in their isotopic composition, e.g. nitrogen and carbon. An investigation on the ICP-MS technique is also described, which allowed for the multi-elemental profiling of trace impurities present in AN and AN-based explosives. These trace impurities may be used to compare samples in order to identify samples that have a similar origin or manufacturing process.

Lab based samples (as analysed in Chapter 2) tend to be considerably simpler to analyse than real samples, so in order to test the validity of the methods developed, DSTO provided realistic HME samples for analysis. These samples were used as they have been prepared in a manner directly analogous to HME samples commonly encountered in a real world scenario. Analysis of these genuine samples is covered in Chapter 3. The analysis of genuine samples highlighted a number of problems with the interpretation of results obtained from a single measurement of the bulk HME sample. These included: contamination, sampling issues, storage issues, dual carbon sources and dual nitrogen sources. The process used to concentrate and purify AN from calcium ammonium nitrate (CAN) also proved to be an important factor for the analysis of AN-based HMEs. The results obtained in Chapter 3 highlights the usefulness of IRMS and ICP-MS for batch-to-batch matching of HME, but indicated that analysis of bulk sample is not sufficient for determining sourcing information and has limited intelligence value.

In Chapter 4 a new technique is described which mitigates the problems determined in Chapter 3. This technique is based on the separation and analysis of the nitrogen sources in AN, namely nitrate ion and ammonium ion. The isotopic ratio of the nitrogen in the nitrate ion was shown to be unchanged regardless of the purification process used, thus is an important marker for determining sourcing relationships. This Chapter described the separation technique and uses IRMS to determine the provenance of AN and CAN based explosives to their source/precursor materials.

Chapter 5 discusses the problem associated with dual carbon sources commonly encountered in fuel-oxidiser-based HME. It details a new method for gaining forensic intelligence from the exploitation of HME comprising CAN/sugar compositions.

Chapter 6 details techniques and methodologies for the analysis of non-explosive components occasionally found in HME compositions. The non-explosive component considered in this examination is glitter. Glitter is often found in paint grade aluminium flake to introduce various lustre effects, however, if this paint grade aluminium flake is used in the fabrication of HME, such as AN/aluminium, then those glitter particles become a

useful marker. The different types of analysis are detailed in this Chapter and the usefulness of this extra layer of information for linking HME samples is demonstrated.

The chemical analysis of a number of organic-based HME is detailed in Chapter 7. A series of experiments illustrating that both IRMS and ICP-MS can be utilised to extract information from samples of organic-based HME. This information can be used for batch-to-batch matching of samples but also to determine the origin of source materials.

The conclusions and recommendations from this research task are detailed in Chapter 8 of this thesis. It describes two new analytical methodologies for the analysis of HME samples using IRMS. These methodologies improve the confidence of source matching, which is important for the provision of chemical intelligence. These techniques highlight a need to change from the bulk analysis of CAN-based HME to the separate analysis of each individual component (carbonate/nitrate) by IRMS. This new methodology has shown potential to be implemented as a way to determine the origin of the CAN used in the preparation of CAN-based HME.

The research described in this thesis has sort to highlight the use of IRMS and ICP-MS for the provision of chemical intelligence in the analysis of HME. By understanding the limitations of bulk analysis and how various processes affect the isotope ratios, or the introduction of trace impurities, it is now possible to link like samples and identify their source materials. The use of the analytical techniques described in this thesis may now be used as an additional layer of information in the general intelligence picture, which when combined with other intelligence collection methods may allow for "attack the network" operations.

Declaration

'I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or a diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person where due reference is made in the text.'

Paul Matthew McCurry

Acknowledgments

This research was performed under the Centre of Expertise in Energetic Martial Arts (CEEM), which is a collaboration between Flinders University of South Australia and the Defence Science and Technology Organisation (DSTO). I would like to acknowledge funding for this project was obtained from the National Security Science and Technology Centre (NSSTC), DSTO and CEEM. I would like to thank these organisations for the opportunity to partake in this project. I would also like to thank Flinders University for awarding me a Research Student Conference Travel Grant, which allowed me to present my research overseas.

I would like to thank my supervising team from DSTO for their expertise, encouragement and guidance on all matters: Dr Benjamin Hall, Dr Philip Davies and Dr David Armit. I would also like to thank the members of both the Explosives and Pyrotechnics group (E&P) and the Threat Mitigation Group (TMG) for their constant guidance and willingness to participate in many aspects of my project. Throughout my time at DSTO I have had the opportunity to participate in a number of once in a lifetime events. I thank them for allowing me to have these opportunities.

From Flinders University, I would like to thank my supervisors for the support, guidance and expertise on all matters: Associate Professor Stewart Walker and Professor Paul Kirkbride. I would also like to thank Professor Hilton Kobus and Associate Professor Claire Lenehan for all their support and guidance through my time at Flinders University. Thanks must also go to the Walker research group and in particular, to Danielle, Christopher and Rachel for their ability to make Flinders an increasingly interesting place.

Thanks for their technical expertise must go to Dr Daniel Jardine and Mr Jason Young from Flinders Analytical. This facility undertook the routine analysis of many of the HME samples reported in this thesis. Daniel and Jason were always willing to offer solutions to technical problems and were always on call to discuss novel ways of tackling the problems highlighted in this thesis. Jason in particular imputed an enormous amount of time and effort into the method development for the ICP-MS work. I cannot thank them enough for all they have done.

This research could not have been undertaken without the wholehearted support of my family. Their continuing encouragement and optimism throughout my studies has facilitated my personal growth and allowed me to fulfil my potential.

I would finally like to thank my friends (especially Vince, Daniel, Michael, Nick and Jess) who have supported me throughout my PhD candidature. You have provided me with friendship, compassion, plenty of laughs and sometimes-valid abuse and I thank you all for being there for me.