IMPROVING DETECTION AND IDENTIFICATION METHODS FOR VOLATILE ORGANIC EXPLOSIVES

By

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Certificate of Authorship and Originality

I, Vitor Cesar Taranto, certify that the work in this thesis has not been previously submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that I am the author of this project and this thesis has been written by me. All the people and institutions involved in the building of this project have been rightfully acknowledged and the information sources and literature used are indicated in the captions and final references of this work.

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DEDICATION

TO MY AUNT AURELIA

COM MUITO AMOR À MINHA TIA LELÉ, A PESSOA MAIS DOCE QUE TIVE O PRAZER DE CONVIVER EM MINHA VIDA.

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List of Abbreviations and Symbols

1D	One Dimensional
2D	Two Dimensional
2-NT	Ortho-Nitrotoluene
4-NT	Para-Nitrotoluene
ANFO	Ammonium Nitrate Fuel
ANN	Artificial Neural Networks
BGE	Background Electrolyte
C^4D	Capacitively Coupled Contactless Conductivity Detection
CAR	Carbowax
CE	Capillary Electrophoresis
CI	Chemical Ionisation
CIT	Cylindrical Ion-Trap
CIT-MS	Cylindrical Ion-Trap - Mass Spectrometer
CMC	Critical Micellar Concentration
CTAB	Cetyltrimethylammonium Bromide
CW/DVB	Carbowax-Divinylbenzene
DDNP	Diazodinitrophenol
DI	Direct Immersion
DMDNB	2,3-dimethyl-2,3-dinitrobutane
DNA	Deoxyribonucleic Acid
DNT	2,4-Dinitrotoluene
DVB	Divinylbenzene
EDDs	Explosive Detection Dogs
EI	Electron Ionization
EOF	Electroosmotic Flow
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-ECD	Gas Chromatography - Electron Capture Detector
GC-MS	Gas Chromatography - Mass Spectrometry
GC×GC	Two Dimensional Gas Chromatography

GC×GC-TOFMS	Two Dimensional Gas Chromatography - Time of Flight Mass Spectrometry
GSR	Gunshot Residue
His	Histidine
HMDs	Home-made Devices
HMTD	Hexamethylene Triperoxide
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High Performance Liquid Chromatography
HS	Headspace
ICAO	International Civil Aviation Organization
IEDs	Improvised Explosive Devices
IMS	Ion Mobility Spectrometry
IR	Infrared
LED-IF	Light Emitting Diode Induced Fluorescence
LIF	Laser Induced Fluorescence
LOAR-1	Lab-on-a-Robot-1
LOAR-2	Lab-on-a-Robot-2
LOAR-3	Lab-on-a-Robot-3
LOC	Lab-on-a-Chip
LOD	Limit of Detection
m/z	Mass-to-charge
MEKC	Micellar Electrokinetic Chromatography
MES	2-(N-morpholino)ethanesulfonic Acid
MS	Mass Spectrometry
MS/MS	Tandem Mass Spectrometry
NB	Nitrobenzene
NFSTC	National Forensic Science Technology Center
ng	Nanograms
NICI	Negative Ion Chemical Ionization
NMR	Nuclear Magnetic Resonance
NSWPDU	New South Wales Police Dog Unit
PA	Polyacrylate
PDMS	Polydimethylsiloxane

PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PETN	Pentaerythritol Tetranitrate
PICI	Positive Ion Chemical Ionization
pg	Picogram
ppb	Parts per billion
ppt	Parts per trillion
QIT	Quadrupole Ion Trap
RDX	Cyclotrimethylenetrinitramine
RNA	Ribonucleic Acid
RSD	Relative Standard Deviation
SDS	Sodium Dodecyl Sulfate
SERS	Surface Enhanced Raman Spectroscopy
SPE	Screen-Printed Electrodes
SPME	Solid Phase Microextraction
TATP	Triacetone Triperoxide
Tetryl	2,4,6-tetranitro-N-methylaniline
TNB	1,3,5-trinitrobenzene
TNT	2,4,6-trinitrotoluene
TOF	Time of Flight
TOFMS	Time of Flight Mass Spectrometry
µg	Micrograms
UV	Ultraviolet
UV-vis	Ultraviolet – Visible Spectroscopy
VOC	Volatile Organic Compound

PUBLICATIONS

Taranto, V., Ueland, M., Forbes, S.L. and Blanes, L. 2019. The analysis of nitrate explosive vapour samples using Lab-on-a-chip instrumentation. *Journal of Chromatography A*. Accepted 3 June 2019.

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ABSTRACT

Although numerous chemical detection methods have been posited and tested for portability and detection of explosives, to date no method has solved the simultaneous issue of speed, reliability, selectivity and sensitivity. In order to advance the chemical and biological detection of explosives as screening tools in search areas, it is necessary to understand the key volatile organic compounds (VOCs) produced and detected by explosives. This thesis aimed to investigate a range of chemical detection methods, including portable and benchtop, to gain a better understanding of the VOCs produced in the headspace of commonly utilised explosives. The first stage of this project focused on the investigation of a previously reported capillary electrophoresis (CE) system coupled to an oscilometric detector (C4D) but with limited success. The second stage of this project focused on the study of commercially-available techniques. A lab-on-a-chip (LOC) was repurposed and successfully used to detect explosive residues in liquid and vapour samples. The Agilent 2100™ Bioanalyzer showed recovery rates of 29, 45 and 75 % for the three nitrate explosives investigated. A transportable gas chromatography-mass spectrometry (GC-MS) system was also tested, however due to several issues presented the instrument was not able to perform headspace analysis. Instead, a benchtop GC-MS and a two dimensional gas chromatograph (GC×GC) coupled to a time of flight mass spectrometer (TOFMS) were investigated. The conventional GC-MS method proved to be inefficient for headspace profiling, whereas the GC×GC-TOFMS was successful in separating and detecting the key VOCs from explosive samples. 2,3-dimethyl-2,3-dinitrobutane (DMDNB), 2,4-dinitrotoluene (DNT), and 1,3-dinitrobenzene (DNB) were identified as the most significant VOCs and subsequently used in the final stage of this project to compare the chemical detection methods with biological detection methods. Accredited explosive detection dogs (EDDs) were exposed to varying concentrations of the three significant VOCs. The study demonstrated that the dogs increased their response over time and with exposure to the standards, demonstrating a learning curve to the target odour. This study has demonstrated comparable sensitivity between EDDs and the benchtop GC×GC-TOFMS method, however canines are still considered the most effective real-time method for screening of explosives, due to their speed and selectivity over large areas. This thesis has advanced our understanding on the VOCs that comprise the odour profile of explosives and will assist with the future enhancement of chemical and biological detection methods.

Keywords: explosive vapours, volatile organic compounds, chemical detection methods, microchip-CE, gas chromatography, mass spectrometry, headspace analysis, explosive detection dogs.