The Development of Novel Micro Paper-based Analytical Devices for the Detection of Explosives

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

By

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Dedication

For Ron, Jim & Esther.

Declaration: Certificate of Authenticity & Originality

I, Natasha Benson, declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Centre for Forensic Science/Mathematical and Physical Sciences at the University.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by an Australian Government Research Training Program.

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Date: 16th of December, 2022

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Abbreviations

4-A-2-NP	4-Amino-2-nitrophenol
ADC	Analogue-to-digital converter
AFP	Australian Federal Police
AlInGaP	Aluminium gallium indium phosphide
AN	Ammonium nitrate
ANFO	Ammonium nitrate fuel oil
ANZPAA	Australian and New Zealand Policing Advisory Agency
ATO	Ammonium titanyl oxalate
b	y-intercept
BD	Bomb disposal
BGE	Background electrolyte
C4 or C-4	Plastic explosive/Composition 4
C^4D	Contactless conductivity detector
CAR/PDMS	Carboxen/Polydimethylsiloxane
C_q	The concentration of the quencher
CE	Capillary electrophoresis
CIE	Commission Internationale d’Éclairage/International Commission on Illumination
CSI/s	Crime scene investigation/investigators
CT	Computer tomography
CTAH	Cetyltrimethylammonium hydroxide
CMC	Critical micelle concentration
CMYK	Cyan, magenta, yellow and key (black) colour scale
1D	One dimension
DI-SPME	Direct immersion solid-phase extraction
D_H	Diameter after heat treatment
DMNB	2,3-Dimethyl-2,3-dinitrobutane
DNA	Deoxyribonucleic acid
DNAN	2,4-Dinitroanisole
1,3-DNB	1,3-Dintirobenzene
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
DNP	Diphenylamine
DMDNB	Dimethlydinitrobutan
D_P	Printed diameter
EC	Electrophoresis
ECD	Electron capture detector
ED	Energy dispersion
EDS	Energy dispersive spectroscopy
EDXS	Energy dispersive x-ray spectroscopy
Ee	Incident irradiance
EGDN	Ethylene glycol dinitrate
EMC	Extended migration channel
EOF	Electroosmotic flow
EPA	Environmental Protection Agency
ESR	Electron spin resonance
f_A	Frequency average

$\Delta f_{A(analyte)}$	Change in frequency change
f_B	Frequency of the blue wavelength
f_D	Output frequency in dark conditions
f_G	Frequency of the green wavelength
f_O	Frequency output
$\Delta f_{O(value)}$	Background subtracted frequency output (generic or unfiltered)
f_R	Frequency of the red wavelength
f_W	Output frequency in white lighting conditions
FBI	Federal Bureau Investigation
FNA	Fast neutron analysis
Eu-MOF	Europium-molecular organic framework
F-CC	Fluorophore-compound complex
F-EC	Fluorophore-explosive complex
FTIR	Fourier transform infrared
GaP	Gallium phosphide
GC	Gas chromatography
GPa	Giga-pascal
G-PLA	Graphene-doped polylactic acid
GSR	Gunshot residue
HCA	Hierarchical cluster analysis
HCl	Hydrochloric acid
HMI	Human-machine interface
HMEs	Home-made explosives
HMTD	Hexamethylene triperoxide diamine
HMX	1,3,5,7-Tetranitro-1,3,5-tetrazacyclooctane
HNS	Hexanitrostillbene
HPLC	High performance liquid chromatography
IC	Ion chromatography
IDE	Integrated development environment
IEDs	Improvised explosive devices
InGaN	Indium gallium nitride
IMDA	Instrumental minimal detectable amount
IMS	Ion mobility spectrometry
IR	Infrared
k_d	The second-order rate constant for dynamic quenching
K_d	Stern-Volmer constant
kHz	Kilohertz
KI	Potassium iodide
KOH	Potassium hydroxide
LC	Liquid chromatography
LDA	Linear discriminant analysis
LOC	Lab-on-a-Chip
LOD	Limit of detection
m	Regression of the line
M	Molar concentration
mAh	Milliamp
MB	Methylene blue
MC	Migration channel
MCDA	Minimal consistently detectable amount
MDA	Minimum detectable amount

MEKC	Micellar electro-kinetic chromatography
MeOH	Methanol
Micro-SD	Micro-sized storage device
MNT	Mononitro-toluene
MS	Mass spectrometry
MTBE	Methyl tert-butyl ether
mW	Mega whatt
(m/z)	Mass-to-charge ratio
$NaNO_2$	Sodium nitrite
NaOH	Sodium hydroxide
NB	Nitrobenzene
NC	Cellulose nitrate, nitrocellulose
ng	Nanogram
NIFS	National Institute of Forensic Science
NG	Glycol trinitrate, nitroglycerine
NMR	Nuclear magnetic resonance
NQR	Nuclear quadrupole resonance
2-NT	2-Nitrotoluene
3-NT	3-Nitrotoluene
4-NT	4-Nitrotoluene
OE	Output enabled
PA	Picric acid - 2,4,6-trinitrophenol
PADs	Paper-based analytical devices
μPADs	Microfludic paper-based analytical devices
PC	Principal component
PCA	Principal component analysis
PDMS	Polydimethylisiloxane
PENO	Plastic explosive containing PETN
PETN	Pentaerythritol tetranitrate
pg	Picogram
PMW	Pulse modulation widths
P-NCEC	Pyrene- nitro-containing complex
PPE	Personal protective equipment
ppt	Parts per trillion
PTFE	Poly-(1,1,2,2- tetrafluoroethylene)
PTFTNA	Pulsed fast/thermal neutron analysis
PRRP	Pyrotechnic reaction residue particles
PYR	Pyrene
PYR-KOH	Pyrene – KOH mixture
R^2	r-squared value
RDX	1,3,5-Trinitro-1,3,5-triazacyclohexane
RGB	Red, green and blue
RH	Relative humidity
RTC	Real time clock
SD	Storage device
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
S/N	Signal/noise ratio
SPE	Solid-phase extraction
SPME	Solid-phase micro extraction

SPR	Surface plasmon resonance
StDev	Standard deviation
TATP	Triacetone triperoxide
TEA	Thermal energy analyser
Tetryl	2,4,6-Tetranitro-N-methylanilne
TLC	Thin layer chromatography
TNA	Thermal neutron analysis
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
UHPLC	Ultra-high performance liquid chromatography
UN	Urea nitrate
UV	Ultra-violet
V. Griess	Variant of Griess reagent
VOCs	Volatile organic explosives
VSC	Video Spectral Comparator
x	x-value
y	y-value
µg	Microgram
ϕ_f^0	In the absence of light intensity
ϕ_f	In the presence of a fluorophore quencher
τ_f^0	Fluorescence lifetime
$\frac{F_O}{F}$	Fluorescence power ratio
σ_{R^2}	Noise
$\sigma_{R^2\ RGB}$	Noise of RGB Image J approach or combined filter or combined f_O of red, green and blue
λp	Peak wavelength
λ1/2	Spectral halfwidth
%RSD	Relative standard deviation

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Abstract

Colourimetric detection, a technique where explosives, constituent functional groups, and taggants may be identified by a change in colour of the reagent, is a rapid and accurate detection method of explosives in-field. However, this approach is presumptive, subjective and inherently relies on the user's ability to distinguish colour changes. Paper-based analytical devices (PADs), using traditional colourimetric detection has overcome some of the limitations of using colourimetric detection alone, and a desirable technique for further development and application in-field.

This thesis presents a method for the improved detection of explosives utilising a 'universal' paper-based analytical device by using traditional colourimetric detection with concomitant fluorescence quenching; where fluorescent chromophore emissions were diminished in the presence of nitro-containing compounds due to complex formation between the compound and fluorophore. *In-situ* and microfluidic PADs (μPADs), were designed and optimised to incorporate both colourimetric and fluorescence quenching reagents, used both independently or combined. *In-situ* and μPADs were designed with two viewing wells per μPAD, and quantitative detection was achieved via a novel transmittance detector under both a white and a 310 nm LED light sources; referred throughout as the eBeagle v.3 detector.

Pyrene and pyrene with sodium dodecyl sulphate (SDS) formulations were found to have superior detection selectivity ranges of nitro-containing explosives compared to other tested fluorophores, detecting between 8 – 9 of the 16 nitro-containing explosives. The eBeagle v.3 detector compared had a detection range of 0.09 ± 0.05 mg – 5.29 ± 2.55 mg using pyrene and 0.22 ± 0.27 mg – 0.75 ± 0.17 mg using pyrene with SDS**,** respectively.

Five out of nine tested traditional and unconventional colourimetric reagents for the detection of organic and inorganic explosives were feasible using *in-situ* or microfluidic PADs and were further optimised with pyrene. A 'universal' two well µPAD using two concomitantly colourimetric detection reagents was developed; 1) a pyrene-KOH mixture for the detection of eight nitro-containing explosives, and sub-classification of some tertiary nitro-aromatic explosives (tetryl, trinitrotoluene (TNT), and trinitrobenzene (TNB)), and 2) an ammonium titanyl oxalate and a variant of Griess reagent performed sequentially to determine the presence of hydrogen peroxide and nitrite-based explosives, respectively. This approach had an instrumental minimum detectable amount (MDA) range of 0.97 ± 0.85 mg – 1.66 ± 1.39 under white lighting conditions and 0.25 ± 0.12 mg – 0.83 ± 0.55 mg under UV lighting conditions.