

**Flexible polyurethane in fire
investigation: detection of hydrogen
cyanide and time until flashover.**

by

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For...

Lorraine Grimwood, who shaped me in her absence;

Michael Dawson, who believed in my ability even when I did not; and

Neil Barnett, who reminded me about the healing qualities of white light.

What matters most is how well you walk through the fire.

Charles Bukowski

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 the 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 the information sources and literature used are indicated in the thesis.

Kate Grimwood

31/03/2014

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Table of contents

Certificate of authorship and originality.....	iv
Acknowledgements.....	v
Table of contents	x
List of figures.....	xiv
List of tables.....	xxi
Abbreviations.....	xxiv
Abstract	xxvii
Chapter 1: Introduction	2
1.1 Fire	2
1.2 The Evolution of Fire Investigation as a Forensic Science Discipline	4
1.3 Fire and Rescue New South Wales (FRNSW) Fire Statistics in Domestic Dwellings.....	8
1.4 Flashover.....	11
1.5 Polyurethane	23
1.5.1 Thermal Degradation	25
1.5.2 The Detection Temperature of Hydrogen Cyanide Detection.....	26
1.6 Fire Effluent Toxicants, Toxicity and Toxicology	27
1.7 Analytical Techniques	32
1.8 Rationale and Structure of Thesis.....	40
1.8.1 Aims.....	41
Chapter 2: Time Until Flashover: Montrose, MN	43
2.1 Introduction.....	43
2.2 Site Description.....	45
2.3 Sample Description.....	47
2.4 Method	49

2.5	Results and Discussion	55
2.5.1	Visual Analysis	55
2.5.2	Environmental Scanning Electron Microscopy (ESEM) Analysis	58
2.5.3	ATR-FTIR Spectrometric Analysis	61
2.5.4	Heat Release Rate (HRR)	64
2.5.5	Time Until Flashover	67
2.5.5.1	Room 1	67
2.5.5.2	Room 2	68
2.5.5.3	Room 3	69
2.5.5.4	Room 4	69
2.6	Conclusion	70
Chapter 3:	Time Until Flashover, Fergus Falls, MN	72
3.1	Introduction	72
3.2	Site Description	73
3.3	Sample Description	76
3.4	Method	79
3.5	Results and Discussion	83
3.5.1	Visual Analysis	83
3.5.2	Environmental scanning electron microscopy (ESEM) Analysis	87
3.5.3	ATR-FTIR Spectrometric Analysis	90
3.5.4	Heat Release Rate (HRR)	94
3.5.5	Time Until Flashover	95
3.5.5.1	Room 1 - Accidental	96
3.5.5.2	Room 2 - Deliberate	96
3.5.5.3	Room 3 - Deliberate	96
3.5.5.4	Room 4 - Accidental	97
3.5.5.5	Room 6 - Deliberate	97

3.5.5.6	Room 7 - Accidental	97
3.5.5.7	Room 8 - Accidental	97
3.5.5.8	Room 9 - Deliberate	97
3.5.6	<i>Further Observations</i>	98
3.6	Conclusion	99
Chapter 4:	Time Until Flashover, QCESA, QLD	101
4.1	Introduction	101
4.2	Site Description	102
4.3	Sample Description	106
4.4	Method	110
4.5	Results and Discussion	119
4.5.1	<i>Visual Analysis</i>	119
4.5.2	<i>Heat Release Rate (HRR)</i>	124
4.5.3	<i>Mass Remaining</i>	127
4.5.4	<i>Time Until Flashover</i>	130
4.5.5	<i>Visual Examination of the Fuel Load, Post Suppression</i>	136
4.6	Conclusion	143
Chapter 5:	Post Suppression Gas Detection Fergus Falls, MN	146
5.1	Introduction	146
5.2	Site Description	147
5.3	Sample Description	147
5.4	Method	147
5.5	Results and Discussion	150
5.6	Conclusion	156
Chapter 6:	Pre-Flame and Post Suppression Gas Detection QCESA, QLD	158
6.1	Introduction	158
6.2	Site Description	158

6.3	Sample Description	158
6.4	Method Development	159
6.5	Method	165
6.5.1	<i>Ion Selective Electrode (ISE)</i>	172
6.5.2	<i>Ultraviolet-Visible Spectroscopy (UV-Vis)</i>	173
6.6	Results and Discussion	175
6.6.1	<i>Ion Selective Electrode (ISE)</i>	175
6.6.2	<i>Ultraviolet-Visible Spectroscopy (UV-Vis)</i>	185
6.7	Conclusion	200
Chapter 7:	Laboratory-based Pre-Flame Gas Detection	202
7.1	Introduction	202
7.2	Site Description	202
7.3	Sample Description	202
7.4	Method	203
7.5	Results and Discussion	208
7.5.1	<i>Experiment A</i>	209
7.5.2	<i>Experiment B</i>	212
7.6	Conclusion	214
Chapter 8:	Conclusions and Further Work	216
8.1	Time Until Flashover	216
8.2	Pre-Flame and Post Suppression Gas Detection	220
8.3	Laboratory-based Gas Detection	222
8.4	Further Work	223
References	226

List of figures

Figure 1.1:	The fire triangle.	2
Figure 1.2:	The fire tetrahedron.....	3
Figure 1.3	Pre-flashover conditions and signs (adapted from [22]).....	14
Figure 1.4	The moments immediately prior to flashover.	15
Figure 1.5	Pre-flashover conditions and signs (adapted from [22]):.....	16
Figure 1.6	a & b) Illustrate the progression of a controlled fire (yellow circles show the ignition of the hot gas and smoke layer and the blue oval show the pyrolysis gases igniting near the entrance to the doorway).	16
Figure 1.7:	Post flashover conditions in a compartment (adapted from [22]).	17
Figure 1.8:	Example of the development of a fire to the post flashover stage.....	18
Figure 1.9:	Diisocyanate and diol reaction to form polyurethane.	23
Figure 1.10:	a)2,4-TDI, b) 2,6-TDI, c)2,4-MDI, d) 2,2-MDI and e) 4,4-MDI	24
Figure 2.1:	The domestic dwelling at 4802 Crowfoot Avenue Montrose, MN.	45
Figure 2.2:	Ground floor schematic of 4802 Crowfoot Avenue Montrose, MN. Not drawn to scale.	46
Figure 2.3:	Example of sofa bed with dimensions included.....	48
Figure 2.4:	Example of the king mattress with two single bases with dimensions included. The red outline indicating the area a sample was collected from.	49
Figure 2.5:	Schematic indicating the location of the bed and the couch in each room. The point of ignition is also indicated by	51
Figure 2.6:	Images indicating the location of the bed and the couch in each room on comparison with the schematic.	52

Figure 2.7:	Exemplar of sofa bed used in each of the experimental burns with the ignition points indicated.....	53
Figure 2.8:	Comparison of the foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4.	56
Figure 2.9:	Comparison of the foam samples collected from the carpet underlay. a) Room 1, b) Room 2, c) Room 4.	56
Figure 2.10:	Latex foam rubber [204].....	57
Figure 2.11:	Comparison of known PU foam samples. a) Density 23, Hardness 130, b) Density 29, Hardness 400 c) Density 36, Hardness 100, d) Activated Chloride Non Flame Retarded, e) Density 30, Hardness 110 and f) Density 15, Hardness 100.....	58
Figure 2.12:	Comparison of the foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4.	59
Figure 2.13:	Comparison of the foam samples collected from the carpet underlay. a) Room 1, b) Room 2, c) Room 4.	59
Figure 2.14:	Comparison of known PU foam samples. a) Density 23, Hardness 130, b) Density 29, Hardness 400 c) Density 36, Hardness 100, d) Activated Chloride Non Flame Retarded, e) Density 30, Hardness 110 and f) Density 15, Hardness 100.....	60
Figure 2.15:	Overlaid spectra of foam samples a) Montrose Room 1 bed, b) Montrose Room 1 sofa bed, and c) Known PU foam samples.	62
Figure 2.16:	Comparison between ATR-FTIR spectra of poly(ester urethane) and poly(ether urethane) contained in the instrument library and that from a sample collected during from the experiments at Montrose, MN.	63
Figure 2.17:	Overlaid spectra of all foam samples collected from Montrose, MN burns room 1 – 4.	63

Figure 2.18:	Comparison ATR-FTIR spectra of Latex contained in the library of the instrument with that of sample collected during from the experiments at Montrose, MN.	64
Figure 3.1:	Lakeland Motel, MN with the administration building shown.	73
Figure 3.2:	Schematic of the 14 connected motel suites. Not drawn to scale.....	74
Figure 3.3:	Section of the building utilised for the burns at Fergus Falls, MN in early stages of the fire.....	76
Figure 3.4:	An example of the quilt, mattress and base used in each room.....	77
Figure 3.5:	a) Pink armchair b) Chairs with padded seat cushions.....	78
Figure 3.6:	a) Dresser b) Desk c) Beside table and lamp.	79
Figure 3.7:	Photographic exemplar of the furniture distribution and schematic that illustrates the layout of the building, the location of the furniture and indicates the location (and mechanism) of ignition. Not drawn to scale.....	81
Figure 3.8:	Foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.....	85
Figure 3.9:	Foam samples collected from the chairs with padded seat cushions a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.	86
3.10:	Foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.....	88
Figure 3.11:	Foam samples collected from the armchair with wood a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.....	89

Figure 3.12:	Overlaid spectra of foam samples a) From the mattress in each suite, b) From the armchair in each suite and c) Chairs with padded seat cushions from each suite, except Room 6.....	91
Figure 3.13:	Overlaid spectra from the armchairs with wood. The sample collected from the armchair with wood used in Room 6 is highlighted blue.....	92
Figure 3.14:	Illustrates the overlaid spectra of the foam samples collected from all of the mattresses and the pink armchairs and the armchair with wood in Room 6... ..	92
Figure 3.15:	Overlaid selected spectra collected from Fergus Falls, MN and Montrose, MN.	93
Figure 4.1:	Warehouse within QCESA facility housing four shipping containers (burn cells).	103
Figure 4.2:	Schematic showing how each scenario was set up, including the couch placement for Burns 1 - 6, two armchair placement for Burns 7 – 12, single armchair placement for Burns 13 – 15 and the placement of the smaller armchair placement for Burns 16 – 18.....	105
Figure 4.3:	Representative exemplar of the larger couches used in Burns 1 – 5.....	107
Figure 4.4:	Couch used in Burn 6.....	108
Figure 4.5:	(a) Larger one seater armchair used in Burns 7 – 15 (b) Smaller one seater armchair used in Burns 16 – 18.....	108
Figure 4.6:	Example of three seater couch placement repeated for Burns 1 – 6.	111
Figure 4.7:	Example of how the two armchair, Burns 7 – 12, were configured.....	112
Figure 4.8:	Example of how the single armchair, in Burns 13 – 18, was configured.	112
Figure 4.9:	Example of the measurements recorded of the distance of the couch from each wall. The values recorded in this schematic are taken from Burn 1. Schematic not drawn to scale.	113

Figure 4.10:	Schematic of k-type thermocouple.....	114
Figure 4.11:	Image indicating the position of the data logger at the edge of the warehouse perimeter. The blue box indicates the thermocouple extension leads spanning from the cell to the edge of the warehouse.	115
Figure 4.12:	Schematic of where thermocouples were introduced into each burn cell.....	116
Figure 4.13:	An example of the point and mechanism of ignition used throughout the experimental burns.	117
Figure 4.14:	PU foam samples collected from the three seater couches used in: a) Burn 1 b) Burn 2 c) Burn 3 d) Burn 4 e) Burn 5 f) Burn 6.	120
Figure 4.15:	PU foam samples collected from each of the two armchairs used in: a) Burn 7 b) Burn 8 c) Burn 9 d) Burn 10 e) Burn 11 f) Burn 12.	121
Figure 4.16:	PU foam samples collected from the single armchairs used in: a) Burn 13 b) Burn 14 c) Burn 15 d) Burn 16 e) Burn 17 f) Burn 18.	121
Figure 4.17:	A) Green, B) Long Yellow, C) Short Yellow, D) Double Layer, E) Yellow Squares.	122
Figure 4.18:	F) Short Pink, G) White Pink, H) Other.	122
Figure 4.19:	Thermal data for Burn 17 - one armchair (smaller).	133
Figure 4.20:	Thermal data for Burn 4 - three seater couch.....	134
Figure 4.21:	Thermal data for Burn 12 - two armchairs.....	135
Figure 4.22:	Thermal data for Burn 15 - one armchair (larger).....	136
Figure 4.23:	Couches used in Burns 1 – 6 post suppression. The circle indicates the area of origin. The narrower arrows indicate a line of demarcation radiating up and out from the area of origin. The larger colour graduated arrow indicates the decline in damage to the couch moving away from the area of origin.	137

Figure 4.24:	Couches used in Burns 1 – 6 post suppression, oriented from the area of origin.	138
Figure 4.25:	Couches used in Burns 1 – 6 post suppression, orientated from the end of the couches opposite the area of origin. The blue arrows indicating the line of demarcation radiating up and out from the area of origin.....	138
Figure 4.26:	Armchairs used in Burns 7 –12 post suppression. The circle indicates the area of origin. The narrower arrows indicate a line of demarcation radiating up and out from the area of origin.....	140
Figure 4.27:	Armchairs used in Burns 7 –12 post suppression that has been orientated from the area of origin.....	140
Figure 4.28:	Armchairs used in Burns 7 –12 post suppression that has been orientated from the end of the armchairs furthest away from the area of origin.....	141
Figure 4.29:	Single armchair used for Burns 13 – 18. Burn 18 is in the foreground.	142
Figure 4.30:	Single armchair used for Burns 13 – 18. Burn 13 is in the foreground.	142
Figure 5.1:	Dräger accuro 2000 pump [207].	148
Figure 5.2:	Schematic of one of the motel suites. The red squares indicate where the atmosphere in the room was sampled from. The numbers indicate the two different pink armchairs. The schematic is not drawn to scale.	150
Figure 5.3:	Detection of HCN and CO from gas analysis of the post suppression atmosphere above the bed. Note that Room 5 was not used in this work. ...	151
Figure 5.4:	Data from gas analysis of the post suppression atmosphere above the chair. Note that Room 5 was not used in this work.....	153
Figure 6.1:	Schematic of apparatus used to house substrates for HCN detection.	161
Figure 6.2:	a) Sampling array from the left. b) Sampling array from the right.	165

Figure 6.3:	a) The outside of cell indicating the neoprene and stainless steel connection. b) Showing the neoprene tubing attached to the Schott bottle containing the KOH solution.....	166
Figure 6.4:	Schematic representation of the gas sampling system from inside the cell...	167
Figure 6.5:	Vacuum pump.	168
Figure 6.6:	Set up for the Stage 2 (heating stage); circles indicate positions of thermocouples directly in front of heat gun at heated surface (red circle) and perpendicular to the surface being heated (blue circle).....	170
Figure 6.7:	Position of the heat gun a) and b).....	171
Figure 6.8:	Calibration curve for Burns 1 & 2.....	178
Figure 6.9:	Calibration curve Burn 7 (a).	182
Figure 6.10:	CN ⁻ Detection Using ISE.....	185
Figure 6.11:	Calibration curve standard solution set one.....	190
Figure 6.12:	Temperature profile during heating stage for Burn 9.....	198
Figure 6.13:	Temperature profile during heating stage for Burn 6.....	199
Figure 7.1:	a) Long Yellow b) Green, PU Foam harvested from the fuel load for the work conducted at QCESA.....	203
Figure 7.2:	Short Yellow PU foam from the fuel load for the work conducted at QCESA.	204
Figure 7.3:	a) Long Yellow and b) Green, PU foam cut into smaller pieces to increase surface area to volume ratio.....	204
Figure 7.4:	a) Short Yellow and b) Grey Density 35, Hardness 200 PU foam cut into smaller pieces for greater surface area to volume ratio.....	205

List of tables

Table 1—1:	The Area of Origin for Fires in Class 1 to Class 4 Structures Determined and Attended by FRNSW 2004 – 2013.	9
Table 1—2:	The Number of Fatalities for Fires in Class 1 to Class 4 Structures Attended by FRNSW 2004 – 2013.	10
Table 1—3:	A Comparison of Flashover Definitions Found in the Literature.	12
Table 1—4:	AS/NZS 4967 2009 Minimum Requirements for Heat Transfer.	22
Table 1—5:	Signs and Symptoms of HCN and CO Inhalation at Different Amounts in Air [129-136].	29
Table 2—1:	Room Dimensions, Ventilation Areas and the Wall and Floor Coverings of the Rooms Used in the Burns Conducted at Montrose, MN.	47
Table 2—2:	Examples of Peak Heat Release Rate Values.	65
Table 2—3:	Estimated Peak HRR (kW) Required for a Flashover Event to Occur compared with the Estimated Peak HRR for the fuel package present.	66
Table 2—4:	Time until flashover: Montrose, MN.	67
Table 3—1:	Room Dimensions and Fixtures: Fergus Falls, MN.	75
Table 3—2:	Peak Heat Release Rates (unconfined burning).	94
Table 3—3:	Estimated Peak HRR (kW) Required for a Flashover Event to Occur compared with the Estimated Peak HRR for the fuel package present.	95
Table 3—4:	Time until flashover (FO), Montrose MN.	96
Table 4—1:	Burn Cell Dimensions and Fixtures, QCESA, QLD.	104
Table 4—2:	Temperature Range and Rainfall.	106
Table 4—3:	QCESA Furniture Dimensions.	110

Table 4—4:	Thermocouple Position in Burn Cells.	116
Table 4—5:	Burn cell use.	119
Table 4—6:	Distribution of PU Foam Per Burn.	123
Table 4—7:	Estimated Peak Heat Release Rates (kW) Required for a Flashover Event to Occur compared with the Estimated Peak HRR for the fuel package present.	125
Table 4—8:	Peak Heat Release Rates.	126
Table 4—9:	Percent Mass Loss, Three Seater Couch.....	127
Table 4—10:	Percent Mass Loss, Two Armchairs.	128
Table 4—11:	Percent Mass Loss, One Armchair.....	129
Table 4—12:	Percent Mass Loss, One Armchair, grouped.	129
Table 4—13:	Time Until Flashover, Three Seater Couch.	130
Table 4—14:	Time Until Flashover, Two Armchairs.	131
Table 4—15:	Time Until Flashover, One Armchair.	132
Table 5—1:	Operating parameters for Dräger accuro 2000 pump.	149
Table 6—1:	Conditions for gas sampling during each stage.....	169
Table 6—2:	Initial ISE calibration curves.	177
Table 6—3:	Calibration Curve Comparison Burns 1 – 6.....	178
Table 6—4:	ISE Response (in mV) to standard solutions over five individual days.....	179
Table 6—5:	ISE Concentration [mol/L] Results Burns 1 – 6.....	181
Table 6—6:	Calibration Curve Equation Comparison Burn 7 and Burn 8.....	183
Table 6—7:	ISE Concentration Results Burns 7 & 8.....	183

Table 6—8: Absorbance (AU) at Specific Wavelengths (nm).	187
Table 6—9: UV-Vis results for maximum absorbance (AU) at 267 nm.	188
Table 6—10: Questioned maximum values for absorbance (AU) at 267 nm.....	189
Table 6—11: Equations for the standard CN ⁻ solutions including all data points.....	191
Table 6—12: Equations for the standard CN ⁻ solutions including all data points (Burns 1 – 6).	191
Table 6—13: Equations for the standard CN ⁻ solutions including all data points (Burns 7 – 12)	192
Table 6—14: Equations for the standard CN ⁻ solutions including all data points Burns 13 – 18).....	192
Table 6—15: UV-Vis results for Burns 1 – 6 (Three Seater Couch).....	193
Table 6—16: UV-Vis results for Burns 7 – 12 (Two Armchairs).	194
Table 6—17 : UV-Vis results for Burns 13 – 18 (One Armchair).....	195
Table 6—18: Type of PU Foam Sampled from The Cushions Used in the Heating Stage.....	197
Table 7—1: Colour, Density and Hardness of the Known PU Samples.....	205
Table 7—2: Conditions for Gas Sampling in the Laboratory.	207
Table 7—3: Equations for the standard CN ⁻ solutions including all data points.	208
Table 7—4: Mass Loss of PU Foam For Experiment A.....	209
Table 7—5: Experiment A Results.	212
Table 7—6: Experiment B Results.....	213

Abbreviations

%RSD	Percent standard deviation
ADG Code	Australian Code for the Transport of Dangerous Goods by Road and Rail
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
CFD	Computational Fluid Dynamic
CMS	Chip Management System
CN ⁻	cyanide ion
CNS	Central Nervous System
CO	carbon monoxide
COHb	carboxyhaemoglobin
DNP	2,4-dinitrophenylhydrazine
EPM	Embedded Piezoresistive Microcantilevers
ESEM	Environmental Scanning Electron Microscopy
FFFD	Fergus Falls Fire Department
FIA	flow injection analysis
FMV	fair market value
FRNSW	Fire and Rescue New South Wales
FTIR	Fourier Transform Infrared spectroscopy
GC-MS	Gas Chromatography Mass Spectrometry
gm	grams
HCN	hydrogen cyanide
HPLC	High Performance Liquid Chromatography
HRR	Heat Release Rate
HS	Head Space
IAAI	International Association of Arson Investigators
IC	Ion Chromatography
IQR	interquartile range
IRS	Internal Revenue Service

ISE	Ion Selective Electrode
KCN	potassium cyanide
kg	Kilograms
KOH	potassium hydroxide
kW	Kilowatts
LEAA	Law Enforcement Assistance Administration
LOD	Limit of Detection
LOQ	Limit of Quantitation
m	meters
MALDI-MS	Matrix-Assisted Laser Desorption Ionization Mass Spectrometry
MDI	methylene diphenyl diisocyanate
MFD	MN Fire Department
mL	Millilitres
mm	Millimetres
MN	Minnesota
MQH	McCaffrey, Quintiere and Harkleroad
mV	Millivolt
N	Hardness
n	Number
N ₂	Nitrogen
NaOH	sodium hydroxide
NBS	National Bureau of Standards
NFPA	National Fire Protection Association
NFPA 921	NFPA 921 Guide for Fire and Explosion Investigations
Ni(OH) ₂	nickel hydroxide
Ni ²⁺	Nickel ion
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance spectroscopy
O ₂	Oxygen
OH-	Hydroxide ion
PPE	personal protective equipment
PU	Polyurethane
Py-GC-MS	Pyrolysis gas-chromatography mass spectrometry
QCESA	Queensland Combined Emergency Services Academy

S&S	Signs and Symptoms
SCBA	self contained breathing apparatus
SCN-	Thiocyanate ion
sec	Seconds
SS	Stainless steel
STD	standard deviation
STEL	Short term exposure limit
SUT	Swinburne University of Technology
TDI	toluene diisocyanate
TGA	Thermogravimetric analysis
The Code	Internal Revenue Code
TWA	Time weighted average
UL	Underwriters Laboratories
UP	ultra-pure
USA	United States of America
USFA	United States Fire Administration
UTS	University of Technology, Sydney

Abstract

Although the majority of fires attended by Fire and Rescue NSW (FRNSW) originate in the kitchen, most fatalities occur in the lounge and bedrooms. These rooms have a comparatively higher proportion of polyurethane (PU) and hence this project sought to focus on the role of PU during the progression of a fire.

The research presented here is a significant addition to the existing body of knowledge and, for the first time, investigates whether the time until flashover is proportional to the amount of PU in a cell. Additional research was undertaken to determine the lowest temperature that hydrogen cyanide (HCN) could be detected in effluent produced from the degradation of polymeric materials, specifically flexible PU.

Thirty large scale burns, which were fuelled with PU-containing furniture, were conducted at three different sites in the United States of America (USA) and Australia between 2007 and 2010. After significant method optimisation (that concentrated on the standardisation of the majority of the experimental parameters) the time until flashover based on the amount of PU in the cell was successfully determined.

Gas analysis was run in parallel to the large scale burns. To facilitate gas sampling an apparatus was developed to remotely trap effluent produced during the progression of a fire, by drawing it through potassium hydroxide (KOH) solution from directly inside the fire cell. The system was used in conjunction with a novel HCN detection method using Ultraviolet Visible (UV-Vis) spectroscopy. The method involved adding nickel (Ni^{2+}) solution to the KOH + fire effluent solution and analysing the resultant solution using UV-Vis spectroscopy. The positive presence of HCN in the fire effluent could be shown by the presence of the tetracyanonickelate (II) complex with a characteristic absorbance at 267 nm. The presence of HCN in fire effluent was quantitatively determined in the pre-flame and at an interval of 30 minutes post suppression in the large scale burns conducted in Australia. In addition a commercially available Ion Selective Electrode (ISE) specific to HCN was used to analyse the KOH + fire effluent solution; though it was found that this technique was best suited to qualitative, rather than quantitative, work.

In a controlled laboratory environment the detection of HCN between 171 °C – 203 °C was investigated. Using a modified version of the method used to detect HCN at the large scale test burns, PU foam was heated in an oven between 171 °C – 180 °C and 184 °C – 203 °C and the resultant effluent was drawn through KOH solution at different time intervals. An amount of Ni²⁺ solution was added to each of the collected sample solutions. The presence of the characteristic absorbance caused by the combination of CN⁻ and Ni²⁺ to form tetracyanonickelate (II) complex was determined using UV-Vis spectroscopy. In some cases the fire effluent was found to contain HCN after heating PU foam for 30 minutes and 50 minutes at both temperature ranges.

The data presented in this body will provide insight to fire investigators when determining the origin and cause of fires, when flashover is suspected to have occurred. This research will certainly benefit the occupant as it provides data to inform the development of a self egress plan that acknowledges the presence of PU in a fire, and its potential hazards. Emergency services members can use the information described in this work to further inform the level of respiratory personal protection equipment (PPE) required when they attend the post suppression scene of a PU fuelled fire. Finally, the research undertaken in this work regarding time until flashover has the potential to inform fire brigades, such as FRNSW, at a strategic level when developing their response time isochrome map (the time taken for an engine to respond to a fire at the furthest point within their area).