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

by

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A thesis submitted for the

Degree of Doctor of Philosophy (Science)

University of Technology, Sydney

March 2014

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

Acknowledgements

This tangible product of blood, sweat and a good deal of tears would never have come to fruition if not for those who inspired me to *be* better and to *do* better. For that I thank all of you, sincerely.

The work contained within these pages is the polished result of embarking on a PhD. What have not been presented here are the lessons I learned, the skills I have acquired and the knowledge that I now hold about myself, and others. It is a knowledge that cannot be forgotten or unlearned and it in itself is worth more to me than anything else.

These acknowledgements are mixed between professional and personal, much like life. They are in no particular order except for the first, who undoubtedly helped me in the best way for the most time and for the longest.

Most special thanks go you to Mark Tahtouh for together we have faced a lot, and amazingly still like and love each other – most of the time anyway. I simply would not have continued to believe I could get this far, if you hadn't reminded me, which you have done often over the years and significantly more so of late. I told a story, just like you suggested, and it's a pretty good one.

My PhD Supervisors both present Claude Roux and Alison Beavis, as well as past. You have all taught me very important lessons for which I am grateful. Without your guidance, getting through this process would have been more difficult.

Thank you to Donna Slusser and Vicki Hoff, my American Moms. Meeting you both was somehow written in the stars, I'm sure, and marked the start of the best adventure of my life thus far. The benefits of our liaison continue to make themselves known and I am so excited for how our lives will be intertwined in the future. I am grateful to both of you then, now and always. Donna if not for you I would not have had the opportunity to learn half of the things I have. I trust you and offer you most grateful thanks. Vicki not only did you lead me astray; you lead me to trust my own instincts (especially when determining origin and cause) with your quiet wisdom. And then, you lead me to Jamie Novak, without whom I would not have

had the opportunity to burn down (legally) half the things I did and my work would not have had the same shape it does today.

Jamie Novak your passion for all things fire inspires me, regularly. I thank you and the MN chapter of the IAAI for all the help you gave me during the early stages of my PhD. Specifically, for acquiring two houses and a hotel to burn down. It's not every day you get to write *that* in a sentence is it? How magnificent! In addition, I would like to express my thanks to Peter Dahl for his contribution and the Fergus Falls Fire Department for their skills in keeping me safe and ensuring the whole place didn't go up in flames before I had a chance to have my way with it. In addition, I would like to thank the gentlemen from the Otter Tail County Detention Facility, for tirelessly setting up the fuel loads at the Fergus Falls burns and for being so polite and respectful.

To those at Queensland Combined Emergency Services Academy (QCESA) who went above and beyond to help me. Thank you, sincerely. It was an incredibly tough period but as you can see here, it paid off.

To little Lisa Johns (nee Mingari) thank you for initially helping me at QCESA. Though I think I still have a little credit left from feeding your maggots whilst you honeymooned, and count excessive amounts of fly carcases on your return. In addition, thank you for being so stoic. All. The. Time. Just hurry up and finish, she said. Stop whinging and do it, she said. Well, now I have.

Ronald Shimmon, at least now I can run an NMR with my eyes closed! I'm still a bit hazy on the freeze-dryer though. Thank you for always ensuring that nothing I asked was ever an imposition and that it was always done with your pleasure. It has been *my* pleasure to know you, and learn from you Aumo.

To Anthea Harris and Gail Grinrod for your technical support (and personal support) when the chips were down. I honestly thought I would never finish running samples on the UV-Vis, but you helped me see the light at the end of the tunnel (and realise it wasn't a train…) thank you.

A big thank you to Norman Booth, Geoff McCredie and The 'Gregs', not only for your technical support and extensive mind blowing knowledge about all things that move, but for allowing me to be so involved in the manufacture of my apparatus.

Bob Crocker thank you for your seemingly endless supply of couches and armchairs, they were worth their weight in gold. If you ever have more I will easily make use of them!

Jim Keegan, Ilona Kramer and David Bishop. Brownie. Need I say more? May the old girl rest in peace and dream of easily separable gas mixtures….

Niamh Nic Daied my thanks to you is mostly for being a shining light, who fights for the underdog because she remembers what it is like to be one. I admire you personally and professionally and I feel blessed to have you as a friend. Your subtle support and appreciation of my path has been a comfort. Don't think I didn't notice and please know that I have always appreciated your thoughts, even from so very far away.

To John DeHaan thank you for once saying to me after I admitted to you I wanted to quit "oh no don't do that we are all interested to see how this turns out". One little sentence, which you probably don't remember uttering, gave me the drive needed to get me through the next bit, and the next bit and the bits after that. Thank you.

Mel Salmon (nee Ruser), an incredibly talented fire investigator and all around amazing woman, thank you for letting me put my theoretical skills into practice. Your guidance and appreciation of my capability as a fire investigator has been refreshing and so very encouraging.

To Paul (PB) Bailey for being supportive, irritating, knowledgeable, caring, dismissive, encouraging, questioning and arrogant. The irritating, dismissive, questioning and arrogant part in you made me want to prove that I could and the supportive, knowledgeable, caring and encouraging part in you helped me do it. I thanked you then. I thank you now and I will probably thank you forever.

Val Ansett, thank you for introducing me to Mel Salmon! But mostly thank you for the times you buoyed my spirits by coming out with the most surprising (and exquisitely inappropriate)

comments at just the perfect time. You are good (and bad) to me and I appreciate you in all your wonder.

From one nerd to another a special mention goes out to Michael Harvey (Fire and Rescue NSW) who shall always be thought of by me as the god of data.

A huge, loud, soft thank you to my Urban Family and I hope you all know who you are. You are so loved and appreciated. You span many years from Year Seven to University to the SES, from Castlecrag to Waitara to Paddington to Perth and to Brisbane and everywhere in between. I appreciate, especially of late, the understanding and support you have shown me when I have had no capacity to think or act outside of my own path. I am so looking forward to getting re-enmeshed in your paths and all the craziness that may ensue; I've missed them and you terribly.

The University Crew. I should just stop right there. How can it all be said in a paragraph? How can you all be individually named? There have been births, marriages, breakups, deaths, engagements, homes bought and sold, holidays, farm stays, parties, driving adventures, boating adventures, uno, gin rummy, conferences, progress reports, travel, secrets, job applications, job applications, job applications, grant proposals, scholarship applications, support, laughter, tears and board meetings. Lots and lots of board meetings. Thank you for the fun times, the hard times, the crazy times and the down times – I have now left the campus. FINALLY!

Special thanks to those I met and become much closer to as a result of working with the ANZFSS, a small and special group, who have shown wonderful support these last few years. Some of you I see regularly and some biennially, but I appreciate you all.

The wonderful people I am lucky enough to earn a crust with, thanks to you all. Especially to Janice 'Wifey' Joss, who came in as a late entrant and had seen me well and truly over the line. Your provision of pep talks, wine times, heartfelt advice and thesis revision is so very much appreciated. I wouldn't have made it without you and I am so pleased that we both got the job! We are kindred. Special thanks to my eternally understanding and supportive work supervisors Malsha and Angela for not letting me come back to work till the draft was done. In addition thanks to the entire Existing Chemicals Team who all know the stress involved and have been very accommodating, in terms of my….idiosyncrasies. Thanks also to Aido, Simran,

Justina, Lew Daddy, Jarrod, Jacqualine, Kylie, Louise, Nick and Mark for providing light entertainment and understanding when needed.

There are a lot of acknowledgements because I have had a lot of help over the years which collectively got me over the line. So in that vein I thank you one and all.

Table of contents

List of figures

List of tables

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 and was found that this technique was best suited to qualitative, rather than qualitative, 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 Ni^{2+}solution was added to each of the collected sample solutions. The presence of the characteristic absorbance caused by the combination of CN^- and Ni^{2+} 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.

Chapter 1: Introduction

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1.1 Fire

Fire can be defined as the result of a rapid oxidation reaction that produces a detectable combination of heat and light [1-3] or as uncontrolled self-sustaining combustion that is visible as a glowing or flaming fire [2, 4]. Though those definitions are correct they do not fully encapsulate the intricacies involved in the development, propagation and sustainment of fire.

Figure 1.1 is a triangular representation of fire that symbolises the factors collectively essential to promote fire: fuel, oxidation and heat. Similar analogies have been discussed in the literature [2].

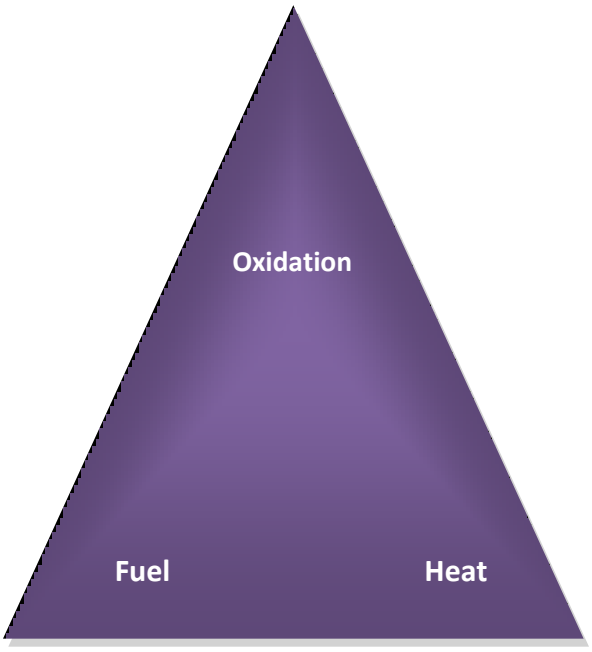


Figure 1.1: The fire triangle.

Using the fire triangle to explain the mechanism of fire is correct but simplistic. A more complete representation of the factors required to sustain fire have been presented in Figure 1.2. The difference between the fire triangle and the fire tetrahedron is that the latter

acknowledges uninhibited rapid chemical chain reactions as a fundamental factor necessary for sustained fire.

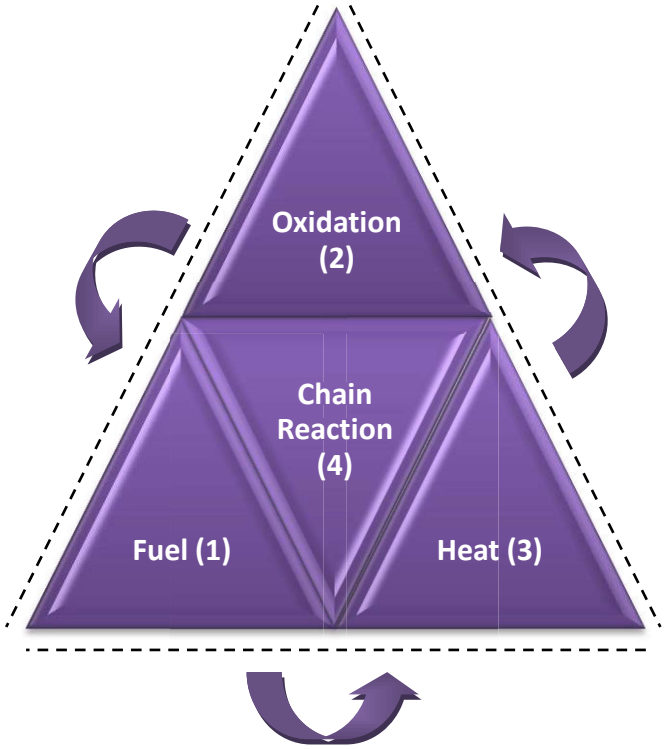


Figure 1.2: The fire tetrahedron.

Using a practical example, consider that a small log fire is represented by the system depicted in Figure 1.1 and Figure 1.2. Applying sufficient water to the system decreases the available heat therefore interrupts access to an essential factor conducive to sustained fire the water absorbs the heat resulting in steam, thus redirecting the heat from the fire. Alternatively, physically removing the logs from the system interrupt the factors required to sustain fire and therefore combustion is interrupted and subsequently the fire would be extinguished. Finally, covering the fire, with a fire resistant medium, disrupts the oxidation process through oxygen starvation consequently extinguishing the fire. The additional aspect included in Figure 1.2 illustrates that each face of the tetrahedron is connected by a chain reaction. Therefore, removing the fuel, heat or oxidation from the situation interrupts the chain reaction impacting on the capacity of the fire to continue.

When the combustion reaction is incomplete, for example in a situation where ventilation fluctuation and smouldering or thermal degradation of the fuel occurs, CO can be a significant

product. In an uncontrolled environment it is rare for complete combustion to occur and it is accepted that CO is present in the atmosphere during the progression of a fire [1].

1.2 The Evolution of Fire Investigation as a Forensic Science Discipline

Fire Investigation is the practice of determining the origin and cause of a fire [3, 5-6]. Today it is recognised as an inclusive process that requires, at the very least, a basic competency (above secondary level) in: fire science, fire chemistry, thermodynamics, thermometry, fire dynamics, explosion dynamics, computer fire modelling, fire investigation, fire analysis, fire investigation methodology, fire investigation technology, hazardous materials, failure analysis and analytical tools [7-8] .

Historically though, the practice itself was at times based on popular, yet unverified, claims regarding the meaning of data gathered during the fire, as well as post suppression fire indicators. Furthermore, the investigative techniques employed to determine the origin and cause lacked a systematic and accepted standardised method when conducting the investigation [9].

In 1977, the now defunct Law Enforcement Assistance Administration (LEAA), which existed as an agency within The United States Department of Justice, assembled a document entitled *Arson and Arson Investigation: Survey and Assessment*. The premise of the document was to consolidate current data pertaining to fire investigation methods and needs, and identify areas where fire investigation could be improved, particularly in the area of validated data and the availability of training to develop existing and future investigators. The report came with a caveat regarding the data collected, indicating that the information was resultant from a survey of fire investigators and the results had not been scientifically validated by the authors. However, the report did make detailed recommendations on the experimental methods that could be used to determine the validity of the data [10-11]. The premise of this document was lost when its contents were included, without undergoing the suggested validation, in *Fire Investigation Handbook, Issue 134* a document published in 1980 by The National Bureau of Standards (NBS), now The National Institute of Standards and Technology (NIST), within The United States Department of Commerce [11-12]. The NBS endorsement of the information published by the LEAA, in addition to subsequent citations, perpetuated the

myths and misinformation rife in fire investigation. This support hindered the introduction of a scientific methodology required to propel fire investigation towards acceptance as a discipline with scientific basis and merit.

The LEAAs original principle, to identify the current methods and needs in fire investigation, was not completely overlooked as a result of the misinterpretation of its 1977 publication. The National Fire Protection Association (NFPA), having become increasingly aware of the variation in the processes used and outcomes recorded by fire investigators during the investigation of fire, moved towards the next step in the advancement of fire investigation from an art to a science.

It is worthwhile to note that the LEAA's 1977 and the NBS's 1980 documents were not the only text perpetuating tradition rather than science, nor was the tradition disseminated by text alone. The responsibility lies with the discipline as a whole and highlights the need for continued regulation in addition to compulsory professional and educational competencies that are overseen by bodies such as NFPA and the International Association of Arson Investigators (IAAI).

An example of how fire investigation started to evolve into an accepted discipline is the NFPAs publication of guidance documents pertaining to fire investigation, among other factors relating to fire safety. Although founded and situated in the United States of America (USA) the NFPA considers itself an international organisation, whose mission is "to reduce the worldwide burden of fire and other hazards on the quality of life by providing and advocating consensus code and standards, research, training and education" [13]. In keeping with the NFPA mission statement, their first guide on fire investigation, *NFPA 921 Guide for Fire and Explosion Investigations (NFPA 921),* was published in 1992 [3] some seven years after it was begun.

The guide, which has done much to dispel the myths associated with fire investigation, was developed by a technical committee comprised of members from the public and private sectors. The members were selected based on their expertise in the techniques, equipment and or facilities developed or used to generate and verify data needed by fire investigators to determine the origin and cause of fire [3]. That is, the guide was developed by a group whose area of expertise was consolidated in a document that provides a holistic method for the fire investigator to determine origin and cause.

As the original NFPA 921 (and subsequent editions) was proposed as a guide, it allows for the periodic revision and update of its contents to reflect scientifically based methods and peer reviewed information from the NFPA, American National Standards Institute (ANSI), American Petroleum Institute (API), American Society for Testing and Materials (ASTM), IAAI, Underwriters Laboratories (UL), U.S Fire Administration (USFA), U.S Government and over 30 individual peer reviewed publications [3]. The result is the culmination of considerable research in disciplines including, but not limited to: fire science, fire dynamics, engineering (fire, electrical and structural), fire chemistry and forensic science coupled with extensive practical knowledge (that is repeatable) from fire investigators.

Despite significant research and the publication of peer reviewed data, to the benefit and development of fire investigators and fire investigation as a discipline, parts of the industry were reticent to embrace the contemporary knowledge. As a result, acceptance of the guide was relatively protracted, even in light of landmark cases such as *Daubert v. Merrell Dow Pharmaceuticals Inc., 509 U.S. 579 (1993)* [14] where it was determined that there is onus on the presiding trial judge to ensure the relevancy, reliability and scientific validity of a scientific experts testimony [15], and *Michigan Millers Mutual Insurance Company v. Janelle R. Benfield*, (*Millers Mutual Insurance Company v. Janelle R. Benfield*, 140 F.3d 915 (11th Cir. 1998) which prevented the testimony of a fire investigator being presented due to the lack of adherence to the scientific method by failing to record appropriate contemporaneous notes [11].

Although acceptance of NFPA 921 was relatively slow, the growing number of legal outcomes reinforcing the need for adherence to the scientific method when investigating fires coupled with the first endorsement and acceptance of NFPA 921 by the IAAI in 2000, propelled the NFPA 921 to become widely accepted as the benchmark in scientific method for the determination of origin and cause.

It is important to highlight though that the NFPA 921 has, in this instance, been used as an example of how fire investigation has progressed over time. The document itself is a guide, not a standard, and more importantly it should be used as intended, as one of numerous tools available for fire investigators when conducting a fire investigation. Fire investigators need to be aware that it is by no means the only tool available and, like any scientific information, it is not infallible and is subject to regular review and updating.

It is unlikely that the confidence in myths and misinformation pertaining to fire investigation was isolated to the USA. Particularly when texts developed outside of the USA, such as Cooke and Ide's Principles of Fire Investigation drew on a significant amount of scientific research to present holistic peer reviewed data regarding fire investigation [16]. The existence of texts such as this seemed to reduce the prevalence of unsubstantiated mythology when determining origin and cause of a fire[9].

In Australia, or internationally, there are no legal requirements to have formal qualifications or a licence to practice as fire investigator; though competencies (above secondary education level) in fire investigation subjects are acknowledged [7]. Tertiary institutions that offer qualifications in fire investigation exist in Australia (Canberra Institute of Technology, Charles Sturt University and the University of Technology, Sydney (UTS)) however, the curriculum is not standardised nor are they all recognised on a national or international basis. Standards, such as the NFPA 1033: Standard for Professional Qualifications for Fire Investigator, suggest minimum levels of competency to qualify as a fire investigator (Ed 1. 1987) though leave the determination of competency up to the prospective or current employer [7]. Like the broad acceptance of NFPA 921, bodies such as the IAAI have been protracted in accepting NFPA 1033 as a basis for qualification having only officially endorsed the standard in 2013 [8].

Considerable development and research occurred in the latter part of the 20th and early part of the 21st century that advanced fire investigation as a scientific and professional discipline. Of which, only those relevant to this project have been referenced in this work.

1.3 Fire and Rescue New South Wales (FRNSW) Fire Statistics in Domestic Dwellings.

The purpose of Fire and Rescue NSW (FRNSW) is to improve community safety, the quality of life and the confidence of NSW by minimising the impact of hazards and emergency incidents on the environment, economy and its 6.8 million residents [6]. Firefighters from FRNSW are responsible for protecting over 90% of the state's population from fires (and other emergency situations like vehicle accidents) and 100% of hazardous material incidents, building collapse and counter-terrorism consequence management [6].

Between January 2004 and November 2013 FRNSW attended over 26000 structural fires in domestic dwellings (Class 1 – Class 4 buildings) [6, 17]. This does not include data involving fires in other structure classes that would likely have polyurethane (PU) present, like office buildings. FRNSW collect a range of data from each fire attended including the area of origin and number of fatalities and the location they are found in. The data presented in Table 1—1 and Table 1—2 do not involve data from other agencies involved in the suppression and investigation of fire.

The data illustrated in Table 1—1 outlines the determined area of origin recorded by FRNSW on attendance to structural fires in Class 1 – Class 4 domestic dwellings, such as single dwellings, attached dwellings, boarding houses and apartments, residential parts of hotels or units attached to commercial buildings. The combination of the two areas where most flexible PU is generally found, the lounge room and sleeping areas, account for a significant portion of the area where the origin is known to have occurred in. The most common area of origin, the kitchen, has also been included. In addition, the culmination of all the remaining areas, termed as 'other', has been included and refers to 53 areas in or around the structure where the area of origin was determined to be and where generally PU is not found in abundance. The areas represented by 'other' include, but are not limited to; awning, external roof surface, external wall surface, external stairwell, small storage area, chimney or flue, patio, crawl space or car port. The 'other' section also includes fires where the area of origin was not determined, or where there were multiple area of origin.

Table 1—1: The Area of Origin for Fires in Class 1 to Class 4 Structures Determined and Attended by FRNSW 2004 – 2013.

	Lounge	Bed	Kitchen	Other	Total
2004	361	572	684	1263	2880
2005	365	533	704	1318	2920
2006	358	501	645	1257	2761
2007	348	505	611	1315	2779
2008	316	459	606	1150	2531
2009	283	461	593	1274	2611
2010	276	420	628	1290	2614
2011	264	433	640	1267	2604
2012	276	403	663	1279	2621
2013 (Nov)	184	297	517	1157	2155
Total	***3031***	***4584***	***6291***	***12570***	***26476***
Percentage	***11***	***17***	***24***	***48***	***100***

For Class 1 – Class 4 structural fires that were attended by FRNSW between 2004 – 2013 it can be seen that the general trend has been repeated. That is, on a yearly basis in the period the data was reviewed, the single area of origin is most commonly the kitchen. The combination of where the majority of flexible PU is found, the lounge room and the sleeping areas, accounts for almost 30 % of a single area of origin and where *other* accounts for the remainder.

From the data presented in Table 1—2 it can be seen that fatalities are generally found in the areas where the highest amount of PU is used to furnish modern homes. The fatalities that were located in the sleeping area and the lounge room account for 50% of the fatalities found at the fires. In this data summary included in the 'other' section represent areas other than

those indicated by Lounge, Bed or Kitchen but do not account for injured victims that may have died after self egress or rescue.

Table 1—2: The Number of Fatalities for Fires in Class 1 to Class 4 Structures Attended by FRNSW 2004 – 2013.

	Lounge	Bed	Kitchen	Other	Total Fatalities	Total Fires
2004	9	6	7	12	34	26
2005	3	8	14	11	36	28
2006	4	2	3	7	16	14
2007	0	1	4	11	16	15
2008	6	6	2	7	21	21
2009	7	9	1	5	22	20
2010	6	6	4	5	21	19
2011	8	17	2	6	33	21
2012	5	7	2	10	24	24
2013 (Nov)	4	6	2	10	21	21
Total	***52***	***68***	***41***	***84***	***244***	***209***
Percentages	***21***	***29***	***8***	***42***	***100***	

The fatality data for Class 1 – Class 4 indicated in Table 1—2 illustrates that the trend indicated for the ten year period is evident in the yearly data also. That is, on a yearly basis in the period the data was reviewed, the majority of the fatalities are found in the areas where the majority of flexible PU is found, the lounge room and the sleeping areas.

It should be noted that the 13 of the 17 fatalities recorded in 2011 occurred at a single incident at an old age nursing home. Three of the deaths were due to thermal injury and the remaining occurred as a result of other injuries, including inhalation injury.

This data is useful for highlighting that there is a commonality between the amount of PU in a room and areas of origin and or fatality. Additional information, such as the mode of injury being a result of thermal, inhalation injury or other, was flashover noted or thought to have occurred or if there was significant PU present is not in the standard scope of data collected by FRNSW.

1.4 Flashover

The term *flashover* appears in literature associated with fire investigation, fire science, fire modelling and fire dynamics, yet there is no one definition that is uniformly accepted. In some incidences there has been variation between definitions published by the same organisation, which adds to the uncertainty surrounding the description of flashover.

In 2002 Kennedy and Kennedy reviewed NFPA codes that defined flashover and found that five standards, codes or guides defined flashover, four of which gave different flashover definitions [18]. The same codes were reviewed in 2013 and were compared with Kennedys 2002 review [19-23]. The definitions have been presented in Table 1—3.

Table 1—3: A Comparison of Flashover Definitions Found in the Literature.

2002 review **[18]**	2013 review [19-23]
NFPA 101: Life Safety Code. 2000 Edition. **Flashover:** A stage in the development of a contained fire in which all exposed surfaces reach ignition temperatures more or less simultaneously and fire spreads rapidly though the space.	**NFPA 101: Life Safety Code. 2012 Edition.** **Flashover:** Unchanged from 2000 Edition
NFPA 402: Guide for Aircraft Rescue and Fire Fighting Operations. 1996 Edition. **Flashover:** All combustibles in a room or confined space have been heated to the point that they are giving off vapours that will support combustion, and all combustibles ignite simultaneously.	**NFPA 402: Guide for Aircraft Rescue and Fire Fighting Operations. 2013 Edition.** **Flashover:** A transition phase in the development of a compartment fire in which surfaces exposed to thermal radiation reach ignition temperature more or less simultaneously and fire spreads rapidly throughout the space, resulting in full room involvement or total involvement of the compartment or enclosed space.
NFPA 555: Guide on Methods for Evaluating Potential for Room Flashover. 2000 Edition. **Flashover:** A stage in the development of a contained fire in which all exposed surfaces reach ignition temperatures more or less simultaneously and fire spreads rapidly though the space.	**NFPA 555: Guide on Methods for Evaluating Potential for Room Flashover. 2013 Edition.** **Flashover:** SAME as 2000 Edition.
NFPA 921: Guide for Fire and Explosion Investigation. 2001 Edition. **Flashover:** A transition phase in the development of a contained fire in which surfaces exposed to thermal radiation reach ignition temperature more or less simultaneously and fire spreads rapidly though the space.	**NFPA 921: Guide for Fire and Explosion Investigation. 2011 Edition**. **Flashover:** A transition phase in the development of a compartment fire in which surfaces exposed to thermal radiation reach ignition temperature more or less simultaneously and fire spreads rapidly though the space, resulting in full room involvement of total involvement of the compartment of enclosed space.
NFPA 230: Standard for the Fire Protection of Storage. 1999 Edition. **Flashover:** See definition of Flameover. **Flameover:** A fire that spreads rapidly over the exposed linty surface of the cotton bales. In the cotton industry, the common terms is flashover and has the same meaning.	**NFPA 230: Standard for the Fire Protection of Storage. 2003 Edition**. **Flashover:** There is no definition for Flashover. **Flameover:** A fire that spreads rapidly over the exposed linty surface of the cotton bales.

As Table 1—3 suitably highlights, these kinds of documents are open to review in order to reflect the most current peer reviewed attitudes towards a subject. It is encouraging to note that the 2013 review of the NFPA documents indicated a clear move towards universal consolidation of the definitions within the organisation.

Individual parties have also defined flashover in terms that originate from different factions of fire science. However, generally the definitions are consistent in their explanation as illustrated by the examples below:

The final stage of the process of fire growth; when all combustible fuels within a compartment are ignited, the room is said to have undergone flashover [2].

A rapid change in a developing room fire to full room involvement [1].

Flashover is a transition from a fire involving one fuel package after another to a fire which involves all available fuel in the compartment [24].

Literature definitions were considered and the following definition was adopted when defining the physical moment that flashover had occurred with respect to the experimental work conducted and presented in this thesis:

A transition phase in the development of a compartment fire in which surfaces exposed to thermal radiation reach ignition temperature more or less simultaneously and fire spreads rapidly though the space, resulting in full room involvement of total involvement of the compartment of enclosed space [3].

For the experimental work the visual cues described in the definition above were observed; though additional visual cues were noted during the progression of the fire as indications that flashover was likely to be imminent. Figure 1.3, Figure 1.5 and Figure 1.7 have been adapted from examples in NFPA 921 that illustrate the progression of a compartment fire [22]. However the figures presented in this work include additional visual signs that were noted. Supplementary physical criteria that were utilised have also been included in the figures.

The information illustrated below in Figure 1.3 provides a stylised example of pre-flashover conditions in a compartment fire [22]. This situation is where the flames have not impinged

on all the available items in the fuel load yet. The temperature at the ceiling is rising, but is not yet relatively uniform from the floor to ceiling.

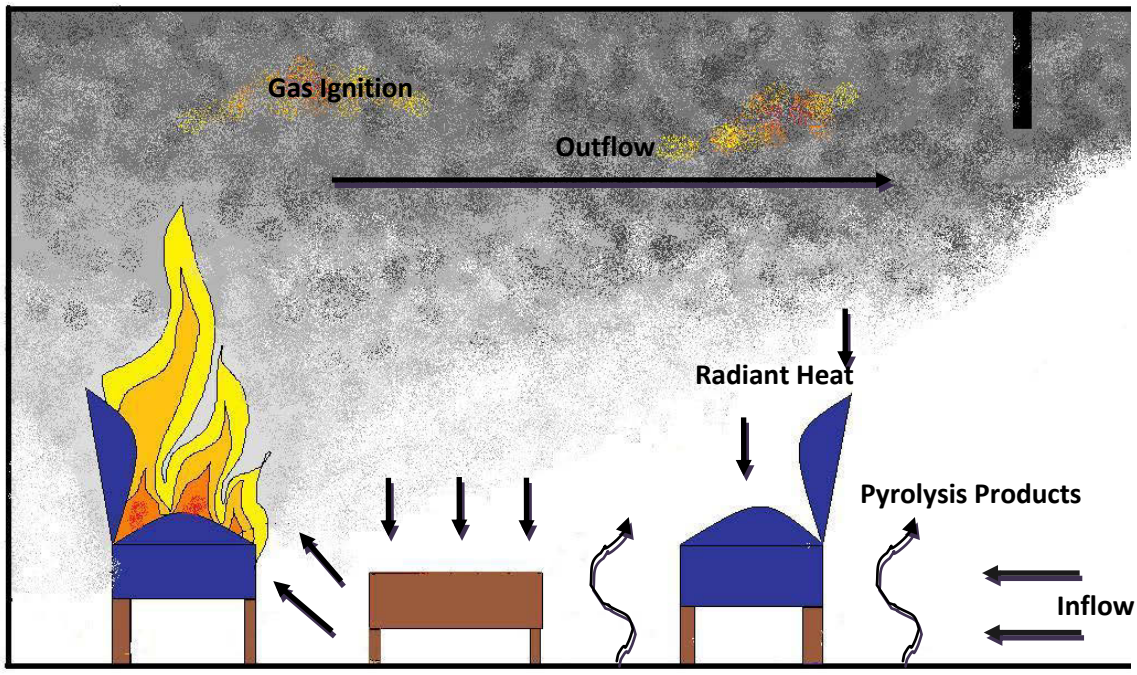


Figure 1.3 Pre-flashover conditions and signs (adapted from [22]).

Additions have been included to illustrate the visual cues watched for in this body of work that suggested flashover could occur shortly. For example, signs of flickering in the hot smoke and gas layer where pockets of gas (and or particulate matter) ignite were watched for as they can generally precede a flashover event. In addition, the occurrence of tracking, where the inflow of cool air disturbs the rising pyrolysis gases to form visible gaseous rivulets flowing horizontally across the floor in line with the inflow, was considered in this instance to be an indication that flashover was forthcoming. At this point the radiant temperature is not significant enough to ignite the floor level pyrolysis gases, nor are they being impinged on by flame.

An example of the tracking being noted has been provided in Figure 1.4 and is from fires conducted during the research presented here. The rivulets of pyrolysis products have been indicated using a blue oval and the flickering in the hot gas layer has been indicated by the yellow circle.

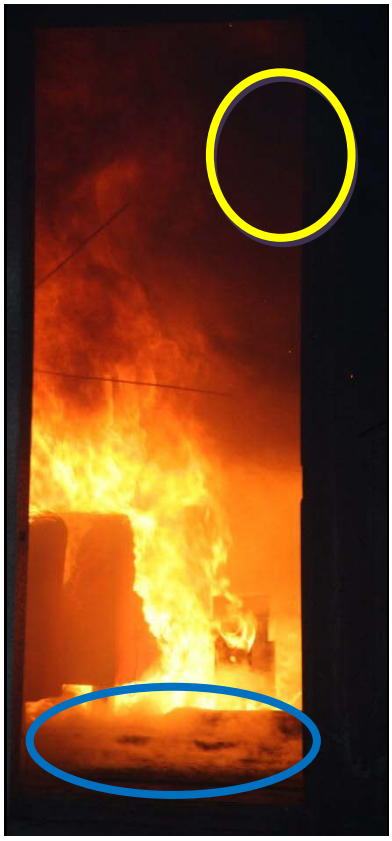


Figure 1.4 The moments immediately prior to flashover.

The progression from the situation illustrated in Figure 1.3 to that illustration in Figure 1.5 is a rapid transition in the progression of a fire. The image depicted in Figure 1.4 was captured in the seconds prior to fire reaching flashover in the cell.

Figure 1.5 is a representation of what is occurring at the onset of flashover. The temperature of the hot gas layer has risen such that the radiant heat is sufficient that those materials in the fuel load that can, undergo thermal degradation, pyrolysis. The resultant gas reaches it auto ignition temperature and ignites. Here surface burning from floor to ceiling is occurring and the hot smoke and gas layer is well ignited. In Figure 1.5 the addition of a temperature gauge indicates a rapid rise in temperature that occurs from floor to ceiling.

Generally it is accepted that the onset temperature for flashover is approximately 600 °C, however it has been reported in a review of the research as being reported to occur between 450 °C – 771 °C with a heat flux range of 15 kW/m^2 to 33 kW/m^2, however flashover has been reported to occur with a heat flux of 170 kW/m^2 [25].

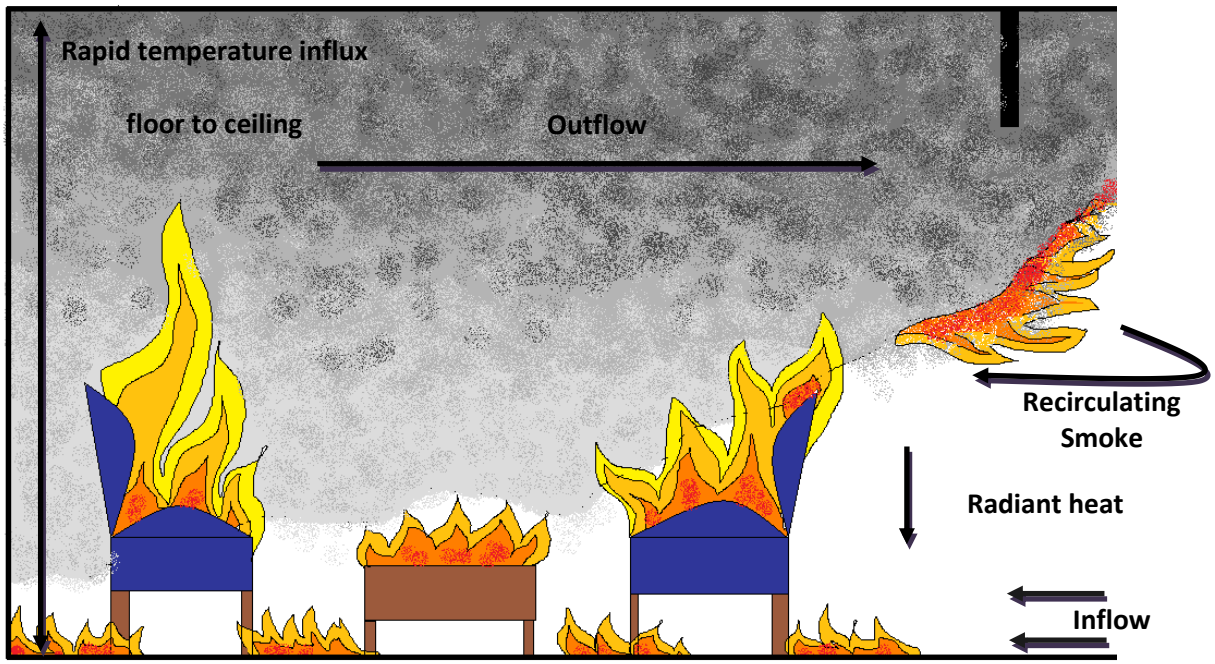


Figure 1.5 Pre-flashover conditions and signs (adapted from [22]).:

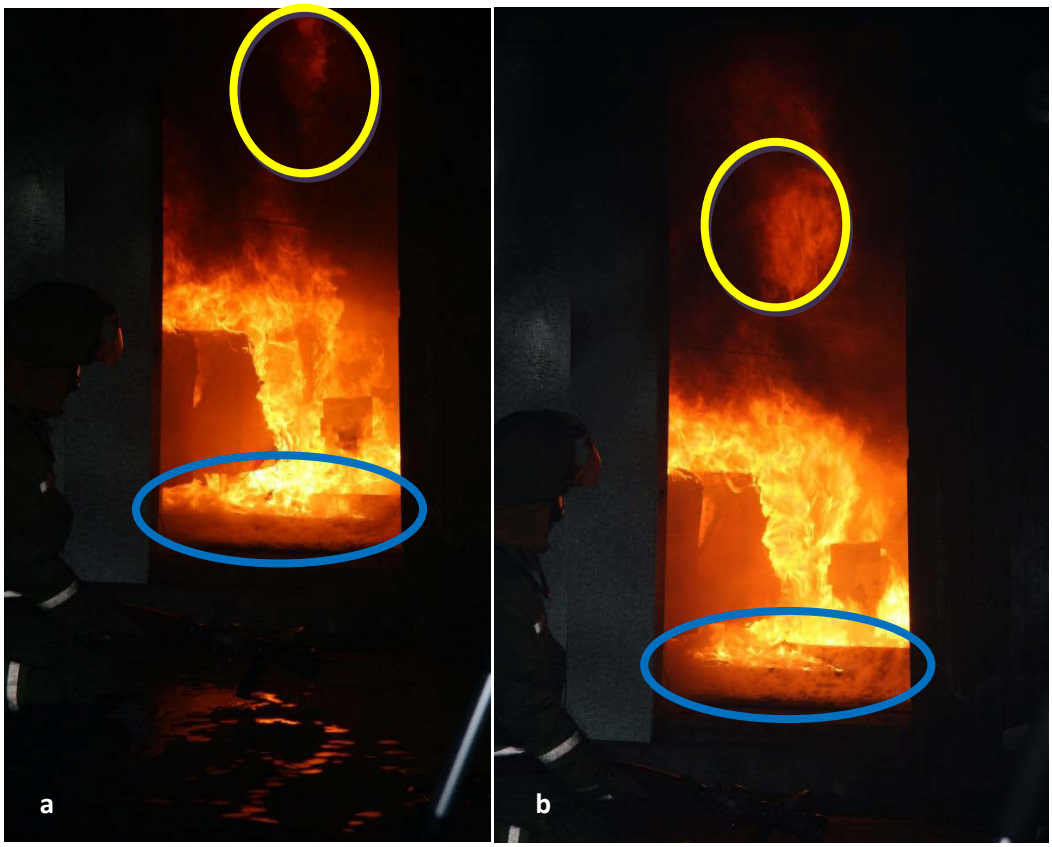


Figure 1.6 a & b) Illustrate the progression of a controlled fire (yellow circles show the ignition of the hot gas and smoke layer and the blue oval show the pyrolysis gases igniting near the entrance to the doorway).

Figure 1.6 includes images taken during the progression of a controlled fire (conducted during the research outlined here) that depict what the schematic in Figure 1.5 is illustrating. For example the yellow circles indicate the ignition of the hot gas and smoke layer and the blue oval indicate the ignition of the pyrolysis gases from the carpet near the entrance to the doorway.

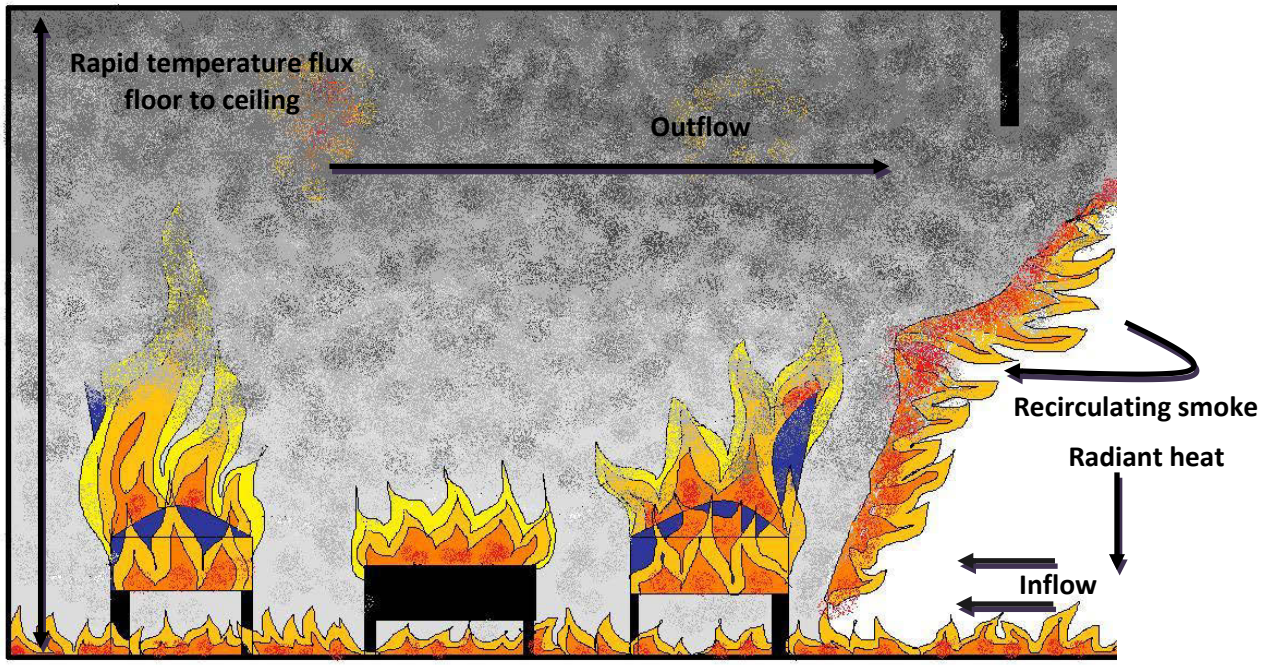


Figure 1.7: ***Post flashover conditions in a compartment (adapted from [22]).***

Figure 1.8: ***Example of the development of a fire to the post flashover stage.***

Though the investigation of post flashover conditions were not included in the work presented in this thesis Figure 1.7 and Figure 1.8 illustrate the transition from flashover into the post flashover stage and total involvement. It can be seen in Figure 1.8 that the pyrolysis gases are ignited at floor level all the way to the door way and that the hot gas and smoke layer is ignited.

It should be noted that the progression of the photographic images displayed in Figure 1.4, Figure 1.6 and Figure 1.8 are the progression of the same fire from pre-flashover conditions to post flashover conditions and took place in an estimated time period of approximately three seconds and were recorded during the research conducted for this body of work. The last image in the series, Figure 1.8, was taken as the firefighter responsible for suppressing the fire was opening the hose to initiate suppression.

In this body of work flashover was predominantly determined visually based on the knowledge and experience of the author in combination with those suppressing the fires. Therefore significant care has been taken to explain the visual nuances associated with

flashover. However other factors, in addition to those that were briefly touched on earlier, contribute in a cascade like manner to the occurrence of flashover.

For example, equations have been developed that estimate the heat release rate (HRR) required for a compartment to reach flashover [1-3, 26].

The following correlations have been proposed by Babrauskas, Thomas, and McCaffrey, Quintiere and Harkleroad (MQH).

$\dot{Q}_{f_0} = 7.8A_T + (378\ A_o)(h_0)^{0.5})$ (Thomas Correlation) [2-3].

$\dot{Q}_{f_0} = (750A_0)(h_0)^{0.5}$ (Babrauskas) [2-3].

Where:

A_T = total surface area of the room (m^2)

A_o = area of the opening (m^2)

h_o = height of the opening (m)

$\dot{Q}_{f_0} = 610\ [h_k A_t A_0 \left(h_0{}^{0.5}\right)^{0.5}$ (MHQ) [26]

Where:

h_k = convection coefficient – this can also be an estimation (calculated by estimating room temperatures and the likelihood of flashover using fire test data correlations)

$h_k = k/\delta$

Where:

k = thermal conductivity of the wall material

δ = wall thickness

Or,

$$h_k = \sqrt{\rho ck}/t$$

where:

ρ = density of the wall material

c = specific heat of the wall material

k = thermal conductivity of the wall material

t = time of exposure

The correlation equations produce estimated HRR values only. For example the ventilation factor, size surface area and material that the fuel load is composed of, the size of the compartment and the type of material the walls are constructed from can all impact of the determination of the HRR. In addition, factors such as the placement of the fuel load can also impact on the growth rate of the fire, thus the HRR of the fire.

While the theorems predict the likelihood of flashover occurring based on prescribed parameters, the time it will take is not. Determining how long the cell or structure will take to reach flashover based on the existing PU fuel load has not been the focus of previous research.

Research has been conducted into the propensity for specific items made from PU reach flashover as opposed to the time [27-28]. There have also been studies conducted regarding the manipulation of different parameters and how they affect or improve predictor fire models, in terms of flashover; though time until flashover is not part of the testing protocol. Notably, in the majority of the experimental work, the experiments were not repeated [25, 29-40]. A small body of work has focused on the precision of Computational Fluid Dynamic (CFD) models as predictive tools to determine the magnitude and spread of fire in a full scale scenario; however the work was unrealistic as spiking occurred (three mattresses were stacked) and the experiment was not repeated [32-33].

There have been several studies that derived models to predict the time until flashover based on the data collected from analysis of samples using cone calorimetry [41-50]. The EN 13823:2000 Reaction to fire tests for building products – Building products excluding floorings exposed to the thermal attack by a single burning item and the ISO 9705 Fire tests – Full-scale room test for surface products feature heavily in the testing procedures [51-52]. Most models were more suited to materials that had prescribed times until ignition, for example the model proposed by Hakkarainen had good results using the cone calorimeter for products that had an ignition time of between 5 – 60 seconds at 50kW/m^2. The model proposed by Östman and Tsantaridis appears to be the most accurate. It uses data collected in the first 300 seconds to predict the time until flashover based on the density of the product, its ignition time, again at 50kW/m^2 [41, 47]. Though some of the methods proposed to determine the time until flashover these studies focused on building materials that did not extend to PU and included extrapolation from bench top experimental work.

Determining if a cell of structure will reach flashover, based on the existing fuel load, is certainly beneficial to fire scientists, investigators and occupants alike, albeit for different reasons. The ability to derive a time until flashover proportional to the existing fuel load would augment the existing capability regarding the likelihood of flashover to occur. The fundamental outcome is the increased potential to save lives and reduce property destruction.

Standards exist to outline the mechanism in which to set up a large scale experiment to ensure that flashover is achieved, or determine if flashover is likely to occur based on known parameters [21, 53]. However the standards do not investigate the time until flashover based on the fuel load, specifically PU.

Of particular note to those attending the fire would be the determination of a time until flashover based on the fuel load. In Australia the personal protective equipment (PPE) worn by firefighters responding to structural fires is governed by AS/NZS 4967:2009 Protective clothing for firefighters-Requirements and test methods for protective clothing used for structural firefighting [54]. In terms of heat transfer, the minimum requirements for turnout gear are as follows:

Table 1—4: AS/NZS 4967 2009 Minimum Requirements for Heat Transfer.

Heat Transfer (Flame) 80 kW/m²	
Heat Transfer Index (HTI)	**Performance**
HTI 24	≥ 17 seconds
HTI 24 – HTI 12	≥ 4 seconds
Heat Transfer (Radiation) 40 kW/m²	
Heat Transfer	**Performance**
t_2	≥ 22 seconds
$t_2 - t_1$	≥ 4 seconds
Mean Transmission Factor 1	≤ 60 %

For the Heat Transfer (Flame) HTI 24 and HTI 12 represent minimum time values that each garment must perform to, in terms of resisting heat transfer, in order to prevent second degree and first degree burns respectively to the wearer. The variance in the heat flux recorded in the literature for flashover has exceeded both those used to determine the minimum requirement for flame and radiant heat transfer and in the case of radiant heat, in some case more than four times. Therefore being able to predict the time until flashover based on the fuel load could certainly be of benefit for those responding to the fire.

Regardless of the definition used to describe flashover or the mechanism of action taking place, for an occupant or other person not wearing fire specific PPE, at the time of flashover the result is fatal. Furthermore, if an emergency services worker is present during a flashover event survival is dependent on the duration of exposure proportional to the level of PPE worn at the time. The nature of the research being carried out sought to take a more holistic

approach to the investigation of what occurred prior to ignition, during a fire and post suppression of a fire.

1.5 Polyurethane

Polyurethane (PU) is an example of a synthesised polymeric material that is widely utilised to manufacture a variety of products. The variety of products, and subsequent applications, can be attributed to the physical properties of PU, such as flexibility. Examples of PU products include flexible and rigid foams, adhesives and rigid coatings [55]. The diversity in the physical properties of PU ensures its use in building and vehicle construction is prolific. In addition to construction, PU is widely used for the internal coverings and furnishings of buildings and vehicles.

The term polymeric material refers to the repetition of monomeric units linked together to form a chain. Principally, PU is the product of an exothermic reaction between an isocyanate and an alcohol which is illustrated in Figure 1.9 by the reaction between a diisocyanate and a diol.

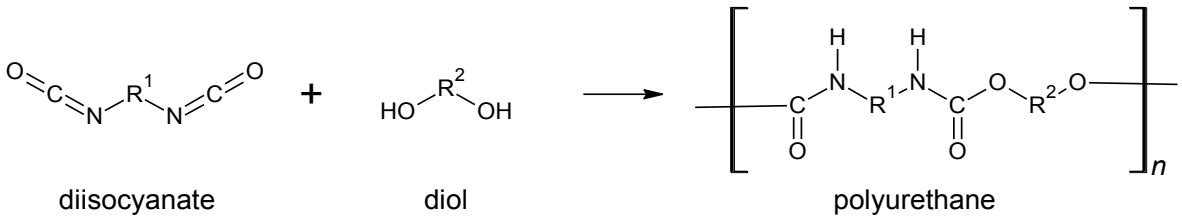


Figure 1.9: Diisocyanate and diol reaction to form polyurethane.

The two most common diisocyanates used are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), illustrated in Figure 1.10. Generally the isomeric mixture of TDI 2,4:2,6 is 80:20.

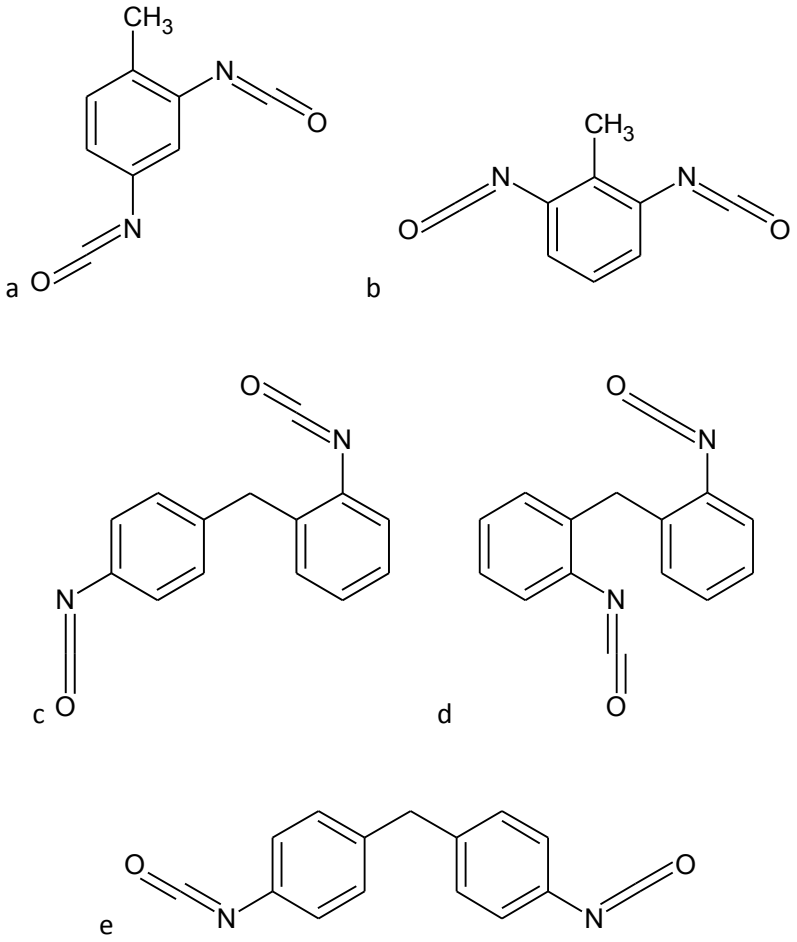


Figure 1.10: a)2,4-TDI, b) 2,6-TDI, c)2,4-MDI, d) 2,2-MDI and e) 4,4-MDI

The alcohols can show greater variation. They have at least two reactive –OH groups and by increasing the active sites the rigidity of the PU can also be increased. Linear PU chains (the general formation of flexible polyurethane) are formed when diols, alcohols with two active –OH groups, undergo reaction with TDI or MDI. When alcohols with three or more active sites, triols or polyols, undergo reaction with TDI or MDI linear PU is formed and cross linking will occur between the adjacent PU chains increasing the rigidity. The process of PU production also includes other components such as catalysts, blowing agents and flame and smoke retardants. Cross linking and chain extension agents can be included to maximise the physical and chemical properties of the PU in order to suit the requirements of the end product. The foam focused on in the practical aspect of the work presented in this thesis was flexible PU. Generally, 95%, of flexible PU uses TDI to form either a polyether or polyester based PU, where the difference is a polyether versus a polyester backbone [56].

1.5.1 Thermal Degradation

Thermal degradation describes the chemical decomposition of materials via the application of heat which causes the degradation of a compound into components. In fire investigation the terms thermal degradation, thermal decomposition and pyrolysis are often used interchangeably, despite slight differences in their respective definitions. Pyrolysis is the thermal degradation of solid fuels and describes the stage without which flaming combustion could not occur. Exceptions to the rule exist and solids that do not experience pyrolysis at all, or as a precursor to the onset of flame, are said to experience a direct transition from solid to gas, called sublimation. While evaporation is the thermal degradation of liquid fuels although in this case there are also exceptions, with some ignitable organic liquid fuels undergoing pyrolysis, rather than evaporation [2, 57-59].

Thermal degradation and pyrolysis have been categorised as occurring at different temperatures, for example the following categories have been described in the literature [57]:

- Thermal Degradation 100 °C – 300 °C;
- Mild Pyrolysis 300 °C – 500 °C;
- Pyrolysis 500 °C – 800 °C; and
- Vigorous Pyrolysis above 800 °C.

For the purposes of this work pyrolysis and thermal degradation will refer to the chemical decomposition of solid material at any temperature, specifically PU foam, as a result of thermal assault.

In a review conducted by Paabo and Levin it was reported that three general pathways for the thermal degradation of polyurethane, in increasing temperature order, were likely [56]:

- Dissociation of the PU to form isocyanate and alcohol;
- A rearrangement to form a primary amine and an alkene; or

- A rearrangement to form a secondary amine.

That mechanism of degradation was further corroborated in the literature [60-61] and an additional step was suggested [60]:

- A transesterification type bi-molecular displacement.

The review also provides a comprehensive list indicating some 120 degradation products detected from oxidative and inert atmospheres [56].

In fire investigation, the term thermal degradation refers to the event that occurs in air meaning in an oxygenated or reduced oxygen environment. Thermal degradation is not a phenomenon specific to fire investigation and the environments can vary depending on the faculty of study. For example, in chemistry materials are pyrolysed or undergo thermal degradation in air, reduced oxygen atmospheres or inert atmospheres, such as nitrogen [58]. The research conducted in this body of work was undertaken in air, or reduced oxygen environments and not in inert atmospheres.

1.5.2 The Detection Temperature of Hydrogen Cyanide Detection

The lowest temperature HCN was detected as PU thermally degraded in air (or reduced oxygen atmospheres) prior to combustion, was determined by conducting a review of the available literature [62-83]. The detection of HCN in inert atmospheres, such as nitrogen, was considered although not regarded as the primary focus of the review. This was due to the work presented in this thesis was based on realistic large scale scenarios, which would be unlikely to occur in inert atmospheres.

From their review Bott et al reported having detected HCN in air at 300 °C utilising Dräger Tubes, infrared and mass spectroscopy [76]. Though Robert and Jones reported the detection of HCN in the range of 200 °C – 400 °C it is unclear in their report, or subsequent citings, where in the temperature range HCN was detected and if it was part of the pyrolysis or combustion products [66]. In much of the literature research in oxygenated and non-oxygenated atmospheres was undertaken and it was largely found that HCN was detected in air at lower temperatures than in inert atmospheres, which lead to the supposition that oxygen had an impact on HCN formation, [56, 77]. Or the individual components used to

form the polymer, including the additives of the PU itself impacted on HCN formation [65]. While the majority of the researchers reported their positive results, others specifically reported not having detected HCN at 220, 300, 320 and 400 °C [65, 84]. For the majority of the research conducted the temperature gradients did not start until 200 °C at the minimum; however there were cases where thermal decomposition was seen from 150 °C although HCN was not included as a compound of interest and the environment was not always air [61, 67-70, 73, 85-91].

It is important to note that a portion of the pyrolysis products formed when PU is degraded thermally are toxic, as discussed in more detail in Section 1.6. In addition the pyrolysis products formed as a result of the thermal degradation of PU, among other materials potentially present in the fuel load of a compartment fire, can ignite thus contributing to the onset of flashover.

1.6 Fire Effluent Toxicants, Toxicity and Toxicology

The dose required to elicit a toxic response from a compound is not uniform; it is specific to the chemical and is dependent on the administration, ability of the toxicant or toxin to reach the site of intoxication and the length of exposure [92]. Toxicants are manmade compounds introduced into the environment, while toxins originate from organisms [93]. This section seeks to provide an introduction to toxicants produced during the combustion and thermal degradation of manmade polymeric material in fires.

It has been suggested that the inhalation of toxic gases present in fire effluent is a more common mode of fatality in fire than thermal injury [83, 94-98]. Jones, McMullen and Dougherty indicate that while HCN is the most toxic gas produced as a result of combustion it is rarely acknowledged as the most significant inhalation hazard [94].

Historically carbon monoxide (CO) has been considered the species responsible for fatalities resultant from asphyxiation in fires. This was substantiated when the available literature on toxicants in fire effluent was reviewed, as CO was a common species of interest. In terms of the toxicity of the effluent tested, CO in the smoke from smouldering, flaming fires or post flashover fires are often the focus, even when the fire has a fuel load that contains nitrogen [95, 99-103]. Hydrogen cyanide (HCN) and other toxicants including: nitrogen or oxygen

containing organic compounds and oxides of nitrogen (NO_x), have steadily gained notoriety since the advent of synthetic nitrogen-containing polymeric materials and their prolific use in the modern world [58]. As discussed in Section 1.5.1 in excess of 120 toxicants have been identified as pyrolysis and combustion productions of PU [56]. Notwithstanding, the use of naturally occurring nitogen containing polymeric material in the home is common and examples include wood and wool [58]. Even so, recent studies involving large scale experimental work focus the toxicity testing on components other than HCN [104]. In this work HCN is focused on and the detection at lower temperatures forms the basis of study for a significant portion of this research conducted in this body of work.

Research that focused purely on the detection or the determination of CO concentration in combustion or pyrolysis products of PU was not conducted prior to the knowledge that HCN was a toxic component of fire effluent, as there are reports of similar vintage that do include HCN in the analysis [105-113]. In addition there are other bodies of research that suggest the likely presence of HCN, though do not include it in their test protocols [114]. The question then is why, considering the potential toxicity and likely presence in fire effluent, has the detection of HCN at lower temperatures not been explored further [72, 96, 108, 115-128]?

The presence of HCN at lower temperatures than previously detected would be of particular interest to occupants, those working to suppress the fire or those involved in the investigation of the fire, as the inhalation of the toxicants can impact on the ability of occupants to self egress, lead to death or impact on those working around the fire scene.

The role of HCN in inhalation injuries from fire victims is recognised by the medical fraternity and more rapid early detection techniques have been developed in a move toward preventing fatalities from inhalation [94, 115]. Australian and International standards and classifications for HCN and CO support Jones et al's recognition of HCN having the higher toxicity of the two [129-133]. A comparison was made between the of humans response having inhaled HCN or CO, in air, which has been presented in Table 1—5.

Table 1—5: Signs and Symptoms of HCN and CO Inhalation at Different Amounts in Air [129-136].

Amount in Air	*HCN Signs and Symptoms (S&S)*	*CO S&S*
10 ppm	8 hrs - Time weighted average (TWA)	
15 ppm	Short term exposure limit (STEL)	
25 ppm	4+ hrs of exposure result in slight symptoms and may lead to chronic poisoning.	
30 ppm		8 hrs – TWA
35 ppm		6 – 8 hrs of exposure result in a slight headache and dizziness.
50 ppm	30 min – 1 hr of exposure causes serious disturbances. Immediate danger to health and life limit	
100 ppm	30 min – 1 hr of exposure causes serious disturbances and could lead to death.	2 – 3 hrs of exposure result in a slight headache.
135 ppm	30 min of exposure death is likely.	
180 ppm	10 min of exposure death is likely.	
200 ppm	Exposure of a few breaths likely to result in death.	2 – 3 hrs of exposure result in a slight headache and loss of judgement.
270 ppm	Immediate death for humans.	
400 ppm	No data found inhalation at these amounts, however the lesser amount would suggest that inhalation at this amount would result in death.	1 – 2 hrs of exposure result in a more pronounced headache.
800 ppm		< 45 mins headache, dizziness, nausea and convulsions occur, < 2 hrs become insensible.
1600 ppm		< 20 mins headache, dizziness, nausea and display tachycardia, < 2 hrs death is likely.
3200 ppm		< 10 mins headache, dizziness and nausea will occur, < 30 mins death is likely.
6400 ppm		< 2 mins headache, dizziness and nausea will occur, < 20 mins death is likely.
12800 ppm		Loss of consciousness will occur in a few breaths, < 3 mins death is likely.

Exposure to HCN can occur via the inhalation, oral, or dermal route; though the general form of exposure in fire scenarios is inhalation and exposure to CO occurs via inhalation [132, 133].

After inhalation HCN enters the bloodstream and is hydrolysed to form the cyanide ion (CN^-). In this form CN^- is rapidly transported around the body's water components providing unrestricted access to the body's tissues. Here CN^- reacts effortlessly with cytochrome oxidase and (or) methaemoglobin to form cytochrome oxidase-cyanide complex and cyanomaethemoglobin, respectively. Fundamentally the cytochrome oxidase-cyanide complex prevents cellular respiration by inhibiting the uptake of O_2 at a cellular level, which leads to cell death. Organs especially affected by cellular respiration interruption are the brain and heart, with symptoms manifesting as bradycardia, cardiac arrhythmia and central nervous system (CNS) depression. Ironically HCN exposure leads to respiratory stimulation, proposed to be a result of the need of chemoreceptor cells for O_2. Hyperventilation occurs which not only involves the intake of additional HCN, but also additional toxicants that may be present. It is generally the respiratory arrest resultant from CNS depression that is fatal [137].

A significant number of casualties and deaths occur yearly that can be attributed to either unintentional or intentional CO inhalation including the inhalation of fire effluent [129-130, 138]. Like HCN, CO can be present in fire effluent as a result of the thermal degradation of polymeric materials or from incomplete combustion [1]. The toxic nature of CO can be attributed in part to its binding capacity with haemoglobin, reported to be in excess of 200 times greater than that of O_2 [130, 138-139]. Historically evidence suggested the biochemical response to CO poisoning was limited to tissue and cell hypoxia, a condition where cells and tissues are deprived of O_2 when CO, instead of O_2, binds to haemoglobin to form carboxyhaemoglobin (COHb) [139]. Recent research indicates a propensity for CO to competitively bind with other haem-containing proteins, such as myoglobin and cytochromes, which indirectly effects cellular respiration, cause arrhythmia and cardiac dysfunction or lead to the breakdown and toxicity of skeletal muscle [139-142]. Exposure to ambient sources of CO, such as inhalation via passive smoking or other air containing CO, can increase the baseline levels of COHb (that occur as a result of cell respiration) to those that would occur from TWA exposure. It is therefore worthwhile to note that baseline amounts of COHb in individuals vary and are not always directly related to smoke inhalation. Recognising CO exposure can be inherently difficult to for the individual or emergency service practitioners to recognise as CO poisoning does not initially display pathognomonic signs and symptoms. The characteristic colouration of the lips and flushed appearance generally only occurs in casualties with a COHb level in excess of 40%, which would occur after inhaling CO

at 1600 ppm for approximately 20 minutes [130, 138]. Regardless of the mechanism, if continued exposure to CO occurs the end result is death.

It has been suggested that there is division within the industry regarding the lethality of HCN. Some fractions tout that, despite evidence to the contrary, CO (in a mixture of HCN and CO) is the sole contributor to inhalation fatalities and that the role of HCN as a toxicant is still unclear [143]. Independently both HCN and CO have been demonstrated to be toxic. There has also been research regarding the synergistic or additive affect, if any, exposure to the combination of both has on the physiological and the psychological response [66, 94, 136-137, 143-160]. Some animal studies have recorded the observation of fatalities from the combination of both chemical species at sub-lethal concentrations; though not from independent exposure [157, 160]. Cohort studies from aviation accident victims reported the cause of death to be asphyxiation from a combination of HCN and CO inhalation. The studies reported both HCN and CO in the blood; although at concentrations below that required for toxicological effects. It should be noted that the results were taken from victims who were alive at the time of the fire [146].

When victims of inhalation at fires show a lethal level of HCN together with a sub-lethal level of CO some research attributes this to the HCN retarding CO uptake [145]; which is unlikely due to difference in the mode of action displayed by HCN and CO in addition to HCN leading to respiratory stimulation, which by default leads to increased uptake of all toxicants in the breathed atmosphere [137, 148, 150]. Studies reported that in acute exposure studies the mortality rate for animals exposed to HCN or a combination of HCN and CO, where the CO concentration was sub-lethal, were not influenced by the presence of CO [148, 150]. A review of the literature conducted by McAllister et al reported incidences where the post-mortem concentration of HCN in blood and tissue had rapidly decreased, or increased during the post-mortem interval [210]. The review recommended that proper collection, storage and rapid analysis (within 24 hours of collection) of the samples should be observed to avoid misleading data regarding HCN concentration being reported [210].

The evidence indicating that the combination of HCN and CO in concentrations that individually would be considered sub-lethal illustrates that the investigation of the lowest temperature HCN can be detected during the progression of a fire is certainly worthwhile.

1.7 Analytical Techniques

In exploring analytical techniques for the detection and analysis of HCN, a number of factors were considered when reviewing the literature in terms of suitability:

- Availability of existing instrumentation;
- Commercially available techniques;
- Capacity for in-field testing to aid emergency responders or other services;
- Portability;
- Practicality;
- Sensitivity of method;
- Ease of use; and
- Cost.

As discussed earlier, HCN intoxication can occur via inhalation, ingestion or dermal routes [132]. Therefore directly analysing biological fluids collected from victims and survivors who had suffered inhalation injuries during fires, or other forms of HCN intoxication such as capital punishment, industrial spills, food intoxication or chemical warfare attacks, would be the ideal way in which to collect samples. In addition, the broad range of potential for intoxication has ensured that the testing of biological fluids is well understood and has been supported with human and animal testing [116-117, 132, 144, 161-164]. Though analysing the matrix used in the published data would be ideal its nature, human or animal biological fluids and or organs, make obtaining these matrices difficult and at times prohibitive due to the regulation surrounding human and animal testing. In some of the data reviewed, the mechanism of analysis was instructive in terms of methods used, which included: chromatography, spectrophotometry, direct gas detection and colorimetric analysis [115-117, 144, 161-162, 165];

Though these specific methods, as used for biological sample analysis, were not considered they highlighted techniques that had the potential for application to this work which warranted further investigation.

Hydrogen Cyanide as a toxin has been noted due to its presence in plants including the cultural staple cassava, almond kernels and the pit of some stone fruits such as peaches, cherries and apricots. The liberation of HCN is not defined by a unique mechanism due to the different starting materials in the plant [2-3]. Although HCN as a toxin is not the focus of this work, it presence in staple food sources has lead to significant research regarding its detection. Therefore the toxicity of HCN as toxin or a toxicant has lead to the development and refinement of many detection methods, which were reviewed for this work.

It was known, from the investigation of the literature to determine the products generated from the thermal degradation of PU, that HCN would not be the only gas present in the effluent produced during the progression of the large scale experiments. The review also indicated that HCN could be detected during the thermal degradation of PU using techniques, including: Thermogravimetric Analysis (TGA), Pyrolysis Gas-Chromatography Mass Spectrometry (Py-GC-MS) and Matrix-Assisted Laser Desorption Ionization (MALDI)-MS. However the detection of HCN was not reported at temperatures below 200 °C [61, 63-64, 66-70, 72-73, 83, 85-91, 166]. Whether this was a question of instrument sensitivity, sample size or the absence of HCN below 200 °C was moot, as access to portable version of the instruments described was not available.

An additional technique that proved effective in the detection of HCN was direct gas analysis using Fourier Transform Infrared (FTIR) spectroscopy either from known HCN samples, simulated room fires or the combustion products of flexible PU [64, 119-120, 167]. The issue again was access to portable FTIR instrumentation and a method of capturing the fire effluent had not been identified that would allow for transportation back to the laboratory for introduction into a gas cell and subsequent testing using the available bench top FTIR spectroscopy.

The knowledge that different components are in fire effluent suggested that further investigation of additional techniques utilised by the separation sciences would be of benefit. Some success had been reported for the determination of HCN in different matrices utilising head space (HS) GC, capillary GC and GC coupled with mass spectrometry (GC-MS) using

columns with a suitable affinity for HCN [116, 118, 168-174]. Additional separation techniques were reviewed that had proved successful in the detection of HCN including ion chromatography (IC) and high performance liquid chromatography (HPLC) [173, 175]. However there were challenges associated with obtaining a sample that was suitable for analysis by these techniques. For example, access to (and in some cases the existence of) instruments that could be taken to the field for onsite sampling, or analysis, utilising these techniques at the time of the experimental work were not available.

It was determined that the techniques indicated above could be useful for the detection of HCN in fire effluent. The challenge was sampling the effluent and introducing it to the instrument. Initially the collection of fire effluent on site for later analysis using commercially available evacuated containers was considered. The technique was shown to be effective in the past [176] although it had only been attempted post suppression of fires in one area of the fire. While it was certainly an effective method of collection, the design of the experimental work required a significant amount of containers. Although not the only mitigating factor, the cost per unit made this avenue of collection prohibitive.

In the vein of directly collecting gas during the development of fire a less financially prohibitive option was considered. Tedlar bags, a commercially available container suitable for the collection of fire effluent were available. The primary factor preventing the Tedlar bags progressing past the stage of consideration was the decreased capacity for bags to contain the sample over 48 hours. The particular limitation would have impacted on the reasonable distance between the site and the laboratory where analysis was to be undertaken, to allow for analysis to occur between sample collection and before the degradation of the bags. The distance of the burn sites from the laboratory made this means of sample collection unsuitable.

The drawback of not collecting raw samples of fire effluent at different stages of the fire development indicated that the determination of a holistic gas profile at different stages in a large scale fire scenario was unlikely. After investigation it was evident that directly collecting gas, to safely transport it back to UTS for later analysis, was not a viable option.

For the large scale burns that were to be conducted internationally, commercially available techniques that allowed for immediate analysis of the fire effluent, were explored. Cost effectiveness, small dimensions and lightweight were characteristics were also highly sought.

Having noted the use of Dräger products to determine the HCN content in the blood samples of fire victims in a mass fatality incident [161] further investigation of the products available from Dräger was undertaken. A Dräger accuro^{R} 2000 pump was available for use and it was determined that that species specific Dräger-tubes could successfully used to analyse the fire effluent post suppression of the large scale burns. The system could be individualised by purchasing compound specific detection tubes and had a relatively broad detection range with acceptable response range. In addition the system was simple to use, easily transportable back to Australia and was reasonably cost effective. The challenge associated with this type of testing lay in the hardware itself. Due to the requirement for the instrument to be manually manipulated sampling the atmosphere during the progression of the fire, prior to suppression, would have put the operator in considerable danger and was not considered as an option.

Investigation into the means of sampling the effluent from fire during the progression of the fire from heating to post suppression continued. It was clear that collecting gas samples for later analysis was difficult, considering budgetary requirement and the available apparatus. As a result other mediums, or means, to trap the gas became the focus of further investigation.

Alternatives to direct atmospheric analysis were also explored. The presence of CN^- in water as an environmental pollutant from industrial or agricultural run-off prompted significant work to develop a method to detect CN^- in water. Flow injection analysis (FIA) using spectrofluorimetry, spectrophotometry and flame atomic absorption spectrometry was shown to have been successful in the detection of aqueous CN^- [177-179]. Although the sensitivity and reproducibility of the results reported were attractive, the challenge lay with the analysis being aqueous solution centric. Trapping gaseous HCN and more importantly keeping it contained in a pH neutral medium was impossible. This resulted in the method being recognised as unsuitable for this kind of work.

Although the FIA technique was not suitable the investigation of the method led to the supposition that alternative, more suitable, trapping mediums would be a suitable way in which to collect samples of the fire effluent for later analysis.

It was found that some work had been done establishing methods to impregnate, or coat, substrates with compounds that elicit a colorimetric response when exposed to CN^- or HCN

[84, 180-185]. Some techniques were discounted initially as little information regarding the reagent used was provided, or the substrate was for use in aqueous solution [84, 181].

Embedded piezoresistive microcantilevers (EPM) address several of the desired criteria for on-site HCN detection; however, some drawbacks have been noted [180]. For example, the EPMs were coated by hand which were reported to lead to a variation in response time of up to 20% and the response would decrease after each exposure. In addition, the sensitivity was not reported to have been tested below 150 ppm, indicating that sensitivity may have been an issue.

The picrate method described by Bradbury et al and Bradbury and Haque for the determination of the cyanogenic potential of cassava flour, initially appeared promising [184-185]. Substrates embedded with picrate solution turned from yellow to brown on exposure to HCN. The degree and intensity of the colour change was proportional to HCN concentration, which was determined by comparison with pre exposed picrate paper to known concentrations of HCN. This method was highly suited for the use it was developed for, although the suitability for this work was questioned. The colorimetric response of the papers was shown to increase with temperature over the range 19 °C – 37 °C. It was likely that the temperature of fire effluent and the ambient temperature the papers would be used in (during the summer months) would exceed or be similar to the range tested. The variation in the response proportional to temperature suggested this method was not suitable for the purposes of the work to be conducted.

The formation of Prussian Blue (*Iron(II,III) hexacyanoferrate(II,III)*) a vivid blue complex occurs when ferrous sulfate is exposed to HCN is well established as a detection method specific to HCN; though it is suggested that the method can lack sensitivity [182, 186]. Fulton and Van Dyke indicate a sensitivity range of 0.05 – 0.3 mg [186]. The method proposed by Gettler and Goldbaum sought to address the issue of sensitivity and reported a sensitivity range of 0.0001 – 0.02 mg; although that was dependant on the width of the orifice of the flange used to house the paper [182]. Their method explained the development of a reagent paper sensitive to HCN. The substrate was saturated with a solution of ferrous sulphate and NaOH then air dried. After exposure to HCN the substrate was washed in a hydrochloric acid solution. Like the method proposed by Bradbury et al the resultant colorimetric change was compared with a standard colour chart [182, 184].

Nakano et al reported a method that provided good selectivity and response when papers were saturated with a mixture of tetrabase (*4,4'bis(dimethylamino)diphenylmethane*), copper (II) acetate, butylhydroxy toluene, glycerine and methanol then exposed to HCN. The response could be detected with the naked eye, although the analysis was done by measuring the reflected light of wavelength 555nm. The detection limit was found to be 0.2 ppm for gaseous HCN [183].

The selectivity and sensitivity of the methods reported by Gettler and Goldbaum and Nakano et al, in addition to the ease of in-field use and cost effectiveness prompted further investigation into these methods which are discussed further in Chapter 6. Though the use of paper infused with reagents proved to be unsuitable for this work; the process of trapping and subsequently detecting HCN via the formation of a complex was becoming increasingly attractive.

In work that had been conducted by Fung et al a method involving the detection of HCN via picrate-resorcinol solution was optimised [187]. Although excellent results were reported in the study the determination of concentration via colour comparison with known samples was thought to not be ideal. A significant drawback of the method was the need to transport picric acid which represents a significant risk, consequently that method was rejected for use in this work. Confirmatory HCN analysis conducted by Fung et al using nuclear magnetic resonance (NMR) spectroscopy was successful [187]. However, the method was considered to be inappropriate for this work as it was anticipated that HCN levels would be outside the detection limits of NMR spectroscopy.

Methods utilising sodium picrate solutions were also considered [121, 188]. In addition to the reservation regarding the transportation of picric acid, other drawbacks presented themselves in both works. The field work reported by Reilly involved access to, or the construction of, a portable Ultraviolet-visible (UV-Vis) spectroscopy analyser, in which neither of the options were easily achieved [121]. The method proposed by Alonso-Amelot and Oliveros involved a two-step trapping system, the first trap is shock sensitive 2,4-dinitrophenylhydrazine (DNP) and the second a solution of sodium picrate [188]. The significant risk involved with transporting DNP suggested that this method was not suitable for the work to be conducted.

The use of the pyridine-barbituric acid method (König reaction) to detect HCN using UV-Vis spectroscopy was described by Kenneth et al and Afkhami et al as being sensitive and selective [189-190]. However, Gümüs et al questioned the selectivity of the method indicating that thiocyanate (SCN^-) ion provided a false positive in the reaction [191]. Baum et al indicated that SCN^- occurs even having used a modified König reaction [192]. The issue of the simultaneous detection of HCN and thiocyanate was effectively dealt with by Afkhami et al who applied a partial least squares regression model based on the difference in the rate of reaction of chloramines-T with CN^- and SCN^-, then the resulting CN^- product reacted with pyridine and barbituric acid. Gümüs et al approached the issue slightly differently opting for separation via a melamine-fomaldehyde resin. Though both methods were successful in terms of returning a positive result at the expected absorption, 578 – 580 nm, the multi step process was considered too laborious to perform in-field and particularly difficult without access to a portable spectrometer.

The determination of CN^- using UV-Vis spectroscopy appeared to fulfil a significant portion of the desired criteria defined for the work to be performed at the large scale experiments. The method was reported as being specific for CN^- via the formation of the stable complex tetracyanonickelate (II) on exposure to the ammoniacal solution without an intermediate species, simplistic to replicate in addition to being cost effective [193-199]. Most significantly this method suggested that direct sampling of the fire effluent into the ammoniacal solution to form the stable complex was possible. The stability would allow for transportation back to the laboratory for analysis using UV-Vis spectroscopy. However, during the preliminary investigation of this method it was determined that a nickel hydroxide $Ni(OH)_2$ precipitate would form if the nickel (Ni^{2+}) ion concentration of the ammoniacal solution was too great. The situation of a $Ni(OH)_2$ precipitate could be avoided by adjusting the Ni^{2+}. This put into question to stability of the starting solution. In addition, the methods described did not allow for in-field analysis using alternative detection techniques, such as ISE. Consequently, the use of the complexation method described to determine the HCN concentration was found deficient in some areas. Though, the positive aspects prompted investigation into alternative methods that would lead to the formation of the tetracyanonickelate (II) complex while allowing for in-field analysis.

Despite the shortcomings identified in the method proposed by Scoggins, it remained the most attractive method in terms of specificity and ease of preparation [193]. It was postulated that an alternative pathway to form the tetracyanonickelate (II) complex was

possible. It was also considered that substituting a stable basic solution, such as potassium hydroxide (KOH) in place of the ammoniacal solution to act as a trapping medium for any acid fractions in the fire effluent specifically HCN, would be suitable as an initial step.

Methods were investigated that utilised a hydroxide (OH^-) solution for the collection as pathway as a pathway to tetracyanonickelate(II) for the complexation of HCN [63, 200].

The titration method described by Suzuki et al involved an improved method of titration from the nickel titration of CN^- ions with murexide (*Ammonium 2,6-dioxo-5-[(2,4,6-trioxo-5-hexahydropyrimidinylidene)amino]-3H-pyrimidin-4-olate*) used as the indicator. Though the method itself was protracted and open to error during the process the authors reported good results for the determination of the equivalence point [200]. The attractive part of the method was the initial dissolution of KCN in OH^- at a pH that kept the CN^- in solution to allow for the tetracyanonickelate (II) complex to form on addition of Ni^{2+} in the presence of ammonium.

The method proposed by Michal went the further to support the postulation that HCN could be trapped in OH^- solution by using that as the procedure to trap the effluent from heating various polymeric materials, including PU [63]. In addition Michal showed the formation of tetracyanonickelate (II) via an alternative pathway by introducing ammonium and nickel salt to the experimentally derived sample solution, instead of having it as part of the original trap. In this way Michal illustrated that the tetracyanonickelate (II) complex could be formed without needing to use a potentially unstable ammoniacal solution initially.

The method proposed by Michal was modified and used for the detection of HCN in fire effluent described in Chapters 6 and 7 of this work.

The use of OH^- solution as a trap allowed for UV-Vis spectroscopy analysis to occur though transportation of the sample back to the laboratory was necessary. However as the fire effluent was being trapped in OH^- solution it allowed for the use of instrumentation such as ion selective electrodes (ISE), that were useful for on-site detection, could be utilised.

The review of the literature discussed above, in addition to further reviews [201-202] illustrated that a number of analysis methods were available when the starting sample was the trapped fire effluent in an OH^- solution.

1.8 Rationale and Structure of Thesis

The author's initial investigations in this area (submitted as her Honours thesis) were undertaken in response to a request from Fire and Rescue NSW for research in the area of HCN emissions from polyurethane. The current work represents her own expanded-scope investigation into the area of detection of HCN emissions at low temperatures, and time until flashover (proportional to the amount of PU in the cell or structure).

A review of the available literature indicates that previous research has focused primarily on the capacity for a cell or structure to reach flashover, based on - but not limited to - criteria such as volume and fuel load. The time until flashover proportional to the fuel load (specifically PU) has not been investigated prior to this study (or at least, no conclusions have been reached in published work.)

The research produced in this work seeks to add to the available scientific knowledge regarding 1) time until flashover and 2) the lowest temperature at which HCN can be detected in effluent produced from the degradation of polymeric materials. Investigators, in addition to occupants and members of emergency services responding to incidents, will benefit from this information when processing scene data or determining the potential for self-egress.

Specifically, the information presented could impact decision-making in the following areas:

- emergency services' approach to firefighting, particularly in risk management/assessment
- advice to occupants regarding formulation of self-egress plans
- determination of cause of death: research presented here may offer evidence to challenge current thinking regarding the role of carbon monoxide alone as the principle factor in fire fatalities where the victim has not been impinged upon by flame
- potentially, safety standards in the manufacture of furniture containing PU.

1.8.1 Aims

- To identify the challenges associated with determining the time until flashover in large scale scenarios when there is variation in the experimental parameters adopted (Chapter 2 and 3);

- To determine the time until flashover in large scale test burns proportional to the amount of PU in the cell (Chapter 4);

- To analyse the post suppression atmosphere of large scale test burns, with a PU fuel load, for the presence of HCN and CO using existing (and available) apparatus (Chapter 5);

- To analyse the pre-flame and post suppression atmosphere of large scale test burns, with a PU fuel load, for the presence of HCN, using the existing method and suggesting a novel method during the natural progression of a fire(Chapter 6); and

- To determine the lowest temperature at which HCN can be reliably detected when heating PU foam in a laboratory setting (Chapter 7).

Chapter 8 offers conclusions and suggests the course of possible future research.

Chapter 2: Time Until Flashover:

Montrose, MN

Chapter 2: Time Until Flashover: Montrose, MN

2.1 Introduction

The focus of this section and the subsequent chapters, of this research was to determine if a relationship exists between the amount of PU present in a cell or structure and the time taken to reach flashover.

Given the limitations of previous research discussed in Chapter 1, this research sought to take a more holistic and realistic approach to the investigation of time until flashover. The focus of this section of the research was to determine if a relationship existed between the amount of PU present in a cell or structure and the time taken to reach flashover. To achieve this, the fuel load remained consistent while other experimental parameters were varied.

The objective of conducting these test burns was to establish if a more holistic experimental model could be designed, in part, to determine if the time until flashover based on the amount of PU in a cell or structure was possible. The test burns at Montrose, MN were performed to gather preliminary data regarding the time until flashover in addition to identifying limitations associated with performing test burns of this nature. A number of challenges associated with the experimental model were identified during the test burns at Montrose, MN.

As discussed in Section 1.4 the term flashover has appeared in the literature associated with fire for the better part of seven decades. Not surprisingly the definition of flashover has evolved as more research was gathered about the phenomenon.

Flashover definitions were considered and the following was adopted for the purposes of this research:

A transition phase in the development of a compartment fire in which surfaces exposed to thermal radiation reach ignition temperature more or less simultaneously and fire spreads rapidly though the space, resulting in full room involvement of total involvement of the compartment of enclosed space [3].

The ambiguity in the literature regarding the full room involvement, full fire involvement and total involvement was also considered and the following was adopted:

At the fully developed stage, flames extend out through the opening and all the combustible material in the enclosure is involved in the fire [63].

During the developmental stage of this research, it was identified that the existing facilities at UTS did not support small or large scale test burns; due in part to the hazards involved with conducting this kind of research. Sourcing appropriate sites in Australia was difficult; a contributing factor was council and state regulations that restricted, or completely banned, the generation of fire effluent the potentially hazardous materials generated from conducting burns of any sort. This prompted an investigation of alternative international sites which could accommodate the proposed test burns including any toxic products generated.

The USAs Internal Revenue Service (IRS) oversees the laws associated with taxation in the US. At the time the experimental fires were conducted it was relatively easy, according to section 170 of the Internal Revenue Code (The Code), for building owners to donate their buildings to a charitable or not for profit organisation. The donation was recognised as such and the value of the building, in the form of a fair market value (FMV), could be claimed as a charity donation deduction.

An example of this is the donation of buildings that have been earmarked for demolition to volunteer fire departments to practice or refine their fire suppression skills. This means large scale test burns become a cost effective exercise if buildings can be acquired in this manner. The existence of that particular tax clause lead directly to the acquisition of sites in the US that could accommodate large scale burns. The initial sites were located in Montrose, MN, were preliminary testing to determine the parameters of the method was undertaken.

Historically furniture filler, or stuffing, of furniture, soft furnishings and bedding commonly consisted of natural fibres such as animal hair or wool or natural latex. Synthetic polymers have since taken over as arguably the most widely utilised medium to upholster furniture [203] particularly PU [64, 66, 70, 168]. Therefore due to its prevalence in modern furnishings PU was the material of focus in this study.

2.2 Site Description

The opportunity arose to perform test burns in conjunction with the Montrose, MN Fire Department (MFD) during a fire suppression training exercise using donated structures. Initially two sites were available at Montrose, MN. The structural stability regarding one of the two properties was questioned and it was concluded that the potential hazard and associated risk involved in utilising that site was too great. Therefore only one of the two sites was used to conduct the experiments.

The site at 4802 Crowfoot Avenue Montrose, MN was a domestic dwelling that consisted of two above ground stories plus a basement. The structure donated, illustrated in below in Figure 2.1, was a three story domestic dwelling that had been scheduled for demolition.

Figure 2.1: The domestic dwelling at 4802 Crowfoot Avenue Montrose, MN.

As the domestic dwelling was scheduled for demolition, there was no furniture remaining and the only remaining internal fixtures were the floor coverings and some doors. However the exterior doors and windows were still in place at the commencement of the test burns.

Although the structure had three levels the rooms on the second story and the basement area of the dwelling were not utilised as each only had one egress point. The risk associated

with suppressing a fire with only one egress point could not be mitigated in this case. In addition, had the volunteer fire fighters been unable to maintain control of the fire in the basement or in the upper story it may have become difficult to salvage the remainder of the building and continue the test burns. As a result, access to the second floor and basement was blocked by attaching ply board over the stairwell entry points. Blocking the stairwell entries also reduced the ventilation introduced by having those points uncovered. Figure 2.2 demonstrates on a schematic of the floor plan the points where access to the second story and the basement were covered over.

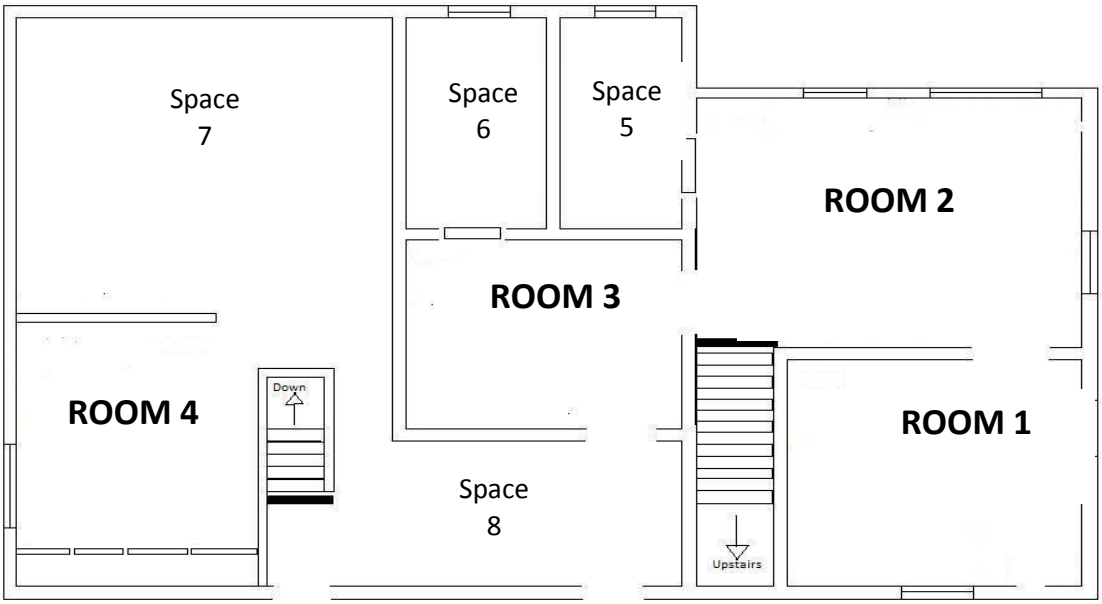


Figure 2.2: Ground floor schematic of 4802 Crowfoot Avenue Montrose, MN. Not drawn to scale.

The structure at Montrose, MN did not have rooms that were identical in size. On the ground floor of the domestic dwelling eight separate spaces had the potential to be set up to use as controlled individual test burn sites. However, only four of the spaces were utilised. The remaining spaces were either too small to accommodate the furniture used for the burns, significantly larger than the other spaces, or in the case of the eighth space the only egress point from the structure.

The room dimensions, the ventilation areas and the room coverings have been provided in Table 2—1.

Table 2—1: Room Dimensions, Ventilation Areas and the Wall and Floor Coverings of the Rooms Used in the Burns Conducted at Montrose, MN.

Features	Room 1	Room 2	Room 3	Room 4
Room Height (mm)	2344	2340	2351	2415
Room Width (mm)	2722	3568	3377	3639
Room Length (mm)	3715	4612	4333	3496
Room Volume (m^3)	23.70	38.51	33.52	30.72
Floor Covering	Carpet	Partial Carpet	Linoleum	Carpet
Wall Covering (over plaster board)	Wood Panelling	Wood Panelling	Wallpaper/Paint	Paint
Ceiling Covering (over plaster board)	Paint	Paint	Paint	Paint
Ventilation Opening Area (m^2)	1.167	1.182	1.266	1.269

The temperature range during the test burns occurred ranged from 20 – 24 °C, there was no rain at the site and little wind during the time of the test burns.

2.3 Sample Description

The furniture and soft furnishing samples used in the test burns were purchased from *Hotel Furniture Liquidators, Inc (1800 University Ave West, Saint Paul, MN)*. It was a consideration that the furniture be the same, or similar, for the test burns. As a result the furniture items that were purchased for this series of testing were of the same design, had been sourced from the same hotel and were of similar age. Although the source of the furniture was known, the manufacturer of the furniture or the PU foam was not known at the time of the test burns.

Four two seater sofa beds were purchased, one for each of the rooms used. The mattress for the sofa bed was included in the purchase and was left in situ for the test burns. Figure 2.3 illustrates an exemplar of the sofa beds with the dimensions indicated. An example of where foam was harvested from on the sofa bed has been illustrated in Figure 2.6.

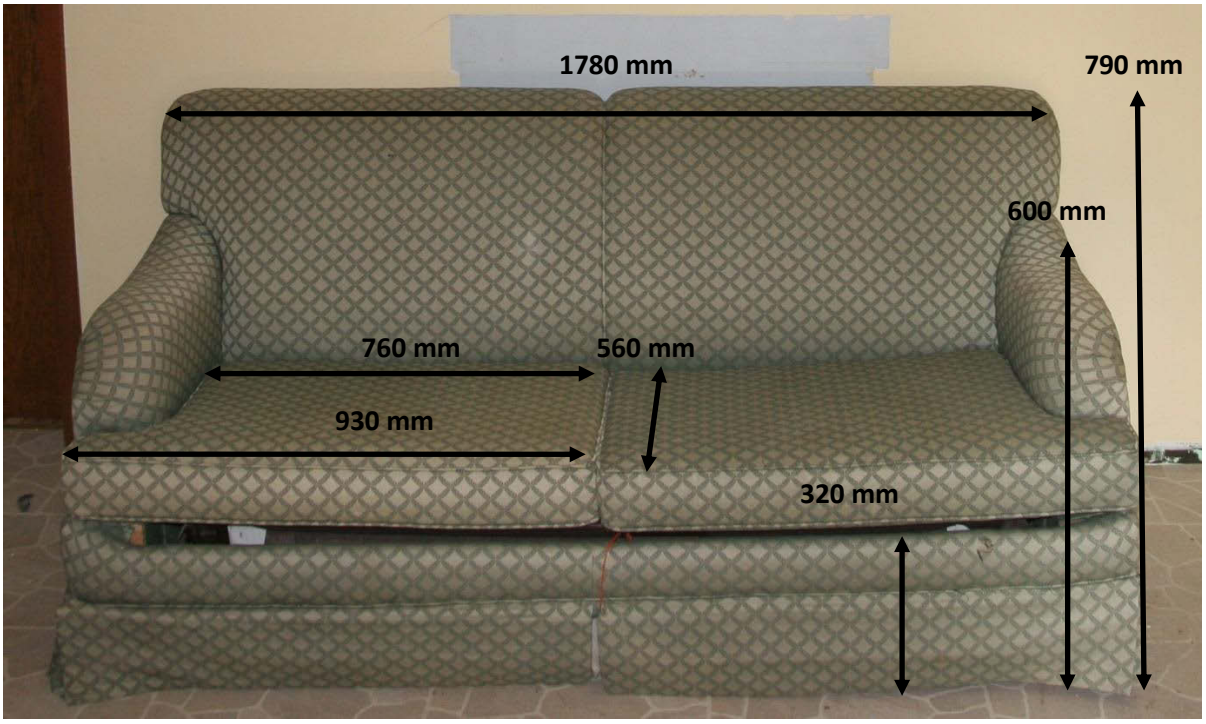


Figure 2.3: Example of sofa bed with dimensions included.

In addition four king size box spring mattresses and eight single bases were purchased and one complete set (consisting of one king size box spring mattress and two single bases) was placed in each of the rooms. The box spring mattress was placed on two single bases to represent a king size bed and base set. Figure 2.4 illustrates the bed set up and the dimensions of the mattress and the base. Although the orientation of the bases and accompanying mattress depicted in Figure 2.4 are not in the correct configuration the image was set in this fashion to illustrate the dimensions of the items in a more succinct fashion.

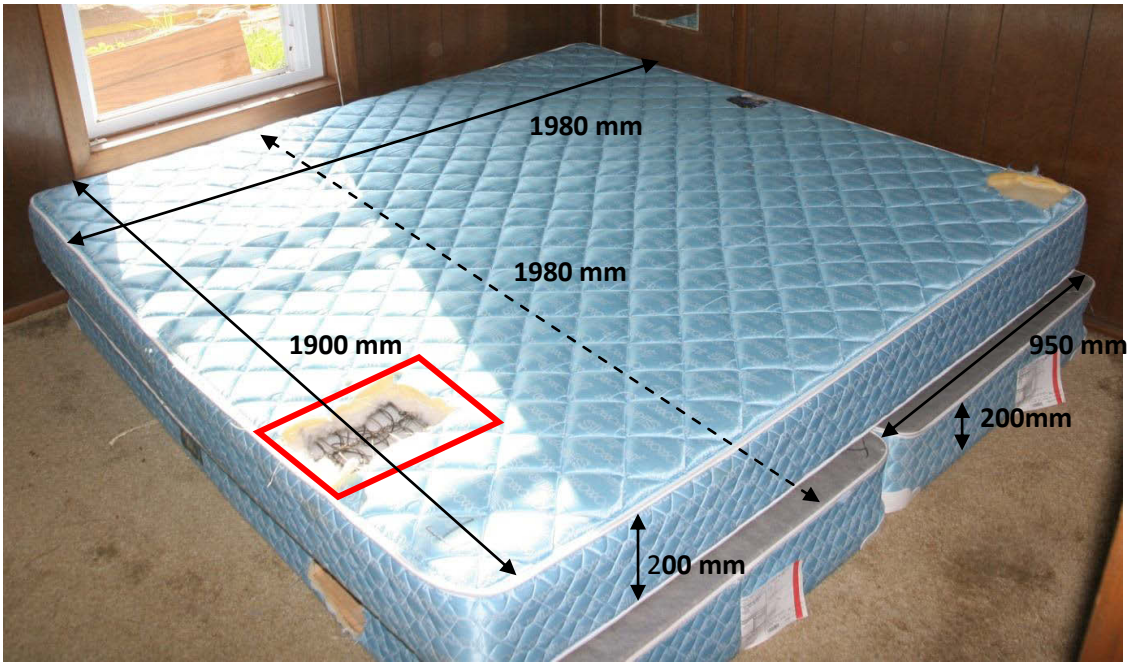


Figure 2.4: ***Example of the king mattress with two single bases with dimensions included. The red outline indicating the area a sample was collected from.***

Four quilts of the same design were purchased for the test burns. The structure of the quilt was a cloth (most likely a poly cotton blend, though a label was not present to confirm) covered Dacron® which was 2700 mm long and 2930 mm wide. Each of the beds was covered with one for the quilts prior to commencement of the test burn.

Purchasing new furniture for each full scale test burn was not within the budgetary constraints of the study and the furniture used in these studies was acquired second hand. As a result, it was not possible to identify the type of filler as this would have required removal of upholstery before purchase. Older furniture predating the widespread use of PU was avoiding in favour of more modern furniture (that were more likely to contain PU), for the large scale burns.

2.4 Method

The test burns at Montrose, MN were conducted as preliminary data gathering experiments in a large scale format, with two specific purposes:

1) to assess the effect on the time until flashover, if the fuel package remained consistent but other parameters, like the following, were varied:

- ventilation area;
- room size;
- fuel package (furniture) placement; and
- point of ignition.

2) to identify as many challenges as possible with conducting large scale events in order to address them for the next series of test burns.

Prior to placement of the furniture items in each room, a section of the foam (approximately $150 \times 200 \times 100$ mm) was collected from each of the items. An example of the size has been highlighted in Figure 2.4 with the use of a red outline and in Figure 2.6 with a blue outline. The section was subjected to preliminary testing to determine the nature of the foam. The preliminary testing comprised of a visual and textural examination. Field testing for the preliminary determination of PU was important to conduct to prevent continuing the experimental work with a material not likely to be PU. The sections of foam were taken back to Australia for additional analysis.

A sofa bed and king size box spring ensemble was then placed in each of the rooms being used for the experiments. The location of the furniture within the rooms has been illustrated in Figure 2.5 and Figure 2.6.

Since the structure at Montrose, MN was a domestic dwelling and not a purpose built test burn facility, consideration was paid to the potential for flame to spread between the rooms being used in the experiments.

During the experimental burns the ambient temperature and the rain fall at the site was recorded.

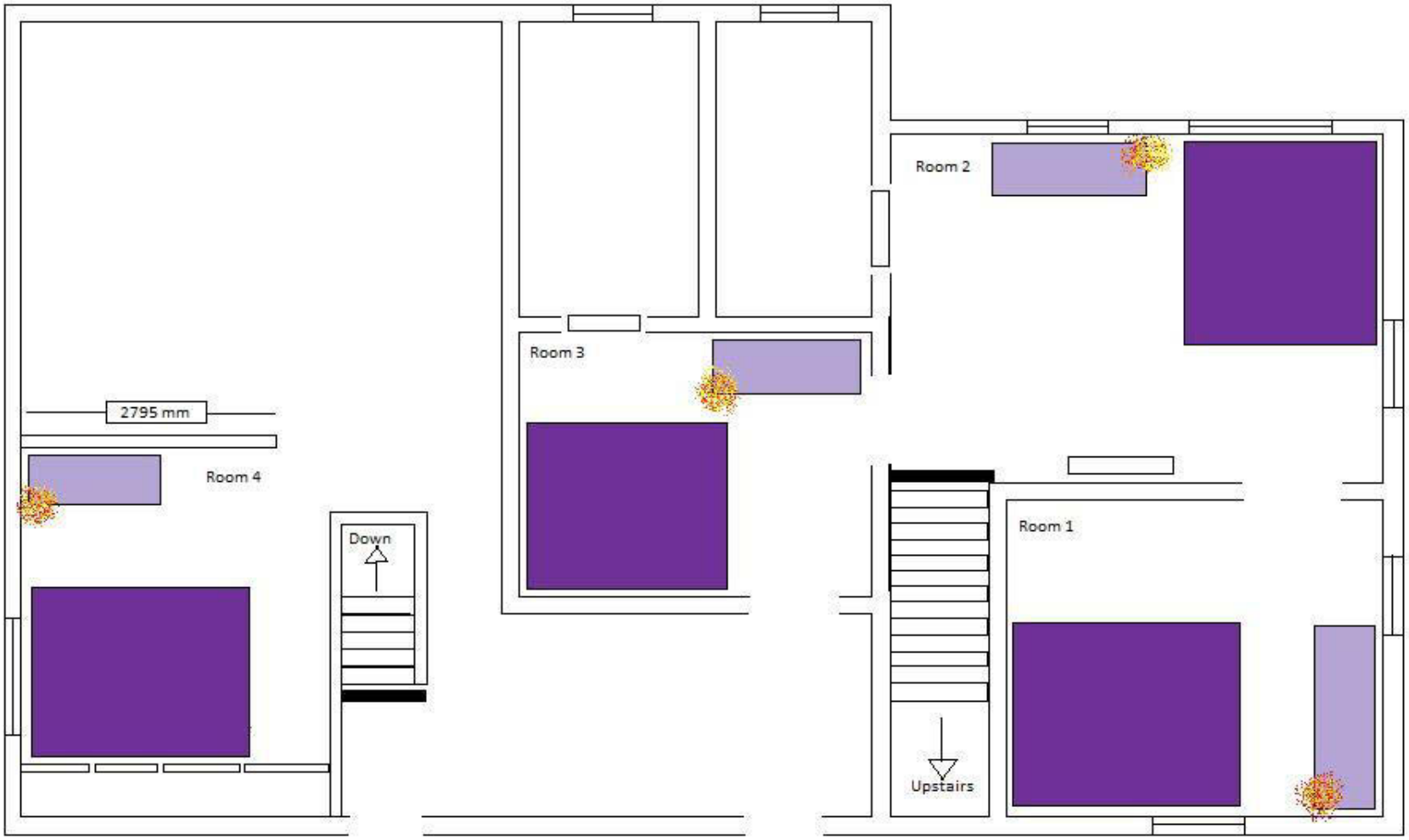


Figure 2.5: ***Schematic indicating the location of the bed and the couch in each room. The point of ignition is also indicated by*** .

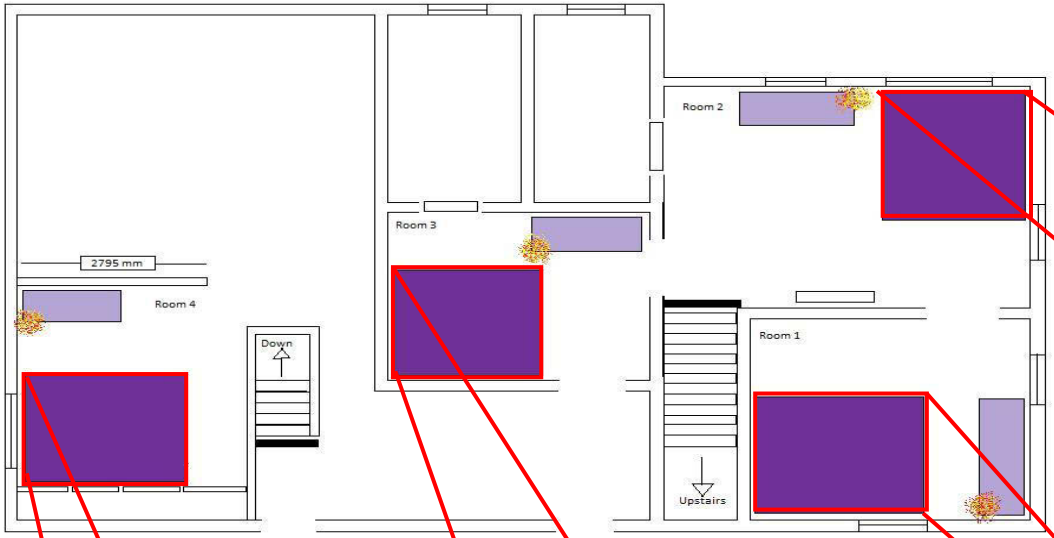


Figure 2.6: *Images indicating the location of the bed and the couch in each room on comparison with the schematic. The blue outline indicates the area a sample was collected from to determine if it was PU.*

As illustrated in Figure 2.5 and Figure 2.6, Room 1 was adjacent to Room 2 which was in turn adjacent to Room 3. For the test burn in Room 1 the top half of the doorway between Room 1 and 2 was covered to curb the potential for flame spread into Room 2 to occur during the experiment. When the test burn in Room 2 was set up the doorway separating Rooms 1 and 2 was completely closed off and a partial cover was placed over the top half of the doorway between Rooms 2 and 3. After the test burn in Room 2 was complete the door way separating Room 2 and 3 was completely closed off. This was done to reduce flame spread and maintain the cell sizes. The doorway to Room 4 was partially covered for the test burn to prevent flame spread to the rest of the house. Despite this being the last test burn, the threat of flame spread to another cell was still considered as the safe egress of the suppression team was important if the fire could not be controlled.

The area of ignition in each room has been indicated in Figure 2.5. Ignition was achieved by applying a flame, from a propane gas hand-held blow torch, directly to the surface of the couch. Prior to commencing the experiments it was decided that the point of ignition would occur on the horizontal surface at the sofa bed at the area closest to the bed. Due to the position of the sofa bed in proximity to the bed, there was variation regarding which side of the sofa bed the flame was applied to.

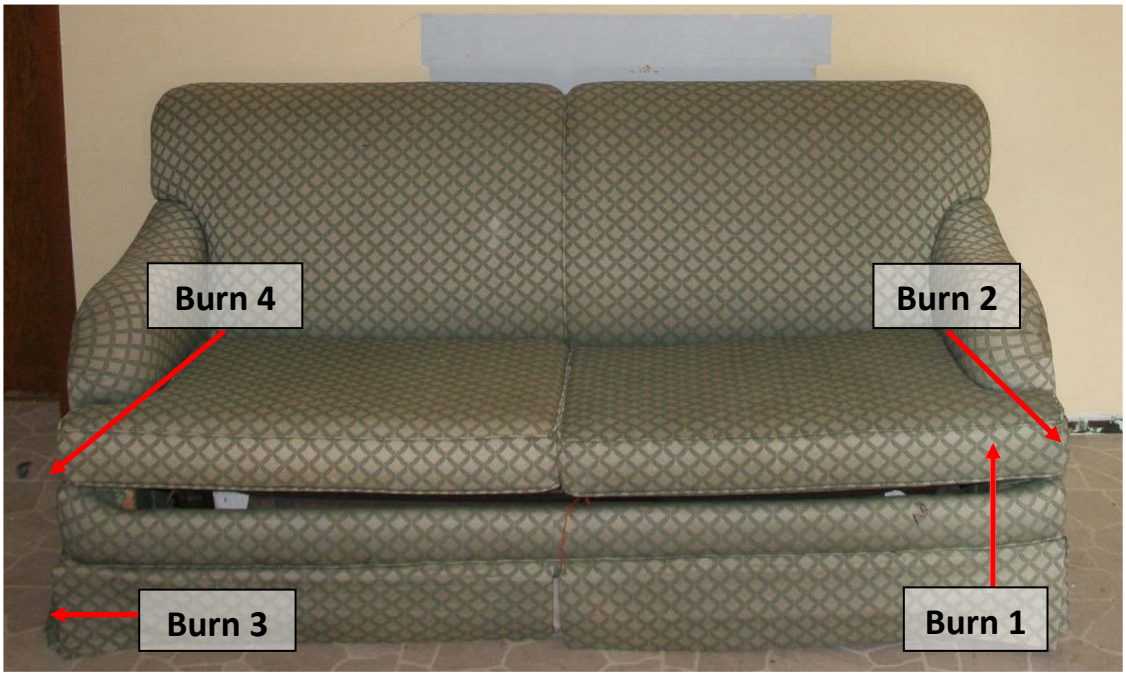


Figure 2.7: Exemplar of sofa bed used in each of the experimental burns with the ignition points indicated.

Burns 1 and 3 were ignited at the front of the sofa bed on the cushion or valance respectively. Burns 2 and 4 were ignited on the valance approximately halfway between the front and back of the couch. The location of the point of ignition for each burn has been illustrated in Figure 2.7.

Determining if a flashover event could be achieved with the parameters used was part of the desired outcome for the experiment; therefore suppressing the fire prior to flashover occurring was not desirable. The fire was allowed to progress until flashover (according to the definition outlined in Section 2.1) then suppression commenced. To avoid pre-wetting the adjacent room the volunteer fire servicemen refrained from using excess water during suppression.

Timing was crucial in this series of test burns as there was significant potential for the fire to spread throughout the house if unchecked, thus destroying the remaining cells. Therefore, as soon as flashover was deemed to have occurred it was agreed between parties that steps would be initiated to suppress the fire. Ideally, the fire progression would be monitored by an observer; however the presence of an observer may have blocked the egress and compromised the safety of the suppression crew. Therefore it was decided that only the suppression crew would be inside the house during the progression and subsequent suppression of the fire. Those parameters in conjunction with the suppression trainer's experience would dictate the occurrence of a flashover event followed by the onset of suppression.

The definitions used to define flashover for this work were discussed with the suppression team trainer who added his knowledge and experience to determine when the flashover event had occurred so the fire could be suppressed. The time until flashover, to the nearest minute, was noted and recorded. As each test burn was recorded digitally a more precise time until flashover was achieved by analysing the video recordings and using the embedded time stamp. It was determined that time zero (T_0) would be defined as when the ignition source was removed from the surface of the couch and the flame was self sustaining.

The sections of foam were taken back to Sydney, Australia and investigated to determine if any differences between the foam could be discerned.

Small subsections of the foam were photographed using a Canon PowerShot SX260 HS Canon, the F-stop was f/3.5, the exposure time was 1/60 sec, the ISO speed was ISO-100,the focal length was 4 mm and the max aperture was 3.625.

Environmental Scanning Electron Microscopy (ESEM) was used to examine visually the foam samples collected from the furniture used in the experiments at Montrose, MN. The ESEM images were collected at a range of magnifications using the low-vacuum mode of an FEI XL30 Environmental Scanning Electron Microscope (ESEM). Low-vacuum mode was used in order to observe the samples in their natural state without the need for specimen coating. The chamber pressure used was 0.8 - 0.9 Torr and the beam accelerating voltage was 20 kV.

Attenuated total reflectance coupled with Fourier transform infrared (ATR-FTIR) spectroscopy was used to determine the polymer type and note any detectable differences between the foam samples. A Digilab FTS 7000 IR spectrophotometer using UMA 600 with an ATR germanium crystal was used to record the spectra. The spectra were collected in absorbance with a resolution of 8 cm^{-1} for 64 scans. Two spectra were collected from each piece of foam that was gathered from the furniture.

2.5 Results and Discussion

2.5.1 Visual Analysis

Generally flexible PU is used as the foam component in modern soft furnishings. It was impossible to destroy the furniture prior to purchasing it to determine if the foam was PU. However, as discussed in the introduction, it would be likely that in more modern furnishings the soft foam component would be flexible PU due to its extensive use. After purchasing the foam was checked, via preliminary testing, to determine if the padding used was flexible PU. Each section of foam was investigated initially in the field via visual and textual examination. The sections of foam were then analysed using ESEM and ATR-FTIR spectroscopy.

Visually the items of furniture appeared to be the same. The majority of the foam was the same, although the sofa bed mattresses in Room 4 had three layers instead of two. The top layer of the foam used in each of the bed mattresses has been presented in Figure 2.8.

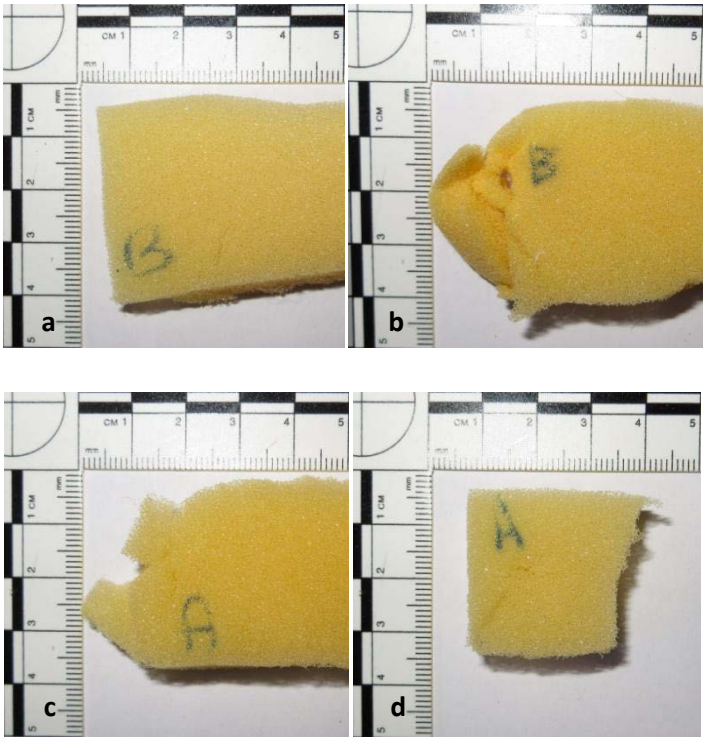


Figure 2.8: ***Comparison of the foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4.***

There was morphological consistency between the majority of the foam samples collected at Montrose, MN except the samples of carpet underlay. The carpet underlay samples displayed inter and intra variation with respect to the samples collected from the furniture, which has been illustrated in Figure 2.9.

Figure 2.9: ***Comparison of the foam samples collected from the carpet underlay. a) Room 1, b) Room 2, c) Room 4.***

The sections were then visually compared with known latex foam samples and images of latex foam rubber presented in Figure 2.10.

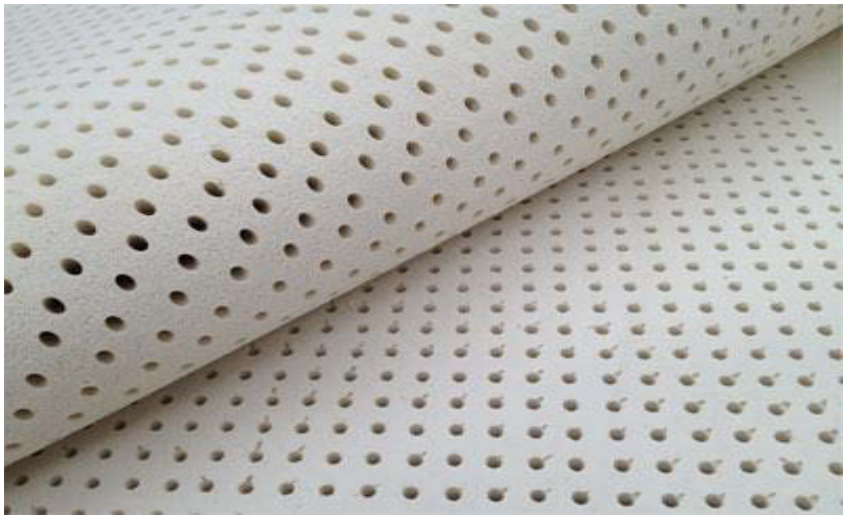


Figure 2.10: Latex foam rubber [204].

The textures of the known latex sample and the sections of foam collected during the experiments at Montrose, MN were compared. The sections of foam were visually and texturally discernible from the known latex samples.

Samples of flexible PU foam with known densities and hardness were collected from *The Foam Booth (554 Cleveland Street, Surry Hills, NSW)* and photographed. Examples of the known samples can be seen in Figure 2.11. There is clear colour variation within the known sample and there is greater rigidity in sample b.

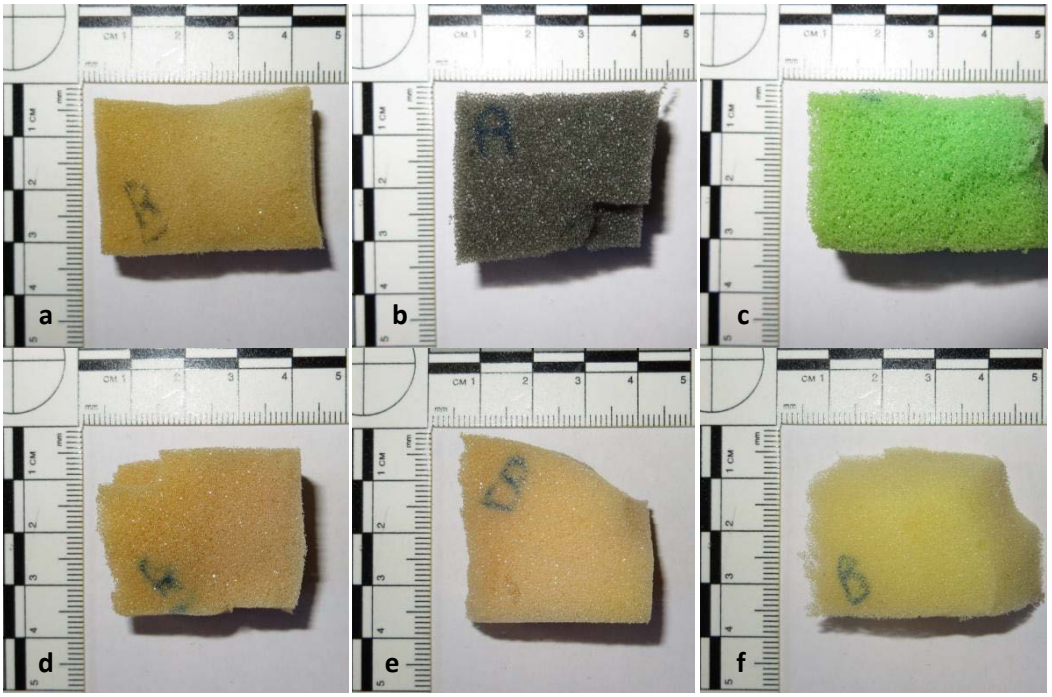


Figure 2.11: Comparison of known PU foam samples. a) Density 23, Hardness 130, b) Density 29, Hardness 400 c) Density 36, Hardness 100, d) Activated Chloride Non Flame Retarded, e) Density 30, Hardness 110 and f) Density 15, Hardness 100.

When compared visually and texturally at the time of the experimental burns, the sections collected at Montrose, MN were indistinguishable from the known flexible PU samples.

Based on the results from the initial field tests it was postulated that the sections of foam collected from the furniture at Montrose, MN were most likely to be flexible PU foam not another form of upholstering material, like latex foam rubber.

2.5.2 Environmental Scanning Electron Microscopy (ESEM) Analysis

The foam samples collected at Montrose were compared using ESEM at the micro level. Figure 2.12 provides an example of the morphology observed throughout the majority of the samples which were consistent.

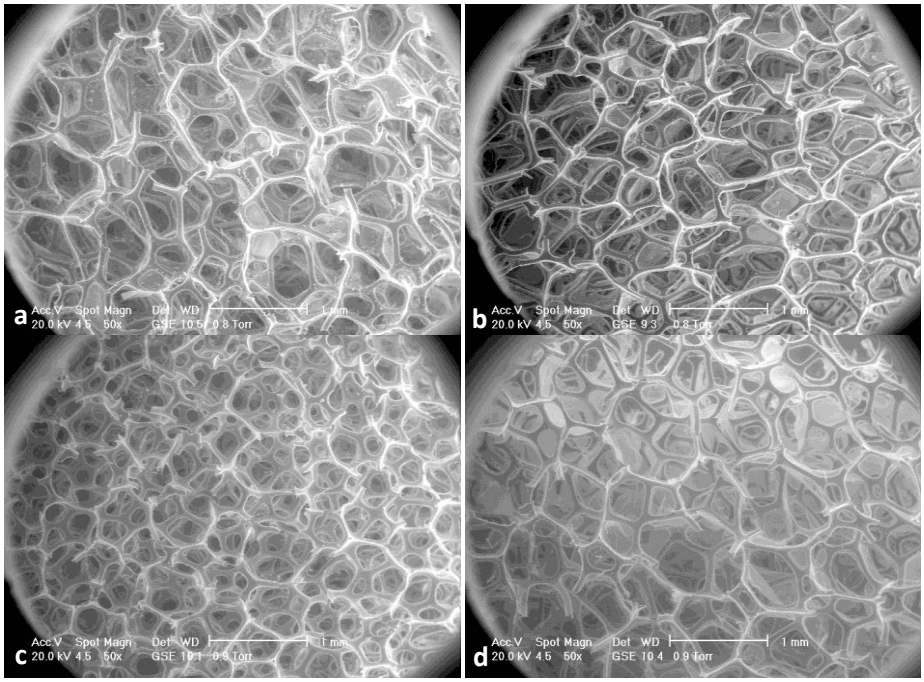


Figure 2.12: Comparison of the foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4.

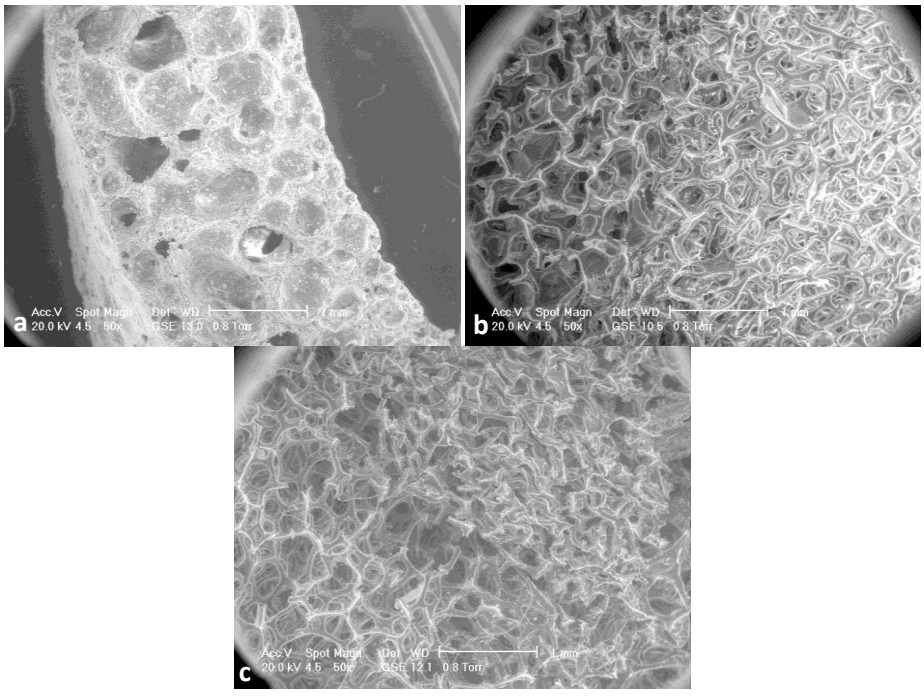


Figure 2.13: Comparison of the foam samples collected from the carpet underlay. a) Room 1, b) Room 2, c) Room 4.

Figure 2.13 illustrates a comparison of the ESEM images of the underlay samples. Figure 2.13 a) illustrates the single sample collected that displayed morphological variation at a micro level. Although Figure 2.13 b) and c) display similar morphological characteristics to each other it is reasonable to suggest that their structure is similar to those illustrated in Figure 2.12 though, due to their placement, repeated compression underfoot has resulted in the cells appearing compressed.

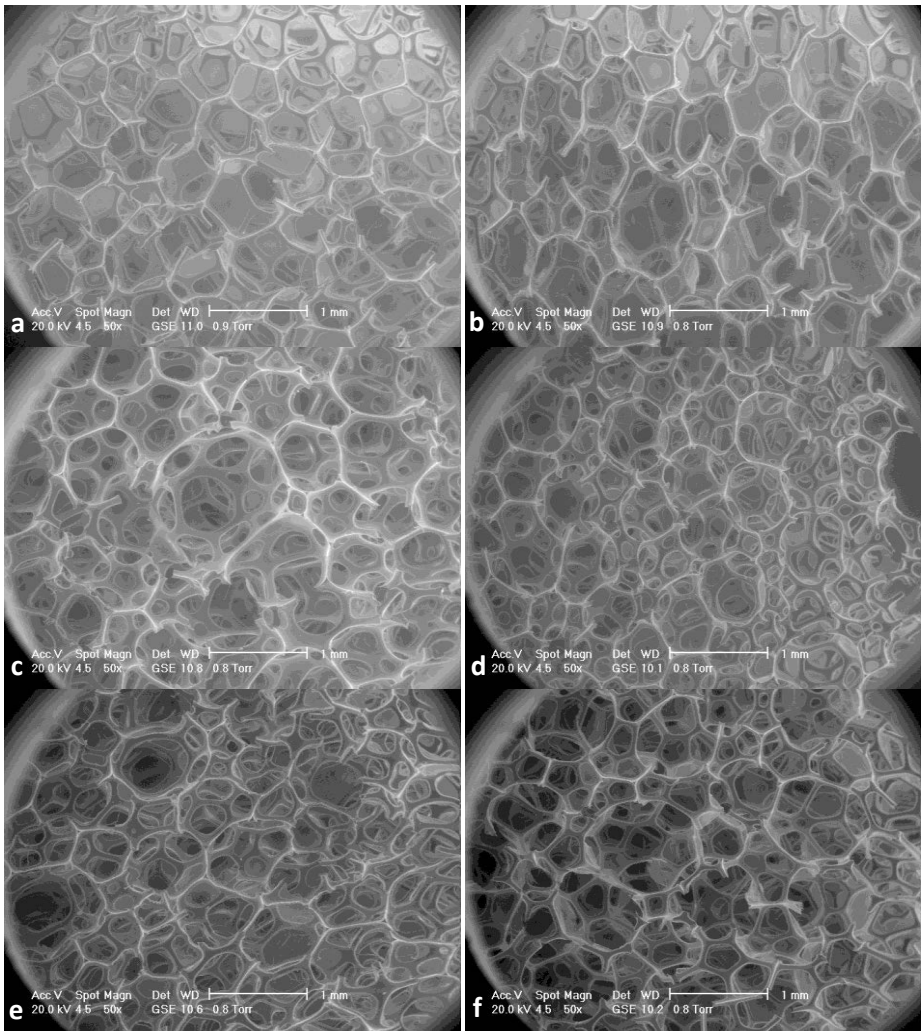


Figure 2.14: Comparison of known PU foam samples. a) Density 23, Hardness 130, b) Density 29, Hardness 400 c) Density 36, Hardness 100, d) Activated Chloride Non Flame Retarded, e) Density 30, Hardness 110 and f) Density 15, Hardness 100.

Morphologically, it has been illustrated that there is consistency between the majority of the foam samples collected during the experimental work conducted at Montrose. In addition, consistency between the known PU samples experimental samples has also been demonstrated.

2.5.3 ATR-FTIR Spectrometric Analysis

Comparison of the foam samples was undertaken using ATR-FTIR spectroscopy. In each room foam was collected from the box spring base of the bed and all the layers of the mattress. In addition, foam was collected from the sofa bed cushions and the sofa bed mattress. Two spectra were collected for each of the sections of foam. Spectra were also collected from PU foam samples of known origin, hardness and density.

Spectra of samples collected from the same item of furniture were overlaid for comparison. It is evident in 2.15 from the samples of foam collected from the bed a) and from the sofa bed b) that there was little variation between the spectra collected from the foam sections taken from the furniture used in the Room 1 burn. These results illustrate that the type of polymer used to make the foam is indistinguishable.

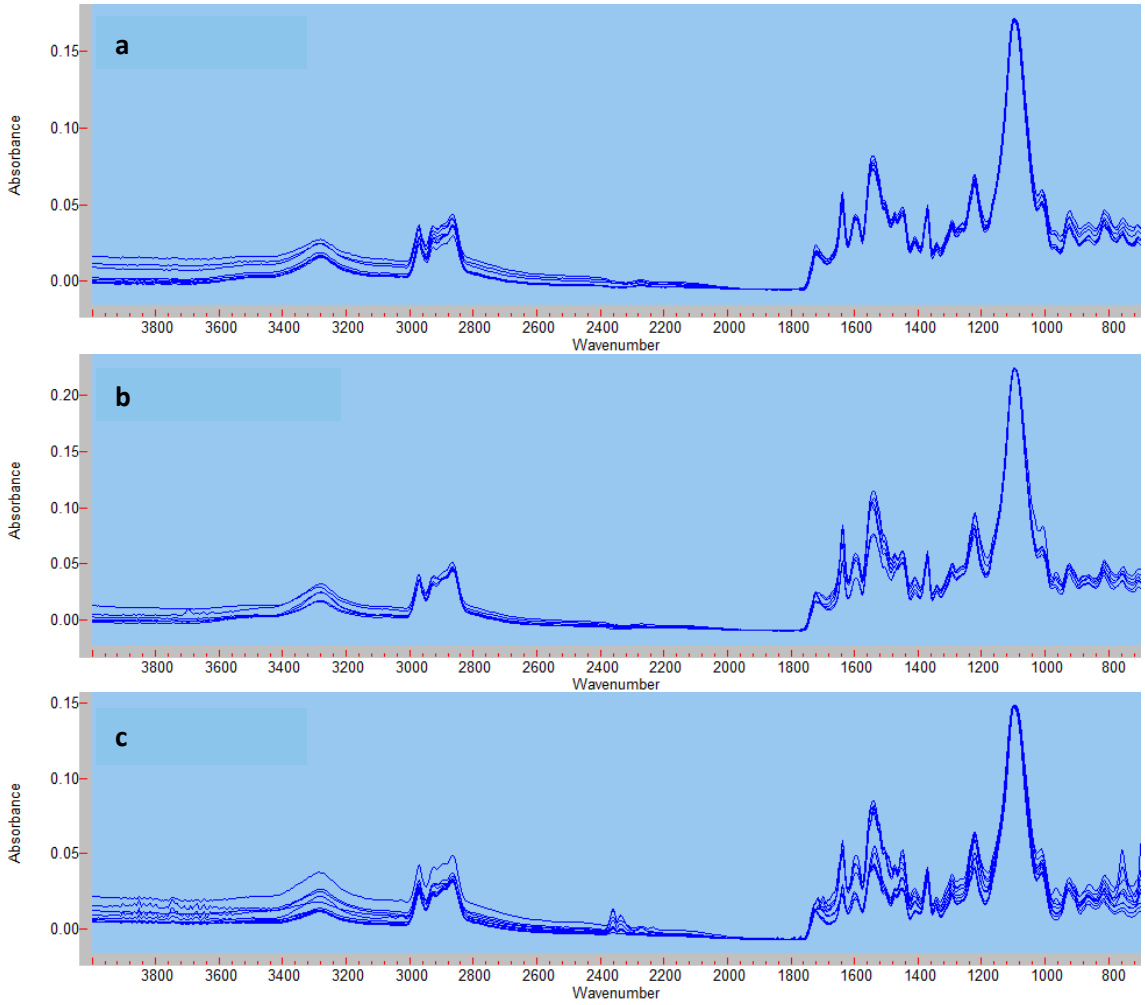


Figure 2.15: Overlaid spectra of foam samples a) Montrose Room 1 bed, b) Montrose Room 1 sofa bed, and c) Known PU foam samples.

In addition, when a comparison was made between the overlaid spectra from the burn conducted in Room 1 and the spectra collected from the known PU samples, the similarity between the sample and reference spectra supports that the sample foam is polyurethane.

Specific characterisation of the sections of foam collected was not of paramount concern; although the foam samples from library search illustrated in Figure 2.16, in addition to data presented in the literature, indicate that the polymer was consistent with polyether urethane [205].

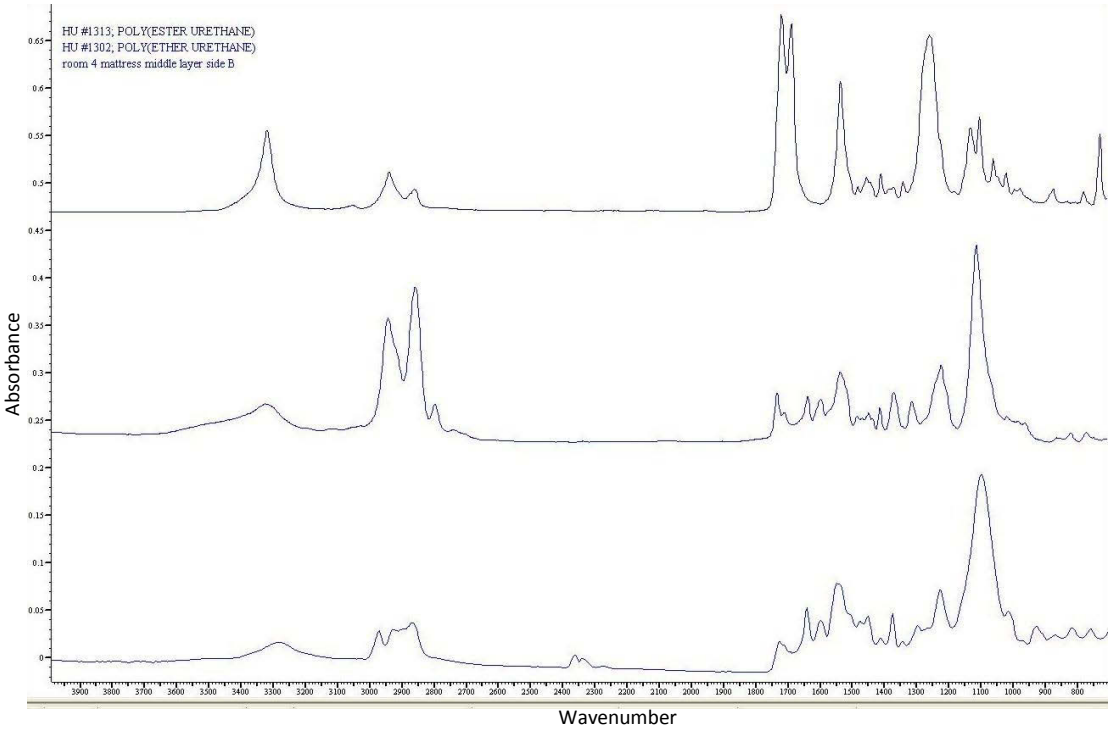


Figure 2.16: Comparison between ATR-FTIR spectra of poly(ester urethane) and poly(ether urethane) contained in the instrument library and that from a sample collected during from the experiments at Montrose, MN.

The spectra collected from all the foam sections were overlaid and have been illustrated in Figure 2.17. It is evident, from the overlaid spectra, that the foam collected from each room is consistent; although, there is one notable variant. The spectrum highlighted in blue was collected from a sample of the carpet underlay used in Room 1, illustrated in Figure 2.9a), is clearly inconsistent with the other foam sections as well as Latex as illustrated in Figure 2.18. Further investigation of the material was not undertaken as it was not a prevalent material.

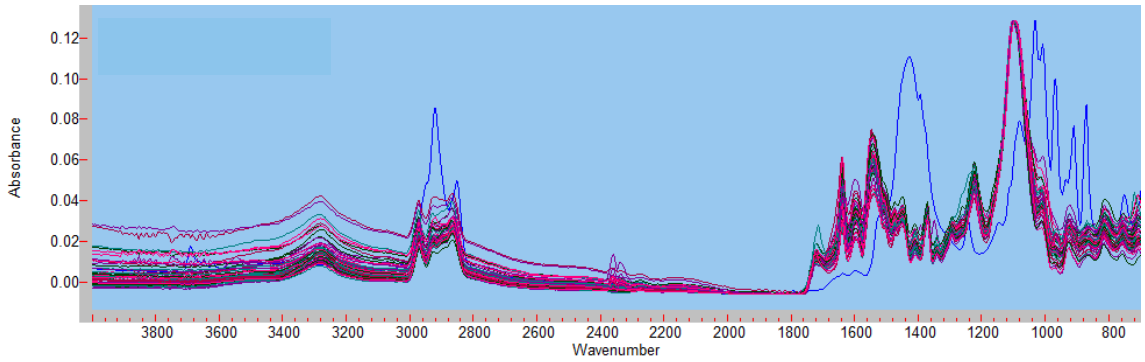


Figure 2.17: Overlaid spectra of all foam samples collected from Montrose, MN burns room 1 – 4.

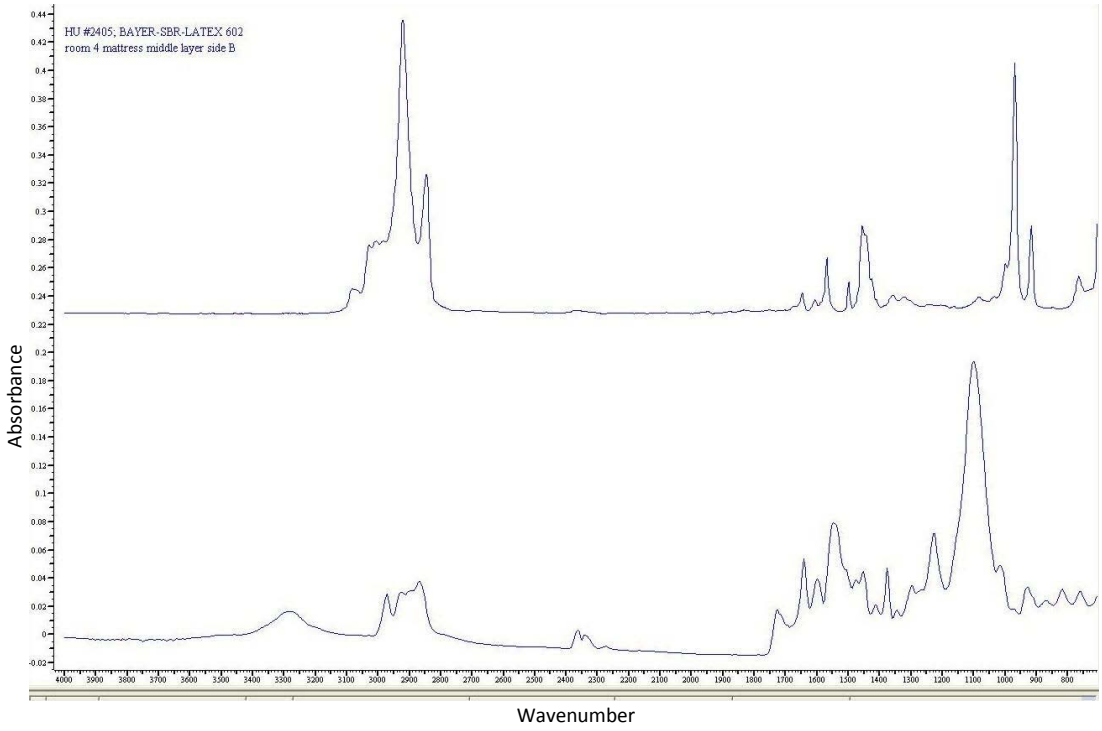


Figure 2.18: Comparison ATR-FTIR spectra of Latex contained in the library of the instrument with that of sample collected during from the experiments at Montrose, MN.

ATR-FTIR was used as confirmatory tool regarding the identity of the samples collected during the experimental work. Due to the size (average molecular weight) of the polymer being analysed some limitations were experienced using this technique. Some aspects such as terminal groups, occlusions in the polymer or organic additives that make up a small portion of the product, are difficult to determine. It is not considered that those components would be significant contributors to pyrolysis, their detection could be used as a means of additional discriminating power if PU from difference manufacturer's had been used. Though, given the potential limitations of this technique when used to analyse large polymers, the results indicate the experimental samples were consistent with the samples known to be PU. Based on the results it is reasonable to suggest that the samples were polyether urethane.

2.5.4 Heat Release Rate (HRR)

The heat release rate (HRR) has been defined as:

The rate at which heat energy is generated by burning which is related to its chemistry, physicals form, and availability of oxidant and is ordinarily expressed as Btu/s or kilowatts (kW) [3].

Measuring the HRR is typically conducted using a cone calorimeter. However as access to a cone calorimeter was not available the HRR of each furniture item was estimated using published data [2-3]. The estimation was then used to predict an overall HRR that could be generated during the fire. Examples of published data have been provided in Table 2—2.

Table 2—2: Examples of Peak Heat Release Rate Values.

Fuel Package	*Reference*	*Mass (kg)*	*Peak HRR (kW)*
Sofa with PU	209	51.3	3120
Sofa (synthetic padding and covering)	2	NA	1000 – 3000
Easy Chair with PU	2	12.2 – 27.7	1350 - 1990
Mattress with PU	209	3.2 – 14.1	810 - 2630
Carpet underlay - PU	2, 209	NA	NA

Table 2—2 highlights that there can be significant variation for an objects reported to have the same end use. For example, the HRR rates of sofas, which have been upholstered with a synthetic material, have been reported in the literature with a 2000 kW range. This is a value that is dictated by a number of factors, including the location of the fire (open versus a compartment) where the data has been gathered from, the surface area to mass ratio of the fuel and other physical properties including density and conductivity. There is also a range depending on the chemical properties of the fuel, for example a sofa upholstered using has a higher range of HRR than a sofa stuffed with cotton that has similar mass and dimensions.

An estimation was made, based on the available data, that the HRR range that could potentially be generated in each room based on the fuel package at the area of origin and then as a whole was item of furniture was approximately 1000 – 5750 kW (see Table 2—3). A HRR value for carpet underlay made from PU was not located in utilised literature. However, this was not considered to be problematic as it would the value would only increased the top estimation for the HRR of the fuel package in Room 2 and Rom 4 (where the PU underlay was located).

It was then projected, using correlations proposed by Babrauskas and Thomas, the HRR required for a flashover event to occur in each of the rooms was as follows:

$\dot{Q}_{f_0} = 7.8A_T + (378\ A_o)(h_0)^{0.5})$ (Thomas Correlation)[2].

$\dot{Q}_{f_0} = (750A_0)(h_0)^{0.5}$ (Babrauskas) [2].

Where:

A_T = total surface area of the room (m^2)

A_o = area of the opening (m^2)

h_o = height of the opening (m)

The range given by the derived correlations were as follows:

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.

Q_{fo}	*Thomas*	*Babrauskas*	*Estimated HRR of Fuel Package (kW)*
Room 1	775.91	1091.8	1000 – 5750
Room 2	841.20	1100.43	1000 – 5750
Room 3	876.97	1212.23	1000 – 5750
Room 4	875.19	1228.93	1000 – 5750

There are other methods of estimating the HRR, but they were not utilised as the data gathered during the experiment did not completely satisfy the requirements of the equations.

It is important to note that the combined HRR for all the items of furniture in a cell of structure do not impact on the growth stage of the fire. For example during the development of a fire if part of the individual objects that comprise the fuel load remain un-impinged on by fire, their individual HRR is not at that moment contributing to the total HRR. However once those items do become involved they contribute, in an additive fashion, to the total HRR of

the fuel load in the cell or compartment. Further evidence to justify the HRR of individual items being indicative, as opposed to definitive, is the manner in which the reference data is collected. Individual testing is generally undertaken in controlled open scenarios which therefore do not consider the impact the fire occurring in a compartment has on the HRR. It would therefore be acceptable to consider the HHR of individual items as base ranges, and that the fire occurring in a compartment will impact on the values by potentially increasing the HRR.

2.5.5 Time Until Flashover

Determining if the time until the occurrence of a flashover event was proportional to the amount of PU in the cell was the primary reason for conducting the test burns. Therefore the flashover event had to occur before the fire could be suppressed. Table 2—4 lists the time until flashover recorded in each room of the Montrose, MN site.

Table 2—4: Time until flashover: Montrose, MN.

Recording Type	*Room 1*	*Room 2*	*Room 3*	*Room 4*
Wrist Watch (min:sec)	16:00	9:00	8:00	8:00
Video Time Stamp (min:sec)	16:15	9:17	8:10	8:02
Room Dimensions	***Room 1***	***Room 2***	***Room 3***	***Room 4***
Volume (m^3)	23.70	38.51	33.52	30.72
Ventilation Opening Area (m^2)	1.17	1.18	1.27	1.27

2.5.5.1 Room 1

Room 1 took significantly longer to reach flashover than then other rooms. One reason for this was that ignition in this test burn was at the surface of the sofa bed cushion on the horizontal plane and flame spread over a horizontal plane generally occurs slower than over a vertical plane [206]. In addition, sustained fire requires an oxygen concentration in air to be between 21% - to approximately 11% in the immediate atmosphere [2-3, 57-59]. Prior to commencing the test burn in Room 1, the top of the door way was covered to reduce the

possibility of the fire spreading to the adjacent room. Consequently, the only significant area acting as a ventilation point for the room had been significantly reduced. The fire was therefore starved of oxygen because the limited ventilation diminished the tracking of oxygen into the room and also prevented the escape of combustion gases from the cell. These two factors (i.e. slower flame spread and inadequate ventilation) are hypothesised to have led to the longer time til flashover.

Further evidence of the above hypothesis can be found in the digital video recording of the progression of the fire in Room 1. Approximately 14 minutes into the recording, the flame had significantly reduced and flameover (also referred to as rollover is a situation where unburned fuel form the fire concentrated in the ceiling layer to such an extent that it ignites and burns [22]) was not in progress. The reduced ventilation and subsequent diminished oxygen levels contributed to incomplete combustion of the fuel load resulting in a visually impervious smoke layer. At that time the east window of Room 1 was manually broken to increase ventilation to the room. Approximately 2 minutes later flashover occurred in Room 1 and the fire was subsequently suppressed.

The burn in Room 1 highlighted how factors, such as the point of ignition and ventilation, influenced the progression of the fire. As the main objective for this series of test burns was to identify any variables that would impact on achieving a flashover event a number of aspects of the test burns were modified. During the test burn in Room 1 the modification of the test parameters occurred during the test. Then in subsequent burns it was ensured that the fire would progress as ventilation controlled not limited, fire.

2.5.5.2 Room 2

The proximity between Room 1 and Room 2 and the method of fire suppression adopted prevented the door between the rooms from being shut during the fire. As a result, preventing the fire in Room 1 impacting on the contents of Room 2 was difficult. The radiant heat resultant from the ignition of the gas layer in Room 1 scorched a semi circular pattern (demarcation line) in the carpet section in Room 2. The carpet was therefore removed prior to commencement of the test burn in Room 2.

Before ignition was initiated in the second room, the doorway between Room 1 and Room 2 was covered. Isolating Room 1 prevented the partially consumed fuel package from being

encroached on by the Room 2 fire. In addition, as discussed in Section 2.4, the top section of the doorway between Room 2 and Room 3 was covered with a ply board to reduce the possibility of the fire progressing to Room 3. To avoid starving the fire of oxygen, by reducing the ventilation area, the north window for Room 2 remained open during the fire.

The point of ignition in Room 2 occurred at the valance of the couch approximately halfway between the front and the back of the couch at the side between the couch and the bed. The increase in the progression of flame over the couch in Room 2 compared to that of Room 1 was evident. The increase of flame spread across the couch could potentially have been attributed to the change in the point of ignition.

Additional variation between Room 1 and Room 2 is apparent in the dimension, volume, ventilation points and areas, floor covering and the placement of the fuel load and these experimental parameters may also have contributed to the increased flame spread and shorter time til flashover.

After the fire was suppressed in Room 2 the room was closed off to prevent future fires spreading into that room.

2.5.5.3 Room 3

As the third room was not adjacent to the fourth, concern regarding flame spread was not as great. As a result, the top of the doorway was not covered. The doorway was the only ventilation point for Room 3 as there were no windows.

The point of ignition in Room 3 was the valance of the couch approximately halfway between the front and the back of the couch at the side between the couch and the bed. The rate of flame spread on the couch was correlated with the initial stages of the Room 2 fire. In addition it can be seen in Table 2—4 that the times until flashover in Room 2 and Room 3 were comparable.

2.5.5.4 Room 4

Room 4 did not share any walls with Rooms 1 – 3 and was not impacted on from heat or flame from the previous burns. In addition, as discussed in Section 2.4, the top section of the

doorway was covered with a ply board to reduce the possibility of fire spread throughout the house. Although, unlike previous tests, the board was erected purely for safety as the remainder of the site was not being utilised for test burns. Ventilation to the room was maintained by leaving one of the windows on the southern wall partially open.

The point of ignition in room 4 occurred at the valance at the front corner of the couch at the wall end between the couch and the bed. The increase of flame spread across the couch could potentially have been attributed to the change in the point of ignition; however other variations in the experimental parameters may also have contributed. For example, the dimension, volume, wall and floor coverings, fuel load placement, ventilation point and area are different from those in the preceding rooms.

2.6 Conclusion

Flashover was witnessed for each burn conducted, and its occurrence was supported by the author's interpretation of post suppression indicators. One significant challenge identified with this series of experiments was that the site was a domestic dwelling. This prevented some experimental parameters (such as room size and ventilation areas) being standardised. The outcome of the work discussed in this chapter highlighted the need for more experimental parameters to be standardised. This was addressed in subsequent experimentation which is described in detail in Chapter 3.

Chapter 3: Time Until Flashover, Fergus Falls, MN

Chapter 3: Time Until Flashover, Fergus Falls, MN

3.1 Introduction

The experimental burns conducted in Fergus Falls, MN were guided by the data and observations recorded at Montrose, MN. Those preliminary test burns were conducted to highlight challenges associated with conducting testing of this nature. The results of the preliminary testing undertaken in Montrose, MN contributed significantly to the modification of the experimental parameters included in the design of the method applied at Fergus Falls, MN that endeavoured to take a more holistic approach to the investigation of what occurred prior to ignition, during and post suppression of a fire.

It was identified that standardising additional parameters, such as the cell size, was desirable to accommodate the repetition of an experiment. It is not standard practice for domestic dwellings to be built to withstand repeated burns significant in duration and damage, therefore finding a location that could accommodate the need for repetition of the burns to occur was a challenge.

A series of structures were donated to the Fergus Falls Fire Department (FFFD) to provide an opportunity for the volunteer fire fighters to refine their suppression skills in a *controlled* training environment. This allowed the owners to take advantage of Section 170 of The Code. The test burns were performed in conjunction with the FFFD during a fire suppression training exercise.

One of the buildings on site had been motel suites. The nature of a motel meant that there would be access to cells of a similar, if not the same, size. Which was idyllic as it satisfied the experimental requirement for repetition in the same size cell.

3.2 Site Description

The site, formerly known as The Lakeland Motel, was located at 1912 Pebble Lake Rd, Fergus Falls, MN part of which has been indicated in Figure 3.1.

Figure 3.1: Lakeland Motel, MN with the administration building shown.

A group of seven buildings were donated that included a single story building containing 14 motel suites (three blocks of four connected by two single suites as illustrated by Figure 3.2) with five additional self contained cabins and a two story house that had been converted into the administration area of the business and private accommodation.

The administration building was immediately discounted for use in the experiments as it was recognised that similar issues encountered at Montrose, MN would have been repeated at Fergus Falls, MN. It was also established that although the five self contained units were comparable in dimension to each other, they were not comparable in size to the 14 motel suites. As a result the self contained units were not included in the study. It was determined that the dimensions of the six of the 14 suites were not comparable and resulted in only eight suites being utilised for the test burns.

Each suite had a bathroom and built in cupboard/wardrobe; both of the additions were located at the east west medial line of the building. To reduce the variables associated with the test burns these spaces were sealed off and were not included in the data collection or data analysis.

Figure 3.2 demonstrates the location of each room that was used in the work completed at Fergus Falls, MN. The figure is a schematic representation only, and is not drawn to scale.

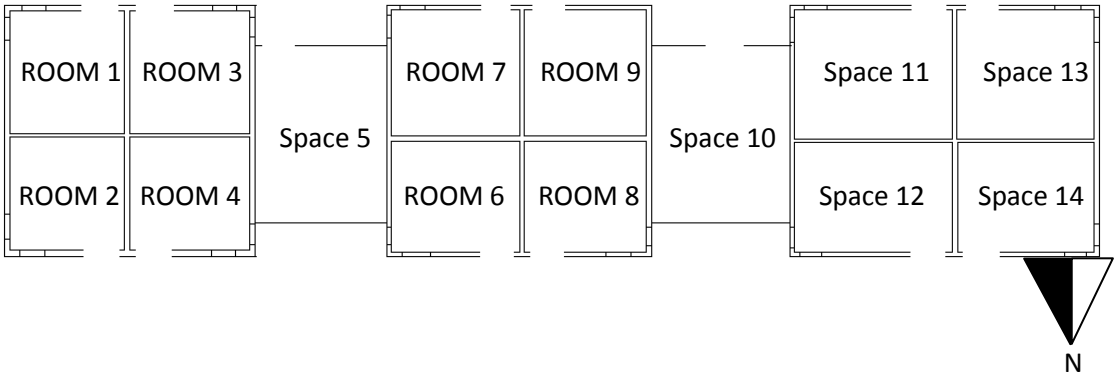


Figure 3.2: Schematic of the 14 connected motel suites. Not drawn to scale.

The site at Fergus Falls, MN was devoid of any furniture and the only remaining internal fixtures were the doors. Table 3—1 catalogues the dimensions of each room, the room volumes and the area of each ventilation point, in addition to the wall and floor coverings.

Table 3—1: Room Dimensions and Fixtures: Fergus Falls, MN.

Features	*Room 1*	*Room 2*	*Room 3*	*Room 4*	*Room 6*	*Room 7*	*Room 8*	*Room 9*
Room Height (mm)	2472	2469	2467	2469	2477	2464	2473	2477
Room Width (mm)	3540	3549	3546	3535	3550	3545	3546	3553
Room Length (mm)	5296	5271	5275	5275	5272	5272	5280	5285
Room Volume (m^3)	46.34	46.18	46.15	46.04	46.35	46.05	46.31	46.50
Flooring	Carpet	Carpet	Carpet	Carpet	Carpet	Carpet	Carpet	Carpet
Wall and Ceiling Covering (on plaster board)	Paint	Paint	Paint	Paint	Paint	Paint	Paint	Paint
Ventilation Area (m^2)	1.609	1.609	1.609	1.811	2.043	NA	1.679	NA

Furniture and carpet was purchased to be placed at the site to act as the fuel load. The items will be described in detail in Section 3.3.

Figure 3.3 illustrates a section of the building utilised for the burns at Fergus Falls, MN. It can be seen that the building is one story with weather board construction. Room 3 is shown in the early stages of the fire. The orientation of the room is west of Room 1 and east of Space 5.

Figure 3.3: Section of the building utilised for the burns at Fergus Falls, MN in early stages of the fire.

It has been illustrated in this image that the suites are connected by a common roof. The connection of a common roof in addition to conjoined roof cavities was considered in the method and is discussed in Section 3.4.

The measurement values were collected with a laser line that had been calibrated, however the recesses attributed to the doors and windows were not included. As a result the volume of each room is an approximation.

The experimental burns took place over three days with maximum temperatures ranging from 23 – 26 °C. Intermittent precipitation was recorded on day one and two of the experimental burns, though there was only one burn conducted on the first day, and at the time there was no rain in the immediate area.

3.3 Sample Description

The furniture and soft furnishing samples used in the test burns conducted at Fergus Falls, MN were purchased from *Hotel Furniture Liquidators, Inc 1800 University Ave West, Saint Paul, MN*. A major consideration was repetition of the experimental procedure. To

accommodate repetition the same, or similar, furniture items were sourced. As with the furniture sourced for the Montrose, MN test burns the furniture used in this series of testing was sourced from the same hotel, of similar age, size and appearance. Although the source of the furniture was known, the manufacture of the furniture or the PU foam was not known at the time of the test burns.

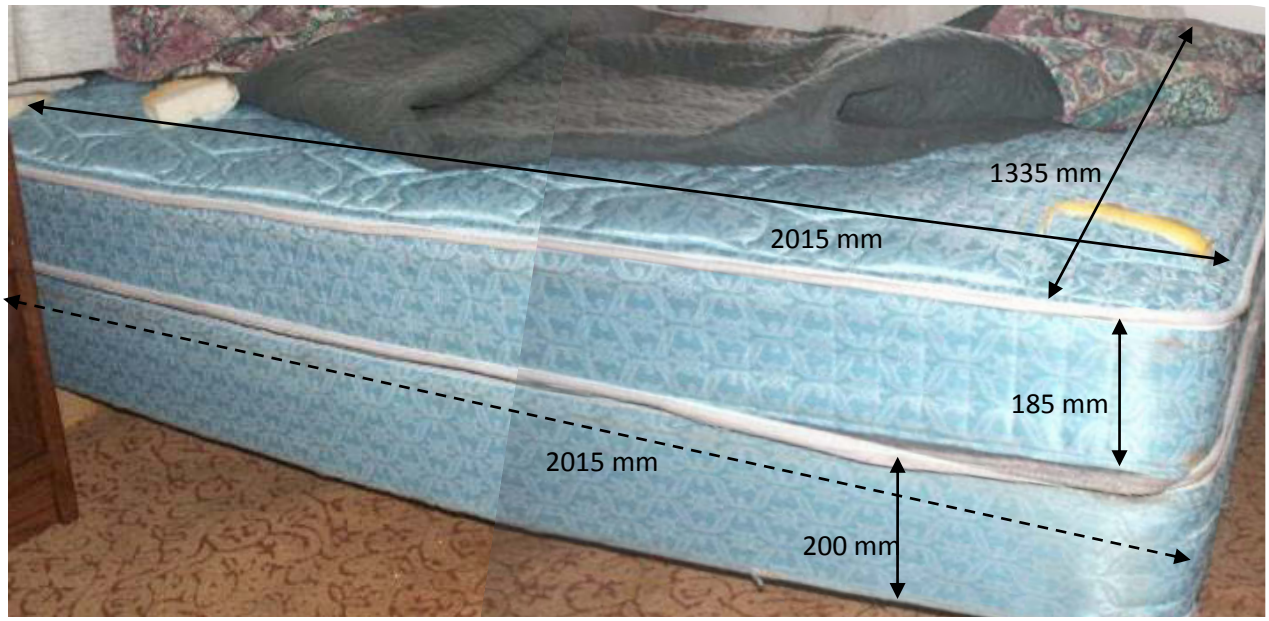


Figure 3.4: An example of the quilt, mattress and base used in each room.

Repeating the type of fuel package was in line with reducing the number of variables in the method. Therefore, the fuel load used in the flaming component of the experiment was sourced from the same supplier, was of similar age, make and design, and had been subjected to the similar environmental conditions. Physically the furniture appeared to be the same; though the PU could not be sampled until after it was purchased as it required damaging the furniture. After the furniture was purchased samples of the PU were collected for later analysis.

Eight double bed box spring mattresses and eight double bases were purchased as a complete set and one was placed in each of the suites being utilised. Unlike Montrose, MN the each bed was raised on four wooden legs, placed at the corners of the bed, that were 140 mm high 165 mm long and 160 mm wide. Figure 3.4 illustrates the bed set up and the dimensions of the mattress and the base. A sample of foam was collected from each box

spring mattress, however the bases were devoid of foam and just upholstered with the material seen in Figure 3.4. Limitations in field prevented the mass of the items of furniture used in the burns being recorded. It was decided to use all of the items of furniture for the burns, rather than lose a repetition of an experiment in order to gain a visual estimation of the amount of PU present in each upholstered item of furniture. Eight quilts were also purchased for the test burns and were of comparable features. The structure of the quilt was a cloth covered Dacron® which was 2800 mm long and 2420 mm wide. Each of the beds was 'made' by covering the mattress with a quilt prior to commencement of the test burn.

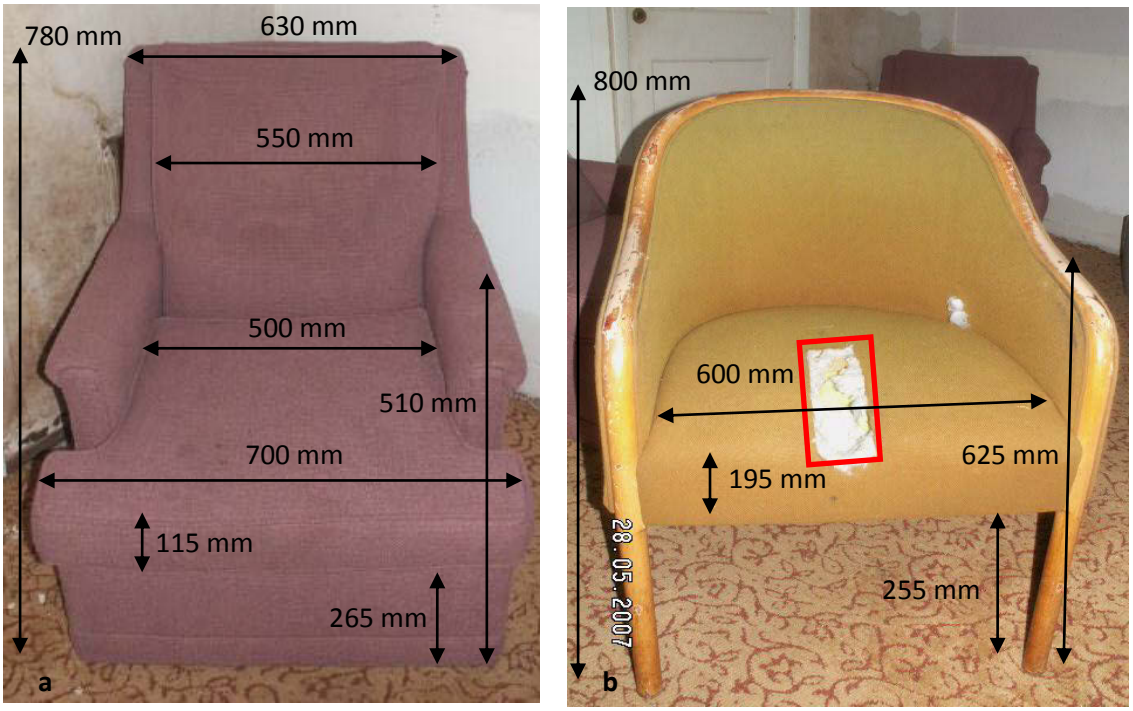


Figure 3.5: a) Pink armchair b) Chairs with padded seat cushions

Although the mattress was considered to be the primary source of PU to be used for the experiments, supplementary items thought to contain PU foam, were purchased for use in the test burns. Sofa beds were not used for this series of burns; instead 16 armchairs and 16 chairs with padded seat cushions were used. Two of each type of chair where included in each suite for the burn. Figure 3.5 illustrates an exemplar of both types of chair used, with the dimensions included. The style of chair shown in Figure 3.5 b) had no foam padding in the back and arm section, as it was just upholstered with the fabric illustrated being drawn taught between the seat and the wooden rail. Although a sample of the foam was collected from each section of the upholstered areas of each chair, consideration was paid to the

amount of foam removed due to the requirement of transportation back to Australia. The red box in Figure 3.5 b) is an example of the approximate size of samples collected.

Additional furniture including a wooden desk, bedside table, dresser, picture frame and two table top lamps (with shades) were placed in each suite. The dimensions of each item have been included in Figure 3.6. The television (TV) included in this image was not repeated in each room and while the sets were of a similar vintage there was a range in size. For that reason the TVs dimensions have not been included in Figure 3.6 as they would not be representative of the whole.

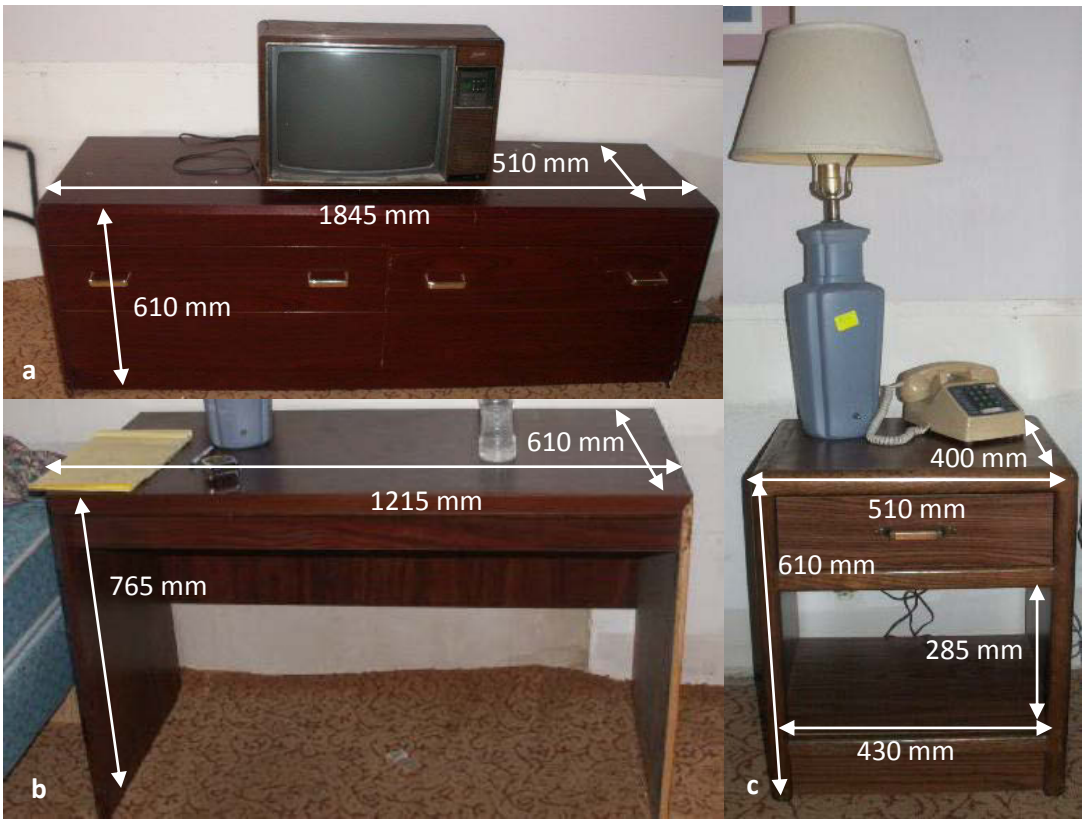


Figure 3.6: a) Dresser b) Desk c) Beside table and lamp.

3.4 Method

The experimental burns at Fergus Falls, MN were conducted using a method that had been modified based on the results recorded at the Montrose, MN burns. Although it had been initially determined that maintaining the fuel package was paramount, the necessity of controlling additional factors, such as cell size, was re-evaluated.

Access to a purpose built facility with the capability to repeatedly conduct burns in the same cell was not available. However, the site described in Section 3.2 had the capacity to support experimental repetition due to the comparable size of eight of the motel suites. This produced a cascade effect that allowed the arrangement of the fuel package to be repeated in each suite; in turn the area of ignition had the potential to be repeated.

A double bed mattress and base, two armchairs and two chairs with padded seat cushions, a bedside table, desk, dresser and two lamps were also included in each suite. The way the fuel package was distributed in each cell has been illustrated in Figure 3.7

Prior to being ignited a section of foam was collected from each item of furniture (approximately 100 x 50 x 200 mm). Preliminary testing was performed on each section of foam that had been collected which involved visual and textural examination. The sections of foam were then collected and sent back to Australia for confirmatory analysis. Figure 3.5 demonstrates the general size of the samples collected.

The burns came under the control of the FFFD, as the buildings were donated to be used in fire suppression training. For this reason the method design had to recognise the needs of the FFFD also. Therefore to ensure that the suppression crews were exposed to more than one scenario some parameters of the burns were altered:

- ignition mechanism; and
- ventilation area.

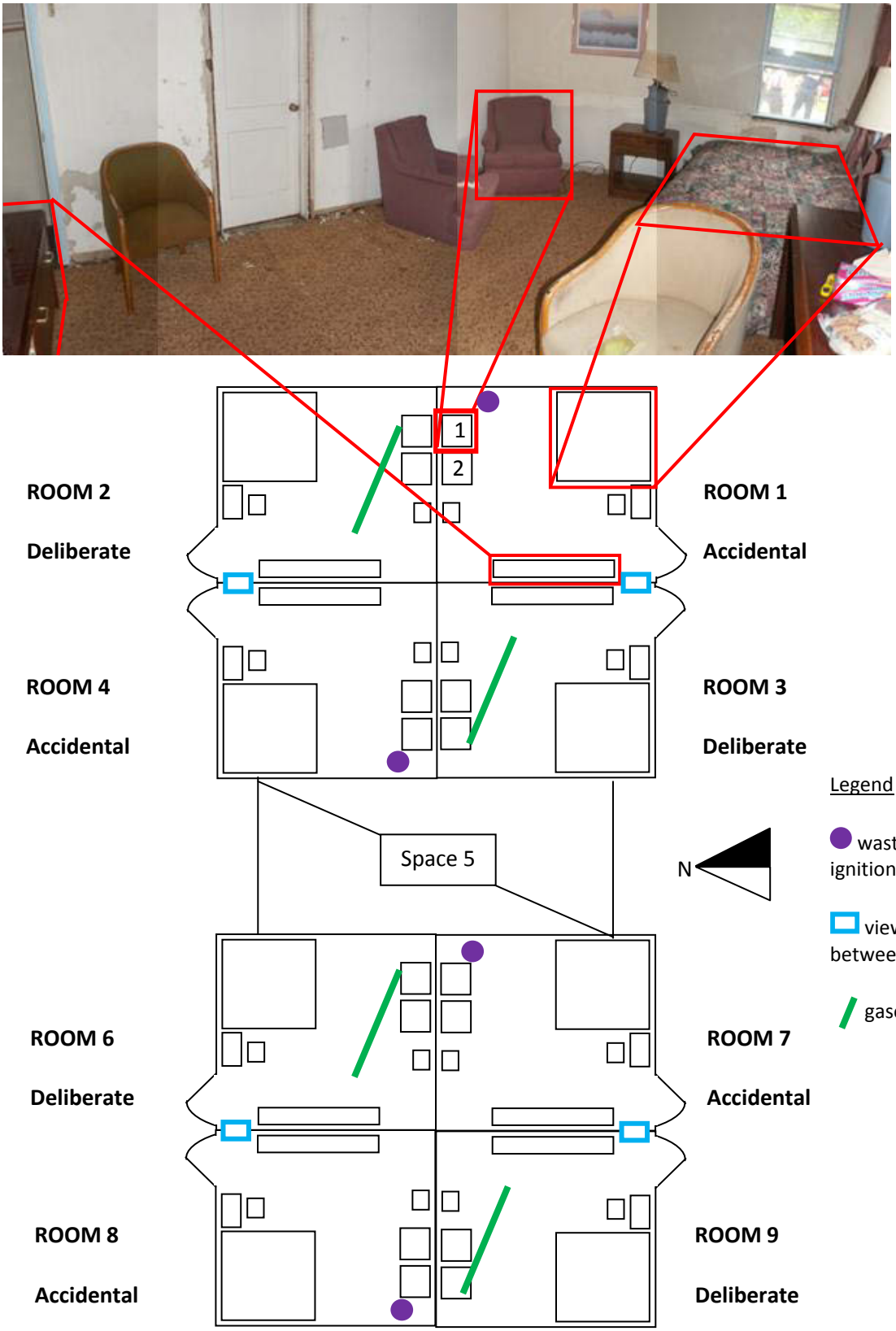


Figure 3.7: ***Photographic exemplar of the furniture distribution and schematic that illustrates the layout of the building, the location of the furniture and indicates the location (and mechanism) of ignition. Not drawn to scale.***

Two different ignition mechanisms were used to simulate either an arson scenario or an accidental fire. To simulate arson approximately 2.0 L of an ignitable liquid, gasoline, was poured in four suites and subsequently ignited using a hand held propane torch. The ignitable liquid was poured in a line approximately 2 m long running SE to NW that started on the corner of the armchair and extended just beyond the end of the bed. The gasoline was ignited at the end of the pour line that was closest to the door. The deliberate ignition occurred in Room 2, Room 3, Room 6 and Room 9 and an example of the pour line is indicated by the green line in Figure 3.7.

In the remaining four suites, Room 1, Room 4, Room 7 and Room 8 the ignition of an accidental fire was simulated using balled newspaper (between 3 to 5 loosely balled sheets of newspaper), which was placed in a rubbish bin, was ignited using a hand held propane torch. The location of the rubbish bin has been indicated on Figure 3.7 by a purple disk.

The chronology of the ignition of each room was Room 1, 3, 7, 9, 2, 4, 6, then Room 8. The time until flashover, including other events such as manual breach of windows or opening of doors, was recorded at the time. Each test burn was recorded digitally which allowed for comparison between both mechanisms of recording. This was beneficial due to the separation of the time keeper from the fire. At times there was a delay between ignition and the message of ignition being relayed to the time keeper.

To better view the flame progression a viewing pane was set up at floor level by cutting a hole in the wall which was subsequently covered with a flame resistant clear cover. The area is indicated with a blue box in Figure 3.7. As was the case at Montrose, MN T_0 for Fergus Falls, MN was defined as the moment the ignition source was removed from the surface of which it was igniting.

The structure at Fergus Falls MN was a motel the suites of which were connected by internal walls and the roof; therefore considerable attention was paid to the progression of the fire. That is, if it became clear that the fire was not going to progress to a flashover situation then suppression was initiated. This was to reduce the chance of the fire breaching the ceiling significantly and spreading laterally through the roof cavity. In addition, after suppression had occurred, the suppression crew thoroughly inspected the roof cavity to ensure that full suppression had occurred.

The sections of foam that had been collected during the experimental work conducted at Fergus Falls, MN were taken back to Sydney, Australia and analysed.

Environmental Scanning Electron Microscopy (ESEM) was used to examine visually the foam samples collected from the furniture used in the experiments at Fergus Falls, MN. The images were collected at a range of magnifications using the low-vacuum mode of an FEI XL30 Environmental Scanning Electron Microscope (ESEM). Low-vacuum mode was used in order to observe the samples in their natural state without the need for specimen coating. The chamber pressure used was 0.8 - 0.9 Torr and the beam accelerating voltage was 20 kV.

ATR-FTIR spectroscopy was used to determine the polymer type and note any detectable differences between the foam samples. A Digilab FTS 7000 IR spectrophotometer using UMA 600 with an ATR germanium crystal was used to record the spectra. The spectra were collected in absorbance with a resolution of 8 cm^{-1} for 64 scans. Two spectra were collected from each piece of foam that was gathered from the furniture.

3.5 Results and Discussion

3.5.1 Visual Analysis

It was determined that differences existed between the foams used in the manufacture of the furniture. Short of purchasing the PU from one manufacturer and ensuring it was produced as part of a single batch prior to the assembly of the furniture, controlling the sample to that extent was unlikely if not impossible.

Although the furniture was from the same source the items had previously been owned and records regarding the manufacturer of the furniture and specifically the PU manufacturer were not available. The specific pathways employed by manufacturers to produce PU are not publically available and information regarding the manufacturer of the PU would have allowed for the investigation into the legislative controls regarding the manufacture of PU in the country, or countries, of manufacture. This in turn would have provided a more detailed appreciation of the chemical composition of the PU.

The pieces of furniture were specifically selected as they were repeat sets salvaged from a hotel. Aesthetically the items were analogous in terms of their physical appearance. Although, when samples of foam were collected from each item of foam containing furniture for analysis it became evident that there was variation in the upholstering of the items.

For example, the mattress used in Room 4, Room 8 and Room 9 were padded using three layers of foam. The remaining mattresses were upholstered using two layers of foam with a layer of Dacron batting between them. In addition variation was noted in the type of foam used to upholster the chairs with padded seat cushions.

There was variation regarding how the individual items were upholstered, there was also variation within the morphology of the samples collected. However; the majority of the foam used to upholster the furniture was similar as has been illustrated in Figure 3.8.

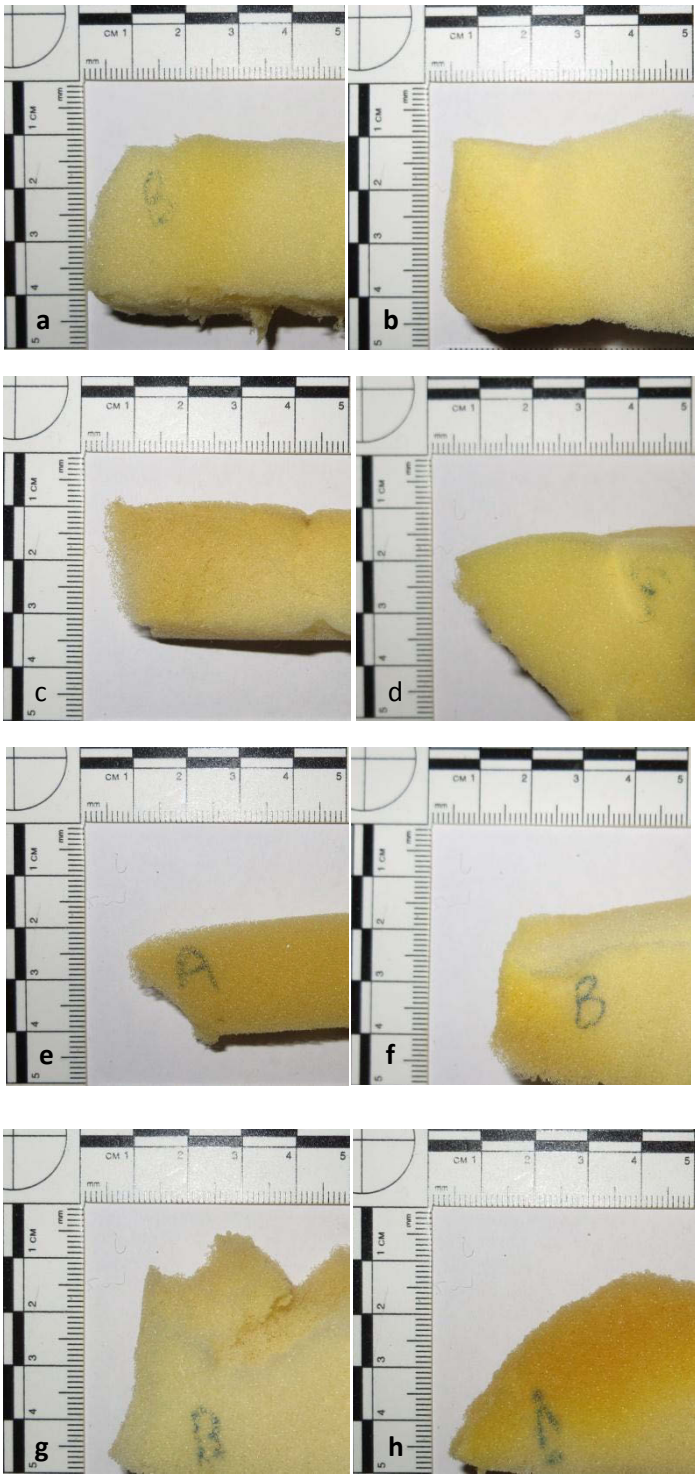


Figure 3.8: ***Foam samples collected from the top layer of the mattress. a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.***

Although the items of furniture displayed similar outward aesthetics, when the sections of foam were collected from individual pieces of furniture it was clear that the foam used to upholster them was not uniform. Figure 3.9 illustrates a morphological difference in the

foam used in the upholstering process. The chairs with padded seat cushions used foam that was green in colour, except for those used in Room 6, which had foam that was similar in colour and texture to the foam used in the other furniture items.

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.***

The sections were then visually compared with known latex foam samples and images of latex foam rubber which has been illustrated in Figure 2.10. The textures of the known latex sample and the sections of foam collected during the experiments at Fergus Falls, MN were compared. The sections of foam were visually and textually discernable from the known latex samples.

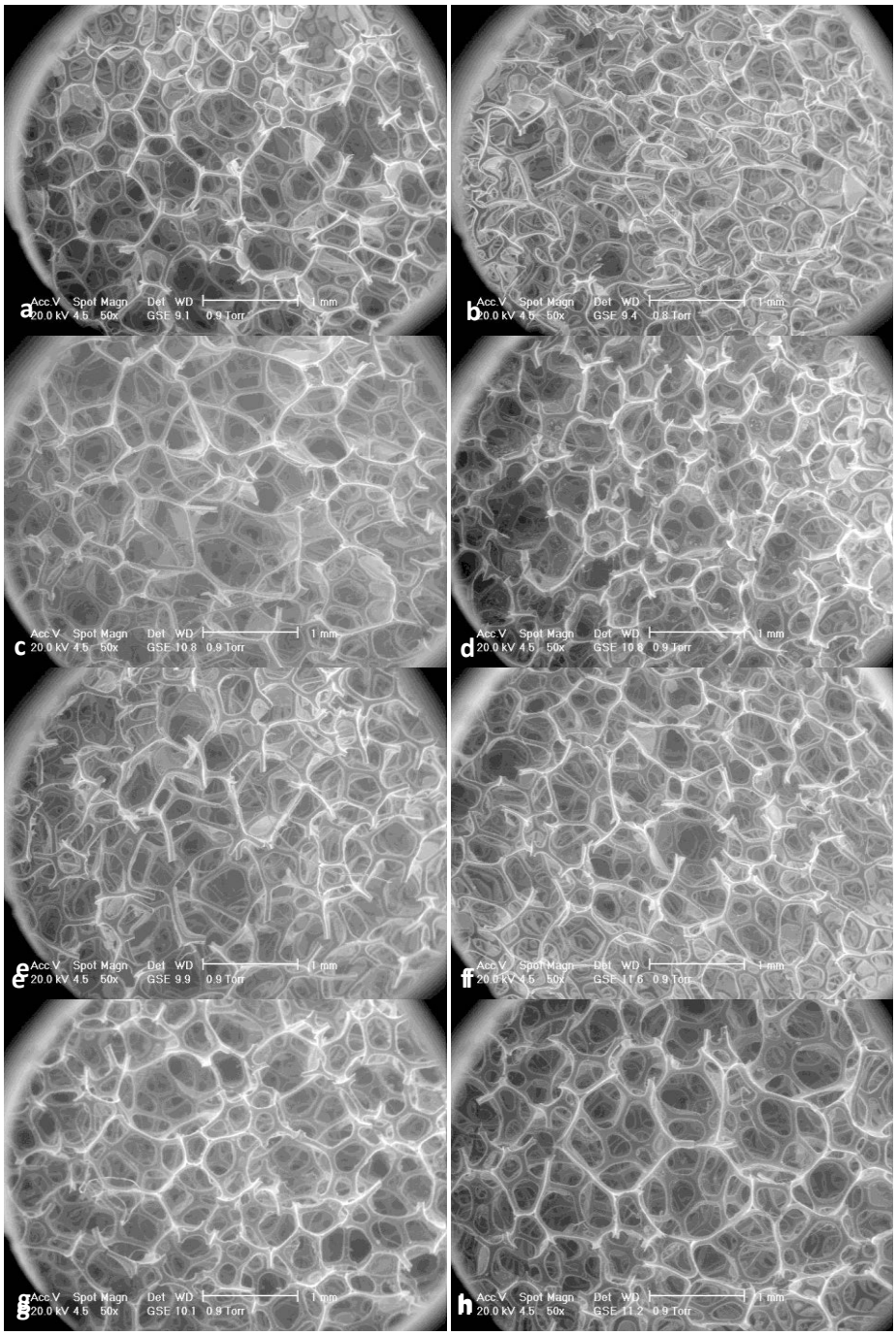
Samples of flexible PU foam with known densities and hardness were collected and photographed which have been illustrated in Figure 2.11. When compared visually and textually at the time of the experimental burns, the sections collected at Fergus Falls, MN were indistinguishable from the known flexible PU samples.

In addition the samples collected at Fergus Falls, MN were visually compared with the samples collected at Montrose, MN (Figure 2.8). Other than a variation in colour, significant differences were not noted between the sections of foam collected.

The variation displayed in the colour of the foam used in the armchairs with wood did not impact significantly on the result of the field tests. It was still postulated that the sections of foam collected from the furniture at Fergus Falls, MN were most likely to be flexible PU foam not another form of padding like latex foam rubber.

3.5.2 Environmental scanning electron microscopy (ESEM) Analysis

The samples were analysed using ESEM to determine if variation between the samples could be detected on a micro scale. It is illustrated in 3.10 that little morphological variation in evident, which is repeated in throughout the remaining samples.



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.

The samples that showed some variation in colour in the macro visual comparison, also display some variation at the micro level. Specifically, part a)-d) and f) and-h) of Figure 3.11display thicker cell walls than the sample in part e, which display thinner walls that are more consistent with the samples in 3.10.

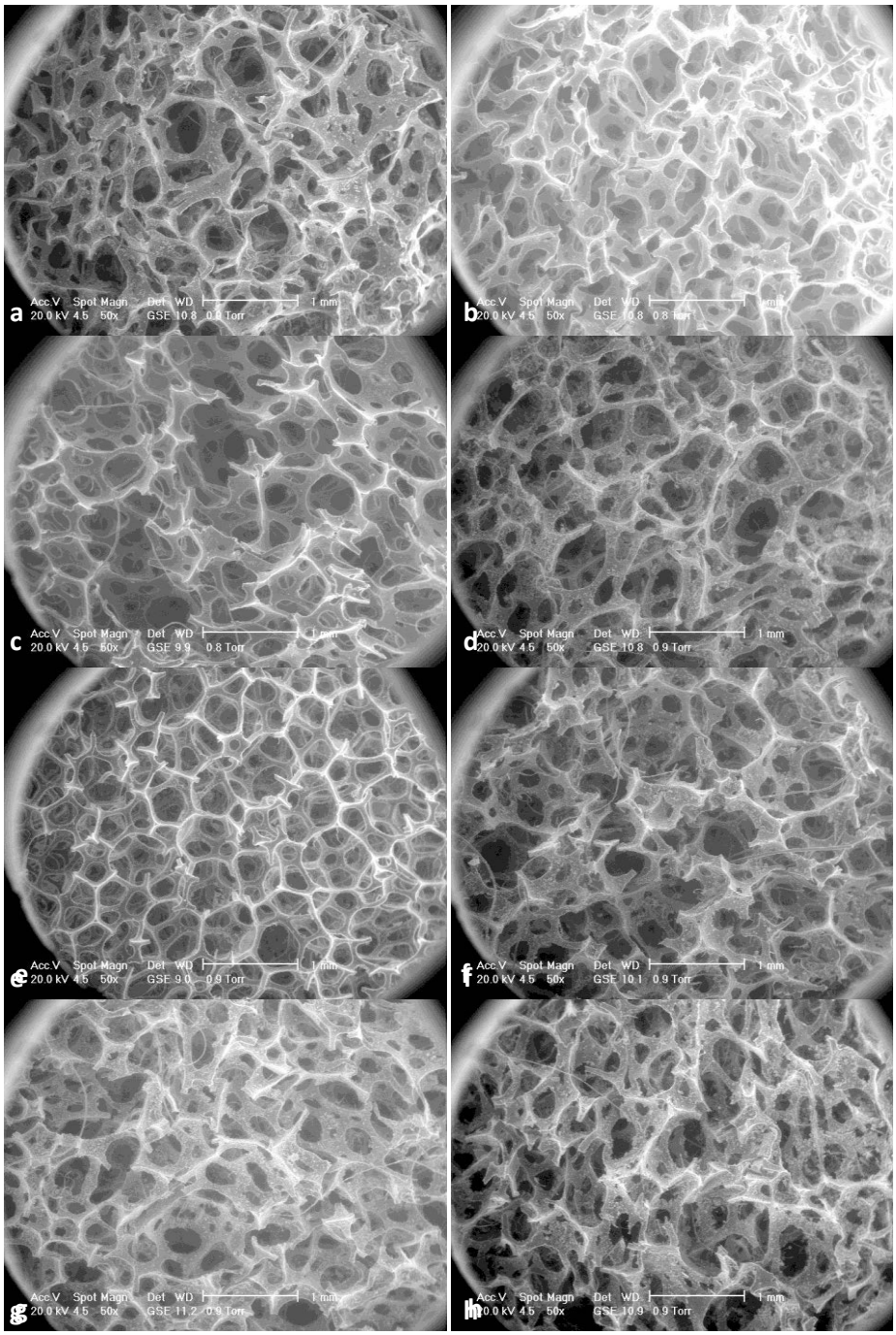


Figure 3.11: ***Foam samples collected from the armchair with wood a) Room 1, b) Room 2, c) Room 3, d) Room 4, e) Room 6, f) Room 7, g) Room 8 and h) Room 9.***

3.5.3 ATR-FTIR Spectrometric Analysis

The samples of foam collected at Fergus Falls, MN were compared using ATR-FTIR spectroscopy. It was noted in Section 3.5.1 and Section 3.5.2 that differences were noted at a macro and micro level respectively. The results illustrated in Figure 3.12 demonstrate that there was little variation detected in the type of polymer used to manufacture the foam.

Spectra were collected from the samples taken from the mattress, the pink armchairs and the armchairs with wood used as the fuel package in each of the motel suites at Fergus Falls, MN.

Spectra of samples collected from the same type of furniture from each suite were overlaid for comparison. It is evident in Figure 3.12 from the samples of foam collected from each of the mattresses (a), and from each of the pink armchair (b) that there was little variation between the spectra collected from the mattress layers and the armchair.

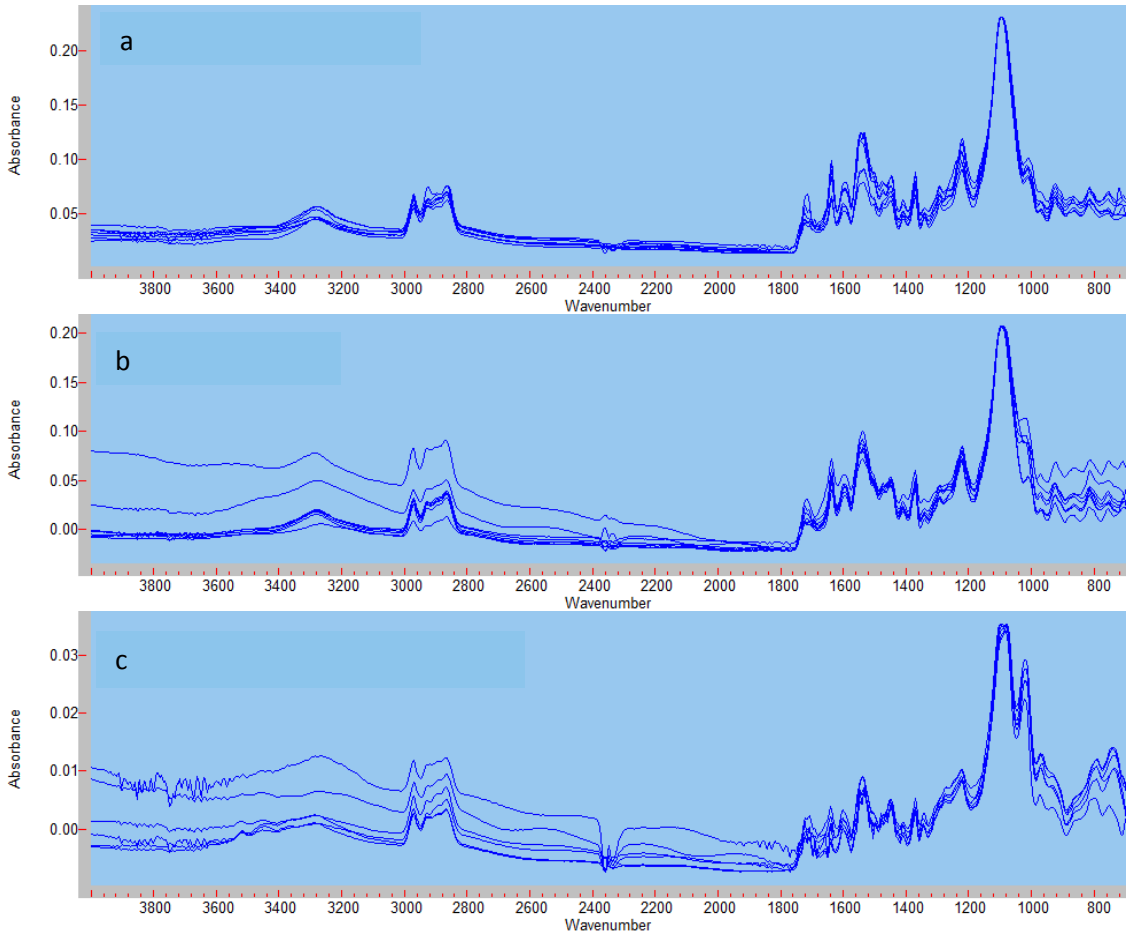


Figure 3.12: Overlaid spectra of foam samples a) From the mattress in each suite, b) From the armchair in each suite and c) Chairs with padded seat cushions from each suite, except Room 6.

The spectra collected from each of the chairs with padded seat cushions were overlaid for comparison and have been depicted in Figure 3.13. The spectrum (indicated with blue) was collected from Room 6 which, as discussed in Section 3.5.1 and Section 3.5.2, displayed some colour variation when compared with the remaining samples collected from the chairs with padded seat cushions. In addition, the sample collected from Room 6 was shown to be more consistent with the samples of foam collected from the mattress layers and the armchair from Room 6 as well as the remaining rooms.

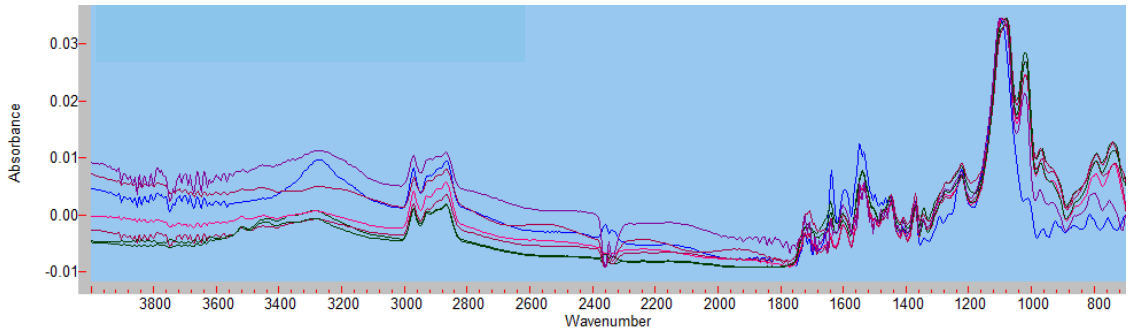


Figure 3.13: Overlaid spectra from the armchairs with wood. The sample collected from the armchair with wood used in Room 6 is highlighted blue.

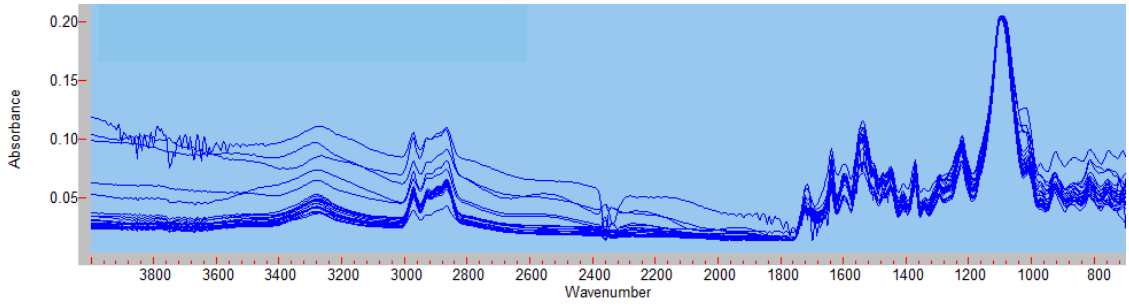


Figure 3.14: Illustrates the overlaid spectra of the foam samples collected from all of the mattresses and the pink armchairs and the armchair with wood in Room 6.

The consistency between the samples collected from all of the mattresses, armchairs and the single sample collected from the armchair with wood in Room 6 has been illustrated in Figure 3.14.

It is evident that there is variation, albeit minimal, between the spectra depicted in Figure 3.13 and Figure 3.14. It is postulated that the variation in the spectra is due to differences in the polymerisation process, which while producing the same polymer has arrived via an alternative pathway resulting in differences in cross linkages or the use of an alternative terminal group.

The variation displayed between the spectra of the samples collected from the armchairs with wood, illustrated in Figure 3.13 and the remaining foam sections collected at Fergus Falls, MN is not significant. The variation is likely to be process related and is not indicative of another individual polymer. This is based on the results presented in this chapter and considers the results of Chapter 2. The limitations of ATR-FTIR, when analysing polymers of

this size, were also considered as discussed in Section 2.5.3. With those aspects of the instrument considered it is suggested that it is reasonable to suggest that the foam used in the experimental burns at Fergus Falls, MN was flexible PU.

The spectra of sections of foam collected at the site in Fergus Falls, MN were overlaid with spectra of samples of sections of foam collected at the site in Montrose, MN and the spectra of sections of flexible PU foam with known values for density and hardness and in some cases a flame retarded sample. The result has been illustrated in Figure 3.15.

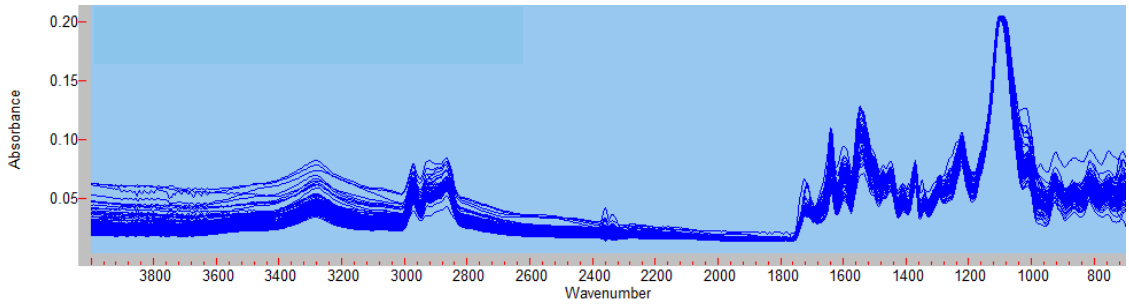


Figure 3.15: Overlaid selected spectra collected from Fergus Falls, MN and Montrose, MN.

When the results from Figure 2.16 and Figure 2.18 are compared with the results presented in Figure 3.15 it is reasonable to suggest that the samples collected from the experimental work conducted at Fergus Falls is PU, were polyether urethane.

3.5.4 Heat Release Rate (HRR)

The HRR for items used in the work conducted at Fergus Falls, MN has been estimated using values presented in Table 3—2.

Table 3—2: Peak Heat Release Rates (unconfined burning).

Fuel Package	*Reference*	*Mass (kg) (gross)*	*Peak HRR (kW)*
Easy Chair with PU	209	12.2 – 27.7	1350 – 1990
Mattress with PU	209	3.2 – 14.1	810 – 2630
Small Chair (some padding)	2	NA	150 – 250
Armchair (modern)	2	NA	350 – 750 (up to 1200)
Television set	209	31.3 – 32.7	120 – 290
Wastebasket, small	209	0.7 – 6.1	4 – 18
Office wastebasket with paper	2	NA	50 – 150
Gasoline in 0.61 m^2 pool	209	19	400

Although a selection of representative HRR values are presented in Table 3—2; not all of the values have been included in estimation for the total HRR required to achieve flashover in each of the rooms during the experimental work conducted at Fergus Falls, MN. Primarily due to the fact that not all of the items listed in Table 3—2 were used in every fire scenario. In addition, the collective HRR based on the combined individual items from the fuel load do not impact on the degree at which the fire progresses in the growth stage of a fire. This is discussed in some detail in Section 2.5.4.

It should be noted that the HRR of the other items in each room, such as the desk, dresser and beside table have not been included in the estimations for each room. They were not included as the main focus of the work was based on PU being a fuel load. As discussed in Chapter 3.4 and illustrated in Figure 3.7 the pink armchairs were used to form the initial fuel load in each room. Although the same furniture used to furnish each of the motel suites,

there were differences in the ventilation areas which impacted on the estimated peak HRR for each room. Based on the results of the estimations presented in Table 3—2, each room had the potential to progress to flashover depending on how many of the furniture items were impinged on my flame.

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.

Q_{fo}	*Thomas*	*Babrauskas*	*HRR of each rooms Fuel Package (kW)*
Room 1	1519.1	1783.5	4 – 10590
Room 2	1488.0	1723.9	400 – 10590
Room 3	1487.6	1723.9	400 – 10590
Room 4	1767.6	2284.7	4 – 10590
Room 6	2008.9	2761.9	400 – 10590
Room 7	1532.0	1788.8	4 – 10590
Room 8	1621.4	1989.0	4 – 10590
Room 9	1502.0	1721.2	400 – 10590

It should be noted that, as per discussion in Section 2.5.4, the McCaffrey, Quintiere and Harkleroads estimation was not utilised as the data required to determine h_k was not collected during the period when the experimental work was conducted.

3.5.5 Time Until Flashover

The record of the time until flashover was recorded, the results of which have been presented in Table 3—4. Additional data is also presented in the table including the volume of each room, the area of the ventilation opening and the mechanism of ignition, to help differentiate between the burns when making comparisons.

Table 3—4: Time until flashover (FO), Montrose MN.

Recording Type	Room 1	Room 2	Room 3	Room 4	Room 6	Room 7	Room 8	Room 9
Wrist Watch (min:sec)	15:20	No FO	7:19	18:23	No FO	No FO	No FO	No FO
Video Time Stamp (min:sec)	15:33	No FO	7:24	17:20	No FO	No FO	No FO	No FO
Volume (m^3)	46.34	46.18	46.15	46.04	46.35	46.05	46.31	46.50
Ventilation Opening Area (m^2)	1.609	1.609	1.609	1.811	2.043	NA	1.679	NA
Point of Ignition	Bin	Gas	Gas	Bin	Gas	Bin	Bin	Gas

3.5.5.1 Room 1 - Accidental

In Room 1 the ventilation point was restricted to the door only. The fire in Room 1 was allowed to progress naturally and after flashover had occurred the fire was suppressed.

3.5.5.2 Room 2 - Deliberate

Room 2 at the ignition of the fire the ventilation point was restricted to the door only. The fire in Room 2 did not achieve flashover and was subsequently suppressed.

3.5.5.3 Room 3 - Deliberate

In Room 3 at the ignition of the fire the ventilation point was restricted to the door only. The fire in Room 3 progressed to flashover and was subsequently suppressed.

3.5.5.4 Room 4 - Accidental

When the fire in Room 4 was ignited the ventilation areas, the door and west window, were fully open. The window design meant that when a window was fully open the area covered by glass when the window was closed was reduced by half. The fire in Room 4 was allowed to progress naturally and after flashover was noted the fire was suppressed.

3.5.5.5 Room 6 - Deliberate

In Room 6 at the ignition of the fire the ventilation points included the door and both windows. The fire in Room 6 did not achieve flashover and was subsequently suppressed.

3.5.5.6 Room 7 - Accidental

Initially, at ignition, the ventilation area in Room 7 was zero as both the windows and the door was shut. It could be clearly seen that the fire was not progressing and if left to develop naturally would not reach flashover. It was determined that the fire had become ventilation controlled and the door was opened at approximately five minutes. In addition, the south and east window were manually breached at approximately 12 and 15 minutes, respectively. Regardless, the fire in Room 7 did not progress to flashover and was suppressed.

3.5.5.7 Room 8 - Accidental

In Room 8 at the ignition of the fire ventilation was via the door and the northern window was half open and the west window was a quarter open. The propagation of the fire was limited and the northern window was manually breached at approximately ten minutes. The fire in Room 8 did not reach flashover and was subsequently suppressed.

3.5.5.8 Room 9 - Deliberate

At ignition the ventilation area in Room 9 was zero as the door and both windows were shut. The fire did not propagate and there was no intervention to introduce ventilation. The fire

self extinguished. At ignition the ventilation area in Room 9 was zero as the door and both windows were shut. The fire did not propagate and there was no intervention to introduce ventilation. The fire self extinguished.

3.5.6 Further Observations

Control over a greater number of experimental parameters was established at the burns conducted at Fergus Falls, MN. This is demonstrated by the uniformity displayed between the items of furniture used as the fuel load, including the foam used in the upholstery and where the furniture was placed in the room. In addition there was consistency among the materials on the surfaces of the walls, ceilings and floors of the rooms in addition to the volume of the rooms. The two methods of ignition were also consistent.

However one parameter, the area of ventilation, was varied. As discussed in Section 3.4 the control of the burns lay with the FFFD for the training of suppression crews and exposure to different types of fire scenarios. As a result a compromise was reached in this one aspect of the experimental design.

The variation in the ventilation was not completely different during each burn. For example Room 2 and Room 3 had the same experimental conditions but the results did not reflect that. Room 2 did not develop to flashover and, as it was clear that it would progress in a steady state, was subsequently suppressed; conversely Room 3 did develop to flashover. In addition Room 1 and Room 7 had all the same experimental conditions but only one of the rooms (Room 7) required intervention in terms of the creation of additional ventilation points and still the experiment did not proceed to flashover.

From the results it can be suggested that no specific trend was observed and that variation in ventilation areas and ignition mechanisms may have been an influence. Without additional repetitions of the experiment (where the ventilation parameters were repeated) it is difficult to substantiate that the use of the same kind of PU foam impacted on the time until flashover. Although, it could be postulated that there was the beginning of clustering of time until flashover for the specific mechanisms of ignition; although, again, the lack of repetition with regard to that parameter in conjunction with ventilation prevents stronger statements being made.

As was discussed in Section 2.5.4, and witnessed again in 3.5.4, having an excess of the estimated range of energy required for a flashover event to occur does not automatically lead to the occurrence of a flashover event occurring; only that it must be considered as a possibility.

3.6 Conclusion

The challenges identified during the work conducted at Montrose, MN were successfully addressed by the work described in this chapter. The site at Fergus Falls, MN had rooms that were comparable in size and construction. Despite improved standardisation of the experimental parameters, not all of the burns progressed to flashover. It is likely that the failure to reach flashover was due to the variation in the ignition mechanism and the area of ventilation. It was identified that additional standardisation of the experimental parameters was necessary in addition to locating a site in Australia. The challenges identified during the work described in this chapter were addressed in subsequent experimentation and has been described in detail in Chapter 4.

Chapter 4: Time Until Flashover, Queensland Combined Emergency Services Academy (QCESA), QLD

Chapter 4: Time Until Flashover, QCESA, QLD

4.1 Introduction

The work conducted at the Queensland Emergency Services Combined Academy (QESCA) was largely driven by the data gathered from prior work performed at Fergus Falls, MN and Montrose, MN. The method employed at Fergus Falls was refined to address the challenges identified while maintaining parameters that reflected a realistic scenario and allowed for repeatability.

The most significant challenge addressed during the three year period between Fergus Falls and QCESA was the search for a location in which further experimental work could be conducted.

Performing the experiments here in Australia significantly reduced logistical challenges associated with running experimental work in the USA. For example, samples could be transported back to the laboratory in Sydney with greater ease, which allowed for a larger sample size to be collected. Also, equipment transport was more economical, which allowed more freedom in the scope of all aspects of the work.

The disadvantage to conducting the experimental work in-country was the considerable financial outlay. Unlike the USA, the Australian Government does not offer a financial benefit (in the US it is in the form of a tax deduction) to those donating a house to a not-for-profit organisation. In addition, obtaining permission to conduct burning of any sort is subject to the discretion of the controlling bodies in each municipality.

Having acknowledged that a site in Australia was desirable, the unique set of challenges associated with conducting large scale test burns and the subsequent sampling of pre- and post suppression atmospheres left the author with only two options. Those were the facilities at Swinburne University of Technology (SUT), Victoria and QCESA, both of which have inbuilt filtration systems. At the time the experimental work was conducted, proactive measures had been taken by QCESA to comply in advance with proposed modification to legislation restricting the concentration of toxicants in the atmosphere.

Although the site at SUT was more attractive in terms of costs, there was significant concern about the location of the cell within an undergraduate teaching facility. The presence of students during teaching periods would have introduced additional logistical and safety challenges. The smaller dimensions of SUT's available cell could not accommodate the parameters for investigating a large scale burn, and the fuel load permissible there was inadequate. However, the facility at QCESA was purpose-built and allowed for the safe management and control of test burns designed and conducted for teaching and research purposes.

Conducting the experimental work at Queensland's purpose-built facility, rather than having to rely on donated structures, alleviated the necessity to collaborate with other parties when sharing their sites. Thus, the need to compromise aspects of the method to align with the requirements of other parties' agendas was eliminated.

4.2 Site Description

The site, known as QCESA, at Howard Smith Drive, Whyte Island, Lytton QLD is a purpose built facility, part of which is dedicated to the practical and theoretical training of probationary fire fighters including competency maintenance training of experienced members. The site also supports research into fire sciences. The section of the site utilised for this study was a facility run by the Queensland Fire and Rescue Service. The site reserved for fire training and fire science related work held a number of structures that were purpose built to allow for the repeated ignition of fires that would mimic realistic fire scenarios.

The area utilised for the work conducted in this series of experiments was located inside a warehouse that had corrugated iron sheeting walls and roof with a concrete floor. Inside the warehouse were four purpose built burn cells. The cells were of comparable size and contained comparable internal coverings. The cells were furnished with items from a common source and that were of similar age. The ignition mechanism and ventilation area was constant throughout the individual burns. Following ignition the time it took for flashover to occur was recorded.

Figure 4.1: Warehouse within QCESA facility housing four shipping containers (burn cells).

The burn cells, which were constructed from shipping containers, were of comparable size and housed within the larger warehouse structure (see Figure 4.1 above). The warehouse had recently been retrofitted with a filtration scrubber system at the apex of the roof. The filtration system had been added as a proactive step taken by the sites administrators to pre-empt proposed changes to environmental pollution legislation in QLD.

Each burn cell casing consisted of one half of a small steel shipping container; except the front wall which had been made from thin metal sheeting and was not lined with plaster board. Plaster board (15 mm thick) was used to line the ceiling and the remaining walls, while the floor was lined with brick and laid with carpet. Additional material, like insulation in the walls and roof tiling, had not been included in the construction of the burn cells.

The burn cell dimensions have been presented in Table 4—1.

Table 4—1: Burn Cell Dimensions and Fixtures, QCESA, QLD.

Features	*Burn Cell A*	*Burn Cell B*	*Burn Cell C*	*Burn Cell D*
Room Height (mm)	2580	2600	2600	2590
Room Width (mm)	2290	2270	2300	2260
Room Length (mm)	2830	2835	2830	2820
Volume (m^3)	16.72	16.73	16.92	16.51
Height of Opening (mm)	2045	2050	2050	2040
Width of Opening (mm)	800	805	805	810
Ventilation Area (m^2)	1.636	1.650	1.650	1.652
Flooring	Carpet laid over brick	Carpet laid over brick	Carpet laid over brick	Carpet laid over brick
Ceiling, Side and Back Wall	Plaster Board	Plaster Board	Plaster Board	Plaster Board
Front Wall	Sheet metal	Sheet metal	Sheet metal	Sheet metal

Each of the burn cells was hard wired with a thermocouple; though the in-house thermocouples were not utilised during the work presented in this chapter as each experimental burn was fitted with an array of thermocouples custom designed specifically for the work.

Figure 4.1 demonstrates that the burn cells were not connected by a roof or walls which eliminated the possibility of fire spread to the next burn cell during an experiment. Note the Figure 4.2 is a schematic representation only and is not drawn to scale.

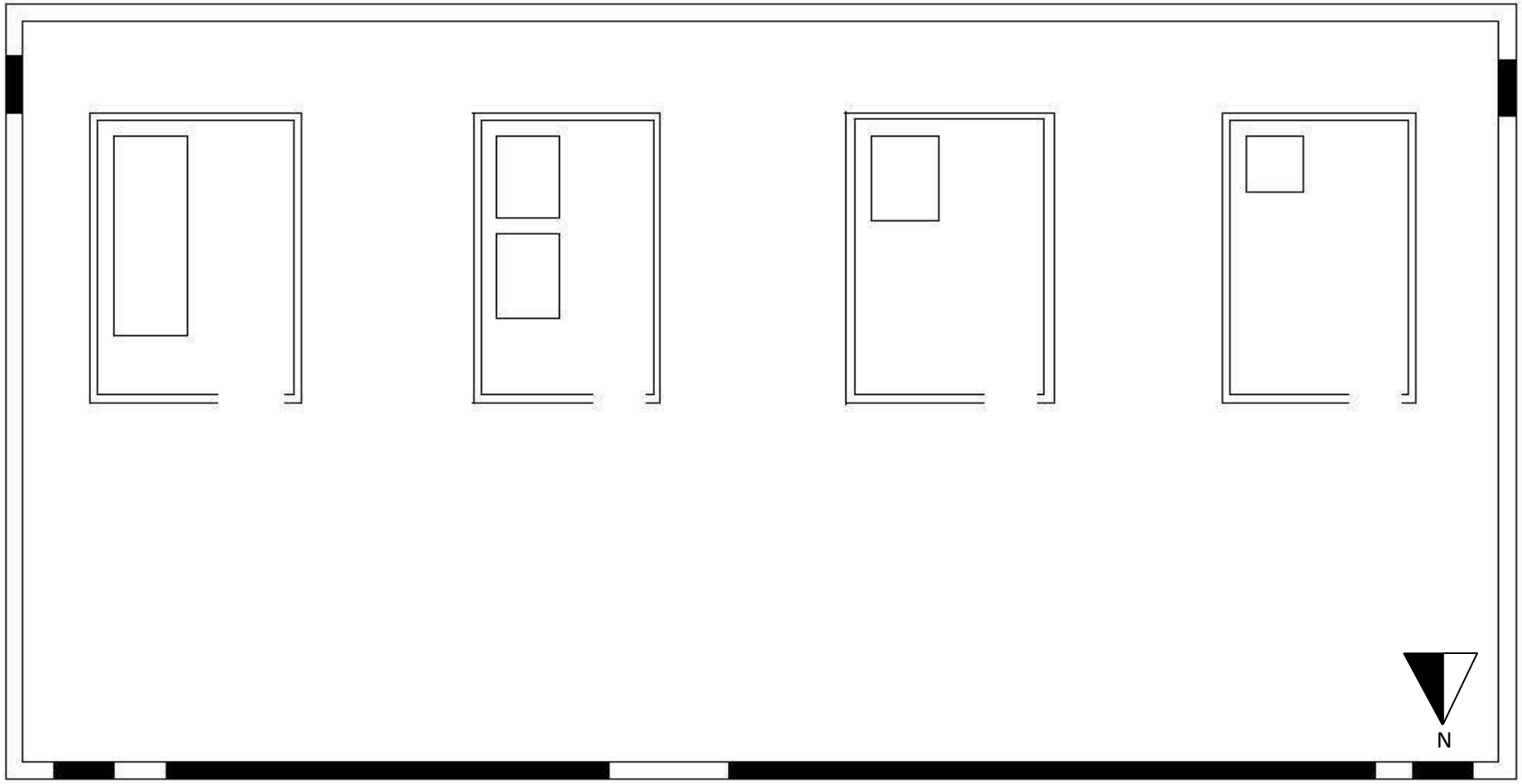


Figure 4.2: ***Schematic showing how each scenario was set up, including the couch placement for Burns 1 - 6, two armchair placement for Burns 7 – 12, single armchair placement for Burns 13 – 15 and the placement of the smaller armchair placement for Burns 16 – 18.***

The experimental work, including experimental set up and the burns themselves, took place over a two week period; though the burns were conducted over seven individual days. The temperature range and rainfall was recorded by the Brisbane Aero and Caltex Refineries respectively and is summarised in Table 4—2.

Table 4—2: Temperature Range and Rainfall.

Dates	*Minimum ˚C*	*Maximum ˚C*	*Rainfall mm*
Burn Day 1 (9/2/10)	21.7	29.1	2.2
Burn Day 2 (10/2/10)	21.5	28.8	7.4
Burn Day 3 (11/2/10)	20.7	29.1	0.0
Burn Day 4 (12/2/10)	20.0	29.6	0.0
Burn Day 5 (15/2/10)	24.0	31.2	0.0
Burn Day 6 (16/2/10)	24.2	30.5	6.2
Burn Day 7 (17/2/10)	21.1	27.8	28.8

The weather was recorded though it is proposed that the impact on the experimental burns of the moisture and temperature gradient would have been negligible. When compared with the work conducted at Montrose and Fergus Falls, MN, as the experimental burns were conducted in cells that were housed inside a warehouse, and were therefore protected to a larger extent from the environment. This brought the work more in line with existing standards and guidelines [21, 52-53]. The effect or lack of effect, the external environment had on the cell environment was illustrated having recorded a consistent temperature inside the cell throughout the day on each burn day. To reduce the potential for the furniture to become moist, which would affect ignition, the items were housed in a secure dry location until needed.

4.3 Sample Description

The furniture used in the test burns conducted at QCESA, QLD was donated by UTS following four years of use in common areas. As with the experimental burns conducted in the USA, the furniture for these burns was obtained from a single source and was of consistent age, size and appearance. However, unlike the furniture sourced for the burns undertaken in the USA, the manufacturer of this furniture and the foam was known to be Australian. The

furniture pieces were from the *Anibou Longreach* design range and the PU foam reported by the manufacturer as having been used in the cushions was *feather-topped fire-retardant foam*. Information pertaining to type of retardant used with the foam was not supplied, or available.

The design of the furniture was consistent and it was manufactured at the same company, therefore it was not initially considered that there would be significant variation in the furniture items. It was not until after the items had been accepted and transported to QLD that the variation in size and mass within the six couches and the 18 armchairs was noted.

Of the six couches there was one that was significantly smaller and it was noted that there was some variation among the remaining five. Figure 4.3 is an exemplar of the larger couches used in Burns 1 – 5, and all five couches in that series were of very similar dimensions (refer to Table 4—3). In total, six three-seater couches and 18 armchairs were divided up and used as the fuel package for 18 experimental burns, which represented three different fire scenarios each repeated six times.

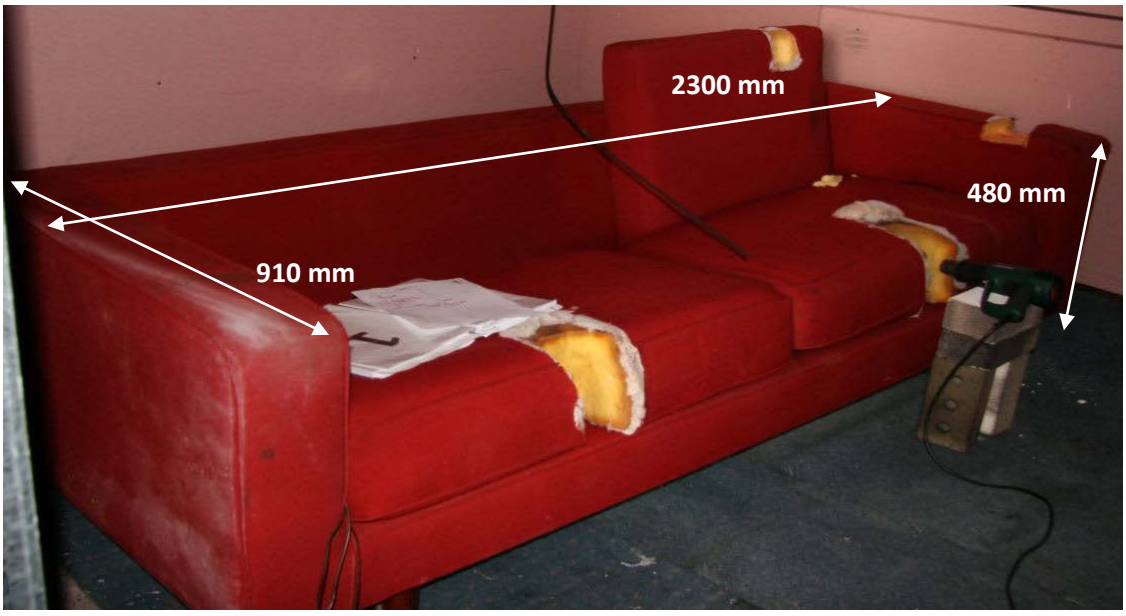


Figure 4.3: Representative exemplar of the larger couches used in Burns 1 – 5.

The image depicted in Figure 4.4 is the couch that was used in Burn 6. From the dimensions included it can be seen that the couch was significantly narrower than those used in Burns 1 – 5 and longer.

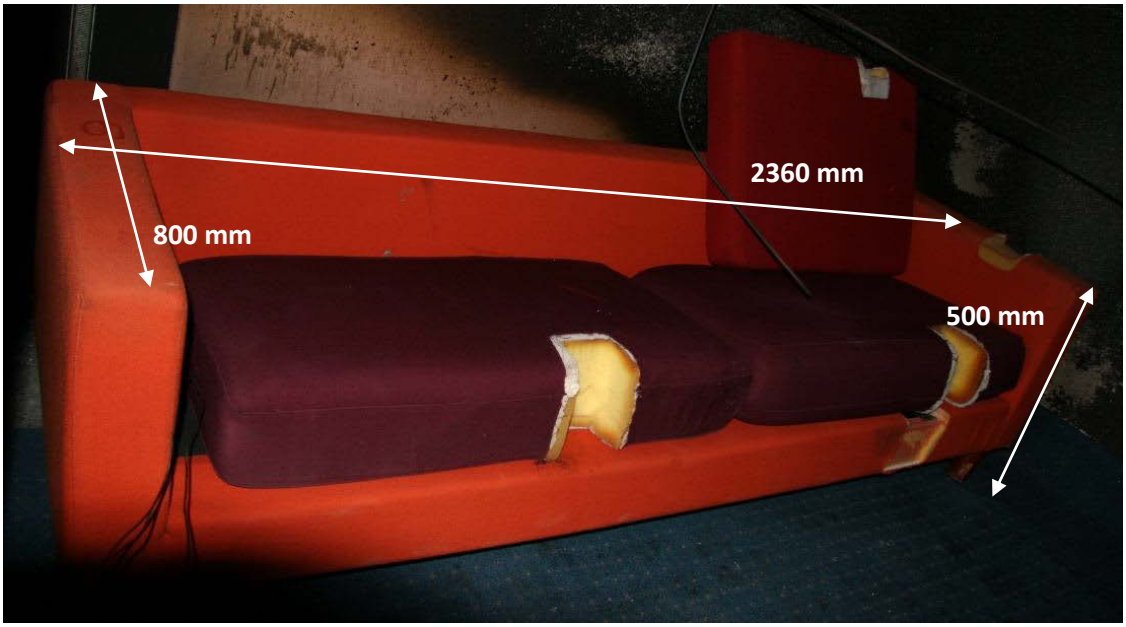


Figure 4.4: Couch used in Burn 6.

It was also noted that, from the group of 18 armchairs, three were significantly smaller. In addition, there was slight variation within the dimensions recorded for the remaining 15 armchairs. Figure 4.5 shows representative exemplars of the armchairs used in Burns 7 – 15 (a) and Burns 16 – 18 (b) respectively.

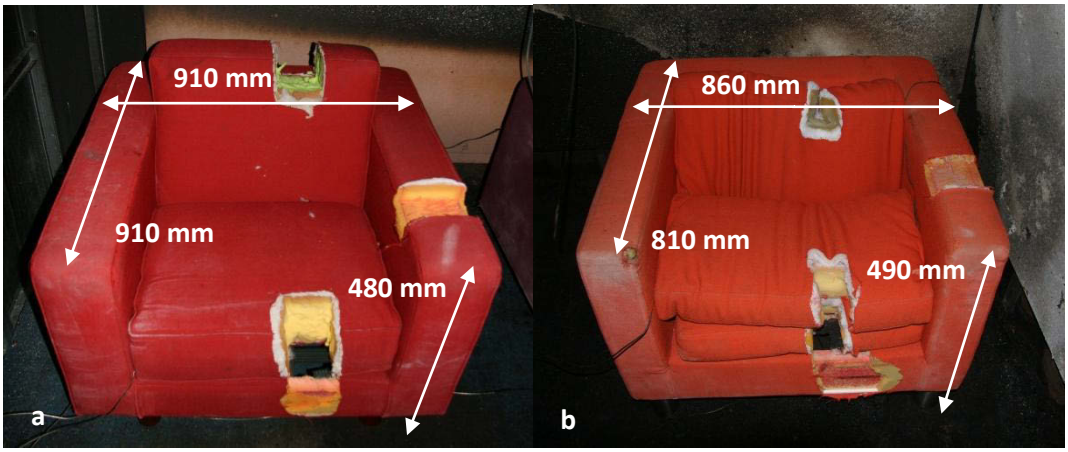


Figure 4.5: (a) Larger one seater armchair used in Burns 7 – 15 (b) Smaller one seater armchair used in Burns 16 – 18.

While it was initially believed, due to their common origin, design and manufacture, that the items sourced were of the same size and mass it can be seen from the data presented in Table 4—3 that even when the same type and style of furniture is obtained there is inter-sample variations. It should be noted here that the height measurement recorded in Table 4—3 was from the ground to the top of the seat cushion. Samples of the PU used in the manufacture of the furniture were collected from each area of the individual piece of furniture, and the mass was recorded after the sample was collected. The area where samples of the PU were collected is clear in Figure 4.3, Figure 4.4 and Figure 4.5. The frame for the couches and the armchairs was constructed from wood.

Table 4—3: QCESA Furniture Dimensions.

	Length (mm)	*Width (mm)*	*Height (mm)*	*Mass (kg) (gross)*
Burn Number	***3 Seater Couch***			
1	2300	920	470	58.00
2	2300	910	480	58.70
3	2310	910	480	58.40
4	2285	910	480	56.55
5	2300	910	480	58.05
6	2360	800	500	47.85
Burn Number	***2 Armchairs***			
7	(i) 900 (ii) 890	(i) 900 (ii) 900	(i) 480 (ii) 480	(i) 34.04 (ii) 33.42
8	(i) 900 (ii) 910	(i) 910 (ii) 910	(i) 480 (ii) 480	(i) 32.86 (ii) 33.90
9	(i) 910 (ii) 910	(i) 910 (ii) 910	(i) 480 (ii) 480	(i) 33.20 (ii) 33.80
10	(i) 890 (ii) 890	(i) 910 (ii) 910	(i) 505 (ii) 500	(i) 33.56 (ii) 33.88
11	(i) 900 (ii) 910	(i) 920 (ii) 910	(i) 450 (ii) 500	(i) 34.00 (ii) 33.70
12	(i) 910 (ii) 910	(i) 920 (ii) 920	(i) 425 (ii) 490	(i) 34.34 (ii) 33.64
Burn Number	***1 Armchair***			
13	890	900	490	34.02
14	900	910	470	34.02
15	900	910	480	33.74
16	860	810	490	23.52
17	860	810	480	23.12
18	870	810	510	21.78

4.4 Method

The test burns took place over a two week period. The temperature range and rainfall was recorded by the Brisbane Aero and Caltex Refineries respectively.

The site was chosen, in part, as the burn cells had the capacity for burns to be repeatedly conducted. This meant that the volume of the cell and the area of ventilation point would remain consistent throughout the experiments. In addition, for the work undertaken in this chapter parameters that had been similar but not strictly consistent were controlled more stringently.

Namely, the fuel package for each experimental burn would be consistently placed in the burn cell. For each burn the placement of each item of furniture was recorded, with respect to its placement from the wall, at a number of points from the couch.

Figure 4.6: Example of three seater couch placement repeated for Burns 1 – 6.

While Figure 4.6 provides a visual representation of the how the three seater couches were placed, and subsequent figures (Figure 4.7 and Figure 4.8) illustrate the how the two armchair and one armchair scenarios were configured respectively, what they do not do is give an appreciation of the how far from the wall the pieces of furniture were.

Figure 4.7: ***Example of how the two armchair, Burns 7 – 12, were configured.***

Figure 4.8: ***Example of how the single armchair, in Burns 13 – 18, was configured.***

The position of where the furniture was with respect to its location to the wall and in the case of Burns 7 – 12 with respect to each other, was recorded and an example has been provided in Figure 4.9.

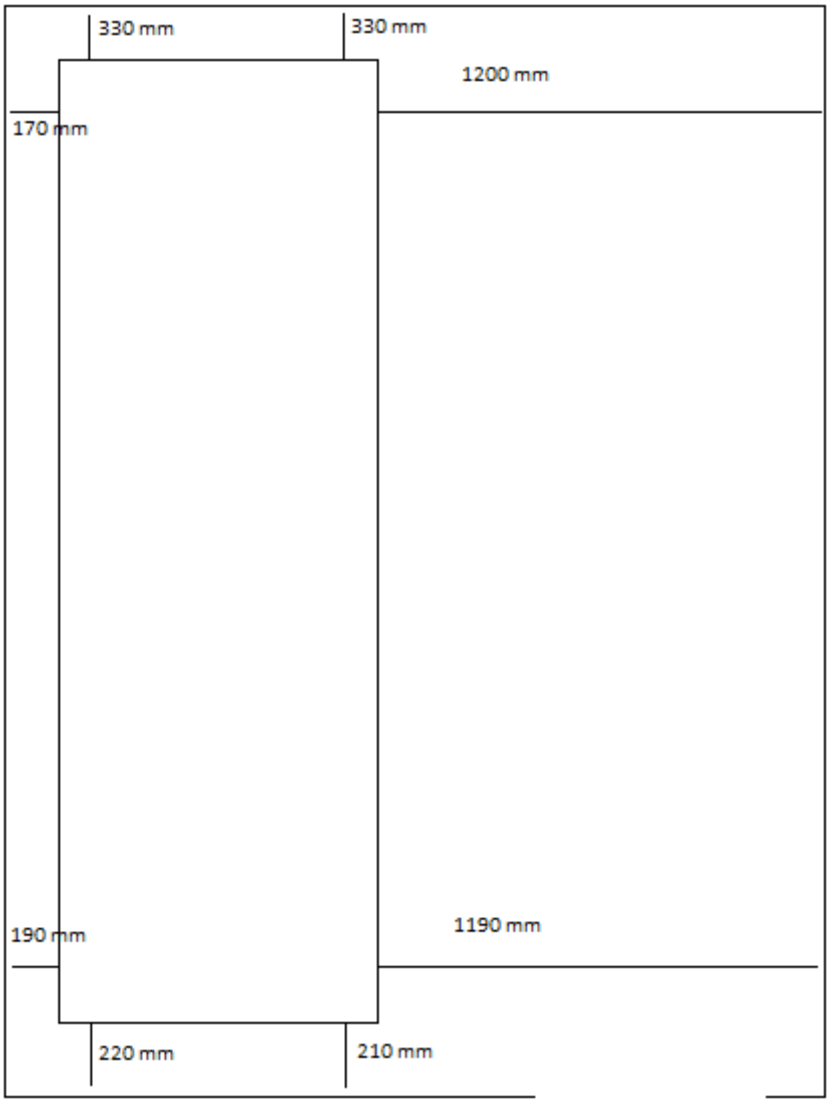


Figure 4.9: ***Example of the measurements recorded of the distance of the couch from each wall. The values recorded in this schematic are taken from Burn 1. Schematic not drawn to scale.***

Unhindered (and safe) visual access to the fire was paramount so that it could be determined when flashover was imminent, or occurring. In addition, an array of thermocouples was placed inside the burn cell to track the growth of the fire based on the temperature gradient. This would verify, after analysis, if flashover based on temperature had occurred. The dimensions and properties of what was considered ideal in a k-type thermocouple were given to *Temperature Controls Pty Ltd*. The schematic presented in Figure 4.10 is what was developed based on the specifications provided.

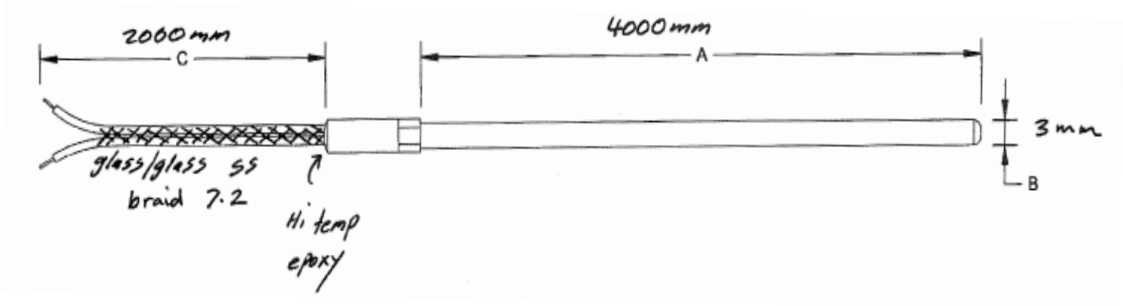


Figure 4.10: Schematic of k-type thermocouple.

It was anticipated that the temperature range during the test burns would range from ambient to approximately 1000 °C. It was essential for the thermocouples to have a number of design features in order to satisfy the recording and safety requirements identified during the development of the method. In order to operate across the anticipated temperature range the hardware of the thermocouple would have to be robust so as to survive multiple exposures to elevated temperatures, they would need to be malleable to allow for manipulation within the cell and they would have to be of sufficient length to allow for the data collection to occur at a safe distance from the test burn.

A number of thermocouples were considered, however it was determined that k-type were the most suitable.

The schematic does not show the addition of an extension lead to extend the distance of the data logger from each burn cell. This was primarily to protect the operator from radiant heat, although there was a measure of protection with respect to the instrument also.

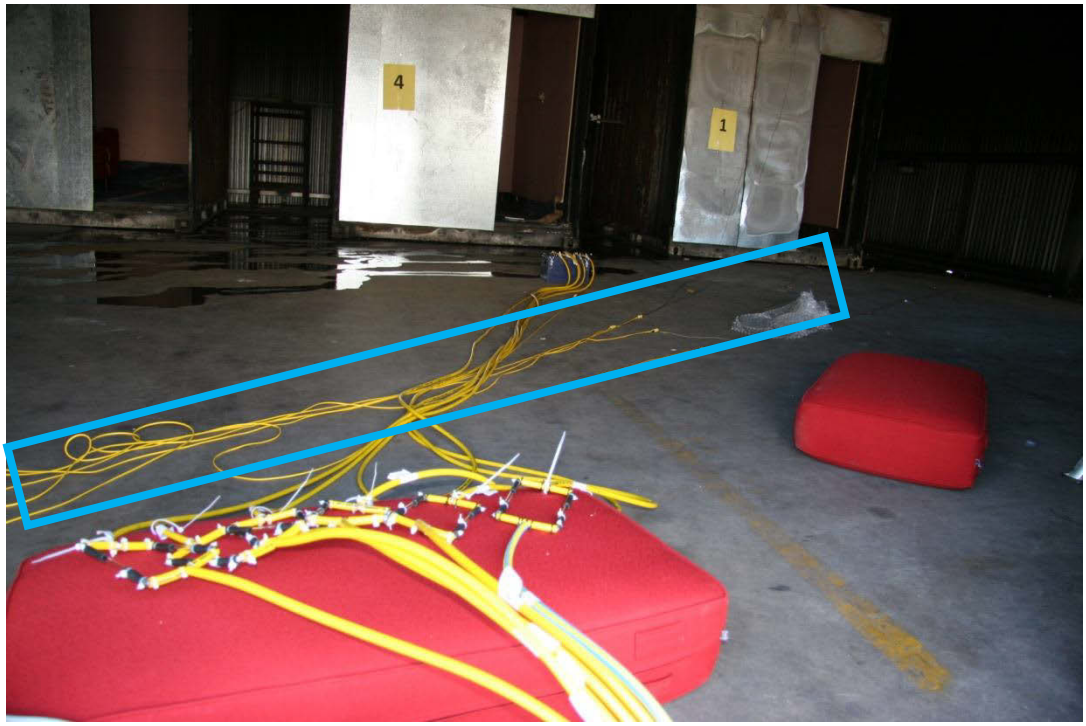


Figure 4.11: Image indicating the position of the data logger at the edge of the warehouse perimeter. The blue box indicates the thermocouple extension leads spanning from the cell to the edge of the warehouse.

Data from the thermocouple array, which included eight thermocouples in the burn cell, was logged at 0.1 sec intervals using a *DeLogger4 Datataker Pty Ltd* to capture the temperature gradient throughout the progression of the fire.

During the set up of the experiments four 5 mm holes were drilled in through the exterior and plaster board of each of the cells to accommodate the threading the thermocouples through. This ensured the uniform positioning of the array for each burn.

The schematic presented in Figure 4.12 indicates where the holes were drilled in each cell. Thermocouple one, two and three were placed inside the couch, or armchair, during the burn.

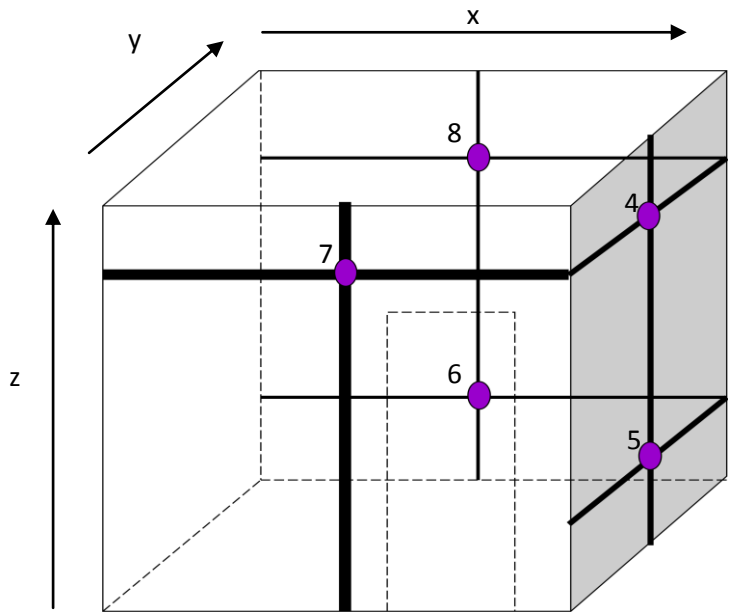


Figure 4.12: Schematic of where thermocouples were introduced into each burn cell.

The position of the thermocouple tip was recorded using an *x, y, z* to define the planes. An example of the position of each of the exposed thermocouples has been presented in Table 4—4. Thermocouple number one, two and three are not included in the table as they were inside the couches, armchairs or at the entrance to the cell, during the fire.

Table 4—4: Thermocouple Position in Burn Cells.

Thermocouple Number	*x (mm)*	*y (mm)*	*z (mm)*
4	2028	1540	375
5	2060	1540	1750
6	1150	2370	2180
7	1130	1260	2230
8	1130	2525	1190

The consistency in the repetition of the placement of the fuel package for each burn allowed for the point (and mode) of ignition to be repeated for all the experimental burns, regardless of the size of the fuel package. For each burn the point of ignition was repeated and the fire was initiated using a hand held propane torch. The flame from the propane torch was applied to the vertical surface of the couch, or armchair, in the area displayed in Figure 4.13.

Figure 4.13: An example of the point and mechanism of ignition used throughout the experimental burns.

The flame from the torch was not removed until the flame on the surface of the couch or armchair was providing the fuel to the fire. No other accelerant, such as an ignitable liquid like petrol, was introduced to any of the scenes.

For each of the experimental burns the fires were allowed to progress without interference to the ventilation areas, as the area of ventilation could not be manipulated (open or closed). Directly after the fire had progressed to flashover it was suppressed. So as not to wet the remaining fuel package extensively, as well as the burn cell, a method of fire suppression designed to reduce the amount of water required for suppression was used.

Each burn was recorded using digital video and the time until flashover was based on the time stamp of the recording. As was the case at Montrose and Fergus Falls, MN T_0 was defined as the moment the ignition source was removed from the surface of which it was igniting.

After suppression, each item of furniture was removed from the cell to allow any residual moisture to dissipate. Then, after at least 24 hours, what remained of the fuel load from each experiment was weighed and the mass remaining was recorded.

Sections of foam from the individual items of furniture were collected, ensuring that samples from each area of the item was represented. The samples were transported back to UTS for analysis.

In conjunction with using a fire suppression method designed to reduce the amount of water introduced to a scene, each burn cell was *rested* between burns. Burn cells were rested for at least twelve hours before being utilised again, and in the case between Burn Day 4 and Burn Day 5 at least 48 hours elapsed due to no burns being conducted over the weekend as the facility was shut. This ensured that the each cell was as dry as possible prior to another fire being initiated. The experiments were conducted using the sequence outlined in Table 4—5.

Table 4—5: Burn cell use.

3 Seater Couch				
Burn Number	**Burn Cell A**	**Burn Cell B**	**Burn Cell C**	**Burn Cell D**
1				Burn Day 1
2		Burn Day 2		
3	Burn Day 2			
4			Burn Day 2	
5			Burn Day 3	
6				Burn Day 3
2 Armchairs				
7		Burn Day 3		
8		Burn Day 4		
9			Burn Day 4	
10			Burn Day 5	
11		Burn Day 5		
12	Burn Day 5			
1 Armchair				
13	Burn Day 6			
14			Burn Day 6	
15				Burn Day 6
16				Burn Day 7
17			Burn Day 7	
18		Burn Day 7		

4.5 Results and Discussion

4.5.1 Visual Analysis

The foam used to upholster the furniture, was labelled by the manufacturer as PU. Therefore, the samples collected from the furniture were subjected to visual analysis primarily for the purposes of logging the morphological features of the samples. Generally, it has been illustrated that the cushions have wider sections of foam and the foam used to upholster the arm and back rest as well as the skirt uses a thinner section of foam. The PU foam samples collected from the three seater couch scenario, Burns 1 – 6, were visually catalogued and have been presented in Figure 4.14.

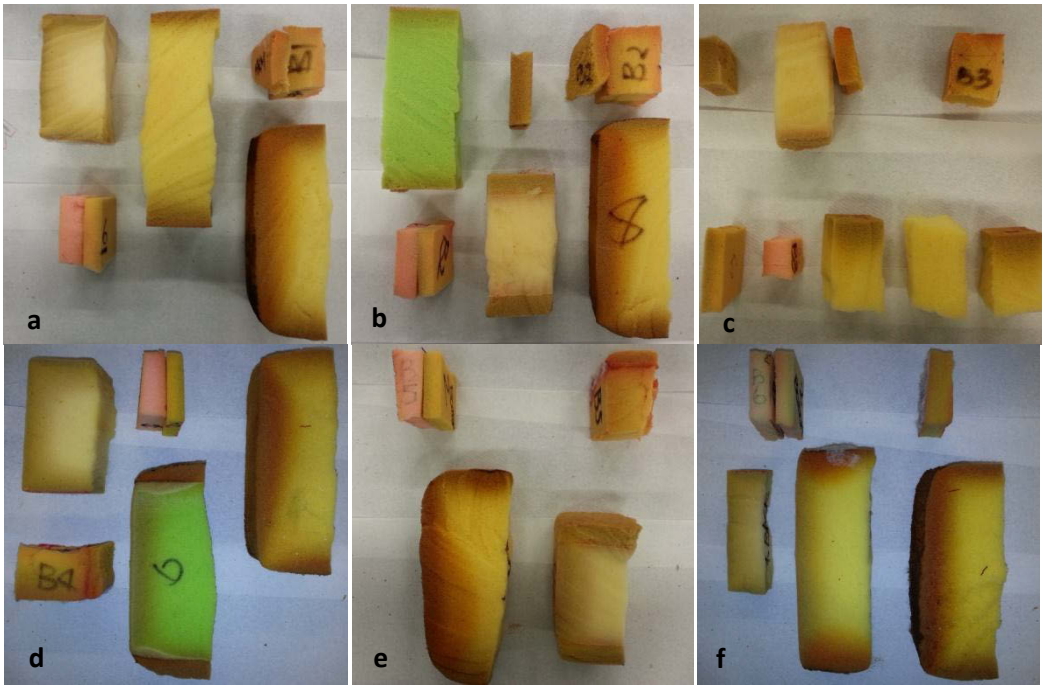


Figure 4.14: PU foam samples collected from the three seater couches used in: a) Burn 1 b) Burn 2 c) Burn 3 d) Burn 4 e) Burn 5 f) Burn 6.

It can be seen in Figure 4.14 that the PU foam used to upholster the three seater couches was not uniform. The foam used for the arm and back rest as well as the skirt is consistent.

Figure 4.6, Figure 4.7 and Figure 4.8 illustrate that the collection site of the PU samples are consistent throughout the different lots of fuel load used in experimental burn. Even though the collection site remains consistent it is clear that variation in terms of the colour of the foam is evident. It was postulated, based on the results from the foam analysis performed in Sections 2.5.2-2.5.4 and 3.5.2-3.5.4, that although morphological variation was noted at a macro and micro level that there was little, if any variation, in the identity of the polymeric material that forms the bulk of the foam.

Figure 4.15 illustrates that the PU foam used to upholster the armchairs used as the fuel load in the two armchair scenarios, Burns 7 – 12. It is evidence that there was greater uniformity with regards to the kind of PU used for the upholstering process of the armchairs.

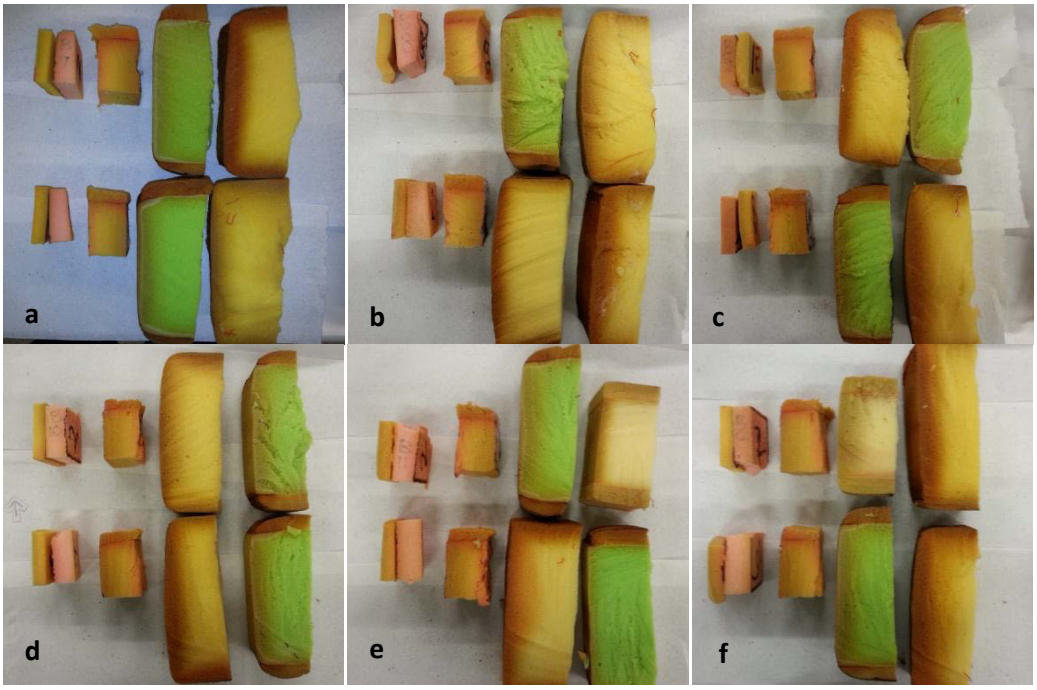


Figure 4.15: ***PU foam samples collected from each of the two armchairs used in: a) Burn 7 b) Burn 8 c) Burn 9 d) Burn 10 e) Burn 11 f) Burn 12.***

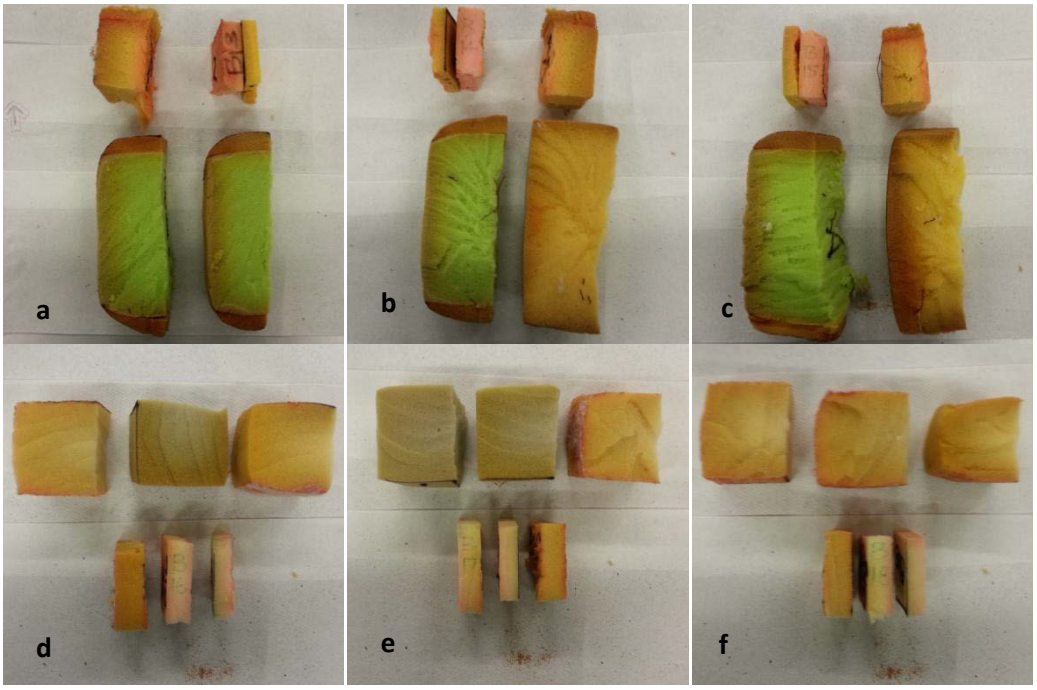


Figure 4.16: ***PU foam samples collected from the single armchairs used in: a) Burn 13 b) Burn 14 c) Burn 15 d) Burn 16 e) Burn 17 f) Burn 18.***

The foam samples collected from the fuel load used for the single armchair scenario, Burns 13 – 18, were compared and have been presented in Figure 4.16. It is clear that there is

consistency between the foam used to upholster the arm and back rest and the skirt, however the variation between the morphology of the foam used for the cushions in Burns 13 – 18 and Burns 16 – 18 is evident.

The assortment of different coloured and sized PU foam prompted consideration of the occurrence of each kind of PU foam in each burn. The foam was sorted based on colour and it was identified that there were eight different colours of foam used in the upholstering of the furniture used. The largest singular pieces of PU were the cushions and were identified as *green*, *long yellow* or *short yellow* and labelled in Figure 4.17 as A, B or C respectively. Thinner samples used to upholster the frame were identified as *double layer* and *yellow squares* which have been labelled in Figure 4.17 as D and E respectively.

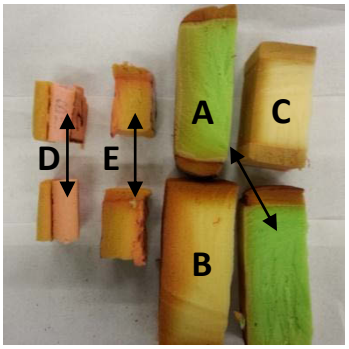


Figure 4.17: A) Green, B) Long Yellow, C) Short Yellow, D) Double Layer, E) Yellow Squares.

The less prevalent PU foam was identified as *short pink*, *white pink* and *other* which have been labelled in Figure 4.18 as F, G and H respectively.

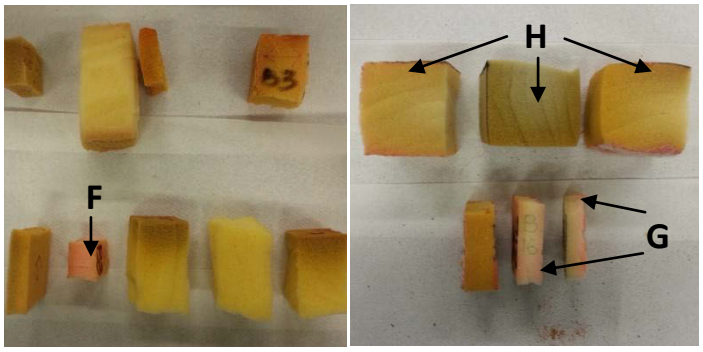


Figure 4.18: F) Short Pink, G) White Pink, H) Other.

To determine the specific spread of the PU foam throughout the burns, the foam used in each burn was itemised. Table 4—6 lists the results of the foam distribution among the experiments.

Table 4—6: Distribution of PU Foam Per Burn.

	3 Seater Couch							
Burn #	**Green (A)**	**Long Yellow (B)**	**Short Yellow (C)**	**Double Layer (D)**	**Yellow Squares (E)**	**Short Pink (F)**	**White Pink (G)**	**Other (H)**
1		Y	Y	Y	Y	Y		
2	Y	Y	Y	Y	Y	Y		
3				Y	Y	Y		Y
4	Y	Y	Y	Y	Y	Y		
5	Y	Y	Y	Y	Y	Y		
6	Y	Y	Y		Y		Y	
	2 Armchairs							
7	Y	Y		Y	Y	Y		
8	Y	Y		Y	Y	Y		
9	Y	Y		Y	Y	Y		
10	Y	Y		Y	Y	Y		
11	Y	Y	Y	Y	Y	Y		
12	Y	Y	Y	Y	Y	Y		
	1 Armchair							
13	Y			Y	Y			
14	Y	Y		Y	Y	Y		
15	Y	Y		Y	Y	Y		
16					Y		Y	Y
17					Y		Y	Y
18					Y		Y	Y

It can be seen from Table 4—6 that the foam common to the majority of the furniture items were the *yellow squares, double layer* and *short pink*, this was not surprising due to those examples of foam being used to cover the frame of the furniture. It can also be seen that *green* and *long yellow* show prevalence in the majority of the experiments due to the use of that foam in the cushions.

The results of the visual analysis conducted on the sections collected at QCESA were compared with the macro results of the known PU foam and latex foam samples that were Australian made which were presented in Section 2.5.1. In addition, the results of the macro visual analysis of the sections of foam collected at Montrose and Fergus Falls, MN, discussed

in Section 2.5.1 and 3.5.1 respectively, were reviewed. It was postulated that as the foam had been identified by the manufacturer as PU, in conjunction with the results of the comparison with earlier results, that the foam was PU and continued analysis would not be required to determine the nature of the foam.

Further, the results from Fergus Falls, MN highlighted that a scenario with consistent PU in addition to repeated experimental parameters, did not reliably lead to uniform results. Therefore, it was recommended that continued analysis to characterise the polymer would not have been beneficial.

4.5.2 Heat Release Rate (HRR)

The method used to estimate the HRR has been repeated in accordance with what was previously outlined in Section 2.5.4. In addition the MQH method of estimating HRR was used as a prediction model.

$$\dot{Q}_{f_0} = 610\,[h_k A_t A_0 \left(h_0{}^{0.5}\right)^{0.5}$$

Where:

h_k = convection coefficient – this can also be an estimation (calculated by estimating room temperatures and the likelihood of flashover using fire test data correlations)

$h_k = k/\delta$

where:

k = thermal conductivity of the wall material (gypsum plaster 0.48 W/mK)[1]

δ = wall thickness

Or,

$h_k = \sqrt{\rho ck/t}$

where:

ρ = density of the wall material

c = specific heat of the wall material

k = thermal conductivity of the wall material

t = time of exposure

The thermal conductivity of the wall material (gypsum plaster) and the thickness of the wall was known (0.015 m) therefore k/δ was used to determine the convection coefficient.

The results of the estimated HRRs from Thomas, Babrauskas and MQH have been presented in Table 4—7.

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.

Q_{fo}	*Thomas*	*Babrauskas*	*MQH*
Cell A	1178.75	1754.65	1025.41
Cell B	1187.72	1772.10	1030.80
Cell C	1189.88	1772.10	1034.57
Cell D	1183.90	1770.10	1025.31

In addition, a more diverse range of the values for Peak HRRs for couches and chairs has been included in Table 4—8 to illustrate that there is variation in values available for modern furniture and to stress that this method of HRR determination is an estimation only based on a number of factors. Alternative HRRs for items of furniture upholstered using natural fibre have also been included in the table for comparative purposes.

Table 4—8: Peak Heat Release Rates.

Fuel Package	*Reference*	*Mass (kg) (gross)*	*Peak HRR (kW)*
Sofa with PU	209	51.3	3120
Sofa (synthetic padding and covering)	2	NA	1000 – 3000
Easy Chair with PU	209	12.2 – 27.7	1350 – 1990
Recliner (synthetic padding and covering)	2	NA	500 – 1000
Armchair (modern)	2	NA	350 – 750 (up to 1200)
Small Chair (some padding)	2	NA	150 – 250
Cotton easy chair	209	17.7 – 31.8	290 – 370
Cotton mattress	209	11.8 – 13.2	90 - 970

Based on the recorded mass of the couches and armchairs used in the experiments (reported in Table 4-2) it can be seen that the value published for *Sofa with PU* and the upper value for *Easy Chair with PU* are below the initial mass recorded of the furniture used in Burns 1 – 6 and Burns 7 – 15 respectively. Therefore the values have been used as a conservative estimate for HHR for the couches and armchairs used in the first 15 burns. The armchairs used in Burns 16 – 18 lie within the mass range published for *Easy Chair with PU*. The values published for HRR that are accompanied with a mass allow for a comparison to be drawn based on the style of the item of furniture in conjunction with the mass. However, the percentage mass of PU present in the furniture, or the mass of the furniture itself is not always indicated [2-3] that illustrates why these values are considered as guidance not absolute.

Thus, when the estimated values for the HRR generated by the fuel load were compared with the estimation of the HRR required for the cells used in this work to progress to flashover, each of the experimental burns were considered to have the potential to progress to flashover.

4.5.3 Mass Remaining

The complete mass of the furniture pre-flame and post suppression was recorded instead of removing the PU from the frame and recording the PU and the frame independently. Primarily this was done to remain consistent with the main ethos of the work which was, to determine the time until flashover based on the amount of PU in a cell or structure, in the most holistic and realistic fashion possible. Fundamentally that meant eliminating as much interference to, or manipulation of, the fuel load (and or the cell) to maintain authenticity.

Therefore a number of realities were considered; extra furniture was not available so choosing one item from each group to destroy to get an estimation of the PU present would have negatively impacted the work. The project, to repeat three realistic situations six times each, would have been compromised by either introducing a dismantled and reassembled fuel load, or by completely removing an exemplar. The reduction of experimental burns in this series of tests would have impacted on the work discussed in Chapter 6. It was therefore determined that recording the initial mass and percentage mass remaining was the best approach.

Table 4—9: Percent Mass Remaining, Three Seater Couch.

Three Seater Couch			
Burn Number	**Burn Cell Used**	**Initial Mass (kg)**	**% Mass Remaining**
1	D	58.00	84.91
2	B	58.70	87.39
3	A	58.40	85.02
4	C	56.55	86.65
5	C	58.05	81.74
6	D	47.85	87.44
Average	-	***56.26***	***85.53***
%RSD		***7.4***	***2.5***

Table 4—9 illustrates the results recorded for the mass remaining of the couches used in the first six burns. It was not known initially that the couch used for the sixth of the *Three Seater Couch* burns was significantly smaller than those used in Burns 1 - 5 until the dimensions and mass of the couch were recorded on site. In addition, when determining the %RSD the results suggested an acceptable experimental variation. The data set was tested, using the interquartile range (IQR) method, to determine if Burn 6 represented an outlier. The results

of the outlier test, based on % mass remaining, indicated that the smaller couch did not represent an outlier.

Table 4—10: Percent Mass Remaining, Two Armchairs.

Two Armchairs			
Burn Number	**Burn Cell Used**	**Initial Mass (kg)**	**% Mass Remaining**
7	B	(i) 34.04 (ii) 33.42	85.98
8	B	(i) 32.86 (ii) 33.90	79.06
9	C	(i) 33.20 (ii) 33.80	80.21
10	C	(i) 33.56 (ii) 33.88	84.02
11	B	(i) 34.00 (ii) 33.70	85.17
12	A	(i) 34.34 (ii) 33.64	89.04
Average	-	***67.39***	***83.91***
%RSD	-	***0.7***	***4.4***

Table 4—10 illustrates the results recorded for the mass remaining of the total of the armchairs used in Burns 7 - 12. Less variation was recorded in the dimensions of the armchairs in this series of burns and this is reflected in the %RSD result with respect to their mass.

Table 4—11 illustrates the % mass remaining recorded for the burns involving one armchair. As highlighted in Section 4.3, the distinction separating the large and small armchairs was not identified until the onsite measurements were being collected. Chronologically the experiments were conducted as presented. The results have been presented as a whole in Table 4—11 and as the natural subsets that resulted from the similarity of the dimensions and mass in Table 4—12.

When the data was treated collectively it can be seen that the %RSD of the initial mass indicates significant variation.

Table 4—11: Percent Mass Remaining, One Armchair.

One Armchair			
Burn Number	**Burn Cell Used**	**Initial Mass (kg)**	**% Mass Remaining**
13	A	34.02	58.50
14	C	34.02	60.73
15	D	33.74	76.17
16	D	23.52	54.34
17	C	23.12	53.07
18	B	21.78	54.82
Average	**-**	***28.37***	***59.61***
%RSD	**-**	***21.6***	***14.4***

It is clear when considering the initial mass of the fuel load from Burns 13 – 18 that there are two distinct data sets represented in this series of experiments. If those sub-sets are recognised as such the results, presented in Table 4—12, of the two data sets reflect more accurately the percentage mass remaining results. The sub-sets also accurately reflect other aspects of the experiment, such as time until flashover, which is discussed in Section 4.5.4.

Table 4—12: Percent Mass Remaining, One Armchair, grouped.

One Armchair (Large)			
Burn Number	**Burn Cell Used**	**Initial Mass (kg)**	**% Mass Remaining**
13	A	34.02	58.50
14	C	34.02	60.73
15	D	33.74	76.17
Average	**-**	***33.93***	***65.13***
%RSD	**-**	***0.4765***	***14.77***
One Armchair (Small)			
16	D	23.52	54.34
17	C	23.12	53.07
18	B	21.78	54.82
Average	**-**	***22.81***	***54.08***
%RSD	**-**	***4.0***	***1.7***

For an experiment such as this, with parameters that are particularly difficult to control, reproducibility is difficult to achieve and hence a high %RSD is expected. The results shown in Table 4—9 to Table 4—12, whereby the majority of the %RSD values are less than 5% for percentage mass remaining, are therefore significant. It should however be noted that only a limited number of experiments (n=3) were conducted for the single armchairs (grouped) so care must be taken in interpreting these %RSD values.

4.5.4 Time Until Flashover

The time until flashover of three different scenarios was recorded, according to the detailed description provided Section 4.4. Burns 1 – 15 progressed to flashover and were subsequently suppressed. The fires in Burns 16 - 18, consumed the fuel load extensively without flashover occurring in the cell; therefore the fire was suppressed when it was apparent that the fire would not progress to flashover. The results, in terms of time until flashover and the relative order in which flashover was achieved, have been reported in the Table 4—13, Table 4—14 and Table 4—15.

It was identified in Section 4.3 that the smaller couch used in Burn 6 had a similar percentage mass remaining the those seen from Burns 1 – 5. The smaller size of the couch used in Burn 6 did not have a significant impact on the %RSD for the total percentage mass remaining. However, it did reach flashover in one case in half the time of its larger counterparts. The results were compared with the time included and excluded for Burn 6, the results have been presented in Table 4—13. As it was the aim to determine if a time until flashover could be determined based on a known PU component, omitting the data recorded for Burn 6 when analysing the results makes sense. Therefore, the results indicated that the average time until flashover, using the parameters described in Section 4.4, was 567 seconds with a 13.4%RSD. Considering the difficulties in reproducibility encountered with experiments of this nature, this relatively low %RSD is considered to be an indication that the experiment has been reproduced within acceptable experimental uncertainty.

Table 4—13: Time Until Flashover, Three Seater Couch.

Three Seater Couch				
Burn Number	**Burn Cell Used**	**Time Until Flashover (sec)**	**Time Until Flashover (sec)**	**Relative order of Flashover**
1	D	609	609	12
2	B	452	452	8
3	A	528	528	10
4	C	616	616	13
5	C	631	631	14
6	D	315	-	1
Average	**-**	***525***	***567***	
%RSD	**-**	***21.4***	***13.4***	

Results pertaining to the time until flashover for the two armchair scenario have been presented in Table 4—14.

Table 4—14: Time Until Flashover, Two Armchairs.

Two Armchairs			
Burn Number	**Burn Cell Used**	**Time Until Flashover (sec)**	**Relative order of Flashover**
7	B	493	9
8	B	379	2
9	C	435	7
10	C	409	3
11	B	422	5
12	A	411	4
Average	**-**	***424***	
%RSD	**-**	***8.9***	

Similar to the trend for the two armchair scenario noted in Section 4.5.3, there were no outliers seen in the data generated from this section of the experimental work. The results indicate that the average time until flashover, based on defined parameters for the two armchair scenario in Section 4.4, was 424 seconds with a 8.9% RSD. This suggests that the experiment can be considered to have been reproduced with acceptable experimental error, suggesting an accurate result.

The results recorded for the time until flashover for the one armchair scenario have been presented in Table 4—15. It was briefly touched on in Section 4.5.3 that it was beneficial to adhere to the two natural sub-sets created in the data created by the variation in mass of the armchairs used for Burns 13 – 18. Primarily due to Burns 13 – 15 progressing to flashover while Burns 16 – 18 did not.

Table 4—15: Time Until Flashover, One Armchair.

One Armchair (Large)			
Burn Number	**Burn Cell Used**	**Time Until Flashover (sec)**	**Relative order of Flashover**
13	A	640	15
14	C	598	11
15	D	423	6
Average	**-**	***554***	
%RSD	**-**	***20.8***	
One Armchair (Small)			
16	D	**DID NOT FLASHOVER**	**DID NOT FLASHOVER**
17	C		
18	B		
Average	-		
%RSD	-		

There is insufficient data to conclude that the results recorded for Burns 13 – 15 are reproducible. However it can be noted that a trend appears to be emerging. Although it is suggested that more repetitions of the scenario using the same size armchair would have been required to see the trend develop further, based on the results of the previous scenarios it is not doubted that similar results would emerge. It is interesting to note that the increase in %RSD could suggest that the amount of PU being used in Burns 13 – 15 is approaching the minimum amount of this type of fuel load, in a cell with the dimensions used here, required to reach flashover.

The remaining burns did not progress to flashover. This was unexpected as, based on the estimated HRR (indicated in Table 4—7and ranged from 1025.41 – 1722.10) for flashover to occur, the estimated HRR of the fuel used (indicated in Table 4—8) exceeded the estimated HRR for flashover to occur in each cell.

Although it was noted that there was different sized foams used for the cushions in Burns 16 – 18, it is unlikely that there was any difference in the PU itself as colour variation in PU noted for other burns had not been seen to impact on the time until flashover results. It is more likely that the relative reduction in cushion size and amount of PU the armchair was upholstered with was the reason flashover was prevented. During the last three burns it was noted that the progression of the burn themselves did not follow the same trend as those

that came before. For example the burns appeared as though they were heading towards flashover, the in-tracking of fresh air at the bottom of the cell was occurring, ignition of the smoke layer was being observed, however the characteristic signs that flashover was imminent did not appear to progress with enough intensity to lead to flashover.

The non-progression to flashover was also reflected in the thermal data gathered and mirrored the visual cues. As discussed in Chapter 4.4 series 1, 2 and 3 representing the thermocouples that were placed inside the chair and are therefore not indicative of the temperature gradient witnessed across the cell. It is clear therefore in Figure 4.19, an exemplar of the data gathered from Burns 16 – 18, that there is no rapid increase of temperature, a characteristic feature associated with flashover. The progression of the fire is more representative of a stylised curve representing the growth, steady state and initial stages (prior to suppression) of decay of the fire.

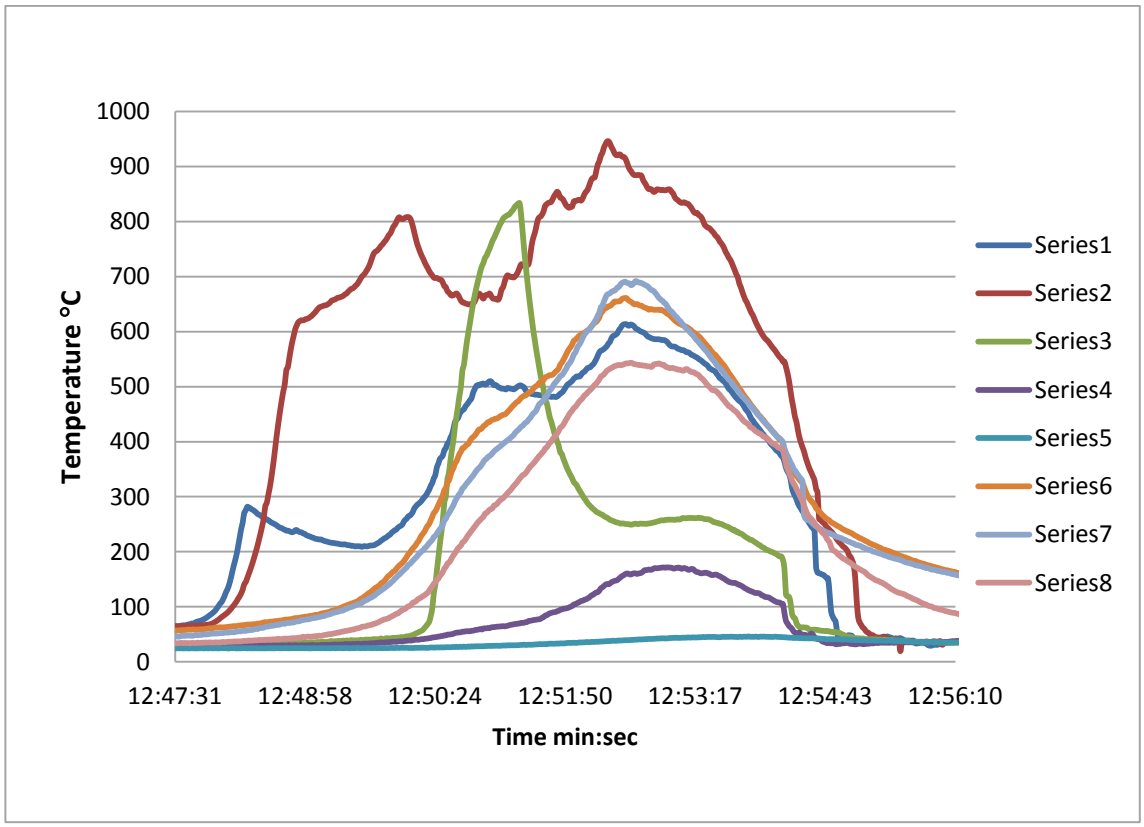


Figure 4.19: Thermal data for Burn 17 - one armchair (smaller (series 1 and 2: armchair near the point of ignition, series 3: armchair away from the point of ignition, series 6 – 8 are inside the cell and illustrate a curve representing the progression and subsequent decay for a fire).

Conversely, the thermal data illustrated by Figure 4.20, Figure 4.21 and Figure 4.22 are an exemplar of the *Three Seater Couch*, *Two Armchair* and the sub-set *One Armchair (Larger)* scenarios, respectively. They indicate a rapid increase in the temperature gradient and mirror the visual cues noted for the occurrence of flashover. The point at which flashover occurs is indicated in Figure 4.20. Again, series 1, 2 and 3 indicate the thermocouples that were inside the fuel load at the point of ignition and therefore give an accelerated view of the temperature gradient seen across the cell, so are therefore overlooked for the purpose of this explanation.

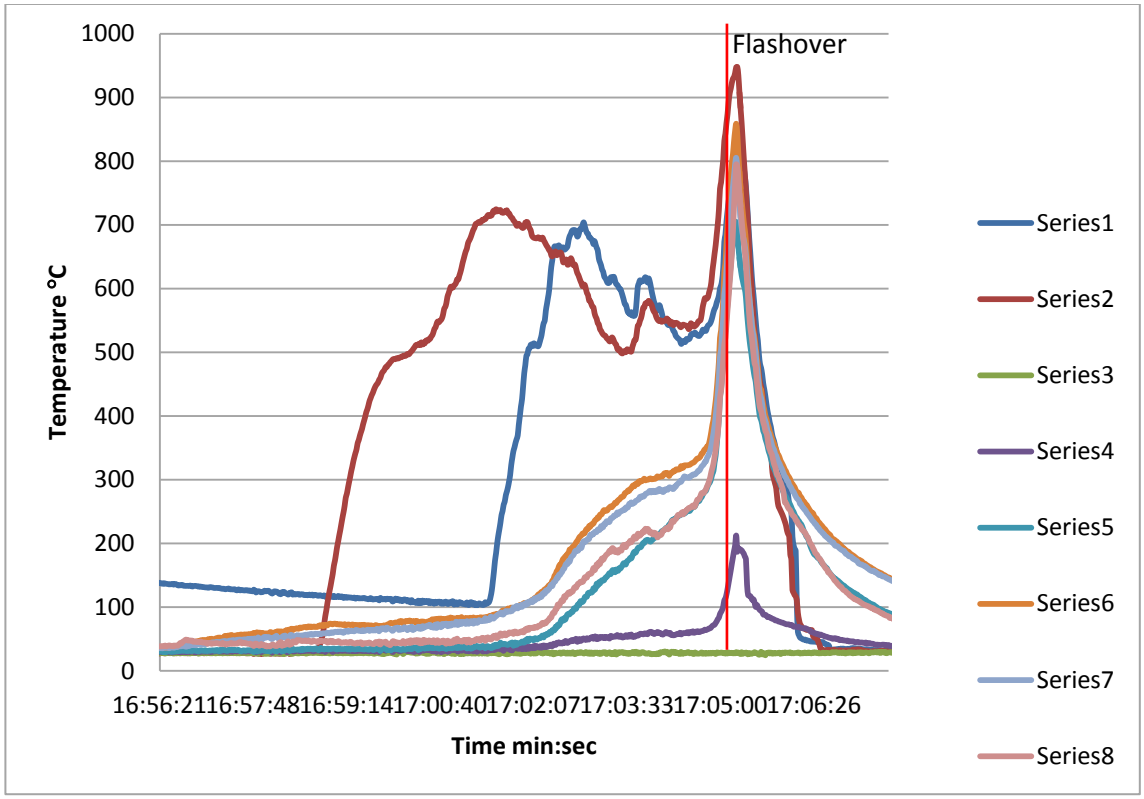


Figure 4.20: Thermal data for Burn 4 - three seater couch (series 1 and 2: inside the couch near the point of ignition, series 3: inside the couch at the end furthest away from the point of ignition, series 6 – 8 are inside the cell indicating the rapid increase in temperature).

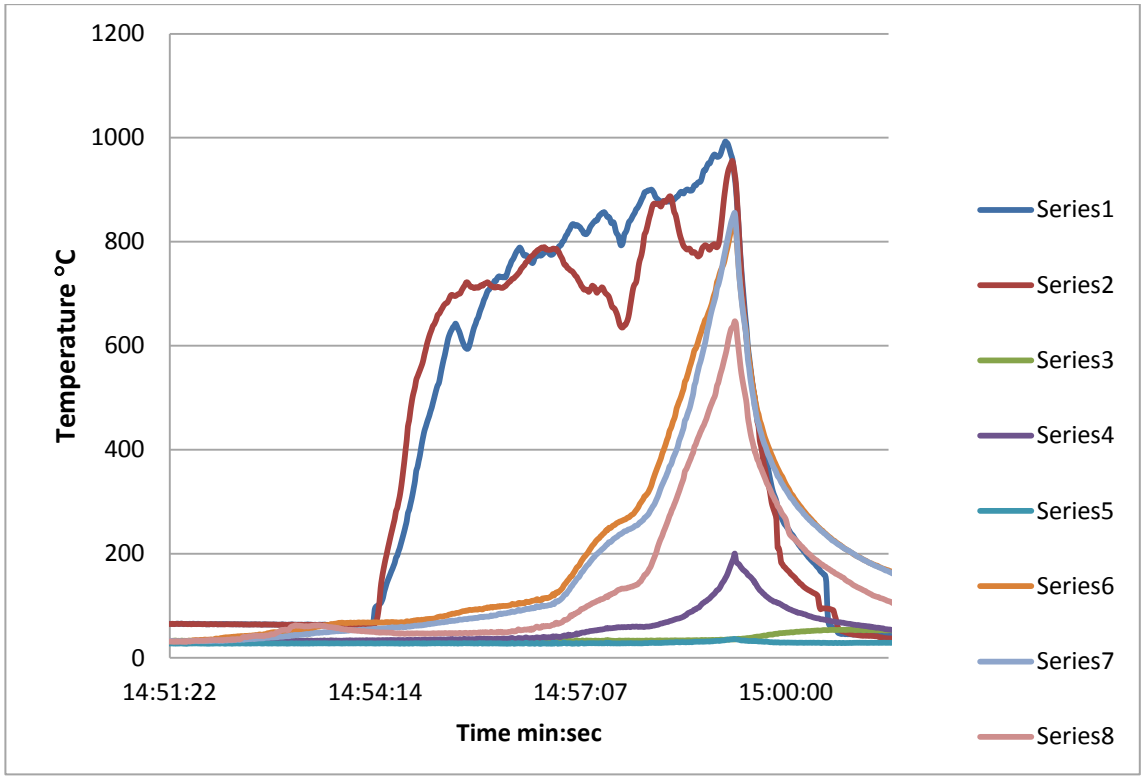


Figure 4.21: Thermal data for Burn 12 - two armchairs (series 1 and 2: inside the armchair near the point of ignition, series 3: inside the second armchair furthest away from the point of ignition, series 6 – 8 are inside the cell indicating the rapid increase in temperature).

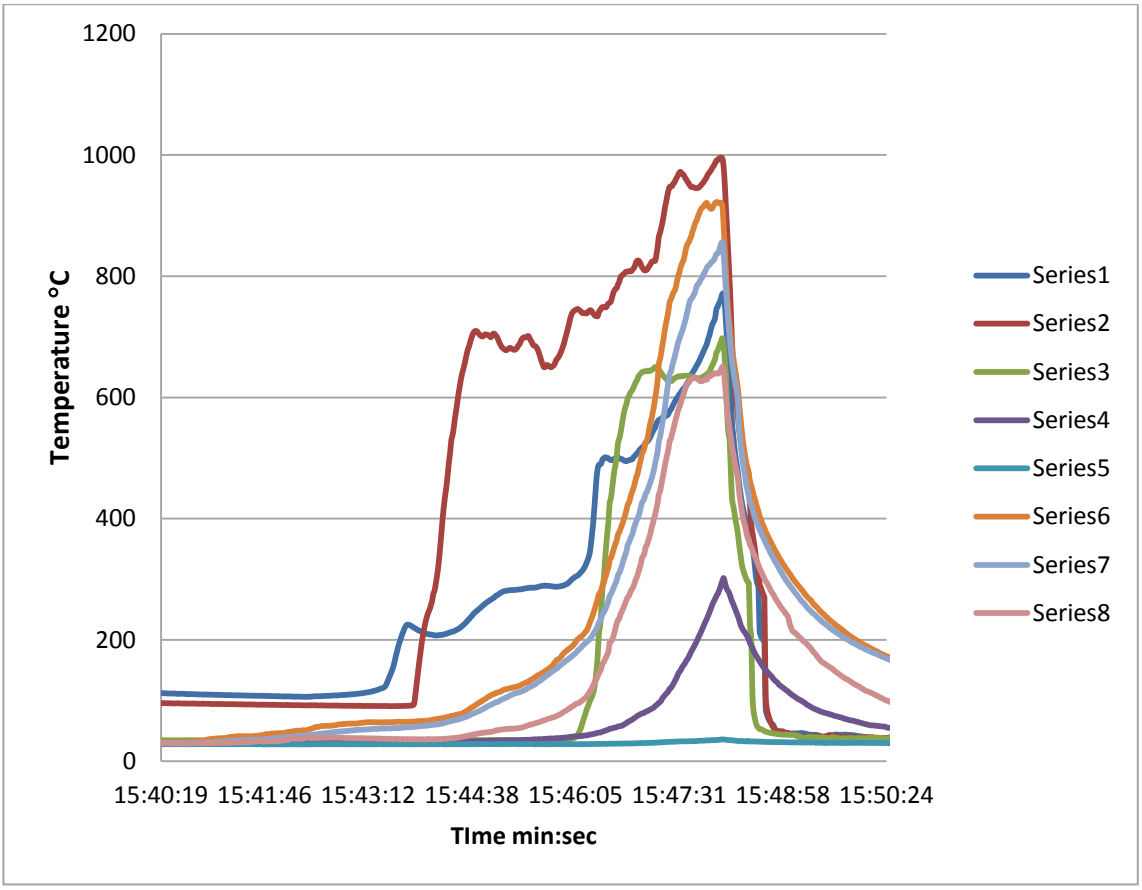


Figure 4.22: Thermal data for Burn 15 - one armchair (larger) (series 1 and 2: armchair near the point of ignition, series 3: armchair away from the point of ignition,series 6 – 8 are inside the cell indicating the rapid increase in temperature).

4.5.5 Visual Examination of the Fuel Load, Post Suppression

After each of the fires had been suppressed, the fuel load was removed and dried. Each of the items were then weighed, the results of which have been present and discussed in Section 4.5.3.

The items of furniture used as the fuel load were then visually compared to determine if the repeatability displayed in the majority of the experiments (and evidenced by the results of the percentage mass remaining and the time until flashover) was mirrored by the post suppression fire indicators on the remaining fuel load. Had the fire been permitted to progress further than flashover and enter the post suppression decay stage, the interpretation of the post suppression fire indicators would have been approached differently.

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.

Figure 4.23 depicts the couches used in Burns 1 – 6. The couch from Burn 1 is depicted in the foreground of the image and the couches represent the burns in increasing sequential burn numbers towards to background of the image.

The cushions were left in situ post suppression of the fire to highlight any demarcation that could be noted. Although the area of origin was known and has been indicated by the blue circle, the heavy damage to that area and the line of demarcation between heavy and lighter flame impingement are indicative of a flame that has initially occurred at a lower level and travelled up and out creating, in this case, a half *v-pattern*. The heavy damage to the area of origin has been repeated the remaining couches, which is demonstrated in Figure 4.24.

Figure 4.24: Couches used in Burns 1 – 6 post suppression, oriented from the area of origin.

The line of demarcation indicating a half v-pattern extended to the opposite end of the couch where less flame impingement was noted. It can be seen that a similar pattern of demarcation has been repeated in each of the couches and is illustrated in Figure 4.25.

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.

Flame damage to the top of the couch is also noticeable in the individual items used in each burn and that the damage decreases in the direction of the arrow used in Figure 4.25. The damage to the top of the couches is the result of direct flame impingement, in the case of the area around the origin, and from the escalating temperature of the hot gas layer which impacted on the fuel load. The escalation of the temperature to a degree where flashover was imminent occurs rapidly, as the majority of published definitions suggest. The rapid escalation of temperature was also indicated by the experimentally derived thermal data presented in Section 4.5.4. Therefore the radiant heat and flame impingement on some areas of the fuel load prior to the fires being suppressed was so rapid that it initially appeared as those there was no damage to the furniture. However even though some of the material remains predominantly intact, it has clearly been damaged by the effects of heat.

A visual account depicting post suppression analysis of the fuel load used in the two armchair scenarios has been presented in Figure 4.26, Figure 4.27 and Figure 4.28. Figure 4.26 illustrates the two armchairs viewed from the front with the items from Burn 7 in the foreground, progressing sequentially to Burn 12 in the background. The area with the most significant damage, indicated by the blue circle, indicates the area of origin. The distance between the armchairs in the cell was indicated in Section 4.4, in Figure 4.26 the distance is greater. That does not take away from the clear line of demarcation indicating a half v-pattern.

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.

It is clear in Figure 4.26, Figure 4.27 and Figure 4.28 that the degree and patination of the flame and heat damage has been repeated in Burns 7 - 12. In addition, that damage was similar to that described in Burns 1 – 6.

Figure 4.27: Armchairs used in Burns 7 –12 post suppression that has been orientated from the area of origin.

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.

The post suppression indicators for the furniture used in the one armchair scenario have been illustrated in Figure 4.29 and Figure 4.30. As has been discussed in Section 4.5.3 and Section 4.5.4 there was variation in the set that leant itself to the formation of two subsets. The smaller of the sub-sets was used as the fuel load for Burns 16 – 18 and is illustrated in the foreground of Figure 4.29. Those experiments did not progress to flashover and it can be seen that there is little of the PU or lighter weight material used as support for the upholstery remaining on these three armchairs.

Figure 4.29: Single armchair used for Burns 13 – 18. Burn 18 is in the foreground.

That is not the case for the armchairs used in Burns 13 – 15, with the armchair from Burn 13 in the background of Figure 4.30. It can be seen in the image that some of the PU and a

Figure 4.30: Single armchair used for Burns 13 – 18. Burn 13 is in the foreground.

portion of soft material remains in the armchair used for Burn 15. It is interesting to note that for Burns 13 – 15 the time until flashover is directly proportional to the degree of damage seen in the post suppression visual analysis of the fuel load. This phenomenon was not noted in the visual analysis of the furniture used in Burns 1 – 6 or Burns 7 – 12. In addition and as expected, a correlation could not be seen between the cells used and the time until flashover.

An interesting aspect of the post suppression visual analysis was the repetition of the patterns caused by flame and heat impinging on the fuel load. Although not completely unexpected, the degree to which the patination was reproduced in each scenario, including the sub-sets of the one armchair scenario although to a lesser extent, was a significant observation. It certainly supported the principle, via accepted fire investigation methods, that each burn had been repeated.

The results attained from the final scenario, the one armchair, are of particular interest. It would seem that the amount of PU containing furniture needed for that cell size to progress to flashover was being approached. It is postulated that the amount of PU containing furniture used for Burns 13 – 15 is approaching a value that below which flashover would not occur. This is thought for a number of reasons 1) the range of the time until flashover is already greater than that displayed in the other two scenarios, 2) there is greater variation in the percentage mass remaining and 3) the temperature gradient is not as steep as the previous scenarios. It is clear though that the PU containing furniture used for Burns 16 – 18 was insufficient for the burns to progress to flashover and as such have provided a base value below which for these parameters flashover would be unlikely. Although without repetition of each sub-set to produce a more statistically viable outcome only suppositions can be made.

4.6 Conclusion

The majority of the challenges identified during the work conducted at Fergus Falls, MN informed the modification to the experimental method which was used for the work conducted at QCESA, QLD. In particular controlling and ensuring consistent ventilation, mechanism and point of ignition ensured consistency and reproducibility of the results.

The defined term (and characteristics) for flashover used in this work were recorded as occurring in 15 of the 18 experimental burns. The results presented in Table 4—13, Table 4—10 and Table 4—15 illustrate that in two of the three scenarios (three seater couch and the two armchairs), the burns with the larger initial mass of PU-containing furniture generally progressed to flashover more rapidly.

The last scenario (one armchair), were split into two unintentional subsets due to a difference in the mass and consisted of three armchairs in each set. Though both sets were thought to be able to yield a sufficient HRR value to facilitate flashover, based on the estimated HRR (flashover) for the cell, only the larger set progressed to flashover.

Based on the results presented here it has been illustrated that determining the time until flashover, proportional to the amount of PU in the cell, was successful and shown to be reproducible.

Chapter 5: Post Suppression Gas Detection Fergus Falls, MN

Chapter 5: Post Suppression Gas Detection Fergus Falls, MN

5.1 Introduction

Historically, CO has been the focus when investigating the primary cause for asphyxiation in domestic dwelling fires. As a result, the examination of possible alternative gases has often been overlooked. With the advent of nitrogen-containing polymeric materials and the subsequent increase of their use in the home, there is a need to re-examine the profile of toxic pyrolysis products from fire development. For this reason HCN was included as a gas of interest.

Recent studies that have sought to determine the profile of toxic gases produced from polymeric materials during heating have concentrated on gases evolved above 200 °C and prior to the suppression of the fire. Data identifying gases that evolve at temperatures below 200 °C and after flame suppression is relatively non-existent. In addition, it was noted that the identity of gases emitted post suppression had only recently begun to be investigated. Furthermore it was recognised that variation between fire scenarios made the collection, comparison and determination of a holistic profile that defined the gases emitted problematic [176].

Although this chapter focuses on post suppression gas detection, the experimental work is a component of a more holistic approach testing several aspects related to the progression of a large scale compartment fire.

As discussed in Chapter 1: Introduction a holistic approach was adopted when setting up the large scale burns to ensure that one event encapsulated the three areas of interest identified. That is i) pre-flame gas detection, ii) time until flashover proportional to the amount of polymeric material present and iii) post suppression gas detection. This chapter focuses on gas detection during the post suppression stages of large scale fires that have been fuelled predominantly with nitrogen-containing polymeric materials, specifically PU.

The preparation and design of this large scale body of work was approached in the same vein as method design of bench top experiments. That is, a repeatable method was developed that sought to control the majority of experimental parameters to allow for the collection and reproduction of quantitative and qualitative data.

5.2 Site Description

The work reported in this chapter was performed in conjunction with the experimental work described in Chapter 3:, refer to Section 3.2 for further details. The point of difference for the work reported in this chapter is that the experimental work was conducted post suppression of the burns.

5.3 Sample Description

The description of the sample in this case refers to the species of gas noted post suppression of a fire that was fuelled predominantly by PU containing furniture. The focuses of the gas species present in this work were CO and HCN. The toxicity of HCN led to its inclusion in the work, in addition to its presence as a reaction product in fire scenarios fuelled by nitrogen-containing polymeric materials. The former, CO, was included as historically it was considered the sole cause for asphyxiation related fatalities in fires. Section 3.3 describes the fuel load that is predicted to be the source of the gaseous species; and is shown pre ignition of the fire.

5.4 Method

The distribution of the furniture in each room has been described in detail in Section 3.4, particularly in Figure 3.7. Figure 3.7 provides a photographic exemplar of the furniture distribution in addition to a schematic that illustrates the layout of the building, the location of the furniture and indicates the location (and mechanism) of ignition.

As reported in Section 3.4 considerable attention was paid to the parameters of the experiment including the size and placement of the fuel load in addition to the continuity of the size of the cell. The progression of the fire was also heavily monitored to reduce flame spread into the adjacent rooms. In addition after the fire had been suppressed the roof

cavity was thoroughly checked to ensure that the fire had not progressed into the roof. For the safety of the crew entering the room, post suppression positive pressure fans were used to speed up the dispersion of the post suppression atmosphere.

After the safety of the cell was established, the atmosphere was analysed to detect and quantify HCN and CO using species specific Dräger-tubes in conjunction with a Dräger accuro^{R} 2000 pump. It can be seen in Figure 5.1 that the ends of the Dräger tube have been removed and one end has been placed into the opening of the hand pump. The area indicated by the hand hold illustrates where the pump is held in one hand and measured pumps, or strokes, are applied to evenly draw the environment of interest through the tube.

Figure 5.1: Dräger accuro 2000 pump [207].

The testing was completed in accordance with the manufacturer's instructions, which are presented in Table 5—1.

Table 5—1: Operating parameters for Dräger accuro 2000 pump.

	Hydrocyanic Acid 2/a for HCN	*Carbon Monoxide 5/c for CO*
Part Number	CH25701	CH25601
Number of Strokes (n) for Measuring Range	n = 1: 10 – 150 ppm (multiply reading by 5) n = 2: 5 – 75 ppm (multiply reading by 2.5) ***n = 5: 2 – 30 ppm (direct reading)***	n = 2: 100 – 700 ppm (direct reading) ***n = 5: 5 – 150 ppm (direct reading)***
Measurement Time	Up to Approx. 1 min.	Approx. 1 min. / approx. 4 mins.
Standard Deviation	+/- 10 – 15%	+/- 10 – 15%
Colour Change	yellow-orange → red	white → pale brown
Reaction Principle	$HCN + HgCl_2 \rightarrow HCl$ HCl + Methyl Red → Red Reaction Product	$H_2S_2O_7$ $5\ CO + I_2O_5 \rightarrow I_2 + 5\ CO_2$ (Pale brown colour owing to formed iodine)

It was postulated that the species of interest would be less concentrated due to the ventilation of the room therefore n = 5 for the strokes required was used. Sampling of the post suppression gas atmosphere was completed manually. To control the process, as much as possible, it was established that the same individual would perform the sampling and subsequent analysis. In addition the positive pressure fans were stopped while the atmosphere was being analysed; although the windows and door remained open during the process.

The location at which the gas was sampled within each cell was consistent between the cells. After the fire was suppressed and the room was rendered safe, Dräger tubes specific for HCN and CO were used to determine the presence of those gas species.

Two areas in the room were focused on, the area directly above the bed and the area directly about one of the two pink armchairs. The positions have been indicated in Figure 5.2 with red boxes.

The analyte of interest was HCN therefore determining if the species was present in the post suppression atmosphere established the order of sampling. Therefore the HCN specific Dräger tubes were used first, starting with the area above the bed then the area about the armchair denoted in Figure 5.2 with the number *1*. The Dräger tubes specific to CO were then used adhering to the same sequence.

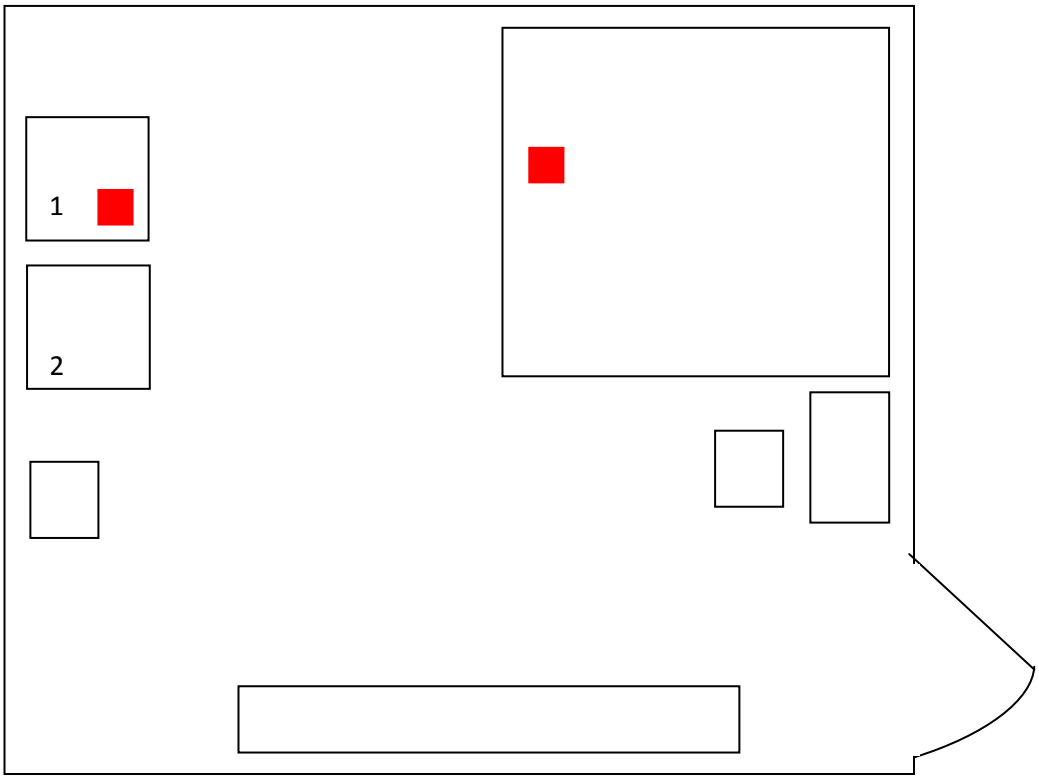


Figure 5.2: Schematic of one of the motel suites. The red squares indicate where the atmosphere in the room was sampled from. The numbers indicate the two different pink armchairs. The schematic is not drawn to scale.

5.5 Results and Discussion

In this series of experiments risk management strategies were employed to ensure the safety of those working in the post suppression fire scene. Specifically, the room was subjected to positive pressure ventilation before manual gas sampling was allowed to occur.

As discussed in Section 5.4 and illustrated in Figure 5.2, the post suppression atmosphere was sampled from the same area in each cell so that replication of the sampling method was observed. The area above the bed and the area above the armchair were chosen as sites to sample the atmosphere due to the high incidences of fires that result in fatalities originating in the bedroom and or lounge/living room [6]. Additionally, in this work it was the fuel load

that was the largest mass of PU used in its upholstery and it was also closest to the area of origin, which made it more likely to have been impacted on by flame.

The technique used to sample atmospheres using the Dräger-tubes and Dräger accuro 2000 Hand Pump can be tailored to account for environments suspected to be rich or poor in the analyte (gas) of interest. Therefore, as it was likely that the concentrations of the analytes of interest had diminished as a result of the positive pressure ventilation, the technique was modified (according to the manufactures parameters) to compensate by drawing a larger volume of air through the tubes.

The data gathered from gas analysis of the post suppression atmosphere above the bed has been presented in Figure 5.3.

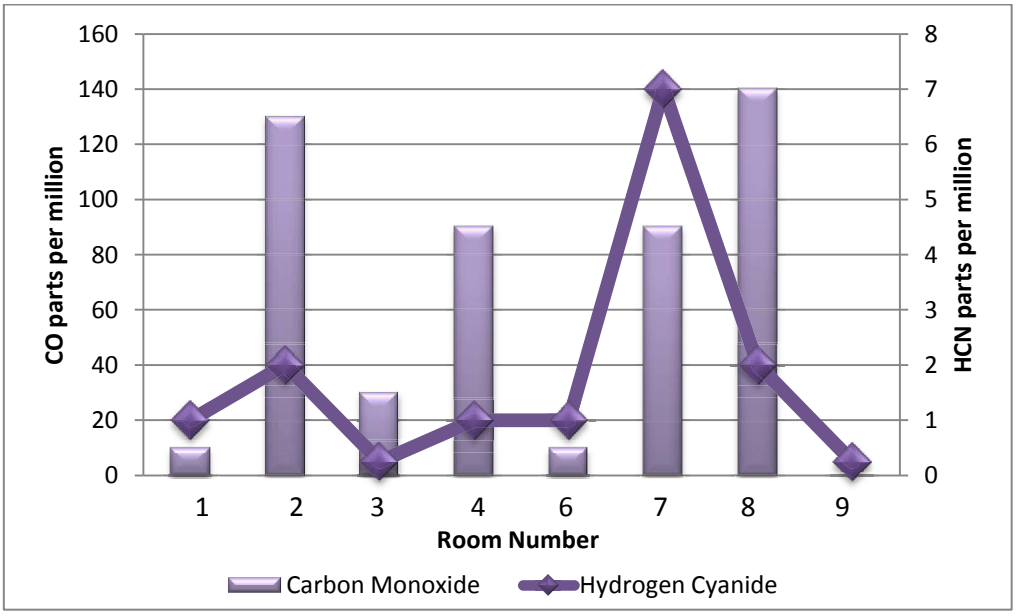


Figure 5.3: Detection of HCN and CO from gas analysis of the post suppression atmosphere above the bed. Note that Room 5 was not used in this work.

It can be seen in Figure 5.3 that results gained from analysis of the environment above the bed in room 3 and 9, the Dräger-tubes specific for HCN displayed discolouration estimated to be approximately 0.25 ppm, and was reported as such. The similarity in the results cannot be attributed to the progression of the fire as the experiment conducted in Room 3 and Room 9, although had the same parameters with respect to fuel load, cell volume and ignition mechanism, there was significant variation in the ventilation parameters. The fire in Room 9 became ventilation controlled due to its windows being shut and the door being closed

moments after ignition. The fire in Room 9 self extinguished in under a minute and the flames did not impact on the mattress at all. The fire in Room 3 was not ventilation controlled to the same extent as Room 9 and subsequently progressed to flashover. This resulted in extensive consumption of the fuel load, suggesting that the possibility of more fire effluent and therefore the capacity to detect a greater amount of toxicants. It is therefore suggested that the introduction of post suppression impacted on the toxicants that remained.

Despite differences in some experimental parameters (i.e. mechanism of ignition and area of ventilation) Rooms 1, 4 and 6 displayed similar post suppression results, for the detection of HCN. Although interestingly Room 1 and Room 4 were both set up to represent accidental fires and both progressed to flashover, the time until flashover and the ventilation areas for the fires differed. Conversely, the burn conducted in Room 6 was set up as a deliberate ignition, had more ventilation to the fire than that reported for Room 1 and Room 4 still the fire did not progress to flashover. However, like the results recorded for the experiments conducted in Room 3 and Room 9 it is not possible to draw strong conclusions as the introduction of positive pressure ventilation post suppression would likely have dispersed the majority of post suppression environment prior to analysis.

The detection of HCN in Room 2 and Room 8 displayed a similar result and the result reported for Room 7 was the greatest value for HCN recorded. Expect for the parameters shared by all the experimental burns, that is, the fuel load including its distribution and the dimensions of the room itself, one additional trait that was repeated for these three experiment; none of the rooms progressed to flashover.

As it has been indicated in Figure 5.3 the results recorded for the detection of CO in the area above the bed also displayed dissimilarity. There was no clear link between the amount of CO detected with the type of PU present, the mechanism of ignition, ventilation of the room or the progression of the fire.

The data gathered from gas analysis of the post suppression atmosphere above the chair has been presented in Figure 5.4.

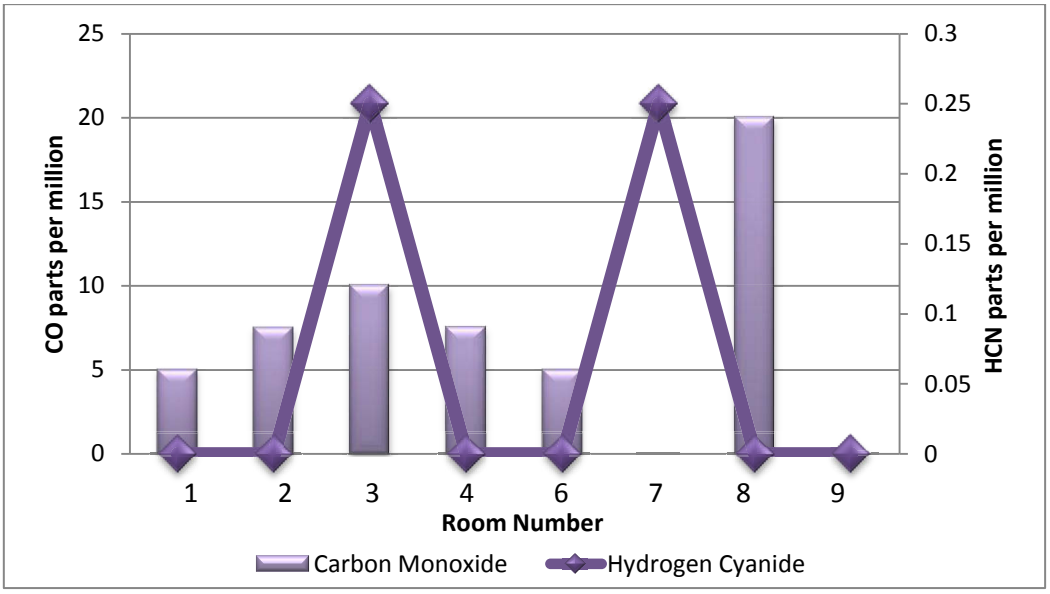


Figure 5.4: ***Data from gas analysis of the post suppression atmosphere above the chair. Note that Room 5 was not used in this work.***

The CO amounts recorded in the area above the chair were relatively low, when compared with the results recorded for the area above the bed. It has been mentioned that the there was little PU remaining on the armchair in Rooms 2, 6 and 8 which would account for the reduction in the detectable amount of CO. In addition the analysis of the area above the chair was the last in the sequence and it is likely that the remaining fire effluent had dispersed somewhat. It is postulated that the result is due to the ambient room concentration due to the lack of remaining PU.

The armchair where the atmosphere was sampled from in Room 2, 6 and 8 had significant fire damage to such an extent that there was no visible PU remaining at the time of sampling. There was PU remaining on the chair in room 1 and 4, however no visible discolouration in the indication layer of the tubes was noted. The data collected when sampling the atmosphere above the chair in Room 3 and 7 the tubes specific for HCN displayed discolouration at the beginning of the indication layer and was estimated to be 0.25 ppm.

As reported in Section 3.5.5.8 and discussed earlier, the fire in Room 9 self-extinguished in under a minute. Prior to extinguishing itself the fire progressed little and did not impact on the items of furniture above which the atmosphere was to be sampled from. This specific circumstance was outside of the method parameters and as a result the post suppression atmosphere in Room 9 was not sampled.

The Dräger-tubes utilised for gas detection in the post suppression environment were within the suggested best usage date range and the associated equipment was in good working condition. In addition, both the tubes and pump were operated in accordance with the manufacturer's specifications. As such the condition of the hardware was not considered as the source for the variation in the results. However it was possible that the design of the equipment used for the experiment impacted the variation recorded in the data collected.

Due to the pumps capacity to physically accommodate a single tube in the unit an order of operation was established, and maintained throughout the test burns, for analysing the post suppression atmosphere in each cell. That was: i) using tubes specific for HCN the area above the bed was tested prior to the area above the chair, then ii) using tubes specific for CO the area above the bed was tested prior to the area above the chair.

Consequently, by adhering to the manufacturers use parameters for the time required to achieve optimal results (including resetting the pump), resulted in the sampling period for each room was between ten to 15 minutes. Therefore repeated testing of the post suppression atmosphere with the equipment available was redundant due to the dynamic nature of the environment and was not attempted.

Although it is likely that the detection of the species of interest was impacted on by the time required for the testing to occur, safety requirements and other method parameters have certainly influenced the result.

For example, inherent hazards are associated with post suppression fire scenes and the safety of the operator was of paramount importance. To mitigate the hazards associated with the experimental work being conducted, some necessary safety procedures were included in the experimental design that took into consideration the level of training, equipment available and the structural stability of the room itself. Two events were deemed a requirement (by the scene safety officer) and had to occur before the operator was allowed to enter the room to begin manual testing of the atmosphere. After the fire had been suppressed the room was assessed for structural stability and to verify that the fire had not progressed into the roof cavity. In addition, as the collector was not certified in the safe use of self contained breathing apparatus (SCBA), a fully encapsulated P3 mask with gas filters was worn. Without the use of SCBA the scene safety officer insisted on ventilating the room, using positive

pressure, before the operator was permitted to enter the cell. During the sampling of the post suppression gas the positive pressure fans were not operating.

Although these safety requirements were important and strictly adhered to, the time it took to assess the stability of the structure, the progression of the fire into the roof cavity and the ventilation of the room would certainly have impacted on the post suppression atmosphere allowing the effluent produced to diffuse.

Another factor that was likely to have impacted on the post suppression environment is the test burn itself, referred to in Chapter 3. It has been emphasised that the work conducted at Montrose, MN and Fergus Fall, MN was undertaken to identify the difficulties associated with developing a holistic approach to recording what occurs during the initial progression and subsequent suppression of a fire. The test burns conducted at Fergus Falls, MN, were designed to allow for a multifaceted solution to addressing multiple questions in one burn. Therefore, while each component of the test burn was treated as an individual experiment, the test burn and how it progressed influenced the subsequent experiment (post suppression atmosphere testing).

Although the volume of the room was maintained, the ventilation areas during the fire were not standard across each burn. It is likely that this affected the extent to which the fire progressed. Therefore if the progression of a fire is controlled by ventilation or other mechanical influence it is likely that the post suppression environment was affected proportionally to the extent at which the fuel load was consumed. The repetition maintained for the fuel load and room size parameters was not observed for the ignition mechanism, the ventilation during the progression of the fire or the time ventilation was applied post suppression of the fire. And, although it is likely that the diversity of the ventilation areas impacted on the progression of the fire, which in turn would have certainly impacted on the toxicants produced when PU is burnt or undergoes pyrolysis, the introduction post suppression ventilation (for varied periods) prevents more definitive statements regarding the variation of the results to be made.

That supposition, coupled with the forced ventilation of the post suppression atmosphere and the uncontrolled rate at which the post suppression atmosphere diffused would certainly have influenced the variation in the detection of the species of interest. It could be considered that this variation was a direct result of the variation in the ventilation areas in

each room. An element of highlighting the challenges associated with creating reproducible results from a method included demonstrating the effect of variation within a specific parameter. Consequently while the volume of the room, the surface coverings and the fuel load were standardised the extent that the windows and doors were opened was varied. This in turn affected ventilation control during the progression of the fire, in addition to the post suppression environment. It was postulated that a number of factors that occurred post suppression contributed to the variation in the results. Specifically the initial ventilation of the room post suppression, the rate at which the gas mixture diffused, the time lapse between collecting the first and last sample in each room and single (as opposed to simultaneous) replicate testing. Although it is not the focus of this chapter, it is further suspected that the variation recorded in how the fire progressed impacted on the post suppression atmosphere.

5.6 Conclusion

The work outlined in this chapter examined the detection of HCN during the post suppression stage of a fire. The experimental work utilised commercially available Dräger accuro 2000 Hand Pump with HCN and CO specific tubes. Two locations were sampled in the post suppression atmosphere, the area above the bed and the area above the pink armchair closes to the corner of the room.

The post suppression positive pressure ventilation of the cell, coupled with the relatively long sampling time, was thought to have negatively impacted on the amount of toxicants available to sample. In addition, in some of the burns, the heat and or flames had not impinged on the area where the atmosphere was being sampled. The results illustrate significant variation was recorded between the concentration of HCN and CO above the bed and then above the chair. As the samples were collected at the same height and it would be unlikely that that a toxicant gradient would be occurring across the room, it is postulated that the variation could be attributed to the sampling time.

The challenges encountered during the work at Fergus Falls, MN prompted the investigation of available techniques that could simultaneously and directly collect fire effluent during the progression of a fire.

Chapter 6: Pre-Flame and Post Suppression Gas Detection QCESA, QLD

Chapter 6: Pre-Flame and Post Suppression Gas Detection QCESA, QLD

6.1 Introduction

This chapter focuses on pre-flame and post suppression gas detection. The primary challenge in designing this section of experimental work was to ensure the sampling of both the pre-flame and post suppression environments without impacting on the natural progression of the fire. The purpose of the work outlined in this chapter was to determine if HCN could be reliably detected in the heating stage of a fire and at different stages post suppression of the fire at the QCESA burns.

6.2 Site Description

The work reported in this chapter was performed in conjunction with the experimental work described in Chapter 4. The particulars of the site that pertain to the experimental work conducted in this chapter have been described in detail in Section 4.2. The point of difference for the work reported in this chapter is that the experimental work was conducted prior to the ignition and post suppression of the fires.

6.3 Sample Description

The fuel load for the burns utilised Australian-made furniture that contained Australian-made PU foam that was of comparable style, size and age. Section 4.3 provides a full description of the PU-containing furniture. Although HCN is produced when wood burns, the majority will come from the PU due to the amount of nitrogen present in the polymer. The effluent produced, specifically HCN, during the pre-flame and post suppression stages of the burns were the focus of the work outlined in this chapter.

6.4 Method Development

The results recorded at Fergus Falls, MN highlighted that existing single sample testing apparatus, like the species specific Dräger-tubes used, did not have the capacity to manage the multiple simultaneous testing desired for this experimental work. Different versions of the tubes did exist (Dräger chip management system (CMS)) that allowed multiple simultaneous sampling to occur remotely by incorporating an extension to a pump however, testing of spot concentrations was still an issue. It was clear that using a detection method that could be operated remotely and allowed for simultaneous testing was required. Although, utilising a colorimetric reaction, paramount to the Dräger-tubes design, was attractive.

A number of methods that could be controlled remotely and were specific for HCN detection were initially identified as being potentially suitable candidates for use in the experiment and hence were explored. The first of which involved the introduction of a solution onto a substrate, such as a filter paper, that would, on contact with HCN, register as a change in colour. The intensity of the colour registration would indicate the concentration of the HCN in contact with the paper. Initially the *Prussian Blue* method was investigated that had been identified by [182, 186].

The method called for a solution of iron (II) sulfate ($FeSO_4$) to be impregnated into filter paper. A substrate of filter paper was fully submerged into a $FeSO_4$ solution until it was saturated. The filter paper was then removed from the $FeSO_4$ solution and allowed to dry. The filter paper was then immersed in a 20% sodium hydroxide (NaOH) solution and dried again ready for use. The filter paper was then exposed to gaseous HCN then *developed* by immersing it into a solution of H_2SO_4 to form the ferriferrocyanide ($Fe_4[Fe(CN)_6]^{3+}$) complex, which is blue in colour.

Another HCN specific method was investigated that involved the saturation of a substrate with a solution. A solution of methanol, 4,4'-bis(dimethylamino)diphenylmethane (tetrabase), copper (II) acetate, butylhydroxytoluene and glycerine was introduced to the filter paper. After the papers were saturated with the solution they were removed from the solution and allowed to dry. On contact with HCN the copper (II) tetrabase solution formed a complex with a blue hue [183].

To avoid the papers being exposed to HCN prematurely or without means of control and to ensure the safety of the operator, a system was developed to house the papers away from the source of the HCN. The schematic described in Figure 6.1 illustrates how the HCN was introduced to the substrate. Two flat faced, bored glass apparatus acted as a conduit that held the paper in place so gas could be drawn through it. The glass components were held together with clamps and neoprene tubing was placed over each of the smaller glass sections.

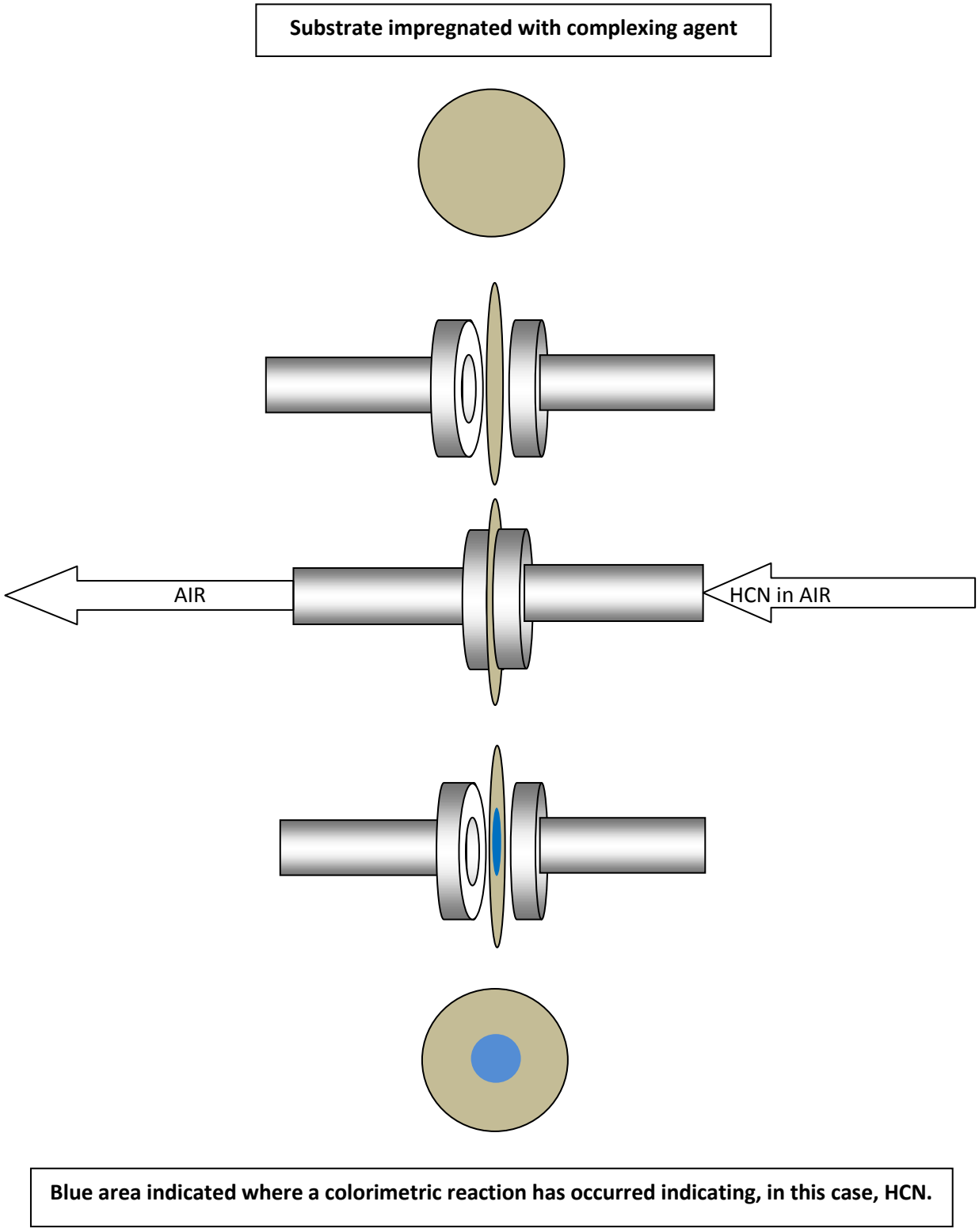


Figure 6.1: ***Schematic of apparatus used to house substrates for HCN detection.***

For both the papers, the intensity of the blue hue formed was proportional to the amount of complex formed, which in turn was proportional to the concentration of HCN. Determining the concentration of HCN occurred by comparing the experimentally derived result with a previously prepared colour chart that represented increases in a known concentration of HCN by its colour.

While both papers produced qualitative and quantitative results; the tetrabase copper (II) acetate papers performed better in terms of reproducibility, when compared with the Prussian blue papers.

Both papers produced qualitative data; though significant challenges were noted. The robustness of the substrate itself was questionable, for example the Prussian blue papers were brittle to the extent a flow rates above 5 L/min shattered the papers drawing the pieces towards the pump. Conversely the glycerine in the tetrabase papers prevented the substrate from completely drying. They therefore remained moist and, when the vacuum was applied, the substrates tended to tear when subjected to fairly modest flow rates. In addition, both of the reaction components on the papers were seen to react in ambient atmosphere, which brought into question their specificity. Finally the papers were seen to have a relatively short life span. This was illustrated by a decrease in the efficacy of the papers in addition to the reaction product fading over time.

As it had already been identified that the manual collection of samples during the progression of the fire was of too great a risk to the collector, and the papers would not survive the temperature gradient associated with the progression of the fire, samples would have to be gathered remotely.

To avoid the atmosphere dissipating prior to being tested, prompt interaction between the cell atmosphere and the reactive paper was ideal. Therefore a rapid flow rate was required to draw the atmosphere through the substrate. However as the substrates were not capable of withstanding even relatively gentle flow rates, even after further optimisation of the method targeting reproducibility, it was clear that this kind of method and apparatus would not be suitable for the intended purpose. In addition, the size of the paper raised the question of surface area and available sites for the reaction to occur, which would be limited by the amount of material impregnated into the substrate.

Furthermore using this method to detect HCN did not allow for secondary or confirmatory testing to occur as a way of validating the results.

Although the success of the papers was limited in this application, investigating their merit led to the exploration of alternative colorimetric mechanisms without the need for a paper substrate. The developed process involved using solutions as a mechanism that would react with the HCN in the fire effluent to form characteristic cyano-complexes. The removal of the substrate resulted in increased sensitivity of the method by increasing the contact between complexing agent and analyte of interest.

The driving force when exploring possible complexing agents was to identify one that:

- was stable;
- would trap the analyte of interest;
- allowed for on-site testing to occur;
- could be safely transported; and
- could be tested using alternative laboratory-based instrumentation.

Complexing agents including picric acid, picrate salts and ammoniacal nickel chloride ($NiCl_2$) solutions yielded promising results during the developmental stage. However they were discounted. The picrate method was rejected for two reasons 1) the concentration of the complex formed was compared with a pre-prepared colour chart that indicated the concentration of the product based on the intensity of the colour. It was considered that the colour reaction could be subjective and it was likely that other aspects of the fire effluent, like soot, would impact on the colour intensity, and 2) picric acid (and some picrate salts) is dangerous to transport and appears in the Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG Code) 6th Ed Vol 2 [208]. Specifically it is listed in Appendix 5: Goods too dangerous to be transported.

Initially the method proposed by Scoggins was considered [193, 195]. However, the results reported by Scoggins were unreproducible. Similar methods utilising an ammoniacal solution were investigated this allowed for the modification of the original Scoggins method and generated reproducible results [63]. When HCN (or CN^- during the testing phase) was introduced to the ammoniacal nickel chloride ($NiCl_2$) solution, a tetracyanonickelate (II) complex is formed. The complex, when analysed using UV/Vis spectroscopy, displays a characteristic absorption at 267 nm. The specificity of the method to form a complex with

HCN, in addition to the simplicity of the solution preparation and lack of subsequent treatment, made this method highly attractive.

Although this method fulfilled a number of the criteria that were initially identified as crucial to satisfying the requirements of the experiment, there were some notable limitations to address. Specifically the instability of the ammoniacal solution required frequent preparation. Remaking the ammoniacal solution was not particularly problematic in a laboratory setting, especially when smaller volumes were being utilised. However preparing a large volume daily, or even the evening before, was difficult as access to the site was strictly limited to the opening hours of the facility which would be dedicated to conducting the burns themselves.

It was estimated that up to four burns per day could be conducted, therefore to accommodate the experimental requirements at least 9.6 L of ammoniacal $NiCl_2$ solution would need to be made daily, regardless of if all was required. Finally this method was restricted to testing via one form of analytical instrumentation.

However, the reproducibility and specificity of the ammoniacal $NiCl_2$ method for the quantitative analysis of cyanide warranted further investigation.

It was postulated that passing the fire effluent through a basic solution to force, and keep, the acidic components of the effluent in solution could be an effective method to trap the gas of interest. The resultant solution could then be tested using different instrumentation depending on the post collection treatment. This was an attractive outcome as it allowed for onsite qualitative analysis to occur in addition to supplementary techniques to be applied at a later date.

During the design process a number of design features were considered imperative. For example, although the premise of the apparatus was to collect samples from a gaseous environment the safety of the operator was of paramount concern and this dictated the design of the sampling apparatus. For example significant attention was paid to the position of the operating mechanism in relation to where the experimental burn was being conducted. In addition a key requirement of the apparatus was to allow for multiple samples to be taken simultaneously and the point at which the sample was collected had to be from the same, or similar, points in each experiment. Finally it was necessary for the sampling

medium to be distanced away from the burn cell to prevent the temperature of the solution rising above ambient. This in turn had a duel effect; increasing the temperature significantly of the trapping medium would either force some of the trapped gas back out or prevent more being dissolved and if a problem occurred with the sampling system or sampling medium it could be addressed in relative safety at a distance from the fire.

It was desirable to collect multiple samples simultaneously during the progression of the fire and be able to replicate the collection position for each subsequent fire. Therefore a rigid and durable apparatus was needed that could be set up in each cell repeatedly. A circular array arrangement was developed using stainless steel tubing and swage locks.

The system developed to hold the papers, shown in Figure 6.1, was modified to allow the effluent from the fire to be drawn through a solution instead of through a substrate. The modifications lead to the instrument used for the method and described in Section 6.5 below.

6.5 Method

The sampling apparatus designed specifically for this work was set up the prior to the commencement of each burn. A hole was cut in each of the cells at the same height and depth on the east wall to allow for the stainless steel (SS) tubing to be passed through. To reduce the impact of turbulence during the fire the section of apparatus pictured in Figure 6.2 was held firmly in place by having the SS tubing fixed through a base plate. A t-bar steel rod (threaded on the vertical portion of the T) was passed through the base plate and secured with a nut on the fire side cell.

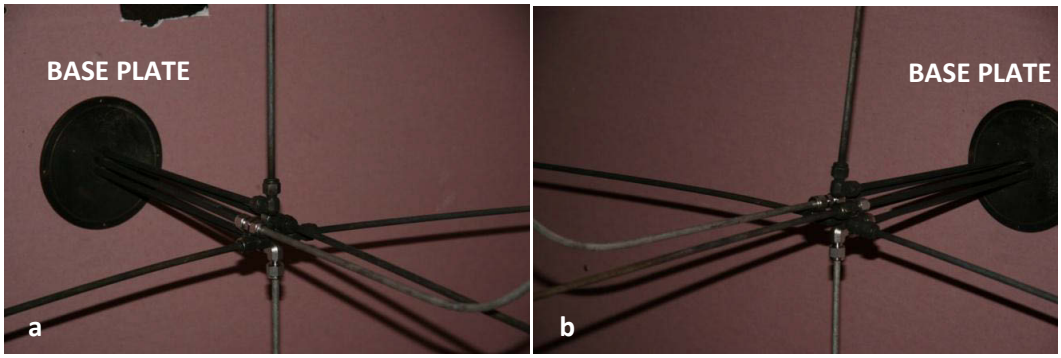


Figure 6.2: a) Sampling array from the left. b) Sampling array from the right.

Figure 6.3 a) depicts the outside of the cell, the extension of the stainless steel tubing illustrated in Figure 6.2. Neoprene was attached to each of the bored SS tubes using swage locks. Stainless steel and neoprene were used due to their relative inertness to corrosive agents.

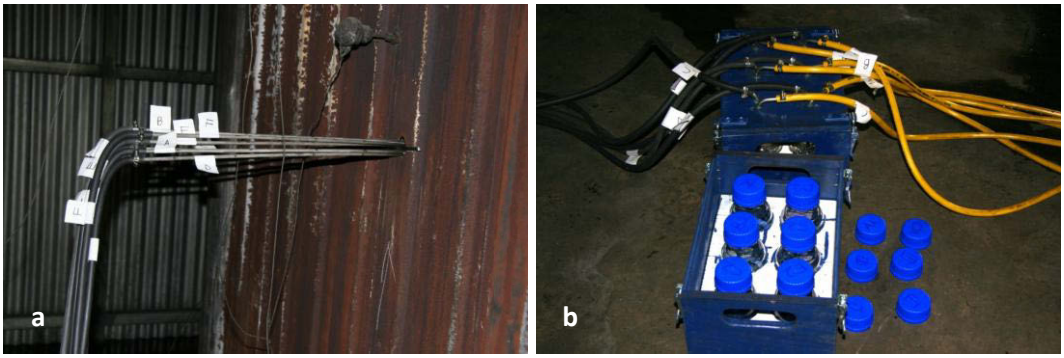


Figure 6.3: ***a) The outside of cell indicating the neoprene and stainless steel connection. b) Showing the neoprene tubing attached to the Schott bottle containing the KOH solution.***

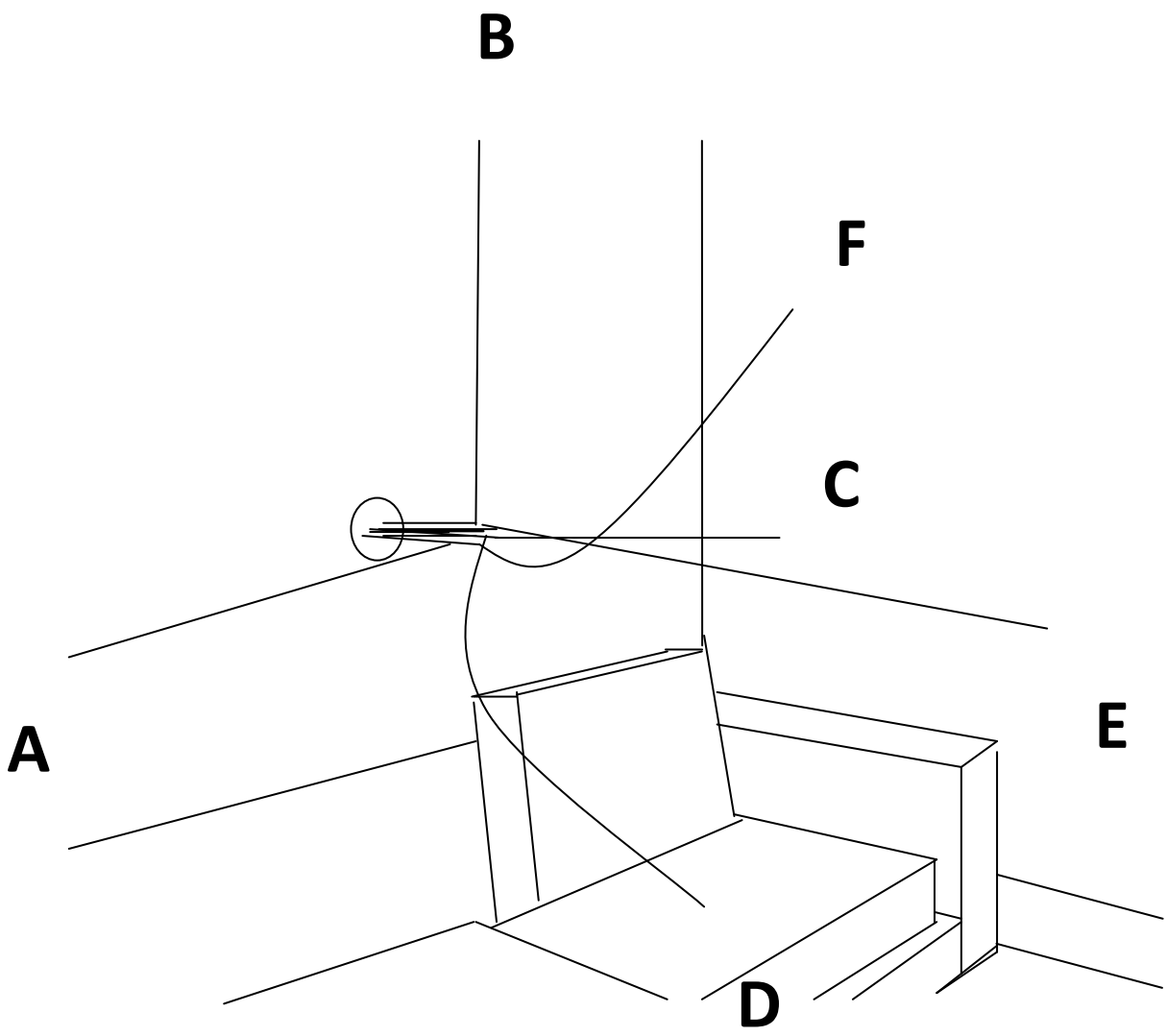


Figure 6.4: Schematic representation of the gas sampling system from inside the cell.

It can be seen in Figure 6.3 that the SS and neoprene tubing have been individually labelled. The labelling was continued to the KOH gas traps to ensure that the area of the cell the fire effluent was being sampled from could be recorded.

On the pump side of the gas trap generic hose was used, this allowed for the pump to be controlled from a safe distance at any time during the progression of the fire. Figure 6.5 illustrates the pump that was used. A manifold was designed and purpose built to accommodate six lines simultaneously. The flow rate was tested at the fire side of the stainless steel tubing rig and just prior to the entry point of the gas traps containing KOH solution using a flow rate meter and determined to be 20 L/min. The flow rate was tested periodically after the burns to determine if any variation was detectable or if there was any particulate matter clogging the lines. Minimal variation in flow rate was noted and the flow rate.

Figure 6.5: Vacuum pump.

A 1.00 mol/L KOH solution was prepared in 2-L batches. Approximately 100 mL of the 1.0 mol/L solution was placed in each of the six Schott© bottles, depicted in Figure 6.3 b). After each Stage was completed approximately 50 mL of the experimental solution was retained for testing and transportation to NSW in two separate glass scintillation vials (25 mL each). The bottles were emptied and rinsed using deionised water then rinsed with stock 1.00 mol/L KOH solution prior to being refilled ready for use again.

The experiment was divided into four sections that the atmosphere would be sampled from before, during and after the progression of the fire. To allow for easy recognition the stages were named accordingly:

- Stage 1: Blank
- Stage 2: Direct Heating of the Exposed Foam
- Stage 3: Post Suppression Time 0 mins
- Stage 4: Post Suppression Time 30 mins

The atmosphere was drawn through the KOH solution according to the conditions outlined in Table 6—1.

Table 6—1: Conditions for gas sampling during each stage.

Conditions	*Stage 1*	*Stage 2*	*Stage 3*	*Stage 4*
Stage Name	Blank	Direct Heating of the Exposed Foam	Post Suppression Time Zero (T_0)	Post Suppression Time Thirty (T_{30})
Temperature	Ambient	190 – 197 °C	Approaching ambient	Ambient
Sampling time	10 min	10 min	10 min	10 min
Flow rate	20 L/min	20 L/min	20 L/min	20 L/min
Collection points	A – F	A – F	A – F	A – F
Sample solution	100 mL 1.00 mol/L KOH (pH 14)	100 mL 1.00 mol/L KOH (pH 14)	100 mL 1.00 mol/L KOH (pH 14)	100 mL 1.00 mol/L KOH (pH 14)
Solution retained	2 x 25 mL	2 x 25 mL	2 x 25 mL	2 x 25 mL

As has been discussed in Chapter 4 the burns were conducted at a purpose built facility at QCESA. Sections 0 and 4.4 describe the size of the cell and the placement of the thermocouples respectively.

As described in Table 6—1 prior to heating the cell, the environment from the ambient atmosphere was drawn through the KOH solution for ten minutes as a blank to determine a baseline reading. The experimental burns were undertaken at a purpose built facility which housed many additional sites where fires were being conducted for training and research.

Therefore the collection of the blank served two purposes; collecting a base atmospheric indication of HCN present that may have not cleared with the use of the scrubber after each test burn, or determining if HCN could be detected from the surrounding work being carried out after the immediate atmosphere had been cleared.

Following the collection of a sample from the ambient atmosphere the heating stage was undertaken. Figure 6.6 illustrates effectively how the heating stage of the experiment was set up. A heating gun (Bosch PHG 360 DCE) was positioned to channel hot air toward the face of the exposed PU foam. The temperature at the face of the PU foam directly in front of the heating gun dictated the distance between the heating gun and the foam.

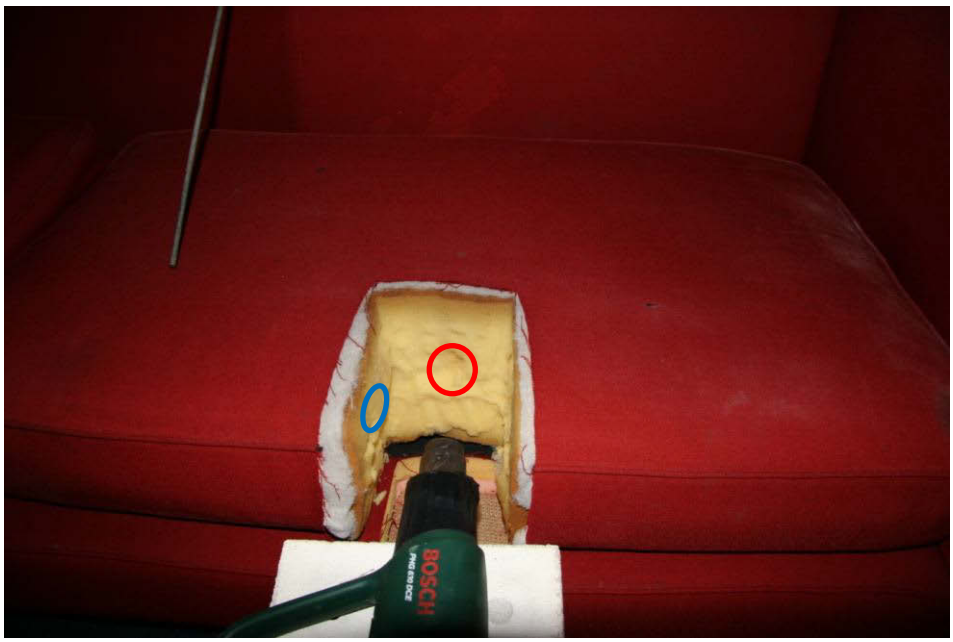


Figure 6.6: Set up for the Stage 2 (heating stage); circles indicate positions of thermocouples directly in front of heat gun at heated surface (red circle) and perpendicular to the surface being heated (blue circle).

The temperature at the face of the exposed foam was monitored and recorded by two k-type thermocouples that had been inserted into the cushion. The tip of each of the thermocouples was pushed through the foam so that the tip was at the exposed surface of the foam. One thermocouple was placed directly in-front of the heat gun, indicated by the red circle in Figure 6.6, and the second was placed on exposed surface of the wall perpendicular to the surface being heated indicated by the blue circle in Figure 6.6.

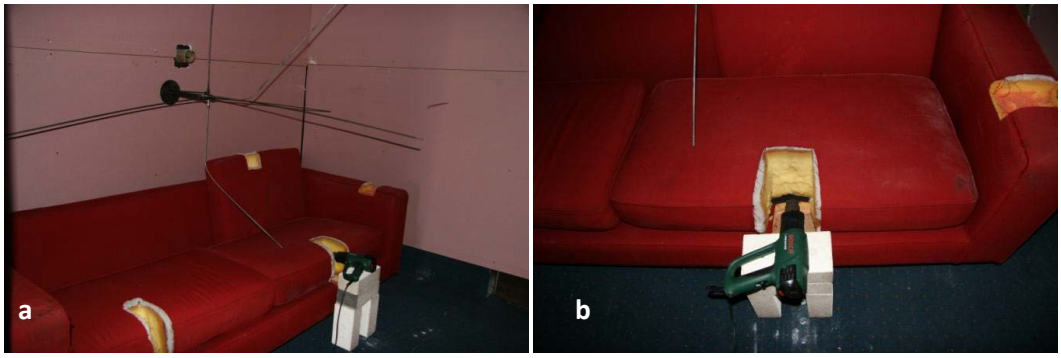


Figure 6.7: Position of the heat gun a) and b).

The distance between the heating gun and the surface of the PU foam was dictated by the temperature being recorded at the face of the PU by the k-type thermocouple rather than the temperature display on the heating gun. The quick response of the thermocouples allowed for real time adjustment if the temperature fluctuated outside of the defined range. The temperature was maintained at 190 – 197 °C for 30 minutes before the atmosphere was drawn through the KOH solution for ten minutes. During that time the temperature at the face of the PU was maintained between 190 – 197 °C.

Following the heating stage of the test burns the fuel load was ignited and the fire was allowed to develop naturally. The details of that section of the fire have been presented in detail in Chapter 4. At the time of initial suppression, T_0, a sample of the atmosphere from inside the cell was collected in accordance with the parameters outlined in Table 6—1 for ten minutes.

At T_{30} the post suppression atmosphere was drawn through the gas trap for ten minutes according to the parameters outlined in Table 6—1.

As indicated in Figure 6.4 the array was labelled from A – F to indicate where the fire effluent was drawn from inside the cell. It is illustrated in Figure 6.3 a) and b) that the identification of the sampling points was continued on into the individual bottles that made up the gas trap. The location that the samples were collected from during each burn was also recorded to account for each sample from any one point in the cell and for accountability and traceability during transportation, storage and subsequent analysis.

6.5.1 Ion Selective Electrode (ISE)

A *TPS uniPROBE Cyanide (CN^-) ISE* was used to conduct the measurements conducted in this section of the work. The ISE used a solid state electrode with a pressed silver iodide pellet. The pellet develops a millivolt (mV) potential proportional to the CN^- ions in the test solution.

In accordance with the product recommendations, the ISE was initially conditioned overnight to ensure that the instrument had stabilised, with minimal drift.

A calibration curve was constructed by creating standard cyanide solutions (with pH adjusted > 12) and measuring the potential of each buffered standard solution. The results were plotted against the concentration and the log of the concentration to form the curve. The latter was easiest to follow visually and used for the majority of the results.

Standard cyanide solutions were made using AJAX potassium cyanide (KCN) salt in half order of magnitude increments from 1.00×10^{-6} mol/L to 1.0 mol/L. To buffer each standard solution 5.00 mL of 10 mol/L sodium hydroxide (NaOH) solution was added to 50 mL of each standard solution.

Starting with the lowest concentration of the buffered standard solutions, 1.00×10^{-6} mol/L, the standard was placed in a 100 mL beaker with a magnetic stirrer and placed on a stirring platform. The ISE was lowered into the buffered standard solution and any bubbles that may have formed on the surface of the tip during the immersion were dislodged by gently tapping the body of the ISE. The mV of each solution was measured using the ISE which was connected to an ion meter. When the reading had stabilised to a drift of < 0.5 mV/min the reading was recorded, but the tip was not held in solution longer than 90 seconds.

After the reading was recorded the ISE was removed from the solution and rinsed with deionised water and blotted dry. The mV for the remaining buffered standard solutions was measured and recorded using the steps outlined for the 1.00×10^{-6} mol/L solution. When the mV for the buffered standard solutions had been recorded, the ISE was placed in the lowest concentration of the standard solution and allowed to re-equilibrate.

During the time the time the ISE was re-equilibrating the calibration curve was constructed. The product statement suggested that an acceptable slope for the response was -57 +/-3 mV,

therefore if that was achieved the calibration curve was adopted for that series of tests, or repeated if the slope was outside that range.

After the drift for the mV measurement had settled to < 0.5 mV/min the ISE was considered ready to use on the experimentally derived samples.

The samples that had been collected during the experimental work were already at a pH > 12 due to the trapping medium and therefore did not require buffering.

For each of the burns conducted at QCESA, six samples were collected during the four stages for each of the 18 burns. Therefore 432 individual samples that had been collected over two scintillation vials producing 864 vials in total. The samples from Stage 2 – Heating, Stage 3 – T_0 Post Suppression and Stage 4 – T_{30} Post Suppression were tested.

Approximately 25 mL of the experimentally derived solution and a magnetic stirrer were deposited into a 50-mL beaker and placed on a stirring platform. The ISE was used to measure the mV of the solutions collected during the experimental work in the same manner as was described for the development of the calibration curve.

After the reading was recorded the ISE was removed from the solution and rinsed with deionised water and blotted dry. This method was repeated for the samples collected from Burns 1 – 6.

The measurements were recorded at ambient laboratory temperature in succession. A calibration curve was developed every day that measurements were recorded from the experimentally derived solutions.

6.5.2 Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-Visible Spectroscopy (UV-Vis) was the technique used to conduct the measurements in this section of the work.

A Hewlett Packard 8453 UV-Vis spectrophotometer was used to record the spectra. The spectra were collected in absorbance from 200 – 400 nm with a 1 cm path length (1 $\times$ 1 cm

quartz cuvette). Spectra were processed using UV-Vis Chemstation Software Version B04.01 (61).

Tetracyanonickelate complex has characteristic absorbance at 267 and 385 nm. A calibration curve was constructed by measuring the primary absorbance, 267 nm, displayed by the tetracyanonickelate complex that was created when standard CN^- solutions were combined with Ni^{2+} and OH^- solutions. The curve was constructed by plotting the absorbance of the complex against each standard concentration of the CN^- solution.

A 1.0×10^{-2} mol/L stock solution of CN^- was made by dissolving 0.3256 g of AJAX KCN in ultra pure (UP) water and making up to volume (500 mL) in a-grade volumetric glassware. A 1.00 mol/L OH^- solution was made by dissolving 56.11 g of KOH in UP water and making up to volume (1.00 L) in a volumetric flask. Serial dilution was employed to make two sets of the standard CN^- solutions:

- Set 1: 1.00×10^{-3}, 5.00×10^{-4}, 1.00×10^{-4}, 5.00×10^{-5}, 4.00×10^{-5}, 3.00×10^{-5}, 2.00×10^{-5}, 1.00×10^{-5} and 5.00×10^{-6} mol/L.

- Set 2: 1.00×10^{-3}, 5.00×10^{-4}, 1.00×10^{-4}, 5.00×10^{-5}, 4.00×10^{-5}, 2.00×10^{-5}, 1.00×10^{-5} and 5.00×10^{-6} mol/L.

Both the standard solutions were made up to volume using the 1.00 mol/L OH^- stock solution.

A 2.00×10^{-3} mol/L stock solution of Ni^{2+} was made by dissolving 0.2363 g of AJAX $NiCl_2$ in UP water and making it up to volume (500 mL).

A 2.00 mL aliquot of 5.00×10^{-6} mol/L of standard CN^- solution was deposited into a 1 cm quartz cuvette using an A-grade glass pipette. As the pH of the solutions, stock and experimental, were not ideal for analysis using UV/Vis spectroscopy the pH of the CN^- was adjusted to between pH 11 – 12 by adding between 780 – 890 μL of 1.00 mol/L sulfuric acid (H_2SO_4). This process also served to suppress any sulfide ions, which would have swamped the absorbance displayed by the cyano complex, which may have been collected during the sampling of the fire effluent. At this point a spectrum was collected of the CN^-/OH^- which was subtracted from the spectrum collected after the addition of the Ni^{2+} and the subsequent formation of the cyano complex.

A (calibrated) air displacement pipette (Gilson) was used to introduce aliquots of the Ni^{2+} solution to the cuvette. To ensure that the species reacted and formed the tetracyanonickelate complex the cuvette was agitated briefly, a spectrum was then collected. The addition of Ni^{2+} solution was repeated until the absorption peak displayed at 267 nm reached its maximum. That maximum value was used as the absorption value when plotting against the CN^- to form the calibration curve.

The cuvette was then emptied, rinsed with UP water and dried. Then the method for measuring an absorbance was repeated through all of the prepared standard solutions.

Over a period of one month nine calibration curves were developed using the same method, three of the curves were constructed using the same solution and six were constructed using a different solution. Both solutions were prepared by the same operator using a-grade glassware.

The experimentally derived solutions from the work conducted at QCESA were tested using the method outlined above. The point of difference was that the solutions with gas collected at QCESA were used in place of the standard CN^- solutions.

6.6 Results and Discussion

6.6.1 Ion Selective Electrode (ISE)

Techniques that drew the fire effluent though a solution were explored and subsequently apparatus that could be used on-site or in field to analyse the solution were used. The criteria for such a technique and apparatus included the capacity to conduct the sampling remotely to increase the distance of the operator to the cell during the test burns. It was desirable for the technique to be, in addition to being qualitative, quantitative and to have the capability to generate results quickly while being relatively easy to use in the field with minimal equipment required. The clear choice was to employ an ISE specific to CN^-.

A number of different ISEs were explored. Sensitivity was a consideration when choosing the ISE due to the uncertainty associated with the amount of HCN being produced in the pre-flame and post suppression stages of the fire. Other factors contributed when deciding the most suitable ISE for this work, including functionality and cost. The TPS uniProbe was a clear

contender for the following reasons: the literature provided with the ISE indicated a linear concentration range between 1.0×10^{-5} mol/L to 1.0 mol/L it was relatively inexpensive when compared with other CN^- specific ISEs commercially available, it did not require a reference probe, which would help the robustness for use in the field and the tip containing the membrane could be replaced by the user with ease. The latter was advantageous for two reasons: the membrane degrades when submerged in solutions containing CN^-, the rate of degradation being proportional to the concentration of CN^- ions present; and if desired other ions can be tested for by introducing a tip specific to that ion.

The calibration standards were made by making an aqueous cyanide salt solution which was adjusted to the appropriate pH using a hydroxide solution. As a result it was postulated that using a basic aqueous solution, such as a hydroxide solution, would be an ideal trapping medium forcing the HCN into solution as CN^-. The chemistry used is straightforward yet effective, forcing CN^- into solution for testing and providing a mechanism for storage and safe transportation.

The rate of formation of HCN is dependent on the pH, a greater pH prevents the loss of HCN as gas.

The method used for this work was included with the ISE by the manufacturer, TPS (Pty Ltd). Although the directions provided with the ISE suggested that the linear portion of the response curve of the electrode would be between 1.0×10^{-5} mol/L – 1.0 mol/L standards are generally chosen one order of magnitude apart. Below 0.3 ppm CN^-, standards should be chosen closer together ie 0.1 ppm and 0.5 ppm. Further on the instructions state that the detection range is 1.0 ppm to 2600 ppm (5.0×10^{-6} mol/L – 1.0×10^{-1} mol/L).

From the published literature it was known that HCN would be produced during the progression of the fire. However it was uncertain if HCN would be detected during the heating stage, or post suppression of the fire, therefore it was difficult to estimate the concentrations in which to construct the calibration curve from.

However it was known from preliminary work during the method development that it was likely to be in the lower concentration range of the linear portion of the apparatus' capacity. In addition, while it was found that measuring the mV of larger concentration solutions, such as 1.0×10^{-2} mol/L and 1.0 mol/L solutions, was rapid it took a significant amount of time to

re-equilibrate the ISE to allow for the smaller measurements to occur. As a result a calibration curve was constructed from 1.0 x 10^{-6} mol/L - 1.0 x 10^{-3} mol/L in half order of magnitude intervals.

After the tip had been conditioned in accordance with the product statement a calibration curve was prepared. The theoretical slope for CN^- is 59/n (n=-1), the suggested an acceptable slope for this particular apparatus is -57 +/-3mV. It has been indicated in Table 6—2that after the initial conditioning period, and subsequent conditioning periods, the slope of the curves generated were greater than -57 +/-3mV and the coefficient of determination (R^2 value) was not ideal. However, as have been indicated in Table 6—2 the R^2 recorded for the third calibration curve was significantly better.

Despite the improvement, the difference in potential between measurements was not performing in accordance with the product usage parameters.

Table 6—2: Initial ISE calibration curves.

Calibration Curve	*Curve equation*	*Coefficient of determination (R^2)*
1	y = -63.309x - 326.37	R^2 = 0.9851
2	y = -75.215x - 367.93	R^2 = 0.9857
3	y = -69.649x - 354.77	R^2 = 0.9922

It was proposed that additional conditioning was required and the tip of the ISE was placed in a < 1.0 x 10^{-6} mol/L CN^- solution overnight. As can be seen by the calibration curve presented in Figure 6.8 the response of the ISE was improved significantly. However, the ISE response had a drift of > 0.5 mV for more than 90 seconds in the 1.0 x 10^{-6} mol/L CN^- standard solution and, as a result, that measurement was not recorded.

The potential of the experimental solutions gathered during Burns 1 and 2 was measured and recorded. The CN^- concentration in the individual solutions was determined by fitting the recorded mV value into the equation of the calibration curve.

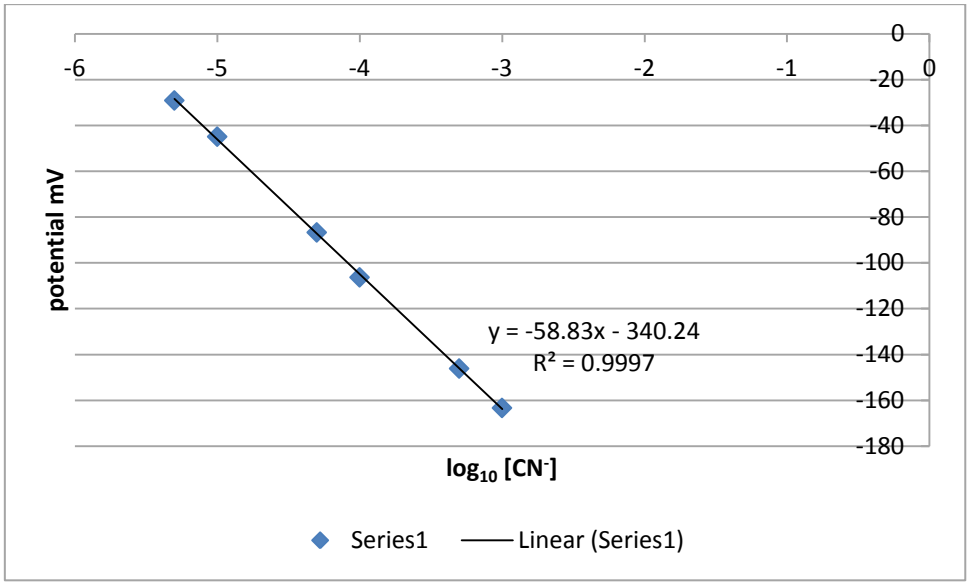


Figure 6.8: Calibration curve for Burns 1 & 2.

The mV measurement recorded for the blank sample collected during the Burn 1 experiments was higher than all the mV measurements recorded (which corresponds to a lower CN^- concentration) for the Heating Stage, both of which fell outside the data set used to create the calibration curve. The curve was extrapolated to derive corresponding concentrations for the mV values recorded. It must be highlighted though that the derived concentration is outside the lower detection limit of the instrument, which is 5.0×10^{-6} mol/L.

The equations for the calibration curves that were developed for the three seater couch series have been presented below in Table 6—3. The limit of detection (LOD) and the limit of quantitation (LOQ) was determined based on the curves and has been included in the table.

Table 6—3: Calibration Curve Comparison Burns 1 – 6.

Calibration Curve	*Curve equation*	*Coefficient of determination*
Burns 1 & 2	y = -58.83x - 340.24	R^2 = 0.9997
Burn 3	y = -54.18x - 294.05	R^2 = 0.9961
Burn 4	y = -54.918x - 298.2	R^2 = 0.9951
Burn 5	y = -62.521x - 339.17	R^2 = 0.9965
Burn 6	y = -59.456x - 319.14	R^2 = 0.9992
	LOD = -1.1 mV	***LOQ = -3.4 mV***

As has been illustrated in Table 6—3 individually the calibration of the ISE had performed particularly well, exceeding the manufacturers specifications. The ISE was consistently returning a linear response between 1.0 x 10^{-6} mol/L - 1.0 x 10^{-3} mol/L, an order of magnitude below indicated by the product statement and 0.5 x 10^{-6} mol/L below the suggested detection response.

The capability for the ISE to be used in field, the tips to be replaced in addition to the LOD advertised by the manufacturer was attractive. Primarily the attraction was attributed to the LOD as the range of HCN to be detected was not known. In addition the potential to rapidly quantify HCN concentration in field using a straightforward cost effective method was particularly appealing.

For its intended purpose the ISE initially exceeded behaviour expectations and detected the presence of CN^- at different stages of fire development. As the analysis continued the challenges associated with utilising this technique became apparent.

Although the curves were developed using the same standard solutions over five individual days, Table 6—4 illustrates how the ISE responds varied over different days. The limited precision of the tip was not wholly unexpected and a comparison of the ISEs response over five different days was made.

Table 6—4: ISE Response (in mV) to standard solutions over five individual days.

	1.00×10^{-6}	5.00×10^{-6}	1.00×10^{-5}	5.00×10^{-5}	1.00×10^{-4}	5.00×10^{-4}	1.00×10^{-3}
Burns 1&2	-	-29.1	-44.9	-86.7	-106.3	-146.1	-163.3
Burn 3	26.4	0.6	-24.5	-60.3	-78.5	-116.1	-131.6
Burn 4	24.1	-1.5	-20.5	-60.0	-78.1	-118.6	-135.7
Burn 5	36.0	-8.3	-20.6	-74.6	-94.8	-130.9	-148.9
Burn 6	35.0	-1.1	-20.0	-64.7	-82.0	-123.4	-140.4
Average	***30.38***	***-7.88***	***-26.10***	***-69.26***	***-87.94***	***-127.02***	***-143.98***
%RSD	***20%***	***157%***	***40%***	***17%***	***14%***	***10%***	***9%***

The data contained in Table 6—3 and Table 6—4 was considered and when comparing inter and intra calibration data it was evident that the ISE could only be used reliably when calibrated at the time the samples were being analysed.

The results recorded from Burns 1 – 6 have been presented in Table 6—5. The potential of the sample solutions were recorded and converted to concentration in mol/L using the equation from each calibration curve. The pale green highlighted values are above the LOD and the dark green highlighted values are above the LOQ. The **+** indicates that positive value was recorded according the calibration on that day; though it was below the overall determined LOD. The **–** indicates that the value recorded was below the value recorded for the blank.

Table 6—5: ISE Concentration [mol/L] Results Burns 1 – 6 (pale green = values above LOD, dark green = values above LOQ, '+' = positive values on calibration curve for the day but below overall LOD, '-' = the value recorded was below that recorded for the blank).

	POSITION IN ARRAY					
	BURN 1					
STAGE	***A***	***B***	***C***	***D***	***E***	***F***
Heating	2.3×10^{-6}	2.1×10^{-6}	2.3×10^{-6}	2.0×10^{-6}	+	+
T_0 Suppression	2.2×10^{-5}	**4.5×10^{-4}**	3.0×10^{-5}	3.0×10^{-5}	3.4×10^{-5}	2.5×10^{-5}
T_{30} Suppression	1.9×10^{-5}	1.4×10^{-5}	1.2×10^{-5}	1.2×10^{-5}	7.1×10^{-6}	6.1×10^{-6}
	BURN 2					
	A	***B***	***C***	***D***	***E***	***F***
Heating	6.0×10^{-6}	8.0×10^{-6}	6.4×10^{-6}	7.0×10^{-6}	5.4×10^{-6}	5.2×10^{-6}
T_0 Suppression	1.2×10^{-5}	**6.7×10^{-5}**	1.5×10^{-5}	1.2×10^{-5}	1.3×10^{-5}	3.3×10^{-6}
T_{30} Suppression	6.3×10^{-6}	2.6×10^{-6}	3.2×10^{-6}	7.9×10^{-6}	5.6×10^{-6}	3.0×10^{-6}
	BURN 3					
	A	***B***	***C***	***D***	***E***	***F***
Heating	+	+	+	+	+	-
T_0 Suppression	1.8×10^{-5}	1.4×10^{-5}	4.2×10^{-6}	4.0×10^{-6}	+	-
T_{30} Suppression	+	**1.1×10^{-4}**	9.0×10^{-6}	8.9×10^{-6}	6.5×10^{-6}	5.0×10^{-6}
	BURN 4					
	A	***B***	***C***	***D***	***E***	***F***
Heating	+	-	-	+	+	-
T_0 Suppression	+	7.3×10^{-6}	+	+	+	+
T_{30} Suppression	-	-	-	-	-	-
	BURN 5					
	A	***B***	***C***	***D***	***E***	***F***
Heating	***VOID***					
T_0 Suppression	+	2.2×10^{-5}	+	+	4.0×10^{-6}	+
T_{30} Suppression	+	+	+	+	+	+
	BURN 6					
	A	***B***	***C***	***D***	***E***	***F***
Heating	+	+	+	+	+	+
T_0 Suppression	5.3×10^{-6}	4.7×10^{-5}	+	5.6×10^{-6}	+	6.2×10^{-6}
T_{30} Suppression	-	-	-	-	-	-

The highest concentration recorded for CN^- was at point B during the T_0 Suppression stage in each burn. This was not unexpected due to the density of HCN, it being a common component of smoke, in addition to the position of smoke layer during and post suppression of fire.

It has been illustrated in Table 6—5 that the heating period for Burn 5 does not have any values. The maximum temperature, 197 °C, used for that stage was exceeded. As a result the face of the exposed PU foam was not maintained; it reached its auto-ignition

temperature and ignited. The fire was swiftly suppressed and did not impact significantly on the mass of the couch; however as flame had occurred the parameters of that stage of the experiment had been exceeded. Therefore the environment for that stage of the experiment was not collected.

The samples collected during Burn 7 were analysed using the curve that had been generated; although in an attempt to improve the response of the curve the ISE was conditioned overnight in accordance with the products instruction. The curve was constructed again the next day with no clear improvement noted. Again the tip was conditioned overnight and the same approach was followed for Burn 8. The results of the construction and reconstruction of the calibration curves have been presented in Table 6—6.

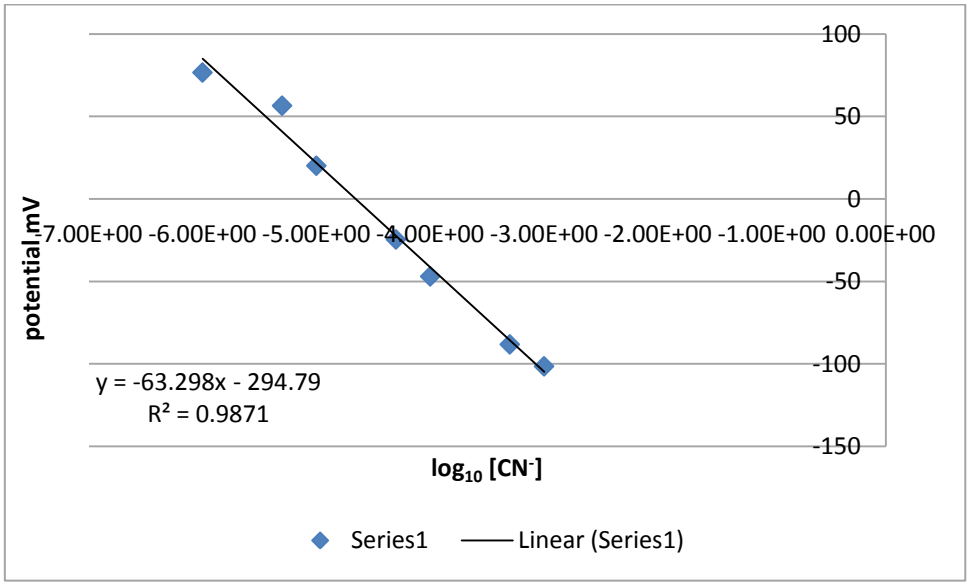


Figure 6.9: Calibration curve Burn 7 (a).

The curves demonstrate that the ISEs performance declined during the analysis of the samples collected from Burn 7 and Burn 8. The LOD and the LOQ, based on the additional calibration curves, was determined and has also been included in Table 6—6.

Table 6—6: Calibration Curve Equation Comparison Burn 7 and Burn 8.

Calibration Curve	*Curve equation*	*Coefficient of determination*
Burn 7 (a)	y = -63.298x - 294.79	R^2 = 0.9871
Burn 7(b)	y = -63.488x - 266.4	R^2 = 0.9739
Burn 8 (a)	y = -60.382x - 241.04	R^2 = 0.9364
Burn 8 (b)	y = -66.588x – 247	R^2 = 0.8909
	LOD = -1.0907 mV	***LOQ = -3.3051 mV***

The results for Burn 7 and Burn 8 have been presented in Table 6—7 using the equation developed from Burn 7 (a) and Burn 8 (a) calibration curves, respectively. The value highlighted in green is above the LOQ, as defined in Table 6—3. The **+** indicates that positive value was recorded according to the days calibration curve; though it was below the overall derived LOD. The – indicates that the value recorded was below the value recorded for the blank.

Table 6—7: ISE Concentration Results Burns 7 & 8 (pale green = values above LOD, '+' = positive values on calibration curve for the day but below overall LOD, '-' = the value recorded was below that recorded for the blank).

	BURN 7					
	Position in the Sampling Array					
	A	***B***	***C***	***D***	***E***	***F***
Heating	**+**	-	-	-	-	-
T_0 Suppression	**+**	4.0×10^{-5}	-	-	-	**+**
T_{30} Suppression	**+**	-	-	-	-	-
	BURN 8					
	Position in the Sampling Array					
	A	***B***	***C***	***D***	***E***	***F***
Heating	-	-	-	-	-	-
T_0 Suppression	-	-	-	-	-	-
T_{30} Suppression	-	-	-	-	-	-

Like the calibration curve developed for Burn 7, the calibration curve being developed for Burn 8 was also losing linearity between 5.0×10^{-6} mol/L and 1.0×10^{-5} mol/L as can be seen in Figure 6.9.

Although initially the ISE exceeded performance expectations, difficulties with the ISE became apparent during the progression of the work. The assurance of a rapid response rate was not experienced with the majority of the samples analysed. It generally took more than 60 seconds per sample, not less than 30 seconds which was prescribed by the manufacturer, for the drift of the apparatus to fall below 0.5 mV/min.

It became clear, during the initial conditioning period, that the tip would need longer to produce an mV response at lower concentrations. Although the basicity of the solutions was in accordance with the manufacturers guidelines it was postulated that the increased response time coupled, and thus time spent in a particularly basic solution, could result in accelerated degradation of the tip. To reduce the effect of high pH on the tip it was not submerged in the standard or test solutions for more than 90 seconds and, where possible, only one burn per day was analysed.

Regardless of the precautions taken to reduce the stress on the tip the results of the calibration curve indicated in Figure 6.9 and Table 6—6 illustrate that the effectiveness of the tip steadily decreased, to the point of being unusable, in a relatively short period of time. This impacted on part of the attractiveness of the apparatus, which was its cost effectiveness.

The results for Burns 1 – 6 and then Burn 7 and 8 have been presented as the concentration based on the calibration curve. Had they been corrected to reflect that values of the blanks collected, in the majority of the experimentally derived samples, the results would have been significantly below the prescribed detection level of the ISE.

The accuracy of the apparatus also impacted on it being appealing for the work undertaken in this chapter. It has been illustrated that the ISE proved useful as a qualitative tool when determining the presence of HCN in the sample solutions. However, it is suggested that for the concentrations seen in this work that there were limits to the ISE usefulness for the quantitative determination of HCN

Therefore, rather than focus on the specific concentrations derived the results were analysed by determining if a general trend could be determined during each burn, specifically in Burns 1 - 6. The generalised results have been presented in Figure 6.10.

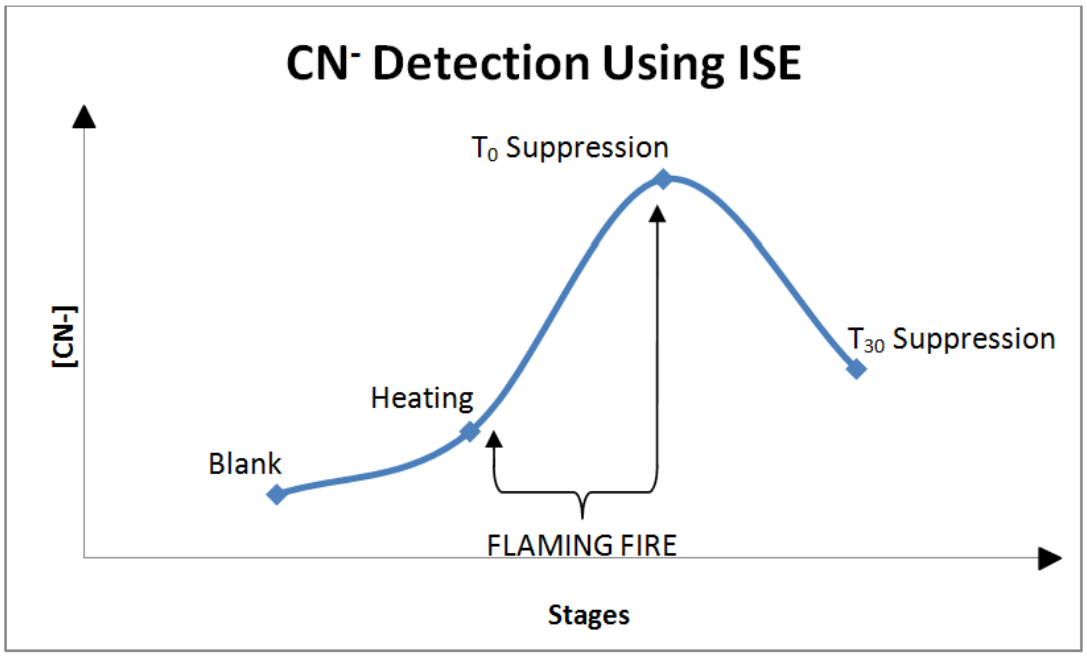


Figure 6.10: CN^- Detection Using ISE.

Comparing the results of the burns was a crucial part of the experimental work to determine if a trend emerged regarding the concentration of HCN at different stages of the fire progression. Without the capacity to directly compare the results of the burns, in addition to the degradation of the tip, there was little reason to continue the analysis of the experimental samples in this manner.

6.6.2 Ultraviolet-Visible Spectroscopy (UV-Vis)

The 1.0 mol/L OH^- solution was used as the medium to trap any acidic components from the fire effluent. As discussed in Section 6.4 trapping the gas in a basic solution would allow for testing to occur in-field. In addition it would allow for safe storage and transportation which permitted secondary methods of analysis (that utilised this type of trapping medium) to be conducted and act as confirmatory testing. The use of UV-Vis spectroscopy was identified as a suitable method.

Scoggins method of tetracyanonickelate complex formation was attractive as analysis using UV-Vis would give rise to a characteristic absorbance spectrum produced by the complex [193, 195]. However, the components necessary to successfully apply Scoggins method were unstable and not deemed suitable for the requirements of experimental work. It was

postulated that as the components of the fire effluent had already been trapped in a basic medium, the OH^- solution, that a Ni^{2+} solution could be added to the trapping medium and the combination of the CN^- present and excess Ni^{2+} would form the tetracyanonickelate complex.

Such a method was not reported in the literature and gave rise to the development of a novel detection method. The method involved the safe collection of gaseous effluent from the heating stage to post suppression of a fire in a OH^- solution medium and later treatment to form tetracyanonickelate which gave a characteristic absorbance when analysed using UV-Vis spectroscopy.

It was discussed in Section 6.6.1 that the ideal pH for use with the ISE was greater than pH 12 which prevented the loss of CN^- as gaseous HCN. The greater pH was proportional to the amount of HCN trapped in solution as CN^-, therefore the pH was maintained at approximately pH 14. While this was considered ideal for the ISE work, the highly basic nature of the solution negatively impacted on the UV – Vis performance by obstructing the signal. As a result the pH of each sample was adjusted to a pH 11 – 12 by introducing approximately (780 – 890 μL) of 1.00 mol/L H_2SO_4 to the cuvette at the time of analysis. The acidification was undertaken at this point to ensure the sample stock would remain at a suitable pH and the gas would certainly remain trapped in solution. An added benefit of acidifying each sample using H_2SO_4 was that any sulfide ions present would be suppressed. Sulfide ions could interfere with the absorbance signal displayed by the tetracyanonickelate complex and hence there removal was required.

The method was validated by reviewing the performance of the instrument by comparing inter and intra data when 22 calibration curves were constructed over a period of eight weeks.

The method of making the stock and standard solutions was described in detail previously in Section 6.5.2. It should be noted though that the ten standard solutions were made up using the 1.00 mol/L OH^- solution in order to replicate the conditions of the experimentally derived samples. The ten standard solutions were made they were made in two sets utilising the same stock solutions.

The first six calibration curves constructed were conducted over a four week period. Three were constructed using one standard solution and the other three curves were developed using a different set of standard solutions. The remaining 16 calibration curves were constructed over a four week period using three different standard solutions.

The characteristic λ maximum for the tetracyanonickelate complex occur at 267 nm and 285 nm. The absorption peak registering at 267 was the primary peak and was therefore used for the construction of the calibration curve. As a confirmatory tool, the presence of the secondary peak, displayed at 285 nm, was recorded. For any given concentration of the standard solutions the absorbance of the peak at 285 nm ranged between 0.45 - 0.65 of the absorbance displayed at 267 nm.

Table 6—8: Absorbance (AU) at Specific Wavelengths (nm).

SPECTRA	*266 nm*	*267 nm*	*268 nm*	*284 nm*	*285 nm*	*286 nm*
1	0.635	**0.656**	0.656	0.277	**0.284**	0.278
2	0.641	**0.661**	0.660	0.288	**0.29522**	0.289
3	0.648	**0.666**	0.665	0.290	**0.297**	0.291
4	0.649	**0.669**	0.668	0.292	**0.299**	0.294
5	0.653	**0.669**	0.668	0.294	**0.301**	0.295
6	0.653	**0.673**	0.672	0.299	**0.306**	0.300
7	0.659	**0.678**	0.677	0.305	**0.312**	0.306
8	03658	**0.677**	0.676	0.305	**0.311**	0.306

To determine which value was to be utilised from the data in the calibration curve predetermined criteria were observed. The maximum was indicated by the highest value in the 267 nm data and corroborated by the corresponding 285 nm value also being the largest values recorded for that wavelength. The values flanking either side of the primary, 267 nm, and secondary, 285 nm, absorptions were also recorded an example of which has been provided in . Table 6—8 highlights the maximum values recorded at 267 nm and 285 nm derived for a 5.0×10^{-4} CN^- solution which are 0.678 and 0.312 nm, respectively. It can be seen that the absorbance value recorded for the peak seen at 285 nm is present, though it is less than the value recorded for 267 nm. In addition the values flanking both highlighted values for 267 nm and 285 nm are all smaller, illustrating the values selected were the maximum.

It has been indicated, by the arrows in Table 6—8 that the initial values for 267 nm was lower than the initial value for 268 nm. As the difference was 3.0×10^{-5} AU at the initial reading this was not considered significant enough to discontinue the determination of the maximum. Had the absorption values for the flanking frequencies, 266 or 268 nm, been considerably higher or occurred further on during the experiment the addition of Ni^{2+} would have ceased at that point. The maximum would then have been taken as the previous value which would have been used for the calibration curve.

The same criteria were upheld when identifying the value to be used for each standard solution to be incorporated into the calibration curve that day. As mentioned previously 22 curves were completed in two one month clusters the results of the first cluster will be discuss in the coming paragraphs. The curves were developed using the same method, utilising two separately made standard solutions. The results have been indicated in Table 6—9 and the lowest (purple) and highest (blue) value for each concentration band has been indicated.

Table 6—9: UV-Vis results for maximum absorbance (AU) at 267 nm.

	Standard Solution 1			***Standard Solution 2***		
[mol/L]	**1**	**2**	**3**	**1**	**2**	**3**
5.00×10^{-6}	0.03317	0.01652	0.02284	0.00808	0.01421	0.00794
1.00×10^{-5}	0.02231	0.01210	NA	0.02461	0.02189	0.01595
2.00×10^{-5}	0.05457	0.05632	0.05096	0.05093	0.06060	0.05708
4.00×10^{-5}	0.09110	0.10799	0.10553	0.09836	0.11314	0.10591
5.00×10^{-5}	0.10929	0.13342	0.13143	0.17722	0.14364	0.18624
1.00×10^{-4}	0.19960	0.22366	0.24708	0.24060	0.22349	0.20723
5.00×10^{-4}	0.75892	0.71736	0.73364	0.79183	0.78134	0.78366
1.00×10^{-3}	1.40780	1.37800	NA	1.51600	1.52500	1.29650

The average, standard deviation (STD) and relative standard deviation (%RSD) were determined. In addition, it was determined if the identified highest and lowest values should remain in the data set. The results of determining average, STD, %RSD of the data sets in addition to determining if the highest and lowest values were to remain in the set have been presented in Table 6—10.

Table 6—10: Questioned maximum values for absorbance (AU) at 267 nm.

Standard CN^-	***Statistical Results***		***Questioned Values***			
[mol/L]	**Average (n=3)**	**%RSD**	**Low**	**High**	**Result**	
5.00×10^{-6}	0.01468	60	0. 76578	2.09977	Y	Y
1.00×10^{-5}	0.01615	29	0.87468	1.82925	Y	Y
2.00×10^{-5}	0.04721	7	1.08501	3.90678	Y	Y
4.00×10^{-5}	0.08887	8	0.31425	3.41539	Y	Y
5.00×10^{-5}	0.12590	21	0.61946	2.25059	Y	Y
1.00×10^{-4}	0.19169	9	0.47271	3.30655	Y	Y
5.00×10^{-4}	0.65246	4	2.36051	5.06978	Y	Y
1.00×10^{-3}	1.18738	7	1.26339	3.90903	Y	Y

In order to determine whether the highest or lowest values could be excluded from the data set as outliers, the average value was subtracted from the questioned value and divided by the standard deviation. Results that returned a value of greater than ten could be discarded as outliers. It can be seen in Table 6—10 that although %RSD results for 5.00×10^{-6} mol/L, 1.00×10^{-5} mol/L and 1.00×10^{-4} mol/L are all above 20%, none of the values could be excluded from the data set.

Calibration curves were constructed by plotting the concentration of the standard CN^- solution and the maximum absorbance at 267 nm measured after the addition of the Ni^{2+} solution. The calibration curve presented in Figure 6.11 has been taken from the data gathered from analysing set one of the standard CN^- solutions.

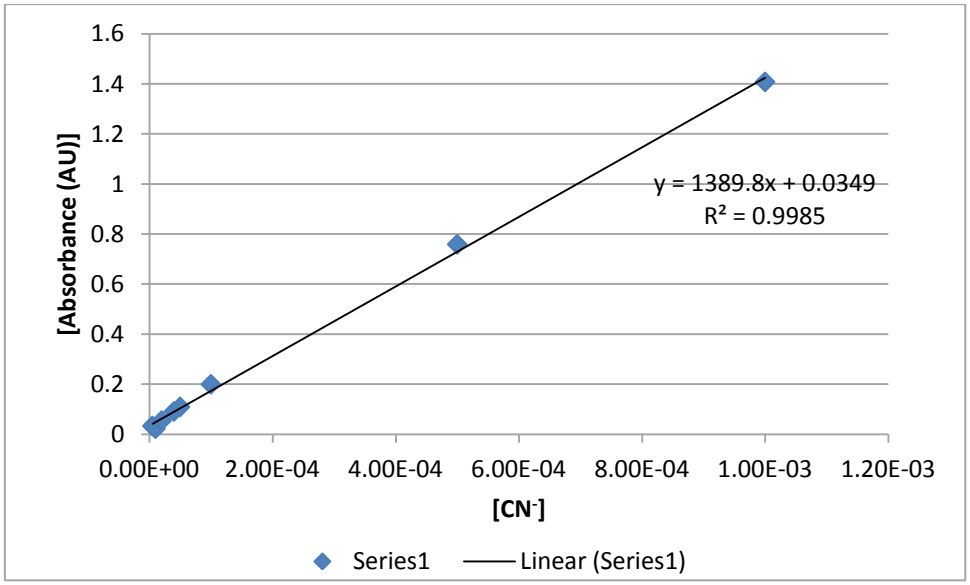


Figure 6.11: Calibration curve standard solution set one.

The equation data from the calibration curves was tabulated to determine the limit of LOD and the LOQ of the instrument.

The LOD was determined using the following equation:

LOQ = 3.3 × (standard deviation of the y intercept / average of the slope)

The LOQ was determined using the following equation:

LOQ = 10 × (standard deviation of the y intercept / average of the slope)

The results have been presented in Table 6—11.

Table 6—11: Equations for the standard CN^- solutions including all data points.

	Burn Number	Slope	y intercept	R^2 value
Standard Solution 1	1	1389.8	0.0349	0.9985
	2	1345.4	0.0406	0.9962
	3	1422.9	0.0371	0.9776
Standard Solution 2	1	1482.2	0.0439	0.9951
	2	1489.4	0.0393	0.9977
	3	1288.6	0.0547	0.9864
Average		1403.05		
STD			0.0064316	
LOD	1.51×10^{-5}			
LOQ	4.58×10^{-5}			

The data gathered for the remaining calibration curves was treated in the same manner as discussed for the initial six, the results have been presented below in Table 6—12, Table 6—13 and Table 6—14.

Table 6—12: Equations for the standard CN^- solutions including all data points (Burns 1 – 6).

	Burn Number	Slope	y intercept	R^2 value
Standard Solution 3	1	3140.3	-0.0065	0.8139
	2	2644.6	0.0075	0.9742
	3	2581.5	0.0169	0.9302
	4	2404.7	0.006	0.9776
	5	2197.8	0.01	0.9795
	6	2543.3	0.0216	0.9828
Average		2585.367		
STD			0.0088816	
LOD	1.13×10^{-05}			
LOQ	3.44×10^{-05}			

Table 6—13: Equations for the standard CN^- solutions including all data points (Burns 7 – 12)

	Burn Number	Slope	y intercept	R^2 value
Standard Solution 4	7	3162.1	0.0146	0.9548
	8	3844.2	0.001	0.95
	9	4160.9	0.0035	0.9778
	10 – 11	3352.5	0.0204	0.9393
	12	3997.5	0.0066	0.9848
Average		3703.44		
STD			0.0072262	
LOD	6.44×10^{-06}			
LOQ	1.95×10^{-05}			

Table 6—14: Equations for the standard CN^- solutions including all data points Burns 13 – 18).

	Burn Number	Slope	y intercept	R^2 value
Standard Solution 5	13	4904.5	0.0241	0.9743
	14	2958.9	0.0205	0.9612
	15	3895.6	0.0004	0.976
	16	4120.8	0.0004	0.9876
	17 – 18	3722.5	0.0034	0.9787
average		3920.46		
STD			0.01036	
LOD	8.72×10^{-06}			
LOQ	2.64×10^{-05}			

The continued performance of the instrument could be considered adequate although it was clear from the results of the regression analysis that there was variation in the outcome. Therefore it was decided that constructing a calibration curve to be used on the day of sample analysis would yield the truest result.

The results from Burns 1 – 6, 7 – 12 and 13 – 18 were converted to concentration [mol/L] using the equation of each corresponding calibration curve, indicated in

Table 6—12, and have been presented in Table 6—15, Table 6—16 and Table 6—17 respectively.

Table 6—15: UV-Vis results for Burns 1 – 6 (Three Seater Couch) (green = vales that lie above the LOQ, orange = values that lie between the LOD and the LOQ, '+' = visible positive result that lies below the LOD, '-' value recorded below the value recorded for the blank).

Three Seater Couch							
		A	**B**	**C**	**D**	**E**	**F**
Burn 1	Heating	-	-	-	-	-	-
	T_0 Suppression	**+**	**+**	**+**	-	1.2024×10^{-5}	**+**
	T_{30} Suppression	**+**	-	-	**+**	-	-
Burn 2	Heating	**+**	**+**	-	-	-	-
	T_0 Suppression	-	2.7352×10^{-5}	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 3	Heating	-	**+**	-	-	-	-
	T_0 Suppression	**+**	**+**	**+**	-	-	-
	T_{30} Suppression	**+**	-	**+**	**+**	**+**	-
Burn 4	Heating	**+**	-	-	-	-	-
	T_0 Suppression	-	-	-	-	**+**	-
	T_{30} Suppression	-	-	-	-	**+**	-
Burn 5	Heating	**VOID**					
	T_0 Suppression	**+**	1.0437×10^{-4}	-	-	**+**	**+**
	T_{30} Suppression	-	-	**+**	-	-	-
Burn 6	Heating	-	**+**	**+**	**+**	**+**	-
	T_0 Suppression	**+**	3.0816×10^{-5}	**+**	-	-	-
	T_{30} Suppression	-	-	**+**	-	-	-

Table 6—16: UV-Vis results for Burns 7 – 12 (Two Armchairs) (green = vales that lie above the LOQ, orange = values that lie between the LOD and the LOQ, '+' = visible result that lies below the LOD, '-' value recorded below the value recorded for the blank).

Two Armchairs							
		A	**B**	**C**	**D**	**E**	**F**
Burn 7	Heating	-	-	-	-	-	-
	T_0 Suppression	-	3.4778×10^{-5}	-	-	-	**+**
	T_{30} Suppression	-	-	-	-	-	-
Burn 8	Heating	-	-	-	-	-	-
	T_0 Suppression	-	1.5889×10^{-5}	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 9	Heating	1.9145×10^{-6}	2.1457×10^{-6}	-	-	-	-
	T_0 Suppression	-	2.2176×10^{-6}	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 10	Heating	-	-	-	-	-	-
	T_0 Suppression	-	**+**	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 11	Heating	-	-	-	-	**+**	-
	T_0 Suppression	-	4.4376×10^{-5}	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 12	Heating	-	-	-	-	-	-
	T_0 Suppression	-	2.5236×10^{-5}	-	-	-	**+**
	T_{30} Suppression	-	-	-	-	-	-

Table 6—17 : UV-Vis results for Burns 13 – 18 (One Armchair) ('-' value recorded below the value recorded for the blank).

One Armchair							
		A	**B**	**C**	**D**	**E**	**F**
Burn 13	Heating	**+**	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 14	Heating	-	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 15	Heating	-	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 16	Heating	-	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 17	Heating	-	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-
Burn 18	Heating	-	-	-	-	-	-
	T_0 Suppression	-	-	-	-	-	-
	T_{30} Suppression	-	-	-	-	-	-

The concentration values that lie between the estimated LOD and the LOQ have been highlighted in orange and the values above the LOQ have been highlighted in green. For the remaining results the concentration values determined from the absorbances recorded were below the estimated LOD except in some cases (indicated by the +) where the HCN absorbance was visible, but below the LOD.

The results clearly show that the HCN can be detected at temperatures below 200 °C in instances where the fuel load is undergoing heating, and not being impinged on by flame. The impact of this finding is that HCN has been detected at previously unreported temperatures. In addition it has been detected as a result of heating only, there was no flame impinging on the PU foam at all. The concentration detected during the heating stage would not be sufficient to kill an adult human immediately [129-136].

It was expected that HCN would be detected immediately after the suppression of the fire and was not the major focus of the work. However, it is interesting to note that the majority of the HCN has been detected at point B in the array (highest point). This is thought to be a consequence of the density of HCN being less than air and hence rising to the upper portion of the structure.

Notably, when comparing all the heating stages, Burns 1 – 6 indicate the most detection of HCN. Specifically Burn 6, the smallest and lightest of the fuel loads in the set, had the most detections of HCN during the heating stage. Detection of HCN was recorded during Burn 6 at four points, B – E, in the array during the heating stage of the experiment.

The type of PU foam that the heat gun was directed at during the Heating Stage of the experiment has been presented in Table 6—18. The foam samples were assigned names initially in Figure 4.6 and Figure 4.7 and have remained consistent in Table 6—18.

Table 6—18: Type of PU Foam Sampled from The Cushions Used in the Heating Stage.

	Long Yellow	*Green*	*Other*
Burn1	**Y**		
Burn 2		**Y**	
Burn 3	**Y**		
Burn 4		**Y**	
Burn 5	**Y**		
Burn 6	**Y**		
Burn 7	**Y**		
Burn 8	**Y**		
Burn 9		**G**	
Burn 10	**Y**		
Burn 11	**Y**		
Burn 12	**Y**		
Burn 13		**Y**	
Burn 14		**Y**	
Burn 15		**Y**	
Burn 16			**Y**
Burn 17			**Y**
Burn 18			**Y**

It is unexpected that any one group would have more, or less, HCN detected in the heating stage as the area being heated was not varied. In addition there is no significant difference in the distribution of PU foam being heated in the initial stage. The detection of HCN in the Post Suppression stages was compared with the PU foam used as the fuel load, which has been illustrated in Table 4—6 (distribution of PU foam per burn). There is no discernible pattern for the distribution of foam compared with the detection of HCN in the either of the post suppression stages. Therefore it is unlikely that the PU foam used is the basis for the variation.

The flow rate at the fire side of the stainless steel lines leading to the gas traps, were checked periodically during the experiments. The flow rate remained consistent throughout the experimental work and no blockages in the line were noted. Therefore, blockages that prevented the fire effluent getting to the gas trap could not have been the cause for the disparity between the HCN values recorded.

It is also clear that carryover between the stages of the burn has not significantly impacted on the results. Initially the volume of gaseous fire effluent remaining inside the gas trap

between sampling times was considered during the design of the method. It was postulated though that any gaseous fire effluent that may have remained in the lines (SS and neoprene) on fire side of the gas trap would have a volume of less than 2 L. This was based on the area of the internal diameter of the stainless steel tube and the length between the fire and the gas trap. As the flow rate was maintained at 20 L/min for the duration of the experimental work 200 L of effluent was drawn through at each stage of the fire. That made the amount potentially left in the dead space of the trap (if it did not dissipate back into the cell as it was unlikely to have undergone passive dissolution into the trapping medium) in the dead space of the trap between sampling stages less than 1% of the volume and as such was considered negligible. The results reflected that any carry over between stages was in fact negligible and this has illustrated in Table 6—16 where all of the relatively large concentration determinations are proceeded by concentration results of zero as there was no absorbance (-) recorded.

It was particularly difficult to maintain a steady temperature and generally when the temperature was maintained close to 200 °C, during the heating stage, the majority of the HCN was detected using this method.

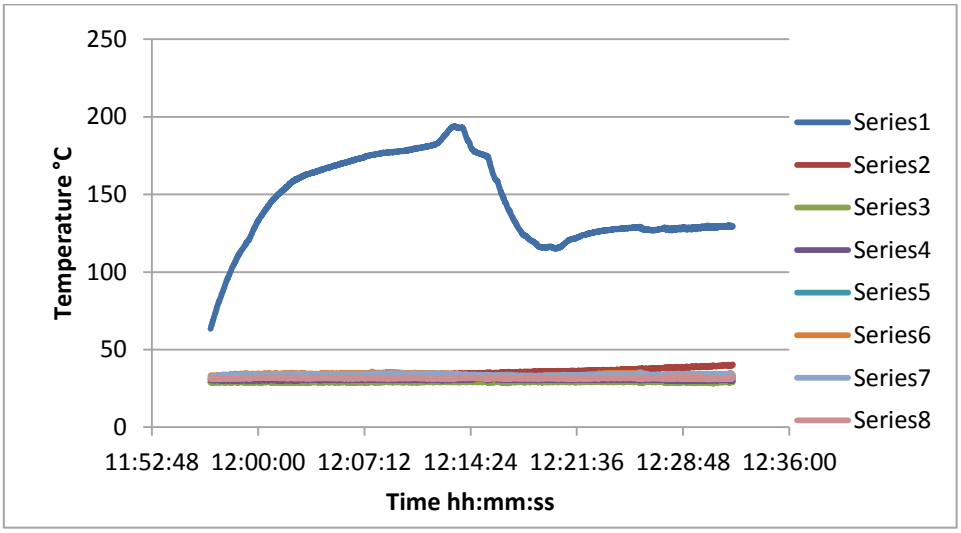


Figure 6.12: Temperature profile during heating stage for Burn 9.

However even in cases where maintaining a steady temperature was not achieved, as seen in the temperature range recorded for Burn 9 seen in Figure 6.12, the results for the heating stage were positive for HCN detection. In Figure 6.12 Series 1 indicates the thermocouple at

the face of the PU where the heat is directed as illustrated in Figure 6.6, Series 2 and Series 3 are in the other area of the armchair. Series 4 – 8 are in situ as indicated in Figure 4.12.

It is postulated that the small amounts of HCN detected can be largely attributed to the small surface area of the foam exposed to temperatures of interest and the insulative properties of PU foam. As discussed and illustrated in Section 6.5 the heat gun was focused at the exposed surface of the PU foam contained in the seat cushion of each couch or armchair. The temperature at the face of the PU foam, where the heat was being directed, was recorded. The temperature was also recorded at the exposed PU foam surface perpendicular to that site.

Figure 6.13 aptly illustrates that the temperature was maintained (at approximately 197 °C) in the area where the heat gun was focused at (indicated by the thermocouple labelled Series 1). It is also illustrated that the temperature drops off significantly outside the area of the heat guns focus. The temperature recorded by the thermocouple labelled Series 2 (the area perpendicular to the head gun has been indicated in Figure 6.6) is only marginally above ambient temperature.

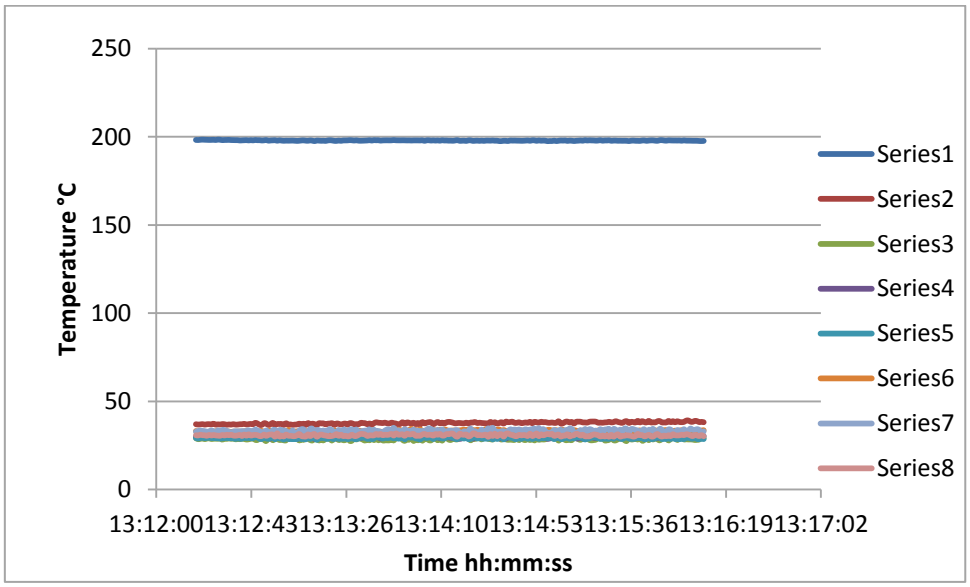


Figure 6.13: Temperature profile during heating stage for Burn 6.

6.7 Conclusion

Addressing the challenges identified at Fergus Falls, MN played a significant role in the modification of the method employed at the QCESA site. The purpose of the work at QCESA was to use a method to determine (via remote sample collection) if HCN could be detected in a full scale fire scenario below previously acknowledged temperatures. Consequently, the modifications applied to the method to address the challenges met at Fergus Falls, MN resulted in improved consistency and repeatability when the results were analysed.

A novel method to sample fire effluent was developed and applied to large scale fire scenarios, where the effluent was directly collected from the fire and passed through KOH solution to trap analytes of interest, HCN.

Commercially available ISE's were used to analyse the KOH solution and fire effluent for the presence of HCN. A decline in the response of the instrument was recorded and was most likely attributed to the degradation of the ISE tip. Though the positive results were recorded, the inaccuracy of the instrument indicated that technique was better suited to the qualitative determination of HCN, when applied in this way.

Further analysis of the sample solutions was undertaken using UV-Vis spectroscopy. A positive response for the presence of CN^- in the sample solution was reported when a characteristic absorbance indicating the tetracyanonickelate (II) complex was noted. HCN was detected at temperatures lower than previously reported and without the PU being impinged on by flame. In addition, HCN was detected at T_{30} post suppression. This method was found to be robust with reasonable reproducibility and HCN was quantitatively determined during the progression of the fire from the Heating Stage to T_{30} Post Suppression

Chapter 7: Laboratory-based Pre-Flame Gas Detection

Chapter 7: Laboratory-based Pre-Flame Gas Detection

7.1 Introduction

Chapter 5 of this work illustrated the successful detection of HCN at post fire suppression scenarios using a commercially available detection method. The challenges associated with the detection method were also discussed. Chapter 6 of this work went on to address the challenges identified in Chapter 5, to yield the successful detection of HCN below temperatures previously reported, in addition to time after suppression, using a novel method in a realistic setting.

The premise of work outlined in this chapter was to determine, in a controlled environment, if HCN could be reliably detected at temperatures lower than those used for the heating stage in the large scale burns conducted at QCESA. Though the foam was considered to be PU foam, there was aesthetic variation in the foam as well as how the foam was distribution between burns, which were discussed in Section 4.5.1. Therefore the work described in this chapter also sought to determine if any specific foam was more likely to have contributed to the detection of HCN during the heating stage of the fire.

7.2 Site Description

The data presented in this chapter are the outcome of work performed solely at the University of Technology, Sydney.

7.3 Sample Description

The foam used in this chapter was harvested from the fuel load used in the work reported on in Chapter 4 which has been described in detail in Section 4.3. The sample itself refers to the atmosphere analysed from heating the foam, specifically HCN. Unlike the large scale burns there were no other aspects, other than PU foam, contributing to the atmospheric fire effluent. Samples known to be PU were also used in this work.

7.4 Method

The gas sample collection method described in Chapter 6 was modified for use within a laboratory. This meant reducing the scale of the experiment whilst maintaining the fundamentals of the method. The modifications were made to the collection method to accommodate the site location. They included the reduction in the length of the Neoprene tubing from the cell to the sampling solution and the use of an oven, rather than a heat gun. The latter was done for two reasons; to apply temperature to a larger surface area of the foam and to reduce the likelihood of igniting the PU foam if the heat gun was in too close a proximity.

Due to the design of the couches and armchairs used at QCESA the bulk of the foam used in the fuel loads was in the cushions. In addition, the foam from the cushions was the focus of the heat gun for the work conducted in the Heating Stage in Chapter 6. Therefore, the foam used in this section of work was harvested from the cushions that were part of the fuel load from the burns conducted at QCESA.

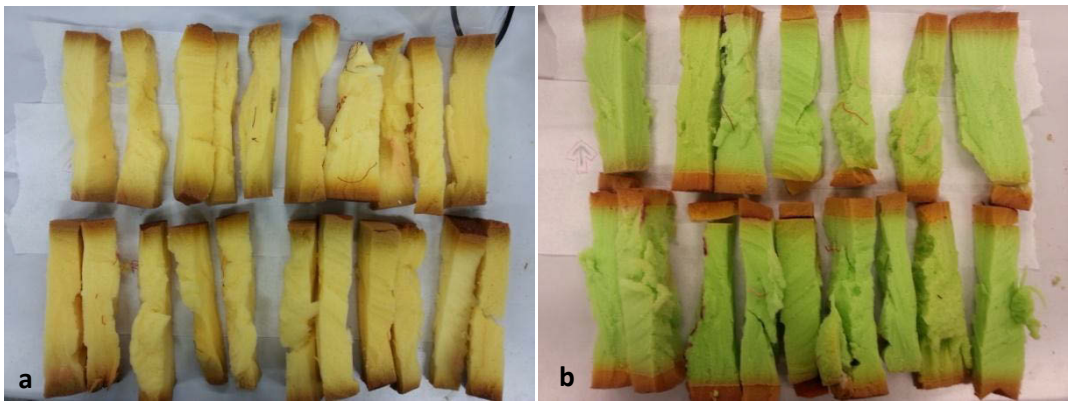


Figure 7.1: a) Long Yellow b) Green, PU Foam harvested from the fuel load for the work conducted at QCESA.

Figure 7.1 indicates the foam arbitrarily named *Long Yellow* and *Green* for the purposes of this work. Long Yellow was the most common cushion foam focused on in the Heating stage as illustrated by Table 4—6 with *Green* being the second common.

Although the *Long Yellow* and the *Green* featured predominantly in the cushions initially being heated, *Short Yellow,* which has been indicated in Figure 7.2, was present as the

material in the secondary and tertiary cushions in Burns 1 – 5 and Burns 11 – 12 as illustrated in Figure 4.14 and Figure 4.15. *Short Yellow* was therefore included in this section of work due to its prevalence.

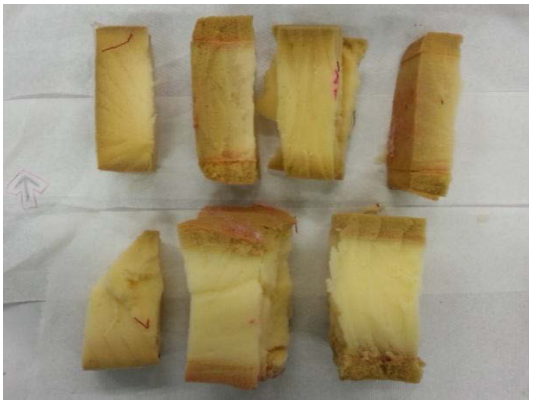


Figure 7.2: Short Yellow PU foam from the fuel load for the work conducted at QCESA.

The considerable insulative properties that PU displays were discussed in Chapter 6. To expose additional surface area of the foam the harvested samples, (Figure 4.14, Figure 4.15 and Figure 4.16) were cut into smaller, approximately cubic, sections of similar size as can be seen in Figure 7.3.

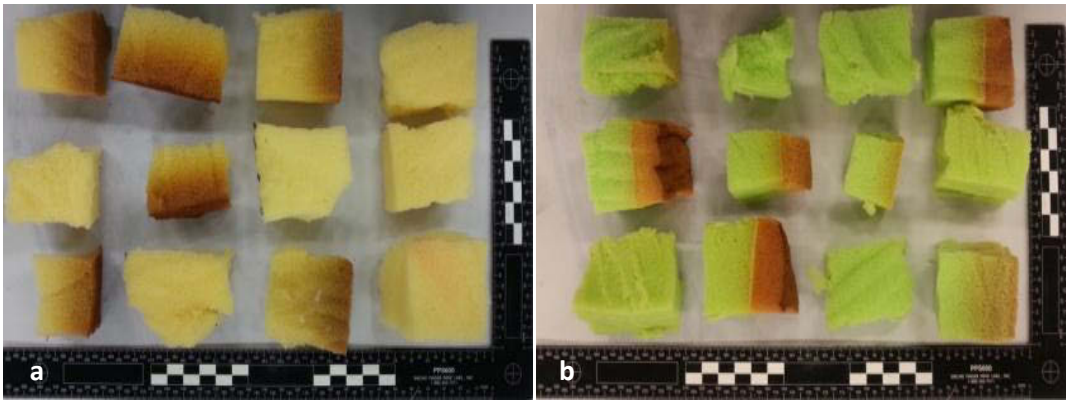


Figure 7.3: a) Long Yellow and b) Green, PU foam cut into smaller pieces to increase surface area to volume ratio.

In addition the remaining foam from QCESA, *Short Yellow*, was treated in the same manner indicated in Figure 7.4 a). Known PU samples were also included in this work and have been listed in Table 7—1. They were treated in the same way as *Long Yellow, Green* and *Short*

Yellow in terms of surface area to volume ratio, an example of which can be seen in Figure 7.4 b).

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.***

The following table lists the known samples of PU foam used in this work.

Table 7—1: Colour, Density and Hardness of the Known PU Samples.

Foam Number	*Colour*	*Density (kg/m^3)*	*Hardness (N)*
1	Grey	35	200
2	Pink	42	500
3	Lemon	25	60
4	Blue	24	160
5	Blue Green	30	130

The foam was difficult to contain so was held in sealable plastic bags. The mass of the foam to be heated was recorded and placed in an oven dish.

A vacuum oven, placed in a fume hood, was used as the mechanism to heat the foam for the experimental work; although the vacuum capacity for the oven was not activated for the experiments. The tip of one of the k-type thermocouples discussed in Section 4.4 was placed in the oven and the oven valves and door were closed. The temperature was recorded and compared with the temperature gauge display on the oven at 197 °C, 190 °C and 180 °C. There was discrepancy between the temperature gauge on the oven and the thermocouple reading, the oven reporting between 3 – 7 °C lower than the thermocouple. To remain consistent in the recording of the temperature the thermocouple was retained.

Consistent with the method used at QCESA four litres of 1.00 mol/L KOH solution was prepared. The solutions were made up to volume in 2.00 L volumetric flasks (A-grade) using UP water from UTS. Approximately 100 mL of the 1.0 mol/L solution was placed in three Schott bottles and placed in the bespoke housing unit, illustrated in Figure 6.3 b). After each of the first three Stages were completed approximately 50 mL of the experimental solution was retained. The bottles were emptied and thoroughly washed, rinsed using deionised water then baked overnight at 100 °C.

After the Blank was collected the vents were shut and the foam was introduced to the oven. The oven was opened briefly and the foam was placed inside. After the temperature returned to above 190 °C the sample was heated for 30 minutes. The atmosphere inside the oven was then passed through the OH^- solution for 10 minutes. During the sampling period the temperature did not drop significantly. After the sampling period the foam continued being heated for an additional 20 minutes. The atmosphere from the oven was then sampled again for 10 minutes. The foam was then removed from the oven, which was allowed to bake and vent at approximately 210 °C for at least an hour.

Each experiment was divided into four sections, three that the atmosphere would be sampled from, during the heating of the fire. To allow for easy recognition the stages were named accordingly:

- Stage 1: Blank
- Stage 2: Heating 1
- Stage 3: Heating 2
- Stage 4: Venting

The atmosphere was drawn through the OH^- solution according to the conditions outlined in Table 7—2.

Table 7—2: Conditions for Gas Sampling in the Laboratory.

Conditions	*Stage 1*	*Stage 2*	*Stage 3*	*Stage 4*
Stage Name	Blank	Heating 1	Heating 2	Vent
Temperature Experiment A	187 – 197 °C	184 – 203 °C	184 – 203 °C	100 °C
Temperature Experiment B	171 – 176 °C	171 – 180 °C	171 – 180 °C	100 °C
Heating time	30 min	30 min	20 min	Overnight
Sampling time	10 min	10 min	10 min	NA
Flow rate	20 L/min	20 L/min	20 L/min	20 L/min
Sample solution	50 mL 1.00 mol/L OH^- (pH 14)	50 mL 1.00 mol/L OH^- (pH 14)	50 mL 1.00 mol/L OH^- (pH 14)	NA
Solution retained	2 x 25 mL	2 x 25 mL	2 x 25 mL	NA

After the foam was removed from the oven the mass was recorded and the mass loss determined.

Experiment B was conducted in the same vein as Experiment A, excepting that the temperature was reduced, as indicated in Table 7—3.

As in Section 6.5.2, UV-Vis spectroscopy was the technique used in this chapter. The method of making an OH^- solution to act as the trapping medium was performed in the similar manner to that outlined in Section 6.5.2. The calibration curve constructed for Burn 17 and 18 in section 6.5.2 directly preceded the work conducted in this chapter and was therefore used for this work. The following concentrations of the standard CN^- solution were used:

1.00×10^{-3}, 5.00×10^{-4}, 1.00×10^{-4}, 5.00×10^{-5}, 4.00×10^{-5}, 2.00×10^{-5}, 1.00×10^{-5} and 5.00×10^{-6} mol/L.

The calibration data from Burns 17 and 18, in addition to the information from the solution as a whole, has been presented in Table 7—3.

Table 7—3: Equations for the standard CN^- solutions including all data points.

	Burn	*slope*	*y intercept*	*R^2*
Standard Solution 5	13	4904.5	0.0241	0.9743
	14	2958.9	0.0205	0.9612
	15	3895.6	0.0004	0.976
	16	4120.8	0.0004	0.9876
	17 – 18	3722.5	0.0034	0.9787
average		3920.46		
STD			0.01036	
LOD	***8.72×10^{-6}***			
LOQ	***2.64×10^{-5}***			

The remaining Ni^{2+} stock solution from the work conducted in Chapter 6 was utilised here.

The experimentally derived solutions from the work conducted at UTS were tested using the method outlined in Section 6.5.2.

7.5 Results and Discussion

The mass loss of the foam was recorded for the experiments that were conducted and has been listed in Table 7—4. The gain in the Pink 42/500 sample after experiment 2 could be due to moisture absorption as the mass was recorded with the sample contained in the same container it was originally housed in and on the same set of scales that had recently been calibrated.

Table 7—4: Mass Loss of PU Foam For Experiment A.

Foam Type	*Pre Heating (gm)*	*Post Heating (gm)*	*Mass Loss (gm)*	*Mass Loss %*
Grey 35/200	148.76	140.82	7.94	5.64
Pink 42/500	147.74	146.39	1.38	0.99
Lemon 25/60	148.59	147.00	1.59	1.01
Blue 24/160	148.71	147.93	0.78	1.01
Teal 30/130	148.87	147.24	0.63	1.01
Long Yellow	201.44	199.65	1.79	1.01
Green	104.15	102.34	1.81	1.02
Short Yellow	79.98	78.12	1.86	1.02
Experiment B				
Grey 35/200	109.24	106.55	2.69	1.03
Pink 42/500	*148.98*	*150.10*	*(+) 1.12*	*(+) 1.01*
Long Yellow	170.35	168.82	1.43	1.01
Green	146.70	145.61	1.09	1.01

The masses were recorded to gauge if loss was occurring and not a quantitative tool. Overall it could be seen that mass loss of approximately 1% was occurring.

7.5.1 Experiment A

The temperature range was indicated in Section 7.4, specifically Table 7—2, and illustrated the extremes in the range. However, the specific range varied for each experiment. It should be noted that temperature range in the experiment used for the samples of PU foam taken from QCESA was maintained at a similar range as that recorded at QCESA. This was done to mimic the method employed during the heating stage, though at a smaller scale in a more controlled environment. The temperature for the known PU samples was lower as it had already been shown, on a large scale, that the detection of HCN was possible below 200 °C. Therefore the premise was to see how low a temperature HCN could be released / detected.

The temperature range for *Grey 35/200* was 186 – 193 °C. The biggest reductions in temperature occurred when the foam was placed in the oven. However a temperature of 189 °C was maintained for 30 minutes during the initial heating stage and maintained at 191 °C for the second heating period. After the first and second sampling period both solutions appeared cloudy. In addition, when the foam was removed from the oven, the foam was darker in colour and it was visibly smoking. Both samples were spun down in the centrifuge which resulted in the separation of the sediment and solution. While centrifuging

the sample appeared to work to the benefit of the solution collected during the first heating stage, it did not for the second solution. As can be seen Table 7—5 sediment remained in the solution and impacted on the detection of the complex.

The temperature range for *Pink 42/500* was 186 – 188 °C. Again the biggest reduction occurred with the insertion of the foam into the oven, as the door had to be opened albeit briefly. The temperature was maintained at 187 °C for 30 minutes for the initial heating period. For the second heating period the temperature was maintained at 188 °C. When the foam was removed there was no noticeable smoke or gas coming from the foam, although it was slightly discoloured. The sample solution had also remained clear.

The temperature range for *Lemon 25/60* was 184 – 193 °C. The temperature was maintained during the heating period for the first sample stage at 187 °C for 30 minutes. For the second heating period the temperature was maintained at 189 °C. The foam was slightly discoloured when removed from the oven although there was no smoke noted and the sample solutions remained clear. There was a strong odour however.

The temperature rage for *Blue 24/160* was 184 – 193 °C. The temperature for both heating periods was maintained at 186 °C. There was no discolouration of the foam nor was any smoke noted.

The temperature range for *Teal 30/130* was 193 – 203 °C. The majority of the first heating period ranged between 196 – 203 °C and the second period the temperature range was between 200 – 203 °C. No smoke, discolouration or odour was observed when the foam was removed from the oven and the sampling solution was clear.

The temperature range for *Long Yellow* was 194 – 198 °C. The initial heating period was maintained at 197 °C with the second heating of a range of 197 – 194 °C. When the foam was removed from the oven there was no smoke observed or odour noted, however the foam was discoloured. The parts of the foam that were initially discoloured, from exposure to light which has been illustrated in Figure 7.3, appeared significantly more discoloured than the areas not initially discoloured. In addition, sediment was noted in the second sampling solution. The solution was centrifuged, which helped separate the larger particulates from the solution, the smaller pieces remained suspended and impacted on the capacity of the light to reach the detector which the sample was introduced to the UV-Vis.

The temperature range for *Green* was 196 – 198 °C. The temperature throughout the heating periods was maintained at approximately 197 °C due to a fluctuation of 1 °C being noted. When the form was removed from the oven there was visible discolouration, albeit slight, to the foam and smoke was in the oven. Though there was smoke present when the oven was open after the cessation of the experiment, none was observed to have remained in the sample solution.

The temperature range for *Short Yellow* was 196 – 200 °C. The initial heating period ranged in temperature from 197 – 200 °C. When it was noted that a temperature spike of 200 °C was occurring, the oven gauge was used to modify the temperature. The second heating period was maintained at 197 °C for the duration.

The results for *Short Yellow* have been questioned, as they do not satisfy the criteria of having an absorbance at 285 nm. For that reason the sample was not tested at a lower temperature.

As was discussed earlier, some sample solutions had noticeable sediment present and were centrifuged in an attempt to separate the particulates from the solution. In some cases it was successful, for example the first heating stage for *Grey 35/200.* In other cases the sediment was too fine and remained suspended in solution, in those cases a spectrum could not be obtained from the sample and those results have been represented in the results by 'sediment'.

The results, listed in Table 7—5, clearly indicate that HCN can be detected when subjected to temperatures comparable to those used at the large scale burns performed at QCESA. The results also indicate that the amount of HCN detected is not necessarily proportional to starting mass, overall mass loss.

Of particular note are the results of the second heating stage. The oven was vented by opening the oven valves and drawing the atmosphere through the sampling solution at 20 L/min for ten minutes to analyse the atmosphere from the first heating stage. The positive results, but decreased amount detected, for the second heating stage could suggest that there is finite time period that HCN is produced when heating PU foam with a static surface area.

Table 7—5: Experiment A Results.

	First Heating Stage		Second Heating Stage	
Foam Type	**Absorbance 1 (AU)**	**[CN^-] (mol/L)**	**Absorbance 2 (AU)**	**[CN^-] (mol/L)**
Grey 35/200	0.3511	9.3405×10^{-5}	Sediment	
Pink 42/500	0.2065	5.4547×10^{-5}	0.0778	1.9984×10^{-5}
Lemon 25/60	NA		NA	
Blue 24/160	NA		NA	
Teal 30/130	NA		NA	
Long Yellow	0.8672	2.3205×10^{-4}	Sediment	
Green	0.6573	1.7566×10^{-4}	0.3259	8.6643×10^{-5}
Short Yellow	0.2197	5.8112×10^{-5}	0.0761	1.9525×10^{-5}

In the first heating stage for Experiment A the samples where absorbance was recorded all were shown to have concentrations above the LOQ, using the calibration data developed in Section 6.5.2 and displayed again in Table 7—5. The second heating stage returned positive results for *Pink 42/500, Green* and *Short Yellow,* all of which were above the LOD determined and *Green* was above the LOQ.

Both *Grey 35/200* and *Long Yellow* had sediment that could not be removed by centrifuging followed with filtration. As a result the particulates remaining in solution hindered the collection of spectra for those samples.

Table 7—5 also indicates that the *Lemon 25/60, Blue 24/160* and *Teal 30/130* did not return a positive result for the detection of HCN, even when the temperature range for the *Teal 30/130* experiment rose above 200 °C it did not return a positive result for HCN. For those reasons, *Lemon 25/60, Blue 24/160* and *Teal 30/130* were not tested again during experiment 2.

7.5.2 Experiment B

The temperature range for this experiment was lower than in Experiment A as the premise of the work was to determine if HCN could be detected at lower temperatures using the foam that was used as the fuel load at the burns conducted at QCESA. Only the PU foam that returned a positive result in experiment was used in Experiment B.

The temperature range for the upper and lower extremes of this experiment was listed in Table 7—2 and as was the case for the temperature profile in Section 7.5.1 the specific range for each run within the experiment displayed variation.

The temperature range for *Grey 35/200* in experiment 2 was 171 – 178 °C. For the initial heating period the temperature ranged between 176 – 178 °C and the second heating period was maintained at 178 °C. When the foam was removed from the oven, neither the presence of smoke, nor discolouration of the foam was noted. In addition there was no sedimentary material in the sample solutions.

The temperature range for *Long Yellow* was 176 – 180 °C. The initial heating period had a temperature range of 176 – 180 °C and the second heating period was maintained at 179 °C. When the foam was removed from the oven there was no smoke observed or odour noted, nor discolouration. However, sediment was noted in the first sampling solution and to attempt to reduce the impact of particulates on obtaining a spectrum the solution was spun down. In this case centrifuging was unsuccessful and sediment acted as an obstruction between the light source and the detector.

The temperature range for *Green* during the second experiment was 171 – 180 °C. The temperature the initial heating period was 178 – 179 °C and the second heating period was maintained at 179 °C. When the form was removed from the oven no discolouration or smoke was observed, nor was there any sediment noted in either of the sample solutions.

Table 7—6: Experiment B Results.

	First Heating Stage		*Second Heating Stage*	
Foam Type	***Absorbance 1 (AU)***	***[CN^-] (mol/L)***	***Absorbance 2 (AU)***	***[CN^-] (mol/L)***
Grey 35/200	0.1016	2.6372×10^{-5}	0.0076	1.1208×10^{-6}
Long Yellow	Sediment		0.0695	1.7760×10^{-5}
Green	0.2281	6.0363×10^{-5}	NA	

The results for Experiment B have been listed in Table 7—6, which indicate that HCN can be detected at more than 20 °C lower than previously reported [56, 61-83, 85-91]. Like the results from Experiment A, there is a suggestion that the amount of HCN detected is not

necessarily proportional to starting mass or overall mass loss. In addition, a similar trend occurs with the second heating stage.

It is suggested that the increased surface area to applied temperature ratio of the foam contributed significantly to the increased detection of HCN. It is also postulated that the reduced volume of the test cell coupled with more tightly controlled ventilation could also be considered a factor.

It was considered that the results recorded were indicative as they were consistent the onset of the thermal degradation of low density PU [73]. However it is accepted that additional repetitions of the experiments could be warranted.

7.6 Conclusion

The purpose of the work presented in this chapter was to determine the lowest temperature that HCN could be detected from PU form (being heated) in a laboratory setting. In addition, the experimental work reported in this chapter was to act as a confirmatory exercise to support the large scale gas detection performed at QCESA.

A modified version of the method used in Chapter 6 was successfully applied in a laboratory setting. Hydrogen cyanide was detected while heating PU foam that is not impinged on by flame; confirming results obtained in full scale experiments (Chapter 6). Results showed that HCN was still detectable from some PU foams heated to temperatures not exceeding 180°C. This is significantly lower than previously reported minimum temperature ranges.

It is likely that the smaller (and contained) volume of the cell, coupled with the increased surface area of the PU exposed to heat, resulted in a larger concentration of HCN being produced than that detected at QCESA. The insulative properties of PU limit the degradation of the polymer to produce HCN, predominantly from the exposed surface. Thus, it is postulated that only a finite amount of HCN, proportional to the exposed surface of the PU, would be produced.

These results support suggest that if a larger surface area of the PU had been exposed (at QCESA) a greater amount of HCN would likely have been detected.

Chapter 8: Conclusions and Further Work

Chapter 8: Conclusions and Further Work

The large scale work presented in this thesis sought to conduct holistic, realistic large scale burns to determine the time until flashover proportional to the amount of PU present in the cell in addition to the detection of HCN in the pre-flame and post suppression stages of the fire. The purpose of the laboratory based work described in this thesis sought to determine the lowest temperature HCN could be detected whilst heating PU foam.

8.1 Time Until Flashover

This aspect of the project sought to examine how the amount of PU within a cell effects the time until flashover. A series of experiments were conducted in three successive sites, with improvements to methodology, consistency and repeatability being realised as the project progressed.

The first site was a domestic dwelling in Montrose, MN. The specific purpose of the work conducted at Montrose, MN was three fold i) to determine the time until flashover, using replica sets of PU-containing furniture, in each of the four rooms being used in the test burns, ii) to illustrate that experimental parameter variation, such as fluctuation in the ventilation areas and room sizes, would impact on the progression of the fire to flashover, and iii) highlight the challenges associated with conducting large scale burns of this nature.

A flashover event was witnessed in each room that satisfied the pre-determined definition (based on existing literature) used for this work. In addition it was noted post suppression, that indicators such as flame damage were evident in each room from floor to ceiling. This further supported the incidence of a flashover event as having occurred.

It was observed that the time until flashover recorded for the burns in Rooms 2 – 4 decreased as the volume of the room decreased; however the burn in Room 1 only progressed to flashover after ventilation was manually introduced. This was most likely due to a reduction in the available oxygen, turning the fire into a ventilation controlled scenario.

The estimated HRR required for flashover to occur based on the fuel load, room size and ventilation area indicated that each room had the capacity to progress to flashover. It was

suggested that Room 1 did not progress to flashover naturally as the fire became ventilation controlled due to a lack of available oxygen in the immediate atmosphere. When air was manually introduced into the cell, flashover was witnessed.

The preliminary results collected at Montrose, MN indicated a decrease in time until flashover as the percentage volume of PU in each room increased. However this could only be suggested as a supposition as the variations between experimental parameters for each burn led to results that were not reproducible and therefore difficult to interpret with any strength.

Though some repetition of the method was achieved (four replica furniture sets were used as the fuel load in each test burn) the design of the structure at Montrose, MN meant significant variations in room size, fuel load configuration, point of ignition, ventilation areas and surface covering were unavoidable. These limitations did however present an excellent opportunity to improve the experimental design for the next series of experiments.

It was identified that locating an available site with rooms, or cells, that had consistent dimensions was desirable. In addition, it was acknowledged that consistency among the surface coverings and ventilation area was advantageous. Further, it was determined that the site would need the capacity to either sustain multiple repetitions of burns in the one cell or have multiples of six cells (the value of six having been chosen due to the attractiveness of six as statistical gold standard) available, to allow for multiple scenarios to be tested. It was also highlighted that greater consistency between point of ignition would be advantageous. Another structural consideration that was noted as preferable was obtaining a site that did not have basement or attic spaces to reduce the potential for flame spread through the site.

The second site was a motel located in Fergus Falls, MN. The site was considered appropriate as it was informed by the data collected at Montrose, MN. That is, the rooms were consistent in size, layout, potential ventilation area and surface coverings. In addition, the site did not have a basement or second level and there were eight rooms considered suitable for inclusion in the experimental work.

An improved experimental model, based on the challenges identified at Montrose, MN, was designed. The purpose of the work at Fergus Falls, MN was to utilise the revised method (with greater standardisation in the experimental parameters that allowed repetition) to

experimentally determine the time until flashover proportional to the amount of PU in the room.

Based on the estimated HRR required for flashover to occur and the combined potential HRR of the fuel load, the fire in each room had the potential to progress to flashover. Though, this depended on the flame spreading to enough of the fuel load at critical times in the progression of the fire to ensure that the total combined HRR of the ignited items of furniture was sufficient to promote an incidence of flashover.

Three flashover events were recorded as having occurred during the eight experimental burns that were undertaken. The ignition mechanism and the ventilation areas of the rooms were varied and it suggested that this impacted on the capacity of some of the rooms to achieve the HRR required to progress to flashover.

The results of the Fergus Falls, MN experimental work indicated more stringent regulation in terms of the variance of the area of ventilation in the rooms and the mechanisms of ignition, was required for future work. It was identified that finding a site that emulated Fergus Falls, MN in terms of repeated cell sizes, ventilation area, surface coverings and fuel load would be ideal. In addition, locating a site within Australia was also desirable. The experimental work conducted at Fergus Falls, MN was the fundamental driver for continuing to pursue a site where all the identified modifications to the experimental design could be incorporated whilst maintaining realistic parameters.

The third, and final, site was identified and subsequently utilised to determine the time until flashover proportional to the amount of PU present in the cell was QCESA, QLD.

The experimental work undertaken at QCESA consisted of three scenarios (three seater couch, two armchairs and one armchair), which were repeated six times each. It was determined that flashover occurred in all of the three seater couch and two armchair scenarios and three (out of six) of the one armchair scenarios. Flashover was determined to have occurred by the visual recognition of characteristic signs, satisfaction of the pre-identified literature definitions and personal experience. In addition, thermal data was collected and used to corroborate the visual analysis, which showed a rapid increase in the temperature gradient an occurrence generally accepted to be an indicator of flashover.

Based on the results recorded at QCESA a trend was observed that indicated the time until flashover decreased as the amount of PU present in the cell increased. The experimental results were reproducible in terms of time until flashover and percentage mass loss of the fuel load.

Reliably reproducing time until flashover, in a large scale (and realistic) fire scenario, proportional to the amount of PU present has implications for a number of parties. Specifically: occupants, emergency services, associated members of the PU foam industry (those who manufacture and/or distribute PU and those manufacturers and/or distribute furniture with PU upholstery) and the insurance industry

The data presented in this work 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). Currently FRNSW guarantee a response time within ten minutes, in 90% of all call outs. Based on the evidence presented in this work it could therefore be necessary to consider (as reproducible data exits surrounding the determination of time until flashover based on the proportion of PU in a cell or structure) how FRNSWs capacity to uphold their mandate of saving life, then property without risk to the responders can be maintained in light of the current response isochrome.

The results reported in this work indicate that the time until flashover, proportional to the amount of commercially available PU-containing furniture in a cell, can be reproducibly estimated. It is realistic to suggest that this data will inform the manufacturers of PU and PU-containing furniture. It is recommended that consideration be paid to this data by legislative bodies and industry when determining if safety advice is required for the consumer.

Of most significance is the impact this data has on occupants. As a result of this work occupants have more data to inform them when developing a self egress plan in response to fire. In addition, the evidence presented in this work provides significant data to consider when deciding how much flexible PU containing furniture, if any, they want in their homes.

8.2 Pre-Flame and Post Suppression Gas Detection

This section of the project investigated the detection of HCN in the pre-flame and post suppression stages of fire. Experiments were conducted at two consecutive sites and improvements were incorporated into the method design as the project progressed. As a result consistency and repeatability of the method was realised.

The first site was a hotel in Fergus Falls, MN. The purpose of the work conducted at Fergus Falls, MN was to two fold i) to identify and use accessible existing techniques to analyse the atmosphere during the progression of a fire (before and after the occurrence of a flashover event) for HCN and CO, and ii) to highlight the challenges associated with conducting atmospheric analysis of this nature.

A Dräger accuro 2000 Hand Pump with HCN and CO specific tubes was used to sample the post suppression atmosphere at two locations (the bed and the corner pink armchair) in each room. The nature of the apparatus (a hand pump) prevented the operator standing in the cell prior to ignition. The area above the bed was tested first, then the area above the chair. Consistently there was more HCN and CO detected in the area above the bed, than the area above the chair and HCN was detected at significantly lower concentrations that that of CO.

The variation in the recorded results occurred for a number of reasons. Primarily the extent of the progression of each burn varied and this certainly impacted how much fuel was impinged on by heat or flame, which consequently affected the amount of toxicants produced. In addition, the safety aspects associated with being in close proximity to residual fire effluent during the manual sample collection (even with PPE) posed a concern and each cell was vented using positive pressure fans prior to analysis of the atmosphere. This would have certainly reduced the toxicants present in the post suppression atmosphere. Further, due to the nature of the analysis technique (which required a relatively lengthy sampling time) it is likely that passive ventilation of the post suppression atmosphere also occurred.

The results recorded at Fergus Falls, MN provided the opportunity to identify the challenges associated with this type of analysis. It was identified that using a Dräger accuro 2000 Hand Pump allowed for single tube analysis during sampling and that the process took a relatively long time. In addition its design prevented safe use (with the available PPE) in the early stages of a fire or directly post suppression.

As a result it was identified that a gas sampling system (that could be operated remotely) with the capacity to collect multiple simultaneous samples was desirable. It was considered that a system that allowed for safe storage and transportation (of the sample to the laboratory) would lend itself to analysis using multiple analytical techniques.

The second site utilised for the detection of pre-flame and post suppression gas was QCESA, QLD. The purpose of the work conducted was to address the challenges identified at Fergus Falls, MN and to improve the method to determine if HCN could be detected in a full scale fire scenario below previously acknowledged temperatures.

A novel apparatus was developed to simultaneously draw fire effluent from six different areas of the cell through six corresponding basic solutions of KOH as gas traps. A commercially available HCN specific ISE was used to analyse the KOH solution presence of HCN. Though the apparatus was used in accordance with the manufacturers specifications the tip degraded rapidly which was reflected in the decline in the response of the apparatus. In addition, while positive results for the presence of HCN were returned, the lack of accuracy (fully acknowledged by the manufacturer) suggested that the technique lent itself to the determination of qualitative, rather than quantitative, results.

Trapping the fire effluent for analysis using the ISE was fortuitous as it provided a medium (the KOH solution) for the gas from the burns to be safely stored and transported in. Transportation of the samples back to the laboratory allowed for complimentary analysis to be undertaken using UV-Vis spectroscopy.

The sample solutions were treated with Ni^{2+} and analysed using UV-Vis spectroscopy. A positive response for the presence of CN^- was indicated by the presence of the characteristic spectrum cased by the tetracyanonickelate (II) complex on addition of Ni^{2+} to a basic solution CN^-. This method was found to be robust with reasonable reproducibility and HCN was quantitatively determined during the progression of the fire from the Heating Stage to T_{30} Post Suppression

HCN was detected at temperatures lower than previously reported and without the PU being impinged on by flame. In addition, HCN was detected at T_{30} post suppression. The detection of HCN at lower temperatures has considerable implications for the occupant, particularly as the presence of HCN in the atmosphere in the early stages of a fire may impede the potential

for self egress of mobile occupants. However, of more significance is the impact on an occupant who may be asleep, less mobile or infirm, as the effects of inhaling HCN for extended periods in the early stages of a fire, without being able to self egress (or raise an alarm) could be catastrophic.

Wearing PPE after the suppression of a fire is not always a consideration when the fire has been suppressed for some time. Therefore, for emergency services workers (or others entering the site) the implications stem from the presence of HCN detected at T_{30} post suppression.

8.3 Laboratory–based Gas Detection

This work sought to determine the lowest temperature HCN could be detected when heating a selection of different flexible PU foam.

One experimental method was developed which involved heating flexible PU foam in an oven, and at two periods during the heating process drawing the atmosphere inside the oven through a KOH solution. The solution was then treated with Ni^{2+} and analysed using UV-Vis spectroscopy for the presence of the tetracyanonickelate (II) complex, a positive indicator for a reaction between CN^- and Ni^{2+}, by it characteristic absorbance peaks in the spectra.

At the higher temperature range (184 °C – 203 °C), five of the eight PU samples tested returned a positive after heating for 30 minutes and three of the eight returned a positive result after being heating for a further 20 minutes. The method was repeated at a lower temperature range (171 °C – 180 °C) using the PU samples that returned strongly positive results in the experiment with the higher temperature parameter. The results indicated that after heating flexible PU samples for 50 minutes at temperatures below 180 °C HCN could still be quantitatively detected.

It was postulated that the result of increasing the surface area of the PU when heating lead to a larger concentration of HCN being produced and in turn detected. In addition it is suggested, due to the insulative properties of PU, that only the exposed surface of the PU was heated to a sufficient temperature to allow pyrolysis to occur. Therefore only a finite amount, proportional to the exposed surface of the PU, of HCN could be produced.

These results support the results recorded at the large scale burns and suggest that if a larger surface area had been exposed a greater amount of HCN would likely have been detected.

8.4 Further Work

Despite the success of this project the work could be continued to gather additional data pertaining to the time until flashover in a cell or structure based on the PU content in the room in addition to the detection of HCN detection.

Further experimental work, pertaining to the time until flashover, could involve using the same method used at the burns conducted at QCESA and altering some of the parameters to include:

- Using the QCESA site to perform multiple repetitions using a different sized fuel load from the one outlined in this body of work.

- Using a different site and different sized fuel load to perform multiple repetitions of defined scenario.

- The use of a solely rigid PU foam (in a realistic representation of that type of fuel load) to determine the time until flashover based on the content of rigid PU in a cell.

- Use a mixture of flexible and rigid PU (as a realistic type of fuel load) to determine the time until flashover based on the ratio of flexible to rigid PU. Then alter the ratio and repeat the process using the same initial foams.

To compliment the continuation of the large scale work to determine a time until flashover proportional to PU In the cell or structure, the detection of HCN work could also be continued during the progression of the scenarios described above.

In addition, it is suggested that the results recorded at QCESA be compared with the results generated by computational models, where the dimensions and fuel load information from QCESA are used as the data to run the model simulation.

The work conducted in the laboratory to detect HCN at temperatures below 200 °C would benefit from additional experimental repetitions. In addition it would be interesting to see how long HCN could be detected for in a consistent temperature range. It is also suggested that the work be extended to include different samples of flexible PU and potentially rigid PU.

It is also suggested that work be conducted to determine concentration of HCN detected over a larger time period. This would be beneficial as it would provide a more representative toxicity profile throughout the progression of the fire.

Preliminary work was commenced to determine if HCN could be detected at lower temperatures than CO. Gas chromatography coupled with mass spectrometry (GC-MS) was fitted with a porapak PLOT Q column to aid the separation of CO and N_2 (atmospheric) samples collected from fire effluent. To further aid separation of CO and N_2 the oven of the GC-MS was cryogenically cooled to -30 °C. Initial success was seen when using samples spiked with a mixture of HCN and CO. However the method requires development to allow for the successful sampling and transportation of fire effluent to the instrument.

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