TEST BURNING OF CARPET AND FOAM AND POTENTIAL INTERFERENCES IN IDENTIFYING PETROL IN ARSON INVESTIGATION BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

RODI SFEROPOULOS,

BSC (PSYCHOLOGY), BSC (MEDICAL, FORENSIC AND ANALYTICAL CHEMISTRY),
BSC (HONOURS) (CHEMICAL SCIENCES)

SCHOOL OF ENGINEERING AND SCIENCE, FACULTY OF HEALTH, ENGINEERING AND SCIENCE, VICTORIA UNIVERSITY

Submitted in fulfilment of the requirements of the degree of Doctor of Philosophy

ABSTRACT

Work described in this thesis contains the results of the study on subjecting carpet and foam to different burning tests and the evaluation, by gas chromatography/ mass spectrometry (GC/MS), of the burnt residues for the purpose of identifying compounds which may potentially interfere with the identification of petrol in arson investigation.

The burning tests conducted on carpet and foam in this study showed that all but one of the 16 important petrol target compounds can either be recovered from the burn tests or produced via pyrolysis. Toluene and ethylbenzene were always the dominant target compounds observed along with lower levels of other aromatics including xylenes, propylbenzene and other C_3 and C_4 alkylbenzenes. Naphthalene was only observed in pyrolysis experiments and an unidentified alkene and styrene were observed in the total ion chromatograms for a number of burning tests.

Results from large room fires, where burning conditions are those encountered in real fires, and furnace fires, which best represent simulated fire scenarios, showed that there were negligible levels of only toluene and ethylbenzene present in the burnt carpet and foam. At the levels found it is unlikely that these interferences would hinder a petrol identification. In the case of interferences from the burning of carpet and foam the analysis of substrate comparison samples may not be necessary.

The results from the small can fire and pyrolysis GC/MS experiments indicate that if there was contribution to a petrol target compound chromatogram from burnt substrates then there may be recognisable indicators such as skewing towards toluene, ethylbenzene and to a lesser extent other C_2 and C_3 alkylbenzenes. Other indicators of interferences include the presence of the unidentified alkene peak and styrene in the total ion chromatograms. Small can and pyrolysis results indicate that it is difficult to misinterpret a petrol target compound chromatogram with that of a burnt substrate.

Small can fires with lid on proved successful in producing target compound profiles from burnt carpet and foam samples and a protocol was developed for the analysis of carpet and foam as substrate comparison samples in arson investigation. Importantly, the entire can and its contents should be sampled when recovering volatile organic compounds as the bulk of the volatile organic compounds are present in the can and not on the lid or burnt sample.

STUDENT DECLARATION

Doctor of Philosophy Declaration

"I, Rodi Sferopoulos, declare that the PhD thesis entitled 'Test Burning of Carpet and Foam and Potential Interferences in Identifying Petrol in Arson Investigation by Gas Chromatography/Mass Spectrometry' is no more than 100,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work".

Signature:

Date:

ACKNOWLEDGMENTS

First and foremost I would like to thank my supervisor Dr. Domenico Caridi for his invaluable support, advice, guidance and more importantly his friendship over the past many years.

Many thanks are also expressed to my co-supervisors, Dr. Jim Pearson and Mr. John Kelleher, as well as the team from the fire and explosives area, from the Victoria Police Forensic Services Centre (VPFSC) for their valuable advice, assistance and for their helpful discussions during the course of this study.

A big thank you goes out to Ms Nicole Harvey from the Country Fire Authority (CFA) and the CFA team in Fiskville, Victoria, for providing the facilities, support and assistance with conducting all the Large Scale Room Fires.

Many thanks also to Mike Culton from the Centre for Environmental Safety and Risk Engineering (CESARE) at Victoria University for his assistance with the temperature logging and helping with the Furnace Fires.

Finally, I would like to thank my family, particularly my husband Theo, my little girl Sienna, my baby boy Xavier and my parents, Helen and Kon, for their ongoing support, patience and more importantly for the never-ending encouragement given to me as I headed towards the finish line.

I wish to acknowledge Godfrey Hirst Pty Ltd, Dunlop Foams and Cryovac for their in kind contributions of carpets, foam, underlay and evidence bags, respectively.

LIST OF PUBLICATIONS AND AWARDS

Keynote Speaker at the ANZFSS Symposium held in Melbourne, October 2008 (abstract in Appendix K): “*The GCMS analysis of fire debris for ignitable liquid residues containing interferences from flooring and furniture padding material”.*

TABLE OF CONTENTS

3. PRELIMINARY STUDIES 96

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1 FOREWORD

Fire is one of the most beautiful and least understood physical phenomena in nature. As a result, there is a natural tendency for people to be impressed by the magnitude, violence and degree of destruction that fires are capable of producing[1, 2].

Since the time humans first learnt to create and control fires, they have become incorporated into daily life and have become an invaluable and necessary asset[1-4]. However, fires are also considered to be a huge public safety concern, largely due to the ease in which they can be lit, become out of control and spread, and also due to their ability to cause great destruction to nature, property and life[3-5].

In Australia alone, fires are estimated to cause damage and losses in excess of $8.5 billion per year[5-8]. Of these fires, only those which appear to be suspicious in origin are investigated and it is estimated that approximately 30% of those fires which are actually investigated, are deliberately lit[5, 8]. Arson can therefore be defined as the deliberate burning of property for malicious or fraudulent purposes and often involves the use of ignitable liquids, which are flammable materials used to spread and increase the rate and intensity of burning[1, 9-17]. The most effective way of reducing the incidence of arson is through the efficient investigation of the fire scene and if possible, the prosecution of those responsible[5, 18].

In order to effectively investigate a suspicious fire, qualified arson investigators are called in to examine and interpret the fire scene. The main aim of the investigation is to determine the origin and cause of the fire[1, 14, 19, 20]. As such, it is imperative that the investigator have a sound understanding about fires in general, as well as the processes and factors which contribute to and control a fire's behaviour[1-4, 21].

Arson investigation for suspicious fires where an ignitable liquid may have been used is made up of two main stages, the first being the initial search of the fire scene for any evidence that the fire may have been deliberately lit, followed by the collection of relevant fire debris samples. The second stage involves the laboratory analysis of the collected samples for any ignitable liquid residues, which may support suspicions that the fire was deliberately lit[1, 19, 22-25]. Laboratory analysis of fire debris samples and the subsequent identification of ignitable liquids is a somewhat complicated task as the debris can contain any number of building materials, such as floor coverings, furniture and structural materials, which may have been burnt, partially burnt or remain unburnt[1, 9, 15, 22, 26-31]. Furthermore some of these materials will be of petrochemical origin and subsequently may share chemical similarities with ignitable liquids, thus when exposed to heat, they can decompose to produce volatile organic compounds which may complicate or interfere with the identification of any ignitable liquids present in fire debris[1, 9, 15, 25-39].

1.2 THE CRIME OF ARSON

Arson is defined as the intentional or malicious act of using fire to destroy property[1, 9-12, 14, 16, 40]. Within this definition there are four core elements, including the actual lighting of the fire, as fire is the fundamental element of arson, intention or wilfulness, malice and property. Of these elements intent is the most crucial as fires can be deliberately lit for many legitimate reasons. However it is possible that the fire may quickly become out of control and spread causing damage to property or even loss of life. Assuming there was no negligence involved and the person(s) responsible did all they reasonably could to keep the fire under control, then this does not constitute arson as there was never any intention to cause damage or harm[1, 41].

Arson fires often involve the use of one or more ignitable liquids, which are utilised to ensure complete ignition and fire spread, so that maximum destruction can be achieved. The most frequently encountered ignitable liquids are typically commercial products such as petrol, kerosene, turpentine and diesel, all of which are complex mixtures of hydrocarbons, that are cheap, accessible, easily ignited and have legitimate uses in private homes[1, 17, 19, 25, 29, 34, 36, 37, 42, 43]. The amount of ignitable liquid used also tends to vary, as an arsonist will generally only use what they can conveniently carry without attracting any undue attention or suspicions[44]. In most instances, ignitable liquids are poured directly on the floor and spread from room to room, creating trails of an ignitable liquid[1]. Due to the volatility and high vapour pressures of ignitable liquids, their presence in a fire will generally enable large amounts of heat to be produced within a short period of time and at specific locations[1, 42]. In many instances ignitable liquids poured directly on the floor are able to be readily detected because a considerable portion of the ignitable liquid may remain unburnt and what does burn usually leaves diagnostic signs, such as burn patterns, which may assist the investigator in tracing the ignitable liquid back to the point of origin, which is the point where the fire began[1, 14, 19, 23, 42].

Although fires are extremely destructive, if ignitable liquids were initially employed significant residue may still remain. However ignitable liquids are volatile and if any does remain it may evaporate, therefore it is imperative that the fire scene be investigated by qualified personnel as soon as the scene is deemed safe to do so[9, 24, 42].

Arson is a difficult crime to investigate and prosecute due to the fact that the crime itself, if successful, destroys any physical evidence rather than creating it as it progresses[1, 45-47]. However arson is still a crime and as such demands to be solved[1].

1.3 ARSON INVESTIGATION

The investigation of a fire occurs in two stages, the first involves the examination of the fire scene to determine the origin, cause and spread of the fire and initially assess if the fire is accidental or suspicious[14]. The second involves the laboratory analysis of the samples recovered from a fire scene. Whilst both of these steps are linked, they may be carried out by different personnel with different backgrounds or experience, such as fire fighters and forensic fire investigation scientists[19, 20].

A fire investigator's understanding of the fundamental principles of fire, combustion and pyrolysis is essential, as this knowledge guides the investigation of the fire[1].

1.3.1 FIRE, COMBUSTION AND PYROLYSIS

Fire, also referred to as combustion, can be defined as the process by which oxygen combines rapidly with a combustible material in an exothermic chemical reaction that proceeds at such a rate that heat and light are produced[1, 48-50]. Whereas pyrolysis is defined as the "...process by which a solid undergoes thermal degradation of its chemicals into smaller more volatile molecules, without interaction with oxygen or any other oxidants"[3, 49].

In order for a fire, or combustion, to occur and sustain itself, sufficient quantities of a combustible fuel and an oxidiser, usually oxygen in air, are essential. An initial source of ignition (heat) is also required and must provide sufficient energy to ignite the fuel. Furthermore the fuel and oxidiser must interact in the self-sustaining chemical reaction that results in a fire[1, 44]. The heat generated by the combustion process radiates onto the surface of the fuel, raising its temperature, causing it to evaporate if it is a liquid or pyrolyse if it is a solid[51]. In the case of a solid fuel, this results in the production of pyrolysis products, which are the gaseous compounds that provide the fuel for combustion, as shown in Figure 1.1[1, 49, 51]. This pyrolytic reaction usually takes place at temperatures between 500°C to 800°C[49, 52].

Hence, ignitable liquids and other solid materials at a fire scene do not burn in their original states, they must first be converted to the gas phase before ignition of the flammable vapours will occur[1, 19, 53]. Therefore, for a liquid to ignite, it must first evaporate and form a flammable mixture with air, however in the presence of a pilot, such as a small flame, ignition will occur when the evaporated liquid fuel has achieved it lower flammable limit[1, 53]. The primary mechanism for igniting solids is pyrolysis, whereby the solid materials are decomposed into gaseous products and once the flammable gaseous products achieve the required concentration, they can also be ignited by a pilot [1, 3, 53].

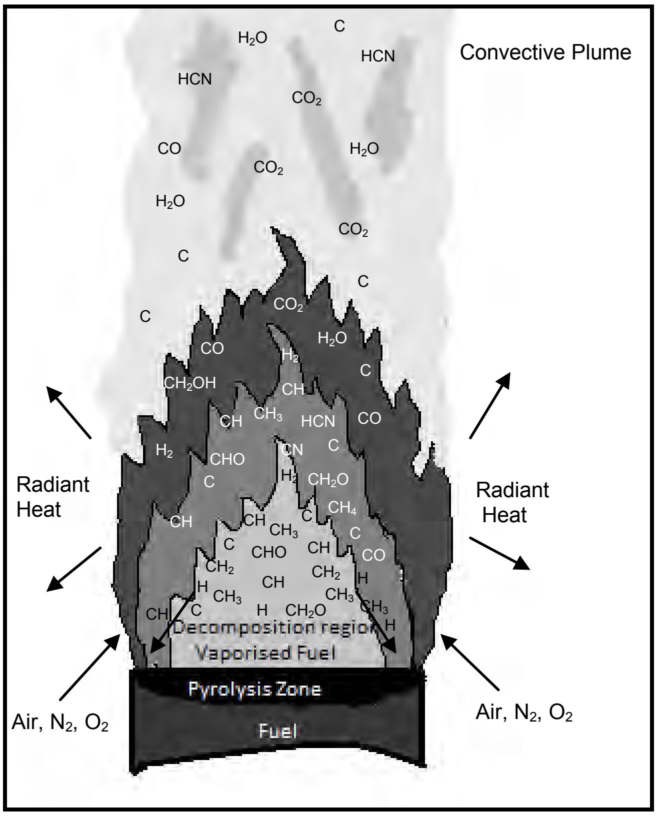


Figure 1.1: Fire Process for Solid Fuels[1] *(reproduced with permission of Pearson Education, Inc., Upper Saddle River, NJ)*

There are four types of fires, including flaming, glowing, explosive and spontaneous combustion, with the primary difference between them resulting from the nature and condition of the fuel and the availability of the oxygen[1, 3, 44].

Flaming combustion is the most typical fire encountered whereby the actual fire is the flame. This type of combustion is the most recognised and cause of nearly all destructive fires[1, 3, 44]. Flaming combustion is a gas to gas reaction, whereby both the fuel and oxidiser need to be in gas form. If this is not the case, the fuel needs to be transformed, which usually occurs by the process of pyrolysis[1, 3, 44, 49]. Glowing combustion, is a solid to gas reaction and is characterised by the absence of a flame and is usually observed at the end of a flaming fire when there is no longer a sufficient amount of oxidiser or fuel present[1]. This type of combustion occurs when solid fuels are not capable of producing sufficient quantities of gas during pyrolysis and as a result are unable to sustain a flame. The resulting glow is due to the presence of very hot materials on the surface on which combustion is proceeding[1, 9-11, 54].

Explosive combustion occurs when vapours, dusts or gases are premixed with the appropriate amount of air and ignited. In this case, the combustion process occurs almost instantaneously because the fuel vapour and oxidant have already mixed and are commonly recognised as an explosion[1, 19, 53]. Spontaneous combustion can be described as a process where a material self heats, eventually exceeding its auto ignition temperature. This results in the material igniting[1, 19, 53].

1.3.2 THE FIRE SCENE

First responders to a scene of a fire are fire fighters. Their role is to primarily save lives and extinguish the fire[55]. Once the fire has been extinguished, the fire fighters will enter the scene and begin a process referred to as overhaul, whereby they will search for hidden fires in walls, ceiling spaces or other areas that are not easily accessible. This phase is imperative in ensuring the fire has been completely extinguished and that the scene is rendered safe. During this process the fire fighters inadvertently alter the fire scene by removing furnishings, flooring, devices, wiring and wall and ceiling materials, thus creating further difficulties for an investigator as any evidence that may remain can be destroyed. Ideally, only the minimum amount of overhaul necessary for safety should be allowed until the origin of the fire has been determined[19, 55].

Once the fire fighters have ensured the fire has been completely extinguished and the scene is rendered safe, the examination begins.

1.3.2.1 Initial Examination

The goal of any successful fire scene examination is to establish if the fire was deliberately or accidentally lit[14, 19, 24]. It is therefore imperative that any evidence relating to the cause and origin of the fire be located, documented and preserved for later analysis. This is especially important if the fire was deemed to be deliberately lit because the investigators will use any evidence collected to assist them in solving the crime[39, 55].

Fire patterns, which are the visible or measurable physical effects that remain after a fire, are the key factor in the determination of the cause and origin of the fire. It is a well known fact that fires produce predictable patterns on materials as they burn and that these patterns represent the history of the fire. Hence, the principal objectives in the determination of the origin and cause of the fire are to recognise and analyse these patterns[1, 19].

A common fire pattern typically observed at fire scenes include ‘V’ patterns, which occur when a fire burns upward and outward from a fuel source. ‘V’ patterns are usually apparent on vertical surfaces such as walls that are directly adjacent to a burning object, with the apex of the pattern being located at the fuel source[1, 19]. Another common pattern is referred to as ‘lines of demarcation’ which are used to assess smoke or fire progression. These patterns are the borders that delineate regions affected by heat and smoke from adjacent unaffected regions[1, 19]. Generally, investigators will also look for any charring of wood materials and although this is quite a common occurrence at fire scenes, the amount and depth of charring is used to evaluate fire spread, intensity and duration of the fire[19].

The point of origin, as the name implies, is the point at which the fire burnt the longest and hottest, and therefore it would be expected that the most destruction would occur at this point[1, 19]. Therefore, the lowest point of burning observed at a fire scene should be examined closely as the potential point of origin and any penetration in the floor should be evaluated to determine the cause, because penetration and associated low burning can indicate the burning of an ignitable liquid[1, 19].

Furthermore, investigators will also attempt to locate pour patterns, which result from the use of ignitable liquids and are strong indicators of arson. These patterns are commonly referred to as ignitable liquid trailers, which is the term used to describe combustible materials or ignitable liquids intentionally placed to spread a fire from one location to another[1, 19]. Figure 1.2 shows some examples of ignitable liquid trailers.

Figure 1.2: Examples of Ignitable Liquid Trailers *(Courtesy of the Fire Investigation Unit at VPFSC)*

Generally, burn patterns can be used to trace the fire back to the origin as gases from combustion flow like a liquid and will follow the path of least resistance around obstructions in an upward manner[1, 19]. However pour patterns may not always be observed as they are dependent on the overall degree of damage and on the ignitable liquid used by the arsonists[11, 56, 57]. However, it is important to note that different ignitable liquids and different quantities used in a fire can produce different burn patterns. Furthermore in some instances burn patterns may actually be misleading in that irregular burn patterns have been produced during the burning process yet no ignitable liquid was used[58, 59].

It is thus essential that the origin and any burn patterns be identified so that the spread and development of the fire can be established. This knowledge facilitates the determination of the cause of the fire and enables the investigator to establish if the fire was accidentally or intentionally lit and subsequently allows for the determination of whether the scene is in fact a crime scene[9, 42, 47].

If the fire was found to be deliberately lit, any evidence relating to the cause must be documented and preserved as soon as possible. This is essential as many ignitable liquids are volatile and therefore, if they do remain they may evaporate. Furthermore, any cleanup or salvage operations may disturb or result in the loss of any physical evidence that may still remain[9, 42].

1.3.2.2 Collection of Samples

To determine the likelihood of arson, the forensic investigator must collect samples for evidence to assist the investigation[9, 11, 56, 57].

The collection of evidence at the fire scene must be conducted in a methodical manner whilst fully documenting the entire scene[26, 60]. The documentation of the scene is an essential process and allows any detected ignitable liquid residues to be placed accurately within the scene[19, 26, 60]. For example, if an ignitable liquid residue is detected at the point of origin, it can be proposed that an ignitable liquid may have been applied to start the fire, however if it was detected away from the origin, then it cannot be proved that the ignitable liquid was used to willingly set the fire as there may be a valid reason for its presence[19, 26, 60].

The handling and packaging of samples is particularly critical and stringent precautions should be taken to avoid contamination and the potential loss of any volatiles[11, 56, 57, 61].
Most ignitable liquids commonly used as accelerants are hydrophobic and tend not to be washed away by water when the fire is extinguished. They instead become sealed into porous substances by the water where they are protected from evaporation. Therefore when collecting samples from a fire scene, it is important to select those materials that have the highest probability of yielding appreciable levels of ignitable liquid residues[22, 45, 62]. These materials should be porous and composed of adsorbent or absorbent materials with a high surface area to retain ignitable liquid residues. Such materials include soil, paper/cardboard, cloth and carpet[45].

Samples should be collected from areas likely to yield ignitable liquid residues and include debris such as ash, soot, and other porous materials. Areas around and below burn patterns and the point of origin are also likely to yield ignitable liquid residues because fires burn upward and ignitable liquids soak downward[4, 23, 42, 43]. In general, when a liquid is poured over a large area it is highly likely that a portion of it will seep into a porous surface, such as upholstery, plaster, carpet and/or cracks in the floor, where it will not always be entirely consumed by a fire and therefore able to be recovered[1, 26, 48, 63].

Substrate comparison or control samples, which are samples believed to not contain any ignitable liquid, should be collected, if applicable, from a nearby undamaged area[1, 26, 43, 64]. Reasons for this are that materials commonly found at structural fires, such as carpet and carpet padding, are of petrochemical origin and may share molecular similarities with an ignitable liquid. Thus, when exposed to heat, these materials can decompose to produce volatile compounds which may complicate the identification of any ignitable liquid present. Consequently, the presence of petrochemical residues in fire debris is not always a definitive indicator of arson[31, 45, 65].

In general, effective containers for the collection of fire debris must be contaminant free and vapour tight as the ignitable liquid residues found in fire debris consist mostly of volatile hydrocarbons[66]. Ideal containers for the collection of debris suspected of containing volatile ignitable liquid residues are clean metal paint cans and sealable glass jars[23]. However, for larger more awkward shaped objects, such as pieces of furniture, bags of nylon or a suitable co-polymer can be used to wrap the item to prevent further loss of any volatiles. Plastic polyethylene bags are not suitable for packaging samples because they react with hydrocarbons and will permit volatile hydrocarbon vapours to be depleted[56, 62]. However, the bags commonly used by forensic laboratories in Australia are Cryovac and Globus branded polyethylene/polyvinylidine dichloride bags. These bags are not prone to puncture or tearing and come in a wide range of sizes. They also offer the benefits of low cost, durability and flexibility[67].

Collected samples should be kept refrigerated at approximately 4°C until analysed by the laboratory in order to prevent further losses from evaporation [11, 56, 57].

1.3.3 LABORATORY ANALYSIS

Upon reviewing all relevant facts and information surrounding the fire, the cause of the fire will be classified by the investigator and any evidence will be collected and preserved for laboratory analysis[56, 68].

The main function of laboratories is to analyse fire debris for suspected ignitable liquids. Therefore the job of the forensic fire investigation scientists is to work with the physical evidence collected at the scene and determine if the fire debris contains any ignitable liquid residues[11, 14, 28, 56, 57]. This is a difficult task as there are a number of possible reasons why an ignitable liquid residue may or may not be found in the debris. For example, if no ignitable liquid residue was recovered from the debris, it is feasible that no ignitable liquid was used. However, ignitable liquids are volatile and therefore the absence of an ignitable liquid in fire debris does not necessarily prove that an ignitable liquid was not used, it merely fails to establish its presence after the fire. Furthermore, the presence of residual ignitable liquids in fire debris is not always a definitive indicator of arson, as further investigation may reveal a legitimate reason for its presence in the debris [9, 11, 28, 46, 69]. If the results obtained in the laboratory are to be used to confirm that the fire was deliberately lit and/or accelerated, the forensic fire investigation scientists must prove the presence of an ignitable liquid unequivocally[9, 11, 70].

Laboratory analysis consists of two main parts, the recovery of ignitable liquid residues from the debris and the subsequent identification of volatiles. There are a number of different recovery methods employed to recover the ignitable liquid residues from the debris, however, gas chromatography (GC), with an appropriate detector is the technique universally employed for the separation and identification of the components present in the ignitable liquid residue[11, 20, 35].

1.3.3.1 Recovery Methods

The first step of fire debris analysis is the extraction and isolation of any volatile hydrocarbons from the sample that may be the remnants of an ignitable liquid[35, 37, 57, 71]. The isolation and recovery of ignitable liquid residues from debris are essential steps in the investigation of arson fires and should be handled by qualified chemists[1, 3].

The common aims of sample preparation are to remove potential interferences from a collected sample, to increase the concentration of the analyte and if required, to convert the analyte into a more suitable form for detection or separation. Furthermore the technique should be robust, reproducible and independent of variations in the sample matrix[43, 72, 73].

In general, recovery methods are efficient at retrieving ignitable liquid residues from fire debris[1, 69]. Several extraction procedures exist, each of which have their advantages and disadvantages, and are applicable based on the character of the sample[1, 9, 11, 24, 69, 70].

Common recovery methods used include heated, passive and dynamic headspace diffusion, solid phase micro extraction (SPME), steam distillation and solvent extraction. However the most common method for extraction of ignitable liquid residues from fire debris samples is passive headspace concentration using activated charcoal strips[15].

Headspace techniques are widely used due to their good sensitivity and the reduced risk of co-extracting compounds from the matrix. These techniques are all based on the principle of extracting and concentrating the vapour phase from above the sample by using an airtight and heated container. The ignitable liquid vapours are then collected on an adsorbent[24]. There are three types of headspace techniques including heated headspace, passive headspace and dynamic headspace.

1.3.3.1.1 Heated Headspace

Heated headspace analysis is the least sensitive, yet fastest method for the recovery of ignitable liquids from fire debris[1, 9, 11, 45]. This method entails heating of the sealed sample container which enables any volatiles in the debris to be driven off and trapped in the headspace of the container. A sample of the headspace vapour is then withdrawn using a gas tight syringe and injected directly into the gas chromatograph[9, 11, 72].

For heavier boiling materials, such as fuel oil and kerosene, the sample container needs to be heated at excessive temperatures to force these ignitable liquids into the vapour phase. This can be problematic in that it encourages the degradation of synthetics (such as carpet), consequently adding to the complexity of the chromatogram, and possibly masking low levels of real ignitable liquid residues [1, 11, 74]. Therefore, if a heavy ignitable liquid is suspected, solvent extraction or dynamic headspace are better recovery methods and will result in a more complete recovery and analysis[1].

This method is a useful screening method, it is quick, simple and particularly effective for polar and highly volatile components[43]. However, the disadvantages of this method include its lack of sensitivity and pronounced discrimination toward low volatility components[43, 45].

1.3.3.1.2 Passive Headspace Diffusion

The most common and simplest method for the recovery of ignitable liquid residues from fire debris is passive headspace diffusion using activated charcoal[13, 45, 63, 75, 76]. A tube containing activated charcoal is inserted into the sample container which is then heated or allowed to equilibrate overnight at ambient temperature. Hydrocarbon vapours become concentrated in the tube, which is then removed and the adsorbed volatiles are extracted from the charcoal with a small quantity of an organic solvent such as diethyl ether[13, 24, 63, 75, 77, 78]. The liquid sample is then injected directly into the gas chromatograph[1, 23, 71, 77].

Variations to this method include inserting plastic or glass beads coated with activated charcoal or inserting a charcoal-coated wire into the sample container, as shown in Figure 1.3[11].

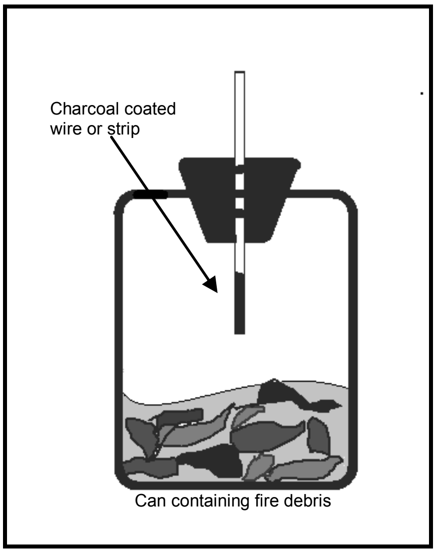


Figure 1.3: Passive Headspace Diffusion Technique[1] *(reproduced with permission of Pearson Education, Inc., Upper Saddle River, NJ)*

This headspace concentration method is best used when a high level of sensitivity is required due to a very low concentration of ignitable liquid residues in the sample and it is also an extremely useful screening method[43, 45, 74, 76, 77]. Furthermore recovery by passive headspace concentration is advantageous in that it is essentially non destructive of the original fire debris, which is an important consideration for items of evidence[45, 77].

The main disadvantages of passive headspace concentration is that the technique is labour intensive[23]. Furthermore this technique relies on the relatively high vapour pressure of hydrocarbons and limitations are imposed by the low vapour pressures of high molecular weight hydrocarbon compounds in accelerants. In addition, the accelerant concentration within a given aliquot of debris vapour can be very low and even vary significantly between samples, causing complications in the interpretation of resulting chromatograms[76]. Recovery by passive headspace is dependent on temperature and time. Generally temperatures above 60°C are required to ensure recovery of the heavier diagnostic compounds, however excessive heating, as well as longer sampling times will result in poorer yields of more volatile components, which become preferentially replaced by the heavier molecules[45, 79, 80].

1.3.3.1.3 Dynamic Headspace

Dynamic headspace uses an adsorptive matrix through which air from the evidence container is drawn or pushed[1, 11, 24, 45, 71]. The matrix is generally charcoal, however polymers such as Tenax may also be used as it has a high recovery rate for a wide range of hydrocarbons. However polymers are not absolutely stable against oxidation and may produce degradation products[1].

The recovery of ignitable liquids using dynamic headspace requires the sample container to be fitted with a modified lid or septum and then heated, forcing volatile compounds to vapourise. At the same time, the headspace of the sample is drawn or pushed through a tube containing the adsorptive matrix, as shown in Figure 1.4. Once the extraction is complete, the adsorbent can either be washed with an organic solvent and the sample can then be injected into the gas chromatograph or it can be thermally desorbed and transferred to the gas chromatograph[1, 45, 57, 71].

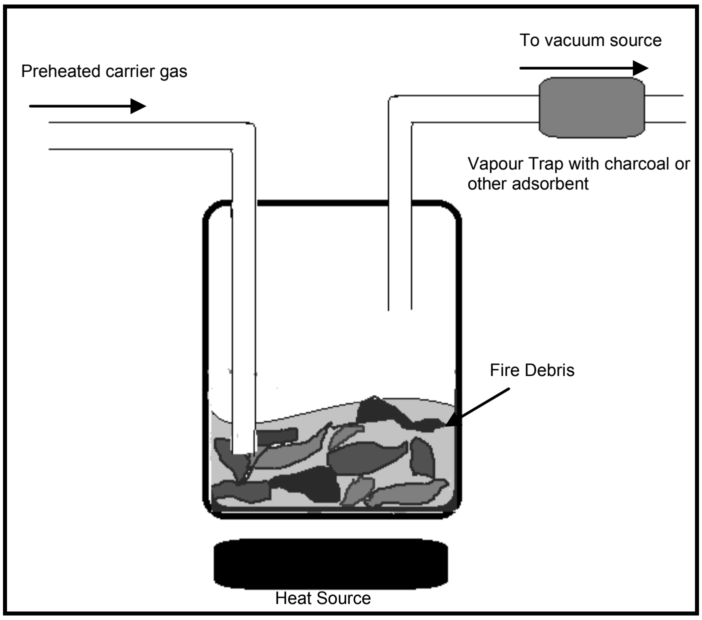


Figure 1.4: Dynamic Headspace Technique[1] *(reproduced with permission of Pearson Education, Inc., Upper Saddle River, NJ)*

Vacuum driven flows or pulsed helium flows can also be used to force volatile compounds onto the adsorbent material. Dynamic headspace extraction methods are more sensitive compared to passive headspace extraction, but it is difficult to conduct additional analyses and the original state of the sample is lost[24, 43]. Although this technique is very sensitive and applicable to all ignitable liquids including alcohols, excessive extraction may result in the loss of lighter fraction ignitable liquids[1, 9, 11, 54, 81, 82].

Limitations inherent to current headspace adsorption/ solvent elution methods include lack of sensitivity and discrimination against low boiling point analytes and the use of hazardous solvents when using adsorption methods. They are also time consuming and cumbersome[30, 82]. Although these techniques are relatively straightforward techniques, water may condense on the adsorbent when the sample is heated which may cause some loss of sample, but overall the recoveries are acceptable[43].

1.3.3.1.4 *Solid Phase Micro Extraction*

SPME is a sensitive technique for the pre-concentration of organic compounds for their subsequent analysis[34, 83-86]. It is a fast, cheap, easy to use and effective technique that requires no sample preparation, eliminates the use of solvents and can effectively isolate ignitable liquid residues from water [1, 15, 23, 37, 45, 77, 83, 87-89]. This technique was found to be capable of detecting trace amounts of petrol from a sample obtained from a real-arson suspected fire, while conventional extraction methods lacked adequate sensitivity for the analysis and the ignitable liquids were not detected[15, 30, 77, 88, 90].

SPME is a very similar technique to heated headspace however this technique consists of a fiber, which has a solid phase adsorbent bonded to it, being inserted into the heated sample container through a hollow needle of the SPME syringe[72, 83, 86, 91-94]. A schematic of the SPME device is presented in Figure 1.5. Any volatiles present in the sample become adsorbed onto the fiber which is then withdrawn and inserted into the gas chromatograph injector where the adsorbed volatiles are thermally desorbed[1, 30, 60, 87, 94].

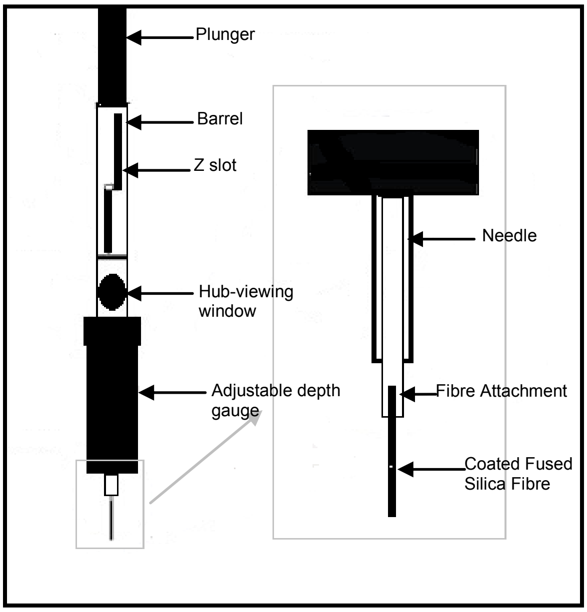


Figure 1.5: Schematic of the Solid Phase Micro Extraction Device

SPME offers the advantage over traditional extraction techniques by integrating the sampling, extraction, concentrating and sample introduction into a single step, furthermore it can be used as an excellent screening method[17, 30, 83, 95]. Although the amount of analytes recovered by SPME is relatively small, there are no analyte losses due to sample handling or transfer and the entire extract is desorbed into the injection port of the gas chromatograph for analysis, thus yielding high sensitivity[96].

The SPME analyses of petrol and kerosene has been compared to headspace, cold-trap and solvent extraction methods and it has been shown to provide accurate information with less interferent peaks [23, 94, 97]. Another study has confirmed the utility of this technique including the lack of interference problems in the presence of wood or plastic pyrolysis products and the ability of SPME to provide reproducible multiple analyses from a single sample. It has also been shown to be effective for recovery of ignitable liquid residues from aqueous samples[17, 23, 90, 94].

It has however been argued that SPME may in fact be overly sensitive, resulting in significant measurement of the petroleum-laced background that is inherent in products manufactured with petroleum derivatives[45, 64, 98]. Other disadvantages of the SPME process include the limited fiber lifetime, inability to archive the SPME extract and an inability to conveniently automate the analytical process using conventional gas chromatograph auto-samplers[98]. Further disadvantages of this method include fiber fragility, high cost of fibers and analyte carry over effects[45, 89, 99].

SPME has received a lot of attention in the field of ignitable liquid residue analysis, however as yet it has not become a common technique in many forensic laboratories around the world[12].

1.3.3.1.5 Steam Distillation

Steam distillation is the oldest procedure of ignitable liquid residue recovery and is employed to separate visible quantities of water insoluble hydrocarbons from fire debris. Therefore this technique is not suitable for the separation of water soluble ignitable liquids and should only be used on samples which have a detectable odour of petroleum distillates when initially examined[1, 43, 45, 79].

Extraction of residues by this method requires specialised equipment to be set up as shown in Figure 1.6[11]. Water is added to the sample and boiled; this generates steam which carries the volatiles into a condenser where they condense and become trapped. Petroleum distillate residues float on top of the column of water and are collected as visible liquids, which are then analysed by GC[43, 60, 100].

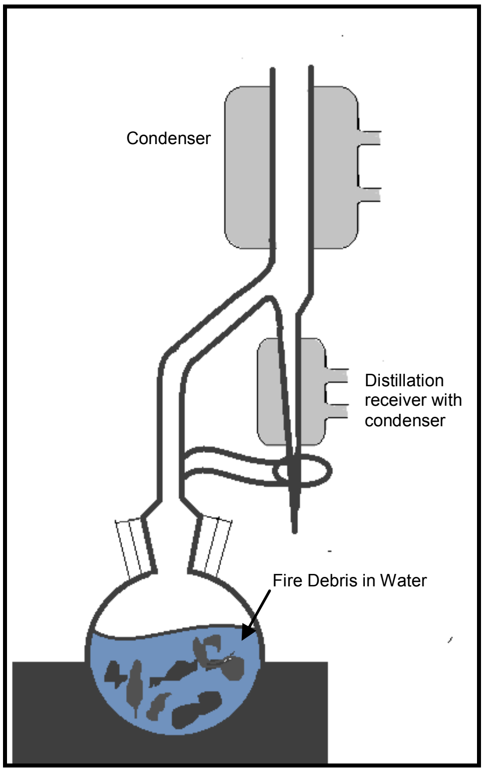


Figure 1.6: Steam Distillation Technique[1] *(reproduced with permission of Pearson Education, Inc., Upper Saddle River, NJ)*

Steam distillation is recommended for samples which have a detectable odour of ignitable liquids at room temperature and which are not amenable to solvent extraction. However limitations to this method include, impurities in the sample may be distilled with the ignitable liquid residues, and the method is relatively insensitive with respect to fuels with low-boiling point components such as petrol due to high losses caused by evaporation. The glassware used requires exhaustive cleaning after each distillation and there is difficulty in collecting very small extracts for injection into a gas chromatograph[17, 43, 45, 77, 101-103].

1.3.3.1.6 *Solvent Extraction*

Solvent extraction is one of the oldest but most direct and simple methods for extracting small quantities of ignitable liquid residues from samples of fire debris. This technique requires the use of an organic solvent, which is used to extract the residue from the sample. The extract is then filtered and concentrated using dry nitrogen or another inert gas and/or filtered air and analysed by GC[9, 11, 24, 27, 28, 45, 77, 78, 104-110].

This method is very sensitive and provides good recovery for heavier petroleum products, such as kerosene but is not suitable for isolating the lighter petroleum distillates due to evaporative losses[1, 9, 11, 27, 28, 49, 77, 104-106, 111, 112]. The solvent has to be evaporated from the sample extract to achieve good sensitivity. This method is very efficient for non volatile products or for a matrix that retains strongly the ignitable products, however it tends to produce complex chromatograms due to co-extraction of compounds from the matrix[24, 45].

1.3.3.2 Analysis of Ignitable Liquid Residues

The vast majority of arsons are initiated by petroleum distillates such as petrol and kerosene, which are complex mixtures of hydrocarbons. GC is therefore the technique of choice for the analysis of ignitable liquids recovered from fire debris as it is capable of efficiently separating the many components that form these complex mixtures, whilst consuming only minute amounts of sample[20, 77]. Furthermore the patterns produced by GC are characteristic of the petroleum distillate and as such quite reproducible. For example, the patterns for the light fractions of petroleum ether, middle distillates like napthas and kerosene and the heavier products such as fuel and lubricating oil are all quite distinct and recognisable[77]. Visual assessment of the gas chromatograms for the identification of ignitable liquid residues can be notoriously difficult and often subjective for a number of reasons. The two main problems associated with visual assessment are weathering, or evaporation of the ignitable liquid and contributions from the fire debris matrix[14, 32, 35, 42, 113, 114].

The analysis of ignitable liquid residues can become complicated as ignitable liquids have high vapour pressures which cause them to evaporate. Therefore when burnt or exposed to air ignitable liquids evaporate, this in effect changes their physical and chemical properties. However this behavior is predictable in that the most volatile components evaporate more quickly than those which are less volatile. As such, ignitable liquids are still able to produce characteristic chromatograms in various stages of evaporation when analysed by GC[1, 9, 26-28, 42, 78, 106, 108, 112, 115, 116]. Generally, when a fire is extinguished with water the rate of evaporation of the volatile components is slowed considerably as water is able to cool and cover the materials whilst not interfering with the gas chromatographic analysis of the ignitable liquid residue[104].

The two most commonly utilised gas chromatograph detectors for fire debris analysis are the Flame Ionisation Detector (FID) and more recently the Mass Spectrometer (MS). GC/FID has conventionally been used for arson evidence because the FID has a very high sensitivity to hydrocarbons and hydrocarbon-related products whilst producing virtually no response to water. These detectors are quite stable however the disadvantage of using a FID is that it yields little chemical information about the compounds that pass through to produce a signal. This is where GC/MS offers a considerable advantage as it is capable of providing structural information about the compounds detected[1, 9, 26-28, 36, 42, 111, 112, 117, 118]. Furthermore, GC/MS has the ability to make complicated GC patterns less complex by utilising data analysis techniques such as extracted ion profiling and/or target compound analysis to minimise the chromatographic interference from the sample matrix[1, 9, 14, 26-28, 42, 78, 106, 108, 112, 115, 116].

1.3.3.3 Data Evaluation

The data produced by GC using either a FID or MS in full scan mode, is primarily evaluated and classified by a technique referred to as pattern comparison. Pattern comparison is commonly employed in the qualitative analysis of complex mixtures such as petroleum products and is a process by which the patterns of GC peaks generated by a sample, referred to as fire residue chromatograms, are visually compared to chromatograms of known ignitable liquid standards which have been obtained under the same GC conditions[39, 54, 91, 106, 108, 111, 116, 117, 119, 120].

Chemometric approaches, which is the application of a mathematical procedure that allows for the statistical comparison of chromatograms has also been used in fire investigation data analysis[121, 122]. Statistical and chemometric methods can be used to group fuel samples based on chemical similarities by statistically quantifying the pattern matching. Principle component analysis (PCA) is one example of a chemometric procedure that can be used to reduce the size of a data set by finding which parts contain the greatest variation. Other chemometric methods, such as linear discriminant analysis (LDA), can be used to compare or classify ignitable liquids for example Sandercock and DuPasquier were able to successfully classify unevaporated petrol samples according to grade, country of origin and season of collection using PCA and LDA. Furthermore a number of other studies have shown the potential to objectively associate an ignitable liquid residue back to a neat liquid, however the process of visual pattern comparison is still the data evaluation method of choice[29, 32, 33, 68, 121-127].

In most cases, visual pattern comparison is sufficient to adequately identify ignitable liquid residues recovered from fire debris, however discernable ignitable liquid patterns may not always be attainable[54, 106, 108, 111, 116, 117, 120]. Complications arise in the identification of an ignitable liquid residue by visual pattern comparison when there is a mixture of ignitable liquids employed or where the ignitable liquid residue is mixed with heat-generated breakdown products of materials burning at the fire scene[35, 39, 54, 106, 108, 111, 116, 117]. In such situations GC/MS may be used as it is capable of providing additional levels of pattern recognition and as such may assist in the interpretation of complex fire residue chromatograms[35].

1.3.3.3.1 Gas Chromatography/ Flame Ionisation Detection

Identification of petroleum products based solely on the chromatographic data obtained by a GC/FID is based on pattern comparison[1, 9, 26-28, 42, 112, 120]. To enable an adequate comparison to be made, the ignitable liquid standards must include both unevaporated and a range of evaporated standards, due to the fact that patterns produced by ignitable liquids can be modified by burning, weathering and other degradation mechanisms[117].

If ignitable liquid residues in the fire debris are present in abundance then identification by pattern comparison is straightforward. However, there are a growing number of ignitable liquids that are not petroleum based and may not be able to produce discernible patterns for comparison[26, 54, 64]. Further complications in the identification of ignitable liquid residues can be due to the actual substrates submitted to forensic fire investigation scientists for ignitable liquid residue recovery. These substrates can be made up of different polymers, which may be of petrochemical origin and be burnt, partially burnt and/or naturally contaminated by everyday use. Therefore, when ignitable liquid residues are present in low enough levels that they start being confused with background then it becomes difficult to render a conclusion because the signal from the ignitable liquid may not be able to be separated from that of the matrix[35, 54, 104, 106, 108, 112, 115]. In these situations, GC/FID patterns may not provide enough information to permit their identification and GC/MS may be used to assist in the interpretation of these complex chromatograms. Hence, the introduction of the mass spectrometer notably enhances the capabilities of the analyst to detect and identify ignitable liquids, particularly in the presence of pyrolysis and combustion products[54, 104, 106, 108, 112, 115].

1.3.3.3.2 Gas Chromatography/ Mass Spectrometry

GC/MS has proven to be a valuable technique for solving difficult problems relating to the detection of ignitable liquid residues in high background samples. Therefore it can be applied to fire debris samples too contaminated for the identification of ignitable liquid residues by GC/FID[49, 111].

Identification of an ignitable liquid residue may become quite difficult when interfering peaks become of sufficient number and intensity that they obscure an ignitable liquid pattern. In such situations, the analyst can take advantage of the fact that petroleum distillates contain small groups of characteristic compounds which occur reproducibly in specific ratios and produce recognisable patterns. Hence the analyst can use the mass spectrometric data system to effectively filter out the contaminating species, producing chromatograms based solely on these characteristic ignitable liquid compounds[38, 104, 109, 128]. Therefore rather than use the mass spectrometer to absolutely identify the compounds, the spectral features characteristic of various classes of compounds can be used in conjunction with basic pattern comparison techniques to analyse the data[42, 104, 128].

Data analysis techniques, such as extracted ion profiling, selected ion monitoring and/or target compound analysis, are designed to identify ignitable liquid residues when they are present in relatively low abundances with respect to co-extracted compounds derived from the sample matrix[78].

1.3.3.3.2.1 Extracted Ion Profiling

Extracted ion profiling, also known as reconstructed ion chromatography or mass chromatography is the most commonly employed method of utilising the mass spectral data characteristics in conjunction with chromatography to analyze ignitable liquid data[78].

This technique allows the full spectral data, referred to as a total ion chromatogram, to be collected throughout the chromatographic run and then allows the analyst to focus on specific compounds by using the data system to effectively filter out other components from the chromatogram[35, 42, 108, 115, 116, 129]. Therefore extracted ion profiling offers the advantage of not omitting any important data whilst still providing a mechanism to minimise contributions from interfering compounds, allowing the analyst to focus only on data of potential interest[104].

Each class of hydrocarbons has specific, characteristic ions which can be extracted to create chromatograms representative of that specific class, for example ions 43, 57, 71 and 85 can be extracted to produce an extracted ion chromatogram which is representative of the alkane profile in the sample[78]. The major classes of hydrocarbons and their characteristic ions are shown in Table 1.1. In order to obtain more simplified chromatographic profiles, the analyst selects the ions characteristic of the compounds of interest via the mass spectral data system, which will then sort through the collected mass spectra from a sample for the presence of these ions and plot the intensities of only these ions as a function of time[108, 116]. Extracted ion profiling provides an efficient process of classifying and identifying ignitable liquid residues in high background samples[104, 108, 128].

Extracted ion chromatograms may be produced as singular or summed profiles and can be applied to each class of hydrocarbons shown in Table 1.1[104, 108, 128]. Single extracted ion chromatograms are produced when individual ions are extracted and evaluated whereas summed extracted ion chromatograms are produced when class specific ions are extracted together for evaluation thus providing direct component abundance comparisons within the class[42, 104, 108, 115, 116, 129].

When using extracted ion chromatograms for the analysis of fire debris there are several general guidelines to which an analyst should adhere, most importantly is the selection of ions. Secondly, the extracted ion chromatograms produced by the fire residue chromatograms must be compared with analogous extracted ion chromatograms obtained from a known standard chromatogram obtained under identical gas chromatographic conditions. Finally it is imperative that the total ion chromatogram still be considered the most important data available for the fire debris analyst[42, 108, 115, 116, 129].

Table 1.1: Classes of Hydrocarbons and their Characteristic Ions[78]

Hydrocarbon Class	Characteristic ions (m/z)
Alkane	43, 57, 71, 85
Cycloalkane and alkene	55, 69
n-Alkylcyclohexane	82, 83
Aromatic-alkylbenzenes	91, 105, 119; 92, 106, 120
Indanes	117, 118; 131, 132
Alkylnaphthalenes	128, 142, 156, 170
Alkylstyrenes	104, 117, 118, 132, 146
Alkylanthracenes	178, 192, 206
Alkylbiphenyls/ acenaphthenes	154, 168, 182, 196
Monoterpenes	93, 136
Ketones	43, 58, 72, 86
Alcohols	31, 45

The major disadvantage with extracted ion profiling is that this technique does not distinguish between a designated ion arising from petroleum hydrocarbons and the same ion arising from non-petroleum sources. Therefore, regardless of the fact that extracted ion profiling may allow for the easy identification of an ignitable liquid, in some instances the sample may contain other compounds, such as pyrolysis products, which are independent of ignitable liquids but may also contain significant levels of the ions of interest and as such these ions will also be profiled along with the compounds of interest. As a result, the extracted ion chromatogram will contain extraneous peaks which may mask or distort the pattern of interest. When this occurs, it may be beneficial for the analyst to observe the individual extracted ion chromatogram or to utilize target compound analysis, as this may help facilitate the identification of an ignitable liquid[35, 108, 117].

A major concern with extracted ion profiling is that when an identification of an ignitable liquid is based on just one or two extracted ions and/or hydrocarbon classes, then the likelihood of extracting interfering compounds which are not part of an ignitable liquid is quite high. Another problem can occur if the relationship of one hydrocarbon class to the other hydrocarbon classes within the sample is not considered, as false identifications of ignitable liquids may be made. To overcome these problems, it is strongly suggested that the number of ions extracted (from different hydrocarbon classes) be increased because the greater the number of different extracted ion chromatograms that match between a fire debris sample and an ignitable liquid, the greater the confidence that an ignitable liquid is actually present[108, 115].

1.3.3.3.2.2 Selected Ion Monitoring

Selected ion monitoring is another technique utilised to analyse the GC/MS data and is similar to extracted ion profiling in that only selected, characteristic ions are analysed. This mode requires only pre-selected ions to be measured and recorded, which results in the detector having fewer ions to measure thus greatly increasing the sensitivity. Furthermore, non-hydrocarbon sample matrix interferences are minimised resulting in cleaner data[4, 7, 19, 42, 108, 115-117, 129].

This technique is more sensitive for ions of interest compared to extracted ion profiling, however it does not collect the full spectral data, therefore compounds present in the mixture that do not have a significant abundance of the monitored ions will not be detected. More importantly however, is that with fire debris analysis the initial analysis should always use a full scanning method due to the limited sample available[108].

Since many arson analyses have extremely limited sample sizes, extracted ion profiling has a distinct advantage over selected ion monitoring as selected ion monitoring techniques force the analyst to select desired ions prior to the sample run, thus precluding the possibility of finding unanticipated compounds in the sample or of more complete compound identification by spectral comparisons at a later time[77, 108, 117].

1.3.3.3.2.3 Target Compound Analysis

Target compound analysis is a technique that uses key specific compounds to characterise ignitable liquid residues in fire debris, thus allowing the analyst to control which gas chromatographic peaks will be extracted and which will be ignored. As a result, this technique allows extraneous peaks, which obliterate the characteristic pattern of an ignitable liquid, to be eliminated making it possible to pick out an ignitable liquid pattern even amongst complex fire residue chromatograms with high backgrounds[77, 104, 108, 117].

Target compound analysis is a more selective data evaluation technique than extracted ion profiling because the requirements are more stringent. Not only must the major ion for the compound elute at the proper retention time but other daughter ions must also be present with the correct intensities relative to the molecular ion[77, 104, 108, 117].

Keto and Wineman originally developed the method of target compound analysis whereby the total ion chromatogram of each sample was processed by a special data analysis program that looked for GC peaks at specific retention times. It then checked the identity of each target compound by considering the relative abundance of two or three characteristic mass-to-charge (m/z) ions. Semi-quantitative data were obtained for the target compounds and used to construct a target compound chromatogram, which is, a bar graph of base ion peak area versus retention time for each target compound identified. Finally the target compound chromatograms were visually or automatically compared with target compound chromatograms generated from standard petroleum samples[37, 117, 130].

The most critical aspect with respect to the effective use of this technique is the selection of the target compounds. Desirable target compounds must be consistently present in ignitable liquids and remain detectable when the ignitable liquid is highly evaporated, diluted and contaminated with high levels of co-eluting substances[35, 104, 117]. Furthermore, target compounds should not be commonly encountered from sources other than from refined petroleum products[78]. The target compounds commonly used for the analysis of fire debris, as per the ASTM (E1618 – 01) ‘Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by GC/MS’, for petrol, medium and heavy petroleum distillates are listed in Tables 1.2, 1.3 and 1.4, respectively[78].

Table 1.2: Petrol Target Compounds as listed in the ASTM (E1618 – 01) ‘Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/ Mass Spectrometry’[78]

Petrol Target Compounds
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Indane
1,2,4,5-Tetramethylbenzene
1,2,3,5-Tetramethylbenzene
5-Methylindane
4-Methylindane
Dodecane
4,7-Dimethylindane
2-Methylnaphthalene
1-1-Methylnaphthalene
Ethylnaphthalenes (mixed)
1,3-Dimethylnaphthalene
2,3-Dimethylnaphthalene

Table 1.3: Medium Petroleum Distillate Target Compounds as listed in the ASTM (E1618 – 01) 'Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/ Mass Spectrometry'[78]

Medium Petroleum Distillate Target Compounds
Nonane
Propylcyclohexane
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
Decane
1,2,3-Trimethylbenzene
n-Butylcyclohexane
Trans-decalin
Undecane
1,2,3,5-Tetramethylbenzene
n-Pentylcyclohexane
Dodecane
n-Hexylcyclohexane

Table 1.4: Heavy Petroleum Distillate Target Compounds as listed in the ASTM (E1618 – 01) 'Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/ Mass Spectrometry'[78]

Heavy Petroleum Distillate Target Compounds
Decane
n-Butylcyclohexane
Trans-decalin
Undecane
1,2,3,5-Tetramethylbenzene
n-Pentylcyclohexane
Dodecane
n-Hexylcyclohexane
2-Methylnaphthalene
1-1-Methylnaphthalene
Tridecane
n-Heptylcyclohexane
1,3-Dimethylnaphthalene
Tetrad cane
n-Octylcyclohexane
2,3,5-Trimethylnaphthalene
Pentadecane
n-Nonylcyclohexane
Hexadecane
Heptadecane
Pristane
Octadecane
Phytane
Nonadecane
Eicosane
Heneicosane

Data evaluation using target compound analysis requires the mass spectral data system to scan the chromatograms for the mass spectra of certain target compounds within a specified retention time[77, 108, 117]. Upon verification of the target compounds, the mass spectral data system produces a list of the compounds with their corresponding peak areas. The comparison of the data from the fire residue samples and standards is then facilitated by target compound chromatograms which are plots of peak area versus retention time for each compound identified[104]. Target compound chromatograms are therefore reconstructed plots that do not have the same appearance as a traditional chromatogram, however they do offer the ability to find components of interest in a highly complex chromatogram in which contributions from pyrolysis are considerable[26, 104, 107, 117]. Figure 1.7 shows a total ion chromatogram and an extracted ion chromatogram for an unleaded petrol sample and Figure 1.8 shows the target compound chromatogram for the same unleaded petrol where peak areas for each target compound, taken from the extracted ion chromatogram, are plotted against each target compound and its retention time. In this thesis, all target compound chromatograms will only include the names of each target compound and not retention times as this allows ready identification of each compound in the target compound chromatogram. However each compound was initially identified via its retention time.

Target compound analysis, like the other methods of ignitable liquid residue data analysis, still chiefly relies on pattern comparison techniques whereby the target compound chromatogram generated for the sample is compared to the target compound chromatogram of a standard or reference ignitable liquid created in the same manner. Therefore, similar to extracted ion profiling, the major disadvantage with target compound analysis is that interfering compounds generated by pyrolysis and/or combustion at the fire scene that are themselves target compounds will not be eliminated. As a result the patterns produced and ratios of ions for the target compounds will not be representative for those of ignitable liquids[104]. This is a frequent problem that cannot be avoided by any type of data manipulation[106].

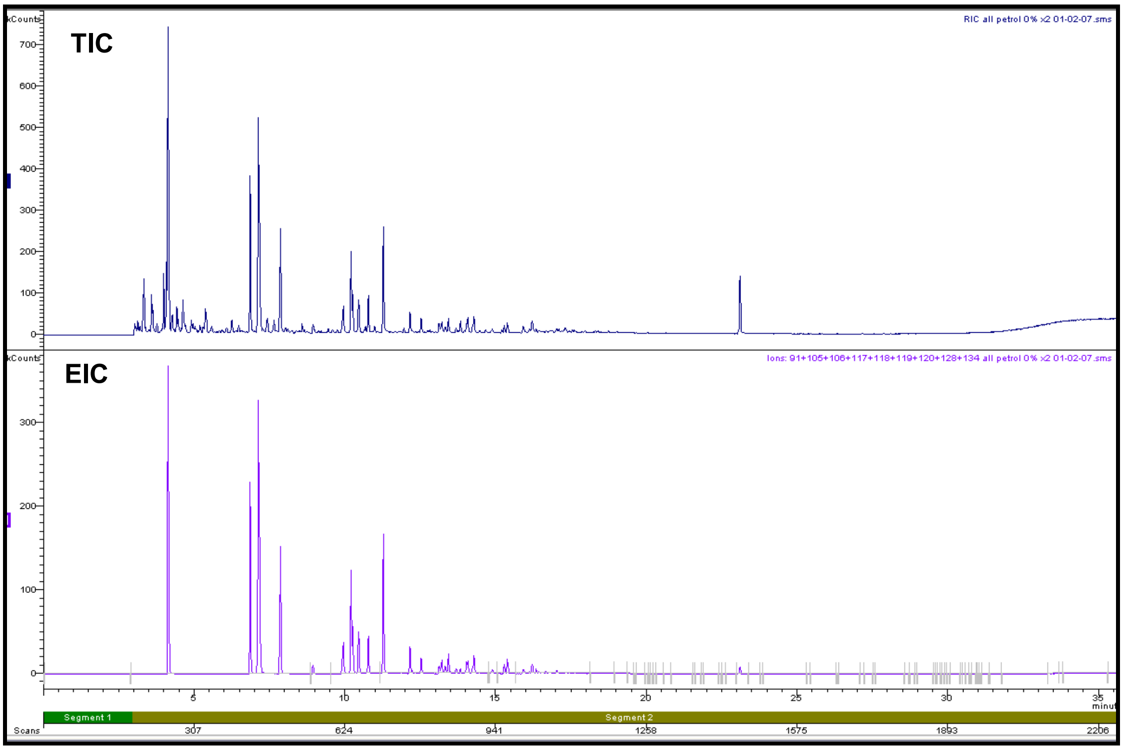


Figure 1.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Unleaded Petrol (Refer to Section 2.5.1 for GC/MS conditions)

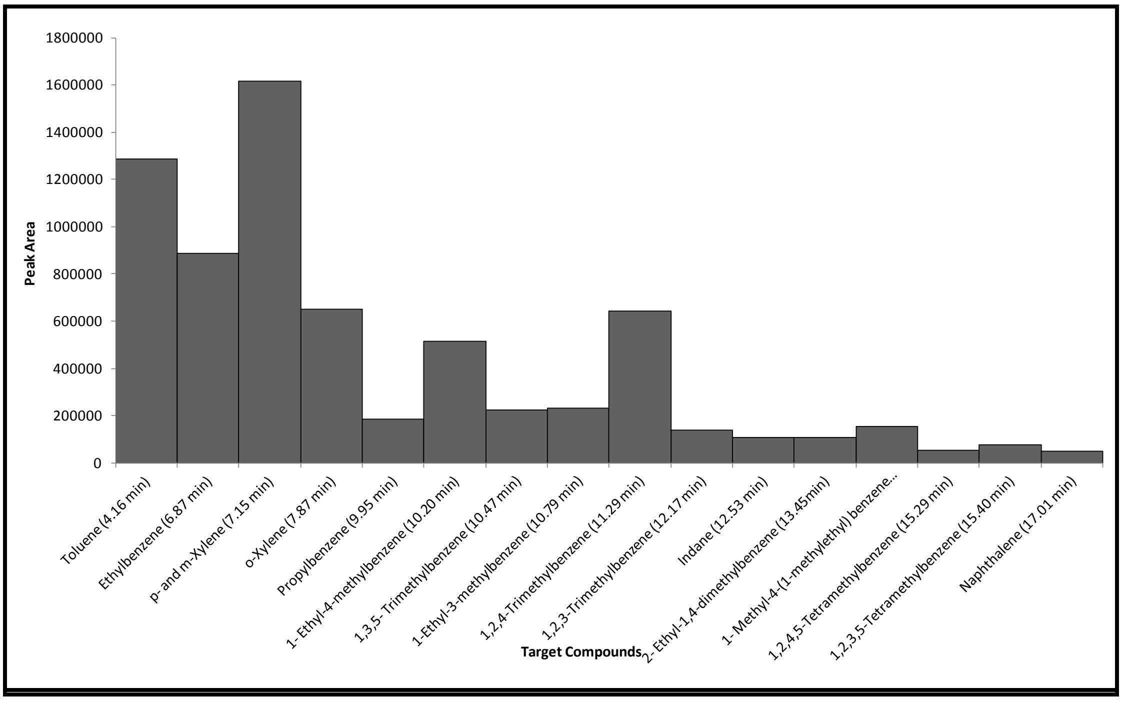


Figure 1.8: Target Compound Chromatogram for Unleaded Petrol

1.3.3.3.3 Gas Chromatographic/ Mass Spectrometric Classification of Ignitable Liquid Residues

Following the interpretation of the chromatographic data, if it has been determined that an ignitable liquid is present in the fire debris the next step is to classify the ignitable liquid residue, to determine what type of ignitable liquid was employed[78, 128, 131, 132]. The data generated by GC/MS generally provides sufficient detail, with respect to the chemical composition and boiling point range, to enable the classification of an ignitable liquid[104]. In order for the classification of an ignitable liquid by GC/MS to be deemed scientifically reliable, certain criteria must be met[64, 78, 104, 108, 111, 117, 129, 132]. First and foremost, the classification must be based on data which has been obtained under the same chromatographic conditions and preferably on the same instrument as a set of standard or reference ignitable liquids. This is important because the chromatographic pattern comparison is the key factor in all ignitable liquid identifications[78, 104, 128, 131, 132].

Furthermore, the standards must incorporate a range of ignitable liquids, with varying boiling point ranges and chemical compositions and in various stages of evaporation[78, 104, 128, 131, 132]. The current classification scheme is the ASTM (E1618 – 01) ‘Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by GC/MS’[78, 104, 131]. This classification scheme (see Table 1.5) consists of nine classes of ignitable liquids, each of which have specific chemical properties that results in diagnostic chromatographic data which allows ignitable liquids to be recognised and subsequently identified[117, 132]. Therefore the classification is based on the elution of specific compounds within a retention time window defined by the *n*-alkane carbon number[112].

The first seven classes listed in this classification are specific to petroleum–based ignitable liquids, with another of the classes being for oxygenated solvents and a miscellaneous class which is reserved for all ignitable liquids which fail to fit into the previous eight[78, 104, 128, 132]. The ignitable liquids are then further classified into three groups entitled light, medium and heavy, based on their boiling point range. In order for an ignitable liquid to be classified as a light petroleum distillate the majority of the pattern in the chromatogram must occur in the range between butane (C_4) and nonane (C_9) with no major peaks above undecane (C_{11}). The medium petroleum distillates generally have a narrow boiling range which typically spans three to four *n*-alkanes with the chromatographic peaks usually centering around C_9, decane (C_{10}) or C_{11}. The heavy petroleum distillates have a broader boiling range, spanning five or more *n*-alkanes and typically center above C_{11}[128].

The classification of an ignitable liquid appears to be quite straightforward, however the data obtained from the analysis of fire debris extracts is usually not only limited to components of ignitable liquids. Any volatile organic compounds in the substrate matrix, including background, pyrolysis and combustion products will be chromatographed along with the ignitable liquid constituents. Therefore the resulting chromatographic patterns may be quite complex and it is the job of the analyst to discern any ignitable liquid components from matrix contributions[32, 105, 117].

The amount and type of matrix contributions is dependent upon composition, quantity, and history, with some matrices producing identifiable diagnostic patterns, whilst others produce random peaks[49, 78].

Table 1.5: Ignitable Liquid Classification Scheme based on the ASTM (E1618 – 01) ‘Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/ Mass Spectrometry’[78]

Class	Light (C_4-C_9)	Medium (C_8-C_{13})	Heavy (C_8-C_{20+})
Petrol	Fresh petrol is typically in the range of C_4-C_{12}		
Petroleum Distillates	Petroleum Ether Some Cigarette lighter Fluids Some Camping Fuels	Some Charcoal Starters Some Paint Thinners Some Dry Cleaning Solvents	Kerosene Diesel Fuel Some Jet Fuels Some Charcoal Starters
Isoparaffinic products	Aviation Gas Specialty Solvents	Some Charcoal Starters Some Paint Thinners Some Copier Toners	Some Commercial Specialty Solvents
Aromatic Products	Some Paint and Varnish Removers Some Automotive Parts Cleaners Xylenes, Toluene-based products	Some Automotive Parts Cleaners Specialty Cleaning Solvents Some Insecticide Vehicles Fuel Additives	Some Insecticide Vehicles Industrial Cleaning Solvents
Naphthenic Paraffinic Products	Cyclohexane based solvents/products	Some Charcoal Starters Some Insecticide Vehicles Lamp Oils	Some Insecticide Vehicles Lamp Oils Industrial Solvents
N-Alkanes Products	Solvents Pentane Hexane Heptane	Some Candle Oils Copier Toners	Some Candle Oils Carbonless Forms Copier Toners
De-Aromatised Distillates	Some Camping Fuels	Some Charcoal Starters Some Paint Thinners	Some Charcoal Starters Odorless Kerosene’s
Oxygenated Solvents	Alcohols Ketones Some Lacquer Thinners Fuel Additives Surface Preparation Solvents	Some Lacquer Thinners Some Industrial Solvents Metal Cleaners/Gloss Removers	
Others Miscellaneous	Single Component Products Some Blended Products Some Enamel Reducers	Turpentine Products Some Blended Products Various Specialty Products	Some Blended Products Various Specialty Products

1.4 INTERFERENCES

The analysis and identification of ignitable liquids from fire debris is a somewhat complicated task, requiring very advanced skills due in part to the presence of interfering products, which are compounds that can mask or distort the pattern of the ignitable liquid, rendering the interpretation of the chromatograms extremely difficult[32, 112].

Interfering products can thus be defined as "…the set of products found in a sample that interfere with the proper identification of an ignitable liquid residue"[78, 105]. Interferences from background materials fall into three basic categories, substrate background products and pyrolysis and combustion products. Substrate background products are those petroleum based products that are inherent to the material or substrate. Hence, substrate background products are usually the result of the natural components in the raw material, the manufacturing process or by contamination [26, 64, 78, 107, 108, 111, 112, 117, 129].

Interferences can occur when a substrate burns and produces pyrolysis products and/or combustion products which are the same as compounds present in ignitable liquids. The difference between these two types of interferences is primarily based on the fact that pyrolysis products are the products released by the material when it is are subjected to heat and do not result from oxidation reactions whilst combustion products require oxygen[49]. Pyrolysis can thus be defined as thermal degradation without interaction with oxygen whereas combustion is a complex process involving the burning of materials in the presence of oxygen[49]. The different sources of interfering products can be seen in Figure 1.9[49].

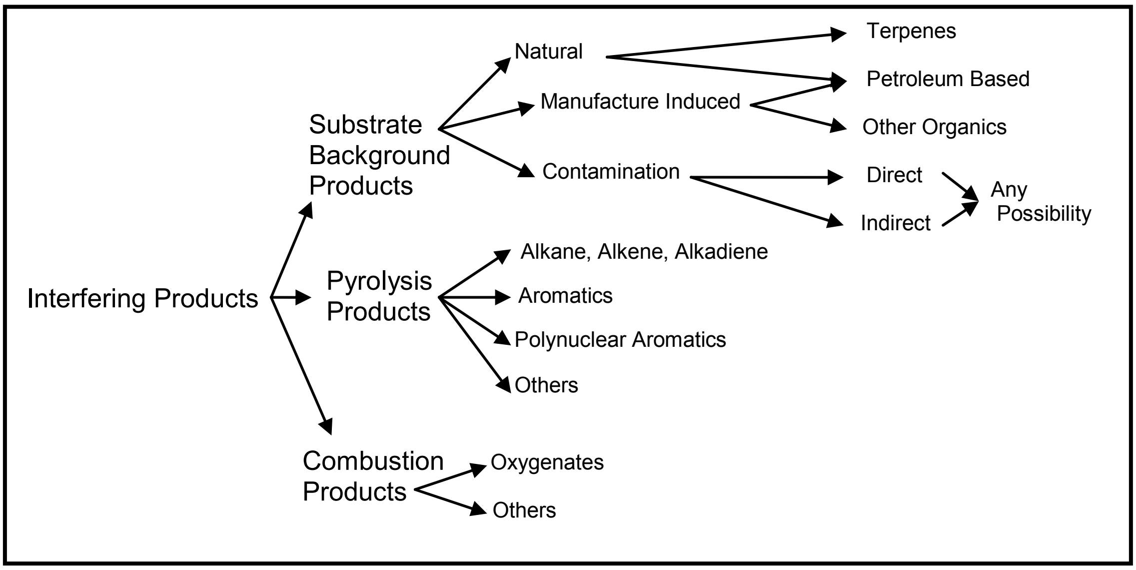


Figure 1.9: Sources of Interfering Products[49] *(reproduced with permission of Taylor & Francis Groups LLC)*

Debris collected from a fire scene as evidence may contain any number of building materials, such as floor coverings, furniture and structural materials. Furthermore these materials may have been burnt, partially burnt or remain unburnt and as such will usually contain pyrolysis products, combustion products and potentially substrate background products [26, 49, 64, 107, 108, 111, 112, 117, 129]. To further complicate matters, petroleum-based distillates are used in the manufacture of many common household products, as diverse as furniture, carpet, carpet padding, insecticides, formulas and tile glue[112]. It is therefore the job of the forensic fire investigation scientist to effectively isolate potential ignitable liquid residues extracted from fire debris from any background products that may interfere with the identification of the ignitable liquid. However, the difficulty lies with the fact that the fire investigation scientist seldom has detailed knowledge of the nature and history of the substrate to be analysed[49, 106].

If interferences from building materials are suspected when analysing fire debris for ignitable liquids, it is strongly recommended that substrate comparison samples are taken if applicable, from a nearby undamaged area thought to contain no additional ignitable liquid. This is to enable the thermal breakdown products of that particular substrate to be determined thus providing further information and assistance in the interpretation of the fire residue chromatograms[3, 49].

1.4.1 SUBSTRATE BACKGROUND PRODUCTS

The natural background products of a substrate are the naturally occurring products found in the raw material and includes products such as terpenes which are found in some wood as well as the ignitable liquid turpentine[3, 49]. The manufacturing induced products result from the manufacturing process and includes such things as solvents which generally stay adsorbed onto the substrate[51, 105]. Substrate background products can also originate from contamination, which may be direct or indirect. Direct contamination occurs as a result of direct contact between two objects, whereas indirect contamination occurs as a result of aerial contamination[49, 51, 105]. Therefore this type of substrate background product encompasses any additional products which have been adsorbed onto the substrate prior to it burning[3, 49].

The only way substrate background products can be determined by the fire investigation scientist is by extracting volatile organic compounds from the unburnt substrates[105].

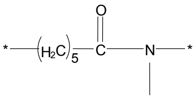
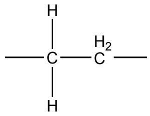
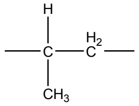
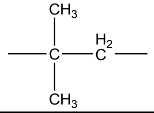
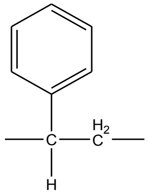
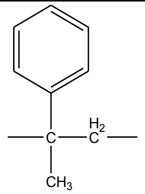
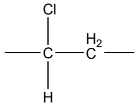
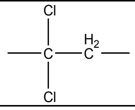
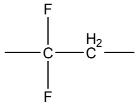
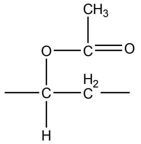
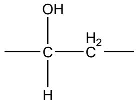
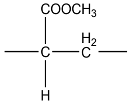
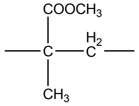
1.4.2 PYROLYSIS PRODUCTS

Pyrolysis is the process by which a substrate undergoes thermal degradation without interaction with oxygen and usually takes place at temperatures between 500-800^{o}C[105]. Between the temperature range of 100-300^{o}C the chemical transformations that take place are commonly referred to as thermal degradation, not pyrolysis. Between 300-500^{o}C the process is referred to as mild pyrolysis and vigorous pyrolysis is said to occur at temperatures above 800^{o}C[3, 49, 51].

Pyrolysis products can significantly complicate fire debris chromatograms because pyrolysis and the resulting pyrolysis products produced are influenced by a number of factors such as temperature and heating rate as well as the presence of oxygen, hydrogen, nitrogen and/or water. However, the most influential of these parameters is temperature. In general, the higher the temperature at which pyrolysis occurs, the smaller the molecules produced. Hence, the ratio of highly volatile compounds to lesser volatile compounds usually increases with temperature. Although the proportion of these compounds change with temperature the actual pyrolysis products themselves are quite similar[3, 49, 105, 112]. Further complications in the interpretation of fire debris chromatograms may also arise when a substrate is burnt in air because most of the pyrolysis products generated will be used to fuel the flame, and some will be adsorbed onto the substrate. As a result, the substrate will not be totally representative of ‘pure’ pyrolysis as combustion products will also be produced[133, 134].

Pyrolysis of polymeric material can occur by one of four methods of degradation, including random scission, side group scission, monomer reversion and cross-linking, however many polymers will undergo pyrolysis using more than one degradation mechanism[105]. In general, the weakest bond in the polymer will usually break first and consequently determine the mechanism by which the polymers will pyrolyse. For example polystyrene will produce styrene as a result of monomer reversion and then degrade further via side group scission to produce aromatic compounds[105]. Table 1.6 shows some commonly encountered polymers and their associated degradation mechanisms[105].

Table 1.6: Commonly Encountered Polymers and their Degradation Mechanisms[49] *(reproduced with permission from Taylor & Francis Groups LLC)*

	Compounds	Chemical Structure	Degradation Mechanism	Pyrolysis Products
Polyamide	Nylon 6		Random Scission Cross-linking	Oxygenated compounds
Polyolefins	Polyethylene		Random scission	*n*-alkanes *n*-alkenes *n*-alkadienes
	Polypropylene		Random scission	Branched alkanes Branched alkenes Branched alkadienes
	Polyisobutylene		Random scission Monomer Reversion	Branched alkanes Branched alkenes Branched alkadienes
Styrene Polymers	Polystyrene		Monomer Reversion Side Group Scission	Styrene Aromatics
	Poly α-methylsytrene		Monomer Reversion	α-methylsytrene
Vinyl Polymers	Polyvinylchloride		Side Group Scission	Aromatics Chlorinated compounds
	Polyvinylidenechloride		Side Group Scission	Aromatics Chlorinated compounds
	Polyvinyidenefluoride		Side Group Scission	Aromatics Fluorinated compounds
	Polyvinylacetate		Side Group Scission	Aromatics Acetic Acid
	Polyvinylalcohol		Side Group Scission	Aromatics
Acrylate Polymers	Polymethylacrylate		Random scission	Methanol Oxygenated compounds
	Polymethylmethacrylate		Monomer Reversion	Methylmethylacrylate

1.4.2.1 Random Scission

Random scission is the degradation mechanism which involves the production of a free radical at some point along the polymers backbone causing it to fragment into smaller, repetitive molecules that differ in chain length by the number of carbons in the original monomer. Polyethylene is a good example of a polymer that degrades by this mechanism. Random scission of polyethylene is shown diagrammatically in Figure 1.10[105].

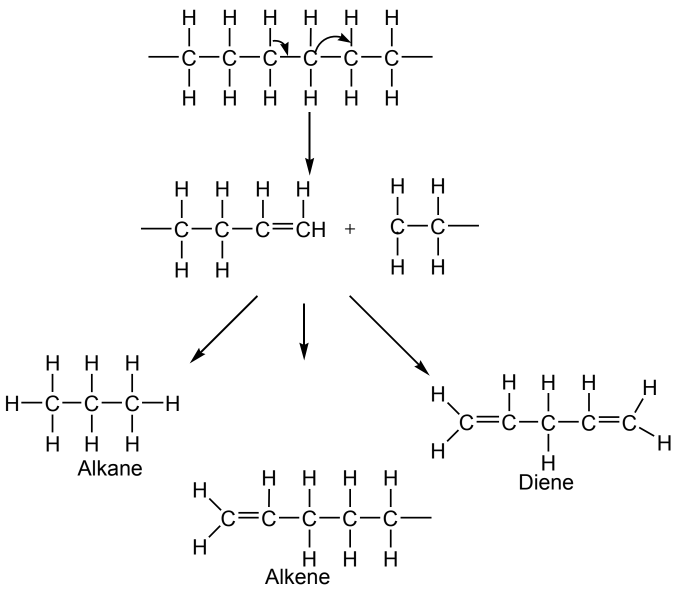


Figure 1.10: Random Scission of Polyethylene

A free radical is formed along the chain of polyethylene causing the chain to break. This produces two molecules, one with an unsaturated end and the other with a terminal free radical. This free radical may take a hydrogen from a nearby carbon which will then produce another two molecules, one with a saturated end and one with a new radical, or combine with another free radical to form an alkane. Multiple cleavages will produce small volatile molecules that when chromatographed will reveal a series of characteristic triplet peaks of a specific chain length[3, 133, 135].

1.4.2.2 Side Group Scission

Side group scission is a degradation mechanism that occurs in two steps. The first step is the elimination of the side groups attached to the backbone of the polymer leaving an unstable polyene macromolecule. This polyene then undergoes further reactions, including the formation of aromatic molecules, scission into smaller fragments and/or the formation of char[3, 135, 136].

Polyvinylchloride (PVC) is a good example of a polymer which undergoes degradation by side group scission. Firstly PVC undergoes a loss of hydrogen chloride (HCl) to form a conjugated polyene macromolecule. This then undergoes further reactions to form aromatic compounds, typically benzene, toluene and naphthalene[3, 135, 136] . The degradation of PVC by this mechanism is shown in Figure 1.11.

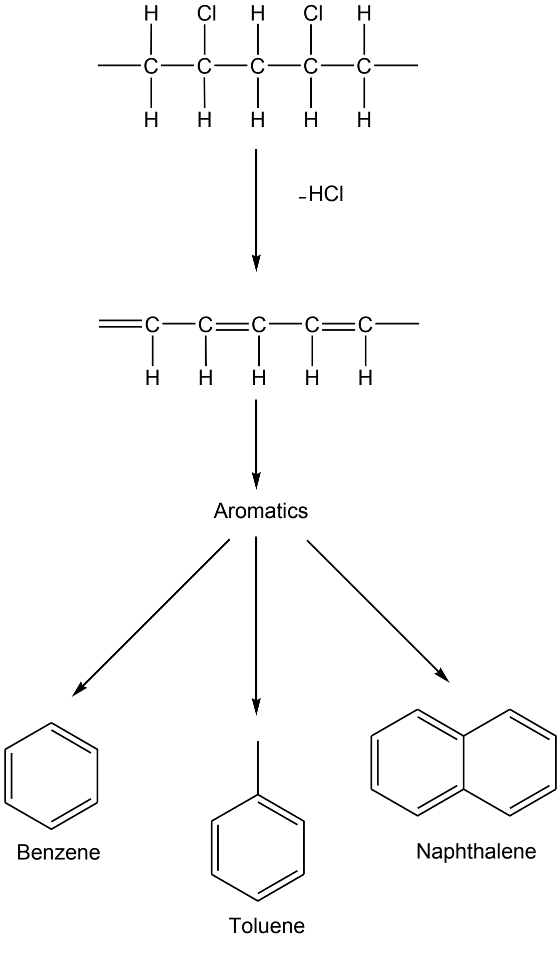


Figure 1.11: Side Group Scission of Polyvinylchloride

Similar polymers that differ only by their side groups also undergo this kind of scission. Hence the resulting pyrolysis products will either be identical or if not, very similar due to the backbone being the same once the side groups are removed[105, 135-137].

1.4.2.3 Monomer Reversion

Monomer reversion is a degradation mechanism also commonly referred to as depolymerisation or unzipping. This mechanism involves the polymer simply unzipping itself and reverting back to its monomeric version. Several polymers degrade by this mechanism including polystyrene and polymethylacrylates. The degradation of polystyrene by this mechanism is shown in Figure 1.12[49, 135, 137].

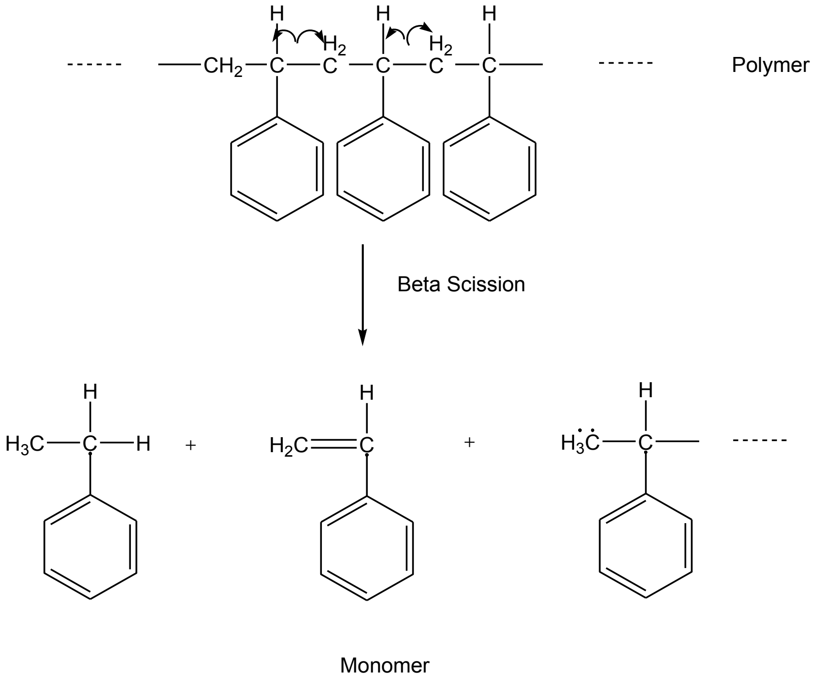


Figure 1.12: Monomer Reversion of Polystyrene

This degradation mechanism is not of much interest to fire debris analysts as this mechanism does not usually interfere too much with the identification of an ignitable liquid residue. It only presents one peak that is predictable when the polymer structure is known and usually the compound is not common to ignitable liquid residues[105].

1.4.2.4 Cross Linking

Cross linking, also known as char formation, is a mechanism by which cross linking occurs within the molecule when it undergoes pyrolysis. This cross linking actually strengthens the molecule thus only creating a small amount of volatile products and as a result this is the pyrolysis mechanism of least relevance to the forensic fire investigation scientist[19, 26].

1.4.3 COMBUSTION PRODUCTS

Combustion is defined as an oxidation process that generates heat and may induce pyrolysis. Therefore depending upon the conditions in which combustion occurs, different products will be released. If, for example, the conditions are ideal, combustion will be complete and in the case of most organic polymers the combustion products will be carbon dioxide and water. However, when limited oxidiser is present other products will be produced which are not completely oxidised or reduced, thus resulting in the creation of incomplete combustion products[3].

At present there is no literature that addresses the exact difference between pyrolysis products and combustion products in fire debris analysis. However it is well known that the differences between pyrolysis products and combustion products are attributed to the fact that combustion products result from oxidation reactions. Hence, this category of products seems relatively restricted with most of the combustion products being oxidised versions of pyrolysis products. As such combustion products are usually not similar to those found in ignitable liquid residues and therefore of no great interest to the fire debris analyst[19, 105].

1.4.4 SUBSTRATE COMPARISON SAMPLES

The use of substrate comparison samples has been recommended to allow potential background interferences to be evaluated[42, 108, 115, 116, 129]. Substrate comparison samples can thus be defined as materials suspected of not containing any additional ignitable liquids and therefore are able to be used to represent the pre-fire condition of the substrate[43, 64, 108, 117, 129].

Substrate comparison samples should assist the forensic fire investigation scientist to more easily discern whether the recovered components originated from an ignitable liquid or from the matrix itself[42, 108, 115, 116, 129, 138]. However, in order for substrate comparison samples to be able to provide useful and adequate information, they must be collected as close to the fire debris sample as practical, ideally in an area which is unburnt and that has not been exposed to water[64, 108, 117, 129]. If the collected substrate comparison samples are unburnt, it has also been strongly recommended that they be analysed and then burnt in the laboratory and re-analysed to provide a good representation of the content of the interfering products, which is particularly helpful in cases where the quantity of ignitable liquid residues present is small[117, 139]. However, problems are frequently encountered as the fire investigation scientist will have little control over a number of factors which may influence the type of interfering products produced[106].

Further problems can also be encountered as fire investigators are not always fully aware of the potential problems associated with certain substrates[106]. For example, samples such as carpet or carpet padding, which may appear to be the logical choice for collection due to their ability to retain ignitable liquids, may in fact complicate or interfere with the identification of any ignitable liquid residues present in the debris. Reasons for this are due to these materials being manufactured from petroleum feed stocks and therefore when exposed to heat they can decompose to produce volatile organic compounds which may be similar to those of ignitable liquids[26, 107].

1.5 CURRENT RESEARCH IN FIRE DEBRIS ANALYSIS

Currently, the literature available in the area of ignitable liquid residue analysis in fire debris containing interferences from common building materials is somewhat limited. The research conducted has explored, to a degree, the effectiveness of GC/MS to rapidly detect specific components of ignitable liquids in samples that have intense background interferences and are thus too contaminated for analysis by GC using pattern comparison alone[112]. However few studies are available in the literature in which the effect of evaporation and matrix interferences on the association of an ignitable liquid residue with the neat liquid are reported[32].

Research in the area of ignitable liquid identification from fire debris, has looked at interferences generated by the off-gassing, i.e., substrate background products, of various materials as well as the pyrolysis and combustion products generated by the burning of a variety of materials which are commonly found at structural fires. The research has illustrated the complicating effects that the presence of interferences can have on the identification of ignitable liquids[3].

Ettling *et al* conducted a study to determine the amounts and types of volatile organic compounds that can be extracted from charred materials and found that in most cases, the amount of volatile organic compounds extracted from the unburnt material was greater than that extracted from the burnt material with or without added ignitable liquid. Therefore they concluded that the amount of volatile organic compounds recovered from the burnt material does not necessarily indicate added ignitable liquids[140].

O'Donnell found that out-gassed volatiles from particle board would seriously interfere with the recognition of paint thinner, whilst new carpet provides a troublesome background for petrol. However, Cavanagh *et al* found that the level of background interferences from substrate background products, for all carpet matrices, decreased visibly with time to such an extent that they do not present significant levels of potential interferences in the chromatographic profile of an ignitable liquid[111]. Although Cavanagh *et al* did find that carpet removed from motor vehicles in the general population can exhibit some of the compounds that are diagnostic for petrol residues they also found that in the majority of cases the chromatographic pattern produced by these components can be easily distinguished from those compounds produced by petrol. These findings have also been supported by Lentini[26, 64].

Keto & Wineman conducted small can fires on common household products, including plywood, vinyl floor tiles, nylon carpeting with jute backing and polyurethane foam underlay. They then used target compound analysis to determine the potential from the burning of these products to interfere with the identification of ignitable liquids. They found that the target compound chromatograms of the pyrolysed samples bore little resemblance to the target compound chromatograms for the unevaporated and evaporated ignitable liquids, subsequently posing no risk for false identification of residual ignitable liquids. They concluded that target compound analysis is a useful approach to identify residual petroleum products in fire debris[64, 108, 117, 129] .

Fernandes *et al* also conducted a study to investigate whether the partial burning of frequently encountered household items such as printed materials (newspapers and magazines), flooring (wood, plastic and polypropylene, wool and nylon carpet with rubber underlay), adhesives and finishing's (wallpaper and paste, plaster and emulsion paint, lacquer) would produce pyrolysis products that could be confused with ignitable liquids. They looked at newly purchased samples and compared the results with samples that had off-gassed for one month. The results from the new samples indicate that polypropylene, nylon and wool carpet produce toluene when burnt, however the amount detected was in such trace levels that it does not indicate the presence of an ignitable liquid in the sample. Polypropylene was also found to produce a number of other pyrolysis products such as limonene and benzene, although limonene is a flammable terpene unlike turpentine, it is not commonly available in the local market and as such can be easily identified. The results also showed that samples that had been allowed to off-gas for one month prior to burning produced far fewer volatiles than the new samples and therefore they are less likely to cause interference in fire debris analysis[113].

Fernandes *et al* found that the most commonly encountered pyrolysis products were benzene, heptane, toluene, styrene, ethylbenzene, and *m*-xylene. Hence they concluded that new household items do contain volatiles that could be sources of interferences and therefore suggested that the analysis of substrate comparison samples would help an analyst in distinguishing any signal from the background in the burnt samples. However the authors do state that in reality substrate comparison samples are not always available and therefore any additional volatile residues may in fact cause misinterpretation of other common ignitable liquids[113].

A study conducted by Bertsch evaluated the interference potential of volatile organic compounds obtained from simulated fire debris samples (samples were burnt in paint cans) and from samples collected in the field. He stated that burnt carpet and carpet padding produce volatile organic compounds that can cause interferences with some ignitable liquids, most notably petrol. He found that variable amounts of alkylbenzenes and naphthalenes are produced along with large quantities of styrene and alkylstyrenes. However the distribution of the alkylbenzenes is quite different from the patterns produced by petrol[141]. Bertsch also stated that the fibres in carpet do not produce significant amounts of volatile organic compounds but found that the carpet backing is a rich source for alkylbenzenes and similar compounds. Furthermore a number of researchers, including Bertsch have identified a number of aromatic hydrocarbons produced from charred carpet including benzene, toluene, ethylbenzene, styrene and alkylstyrenes[43, 116, 129, 141].

DeHaan and Bonarius conducted controlled burn experiments, with and without ignitable liquids, in rooms containing a variety of floor coverings. The results of the experiments indicate that in the absence of ignitable liquids, nylon carpets produce traces of light volatiles and isolated peaks in the medium petroleum distillate range. In the presence of ignitable liquids, they found that although polyester carpet yields a very complex chromatogram, the chromatograms of the ignitable liquids were still readily identifiable in samples of both carpets. The experiments also found that when using charcoal trapping to recover ignitable liquids, the urethane foam underlay yields a complex mixture in the medium petroleum distillate range. Additionally, DeHaan and Bonarius noted that although the burning of synthetic material produces significant levels of various specific aromatics, including toluene, xylene and styrene, the burning of common floor coverings poses no problems to the identification of common petroleum distillates, even though they do occupy volatility ranges common to the medium petroleum distillates[129].

Stauffer conducted a study focusing on identifying and characterising interfering products in fire debris. He examined the substrate background products, pyrolysis products and combustion products of a number of different substrates in order to identify all the interfering products that may be released. He found that the presence of the interfering products is not always constant however some of the interfering products are in fact similar to the products found in ignitable liquids. He concluded that it is difficult to extrapolate data about interfering products to other cases and emphasised the importance of collecting and analysing substrate comparison samples in fire debris analysis. He states that substrate comparison samples should be taken, and where possible should be unburnt, to provide the fire debris analyst with a good indication of the substrate material involved. He advises that the substrate comparison samples should then be burnt and analysed so that a good representation of the interfering products can be provided[64].

Almirall and Furton conducted an extensive study to determine the substrate background products, pyrolysis products and combustion products in a number of different materials commonly found at structural fires, such as carpets and other flooring materials as well as paper and plastic products. They found that there was little difference in the pyrolysis products and substrate background products extracted between burnt and unburnt wood, however several differences were noted between burnt and unburnt synthetic flooring. They also noted that the most frequently encountered pyrolysis products and combustion products were toluene, styrene, naphthalene, benzaldehyde, ethylbenzene, indene, phenylethyne, and α-methylstyrene and subsequently concluded that substrate comparison samples need to be taken[64, 108, 117, 129] .

The studies conducted by Keto, Lentini *et al* and Howard and McKague demonstrates the extent to which a petroleum-like chromatographic profile can be obtained from the extracts of the debris from common building materials, to which no ignitable liquids have been added, thus yielding a false positive or misleading information[78]. Howard and McKague analysed a sample of charred carpet from a real fire scene, which had a pronounced solvent like odour and found that virtually all the peaks in the chromatogram of the charred carpet were styrene and butadiene related compounds, which could be explained by the combustion of carpet materials unaided by an ignitable liquid[78, 105]. In addition to this, Lentini *et al* stated that a finding of toluene, xylene or styrene in a sample might be of little or no significance because such compounds are commonly found as pyrolysates of common building materials[26, 64, 78, 107, 108, 111, 112, 117, 129]. These studies suggest that target compound analysis can be used to overcome such problems, as target compound chromatograms for unevaporated and evaporated ignitable liquids are sufficiently specific to allow their identification in high-background arson samples[78].

A study by Tan *et al* evaluated a number of substrates including polyolefin, nylon and polypropylene carpet and white pine, oak and poplar wood. They found that carpet was a better substrate for sample collection and when spiked with an ignitable liquid, results were similar to the unevaporated ignitable liquid samples. They found that pyrolysing polyolefin carpet produces compounds that can obscure an ignitable liquid pattern making an identification of an ignitable liquid difficult. However when the same carpet is burnt in air, these interfering compounds are not produced[118].

Borusiewicz *et al* conducted two studies to evaluate the influence of a number of factors on the identification of ignitable liquids. The factors examined included the influence from a fire extinguishing medium, the type of substrate and their corresponding pyrolysis products, type of ignitable liquid, length of time between lighting and extinguishing the fire and the air availability level. The results show that out of all the investigated factors that influence the possibility of detecting and identifying potential ignitable liquids, substrate type is the most important whilst fire fighting agents were least important. It was found that for carpet spiked with an ignitable liquid, traces of an ignitable liquid residue were easily recognisable regardless of the burning time, however for the deciduous wood samples ignitable liquid traces were only detectable in a few samples and for chipboard no ignitable liquid was detected after burning[25, 142].

Borusiewicz *et al* found that carpet has a tendency to spontaneously extinguish before it burns completely unless additional heat is provided. However, they did find that the inner layers of the carpet are isolated from open air by an exterior layer of charred material, which is why ignitable liquid traces are easily detectable in the debris thus supporting the findings of Tan *et al* that carpet is the better substrate for sample collection. The authors also emphasise the importance of analysing blank samples and collecting substrate comparison samples in ignitable liquid analysis to ensure false positive results are avoided[25, 142].

The ASTM (E1618 – 01) 'Standard Test Method for ILRs in Extracts from Fire Debris Samples by GC/MS' has recently been revised and is especially appropriate for analysing fire residue extracts that contain high background levels of substrate materials or pyrolysis products. This test method describes the use of GC/MS, utilising both extracted ion profiling and target compound analysis techniques, to facilitate the identification of an ignitable liquid in the extract of fire debris by reducing interferences from components generated as products of pyrolysis. The method relies on the pattern comparison of the sample with standards obtained under the same conditions. Where the interfering compounds are also target compounds for an ignitable liquid, the method states that proper classification of the sample can only be made when sufficient ignitable liquid product compounds remain. It also states that when the pattern becomes overwhelmed by the extraneous compounds then identification by this method is not possible. Furthermore, if there is suspicion that an ignitable liquid found might be indigenous to the substrate, the method states that a comparison sample should be analysed. Interestingly enough, the standard test method also states that whilst target compound analysis provides useful information, it should not be the sole basis for the identification of an ignitable liquid residue[78].

Where potential interferences may exist, the literature suggests two methods to allow these interferences to be accounted for, firstly by taking substrate comparison samples, where applicable, and secondly, by subjecting the sample to extracted ion profiling and/or target compound analysis. Substrate comparison samples can provide the investigator with the thermal breakdown products of the substrate, however as yet there is no standard method of analysis for substrate comparison samples. The literature merely states that substrate comparison samples should be taken and analysed. Whilst extracted ion profiling and target compound analysis allow specific ignitable liquid patterns to be extracted from chromatographic data, problems occur when interfering products are themselves target compounds.

1.6 SIGNIFICANCE OF RESEARCH

Many common household materials, such as floor coverings and furniture padding materials, are of petrochemical origin and therefore when exposed to heat, can decompose to produce volatile organic compounds, which may interfere with the identification of ignitable liquid residues in fire debris. Even though the types of substrate background products, pyrolysis products and combustion products produced by these materials can be predicted from the known degradation mechanisms and by pyrolysis experiments, the application of this information in fire investigation should be made with great caution because conditions in a real fire are very different to those in laboratory burning tests.

When analysing fire debris chromatograms, GC/MS does give the forensic fire investigation scientist the ability to extract specific ignitable liquid patterns. However, when interferences from the burning of common household materials are themselves target compounds there is little information as to how these interferences impact on arson investigation using target compound analysis.

When the fire investigator deems it necessary to collect and burn substrate comparison samples for the purpose of evaluating interferences in the fire debris chromatograms, there is no standard technique or guidelines available on how this should be done. In small scale laboratory tests there is also an issue in that the burning method will not reproduce the exact burning conditions encountered in the fire because real fire conditions are inherently variable. This is unlike other areas of forensic science where appropriate standards and techniques are available to identify and compare physical evidence, and the best that can be hoped for in the area of substrate comparison samples is a laboratory test method that can be standardised.

In this study examples of common household carpet and foam are subjected to four different burning tests and burnt residues evaluated by GC/MS, for the purpose of identifying what potential there is for interference with the identification of petrol in arson investigation using target compound analysis. Two of the tests are on a larger scale, being large scale room fires where the burning conditions are those encountered in real fires, and furnace fires which represent simulated fire scenarios. The other two tests are not representative of a real-life fire, but are small can fires and pyrolysis GC/MS where the burning conditions are artificial. However, the information obtained from the burning tests will be used to develop a laboratory test method for analysing substrate comparison samples.

1.7 AIMS OF RESEARCH

The aims of this study are:

1. Using standard methodology for the recovery and analysis of ignitable liquid residues from fire debris, analyse common domestic carpets and furniture foam which have been subjected to various burning tests, to ascertain if any compounds are recovered that could potentially interfere with an ignitable liquid identification.

   The burning tests to be investigated include:

   a. Large scale room fires - these will be conducted in $10m^2$ concrete bunkers available at the Country Fire Authority training facility in Fiskville, Victoria, Australia.

   b. Furnace fires - these will be conducted in an 8m^3 gas fired furnace available at Centre for Environmental Safety and Risk Engineering at Victoria University, Werribee Campus, Victoria, Australia.
   c. Small can fire - these will be conducted in 1L metal paint cans.
   d. Pyrolysis GC/MS.

2. From test fires obtain knowledge about each substrate with respect to its likelihood to interfere with an identification of an ignitable liquid and investigate its impact in arson investigation using target compound analysis.

3. Further explore the potential of small can fires to develop a laboratory test method for the burning of substrate comparison samples.

2. EXPERIMENTAL

2.1 INTRODUCTION

This chapter reports details of the samples, equipment and methodologies utilised in this study. Details are given for:

- Type and source of petrol.
- Type and source of carpet, foam and underlay.
- Preparation of petrol standards for both liquid and headspace petrol standards.
- Ignitable liquid headspace recovery method (as used by the VPFSC).
- GC/MS parameters used for all standard and samples in this study.
- Pyrolysis GC/MS parameters.
- Infrared (IR) confirmatory analysis of carpet.
- Large Scale Room Fires including temperature measurements.
- Furnace Fires.

2.2 SAMPLES

2.2.1 PETROL

Unleaded petrol was purchased locally at the BP service station on Morris Rd, Hoppers Crossing near the Werribee campus of Victoria University, Victoria, Australia. It was collected on the 7th February 2006 at approximately 10.15am from bowser (petrol pump) 2. The petrol was placed in a brand new 5L metal fuel can and sealed until use. The same petrol was used for all experiments.

2.2.2 CARPET

Samples of carpet were obtained from Godfrey Hirst Pty Ltd, South Geelong, Victoria, Australia. Godfrey Hirst Pty Ltd provided samples of the most commonly used carpets in Melbourne (based on sales). These samples included 100% Nylon, 100% Natural Wool, 100% Polypropylene and a 50% Polypropylene-Wool blended carpet and represent the carpet types most demanded by consumers.

Godfrey Hirst Pty Ltd provided a number of off-cuts of each of the aforementioned carpet samples and therefore the colour and pattern of the carpet was not considered for the purpose of this study.

2.2.2.1 NYLON CARPET

The nylon carpet was a versatile nylon 6 carpet most commonly used in residential buildings. This is a highly versatile fibre type and can be constructed into virtually any style. Furthermore the synthetic nylon fibres are extremely resistant to stains[143].

2.2.2.2 POLYPROPYLENE CARPET

The polypropylene carpet is the most cost-effective carpet available. It is manufactured using synthetic polypropylene fibres and has many similar properties and benefits as nylon fibres[143].

2.2.2.3 WOOL CARPET

The wool carpet is made of 100% premium wool. It is durable and hardwearing with innate stain resistant properties. It is also flame retardant and acts as an insulator, helping to reduce ambient noise[143].

2.2.2.4 50-50 CARPET BLEND

The polypropylene-wool blended carpets are made up of varying percentages of synthetic and wool fibres giving it the natural appearance and luxurious feel of wool[143]. The blended carpet utilised in this study consisted of 50% polypropylene and 50% wool fibres and as such is referred to as 50-50 polypropylene-wool carpet.

2.2.2.5 CARPET BACKING

The composition of the carpet backing was obtained from Godfrey Hirst Pty Ltd. The backing is a combination of latex, ground limestone (filler) and negligible amounts of thickener, surfactant and water. The latex is a carboxylated styrene/butadiene polymer suspended in water containing a bactericide. The ground limestone is made of 70-90% calcium carbonate, 6-12% magnesium carbonate, silicon dioxide, aluminium oxide and ferric oxide[144].

2.2.2.6 CARPET FIBRE STANDARDS

In order to verify the types of carpet received, Godfrey Hirst also supplied yarn samples of 1 ply 100% polypropylene, 1 and 2 ply 100% dyed nylon, 2 ply nylon 6, 2 ply 50-50 polypropylene-wool, and 2 ply 100% wool.

2.2.3 UNDERLAY

The underlay was obtained from Dunlop Foam in Deer Park, Victoria, Australia. The underlay is reconstituted flexible polyurethane foam, which is also known as REPOL® or re-bonded foam. According to Dunlop, these rebonded or reconstituted Dunlop REPOL® foams are made from the shredded off cuts produced by the foam cutting process. The foam chips are combined with a urethane adhesive, compressed and then steam cured. The result of this process is a dense, firm foam with a melting/thermal decomposition temperature of greater than 200°C, flash point greater than 250°C and auto ignition temperature greater than 260°C short term[145].

This underlay is used in approximately 60% of residential homes, the other 40% use Bridgestone (rubber) airstep underlay, which was not examined in this study due to time restraints[146].

2.2.4 FOAM

The furniture foam used in these experiments was provided by Dunlop Foam, Dandenong, Victoria, Australia and is the standard conventional polyurethane foam used in furniture.

2.3 PETROL SAMPLE PREPARATION PRIOR TO GAS CHROMATOGRAPHIC /MASS SPECTROMETRIC ANALYSIS

Petrol samples were prepared for GC/MS analysis by adding 100μL of either unevaporated or evaporated petrol (see Section 2.3.1 below) to 900μL of diethyl ether (Univar, AR. Grade) in 12 x 32mm amber screw cap vials (Alltech, part no. 95194). Both the petrol and diethyl ether were delivered using a 1mL graduated pipette.

2.3.1 PREPARATION OF EVAPORATED PETROL SAMPLES

Evaporated petrol samples were prepared by boiling down 50mL of unevaporated petrol on a hot plate with stirring (magnetic flea) in a fume cupboard.

A 50mL beaker was marked externally, using a permanent marker, at levels corresponding to 50, 37.5, 25, 12.5, 5 and 2.5mL. The levels were determined by adding to the beaker the same volume of petrol with an appropriately sized pipette. When the petrol had boiled down to each level, a 100μL aliquot was taken and prepared for analysis as described above. Table 2.1, shows the levels marked on the beaker, that is, the remaining petrol from a starting volume of 50mL, and the corresponding percent evaporation.

Table 2.1: Volume and Corresponding Percent Evaporation for Petrol Standards

REMAINING PETROL VOLUME (mL)	PERCENT EVAPORATION (%)
50	0
37.5	25
25	50
12.5	75
5	90
2.5	95

2.3.2 PREPARATION OF HEADSPACE STANDARDS

Headspace petrol standards where prepared by spiking petrol, at the various evaporation states stated in Section 2.3.1, on KimWipes, as has been done by previous researchers[70, 80, 94, 119]. KimWipes are manufactured by Kimberly-Clark Professional and are a commercial grade paper wipe that are highly absorbent and yet delicate enough to be used for cleaning those surfaces where the presence of minimal lint or dust can lead to serious errors or abrasions[147].

After spiking, the Kim Wipe was immediately placed in the evidence bags, along with a charcoal tube and prepared for analysis as described in Section 2.4.

2.4 RECOVERY OF VOLATILES FROM SAMPLES PRIOR TO GAS CHROMATOGRAPHIC/ MASS SPECTROMETRIC ANALYSIS

Samples of unburnt and burnt carpet, underlay and furniture foam were collected and prepared for analysis by GC/MS as per the methods currently utilised by VPFSC.

- The samples were collected and placed in evidence bags (Omni, standard, loose, plain barrier bags, made of polyvinylindene dichloride, 450mm x 900mm in size, supplied by Cryovac, Altona, Victoria, Australia).

- The bags were tied in a secure knot (ensuring that as much excess air is removed prior to sealing) and transported to the laboratory.
- At the laboratory, a scalpel was used to split the bag so that a charcoal tube could be inserted (the tubes were SUPELCO ORBO standard charcoal adsorption tubes shown in Figure 2.1).

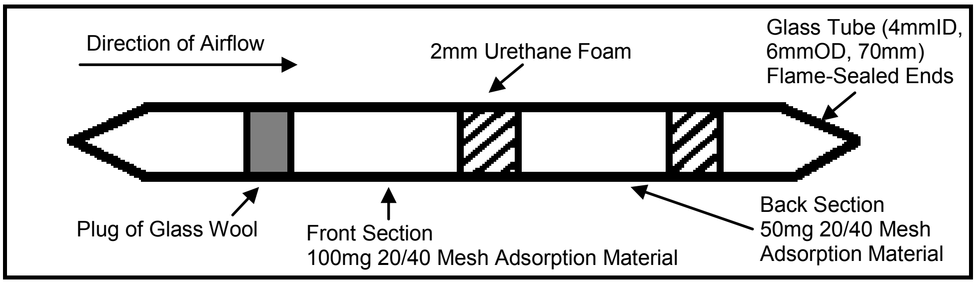


Figure 2.1: Solvent Desorption Adsorption Charcoal Tube

- The tube ends were snapped off and placed inside the bag.
- The bag was resealed with tape and heated in an oven preset to 70°C for 17 hours.
- After this time, the bags were removed from the ovens and the tubes were located in the bag and used to pierce the bag and then immediately attached to a vacuum.
- The remaining headspace was pulled through the tube with the vacuum (approximately 30 seconds).
- The tube was then removed and the bag was resealed.
- 1mL of diethyl ether (AR Grade supplied by Univar Chemicals) was used to elute the volatiles from the tube into test tubes.
- The eluant was then transferred into GC vials by Pasteur pipette, for analysis by GC/MS.

2.5 INSTRUMENTATION

2.5.1 GAS CHROMATOGRAPHY/ MASS SPECTROMETRY CONDITIONS

GC was conducted using a Varian 3400 GC and Saturn MS with the Varian Star Software version 5.52. Injections were performed by a Varian 8200 Auto Injector.

The GC/MS conditions are listed below:

Column: Varian Factor Four, 30m x 0.25mm x 0.25μm, VF-5MS.
Carrier: Helium at 1.2mL/min (17psi) at 35°C.
Injector: 1μL (isothermal at 200°C).
Split Ratio: 50:1.
Temp Program: 35°C (hold 3min), 5°C/min to 100°C, 10°C/min to 210°C, 15°C/min to 300°C(hold 3min).
Detector: MS.
Ion Trap: 220°C.
Manifold: 50°C.
MS Transfer line: 280°C.
Solvent Delay: 3 min.
Scan Rate: 1.0 second/scan.
Scan Range: 40 – 650 amu.
Tuning Procedure: Auto tune.
Mass spectral confirmation: NIST library.

2.5.2 PYROLYSIS

An SGE Pyrojector™ was used for pyrolysis GC/MS. It is a continuous mode micro furnace pyrolysing injection system which is designed to operate at any temperature less than 1000°C for extended periods without Curie point gaps and is highly reproducible.

This Pyrojector™ operates on the existing GC injection port and therefore can easily be attached and removed. Sample introduction results in immediate pyrolysis and transfer of the breakdown products to the head of the column. The samples were prepared for pyrolysis using the SGE solid sampling kit (see Section 2.5.2.3) which consisted of a sampling head which is screwed onto the top of the Pyrojector™ furnace. The carrier gas is then connected directly into it.

The details of the pyrolysis temperatures, pressure, sampling procedure and the GC bake program to run between the samples are as follows:

2.5.2.1 PYROLYSIS TEMPERATURES

Pyrolysis was conducted at 450°C, 600°C, 750°C and 900°C. It was extremely difficult to pyrolyse at temperatures lower that 450°C as the samples were not pyrolysing entirely. This resulted in blocking of the transfer line and contamination of the MS ion trap.

2.5.2.2 PYROLYSIS PRESSURE

The Pyrojector™ was plumbed to a separate Helium cylinder than the gas chromatograph to ensure that both the Pyrojector™ and gas chromatograph were independent of each other and therefore allowed for the monitoring of the flow through the Pyrojector™. The Pyrojector™ pressure was set at 5psi above column head pressure. This was optimised and the experimental data is presented in Section 3.4

2.5.2.3 SAMPLING PROCEDURE

Samples were introduced by utilising a solid sampling kit which consisted of a sampling head which is screwed onto the top of the Pyrojector™ furnace. The kit provided a stainless steel tubular cutter which incorporates a plunger with a gas tight seal. Therefore using the cutter, a section is cut or "bored" from the sample (see Figure 2.2) conveyed within the tube to the Pyrojector™ inlet where it is transferred into the furnace by depressing the plunger[148].

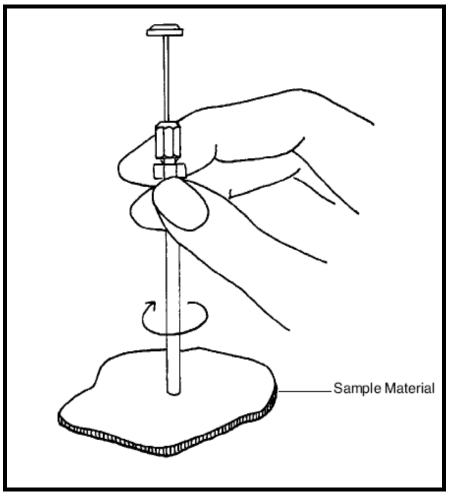


Figure 2.2: Tubular Cutter Obtaining Sample[148]

This cutter allowed the diameter of the sample to remain consistent. However the depth of the sample was variable.

2.5.2.4 GAS CHROMATOGRAPH BAKE PROGRAM

To ensure there was no carry over between pyrolysis experiments, a GC bake program, which was optimised using underlay, was run between each of the experiments. Underlay was chosen as it had very late eluting peaks compared to the other carpet and foam samples. The bake program used is as follows:

GC Temperature Program: 80°C, 40°C/min to 310°C (hold 0.25min)

2.6 CONFIRMATORY ANALYSIS OF CARPET FIBRES

To confirm the identity of the carpets they were compared to the yarn standard by pyrolysis GC/MS and using a Bruker VECTOR 22 Fourier Transform Infrared (FTIR) microscope with Opus Version 2.2 software. A DC-2 diamond compression cell from Specac was used to compress and flatten the carpet fibres to ensure they were thin enough for transmission FTIR.

2.7 LARGE SCALE ROOM FIRES

Large scale room fires were conducted at the CFA training facility in Fiskville, Victoria, Australia. The facility includes a set of three adjoining, reusable, $3m^3$ concrete rooms (two of which are shown in Figure 2.3 below) used for CFA fire-fighting training and investigation. These rooms were used to safely burn all carpet and foam samples investigated in this study under real fire conditions. Prior to burning carpet and foam samples, the rooms were thoroughly cleaned and fitted with new windows, doors and plasterboard. The rooms could then be furnished so as to resemble different household rooms such as a lounge room, bedroom, study etc. Furnishings included old beds, couches, desks, chairs, bookcases, carpet, clothing etc.

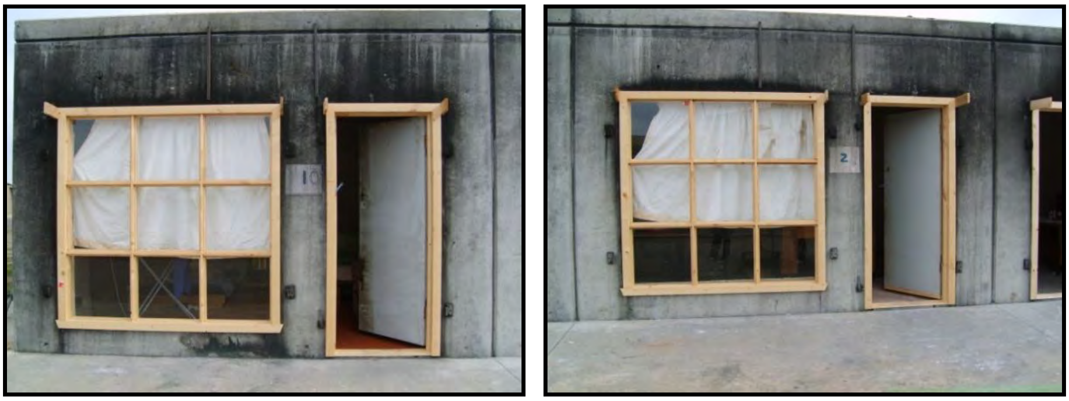


Figure 2.3: Two of the Concrete Rooms used for Large Scale Room Fires

The swatch sizes for the carpet and foam samples burnt for this study also had to represent typical sample sizes collected in fire investigation. Consultation with the fire investigation scientists at VPFSC indicated that sample sizes up 1m x 0.5m for carpet and underlay samples and foam samples typical of a couch cushion (0.5m x 0.5m x 0.1m) would be reflective of a realistic sample size in a fire investigation scenario[59]. Aluminium oil drip trays measuring 90cm x 40cm in size were used to place carpet and foam samples in the large rooms for the fire experiments. These oil drip trays served two purposes, firstly to enable realistic sample sizes to be used (90cm x 40cm for carpet and underlay and 0.5m x 0.4m x 0.1m for foam) and secondly to prevent cross contamination between samples during burning and extinguishment. The aluminium oil drip trays were thoroughly cleaned (soap, rinsed with water and air-dried) prior to use. This cleaning procedure proved to be effective in removing any potential contaminants as shown by diethyl ether swabs of the trays which showed no GC/MS peaks when analysed. Initial trials showed that when the carpet caught fire it tends to curl inwards from the edges and results in the carpet fibres being protected from the fire. Therefore in order to prevent curling the samples were tied to the oil drip trays with steel wire.

2.7.1 TEMPERATURE DATA COLLECTION

Thermocouples used for the temperature measurements of the test fires and control burns were purchased from Industrial Thermocouple Supplies in Thomastown, Victoria, Australia. They were 6m long, type k – 1.5mm MIMs with insulated hot junction. The plugs were also type k – male mini plugs with a 200mm tail and have an uncertainty of $\underline{+}$ 1.1°C ($\underline{+}$ 0.4%)[149].

The data logger for temperature collection was an Agilent bench link data logger 3.

2.8 FURNACE FIRES

The furnace available was an 8m^3 natural gas-fired furnace pictured in Figures 2.4 and 2.5 which was designed for fire testing building materials and small structures and is operated based on a time-temperature program. The furnace contains two gas burners with valves that control the supply of the natural gas and air required for burning, a thermocouple and an exhaust which are highlighted in Figure 2.5.

Furnace burns were only conducted on the nylon, polypropylene and wool carpets. These furnace burns did emit smoke in the immediate environment of the furnace and this required the use of protective respiratory masks. Due to the fact that smoke was released it was decided that foam samples would not be burnt in this manner as they produce toxic/deadly hydrogen cyanide and carbon monoxide vapours[150, 151].

Figure 2.4: Exterior of Furnace

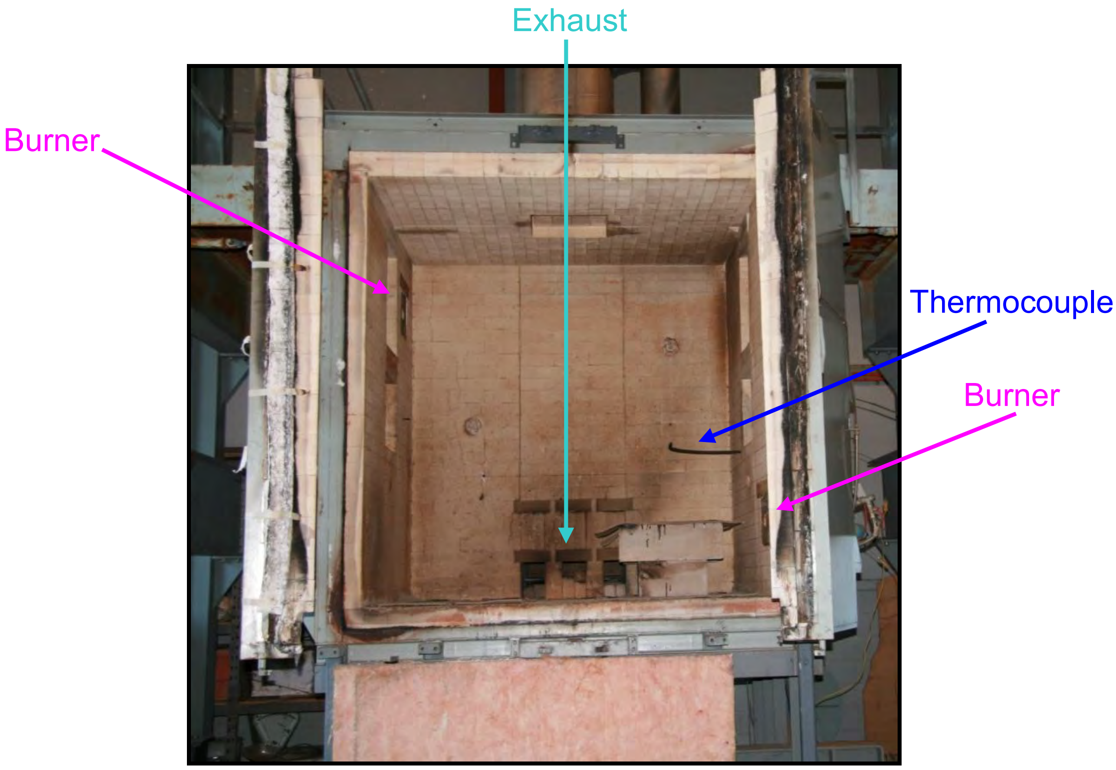


Figure 2.5: Interior of Furnace, showing Burners, Thermocouple and Exhaust

The furnace burns were conducted using a time-temperature program based on the 'Australian Standard AS 1530-4-2005: Method for Fire Tests on Building Materials, Components and Structures'[152], presented in Table 2.2.

Table 2.2: The Time-Temperature Program utilised for the Furnace Burns[152]

Time (min)	Temperature (ºC)*
0	20
5	576
10	679
15	738
30	841
60	945

**Uncertainity of ± 0.5°C.*

2.8.1 PROCEDURE

A large swatch of carpet (approximately 2m x 1m) was placed on the bottom of the furnace and four hebel bricks were strategically placed around the edges to prevent the carpet from curling, this is shown in Figure 2.6. Similar to the large scale room fires, a thermocouple was placed above the carpet fibres (approximately 10mm) to allow the temperature to be recorded at this height. The furnace doors were securely closed and the time-temperature program started. The program includes an initial 3 minute air purge after which the burners were ignited and the temperature began to rise. At the desired temperature, the furnace program was stopped, the doors opened and if the sample was alight it was extinguished with a fine spray of cold water. Once the sample was cool enough to touch (approximately 10 minutes) it was cut with a Stanley knife into appropriate pieces (approximately 1m x 0.5m in size) so that it could be rolled and placed into evidence bags. This is a realistic sample size and was similar to that used for the large room fires. For carpet samples that had undergone minimal overall burning these could be cut into four pieces (referred to as the left side of furnace, front and back and right side of furnace, front and back, see Figure 2.7). Where burning was more extensive less than four pieces were collected and in some cases the carbonised residue remaining from the entire swatch was collected.

Figure 2.6: Nylon Carpet Swatch placed on Bottom of Furnace with Hebel Bricks

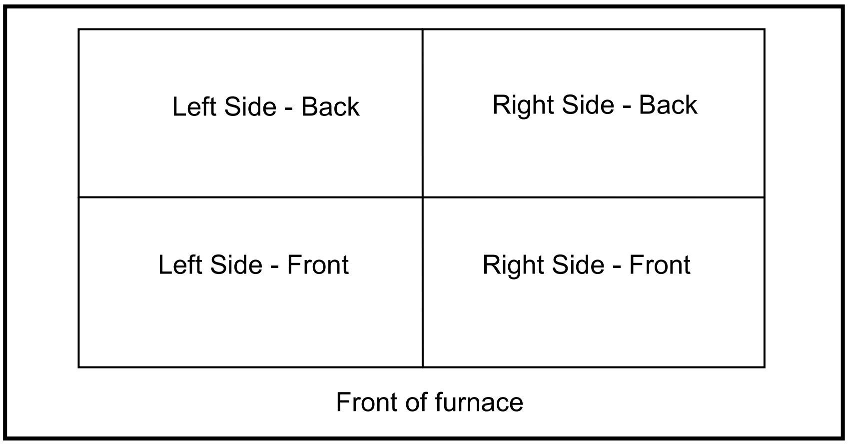


Figure 2.7: Schematic showing how Carpet Swatches were cut for collection

3. PRELIMINARY STUDIES

3.1 INTRODUCTION

This chapter reports the results of the various preliminary studies required for this work. These include:

- Generation of standard target compound chromatograms for unevaporated and evaporated petrol.
    - Liquid Petrol Standards.
    - Headspace Petrol Standards.
- Identification of carpet by IR.
- Pyrolysis sample size and pressure experiments.
- Preliminary studies for pyrolysis experiments.
- Fire temperature studies for pyrolysis experiments.

3.2 GENERATION OF STANDARD TARGET COMPOUND CHROMATOGRAMS FOR UNEVAPORATED AND EVAPORATED PETROL

The compounds present in petrol are quite well-known as there has been a large amount of research conducted in this area over the past couple of decades. Furthermore, the compounds which are characteristic of petrol and that can be used to identify it in the presence of extraneous compounds, have also been extensively studied[26, 57, 108, 111, 117, 130, 153]. Presently, there is a standard test method available through the ASTM which provides the names of 15 compounds which can be utilised to produce a target compound chromatogram to enable petrol to be identified in high background samples (shown in Table 3.1)[78].

Table 3.1: Petrol target compounds as listed in the ASTM E 1618 -01 'Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/ Mass Spectrometry'[78]

ASTM Petrol Target Compounds
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Indane
1,2,4,5- Tetramethylbenzene
1,2,3,5- Tetramethylbenzene
5-Methylindane
4-Methylindane
Dodecane
4,7- Dimethylindane
2- Methylnaphthalene
1-1- Methylnaphthalene
Ethylnaphthalenes (mixed)
1,3 -Dimethylnaphthalene
2,3 -Dimethylnaphthalene

A sample of common Australian unleaded petrol was subjected to GC/MS to see what compounds would be important target compounds. Unevaporated and evaporated petrol was prepared as a 10% (v/v) solution in diethyl ether as described in Section 2.3.1 and analysed using the GC/MS method detailed in Section 2.5.1. Figure 3.1 shows the total ion chromatogram of the diethyl ether solvent.

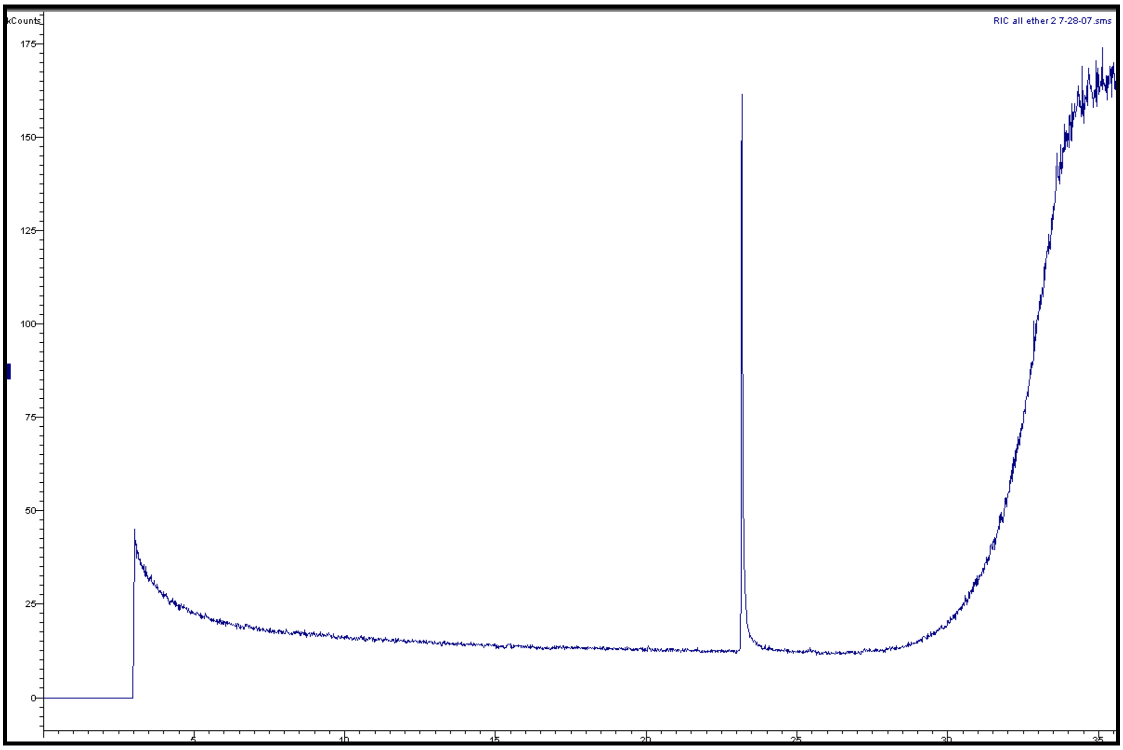


Figure 3.1: Total Ion Chromatogram of Diethyl ether (Refer to Section 2.5.1 for GC/MS conditions)

The diethyl ether solvent produces one peak at 23.13 minutes and this peak was identified as butylated hydroxytoluene and is commonly added to diethyl ether to inhibit the formation of organic peroxides. From here on in, this peak will be labelled as 'Ether' should it be present in the total ion chromatograms or extracted ion chromatograms. Figure 3.2 shows the total ion chromatograms of the unevaporated and evaporated petrol samples. As can be seen in Figure 3.2 as the petrol evaporates the levels of the more volatile compounds decrease whilst the levels of the heavier compounds become more pronounced. However, regardless of evaporation state some peaks remain dominant and these include toluene, ethylbenzene, xylenes and trimethylbenzenes. It should be noted that in Figure 3.2 each chromatogram is displayed using the scale that allows the most abundant peaks to be at full scale. This allows for the distinctive petrol pattern utilised by the fire investigation scientists at VPFSC to be visualised at all stages of evaporation. Although the 'Ether' peak in the unevaporated chromatogram, at the top of Figure 3.2, appears larger than the other chromatograms it has to be noted that it is not larger but appears that way due to different scaling used to display the chromatograms. It is also important to note that the front end of the chromatograms is missing as the GC program (described in Section 2.5.1) used has a three minute solvent delay.

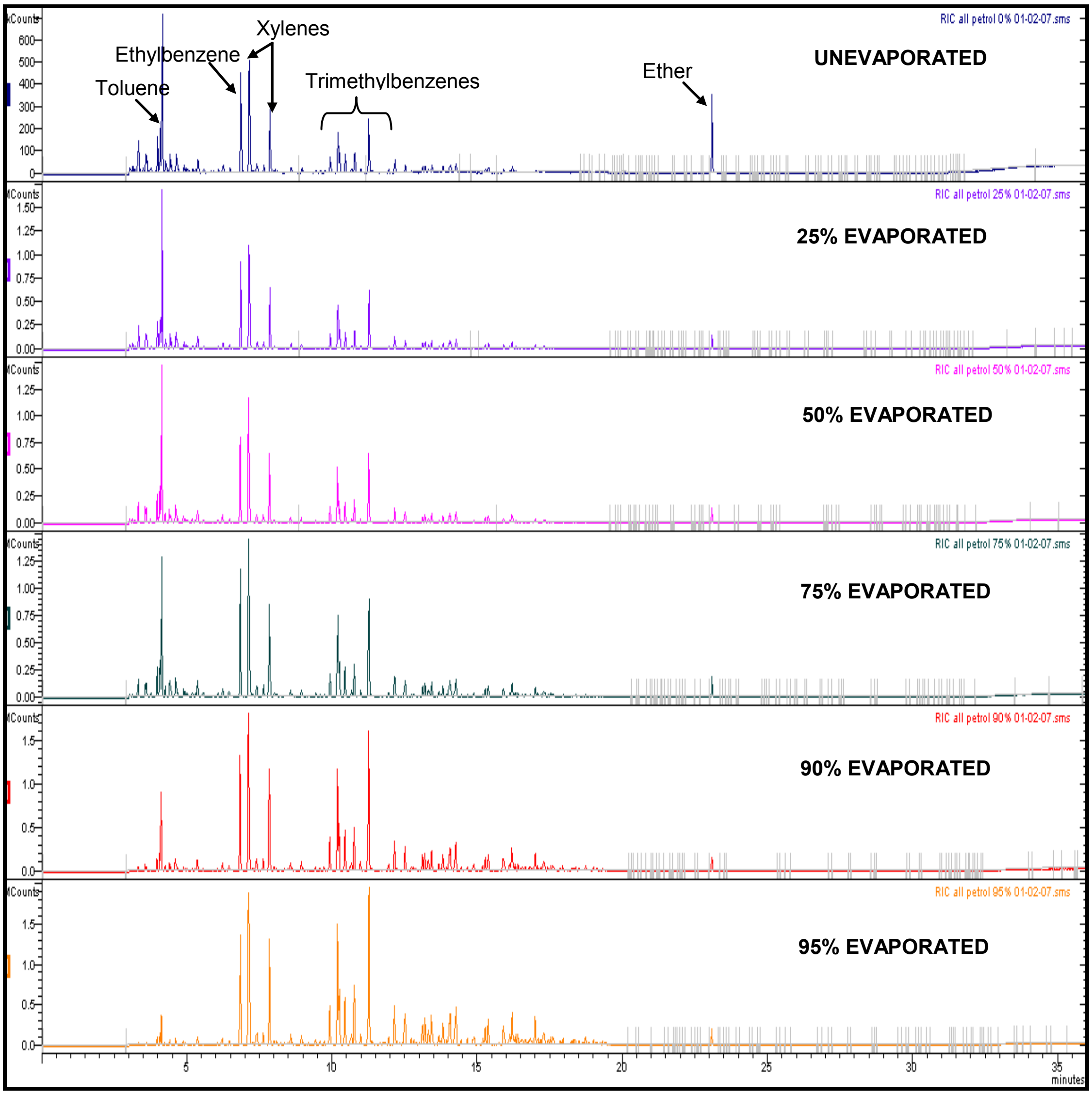


Figure 3.2: Total Ion Chromatograms of Unevaporated Petrol (blue), 25% Evaporated (purple), 50% Evaporated (pink), 75% Evaporated (green), 90% Evaporated (red) and 95% Evaporated Petrol (orange), respectively (Refer to Section 2.5.1 for GC/MS conditions)

Figure 3.3 shows the total ion chromatogram of a 75% evaporated petrol sample where 24 peaks which represented compounds that could be identified by mass spectral matching with the NIST library are labelled, these are listed in Table 3.2. The MS software allows for both automatic and manual background subtraction where manual background subtraction was used as it gave better library matches. Unlabelled peaks were either present in very low abundances or did not produce a good library match.

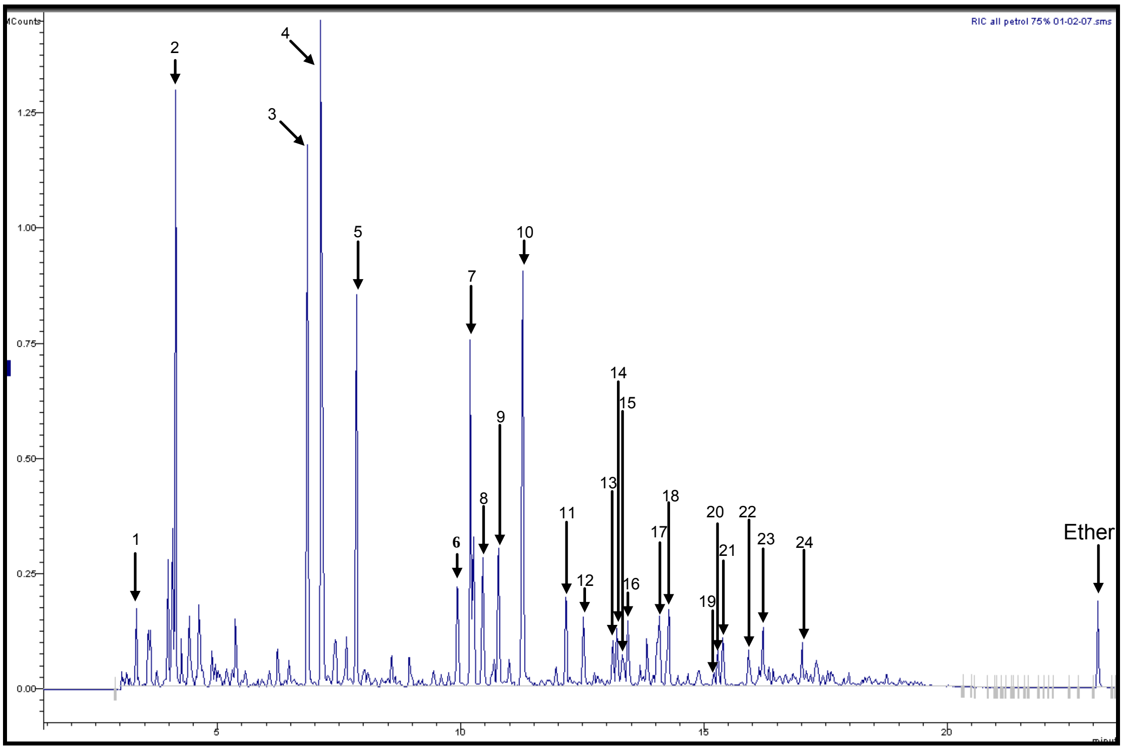


Figure 3.3: Total Ion Chromatogram of Petrol Indicating Peak Numbers for Identification (Refer to Section 2.5.1 for GC/MS conditions)

The compounds present in the greatest abundance include toluene, ethylbenzene, *p-* and/or *m-*xylene, *o-*xylene, propylbenzene, 1-ethyl- 4-methylbenzene, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene and 1,2,4-trimethylbenzene. The dimethylbenzene peak at 7.15 minutes (peak number 4 in Figure 3.3) represents both *p-* and *m-*xylene as these are difficult to separate and do co-elute. Because all three dimethylbenzenes have similar mass spectra it could not be determined if the peak at 7.15 minutes was *p-* or *m-*xylene but more than likely both are present. From here on in, the first xylene peak will be labelled *p-* and *m-*xylene.

Interestingly a number of the target compounds included in the ASTM E 1618-01 were not able to be identified even in the highly evaporated petrol standards. These compounds include 5-methylindane, 4-methylindane, dodecane, 4,7-methylindane, 2-methylnaphthalene and 1-1-methylnaphthalene, ethylnaphthalenes, 1,3-dimethylnaphthalene and 2,3-dimethylnaphthalene[78].

Table 3.2: Peak Identities

Peak Number	Retention Time (min)	Library Identification
1	3.35	Methylcyclohexane
2	4.16	Toluene
3	6.87	Ethylbenzene
4	7.15	*p*- and *m*-Xylene
5	7.87	*o*-Xylene
6	9.95	Propylbenzene
7	10.20	1-Ethyl-4-methylbenzene
8	10.47	1,3,5-Trimethylbenzene
9	10.79	1-Ethyl-3-methylbenzene
10	11.29	1,2,4-Trimethylbenzene
11	12.17	1,2,3-Trimethylbenzene
12	12.53	Indane
13	13.13	1,3–Diethylbenzene
14	13.23	1-Methyl-2-propylbenzene
15	13.35	1-Methyl-3-propylbenzene
16	13.45	2-Ethyl-1,4-dimethylbenzene
17	14.08	1-Methyl- 4-(1-methylethyl)benzene
18	14.29	1-Methyl-2-(1-methylethyl)benzene
19	15.22	Undecane
20	15.29	1,2,3,4- Tetramethylbenzene
21	15.40	1,2,4,5- Tetramethylbenzene
22	15.92	2-Ethenyl-1,4-dimethylbenzene
23	16.21	1-Methyl- 4(2-propenyl)benzene
24	17.01	Naphthalene

These results show that, not surprisingly the Australian petrol is different to that used for the ASTM standard and as a result a number of target compounds, which are more suited to Australian petrol were selected for this study.

In total 16 of the compounds shown in Figure 3.3 and listed in Table 3.2, were selected as petrol target compounds (refer to Table 3.3). The majority of the compounds were selected based on their abundance in the total ion chromatogram of petrol at all evaporation states however a few were selected because they are characteristic of petrol. The major ions for these compounds are also listed in Table 3.3. These ions were used throughout the remainder of the study to produce extracted ion chromatograms. These identified compounds will be utilised throughout the remainder of this study and will from here on in, be referred to as the petrol target compounds.

Table 3.3: Selected Petrol Target Compounds and their Major Ions

Peak Number (Figure 3.3)	**Retention Time (min)**	**Library Identification**	**Major Ions**
2	4.16	Toluene	91
3	6.87	Ethylbenzene	91, 106
4	7.15	*p*- and *m*-Xylene	91, 106
5	7.87	*o*-Xylene	91, 106
6	9.95	Propylbenzene	91, 105, 120
7	10.20	1-Ethyl-4-methylbenzene	105, 120
8	10.47	1,3,5-Trimethylbenzene	105, 120
9	10.79	1-Ethyl-3-methylbenzene	105, 120
10	11.29	1,2,4-Trimethylbenzene	105, 120
11	12.17	1,2,3-Trimethylbenzene	105, 120
12	12.53	Indane	117, 118
16	13.45	2-Ethyl-1,4-dimethylbenzene	119, 134
18	14.29	1-Methyl-2-(1-methylethyl)benzene	119, 134
20	15.29	1,2,3,4-Tetramethylbenzene	119, 134
21	15.40	1,2,4,5-Tetramethylbenzene	119, 134
24	17.01	Naphthalene	128

3.2.1 LIQUID PETROL STANDARDS

The 16 target compounds selected above were used to generate a set of standard petrol target compound chromatograms. Target compound chromatograms were generated based on the guidelines provided in the

ASTM E 1681-01 standard test method where the target compound chromatograms are bar graphs of petrol target compounds plotted against peak area (counts)[78]. They are generated to enable a pattern to be produced without any extraneous compounds being present, thus making it much easier to view and perform the visual pattern comparison procedure required to make an identification of petrol. As the y-axis of each of the target compound chromatograms is based on peak area, the scale differs for each of the target compound chromatograms.

Evaporated petrol samples were prepared as described in Section 2.3.1 and these samples were diluted with diethyl ether to a concentration of 10%, 1%, 0.1%, 0.01% and 0.001% (v/v). Each diluted sample was analysed in triplicate by GC/MS using the chromatographic conditions outlined in Section 2.5.1. The above procedure was repeated seven times and retention time reproducibility was less than 1% and peak area reproducibility showed relative standard deviations (RSD) ranging from 0.04 to 7.1% for the 16 target compounds. This indicated there was good reproducibility in the preparation procedure and good chromatographic run to run reproducibility in the GC/MS. Total ion chromatograms (denoted TIC), extracted ion chromatograms (denoted EIC) and target compound chromatograms for liquid petrol standards at various evaporation states and at various dilutions in diethyl ether is shown below. Figures 3.4 to 3.9 show petrol standards for unevaporated, 50% evaporated and 95% evaporated petrol diluted to 10% (v/v) in diethyl ether. Figures 3.10 to 3.15 show the unevaporated and evaporated petrol diluted to 1% (v/v) in diethyl ether. Figures 3.16 to 3.21 show the petrol, at the same evaporation states, diluted to 0.1% (v/v) in diethyl ether and Figures 3.22 to 3.27 show the unevaporated and evaporated petrol diluted to 0.01% (v/v). Dilutions at 0.001% (v/v) for the unevaporated, 50% evaporated and 95% evaporated petrol are shown in Figures 3.28 to 3.33, respectively. It should be noted that the chromatograms produced show no unexpected peaks and are similar to petrol standard chromatograms produced in this laboratory using a number of different brands of petrol and are also similar to those used as standards by VPFSC[59, 154].

3.2.1.1 10% (V/V) PETROL STANDARDS

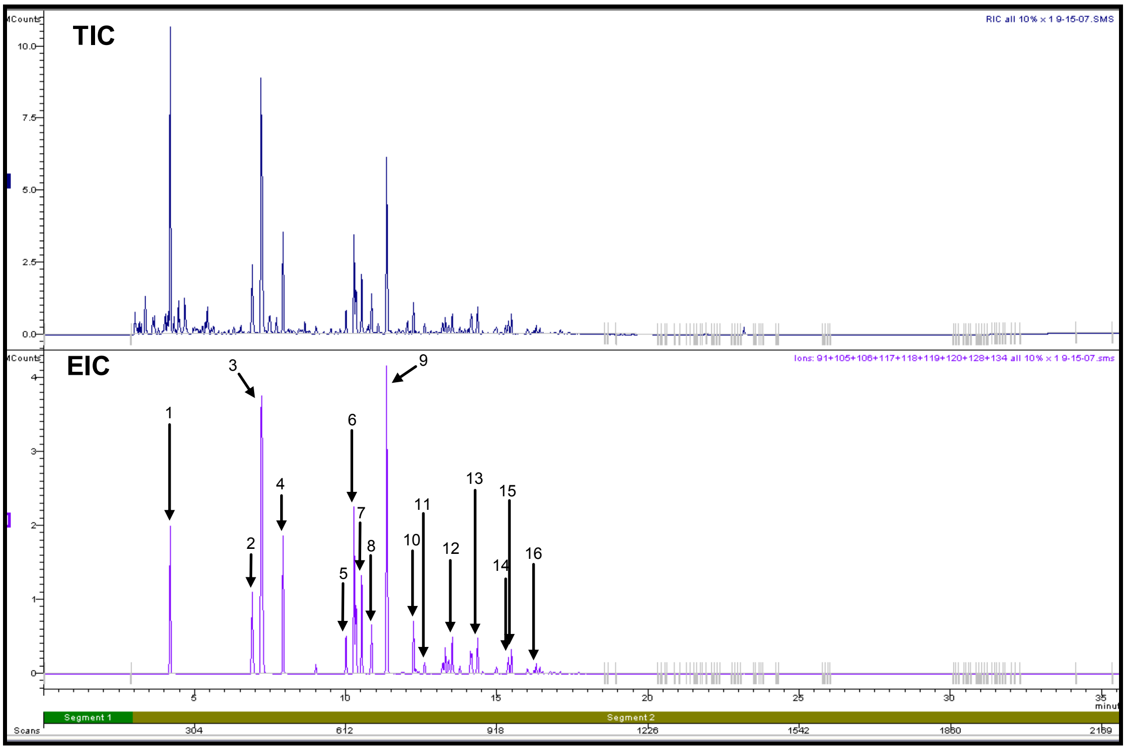


Figure 3.4: Total Ion Chromatogram and Extracted Ion Chromatogram for Unevaporated Petrol Diluted to 10% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3- Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

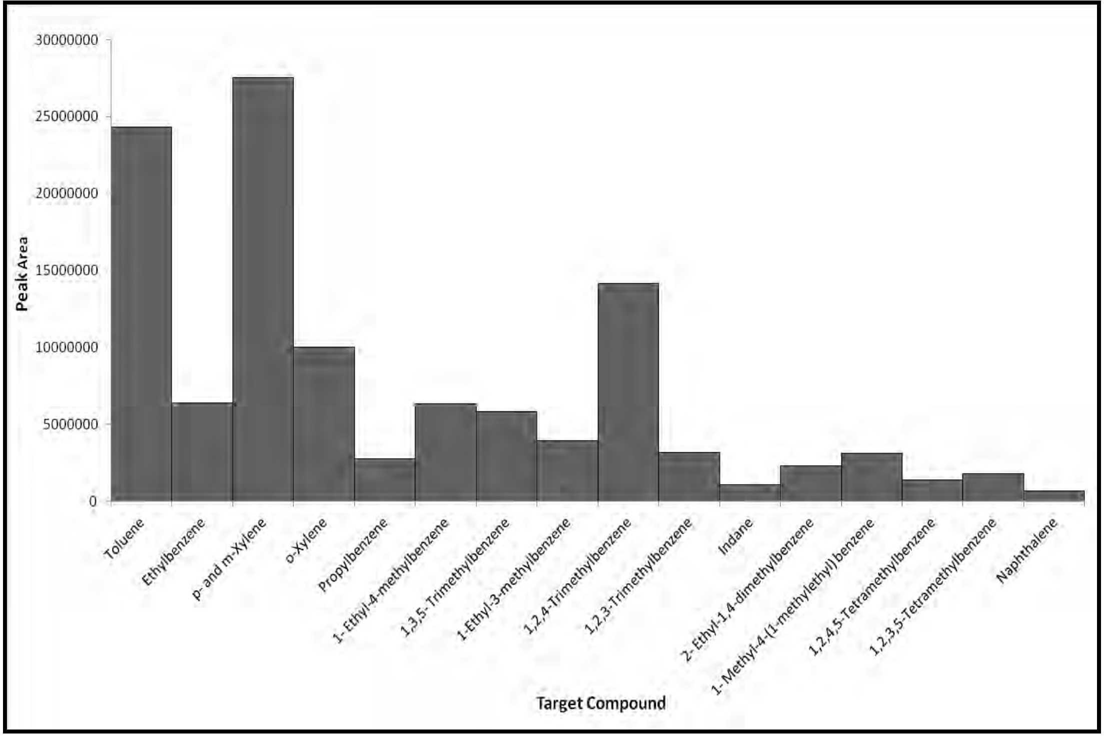


Figure 3.5: Target Compound Chromatogram for Unevaporated Petrol Diluted to 10% (v/v)

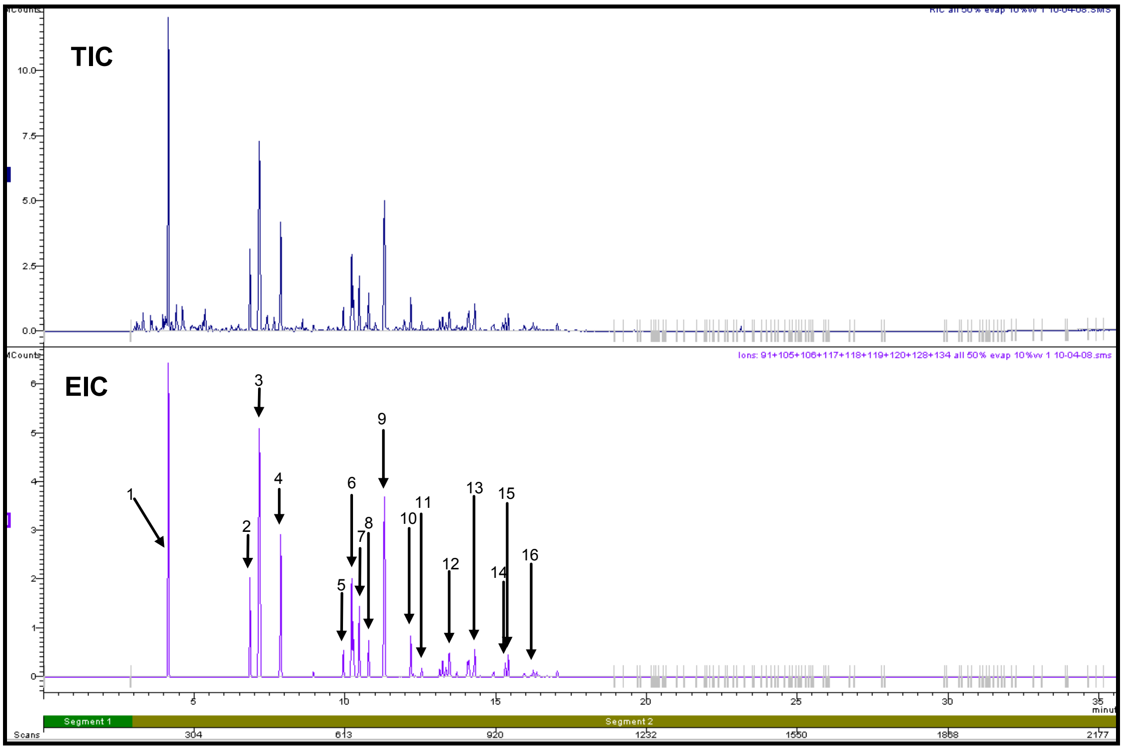


Figure 3.6: Total Ion Chromatogram and Extracted Ion Chromatogram for 50% Evaporated Petrol Diluted to 10% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3- methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

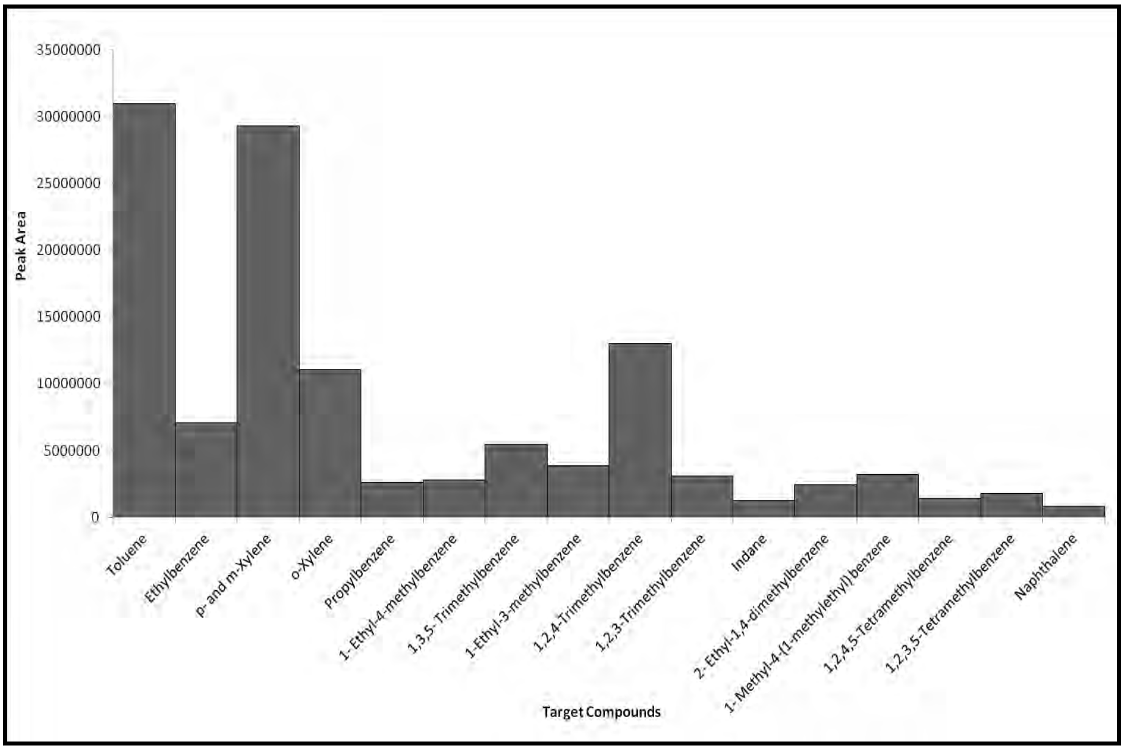


Figure 3.7: Target Compound Chromatogram for 50% Evaporated Petrol Diluted to 10% (v/v)

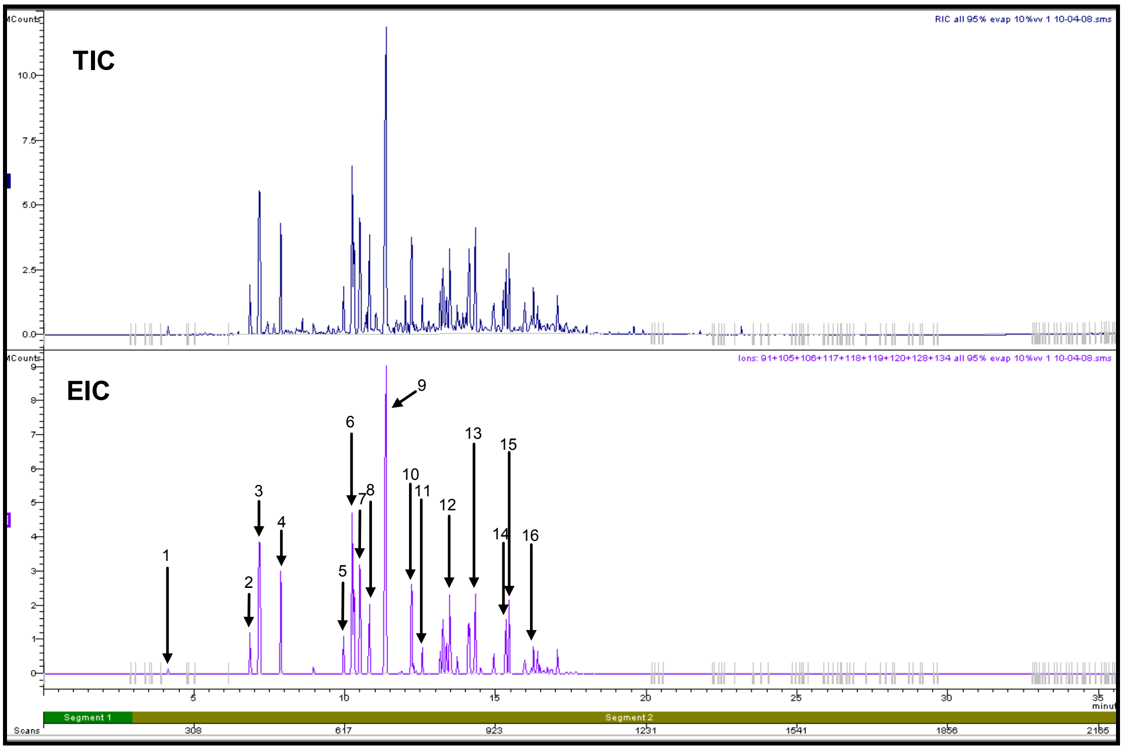


Figure 3.8: Total Ion Chromatogram and Extracted Ion Chromatogram for 95% Evaporated Petrol Diluted to 10% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5- Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

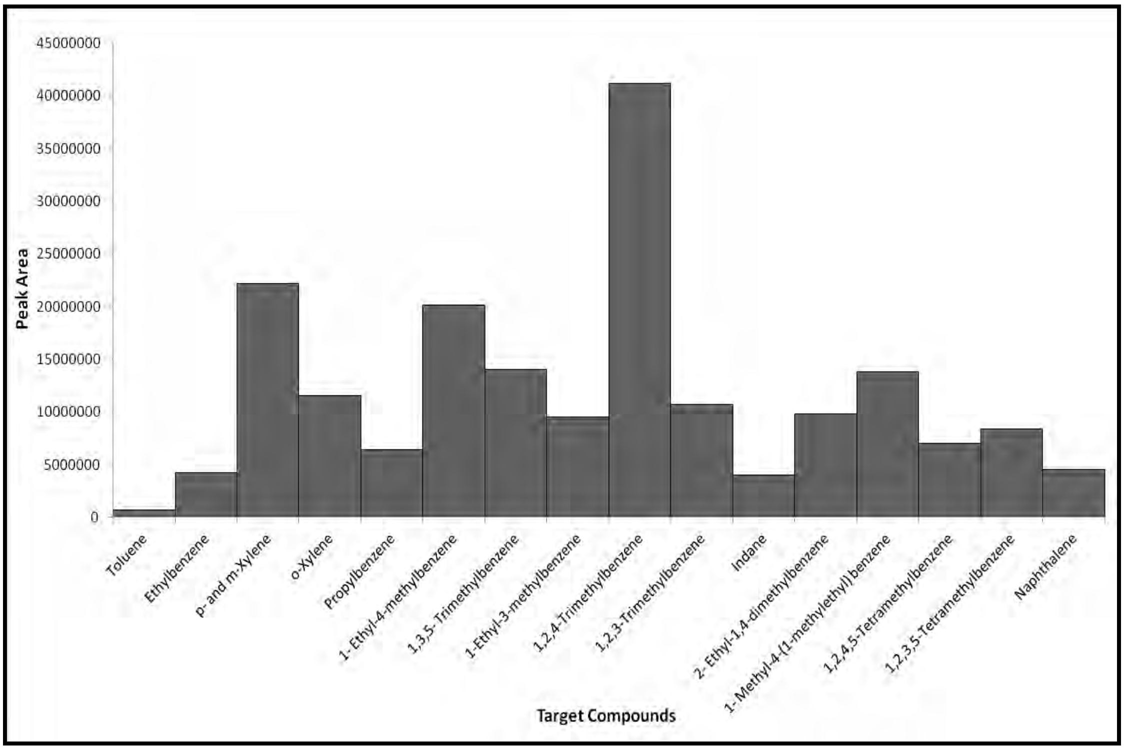


Figure 3.9: Target Compound Chromatogram for 95% Evaporated Petrol Diluted to 10% (v/v)

3.2.1.2 1% (V/V) PETROL STANDARDS

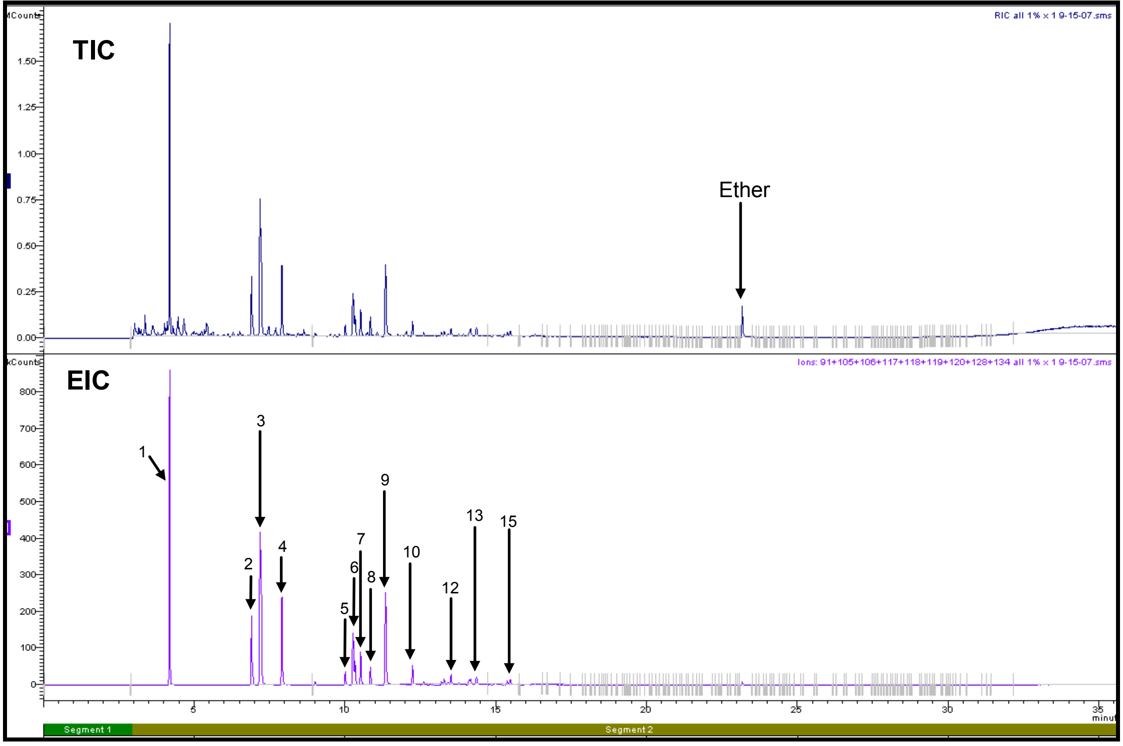


Figure 3.10: Total Ion Chromatogram and Extracted Ion Chromatogram for Unevaporated Petrol Diluted to 1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 15= 1,2,3,5-Tetramethylbenzene

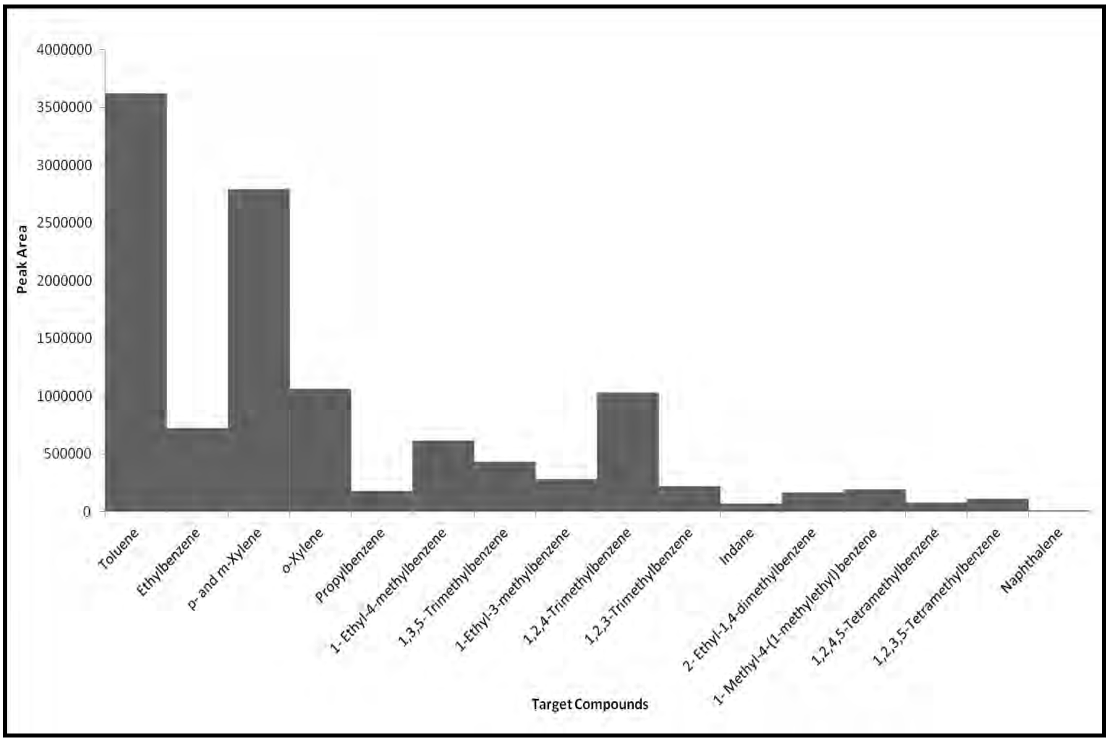


Figure 3.11: Target Compound Chromatogram for Unevaporated Petrol Diluted to 1% (v/v)

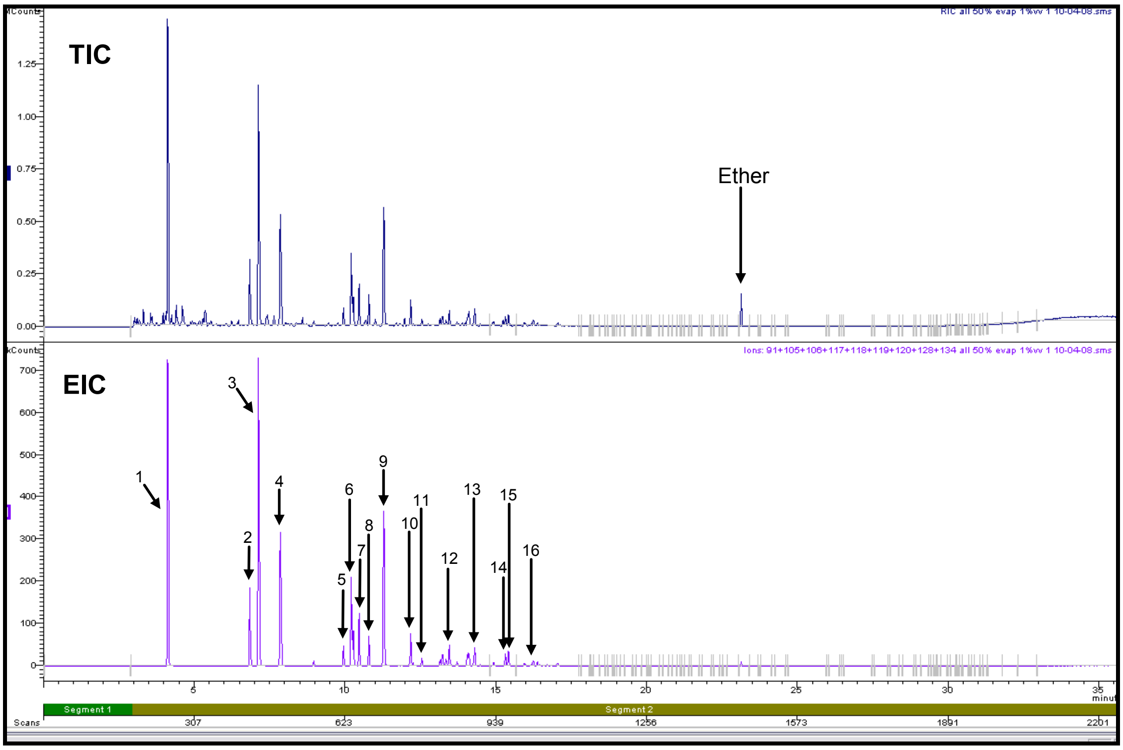


Figure 3.12: Total Ion Chromatogram and Extracted Ion Chromatogram for 50% Evaporated Petrol Diluted to 1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4- Trimethylbenzene, 10= 1,2,3- Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

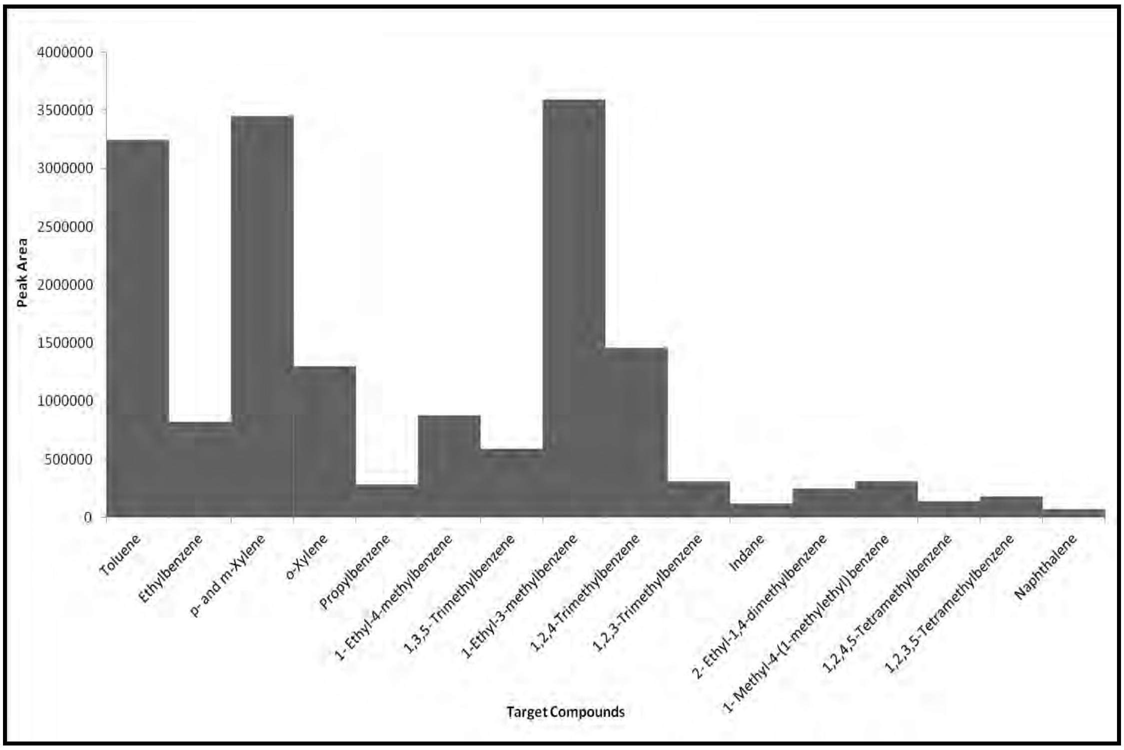


Figure 3.13: Target Compound Chromatogram for 50% Evaporated Petrol Diluted to 1% (v/v)

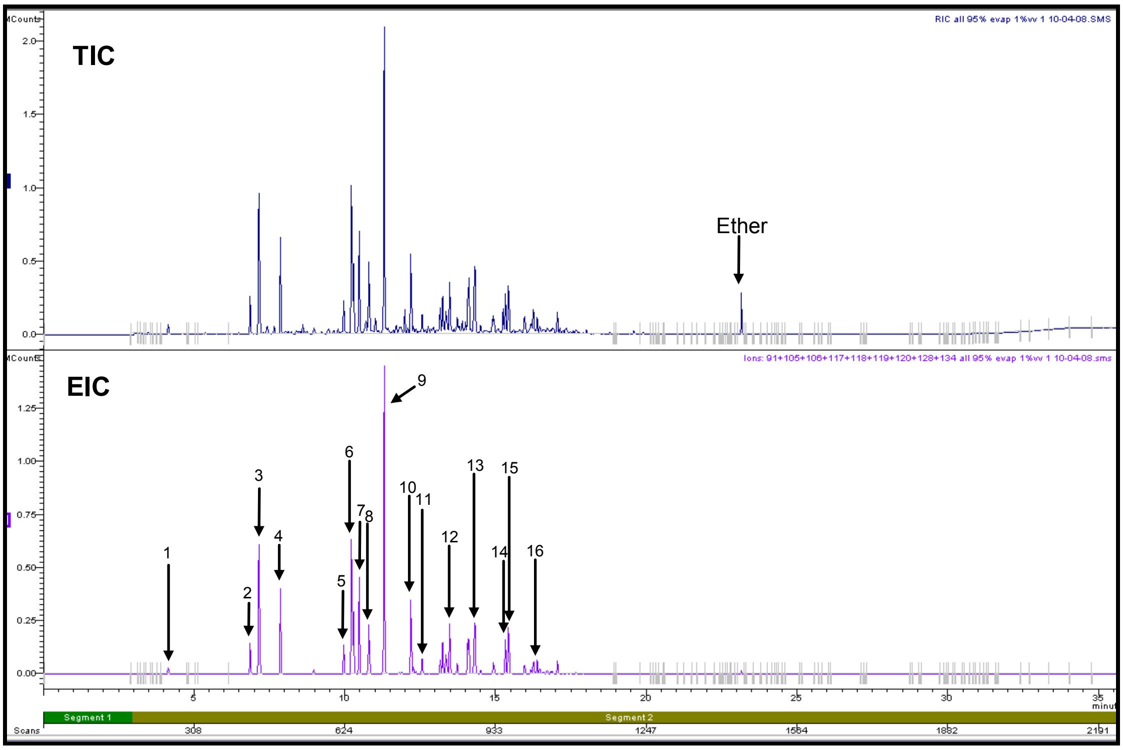


Figure 3.14: Total Ion Chromatogram and Extracted Ion Chromatogram for 95% Evaporated Petrol Diluted to 1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

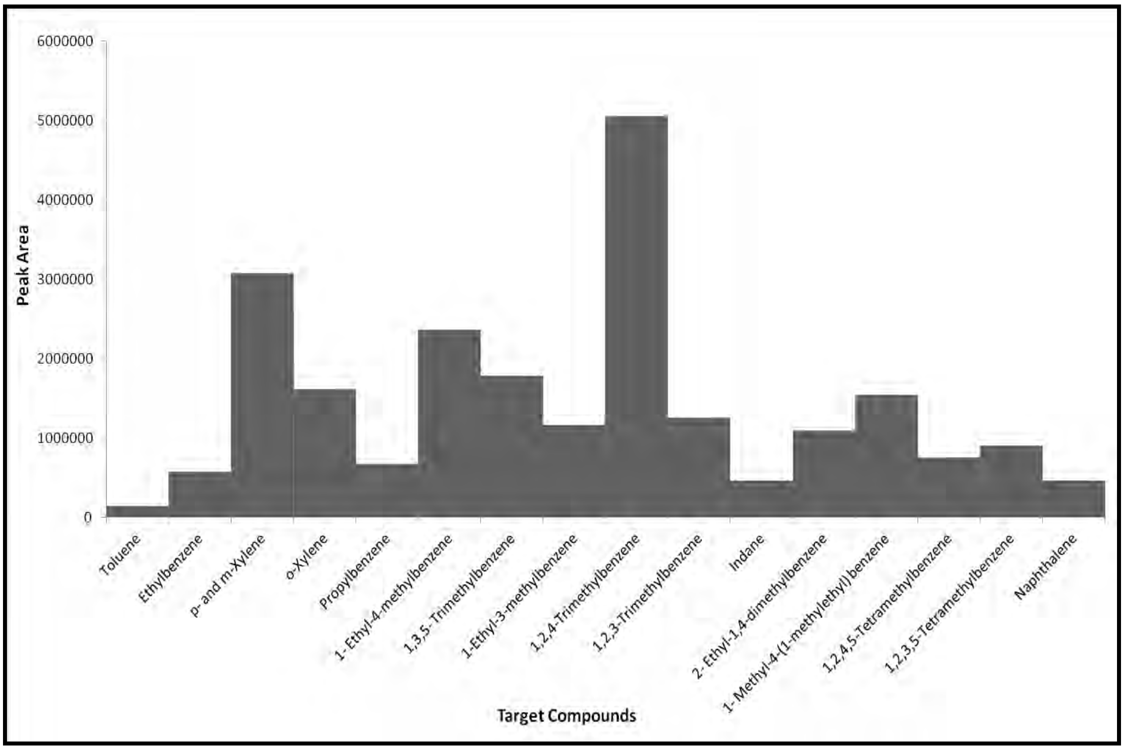


Figure 3.15: Target Compound Chromatogram for 95% Evaporated Petrol Diluted to 1% (v/v)

3.2.1.3 0.1% (V/V) PETROL STANDARDS

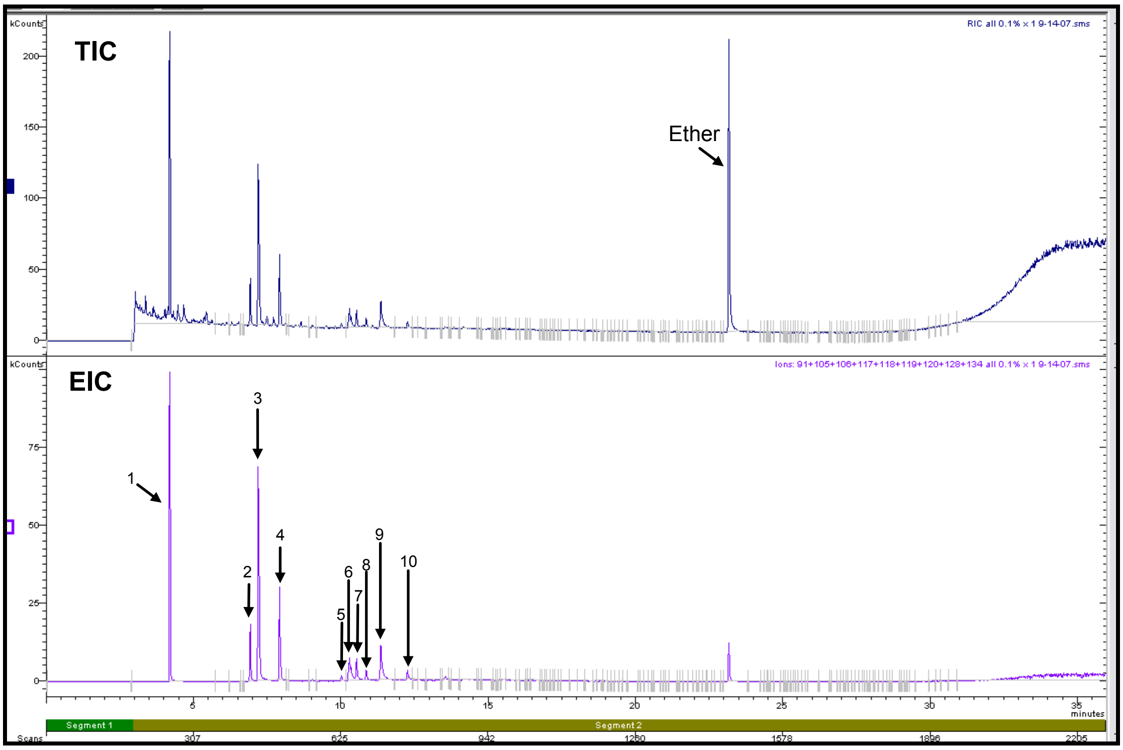


Figure 3.16: Total Ion Chromatogram and Extracted Ion Chromatogram for Unevaporated Petrol Diluted to 0.1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3- Trimethylbenzene

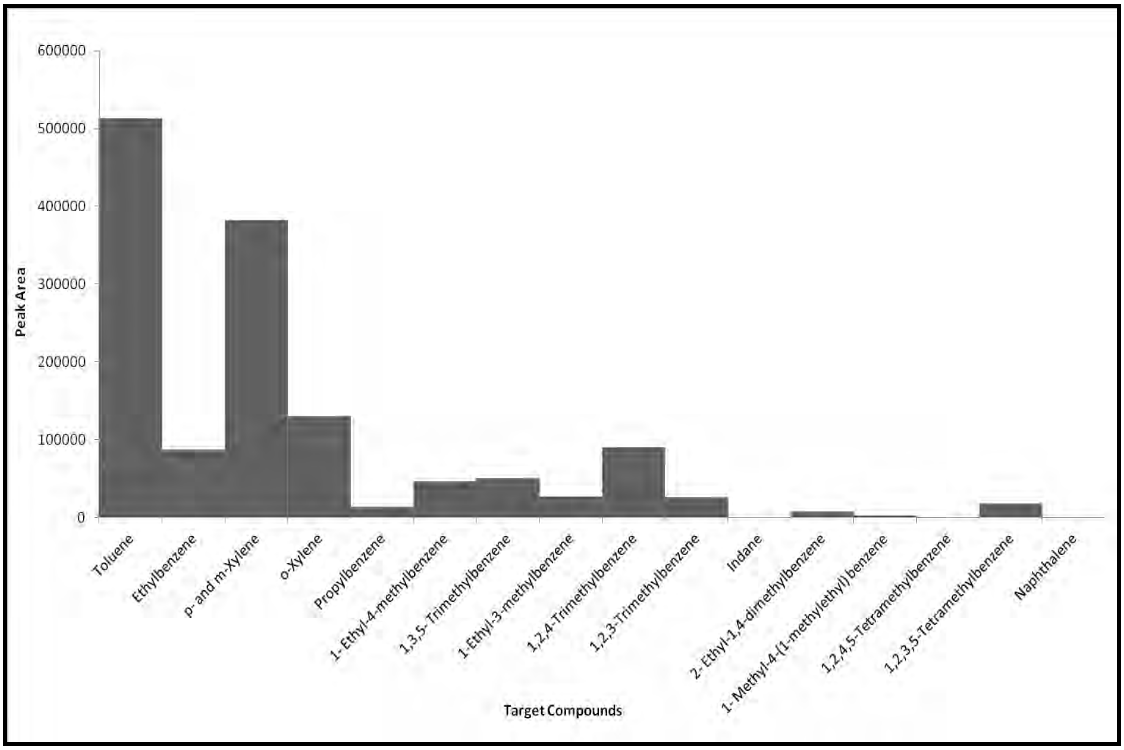


Figure 3.17: Target Compound Chromatogram for Unevaporated Petrol Diluted to 0.1% (v/v)

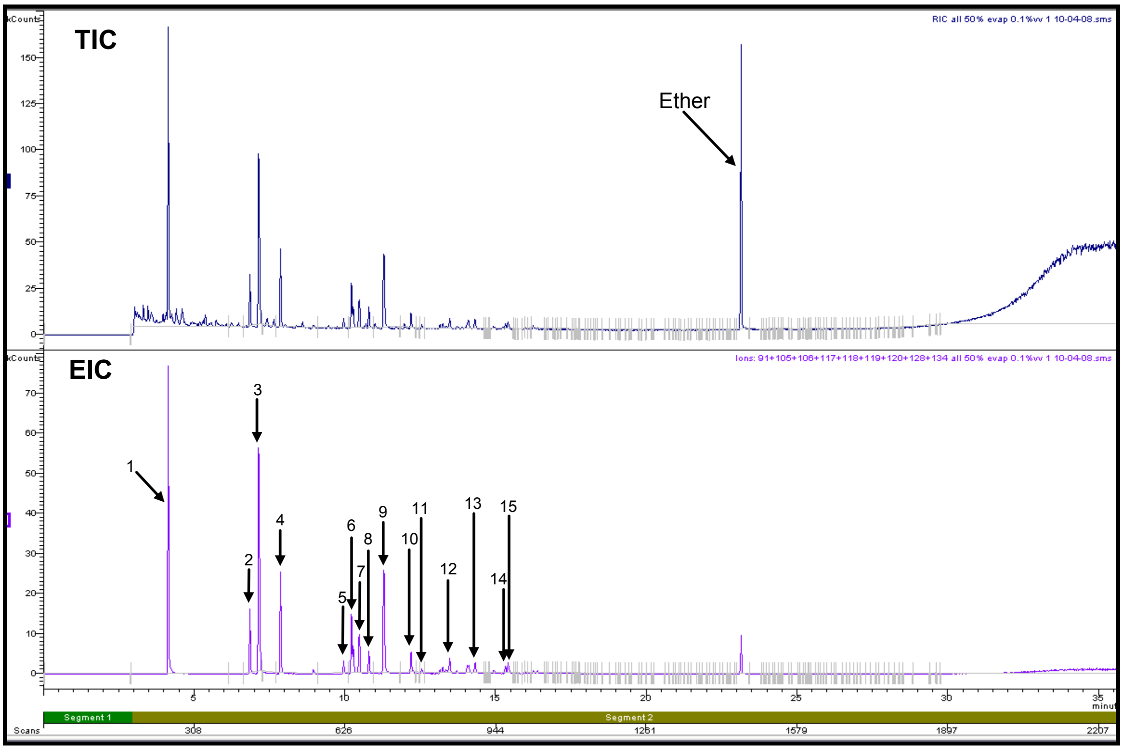


Figure 3.18: Total Ion Chromatogram and Extracted Ion Chromatogram for 50% Evaporated Petrol Diluted to 0.1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3- Trimethylbenzene, 11= Indane, 12= 2- Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5- Tetramethylbenzene, 15= 1,2,3,5- Tetramethylbenzene

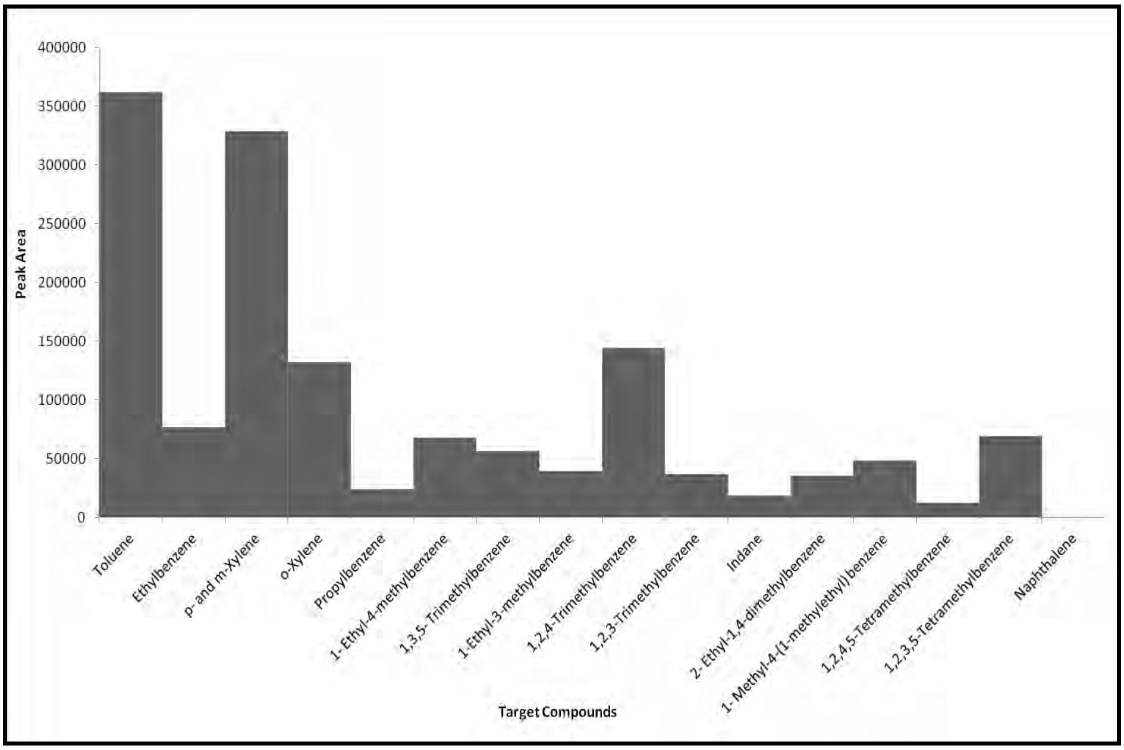


Figure 3.19: Target Compound Chromatogram for 50% Evaporated Petrol Diluted to 0.1% (v/v)

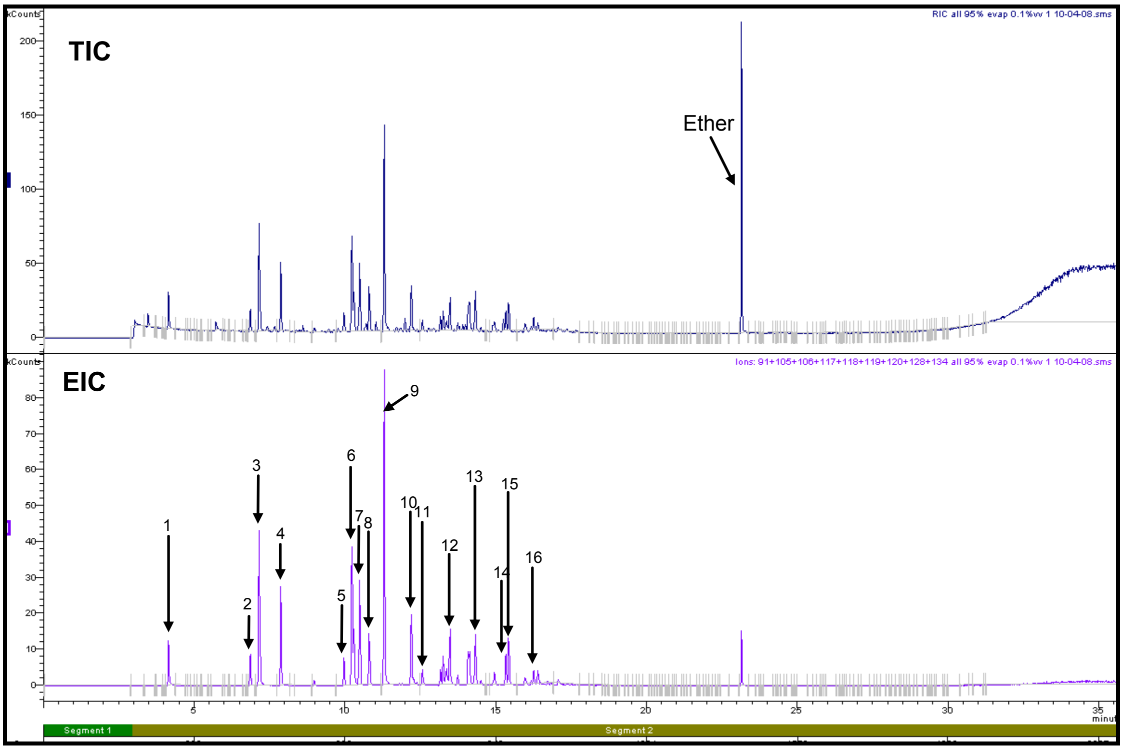


Figure 3.20: Total Ion Chromatogram and Extracted Ion Chromatogram for 95% Evaporated Petrol Diluted to 0.1% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene, 16 = Naphthalene

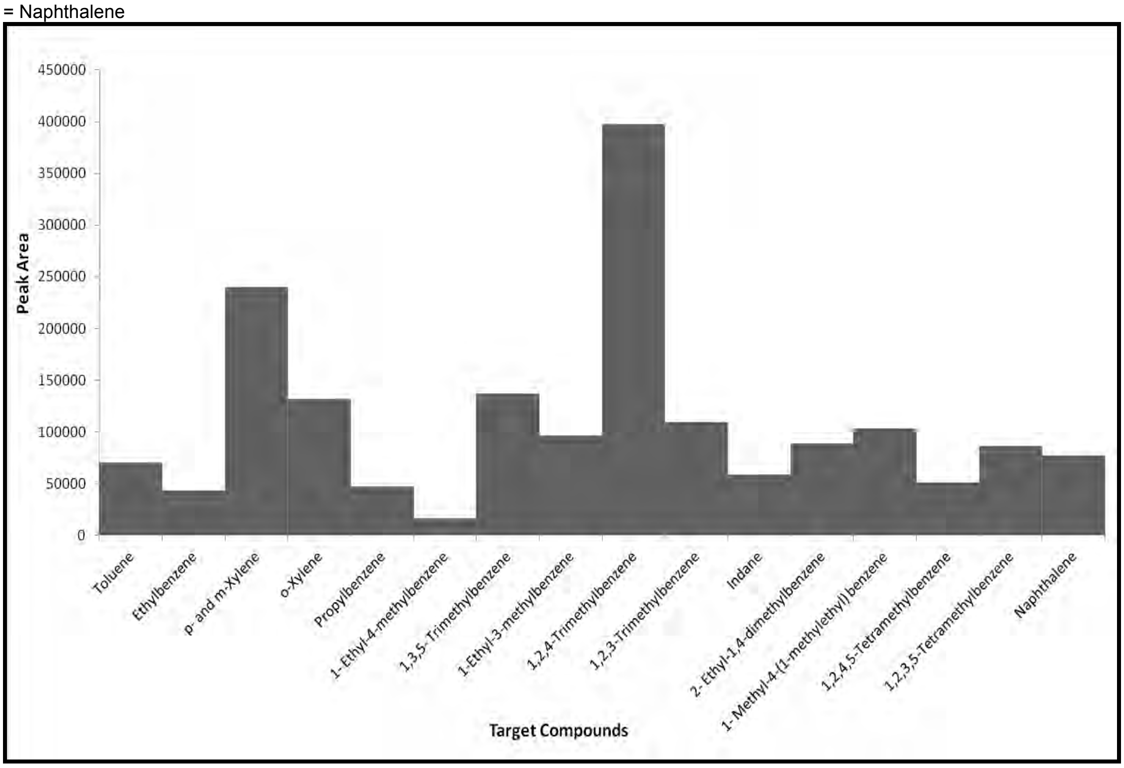


Figure 3.21: Target Compound Chromatogram for 95% Evaporated Petrol Diluted to 0.1% (v/v)

3.2.1.4 0.01% (V/V) PETROL STANDARDS

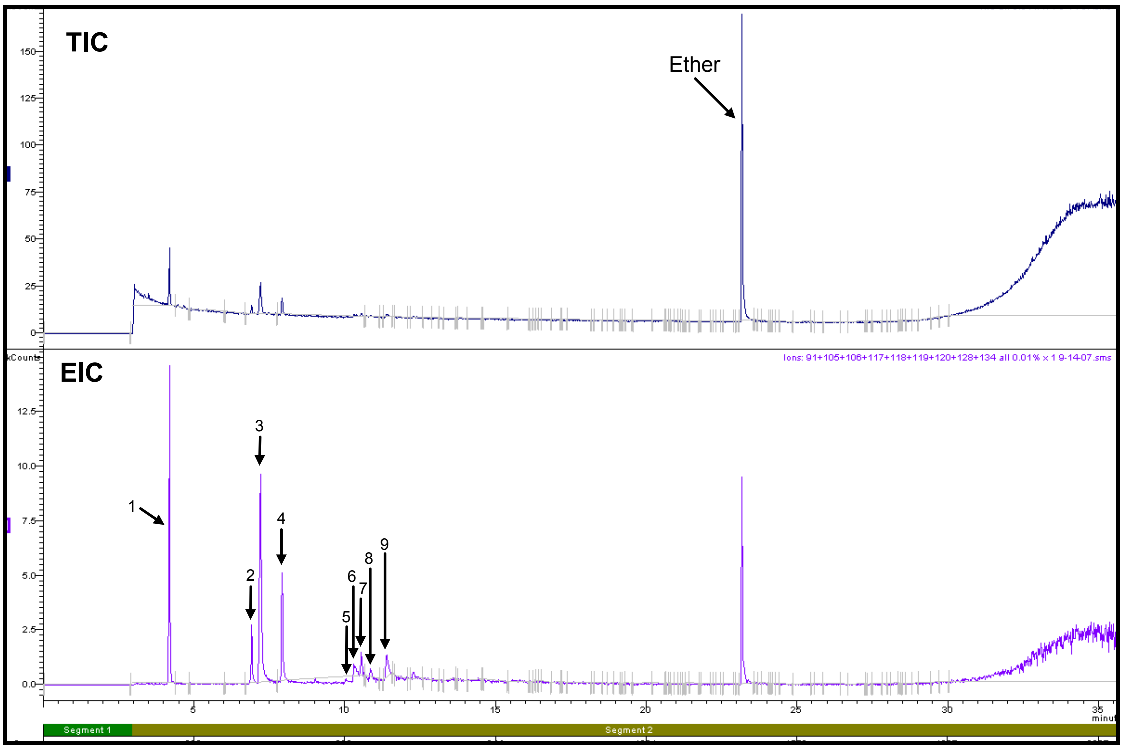


Figure 3.22: Total Ion Chromatogram and Extracted Ion Chromatogram for Unevaporated Petrol Diluted to 0.01% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene

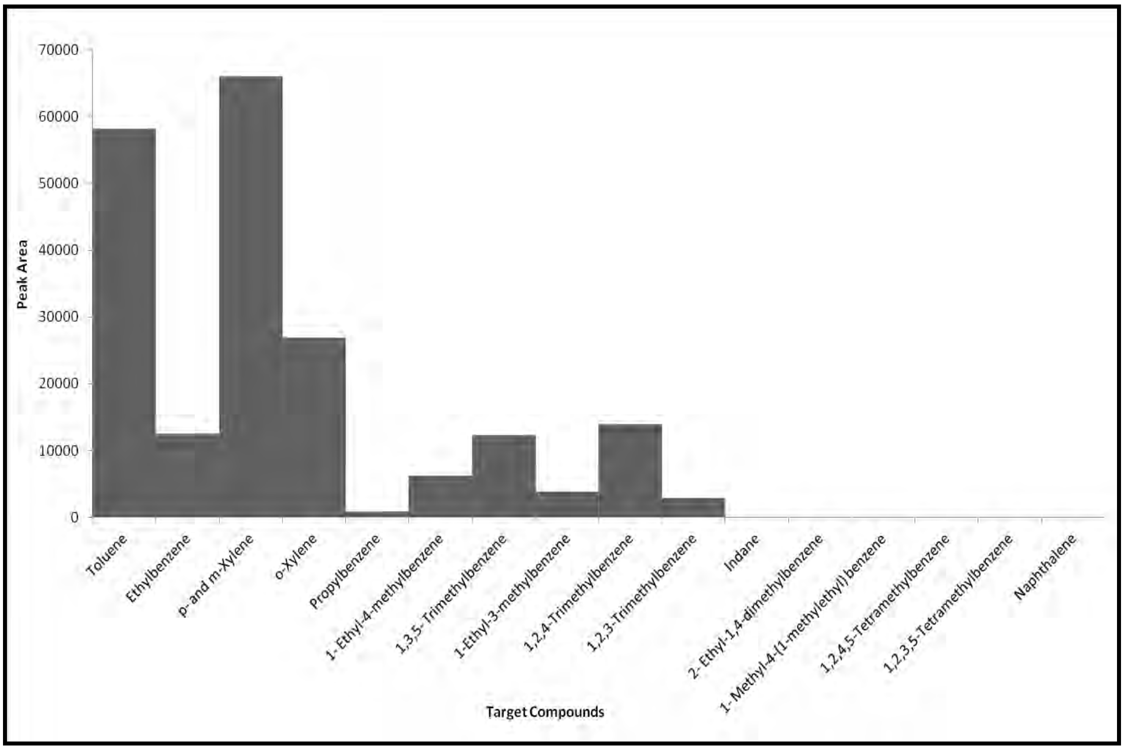


Figure 3.23: Target Compound Chromatogram for Unevaporated Petrol Diluted to 0.01% (v/v)

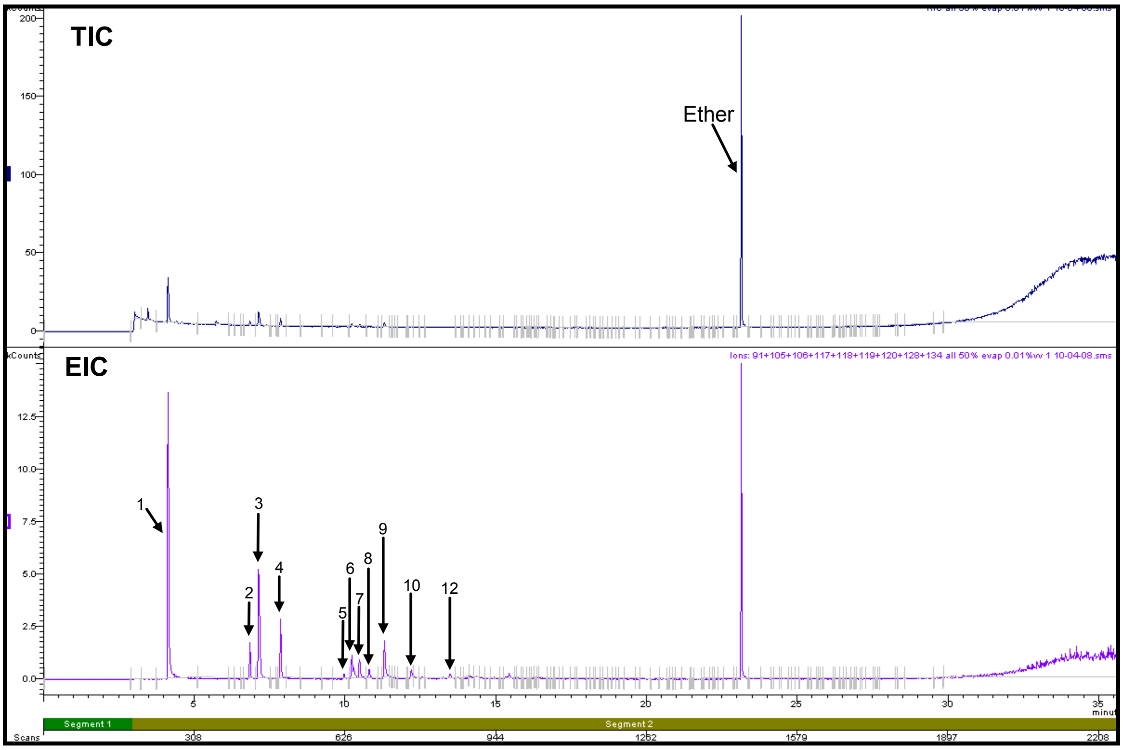


Figure 3.24: Total Ion Chromatogram and Extracted Ion Chromatogram for 50% Evaporated Petrol Diluted to 0.01% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4- Trimethylbenzene, 10= 1,2,3- Trimethylbenzene, 12= 2-Ethyl-1,4-dimethylbenzene

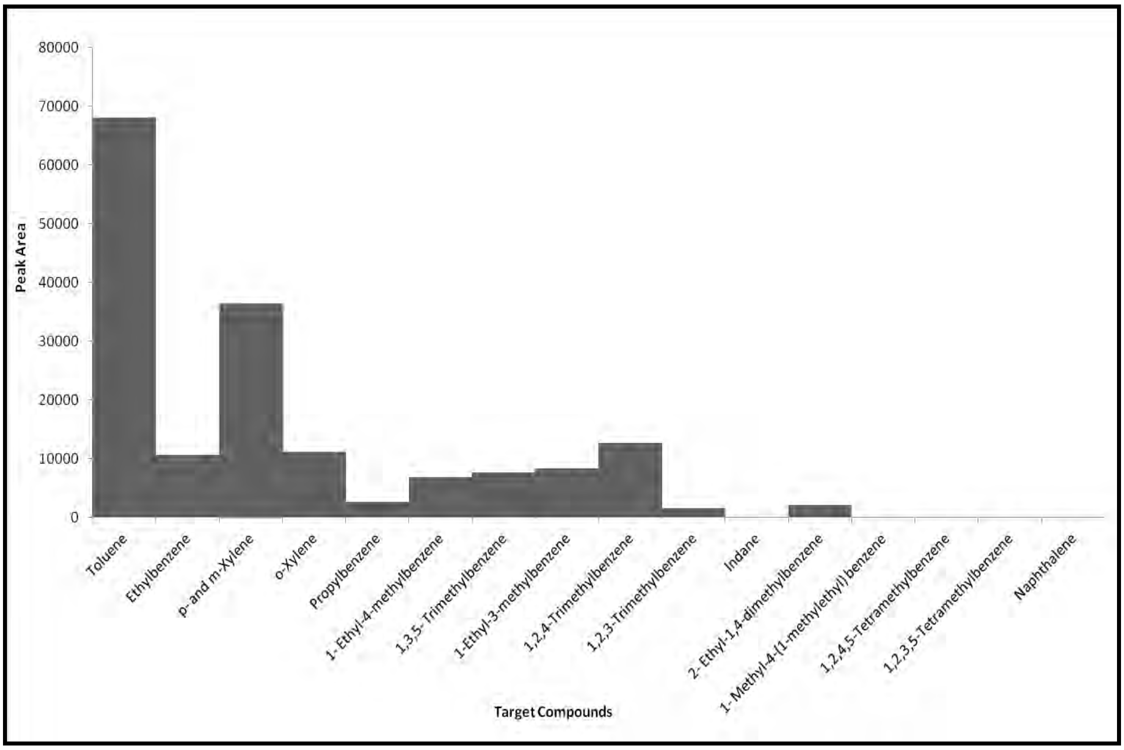


Figure 3.25: Target Compound Chromatogram for 50% Evaporated Petrol Diluted to 0.01% (v/v)

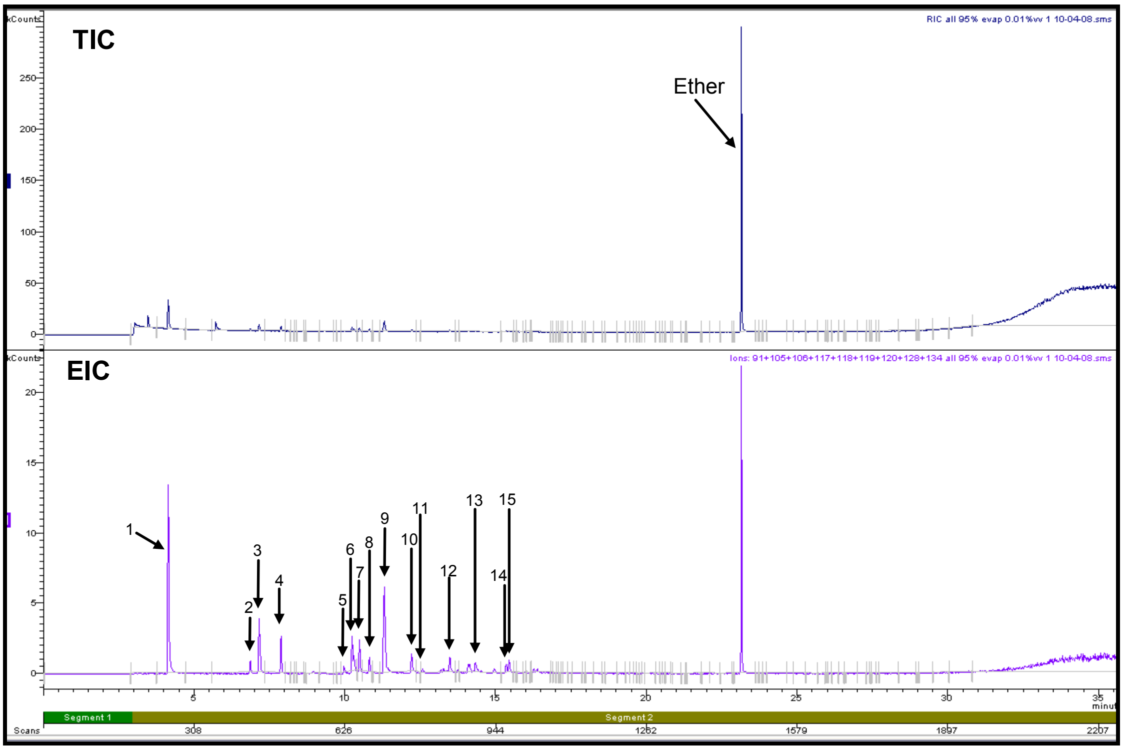


Figure 3.26: Total Ion Chromatogram and Extracted Ion Chromatogram for 95% Evaporated Petrol Diluted to 0.01% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5- Tetramethylbenzene

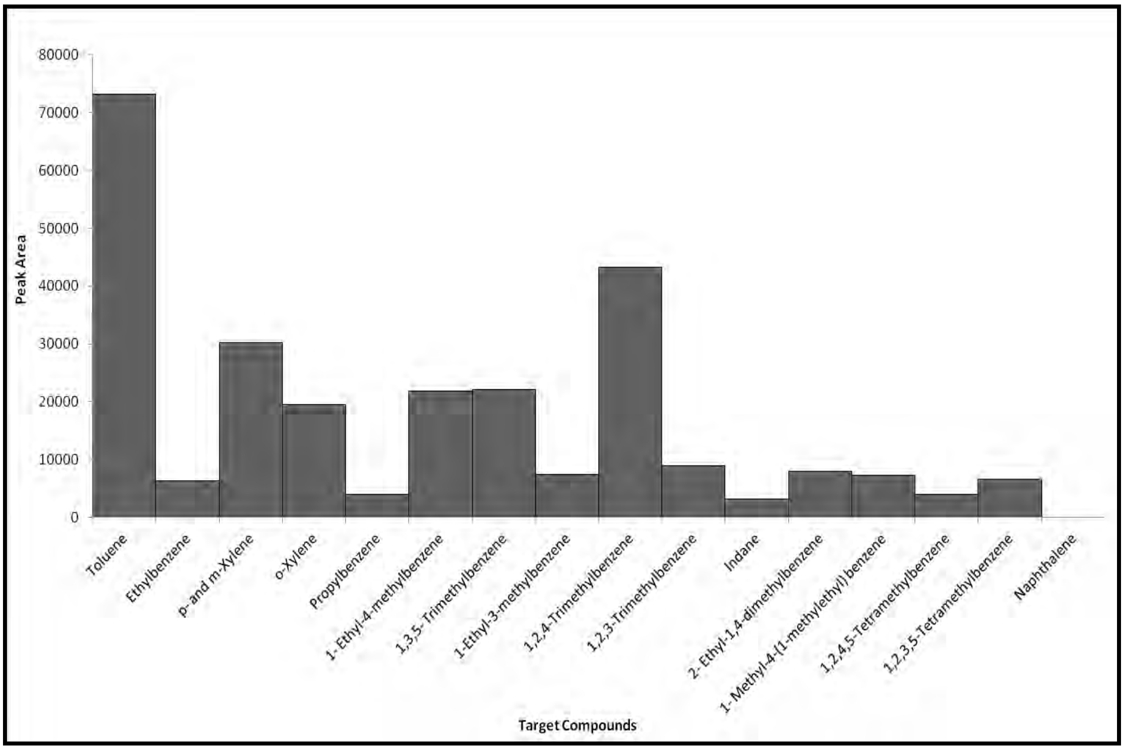


Figure 3.27: Target Compound Chromatogram for 95% Evaporated Petrol Diluted to 0.01% (v/v)

3.2.1.5 0.001% (V/V) PETROL STANDARDS

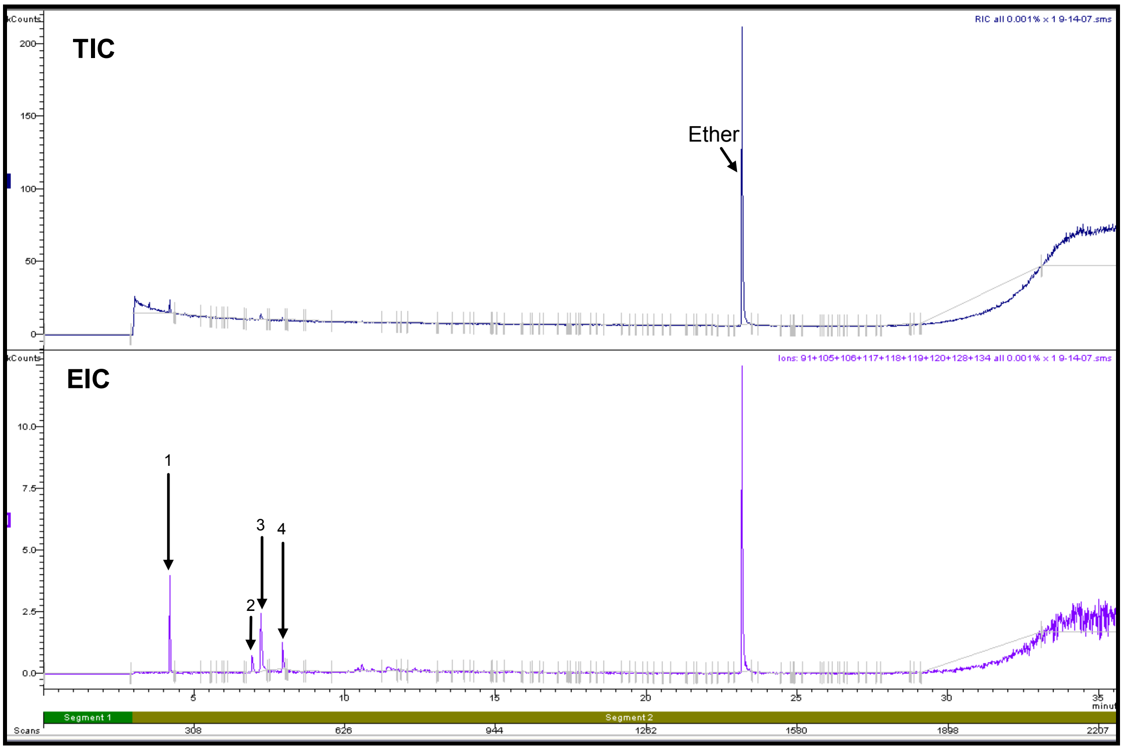


Figure 3.28: Total Ion Chromatogram and Extracted Ion Chromatogram for Unevaporated Petrol Diluted to 0.001% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene

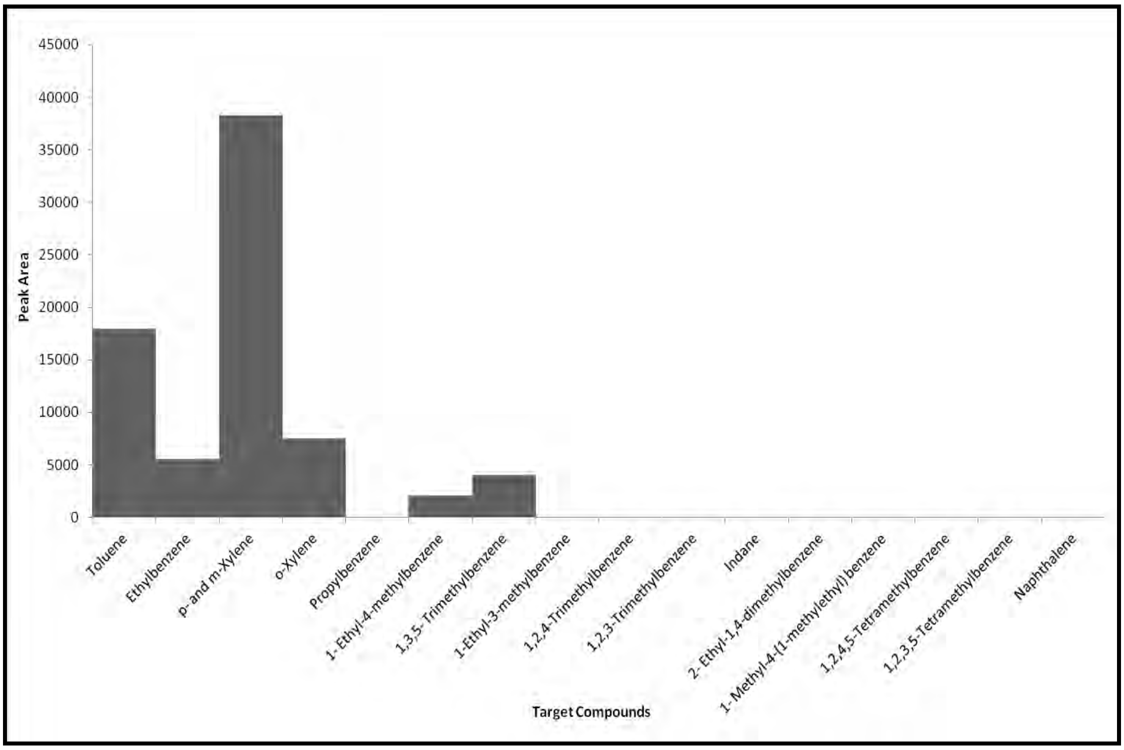


Figure 3.29: Target Compound Chromatogram for Unevaporated Petrol Diluted to 0.001% (v/v)

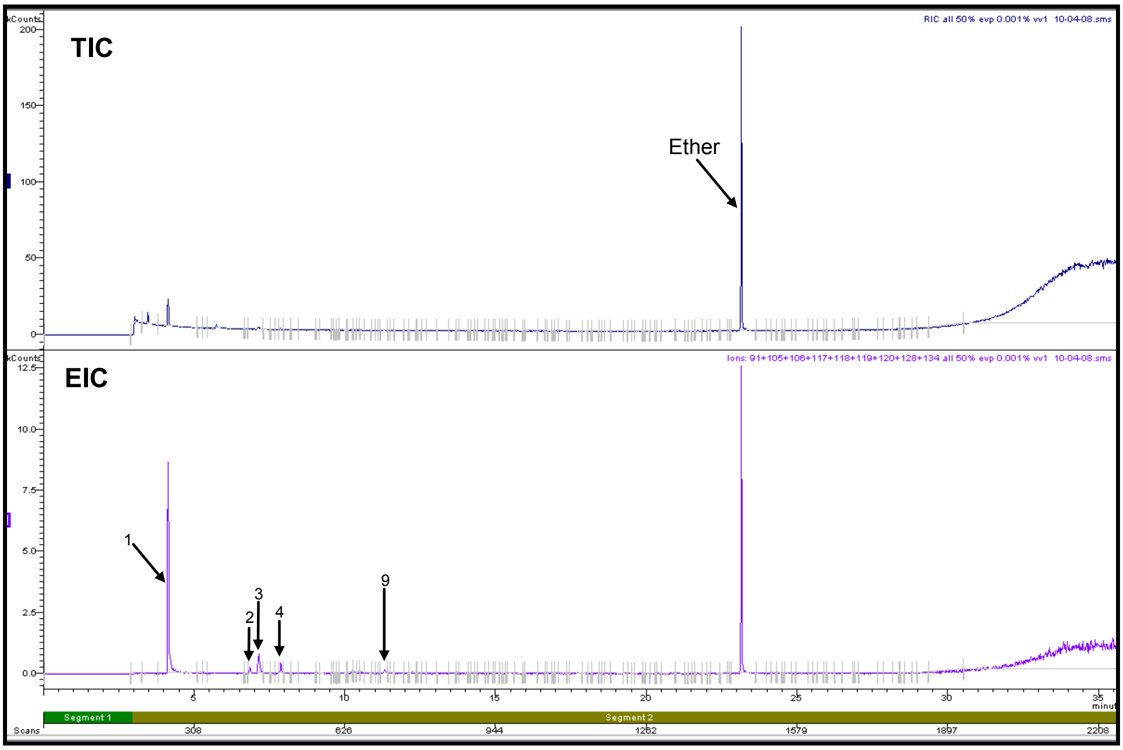


Figure 3.30: Total Ion Chromatogram and Extracted Ion Chromatogram for 50% Evaporated Petrol Diluted to 0.001% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 9= 1,2,4-Trimethylbenzene

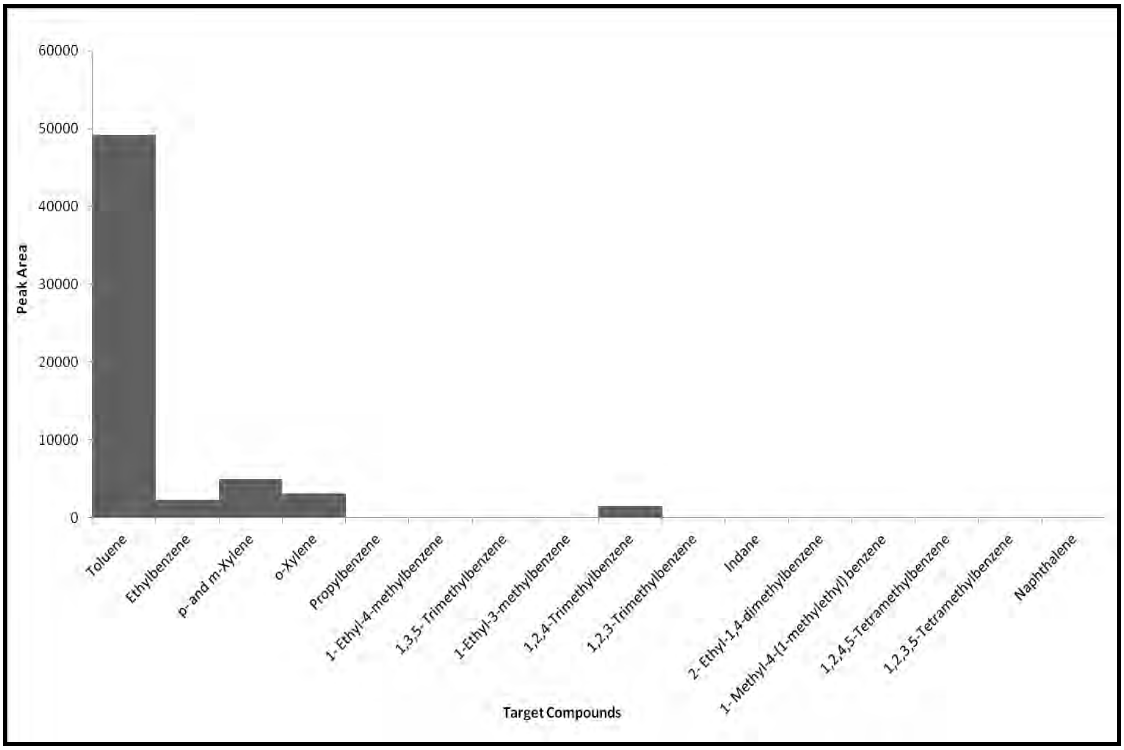


Figure 3.31: Target Compound Chromatogram for 50% Evaporated Petrol Diluted to 0.001% (v/v)

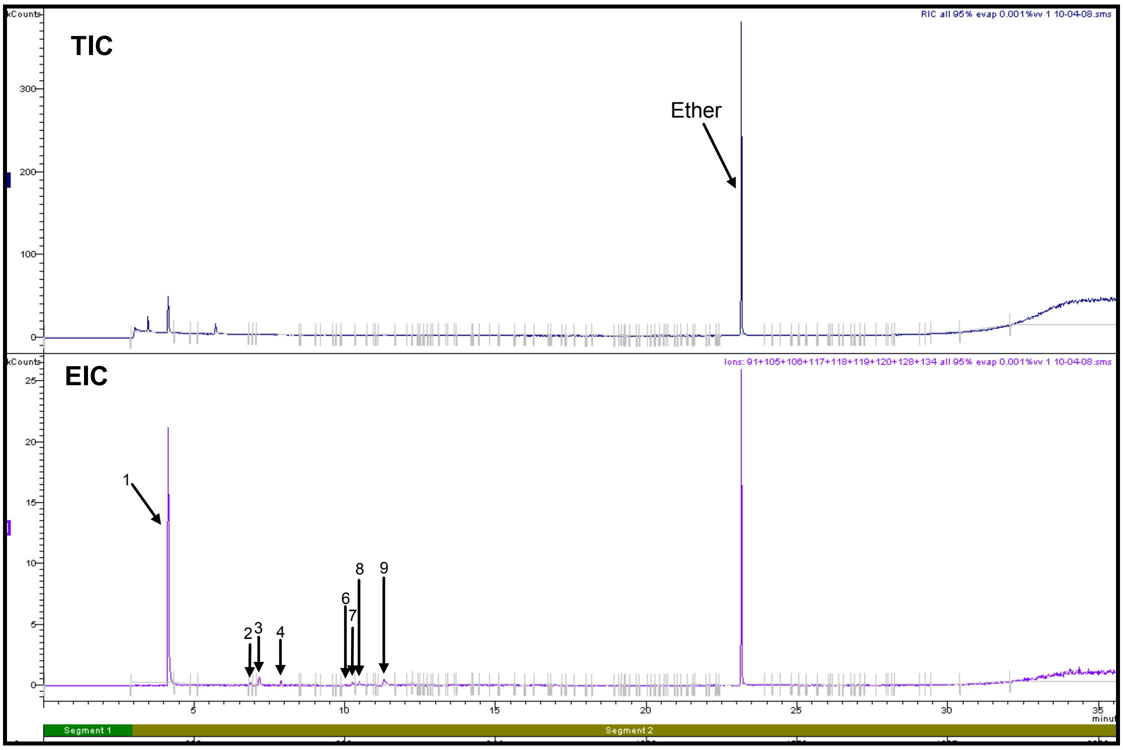


Figure 3.32: Total Ion Chromatogram and Extracted Ion Chromatogram for 95% Evaporated Petrol Diluted to 0.001% (v/v) (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene

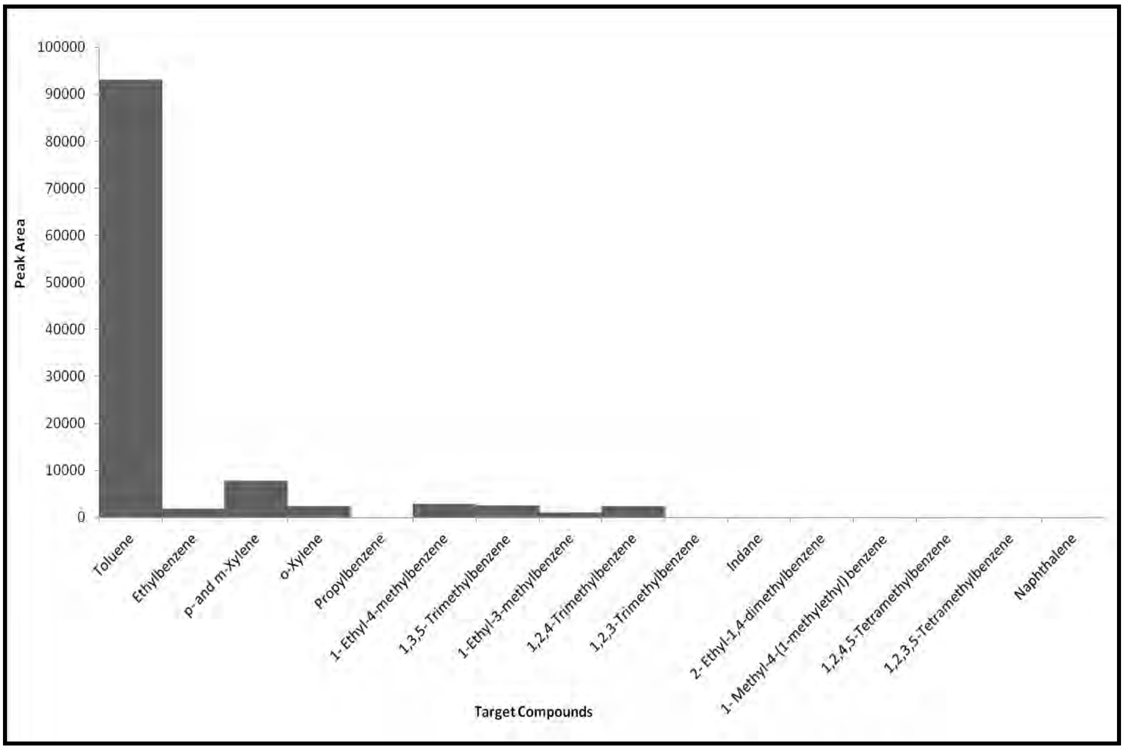


Figure 3.33: Target Compound Chromatogram for 95% Evaporated Petrol Diluted to 0.001% (v/v)

3.2.1.6 SUMMARY

The target compound chromatograms show that for dilutions down to 0.01% (v/v) in diethyl ether the majority of the 16 target compounds are present for all three evaporation states of petrol. For these dilutions the characteristic peaks for toluene, ethylbenzene, xylenes and trimethylbenzenes are evident. The target compound chromatograms for the 95% evaporated petrol show the loss of the early eluting target compounds, in particular toluene, and the later eluting peaks are now present in greater abundance relative to the early eluting compounds.

The total ion chromatograms show that for standards at dilutions below the 0.1% (v/v) there is no MS response for the amount of petrol standard injected, that is only baseline is observed in the total ion chromatogram. However extracted ion chromatography offers extra sensitivity and there is MS response for dilutions down to 0.001% (v/v) and therefore target compound chromatograms can be generated down to this level. With respect to pattern comparison using the generated target compound chromatograms a characteristic profile of toluene, ethylbenzene and the xylenes is still produced at the 0.001% (v/v) level, however at this level not enough target compounds are recovered to enable a conclusive identification of petrol. The 0.001% (v/v) level is approaching the MS (in extracted ion mode) detection limit. At the 0.01% (v/v) level there is sufficient MS response and enough target compounds present including the characteristic peaks for toluene, ethylbenzene, xylenes and trimethylbenzenes for all evaporation states to allow for a petrol identification and therefore this level becomes the limit for pattern comparison.

From the above it is important to consider that the limit for pattern comparison represents very low levels of petrol standard injected onto the column. Given the GC conditions used for this study, for a 1μL injection volume and a 50:1 split ratio, for the 0.01% (v/v) standards only 2nL has been introduced onto the column. For the 0.001% (v/v) where the MS detection limit is approached, 0.2nL of petrol has been injected on the column.

3.2.2 HEADSPACE PETROL STANDARDS

Liquid standards, like those prepared above, are commonly used for pattern comparison in fire investigation. It was of interest to observe the difference between target compound chromatograms for liquid standards and those for standards prepared using the passive/dynamic headspace technique utilised in this study for the recoveries of volatile organic compounds from the burning of the carpet and foam samples.

Headspace petrol standards where prepared using the same petrol samples used to generate the liquid standards (see Section 2.3.1) and these petrol samples were used to spike KimWipes. The KimWipes were then immediately placed in evidence bags along with a charcoal tube and prepared for the recovery of volatiles by the passive/dynamic recovery technique where volatiles were desorbed from the charcoal tube using diethyl ether as described in Section 2.3. Each sample was analysed in triplicate by GC/MS using the chromatographic conditions outlined in Section 2.4.1. The above procedure was repeated seven times and retention time was less than 1% and peak area reproducibility showed RSD ranging from 3.3 to 9.2% for the 16 target compounds. This indicated there was good reproducibility in the preparation procedure and good chromatographic run to run reproducibility in the GC/MS.

It was important to determine if the evidence bag and tube (method recovery blank) produced any interferences and Figure 3.34 shows the total ion chromatogram and extracted ion chromatogram of the empty evidence bag containing the charcoal tube which was subjected to the passive/dynamic recovery method. The peaks numbered in the total ion chromatogram were tentatively identified by mass spectral matching with the NIST library and are listed in Table 3.4. The peaks recovered from the evidence bag are predominately alkanes with the major one at 11.71 minutes (number 5 in

Figure 3.34) which was tentatively identified as 2,2,4,6,6-pentamethylheptane. For conclusive identification, this would require retention time matching with a standard (not available) but this was not attempted and from here on in, this peak will be labelled as 'Bag'. Furthermore, when comparing these compounds to the petrol target compounds selected, the evidence bag contains no similar or co-eluting peaks. This result differs to that found by Kocisko whereby they claim that petrol cannot be identified due to interfering peaks contributed by the bags[67].

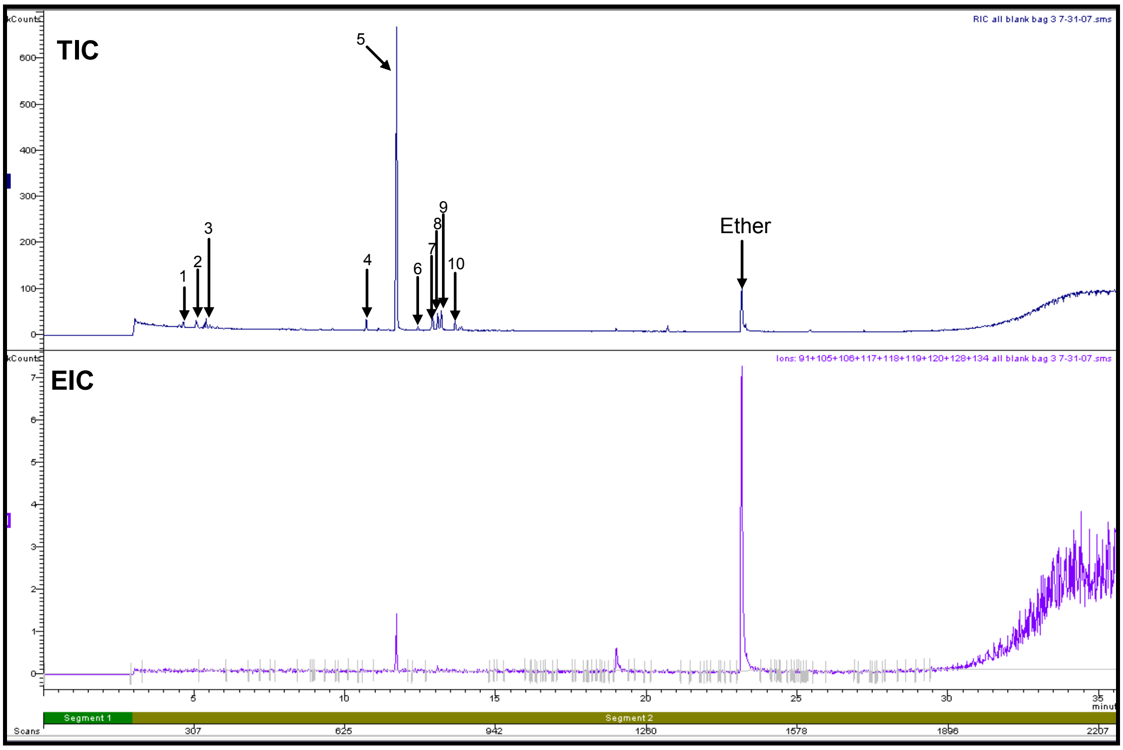


Figure 3.34: Total Ion Chromatogram and Extracted Ion Chromatogram of Evidence Bag with Charcoal Tube (Refer to Section 2.5.1 for GC/MS conditions)

Table 3.4: Peak Identities of Compounds in Evidence Bags

Peak Number	Retention Time (min)	Library Id
1	4.66	3,4-Dimethylhexane
2	5.09	?
3	5.42	2,4-Dimethylhexane
4	10.72	2,2,3,4-Tetramethylpentane
5	11.71	2,2,4,6,6-Pentamethylheptane
6	12.42	2,2,3-Trimethyldecane
7	12.91	3-Ethyl-2,2-dimethylpentane
8	13.09	Ditertbutyldicarbonate
9	13.21	2,2,3,4-Tetramethylpentane
10	13.65	2,3,6-Trimethylheptane

Figure 3.35 shows the total ion chromatogram and extracted ion chromatogram of a blank KimWipe placed in the evidence bag with a charcoal tube and subjected to the passive/dynamic recovery method.

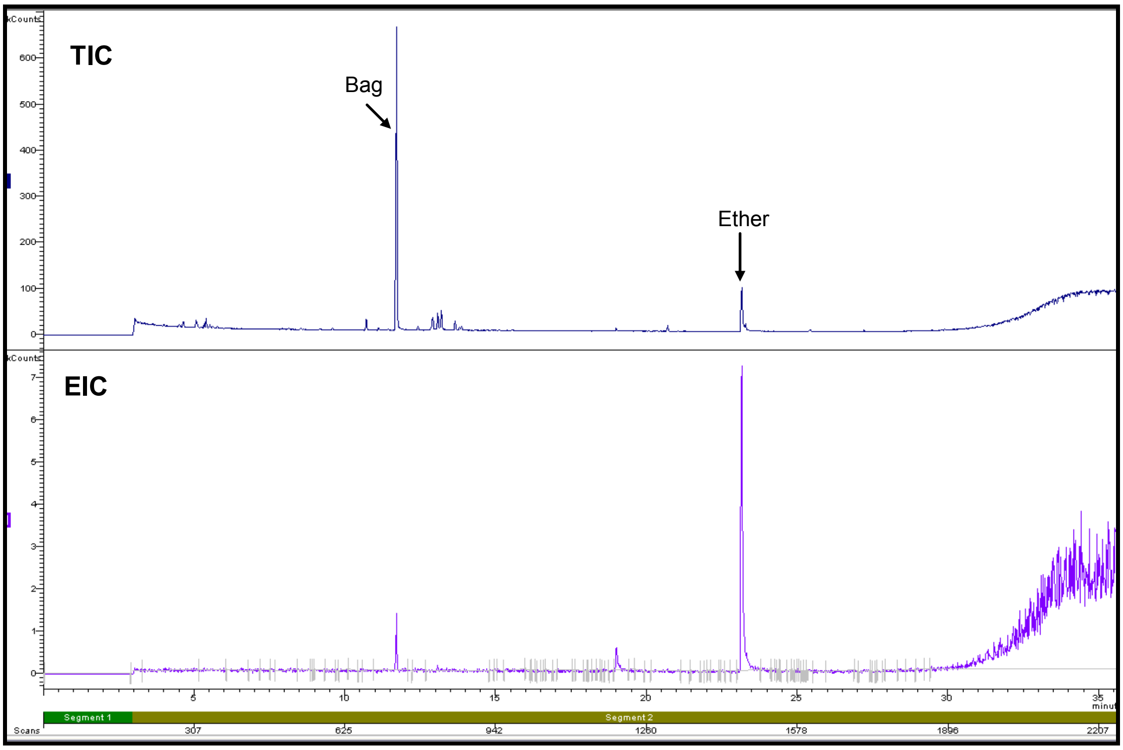


Figure 3.35: Total Ion Chromatogram and Extracted Ion Chromatogram of blank KimWipe (Refer to Section 2.5.1 for GC/MS conditions)

The total ion chromatograms, extracted ion chromatograms and target compound chromatograms for headspace petrol standards at the various evaporation states and volumes are shown below. Figures 3.36 to 3.41 show the headspace petrol standards for the KimWipes spiked with 100µL of unevaporated, 50% and 95% evaporated petrol, respectively. Figures 3.42 to 3.47 show the KimWipes spiked with 10µL of petrol at the same evaporation states as stated previously and Figures 3.48 to 3.53 show the KimWipes spiked with 2µL of the unevaporated, 50% and 95% evaporated petrol.

3.2.2.1 KIMWIPE SPIKED WITH 100µL OF PETROL

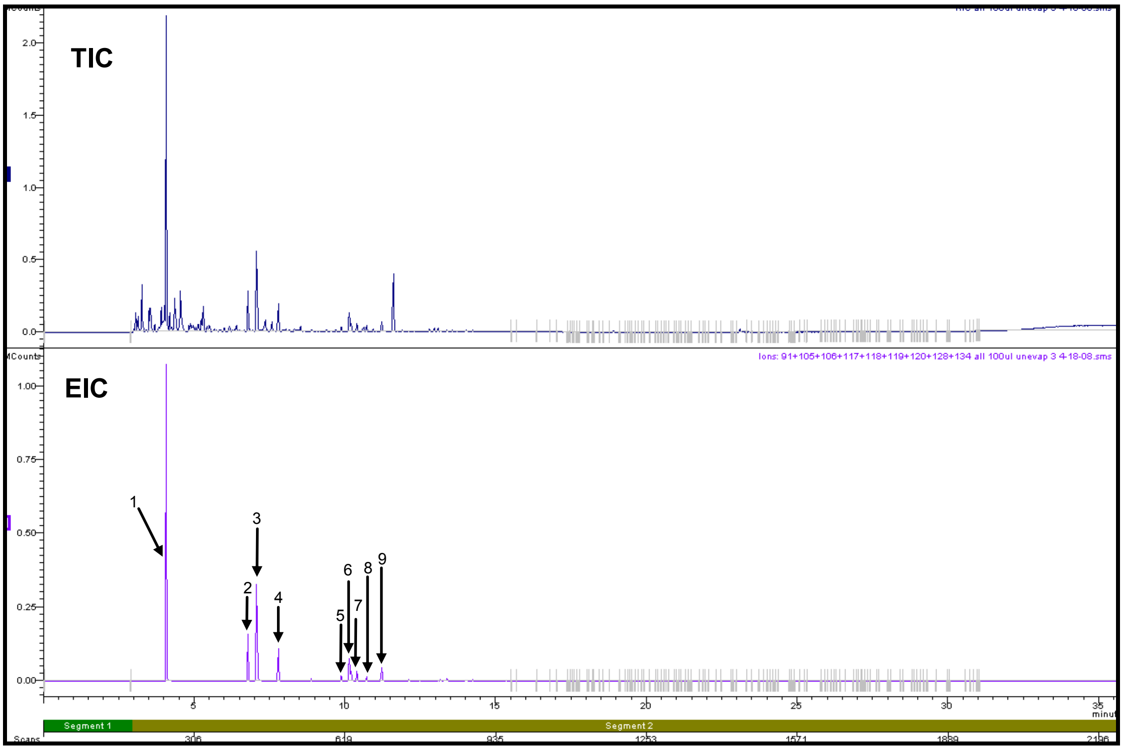


Figure 3.36: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 100µL of Unevaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene

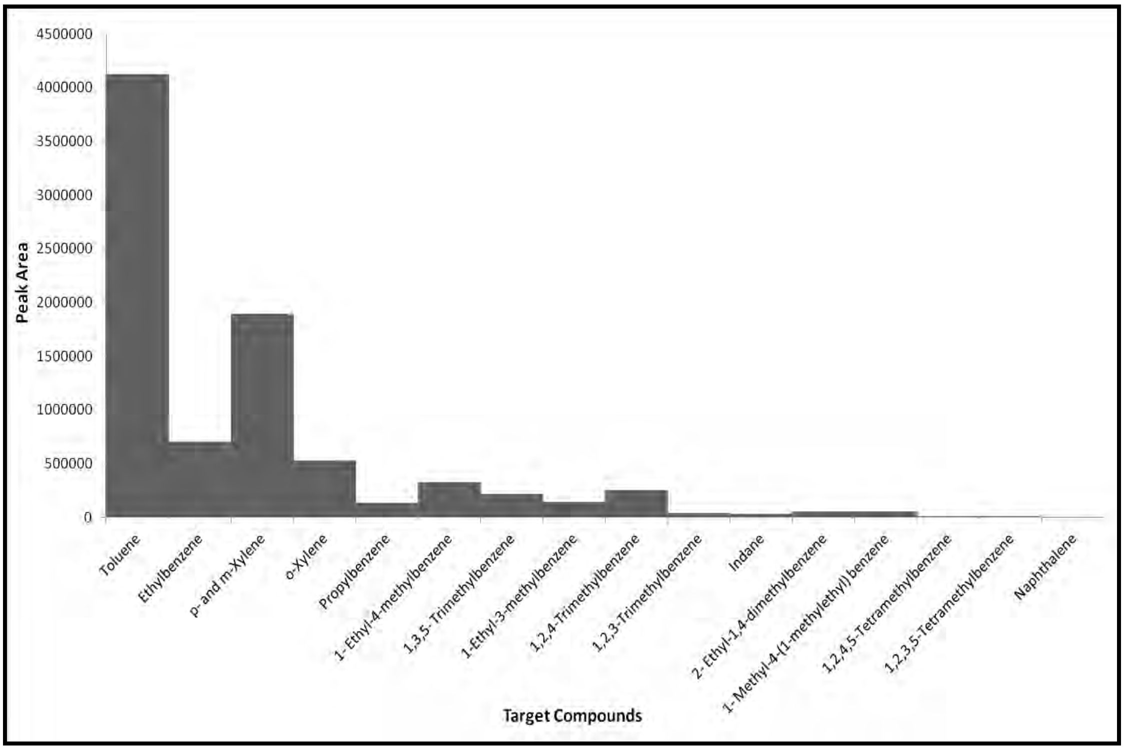


Figure 3.37: Target Compound Chromatogram of KimWipe spiked with 100µL of Unevaporated Petrol

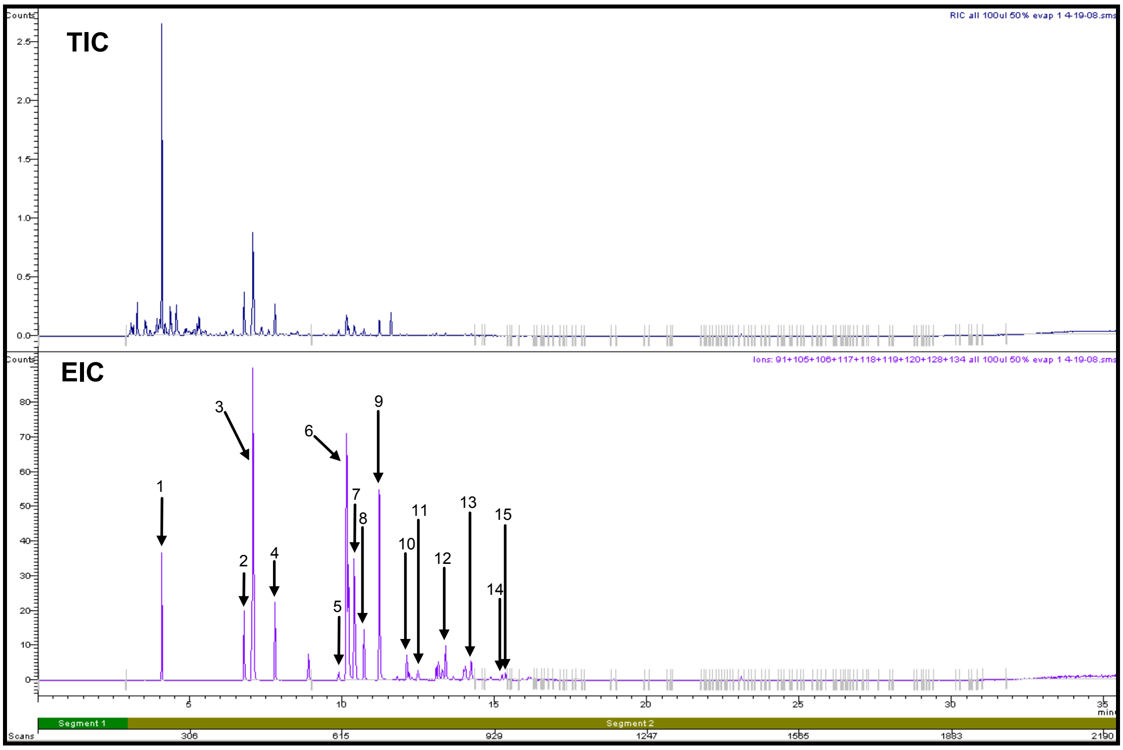


Figure 3.38: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 100µL of 50% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5-Tetramethylbenzene

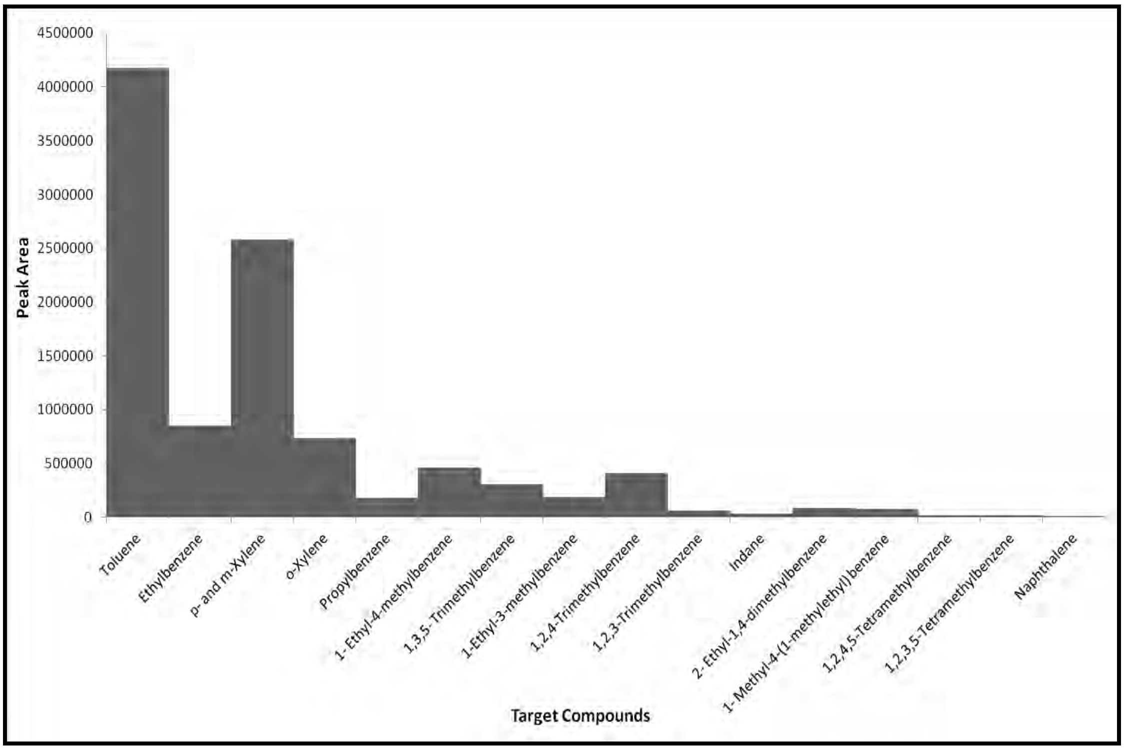


Figure 3.39: Target Compound Chromatogram of KimWipe spiked with 100µL of 50% Evaporated Petrol

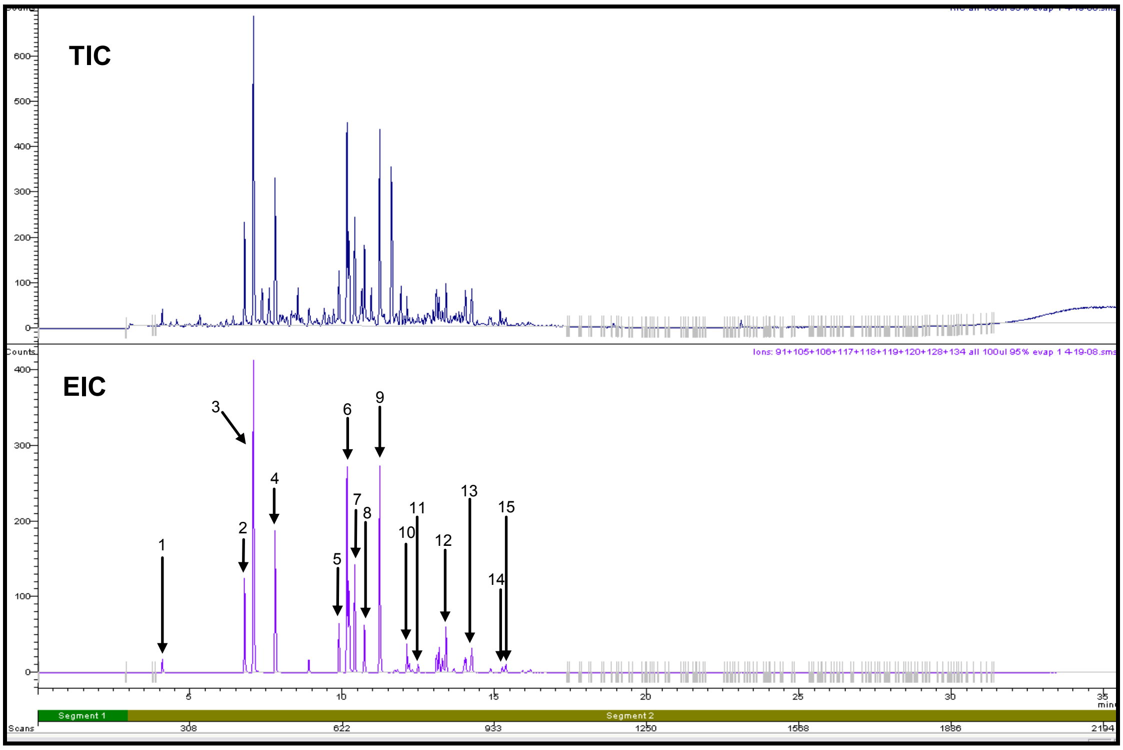


Figure 3.40: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 100µL of 95% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methyl benzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5- Tetramethylbenzene.

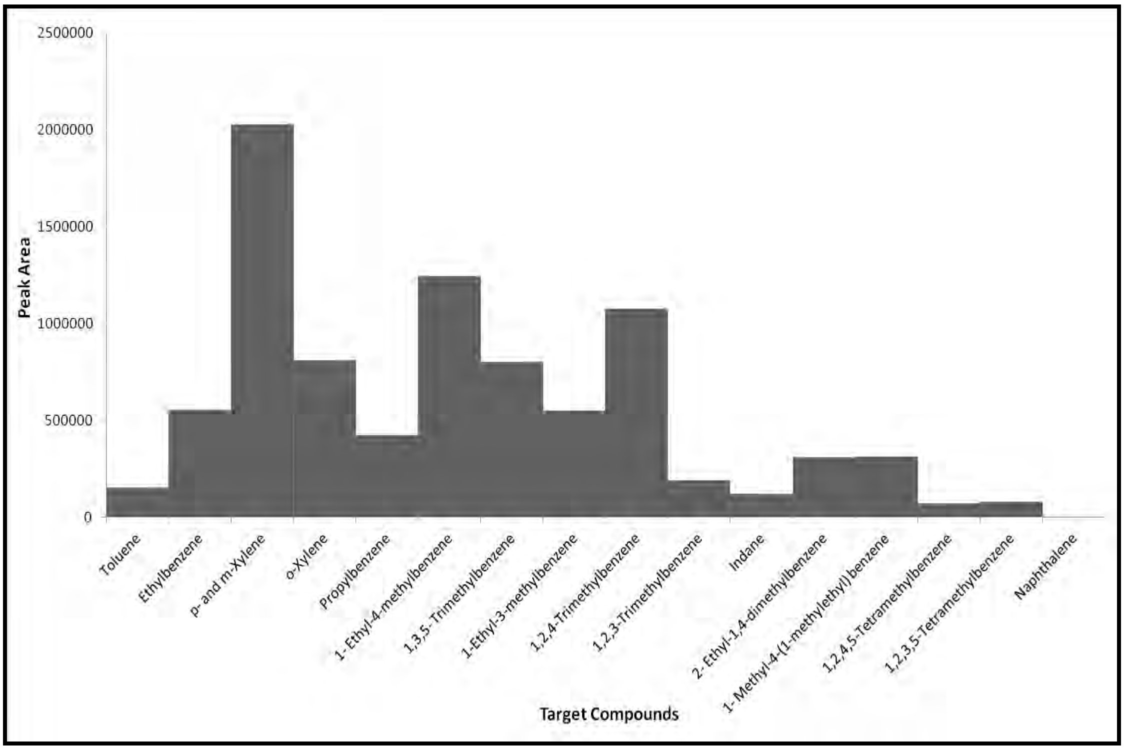


Figure 3.41: Target Compound Chromatogram of KimWipe spiked with 100µL of 95% Evaporated Petrol

3.2.2.2 KIMWIPE SPIKED WITH 10μL OF PETROL

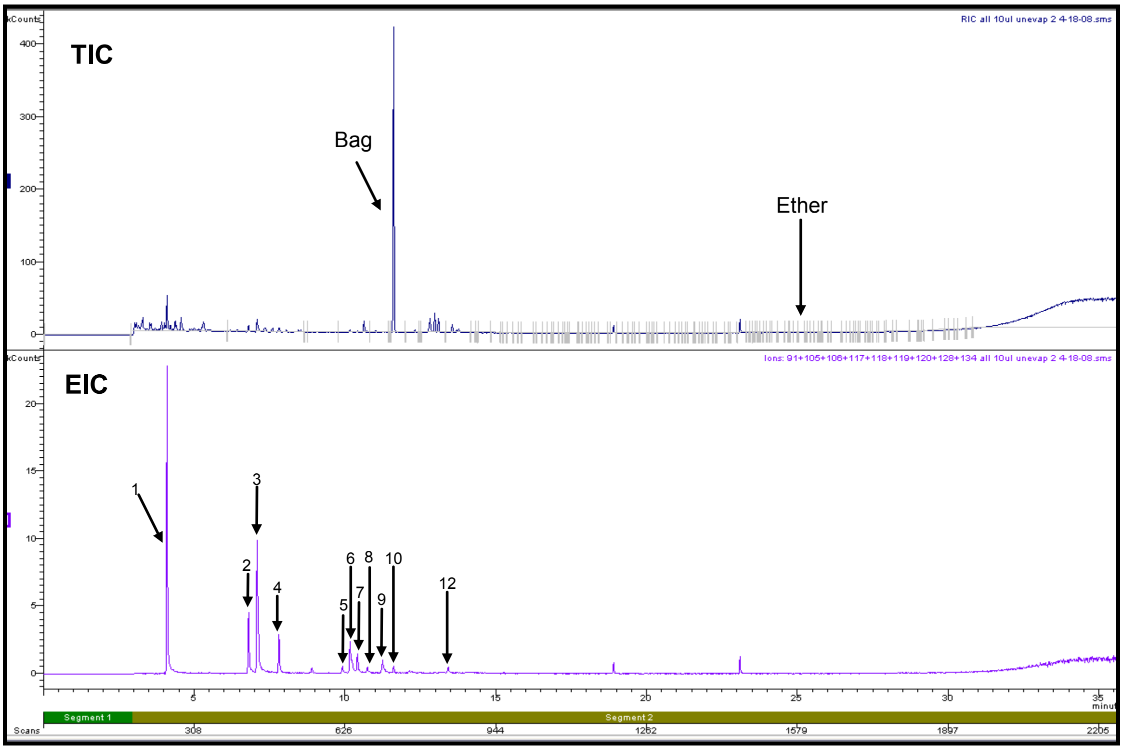


Figure 3.42: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 10μL of Unevaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethyl benzene, 12= 2-Ethyl-1,4-dimethylbenzene

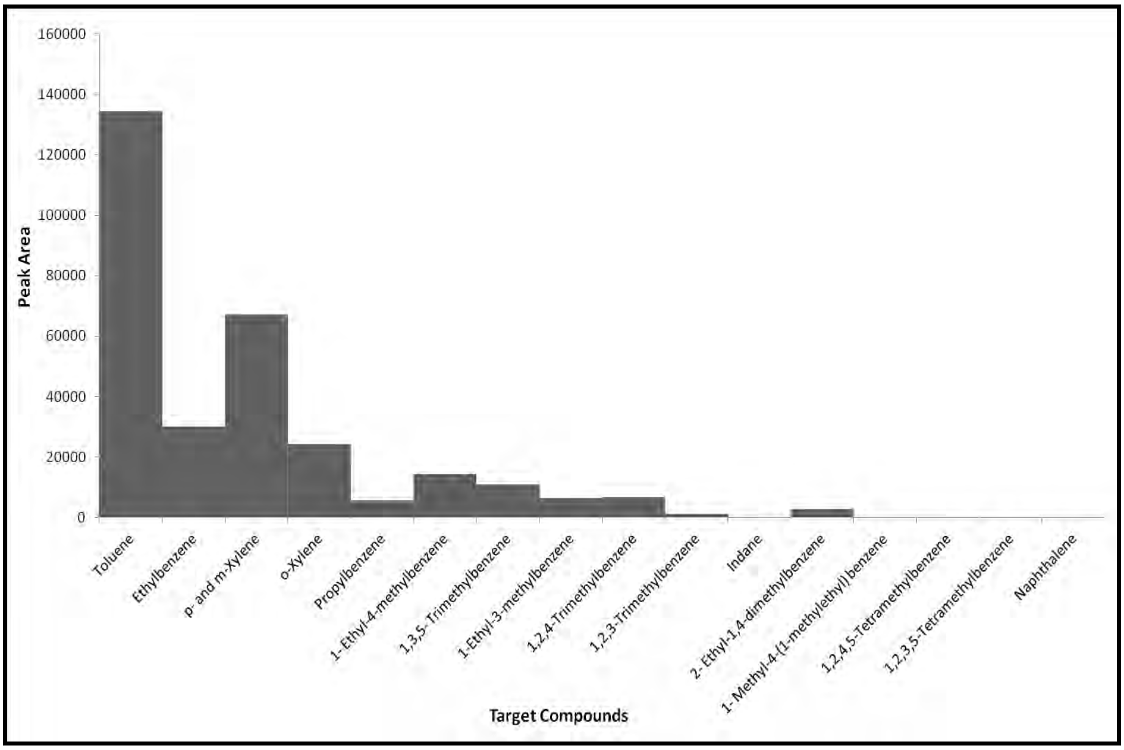


Figure 3.43: Target Compound Chromatogram of KimWipe spiked with 10μL of Unevaporated Petrol

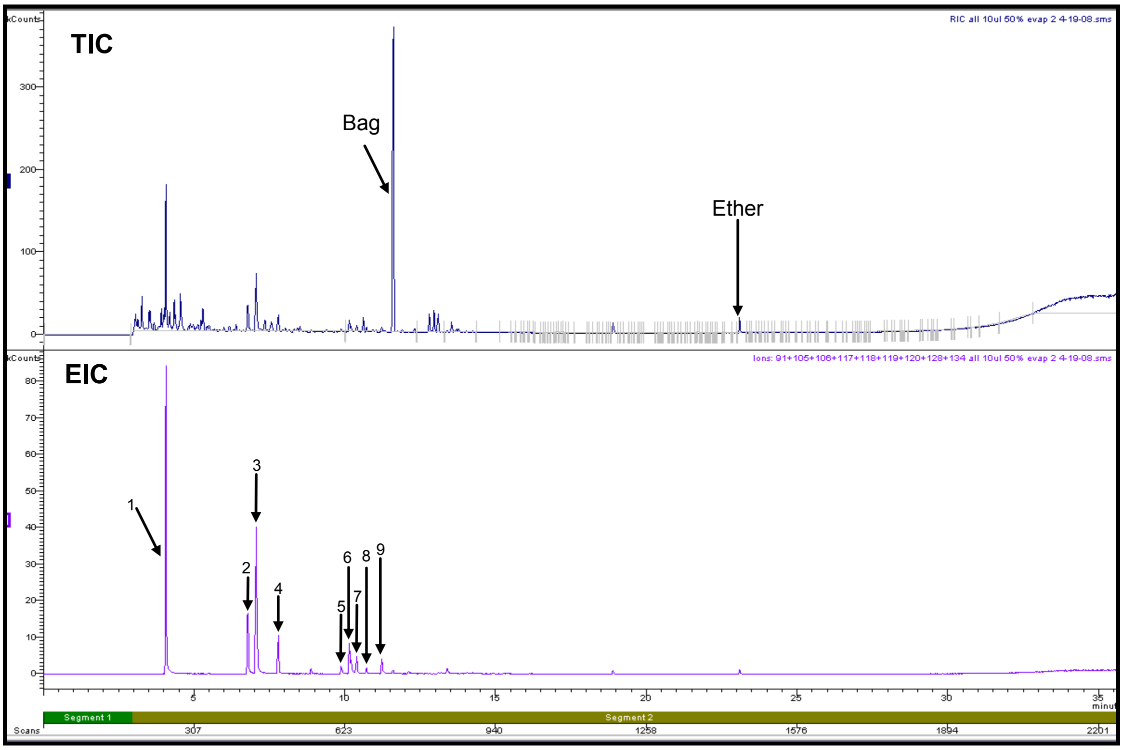


Figure 3.44: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 10µL of 50% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene

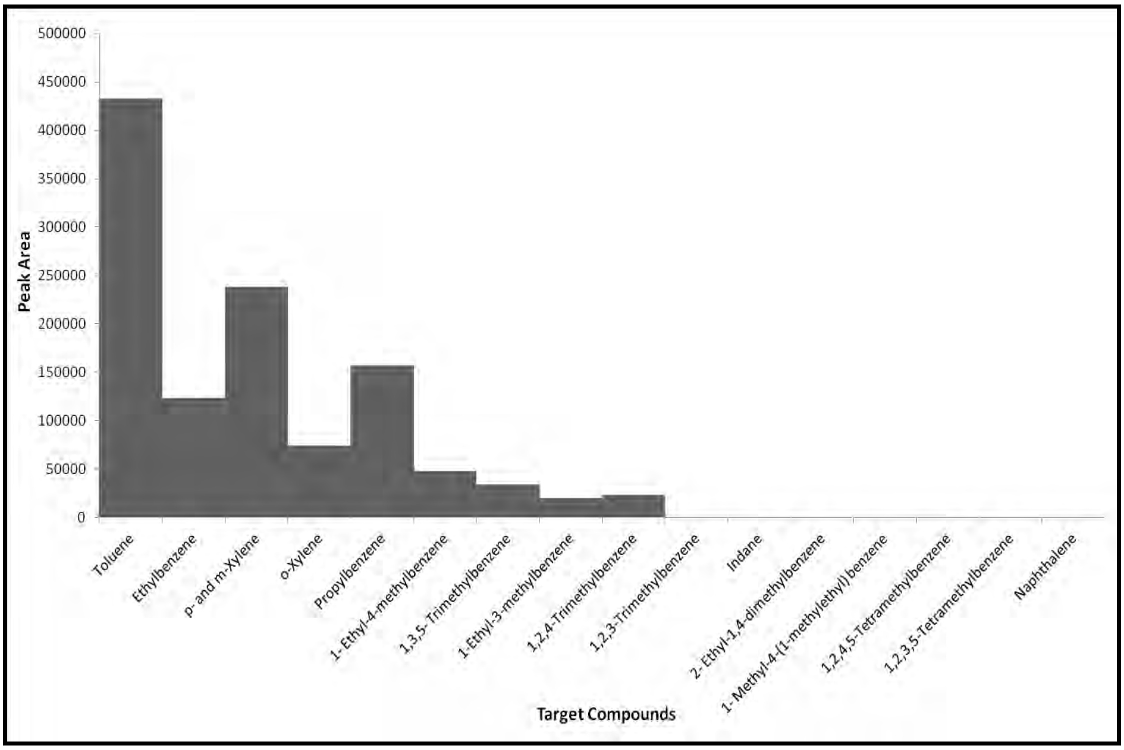


Figure 3.45: Target Compound Chromatogram of KimWipe spiked with 10µL of 50% Evaporated Petrol

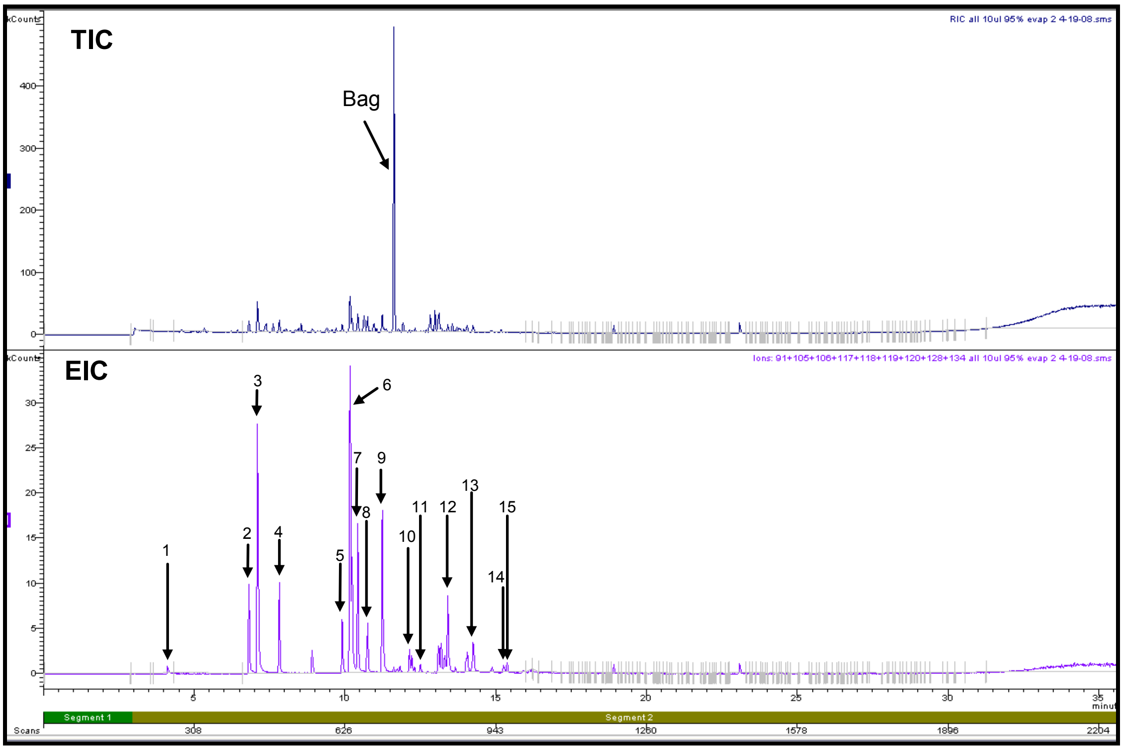


Figure 3.46: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 10µL of 95% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 12= 2-Ethyl-1,4-dimethylbenzene, 13= 1-Methyl-4-(1-methylethyl)benzene, 14= 1,2,4,5-Tetramethylbenzene, 15= 1,2,3,5- Tetramethylbenzene

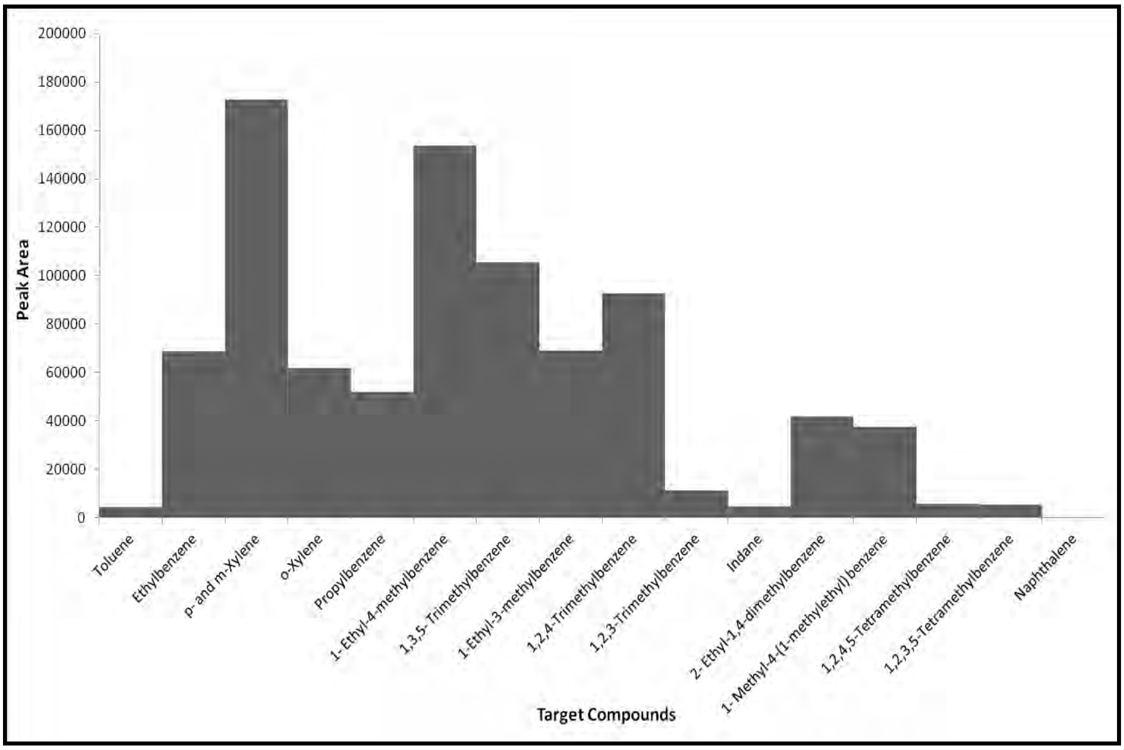


Figure 3.47: Target Compound Chromatogram of KimWipe spiked with 10µL of 95% Evaporated Petrol

3.2.2.3 KIMWIPE SPIKED WITH 2μL OF PETROL

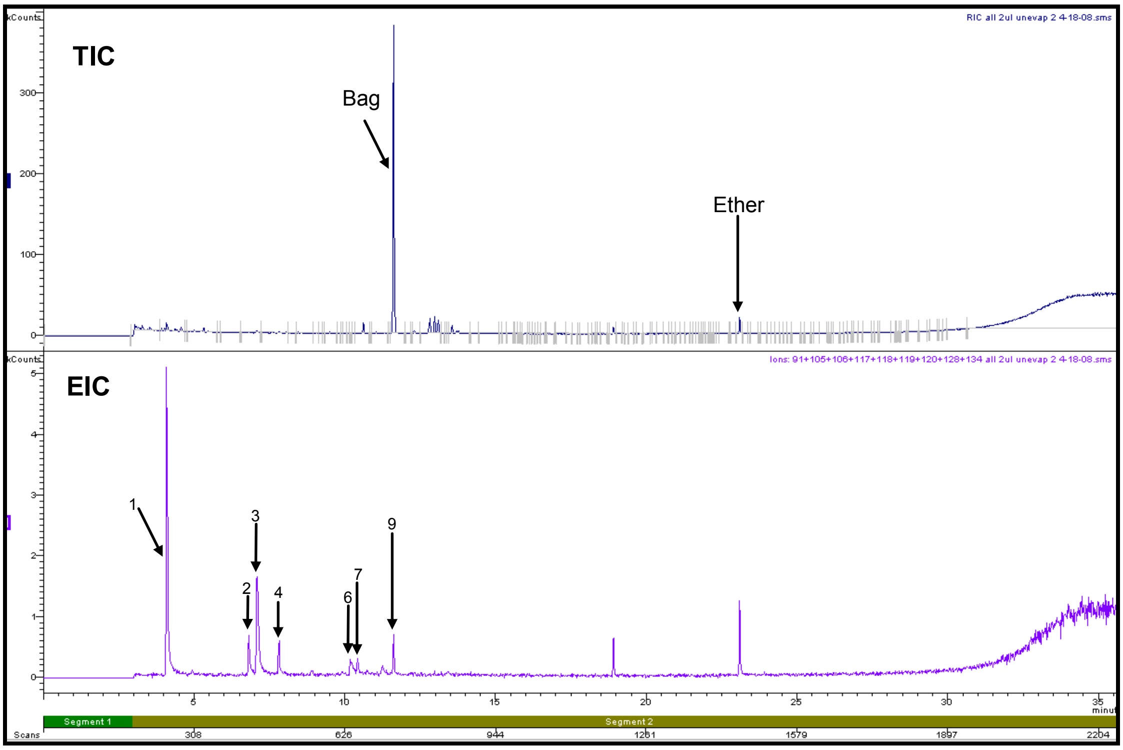


Figure 3.48: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 2μL of Unevaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 9= 1,2,4-Trimethylbenzene

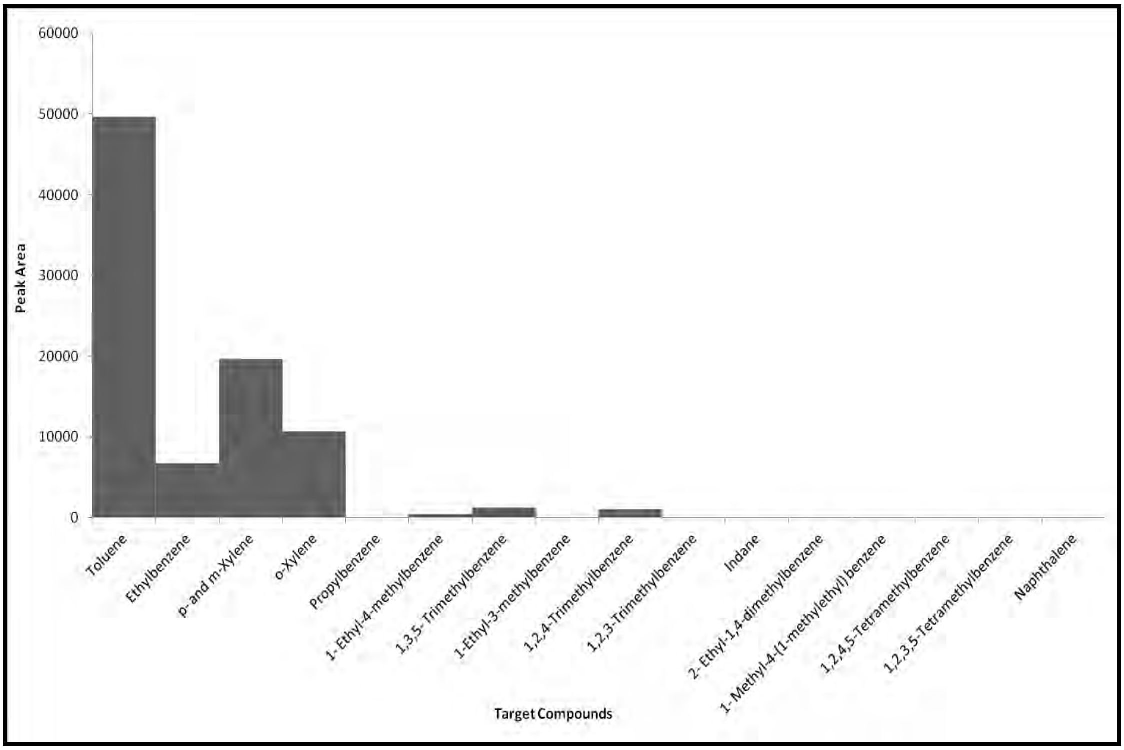


Figure 3.49: Target Compound Chromatogram of KimWipe spiked with 2μL of Unevaporated Petrol

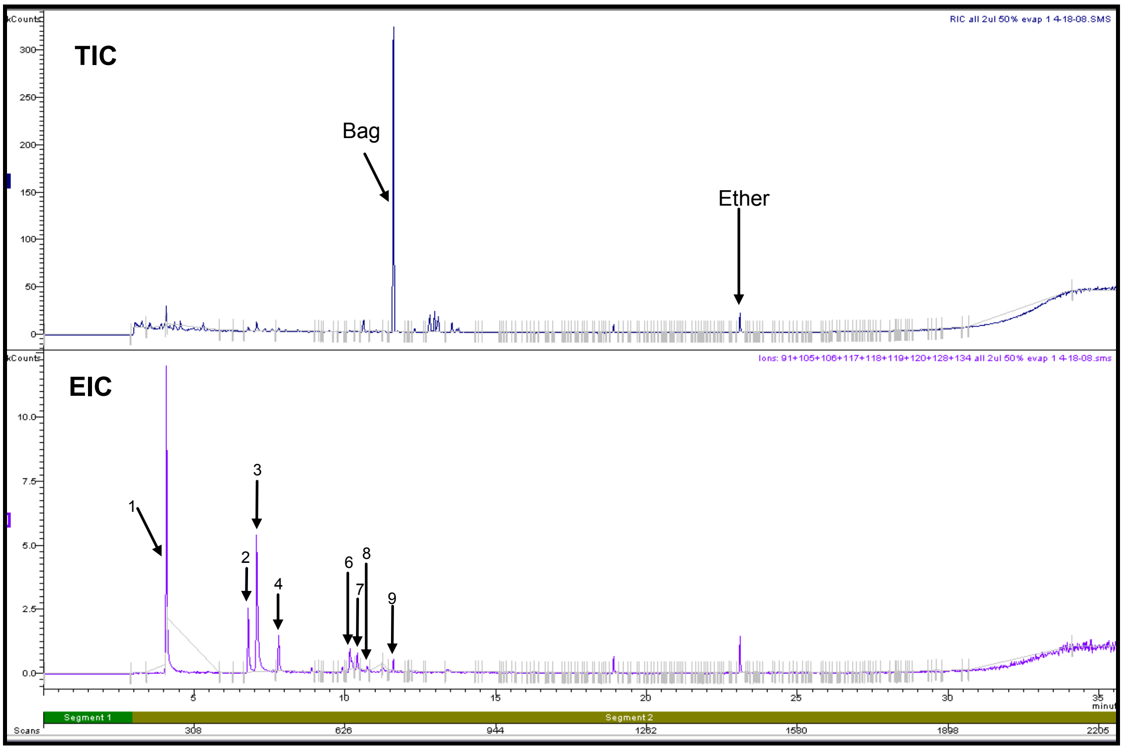


Figure 3.50: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 2μL of 50% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene

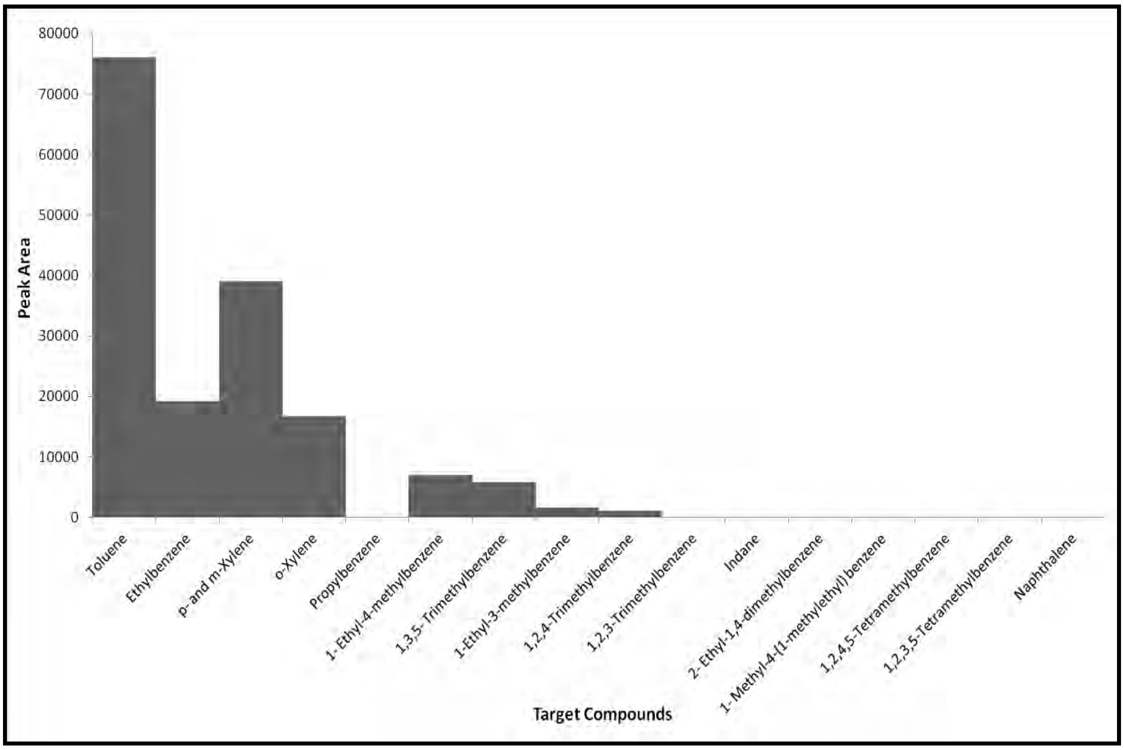


Figure 3.51: Target Compound Chromatogram of KimWipe spiked with 2μL of 50% Evaporated Petrol

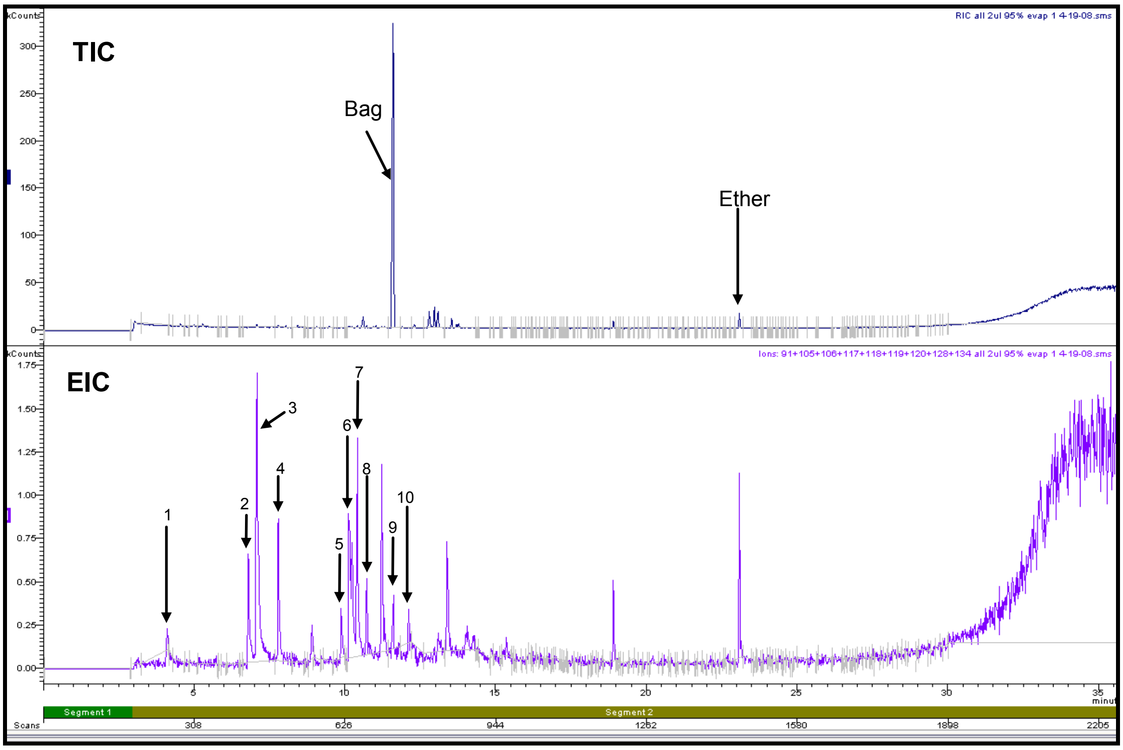


Figure 3.52: Total Ion Chromatogram and Extracted Ion Chromatogram of KimWipe spiked with 2μL of 95% Evaporated Petrol (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4-Trimethylbenzene, 10= 1,2,3-Trimethyl benzene

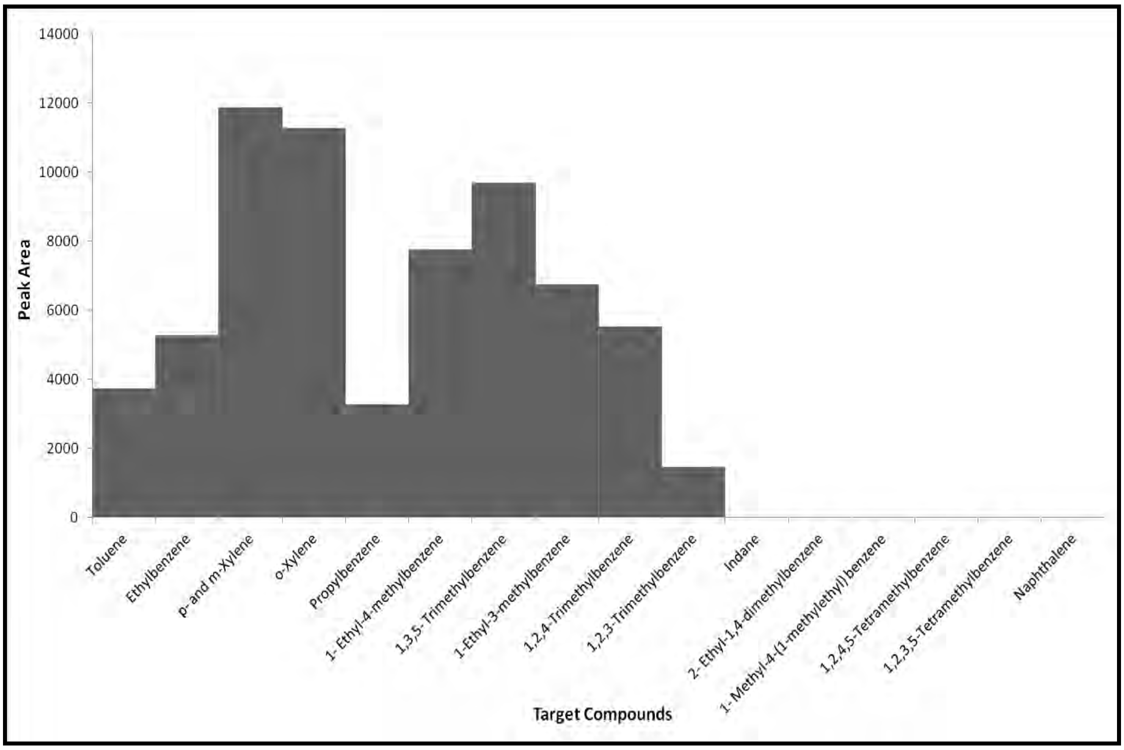


Figure 3.53: Target Compound Chromatogram of KimWipe spiked with 2μL of 95% Evaporated Petrol

3.2.2.4 SUMMARY

The target compound chromatograms produced when spiking the KimWipe with the larger volumes (100µL and 10µL) of unevaporated and 50% evaporated petrol show that the lighter compounds are recovered in much greater amounts when compared to the heavier compounds and this is expected as the heavier compounds would have much lower vapour pressures[45, 76, 79, 80]. The target compound chromatograms for the KimWipes spiked with the larger volumes of 95% evaporated petrol showed naphthalene was the only target compound unable to be recovered. Furthermore, as expected the later eluting peaks shown in the target compound chromatograms for the KimWipes spiked with 95% evaporated petrol are now present in greater abundance relative to the early eluting compounds.

The total ion chromatograms show that for the 2μL headspace standards there is no MS response for the amount of petrol standard injected into the GC that is, only baseline is observed in the total ion chromatogram. For the 10μL headspace standards the total ion chromatogram shows that there is MS response but it is just above baseline. When considering the extracted ion chromatograms and target compound chromatograms there is sufficient MS response to allow a characteristic pattern for toluene, ethylbenzene, xylenes and trimethylbenzenes for all petrol volumes spiked even for the lowest volume of 2μL. Therefore this standard is the limit for pattern comparison and it must be noted that at this level very low amounts of petrol are introduced onto the GC column. Assuming that the entire 2μL spiked onto the KimWipes was recovered onto the charcoal tube and washed into 1mL of diethyl ether, then given the GC conditions used for this study, for a 1μL injection volume and a 50:1 split ratio, only 0.04nL has been injected onto the column.

Although the target compound chromatograms produced by spiking the KimWipes with unevaporated petrol look similar to the target compound chromatograms for the liquid petrol standards, the total compound chromatograms produced by spiking the KimWipes with 50% and 95%

evaporated petrol look considerably different to the target compound chromatograms produced by the liquid standards. This emphasises the importance of subjecting the sample and standards to the same recovery conditions.

3.3 IDENTIFICATION OF CARPET BY INFRARED

Carpet fibre identity was confirmed by FTIR microscopy using a diamond compression cell. Verification of the carpet fibres was performed by FTIR microscopy as it is a rapid and reliable method for analysing fibres because synthetic fibres are able to selectively absorb IR light in a characteristic pattern[9]. FTIR spectrometers with microscope attachments are considered to be standard equipment in a forensic laboratory and are utilised routinely to analyse fibres to determine their class (e.g. nylon, acrylic)[9, 155, 156]. Furthermore, the IR data obtained can also provide identification of the fibres subgeneric class or polymer composition (e.g. nylon 6,6)[155, 156].

The FTIR analysis of each of the fibre types was performed as described in Section 2.6. The FTIR spectrum obtained for each of the carpet fibres was initially compared to the instrument's library database and then to the IR spectra of the yarn standards supplied by Godfrey Hirst Pty Ltd.

3.3.1 NYLON FIBRES

Nylon is the generic name referring to a series of man-made synthetic polymers known as polyamides[157, 158]. There are a number of nylons available, however nylon 6 and nylon 6,6 are the mostly widely manufactured[49, 157]. Both types of nylon are used to make clothing with nylon 6 also being used to make bristles for toothbrushes, ropes, nets and bags whereas nylon 6,6, is predominately used as carpet fibres[49].

The structures of nylon 6 and nylon 6,6 can be seen in Figures 3.54 and 3.55, respectively. Nylon 6 was developed after nylon 6,6 with the intention of mimicking the physical properties of nylon 6,6 without violating the patent.

Hence, the physical properties of nylon 6 and nylon 6,6 are quite similar even though their chemical structures are not.

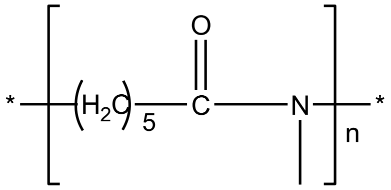


Figure 3.54: Structure of Nylon 6

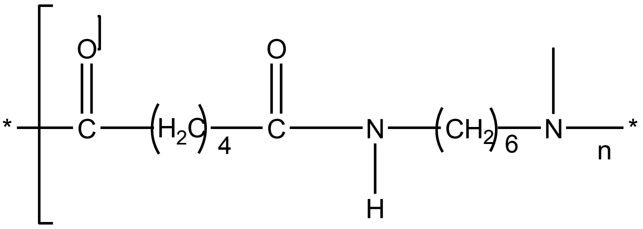


Figure 3.55: Structure of Nylon 6,6

Nylon carpet fibres and fibres from the nylon yarn standards (1 and 2 ply) were subjected to FTIR microscopy. The spectra are shown in Figures 3.56 to 3.59. The IR spectra of the nylon carpet fibres matched those of the nylon yarn standards as well as the instrument library spectra of nylon. Therefore the nylon carpet was positively identified as nylon.

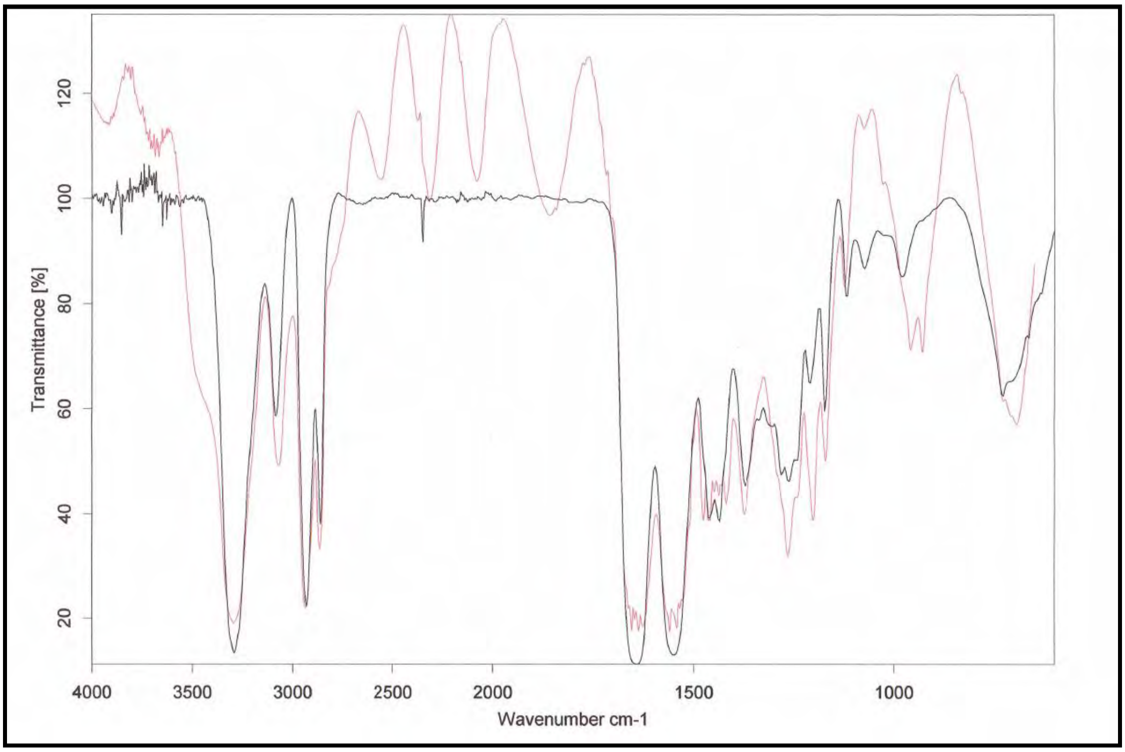


Figure 3.56: FTIR Spectra of the Carpet Sample (red) compared with Library Spectra of Nylon (black)

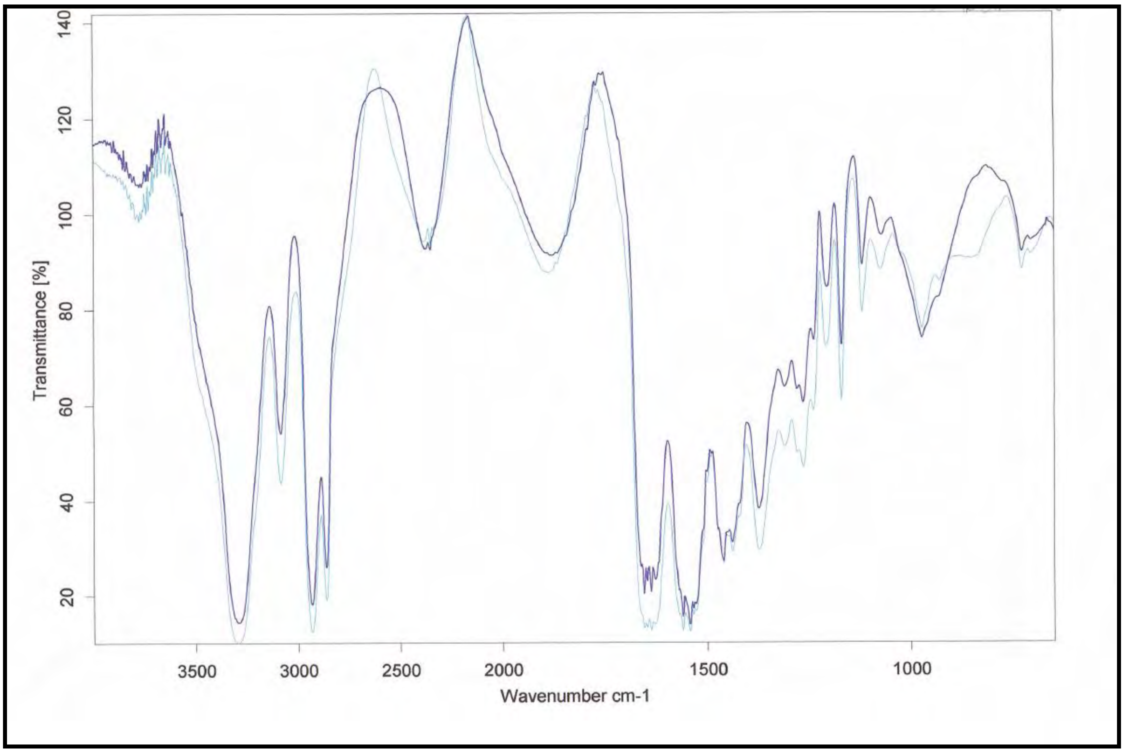


Figure 3.57: FTIR Spectra of 1 ply 100% Dyed Nylon Standard (dark blue) compared with 2 ply 100% Dyed Nylon Standard (light blue)

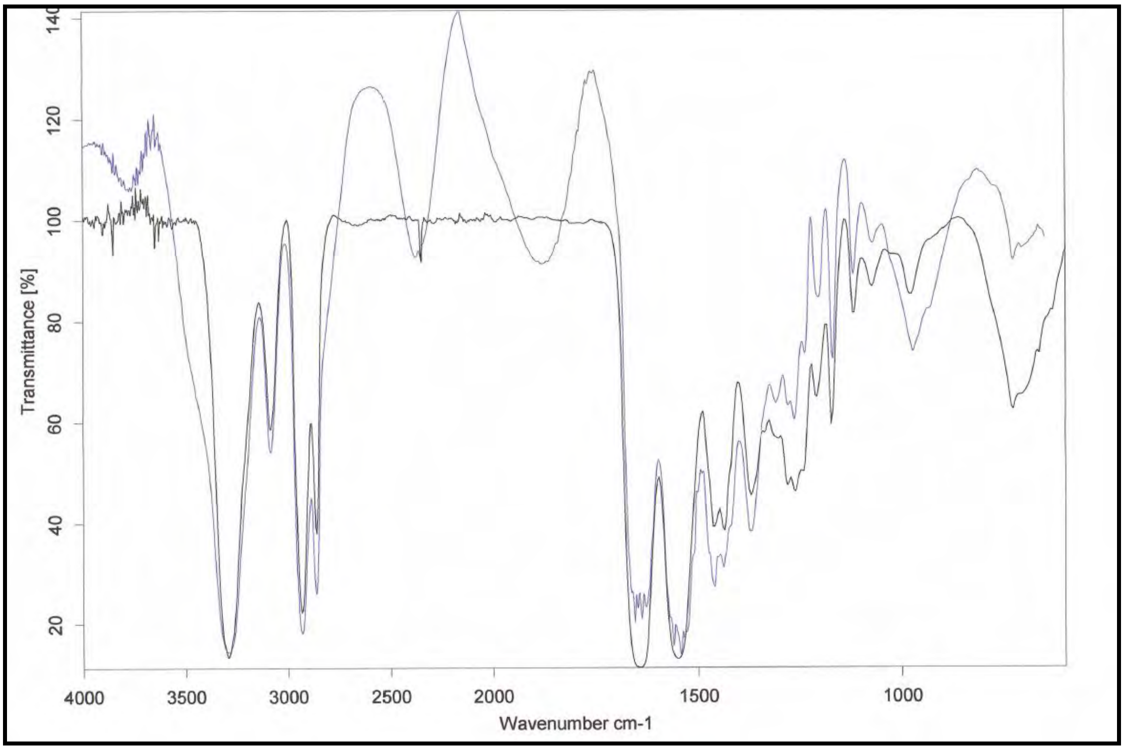


Figure 3.58: FTIR Spectra of the 1 ply 100% Dyed Nylon Standard (dark blue) compared with Library Spectra of Nylon (black)

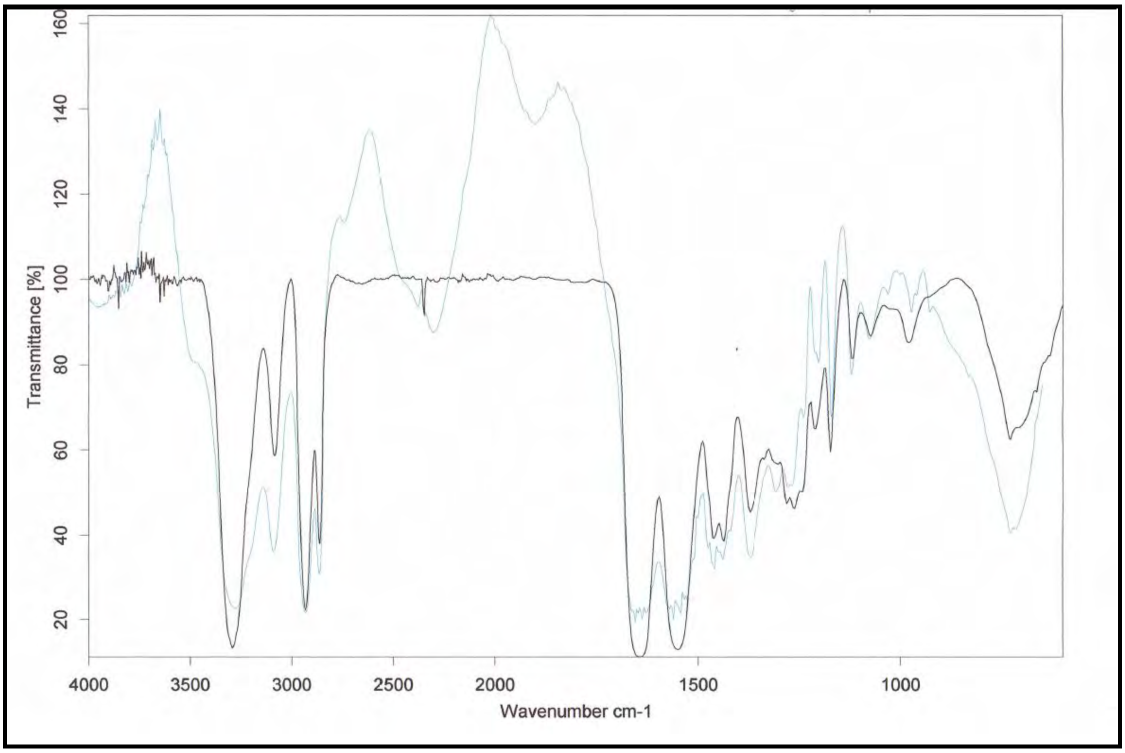


Figure 3.59: FTIR Spectra of the 2 ply 100% Dyed Nylon Standard (light blue) compared with Library Spectra of Nylon (black)

3.3.2 WOOL FIBRES

Wool is a natural fibre that comes, most commonly, from sheep, however wool can also come from other animals including lamas, alpacas, cashmere goats and in some cases camels. The wool from Godfrey Hirst Pty Ltd is sourced from sheep and is composed of the protein keratin as well as small amounts of fat, calcium and sodium[157, 159].

The FTIR microscope's library database did not contain a spectrum of wool and as such a direct comparison between the wool carpet fibres and the library was unable to be attained. However the spectra obtained for the wool carpet fibre from the sample matched that of the wool yarn standard, as shown in Figure 3.60 and as such was confirmed to be wool.

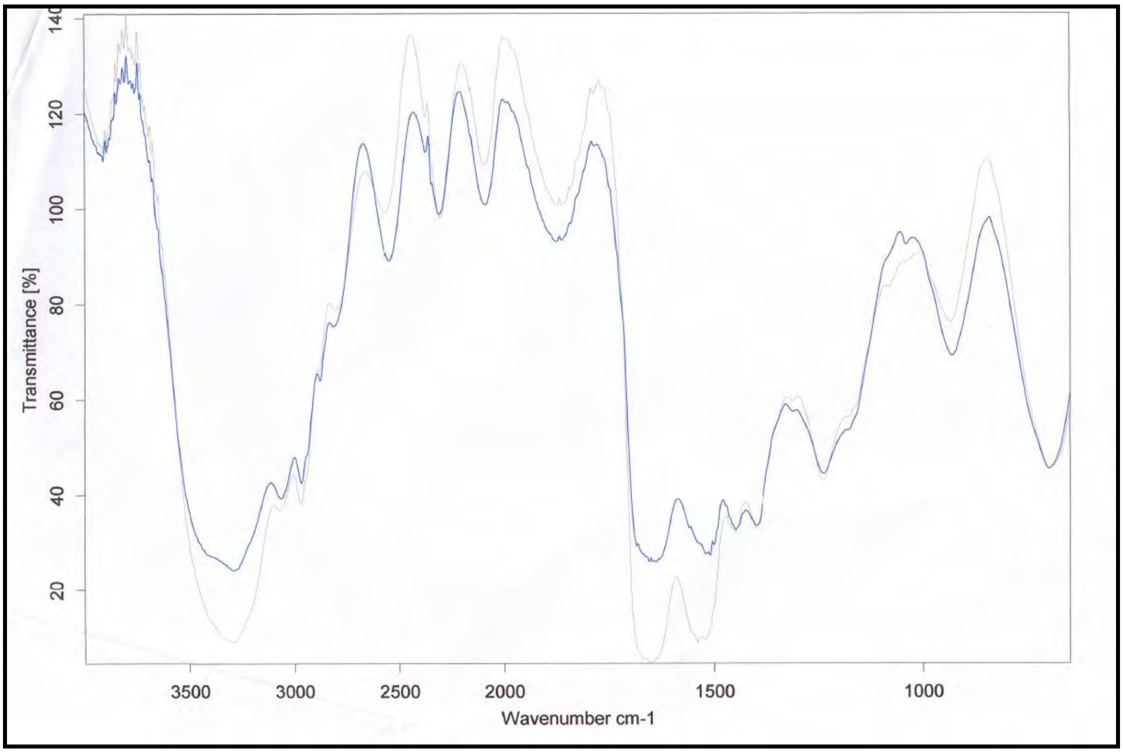
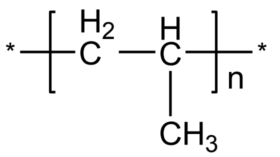


Figure 3.60: FTIR Spectra of Wool Standard (grey) compared with Wool Carpet Fibres (blue)

3.3.3 POLYPROPYLENE FIBRES

Polypropylene polymers are polymerised from propylene which is a petroleum based compound, the structure of polypropylene is presented in Figure

3.61[155]. Polypropylene is an extremely versatile polymer which is commonly used as a plastic and as a fibre. The use of polypropylene in carpet has increased significantly over the past decade as polypropylene is extremely resistant to stains and will not absorb water[143].



$$*-\left[\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right]_n-*$$

Figure 3.61: Structure of Polypropylene

Polypropylene carpet fibres and fibres from the polypropylene yarn standard (1 ply) were subjected to FTIR microscopy. The spectra are shown in Figures 3.62 to 3.63. In both cases the spectra matched and also matched that of the instrument's library database and as such were identified as polypropylene.

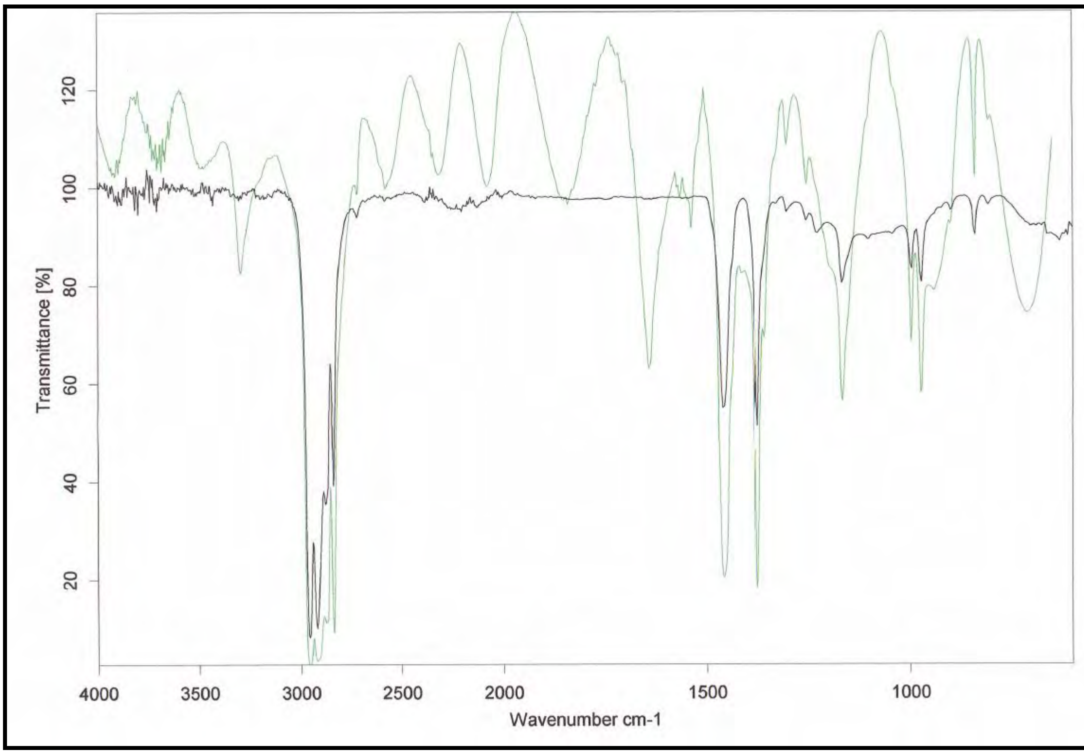


Figure 3.62: FTIR Spectra of Polypropylene Carpet Sample (green) compared with Polypropylene from Library (black)

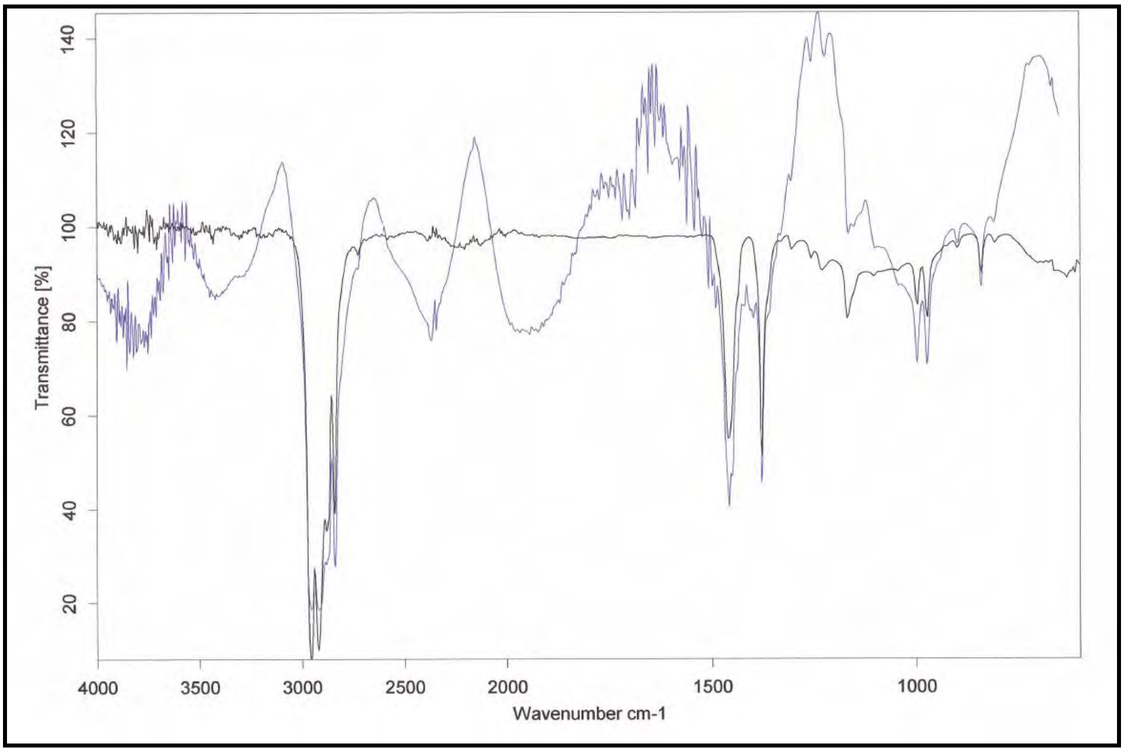


Figure 3.63: FTIR Spectra of 1 ply 100% Polypropylene Standard (blue) compared with Polypropylene from Library (black)

3.3.4 50-50 POLYPROPYLENE-WOOL FIBRES

The 50-50 polypropylene-wool carpet contained alternating rows of black and beige carpet fibres. Therefore, an FTIR spectrum was obtained for both the black and the beige fibres to determine their identity and as can be seen in Figure 3.64 the fibres were different.

The black fibre produced an FTIR spectrum similar to that produced by the wool and when compared to the wool yarn standard (see Figure 3.65) it was shown to be wool. The beige fibre produced a spectra similar to polypropylene and when compared to the polypropylene yarn standard (see Figure 3.66) it was shown to be polypropylene.

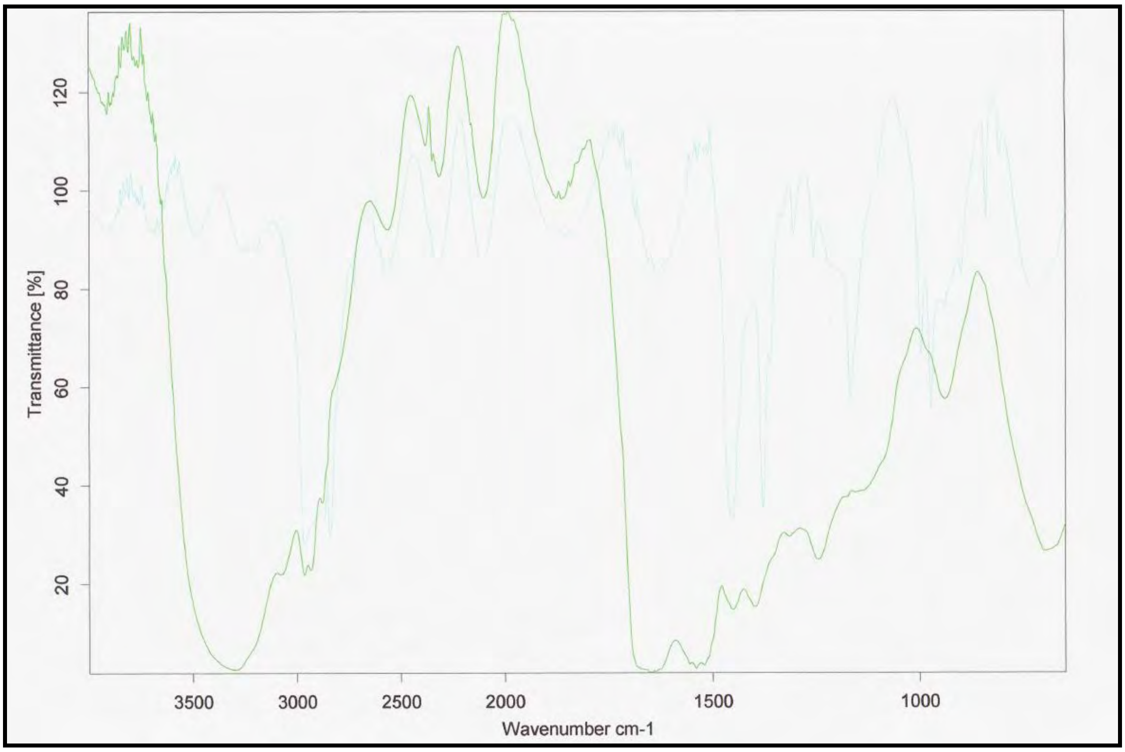


Figure 3.64: FTIR Spectra of Black Carpet Fibre (green) compared with Beige Carpet Fibre (blue)

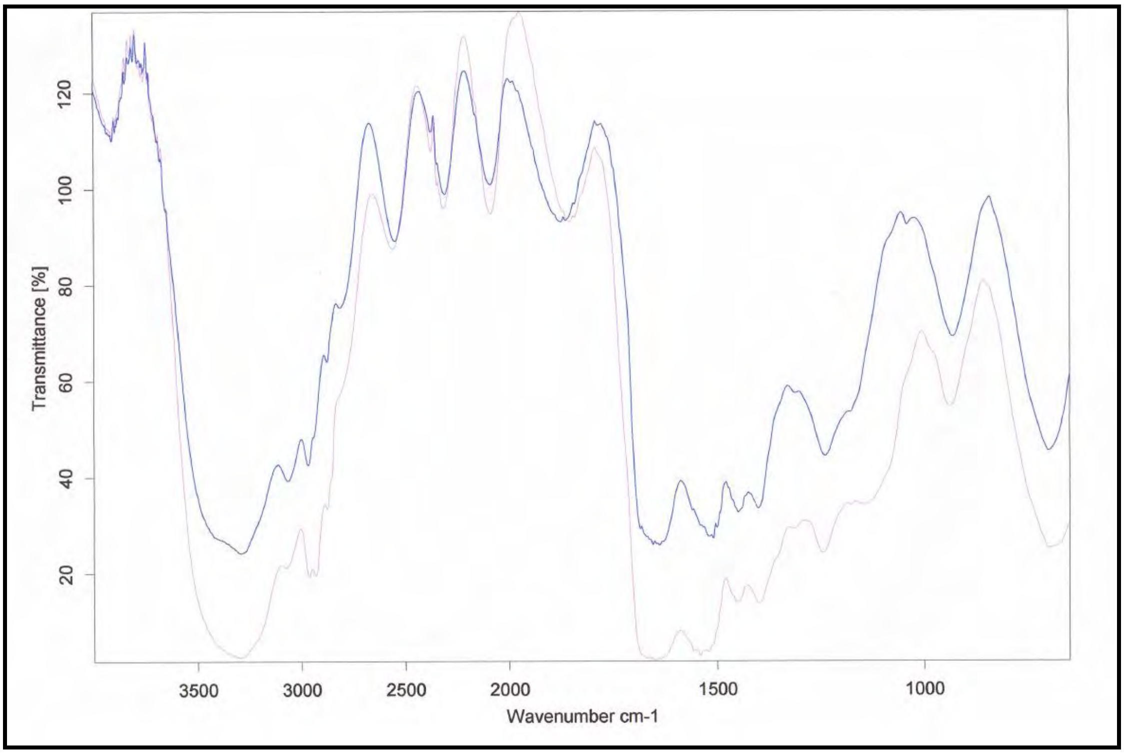


Figure 3.65: FTIR Spectra of Black 50-50 Carpet Fibre (pink) compared with Wool Standard (blue)

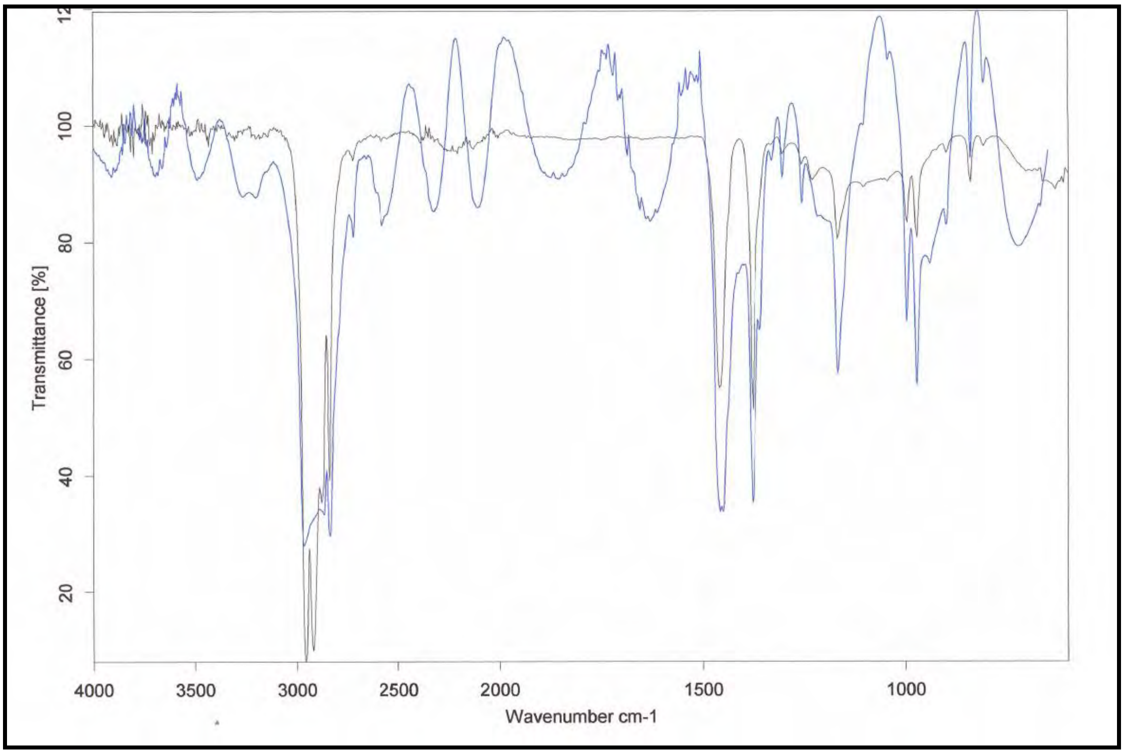


Figure 3.66: FTIR Spectra of Beige Carpet Fibre (blue) compared with the Polypropylene from Library (black)

3.4 PRELIMINARY STUDIES FOR PYROLYSIS

A number of preliminary studies were conducted for the pyrolysis experiments, two parameters of particular importance were optimised prior to conducting the pyrolysis experiments, these included, sample size and pyrolysis pressure. The details of these are as follows:

3.4.1 SAMPLE SIZE

Pyrolysis GC requires very small samples so it was important to optimise sample size in order to produce pyrograms which displayed good chromatography with respect to peak shape and resolution. Effect of sample size was initially trialled using a polystyrene cup. The first sample taken was the thickness of the cup and the chromatograms displayed overloaded peaks. To further reduce sample size, a section of polystyrene cup had its thickness reduced by a third using a scalpel and again the chromatogram of this sample displayed overloaded peaks. To further reduce sample size the thickness of the sample was further reduced to approximately one tenth of the original size and the GC split ratio was increased from 50:1 to 100:1. The pyrogram for this sample, shown in Figure 3.67, displayed excellent chromatography.

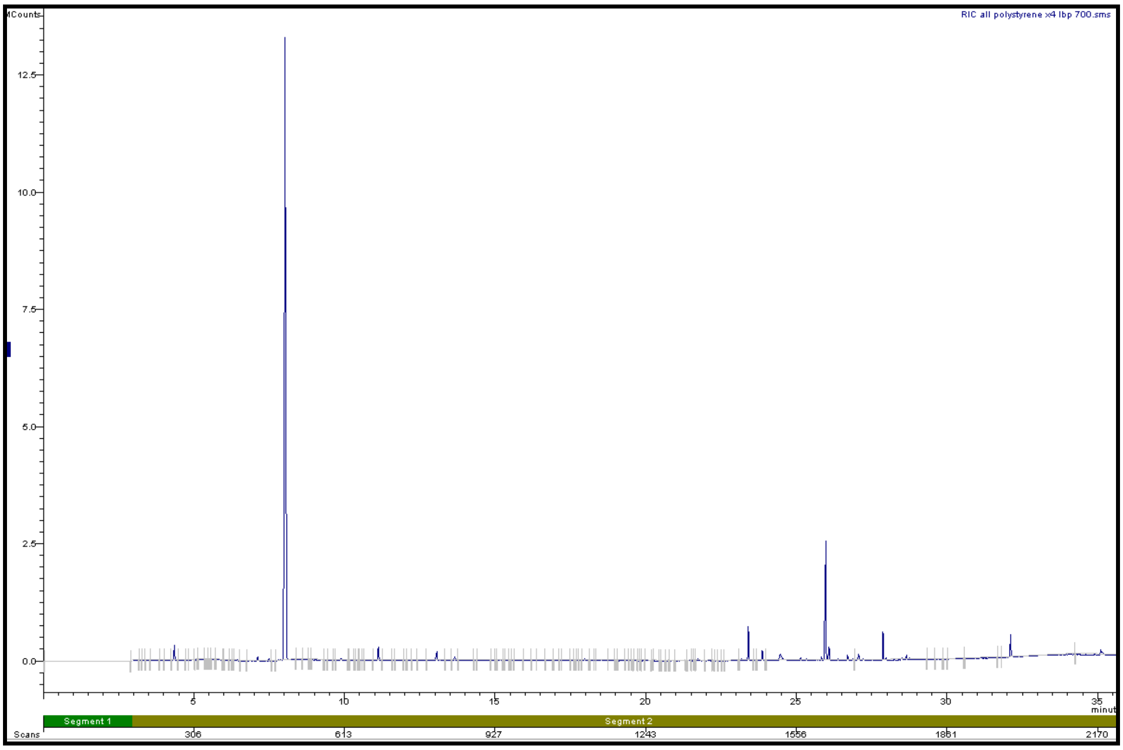


Figure 3.67: Pyrogram of Thin Piece of Polystyrene Pyrolysed at 700°C with Split Ratio Increased to 100:1 (Refer to Section 2.5.1 for GC/MS conditions)

3.4.2 PYROLYSIS PRESSURE

The Pyrojector™ was plumbed to a separate Helium cylinder than the gas chromatograph to ensure that both the Pyrojector™ and gas chromatograph were independent of each other and therefore allowed for the monitoring of the flow through the Pyrojector™. The optimisation of pyrolysis pressure was conducted using polystyrene from a polystyrene cup. A slither of polystyrene was sliced from the cup (approximately 0.5mm thick) and a small sample taken using the tubular cutter and introduced into the Pyrojector™.

The Pyrojector™ manual recommends Pyrojector™ pressure to be set at 5psi above GC column head pressure as this ensures that the residence time of the sample in the Pyrojector™ is enough to produce sufficient pyrolysis of the sample, with minimal secondary pyrolysis and also to produce good chromatography. The Pyrojector™ pressures investigated included 12, 17, 22 and 27 psi. Table 3.5 shows the GC and Pyrojector™ conditions at the various Pyrojector™ pressures investigated. When Pyrojector™ pressure is higher than that of the GC column head pressure the GC split flow changes, due to more gas entering the GC.

Table 3.5: Gas Chromatograph and Pyrojector™ Conditions

Pyrojector™ Conditions		GC Conditions			
Pressure (psi)	**Purge Flow (mL/min @ 600°C)**	**Column Head Pressure (psi)**	**Column Flow (mL/min @ 35°C)**	**Septum Purge Flow (mL/min)**	**Spilt Flow (mL/min)**
Not Connected to GC		17	1.2	3	50
12	5	17	1.2	3	50
17	5	17	1.2	3	50
22	5	17	1.2	3	76
27	5	17	1.2	3	106

The pyrogram for 22 psi is shown in Figure 3.68 and shows a styrene monomer at 8.24 minutes, styrene dimer at 25.97 minutes and the trimer at 32.13 minutes, respectively. The pyrograms for the 17 and 27 psi were similar to that for the 22 psi (Figure 3.68). However the pyrogram for 12 psi showed no visible styrene peak indicating there was not enough gas pressure present to keep the pyrolyser pressurised and transfer pyrolysis products into the GC. It was decided to use a Pyrojector™ pressure of 22 psi, (5 psi above GC column head pressure), confirming manufacturers recommendation for pyrolysis studies as at this pressure the Pyrojector™ gas flow was sure to enter the GC injector (as confirmed by the increase to GC split flow) and the results from the pyrolysis of polystyrene showed good chromatography.

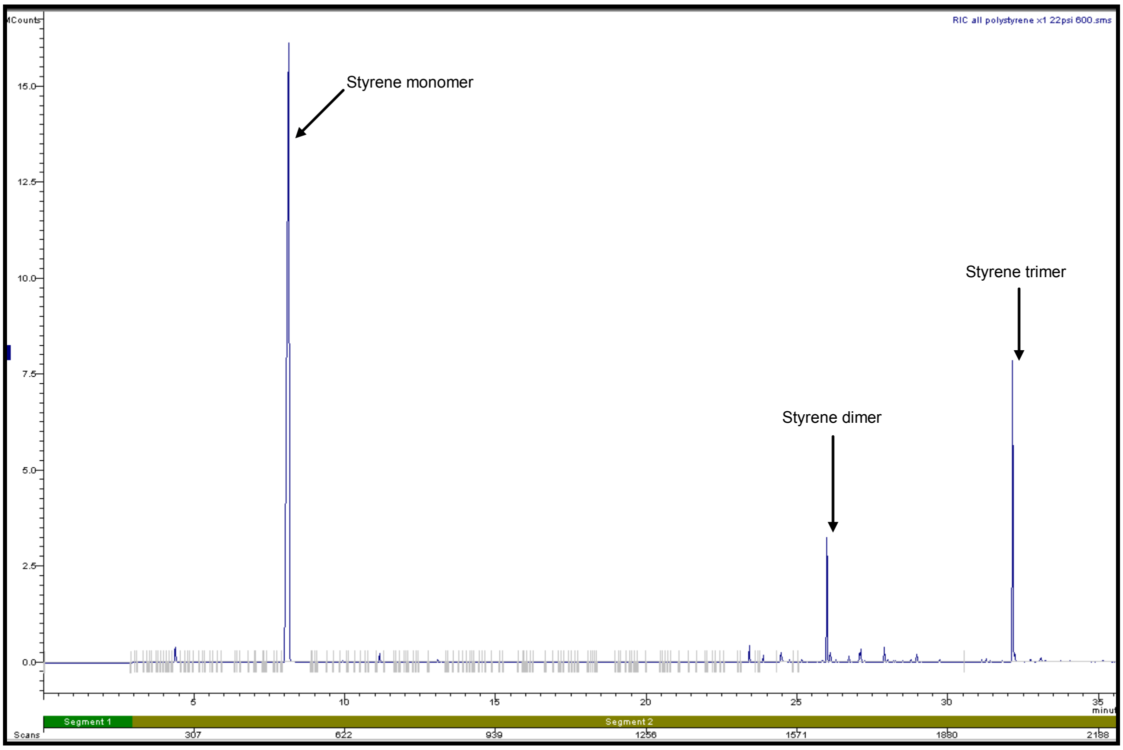


Figure 3.68: Pyrogram of Polystyrene Pyrolysed at 600°C at 22psi (Refer to Section 2.5.1 for GC/MS conditions)

3.5 FIRE TEMPERATURE STUDIES FOR PYROLYSIS EXPERIMENTS

The temperatures required for the pyrolysis experiments were determined after a series of controlled burns were conducted in collaboration with the Country Fire Authority (CFA) at their training college in Fiskville, Victoria, Australia. The aims of these burns were to conduct real fires using different room settings, fuel loads, ignition methods and amounts of ignitable liquid to enable temperature data to be collected throughout the course of the fire, from pre-ignition to extinguishment. Temperature data was collected at floor level given that carpet is laid on the floor.

These controlled burns were conducted on two separate occasions, with each of the burns consisting of three separate room fires. Each fire was conducted in a concrete room that has been specifically designed for this purpose (see Figure 2.3). The fires were ignited, monitored and extinguished with water once flashover was achieved by qualified CFA fire fighters.

Temperature data was collected at three levels in each of the rooms; just above the carpet fibres (10mm), between the carpet and the underlay and on the concrete slab. It was of interest to collect temperature data at all three levels to observe the temperature profile experienced by both the carpet and underlay during a fire. Thermocouples, as described in Section 2.7.1, were used to collect temperature readings throughout the fire. Figures 3.69 to 3.71 show the thermocouples placed on the concrete below the underlay (secured with aluminium tape), the thermocouple placed between the carpet and underlay (also secured with aluminium tape) and the thermocouple placed 10mm above the carpet fibres which was secured in place by a stainless steel plate, respectively. To ensure that the data was collected within the same vicinity in the room, the thermocouples were placed directly above each other.

Figure 3.69: Thermocouple placed on Concrete

Figure 3.70: Thermocouple placed between Underlay and Carpet

Figure 3.71: Thermocouple placed 10mm above Carpet Fibres

3.5.1 ROOM FIRES – FIRST SERIES

The first series of fire experiments were conducted to enable temperature data to be collected in three different room scenarios. In Figures 3.73, 3.75 and 3.77, the temperature profiles referred to as top, mid and bottom refer to the thermocouples placed above the carpet, between the carpet and the underlay and at concrete level, respectively. Ambient temperature was also recorded and was approximately 22.5°C for this series of burns.

3.5.1.1 Room 1

Room 1 was set up as a bedroom, consisting of two beds, two mattresses, a cupboard, television, armchair, bedding, lamp, vacuum cleaner, clothes iron and an ironing board. The layout and pictures of this room can be seen in Figure 3.72.

The fire in this room was initiated on the pile of bedding. The scenario utilised was supposed to mimic a deliberately set fire utilising a hot clothes iron being left on the bedding. The metal ironing surface of the clothes iron was heated by a propane torch (referred to by the CFA as a flame thrower) and placed on the bedding causing it to ignite.

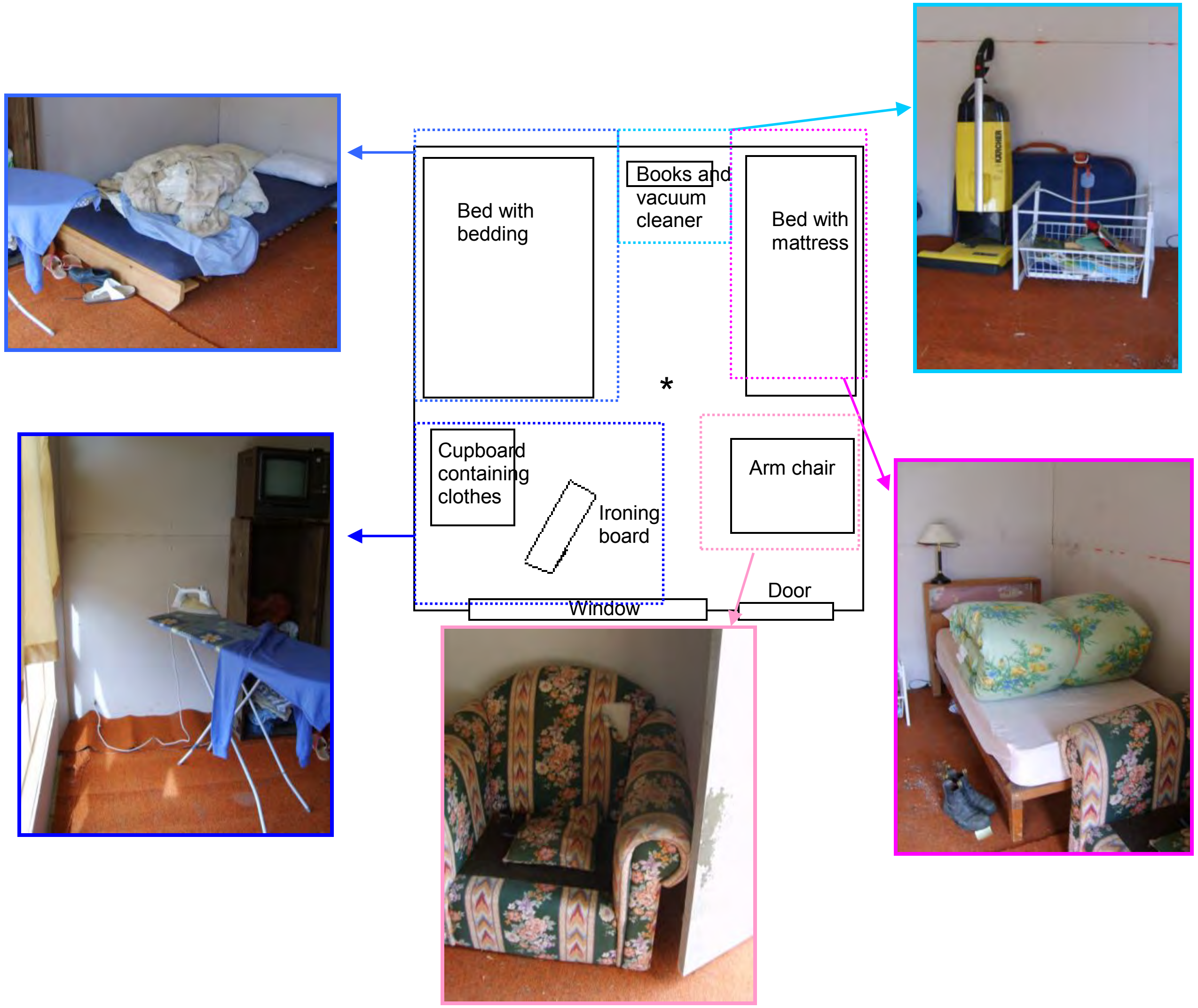


Figure 3.72: Layout of Room 1, with asterisk showing placement of the Thermocouples

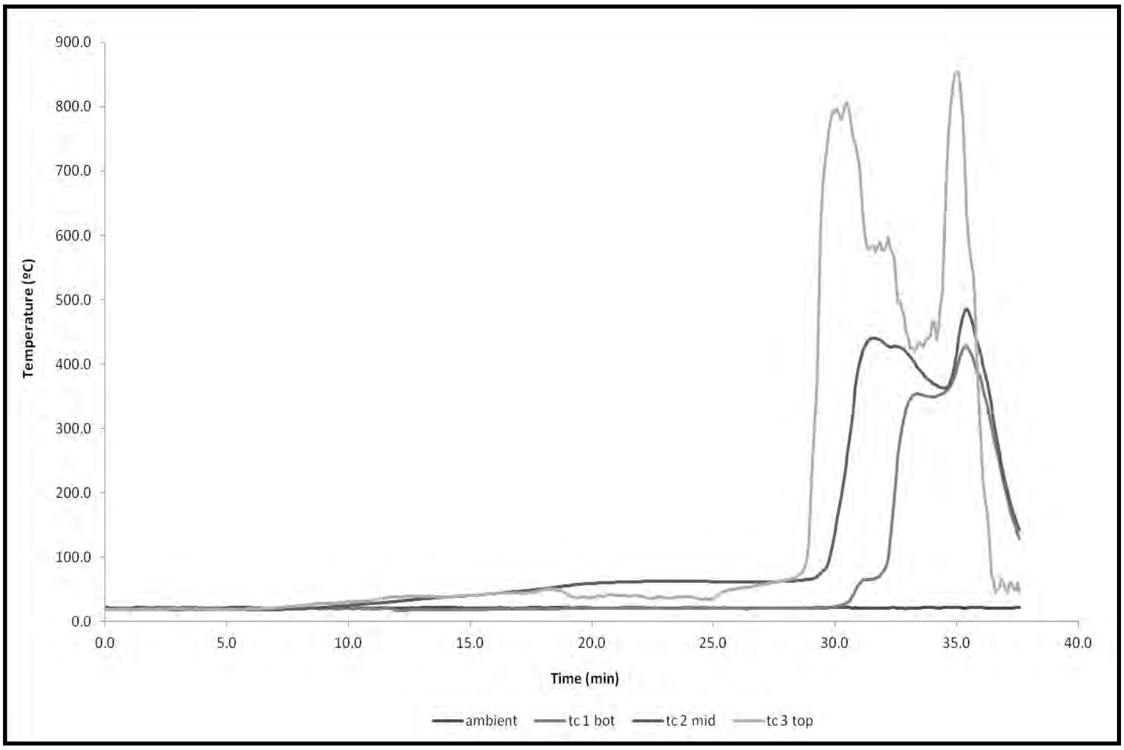


Figure 3.73: Temperature Data collected for Room 1

Figure 3.73 shows the temperature data collected for room 1 where data logging began at 0 minutes and the hot iron was placed on the bedding (ignition) at 5 minutes. The temperature profile shows that flashover was achieved twice which confirms the visual observations made during the fire. The first time flashover was achieved was after burning for approximately 24 minutes and the second after approximately 30 minutes of burning. The fire was extinguished very soon after (approximately 31 minutes after ignition).

The highest temperatures reached for the thermocouples placed at concrete level, between the carpet and underlay and above the carpet, were 427.8°C, 485.7°C and 854.6°C, respectively.

3.5.1.2 Room 2

Room 2 was set up as an office, consisting of a three desks, a number of printers, computers, kettles, toaster, a microwave and a bag of paper. The layout and pictures taken of this room can be seen in Figure 3.74.

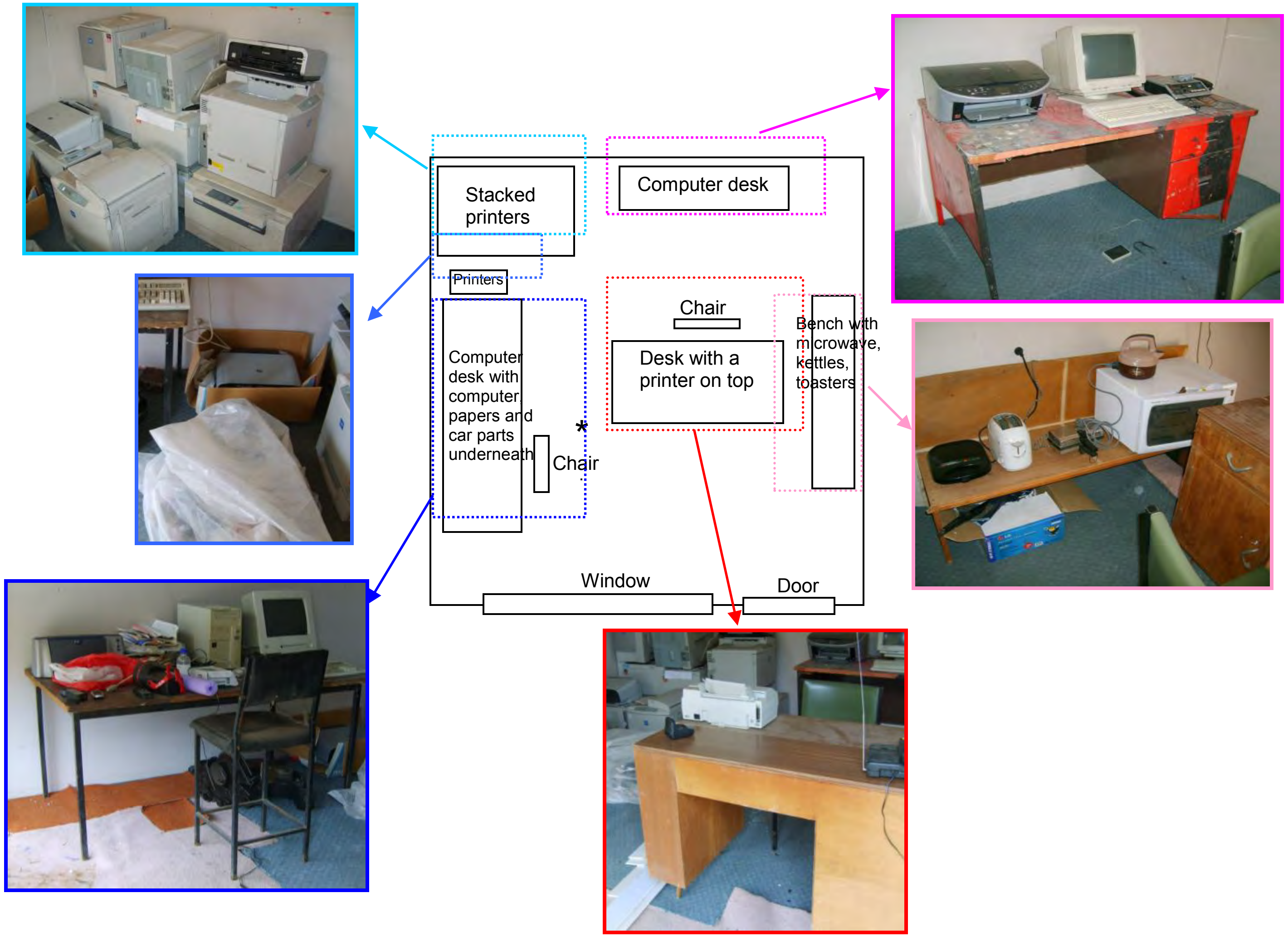


Figure 3.74: Layout of Room 2, with asterisk showing placement of Thermocouples

This fire was started by igniting a pile of paper near the desk with a match. Prior to ignition, two empty beer bottles were thrown through the window causing them the break, thus allowing more air to flow into the room.

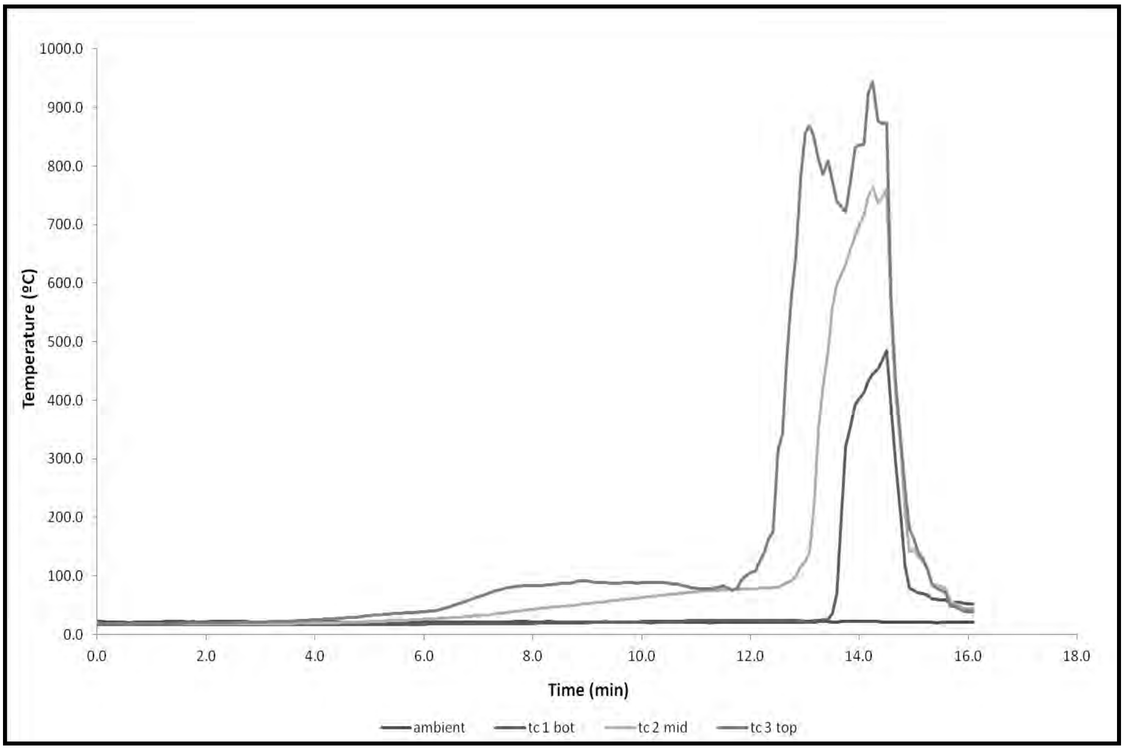


Figure 3.75: Temperature Data collected for Room 2

Figure 3.75 shows the temperature data collected for room 2 where data logging began at 0 minutes and the fire was ignited at 4 minutes. Flashover occurred after burning for approximately 9 minutes (at 13 minutes) and the fire was extinguished after burning for 11 minutes. As compared to the fire in room 1, higher temperatures were recorded in a shorter time period with the highest temperatures reached for the thermocouples placed on the concrete, between the underlay and carpet and above the carpet being 484.6°C, 763.8°C, and 943.3°C, respectively.

3.5.1.3 Room 3

The layout of room 3 replicated a lounge room, consisting of two couches, two desks, computer, television, microwave, empty alcohol bottles and a number of piles of books and papers. A schematic of the room, including photographs can be seen in Figure 3.76.

The fire in this room started when a petrol spill (approximately two litres) was ignited by a match, with the point of ignition occurring in close proximity to the heater. In order to prevent an explosion, resulting from a build up of ignitable liquid vapours in the room, the windows in the room were all broken prior to ignition.

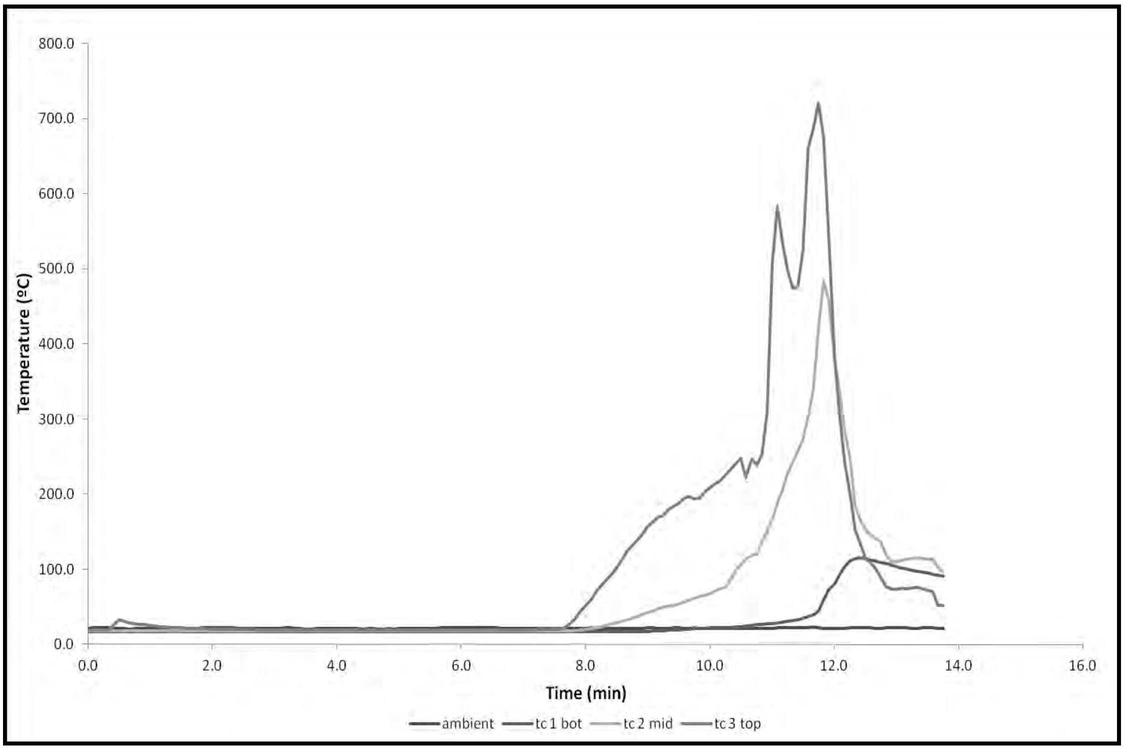


Figure 3.77: Temperature Data collected for Room 3

Figure 3.77 shows the temperature data collected for room 3 where data logging began at 0 minutes and the fire was ignited at approximately 6 minutes. The room reached flashover about 5 minutes after ignition and was allowed to burn for approximately 6 minutes in total, at which point it was extinguished.

The highest temperatures reached for the thermocouples placed on the concrete, between the underlay and the carpet and above the carpet were 114.9°C, 483.6°C, and 721.8°C, respectively.

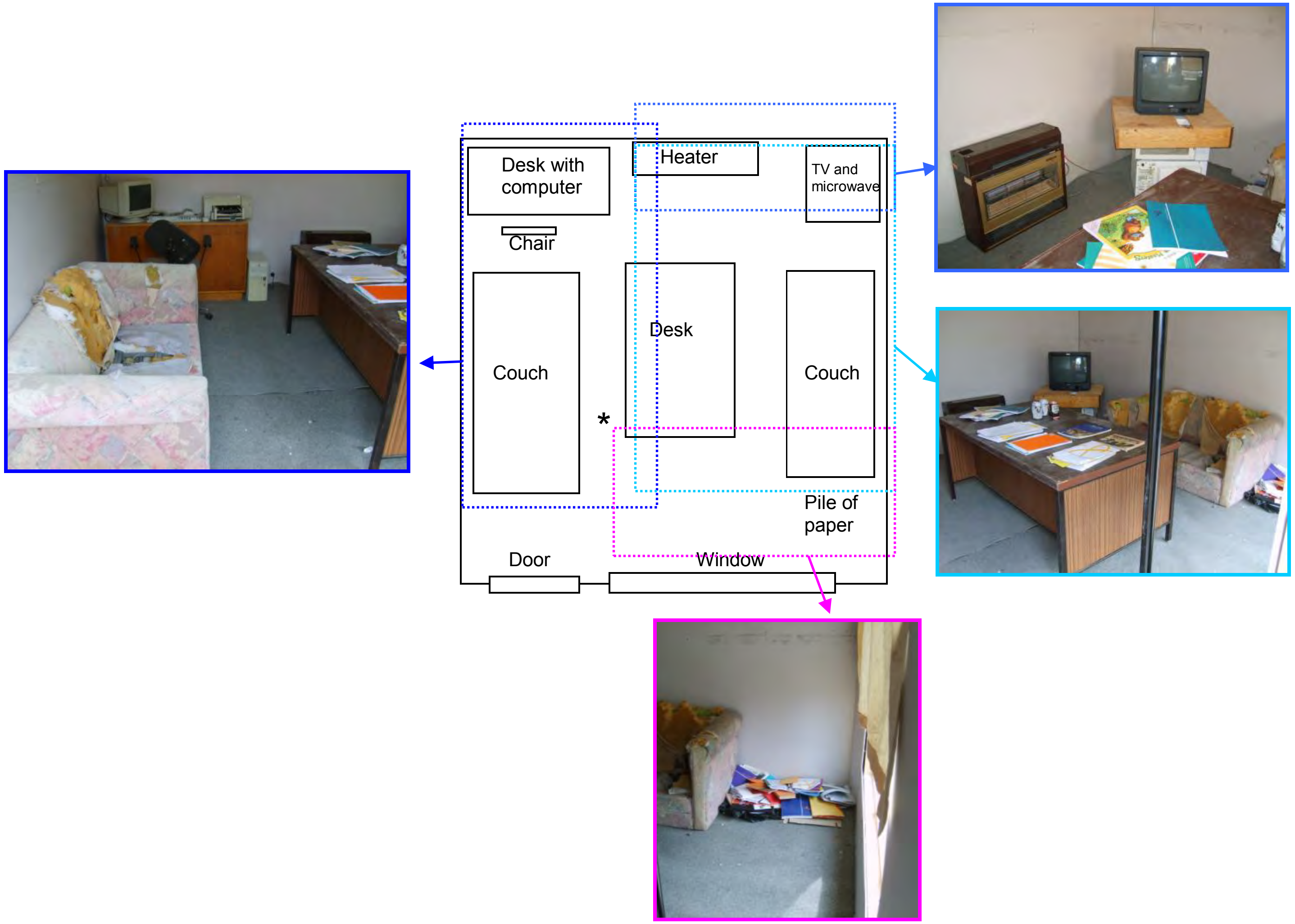


Figure 3.76: Layout of Room 3 with asterisk showing placement of Thermocouples

3.5.2 ROOM FIRES – SECOND SERIES

A second series of fire experiments were conducted on another day when the ambient temperature was approximately 16.4°C. In Figures 3.79, 3.81 and 3.83, the temperature profiles referred to as top, mid and bottom refer to the thermocouples placed above the carpet, between the carpet and the underlay and at concrete level, respectively.

3.5.2.1 Room 1

There was no specific set up of the first room in this instance. It consisted of pieces of furniture and rubbish being scattered throughout the room. The layout and pictures of this room can be seen in Figures 3.78.

An armchair and stack of shelves placed just outside the window were doused in petrol and ignited. The fire spread into the room which was then allowed to burn for approximately 14 minutes. Due to a fault with the data logger no temperature data was collected for the 'mid' thermocouple.

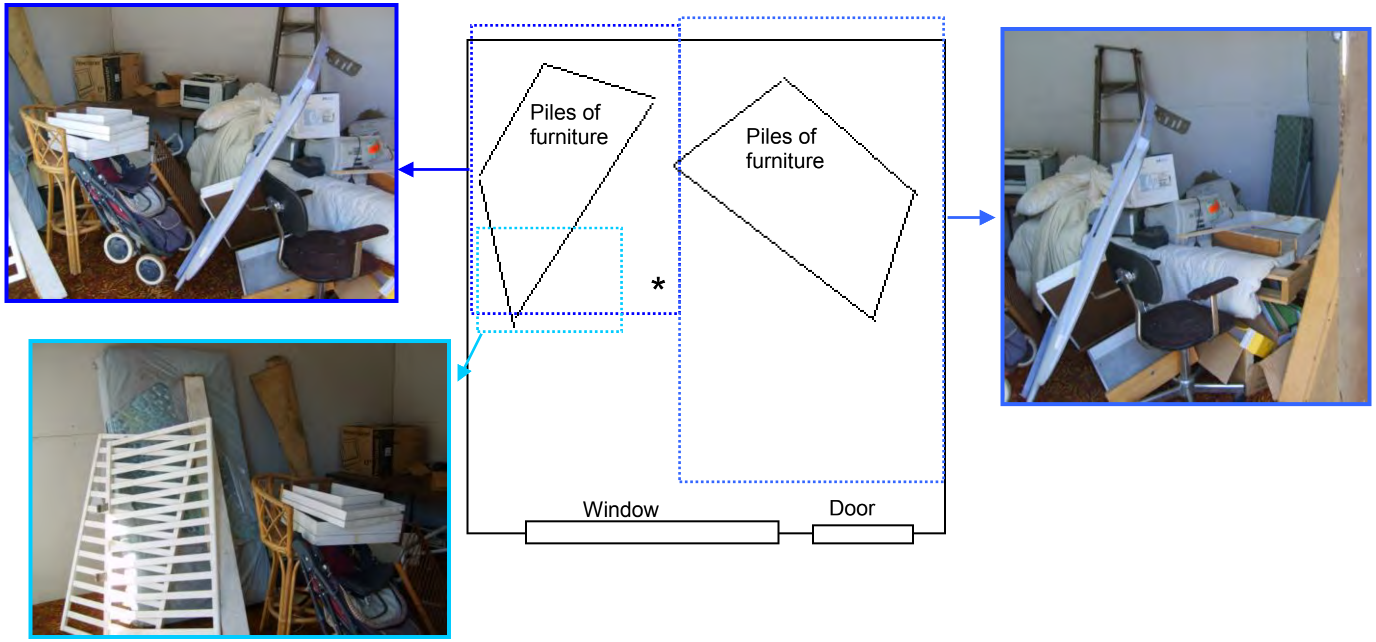


Figure 3.78: Layout of Room 1 with asterisk showing placement of Thermocouples

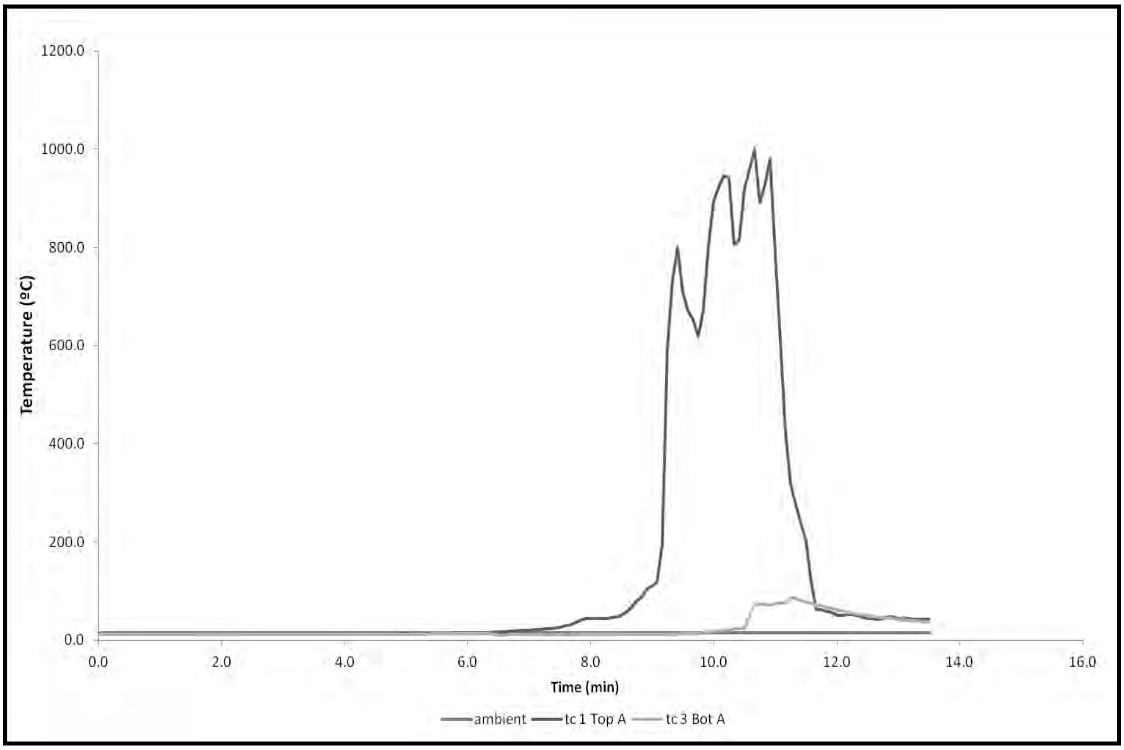


Figure 3.79: Temperature Data collected for Room 1

As shown in Figure 3.79, the highest temperatures recorded for the thermocouples at concrete level and just above the carpet and were 97.8°C and 999.2°C, respectively.

3.5.2.2 Room 2

Room 2 consisted of two desks, a number of computer screens, computers, computer parts, a television, couch and an armchair and as such could be considered as an office. The layout and pictures taken of the room can be seen in Figures 3.80.

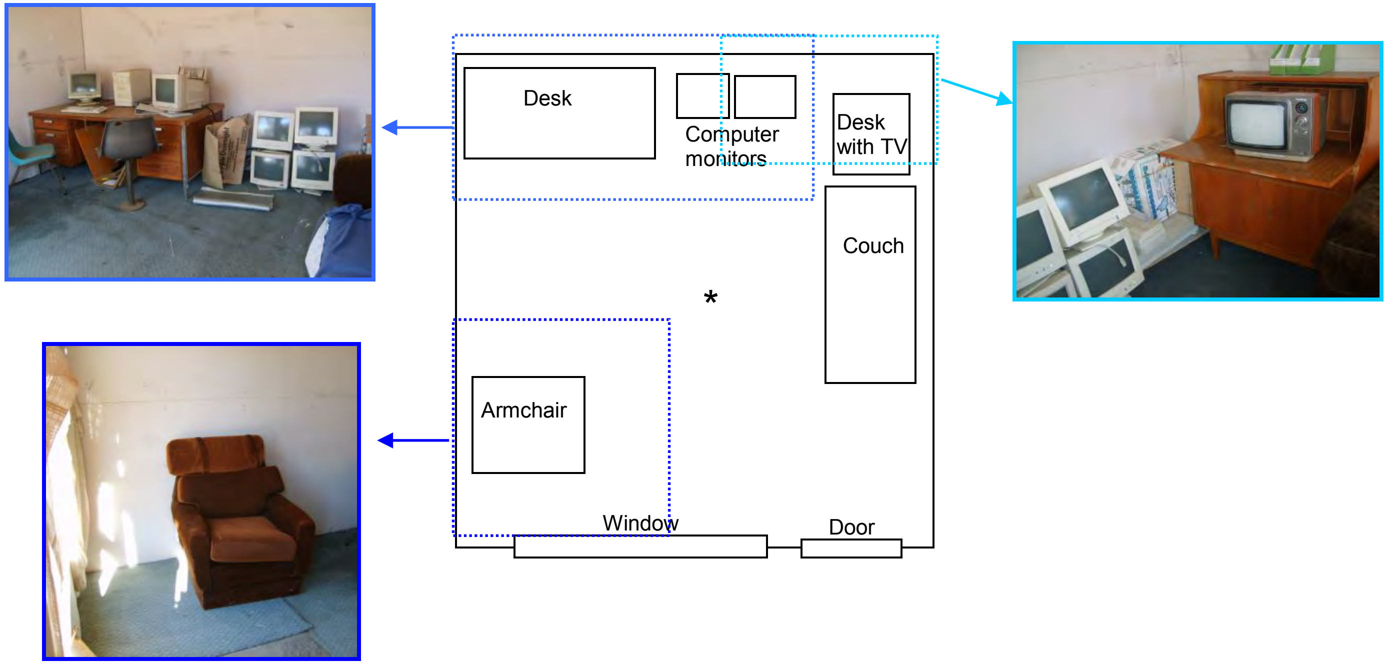


Figure 3.80: Layout of Room 2, with asterisk showing location of Thermocouples

This room fire did not utilise any ignitable liquid for ignition. The fire was started by one of the fire fighters using the flame thrower to light cardboard after which the fire spread quite quickly. Due to a fault with the data logger no temperature data was collected for the 'mid' thermocouple, furthermore there was a delay in starting the data logger and as a result temperatures were only able to be collected during flashover.

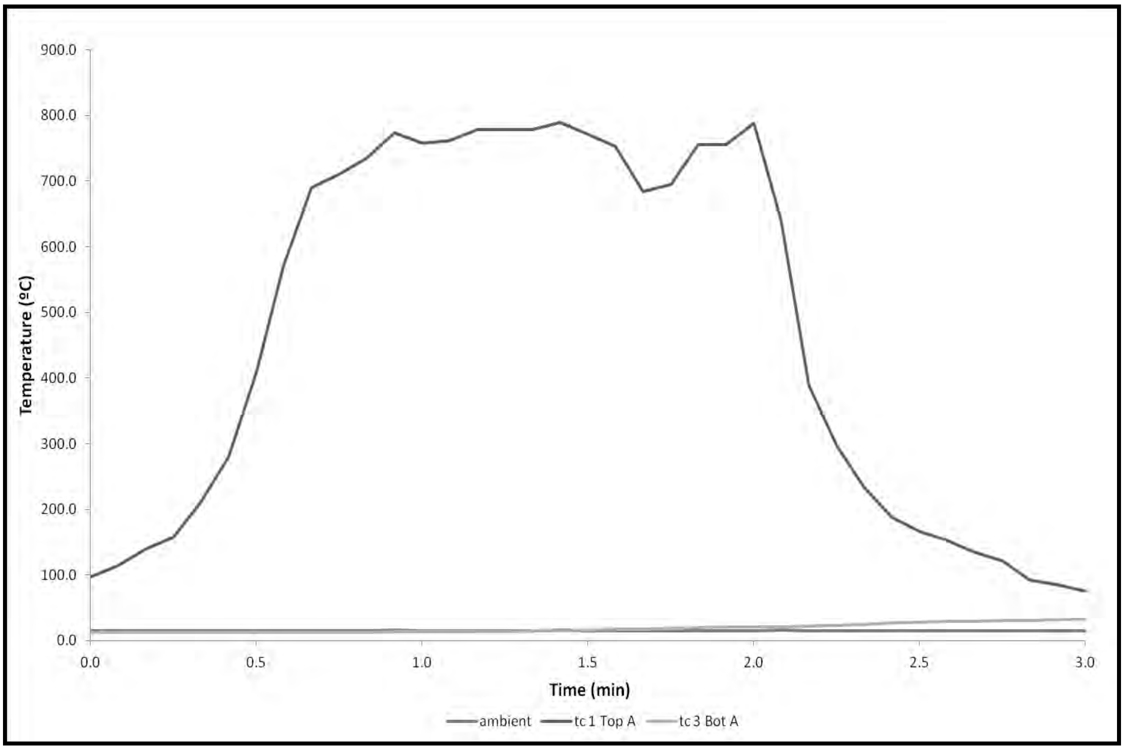


Figure 3.81: Temperature Data collected for Room 2

As seen in Figure 3.81, the highest temperatures reached for the thermocouples placed at concrete level and just above the carpet were 33.1°C and 788.2°C, respectively.

3.5.2.3 Room 3

To enable more comprehensive temperature data to be collected with regard to a petrol fuelled fire, this room was set up with three sets of the three thermocouples. The layout of room 3 can be seen in Figure 3.82.

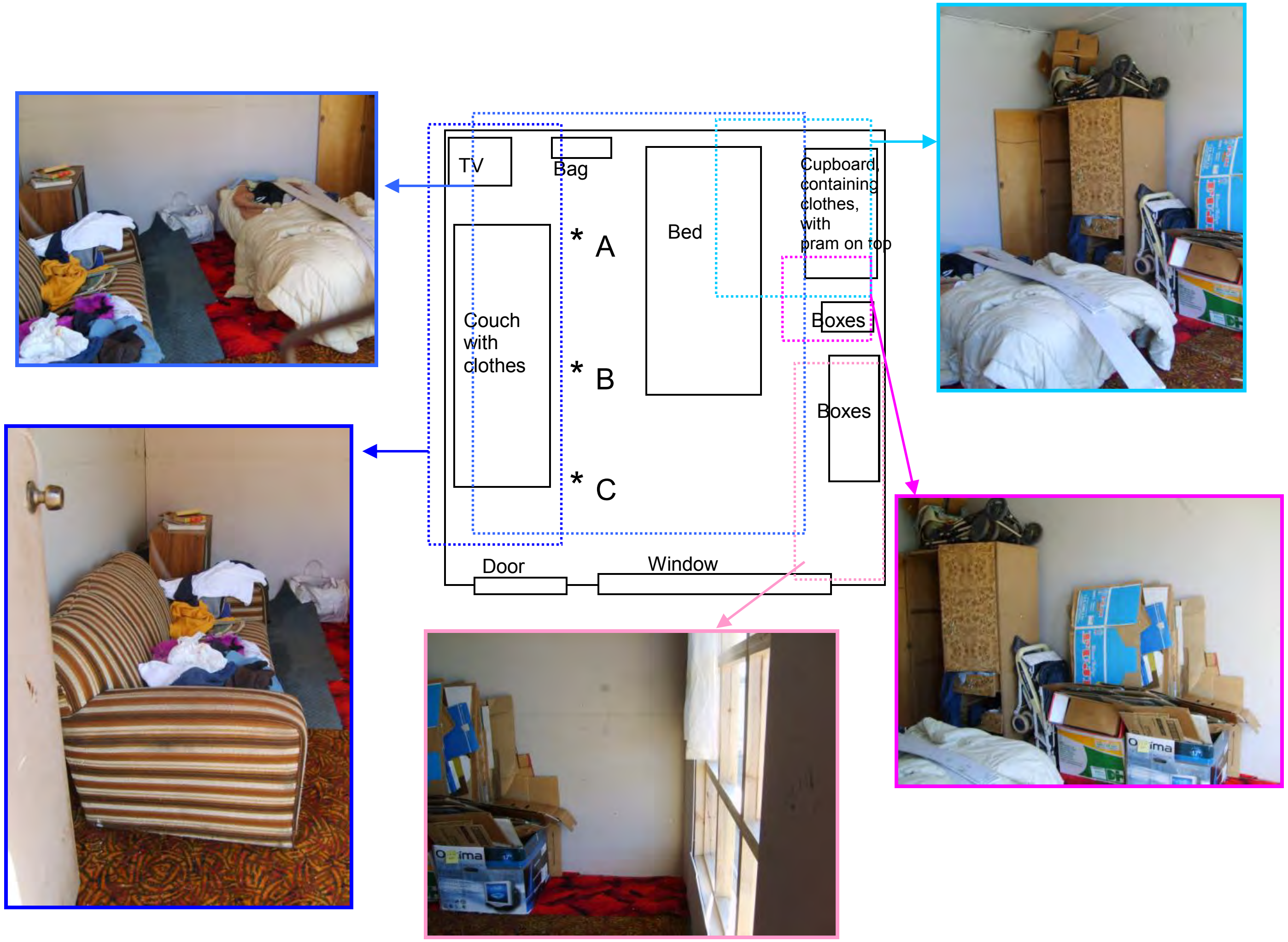


Figure 3.82: Layout of Room 3 with asterisks showing where each group of three Thermocouples were placed

The room was set up to replicate a bedroom and consisted of a bed, couch, cupboard with clothing, a television, bag and a number of boxes. The three sets of thermocouples were placed at positions marked A, B and C, as seen in Figure 3.82. Petrol was poured in a semi-circular pattern starting at position A where a pool of liquid collected, then a trail poured from position A over the bed to near position B. In total two litres of petrol was used. The pour pattern involved position A being in the centre of the spill, position B being on the outskirts of the spill and position C being well away from the spill. Vapours were allowed to collect for a short period of time, after which a lit match was thrown into the room and the fire initiated.

After ignition the room was then allowed to burn for approximately 4 minutes and flashover was achieved after approximately 2 minutes.

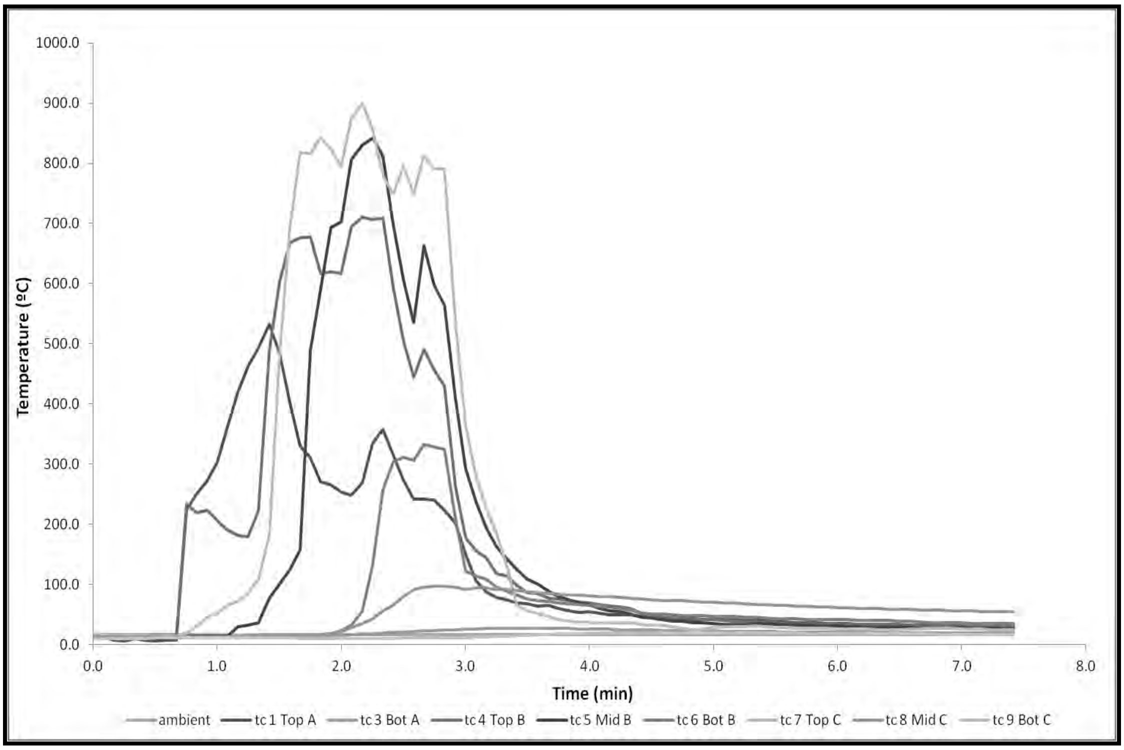


Figure 3.83: Temperature Data collected for Room 3

The highest temperatures reached for thermocouples at concrete level and just above the carpet fibres for group A, which were located in the middle of the petrol spill, were 16.7°C and 533.3°C, respectively. Due to a fault with the data logger no temperature data was collected for the ‘mid’ thermocouple in position A. The temperatures at the perimeter of the petrol spill (group B) were 332.3°C, 842.8°C and 710.3°C for the thermocouples at concrete level, between the carpet and underlay and on the top of the carpet, respectively. The temperatures away from the spill (group C) for the thermocouples at concrete level, between the carpet and underlay and on the top of the carpet were 19.8°C, 97.1°C and 900.2°C.

Once the fire was extinguished, it was observed that the carpet and underlay where the petrol was initially spilt and pooled (where group A thermocouples were situated) had not burnt (see Figure 3.84) even though the temperature recorded just above the carpet level still reached 533.3°C. The perimeter of the spill, where thermocouples in group B were located, exhibited the most intense burning. It was observed that the thermocouples between the carpet and the underlay and at concrete level had become exposed during the course of the fire. At this position, as can be seen in Figure 3.85, the fire actually burnt through the carpet and underlay exposing the concrete, hence explaining why temperatures at concrete level and between the carpet and underlay in this position were found to be the highest.

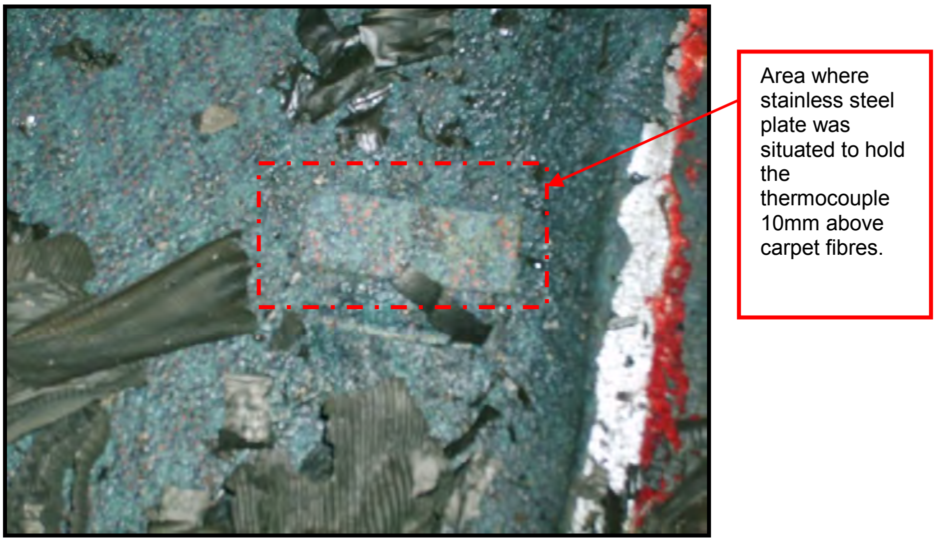


Figure 3.84: Carpet at centre of Petrol Spill after the Fire (where group A Thermocouples were located)

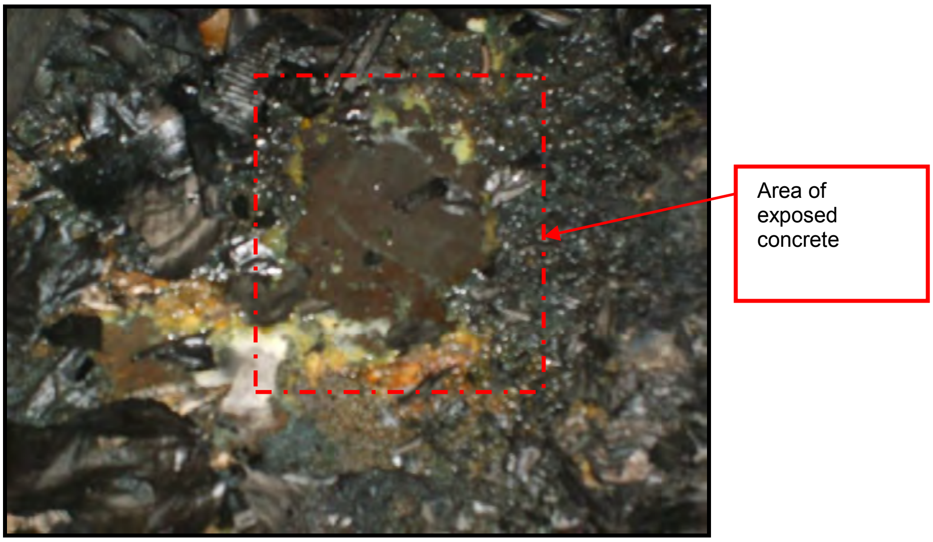


Figure 3.85: Carpet and Underlay at Perimeter of Petrol Spill after the Fire (where group B Thermocouples were located)

In the area where the group C thermocouples were placed, which was away from the actual petrol spill, only the top carpet fibres were burnt as shown in Figure 3.86(a), whilst the carpet backing and underlay remained intact and unburnt, as shown in Figure 3.86(b).

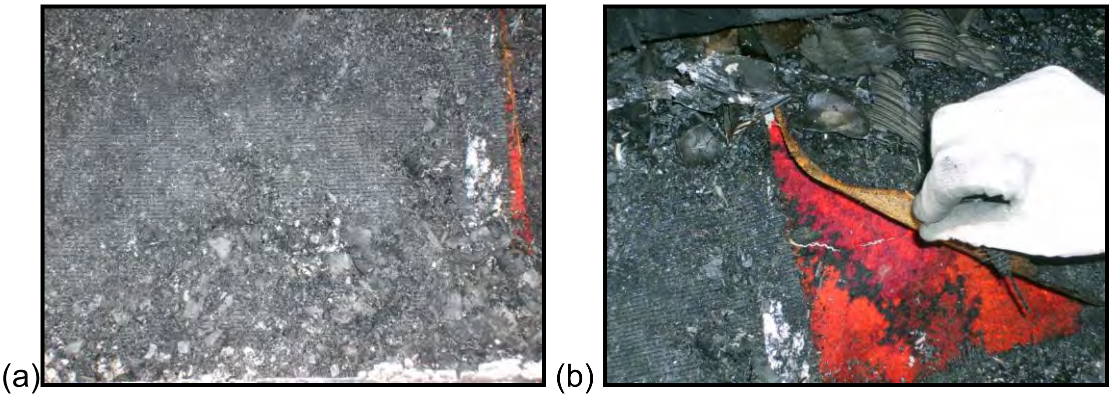


Figure 3.86: (a)Top of Carpet and (b) Underneath the Carpet in the Area located away from the Petrol Spill after the Fire (where group C Thermocouples were located)

3.5.3 SUMMARY

Table 3.6 shows the temperature data collected in the room fires.

Table 3.6: Temperature Data Summary*

Series 1				Series 2			
Room	**Concrete (°C)**	**Underlay (°C)**	**Carpet (°C)**	**Room**	**Concrete (°C)**	**Underlay (°C)**	**Carpet (°C)**
1	427.8	485.7	854.6	**1**	97.8	Not collected	999.2
2	484.6	763.8	943.3	**2**	33.1	Not collected	788.2
3	114.9	483.6	721.8	**3A**	16.7	Not collected	533.3
				3B	332.3	842.8	710.3
				3C	19.8	97.1	900.2

**Uncertainty is ± 1.1°C*

Temperature data and visual observations show that temperatures above the carpet fibres can range from 500°C to 1000°C, where depending upon the extent of burning of the top carpet layer, the top and/or bottom of the underlay can also experience temperatures ranging from 16°C to 850°C.

Furthermore, after discussions with qualified fire investigators it was discovered that it is quite uncommon for carpet to burn right through as the fire brigade usually arrives at or around flashover, with the Metropolitan Fire and Emergency Services Board (MFB) responding to a residential fire typically within 7 minutes from the time of the emergency call, which equates to approximately 12 minutes from the start of the fire. Further discussions with CFA personnel advised that the CFA take 90 seconds to be in their trucks on the way to a fire and therefore will also arrive just after flashover, where in most cases the carpet will remain intact.

Based upon the observations made during these room fire experiments, the temperatures that carpet and underlay are exposed to during a fire were found to vary considerably but can reach temperatures nearing 1000°C. It was thus concluded that the temperatures to be used for the pyrolysis experiments would need to cover the range of burning temperatures observed. The temperatures used for pyrolysis were 900°C, 750°C, 600°C and 450°C which covered the range of temperatures experienced by the carpet and underlay in the room fires. As will be shown in Section 4.6, pyrolysis could not be conducted below 450°C due to blockage of the pyrolyser even though this temperature was well above the melting points of the carpet fibres. The melting points of nylon 6, nylon 6,6 and polypropylene are 220°C, 265°C and ~160°C,respectively[158].

4. RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter reports the results from the test burning of carpet and foam samples and subsequent GC/MS analysis of volatile organic compounds recovered from the burnt samples. It explores the potential of these volatile organic compounds to interfere with identifying petrol in arson investigation. The volatile organic compounds of particular interest are those which have been identified as petrol target compounds (see Section 3.2). Results are presented as follows:

- Determination of substrate background products (Section 4.2).
- Large scale room fires (Section 4.3).
- Furnace fires (Section 4.4).
- Small can fires (Section 4.5).
- Pyrolysis GC/MS (Section 4.6).

In the conclusion (Chapter 5) the potential of the volatile organic compounds produced from the burning tests to interfere with the identification of petrol in arson investigation using target compound analysis, will be described with respect to the impact in arson investigation. The conclusion will also describe a protocol for the burning of substrate comparison samples using small can fires.

Carpet, underlay and foam samples are described in Section 2.2.2, 2.2.3 and 2.2.4, respectively. The recovery of volatile organic compounds from burnt samples using passive/dynamic headspace is described in Section 2.4. GC/MS conditions are given in Section 2.5.1 and were the same for all experiments. Pyrolysis GC/MS was performed using an SGE micro-furnace pyrolyser and conditions are given in Section 2.5.2.

Total ion chromatograms and extracted ion chromatograms were generated for each sample. The extracted ions used to generate the extracted ion chromatograms were those which are representative of the selected petrol target compounds (refer to Table 3.3). As described in Section 3.2.1 and 3.2.2, the diethyl ether, evidence bag and charcoal tube contain no similar or co-eluting compounds to the petrol target compounds selected. It should be noted that the total ion chromatograms produced from carpet and foam samples contain two peaks at 23.12 minutes, and 11.71 minutes which are due to the diethyl ether and the bag (see Sections 3.2.1 and 3.2.2) These two compounds will here on in be referred to as being attributed to the blank sample and will be labelled as ‘Ether’ and ‘Bag’ in the total ion chromatograms. It should be noted that in this chapter, where it is indicated that no target compounds were recovered the total ion chromatograms and extracted ion chromatograms were similar to that shown in Figure 3.34 for the evidence bag.

The identification of GC peaks was conducted by retention time and MS library matching with the selected target compounds in petrol.

4.2 DETERMINATION OF SUBSTRATE BACKGROUND PRODUCTS

Unburnt subsamples of all carpet and foam samples used in this study were subjected to the same recovery procedure used for burnt samples (Section 2.4) in order to determine if any substrate background products were present, in particular any compounds identified as petrol target compounds. This information would be important when analysing burnt samples for volatile organic compounds especially to ensure that observations were due the burning of the substrate rather than off-gassing.

A swatch of each of the carpets and underlay (approximately 1m x 0.5m in size) was loosely rolled and placed in an evidence bag containing a charcoal tube and tightly sealed. A piece of foam (0.5m x 0.5m x 0.1m) was also placed in an evidence bag with a charcoal tube and tightly sealed. The samples were then subjected to the passive/dynamic headspace technique described in

Section 2.4. The extracted ion chromatograms were produced using the petrol target compound ions discussed in Section 3.2.

No substrate background products were recovered from the nylon, polypropylene and wool carpet, nor were any recovered from the furniture foam and underlay (the total ion chromatograms and extracted ion chromatograms produced were similar to that of the blank evidence bag in Figure 3.34). The only sample found to still be off-gassing any substrate background products was the 50-50 polypropylene-wool carpet where toluene was recovered. The total ion chromatogram and extracted ion chromatogram for this substrate is shown in Figure 4.1.

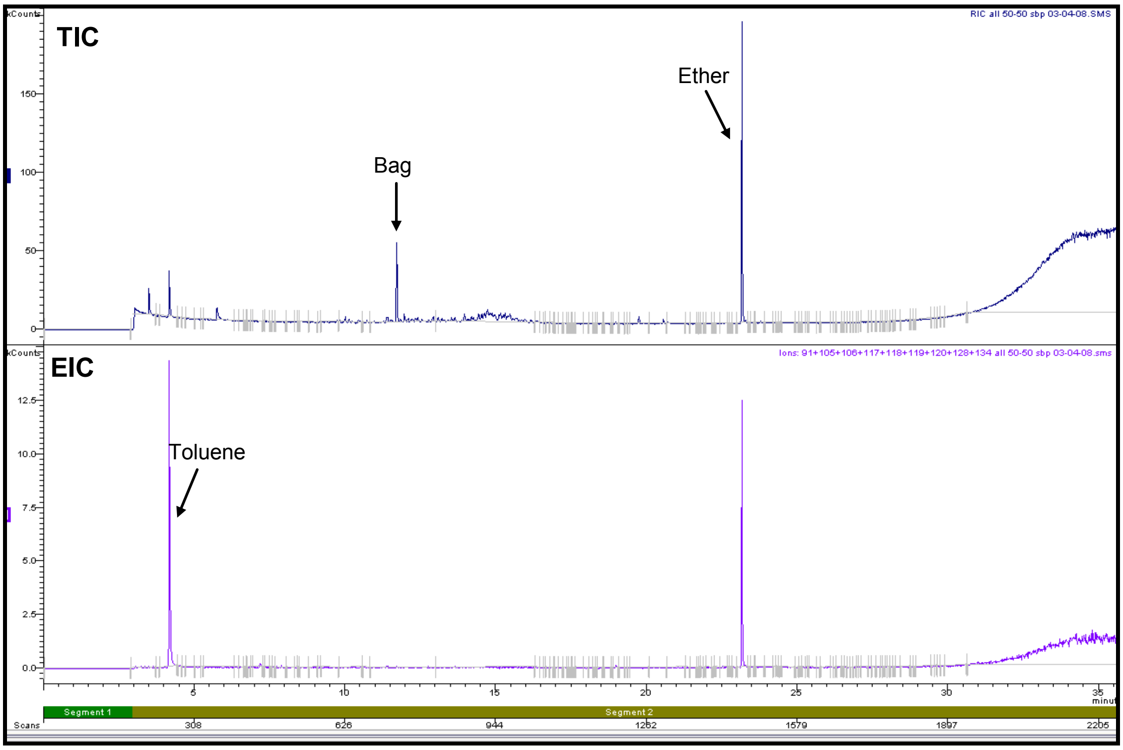


Figure 4.1: Total Ion Chromatogram and Extracted Ion Chromatogram of the Substrate Background Products recovered from the 50-50 Polypropylene-Wool Carpet (Refer to Section 2.5.1 for GC/MS conditions)

The total ion chromatogram shows that the abundance of toluene was low as it was just above baseline and the abundance in the extracted ion chromatogram was at levels comparable to the limit for pattern comparison standards (see Section 3.2). It is highly unlikely that at these low levels toluene off-gassing from the 50-50 polypropylene-wool carpet would interfere with the analysis of substrates used in this study. The studies to determine substrate background products above showed that the carpet and foam samples used for this study had negligible potential to off-gas any interfering petrol target compounds.

It is common knowledge that carpet samples off-gas after production, with a study conducted by O'Donnell finding that new carpet can provide a troublesome background for petrol[107]. However, the results of this study are supported by Cavanagh *et al* who found that the level of background interferences from substrate background products, for all carpet matrices, decreased visibly with time to such an extent that they do not present significant levels of potential interferences in the chromatographic profile of an ignitable liquid[26].

The carpet and foam samples analysed in this study were not new (they had been stored for approximately one year before use) and as such they were expected to have already off-gassed any volatiles. However, the result for the 50-50 polypropylene-wool carpet showed that even after a storage time of one year some volatile organic compounds were still off-gassing. Perhaps the rate of off-gassing had been slowed down due to the carpets being stored as a roll rather than flat.

4.3 LARGE SCALE ROOM FIRES

The aim of these large scale room fire experiments was to determine what volatile organic compounds are produced from the burning of carpet and foam samples in a real fire situation.

Although it would have been ideal to conduct large scale room fires on each individual sample type this would have been time consuming, involving excessive financial, staffing and room fitting resources. It was thus decided to burn all samples simultaneously by using a small swatch of each sample per room (refer to Section 2.7).

Two large room fires were conducted on the same day with both rooms set up as similar as possible. Both rooms were setup as bedrooms (containing a bed/mattress, armchair, couch and TV with stand) and were similar in content and layout except for the position of the door (see Figures 4.2 and 4.3). Each of the rooms contained a swatch of nylon, wool, polypropylene and 50-50 polypropylene-wool blended carpet, as well as furniture foam and underlay. The rooms also contained another three swatches of nylon carpet which were spiked with 10mL, 50mL and 100mL of unevaporated petrol. These three samples were included to ensure that the recovery method utilised in this study (Section 2.4) was able to recover ignitable liquid residues (see Section 4.3.2).

Thermocouples, described in Section 2.7.1, were utilised in both rooms to enable temperature data to be recorded throughout the course of the fire in order to compare the fire conditions in each room. In each room, three thermocouples were placed in different areas of the room (referred to as T1, T2 and T3 in Figures 4.2 and 4.3), approximately 10mm above floor level which represented the height of the carpet when placed in the oil drip trays.

Carpet and foam samples were positioned as shown in Figures 4.2 and 4.3 and abbreviations used in these figures are described in Table 4.1.

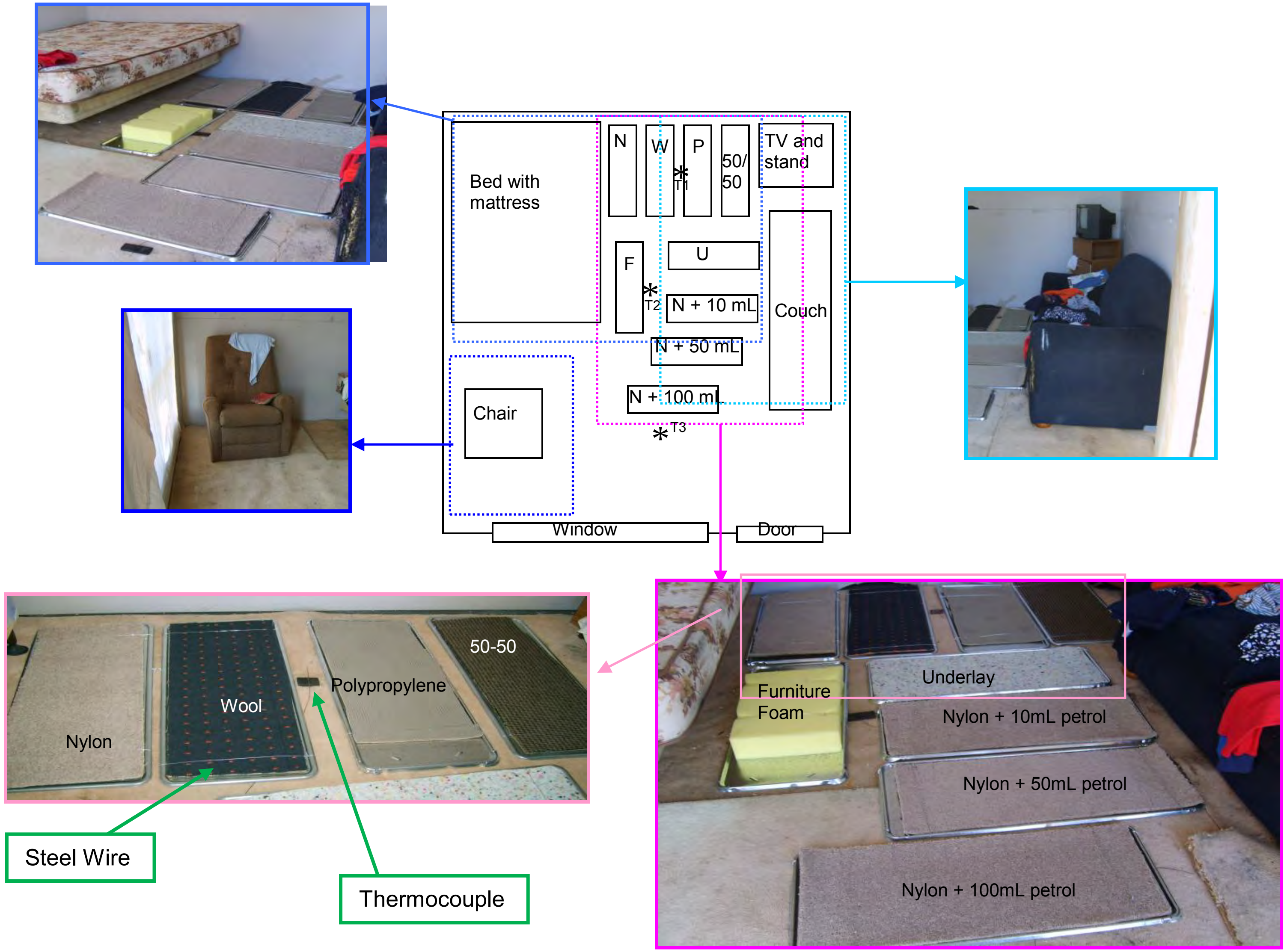


Figure 4.2: Layout of Room 1, with asterisk showing placement of the Thermocouples

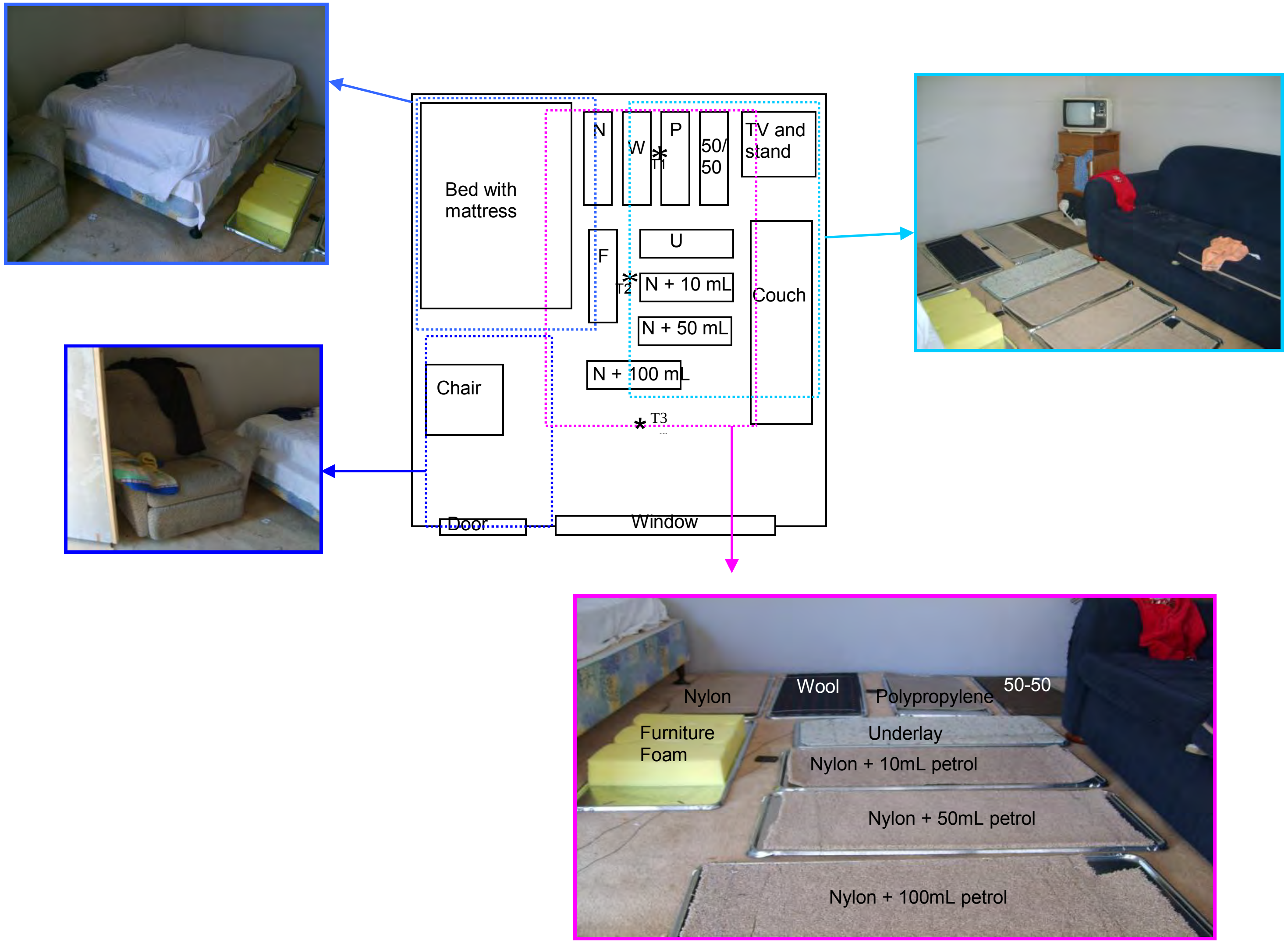


Figure 4.3: Layout of Room 3, with asterisk showing placement of the Thermocouples

Table 4.1: Abbreviations and Definitions from in Large Scale Room Fire Schematics

Abbreviation	Definition
N	Nylon Carpet
W	Wool Carpet
P	Polypropylene Carpet
50-50	50-50 Polypropylene-Wool Carpet
U	Underlay
F	Furniture Foam
N + 10	Nylon Carpet with 10mL of unevaporated petrol
N + 50	Nylon Carpet with 50mL of unevaporated petrol
N + 100	Nylon Carpet with 100mL of unevaporated petrol
T1	Thermocouple 1
T2	Thermocouple 2
T3	Thermocouple 3

The fires were ignited using a propane torch, monitored and extinguished by qualified CFA fire-fighters. Observations made during the temperature data collection experiments (Section 3.5), revealed that the floor only caught fire during flashover which is consistent with research which states that during flashover the radiant heat fluxes produced causes carpets and other flooring materials to be rapidly ignited[1, 44]. Therefore, these rooms were allowed to burn until flashover was achieved. The bed and couch in both rooms were initially ignited and they were extinguished approximately 1 minute after flashover by the CFA fire-fighters. The fires were extinguished, following standard CFA procedure, using a fine spray of water from the fire hose (approximately 30 to 40 L/min).

The major difference in how both fires proceeded was when the floor area caught fire. The CFA left the doors open at the beginning of the fires, where in room 1 the door was able to be left fully open however the door in room 3 could only be left partially open due to a chair being placed behind it. During the burning of room 1, where the door remained open for the entire fire, it was observed that the floor area (where thermocouples and samples were situated) did not catch fire until flashover was achieved. The door in room 3 closed soon after the fire was ignited and the CFA fire-fighters were asked to open the door to enable the fire progression to be observed. Upon opening the door it was noticed that all the samples were on fire even though flashover had not been reached. Flashover in room 3 occurred approximately three minutes after the door was opened and the fire was extinguished approximately 1 minute after that. After the fires were extinguished the samples were left in the room for approximately half an hour in order to mimic a real fire situation where samples would not be collected until fire investigators arrived at the scene.

Even though every attempt was made to conduct two similar fires, as described above the fires burnt quite differently, this is further highlighted in the temperature profiles and visual observations of the burnt carpet and foam samples discussed below.

4.3.1 TEMPERATURE DATA AND OBSERVATIONS

The temperature data collected from the burning of rooms 1 and 3 are presented in Figures 4.4 and 4.5, respectively.

The highest temperatures recorded in room 1 occurred at flashover. These temperatures were 315ºC, 601ºC and 690ºC for the thermocouples placed near the back wall, middle of the room and nearest the door (T1, T2 and T3), respectively. Once flashover was achieved the room was allowed to continue burning for approximately 1 minute after which the fire was extinguished.

The fire in room 3 progressed differently to that in room 1 and this is evident when comparing the temperature profile of the two rooms. The highest temperatures, recorded at flashover in room 3, were 474ºC, 671ºC and 921ºC for the thermocouples placed at the back wall, the middle of the room and closest to the door (T1, T2 and T3), respectively.

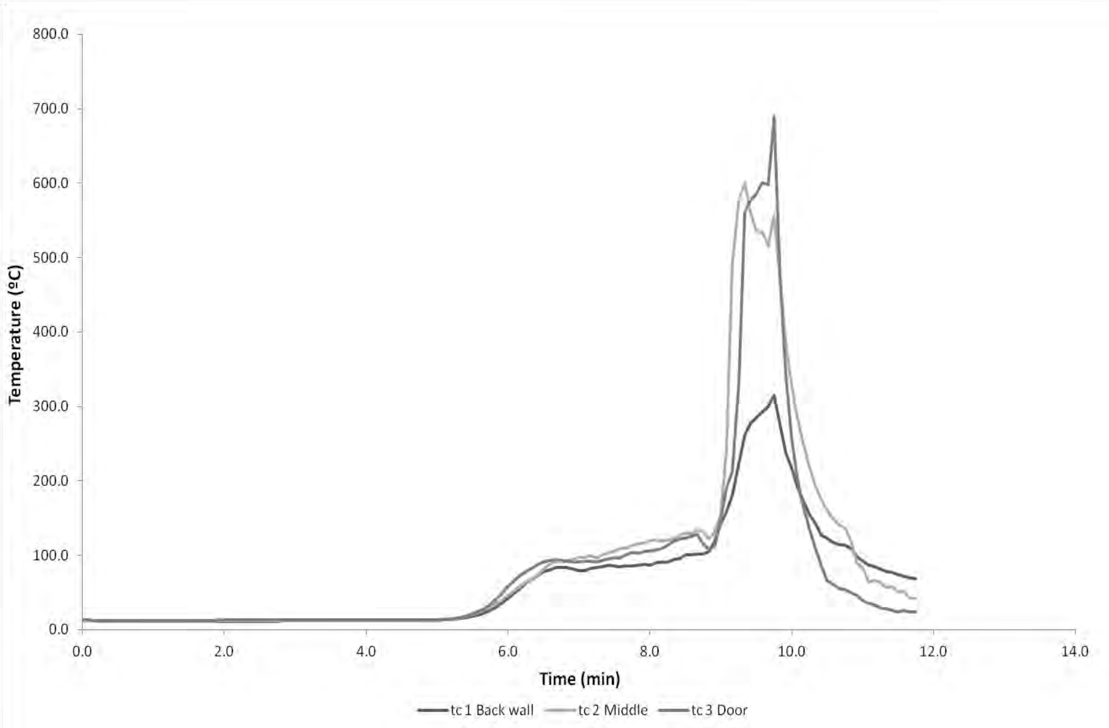


Figure 4.4: Temperature Data collected from Room 1

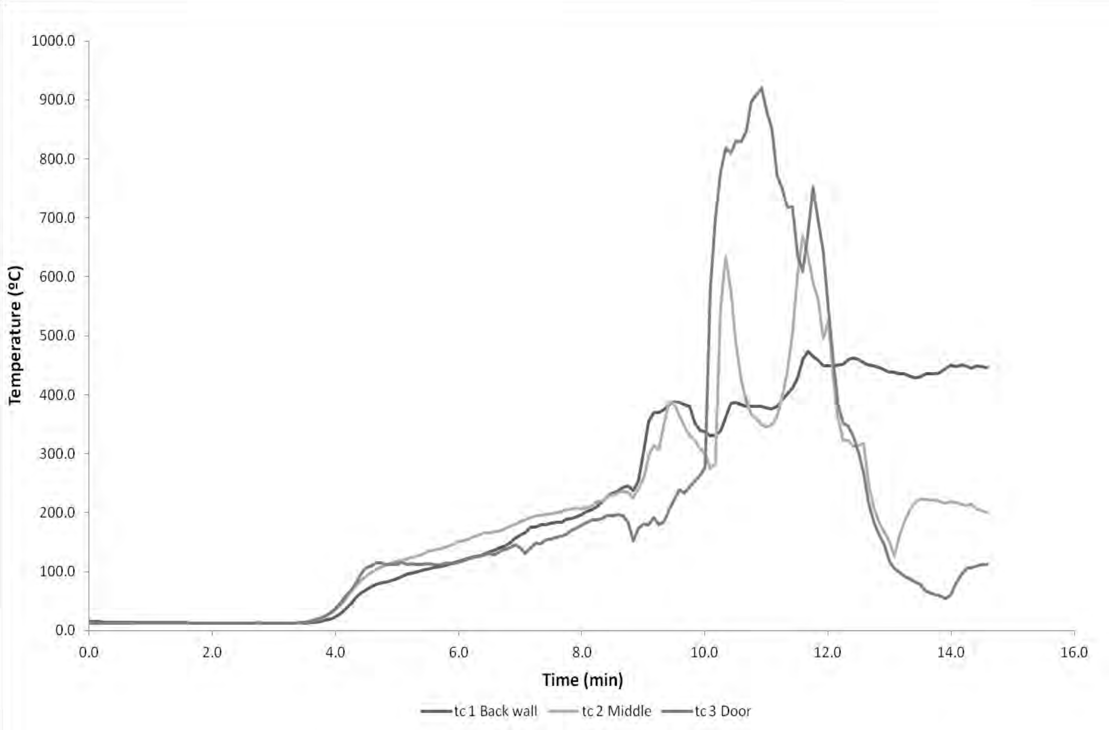


Figure 4.5: Temperature Data collected from Room 3

The temperature profiles collected for both rooms 1 and 3 show that the two fires did in fact burn quite differently. In particular, temperatures reached in room 3 were much higher than those in room 1. Floor temperature profiles in both rooms also showed that at different areas within the room, temperatures were not consistent and found to vary greatly from one spot to another (there was only approximately 1m separating each of the thermocouples). It is interesting to note that in both rooms, the temperatures reached at flashover near the back wall, where T1 was situated, were much lower than the temperatures recorded in the middle of the room (T2) and nearest the door (T3). This may have been the result of the windows in the room breaking at flashover allowing more oxygen to be sucked into the room, causing the fire to burn hotter, thus accounting for the higher temperatures observed nearest the doors and windows.

Samples in room 1 ignited at flashover and were allowed to burn for 1 minute. When collected these carpet samples remained intact and all exhibited slight burning around the edges. The nylon and polypropylene carpet fibres had melted and the 50-50 wool-polypropylene carpet fibres appeared to have only partly melted. The wool carpet fibres only displayed signs of singeing. Due to the carpet samples remaining intact they were able to be rolled up and placed in evidence bags. The furniture foam and foam underlay appeared to have melted before burning away and when collected the residue had to be scraped into the evidence bag.

Samples in room 3 ignited prior to flashover and were alight for at least 4 minutes prior to extinguishment. Carpet and foam samples were extensively burnt and only a residue remained which was then scraped into the evidence bag.

Table 4.2 summarises the observations made during both large room fires.

Table 4.2: Summary of Room Fire Temperatures and Observations

Samples		**Room 1**			**Room 3**		
	Ignition Temp	Temp at flash over	Ignition	Observations	Temp at flash over	Ignition	Observations
Nylon Carpet	424°C-532°C	315ºC	At flashover	The carpets caught fire at flashover. The synthetic carpets appeared to have melted fibres whilst the wool carpet showed evidence of slight singeing. All samples were still intact.	474ºC	~ 3 minutes before flashover	All carpets were extensively burnt and scraped into evidence bags as a carbonised residue.
Polyprop Carpet	570°C	315ºC	At flashover		474ºC	~ 3 minutes before flashover	
Wool Carpet	228°C-230°C	315ºC	At flashover		474ºC	~ 3 minutes before flashover	
50-50 Carpet	228°C-532°C	315ºC	At flashover		474ºC	~ 3 minutes before flashover	
Underlay	416°C	601ºC	At flashover	These samples had burnt away and only a small amount of residue was able to be collected.	671ºC	~ 3 minutes before flashover	These samples had burnt away. Only a small amount of residue was able to be collected.
Foam	416°C	601ºC	At flashover		671ºC	~ 3 minutes before flashover	
Nylon+ 10mL petrol	424°C-532°C	601ºC	At flashover	The carpets appeared to have melted fibres and burning around the edges. All samples were still intact.	671ºC	~ 3 minutes before flashover	The carpets were extensively burnt and scraped into evidence bags as a carbonised residue.
Nylon+ 50mL petrol	424°C-532°C	601ºC	At flashover		671ºC	~ 3 minutes before flashover	
Nylon+ 100mL petrol	424°C-532°C	690ºC	At flashover		921ºC	~ 3 minutes before flashover	

4.3.2 SPIKED NYLON SAMPLES

For the three spiked samples in room 1, ignitable liquid residues were only recovered from the carpet spiked with 10mL and 100mL of petrol. The total ion chromatograms and extracted ion chromatograms for these samples are presented in Figures 4.6 and 4.7, respectively. No ignitable liquid residues were recovered from the carpet spiked with 50mL in room 1 which was a strange result.

The results from the carpet spiked with 10mL and 100mL of petrol confirms the success of the recovery method to recover petrol target compounds from a swatch of carpet after a fire. In the case of the carpet spiked with 10mL of petrol low abundances of target compounds were recovered, as no target compounds were observed in the total ion chromatogram and only four were observed in the extracted ion chromatogram, and therefore there were not enough target compounds recovered to attempt pattern comparison. In the case of the carpet spiked with 100mL of petrol, eight target compounds were recovered in appreciable levels and pattern comparison showed that the target compound chromatogram pattern matched that of the headspace ignitable liquid standard target compound chromatogram (2μL of the 50% evaporated petrol), as shown in Figures 4.8 and 4.9, respectively.

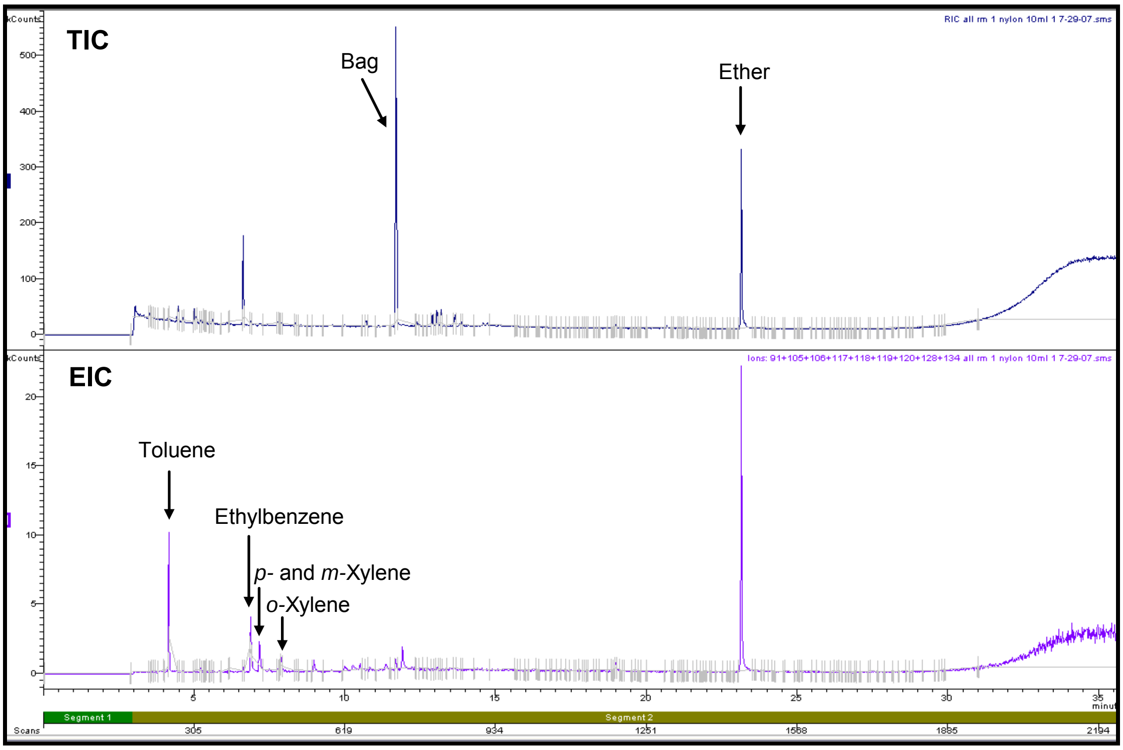


Figure 4.6: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Carpet spiked with 10mL Petrol burnt in Room 1 (Refer to Section 2.5.1 for GC/MS conditions)

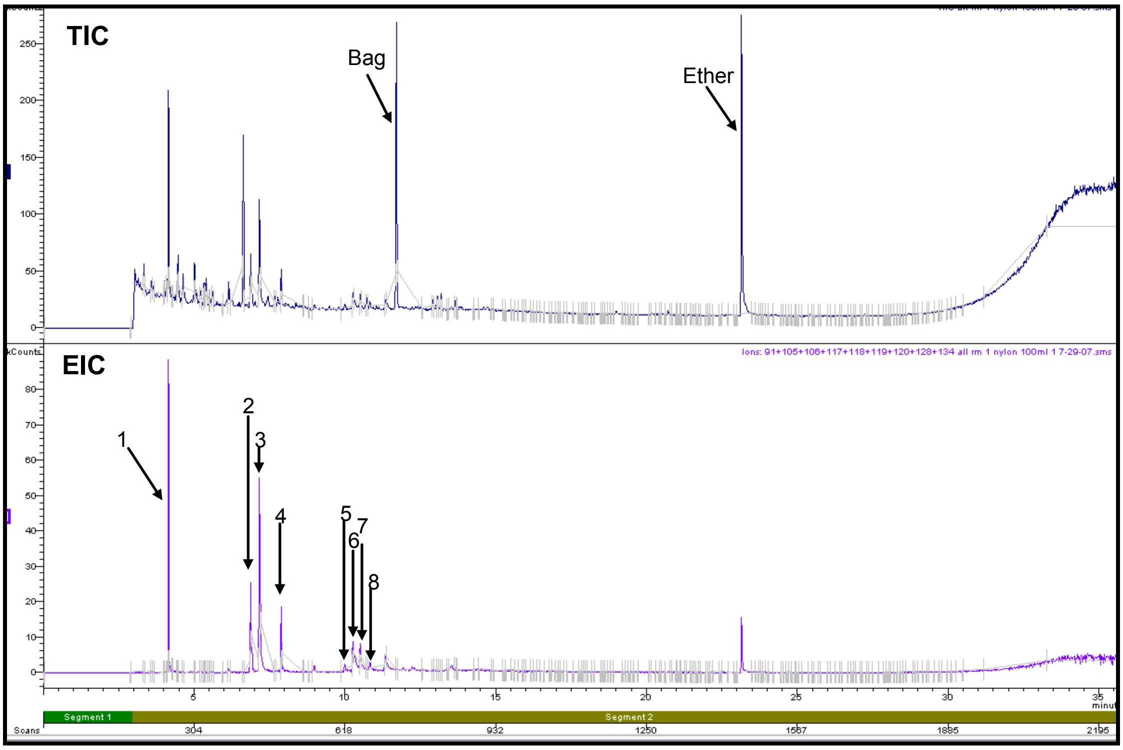


Figure 4.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Carpet spiked with 100mL Petrol burnt in Room 1 (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= 1-Ethyl-4-methylbenzene, 6= 1,3,5-Trimethylbenzene, 7= 1-Ethyl-3-methylbenzene, 8= 1,2,4-Trimethylbenzene

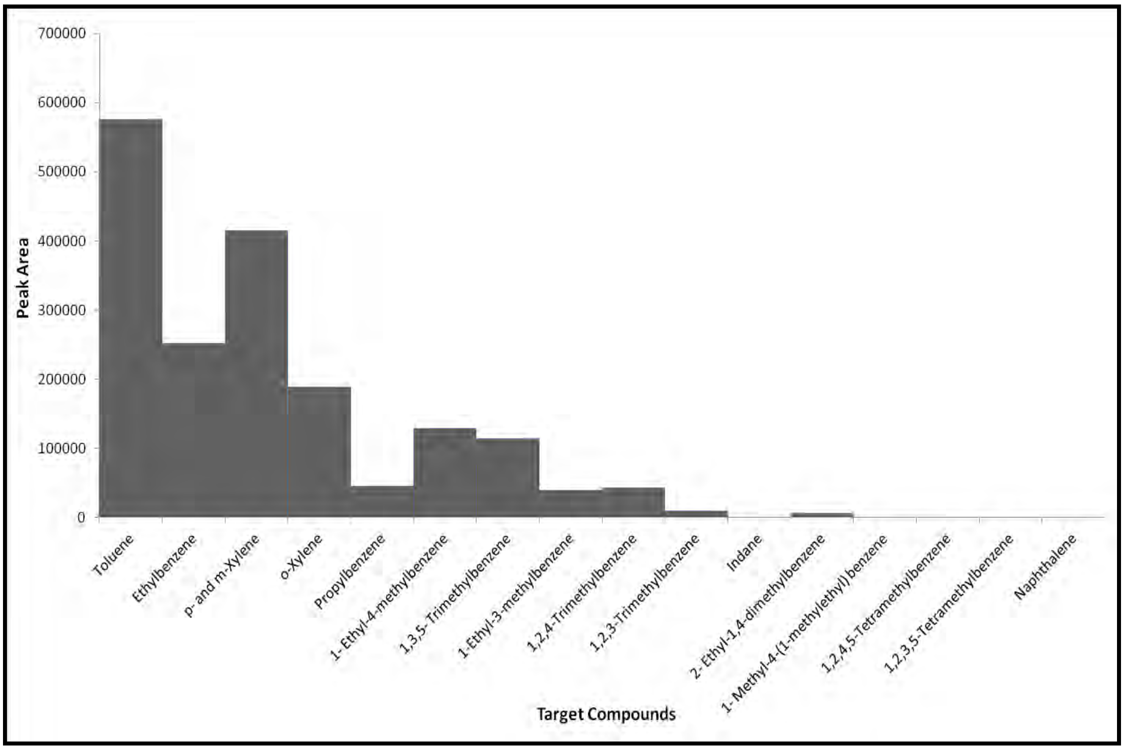


Figure 4.8: Target Compound Chromatogram of Nylon Carpet spiked with 100mL Petrol burnt in Room 1

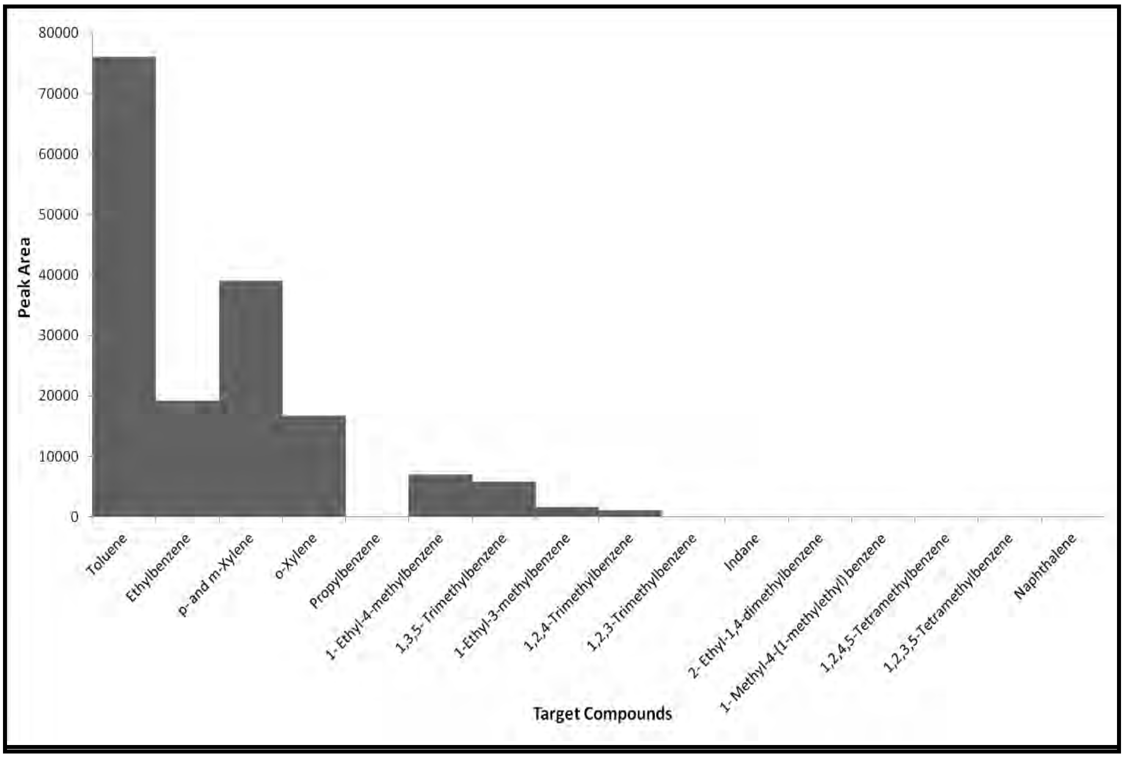


Figure 4.9: Target Compound Chromatogram of KimWipe spiked with 2μL 50% Evaporated Petrol

From the three spiked samples placed in room 3 which had burnt excessively with only a carbonised residue remaining, no petrol target compounds were able to be recovered.

4.3.3 RECOVERY OF VOLATILE ORGANIC COMPOUNDS FROM ROOM 1

Samples in room 1 ignited at flashover and were allowed to burn for 1 minute before being extinguished. Observations after burning showed that for the synthetic carpets the fibres had melted, for the wool carpet the fibres had singed and for the foam and underlay samples only a carbonised residue remained. For the room 1 fires, a petrol target compound was able to be recovered from the wool, 50-50 polypropylene-wool carpet and furniture foam samples. Figures 4.10 to 4.12 show the total ion chromatograms (top) and extracted ion chromatograms (bottom) for the wool, 50-50 polypropylene-wool carpet and furniture foam samples burnt in room 1. The total ion chromatograms and extracted ion chromatograms for the nylon carpet, polypropylene carpet and underlay are not shown as no target compounds were recovered.

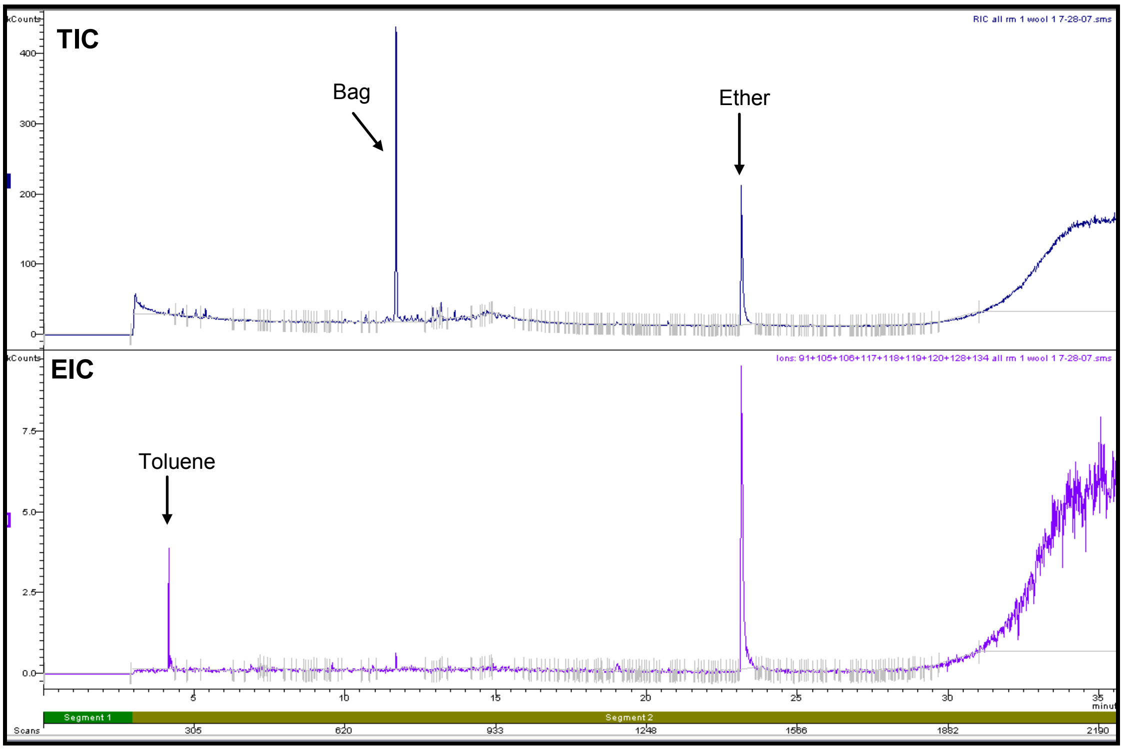


Figure 4.10: Total Ion Chromatogram and Extracted Ion Chromatogram of Wool Carpet burnt in Room 1 (Refer to Section 2.5.1 for GC/MS conditions)

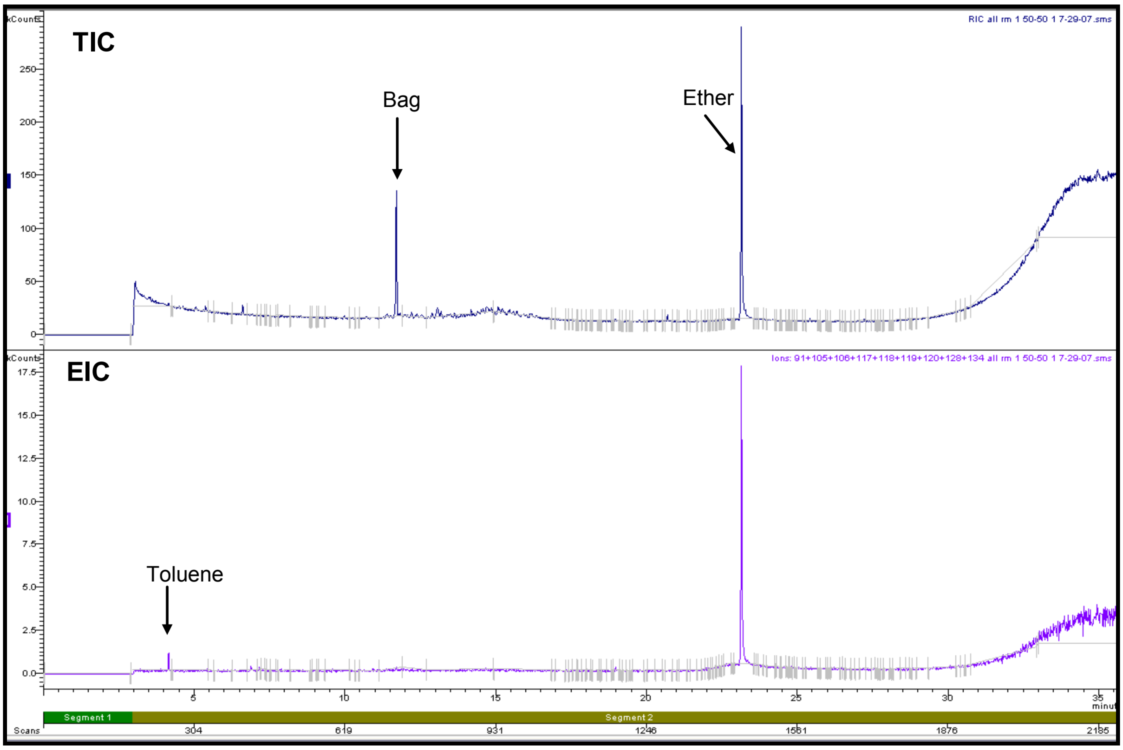


Figure 4.11: Total Ion Chromatogram and Extracted Ion Chromatogram of 50-50 Polypropylene-Wool Carpet burnt in Room 1 (Refer to Section 2.5.1 for GC/MS conditions)

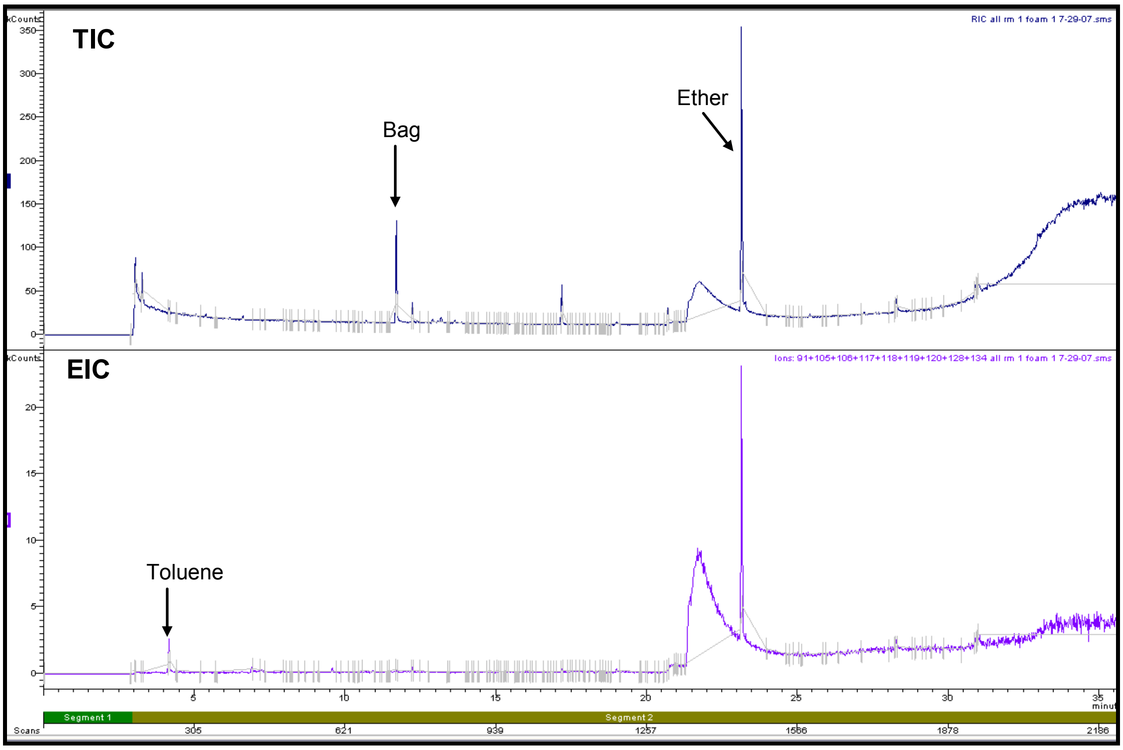


Figure 4.12: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam burnt in Room 1 (Refer to Section 2.5.1 for GC/MS conditions)

The only target compound recovered from wool, 50-50 polypropylene-wool carpet and the furniture foam was identified as toluene. The abundance of toluene was extremely low as it was not present in the any of the total ion chromatograms and present just above the baseline in the extracted ion chromatograms. In the case of the 50-50 polypropylene-wool carpet, toluene was also observed as a substrate background product but given that the carpet was allowed to burn for 1 minute it is unlikely that the toluene recovered for this carpet was a result of off-gassing. In all three cases toluene appeared to be a product of burning and the low levels are a result of it being consumed or otherwise lost during the burning process. What is interesting is that the same petrol target compound and at very similar low levels was recovered for samples that had undergone burning to differing extents. These results are supported by a number of other studies where toluene was found to be produced in low levels from the burning of carpet[43, 64, 102, 116, 117, 129, 141]. This finding is extremely interesting and suggests that perhaps extent of burning has little bearing on levels of volatile organic compounds that can be recovered but suggests rather, that in this real fire situation levels of volatile organic compounds present in the burnt sample are negligible because they are consumed or otherwise lost during this type of fire.

Samples burnt in room 1 were also subjected to steam distillation to see if heavier target compounds were present and could be recovered. An account of this experiment, including pictures, is given in Appendix A. The results from the steam distillation experiments showed that no other target compounds were recovered except again for toluene from the foam sample.

4.3.4 RECOVERY OF VOLATILE ORGANIC COMPOUNDS FROM ROOM 3

Samples in room 3 ignited at least 3 minutes prior to flashover and were allowed to burn for another minute before being extinguished. Observations after burning showed that for all samples only a carbonised residue remained. For the room 3 fires, nylon carpet was the only substrate from which petrol target compounds were recovered, the total ion chromatogram and extracted ion chromatogram is shown in Figure 4.13.

Interestingly, from the nylon carpet which had undergone extensive burning two target compounds, toluene and ethylbenzene, were recovered. The abundance of these two compounds was extremely low as they were not present in the total ion chromatogram and present just above baseline in the extracted ion chromatogram. Similar to room 1, these petrol target compounds may in fact be products of burning and the low levels again suggests that in this real fire situation, levels of volatile organic compounds present are negligible because they are consumed or otherwise lost during this type of fire.

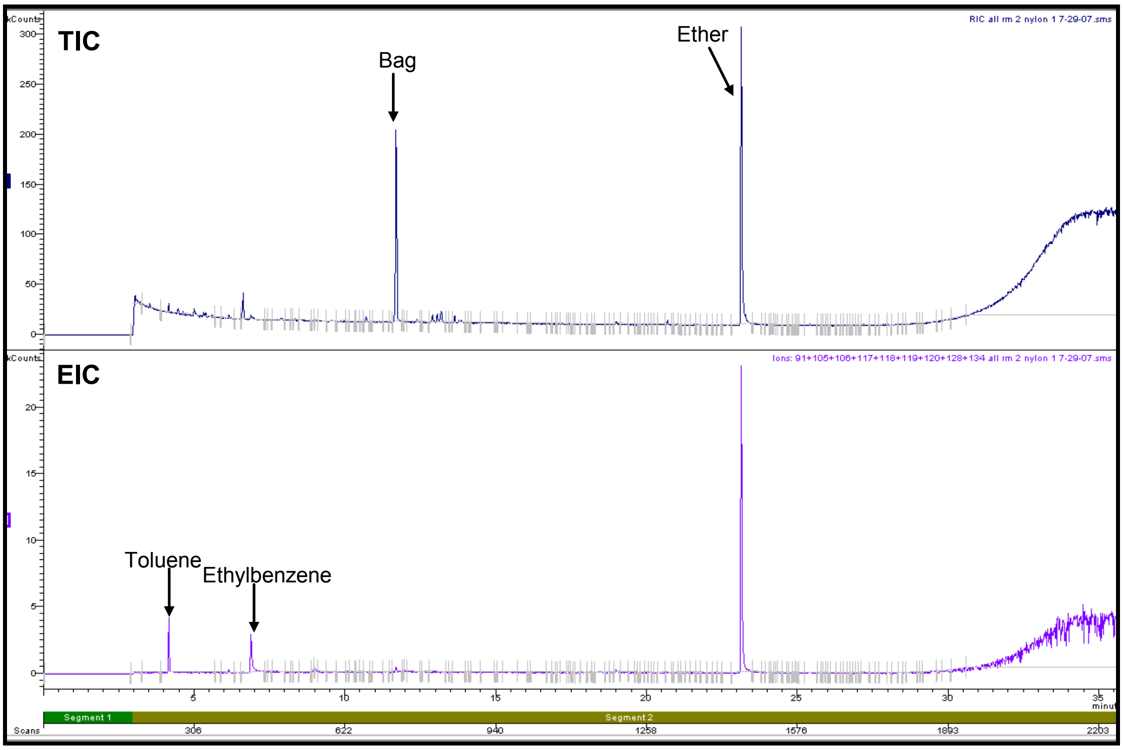


Figure 4.13: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Carpet burnt in Room 3 (Refer to Section 2.5.1 for GC/MS conditions)

The results from these experiments are consistent with the results from the full scale fire experiments conducted by Borusiewicz whereby for carpet, regardless of burning time, traces of used accelerants were easily recognisable[142]. Furthermore a study conducted by Dehaan and Bonarius found that depending upon the type of polymer, burning could result in the formation of compounds such as toluene, xylene and other complex volatiles[112]. Bertsch also showed that while neither carpet itself nor carpet padding produce volatiles that could be misidentified as being petroleum based, it is the carpet backing that is the prime source of interfering compounds[45, 141].

4.3.5 SUMMARY

The large scale room fires along with the carpet and foam sample sizes burnt and collected for ignitable liquid residue recovery represented a real fire investigation scenario. Results from the room fires confirm that there are a number of variables that cannot be kept consistent when trying to conduct real fires. Even though the rooms were set up as similar as possible, the fires burnt quite differently, particularly when the floor area in each room caught fire. In room 1 the door was able to be left fully open throughout the course of the fire and some samples remained intact with only melting or singeing of carpet fibres. Whereas in room 3, where the door was closed during the fire, the samples were completely carbonised. Extremely low levels of toluene and/or ethylbenzene were recovered from the various samples and the results indicated that the extent of burning had little bearing on the levels of target compounds recovered, but rather negligible levels are present in the burnt substrates because they are consumed or otherwise lost during burning in a real fire situation. This is a significant finding and suggests that in a real fire situation it would be unlikely to encounter interferences from the burning of carpet and foam that would hinder a petrol identification. When considering the levels of toluene and/or ethylbenzene recovered are below the limit for pattern comparison, then it is unlikely that at these levels these compounds would interfere with a petrol target compound chromatogram to any significant extent. It must be remembered that the limit for pattern comparison represents trace amounts of petrol and the relevance of this point to fire investigation is considered below where a hypothetical situation is used to show that the levels of toluene and ethylbenzene recovered from the large scale room fires is indeed extremely low.

The limit of pattern comparison standards were prepared by spiking a KimWipe of approx 250cm^2 (21.4cm x 10.5cm) with 2μL of 0, 50 and 95% evaporated petrol followed by passive/headspace recovery. This level of petrol present on the KimWipes can be related back to a typical room of 20m^2 where there is 1.6mL of petrol residue for recovery. Calculating how much unevaporated petrol would be present before a fire gives the following: 1.6mL if the petrol recovered was unevaporated, 3.2mL if the petrol recovered was 50% evaporated and 32mL if the petrol recovered was 95% evaporated. These initial levels of petrol are not realistic when considering an arsonist might typically use 1L of petrol to initiate a fire in a 20m^2 room. Using this simple estimate, the limit for pattern comparison is well below, ranging from

30 – 600 times below based on the knowledge and expertise of the fire investigation scientists at VPFSC, the levels at which these fire investigation scientists would expect to be working[59].

Of course the major assumption with the above is that the petrol was spread evenly through the room. Considering that petrol would be splashed through the room and would be concentrated in some areas more than others, and samples would be taken from the areas of greatest concentration, the limit for pattern comparison is far below the range in which these fire investigation scientists would work.

4.4 FURNACE FIRES

The large room fires displayed the typical, unpredictable nature of real fires where burning could not be controlled, resulting in samples that displayed either minimal burning or that were totally burnt. Furnace fires offered the possibility to better control the fires hence the extent of burning and study the volatile organic compounds produced during burning. A description of furnace, procedure, sample size and the time-temperature program utilised for these experiments is presented in Section 2.8. Furnace burns were only conducted on the nylon, polypropylene and wool carpets.

When burning carpet samples, the furnace was stopped at a selected temperature after which samples were collected for analysis. Initial trials where the program was stopped at high temperatures (above the carpets ignition temperature) resulted in excessive burning. The main disadvantage with the furnace was that the extent of burning could not be controlled as the carpet was unable to be observed during the burning process when the furnace doors were closed. Further trials saw the program stopped at ignition temperatures and based on extent of burning subsequent burning temperatures were decided.

With respect to sample size, initially small swatches of carpet (90cm x 40cm) were placed in the furnace but because of the positioning of the burners, burning conditions were not consistent across the floor of the furnace, resulting in some carpet pieces burning excessively while others experienced little burning. In order to take into account the varying burning conditions across the floor it was decided that a single large swatch of carpet would be used and placed on the furnace floor. However, the carpet swatch was too big to be placed in a sampling bag and had to be cut into pieces that represented the left or right side of the furnace.

Table 4.3 lists the temperatures at which the furnace burns were stopped.

Table 4.3: Furnace Burn Experiments

Carpet type	Temperature Furnace stopped (°C)*		
Nylon	483 (ignition)	433	383
Polypropylene	570 (ignition)[62]	470	370
Wool	230 (ignition)[62]	280	330

* *Uncertainty ± 0.5°C*

4.4.1 FURNACE BURNS FOR NYLON CARPET

As the ignition temperature of nylon is known to range between 424ºC and 532ºC, it was decided that the first fire would be stopped at the mid-point of approximately 480ºC[62]. Another two burns were subsequently performed at 50ºC and 100ºC below the mid–point ignition temperature (shown in Table 4.3). Figure 4.14 (a-b) shows the photos of the carpet when the furnace doors were open (at ignition temperature) and after extinguishment, respectively. After extinguishment, the carpet was almost completely burnt near the left side. However around the mid section, there were areas of the carpet that did not burn completely.

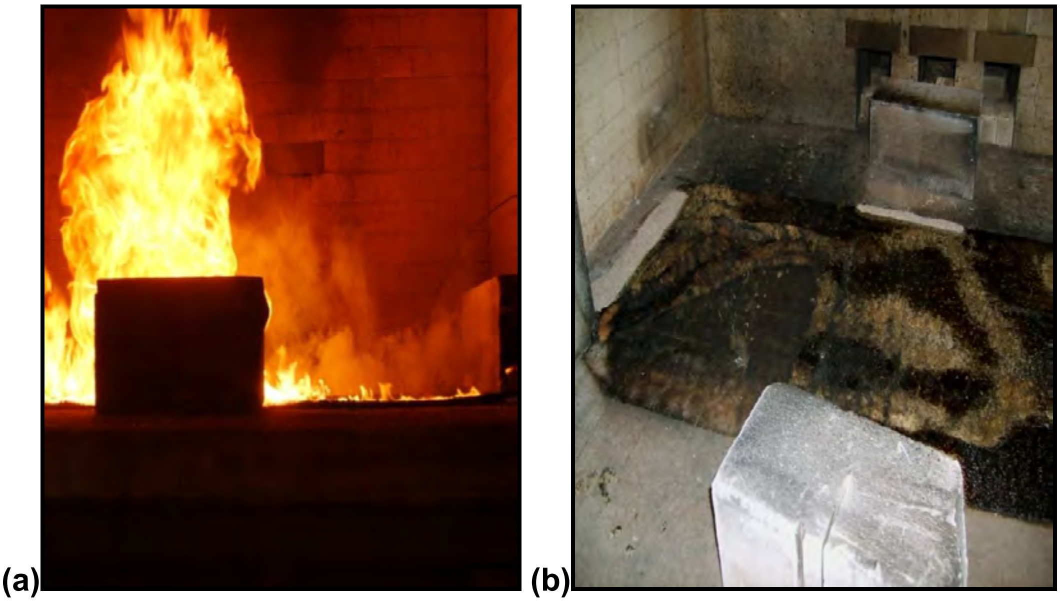


Figure 4.14: Nylon Carpet after Furnace Burn at 483ºC (a) When Doors were Opened (b) After Extinguishment

For the furnace burns which were stopped at 433°C and 383°C, the carpet was not on fire when the doors were opened and photos of the carpet are shown in Figures 4.15 and 4.16, respectively. Upon inspection of the carpet swatch burnt in the furnace at 433°C, it was observed that some areas of the carpet showed a considerable amount of burning whilst in other sections the fibres had only melted; this can be seen in Figure 4.15. The carpet burnt in the furnace at 383°C showed no evidence of burning, the fibres had merely melted.

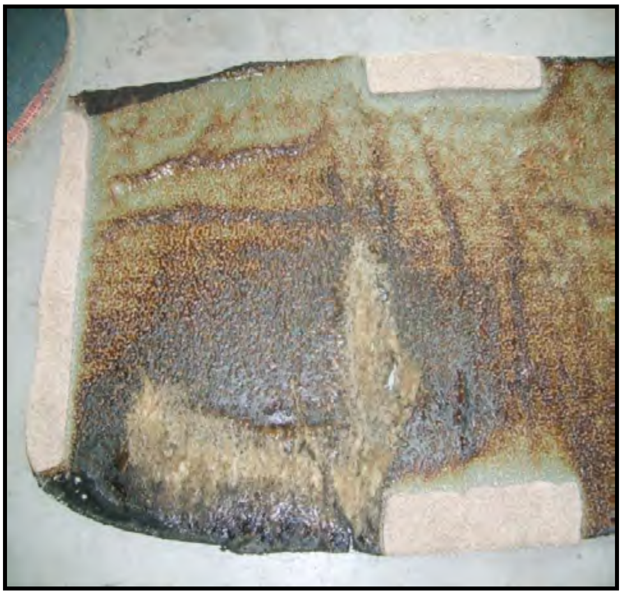


Figure 4.15: Nylon Carpet after Furnace Burn at 433ºC

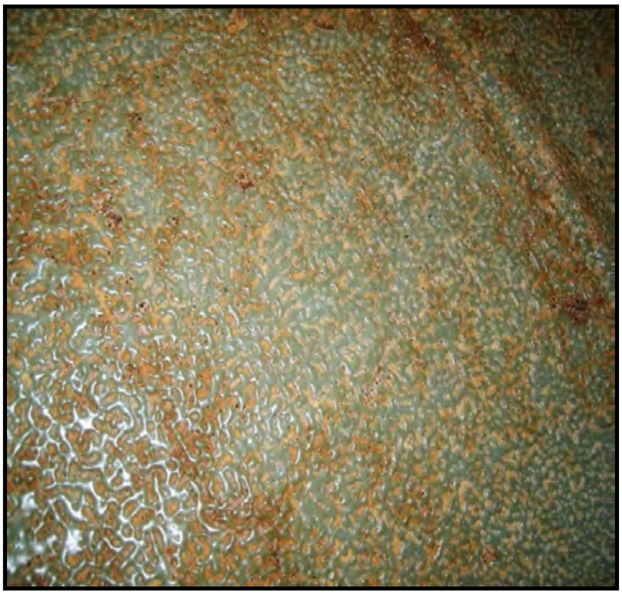


Figure 4.16: Nylon Carpet after Furnace Burn at 383ºC

The burnt nylon carpet samples were allowed to cool then cut into pieces. These pieces were then collected and analysed as described in Section 2.4 and 2.5.1. Table 4.4 lists the pieces of nylon carpet, the area of the furnace they occupied, their extent of burning and the petrol target compounds recovered.

Table 4.4: Observations and Target Compounds Recovered from Furnace Fire Experiments for Nylon Carpet

Temperature (°C)	Area of Furnace where Sample was Collected	Observations	Target Compounds Recovered
483	Left Side	Extensively burnt, including backing. Carbonised residue remaining.	Toluene, Ethylbenzene
	Right Side-Front	Heavily burnt fibres but not through to backing.	Toluene
	Right Side-Back	Heavily burnt fibres in some areas but not through to backing. Small areas with less burning	Toluene, Ethylbenzene
433	Left Side-Front	Heavily burnt fibres but not through to backing in some areas.	Toluene, Ethylbenzene
	Left Side-Back	Fibres melted with some areas having burnt.	-
	Right Side-Front	Minimal burning, backing had started to burn in some areas, fibres melted	-
	Right Side-Back	Minimal burning, backing had started to burn in some areas, fibres melted	-
383	Left Side	No burning, fibres melted	-
	Right Side	No burning, fibres melted	-

The total ion chromatograms and extracted ion chromatograms for the nylon carpet pieces burnt at 483°C are presented in Figures 4.17 (a-c).

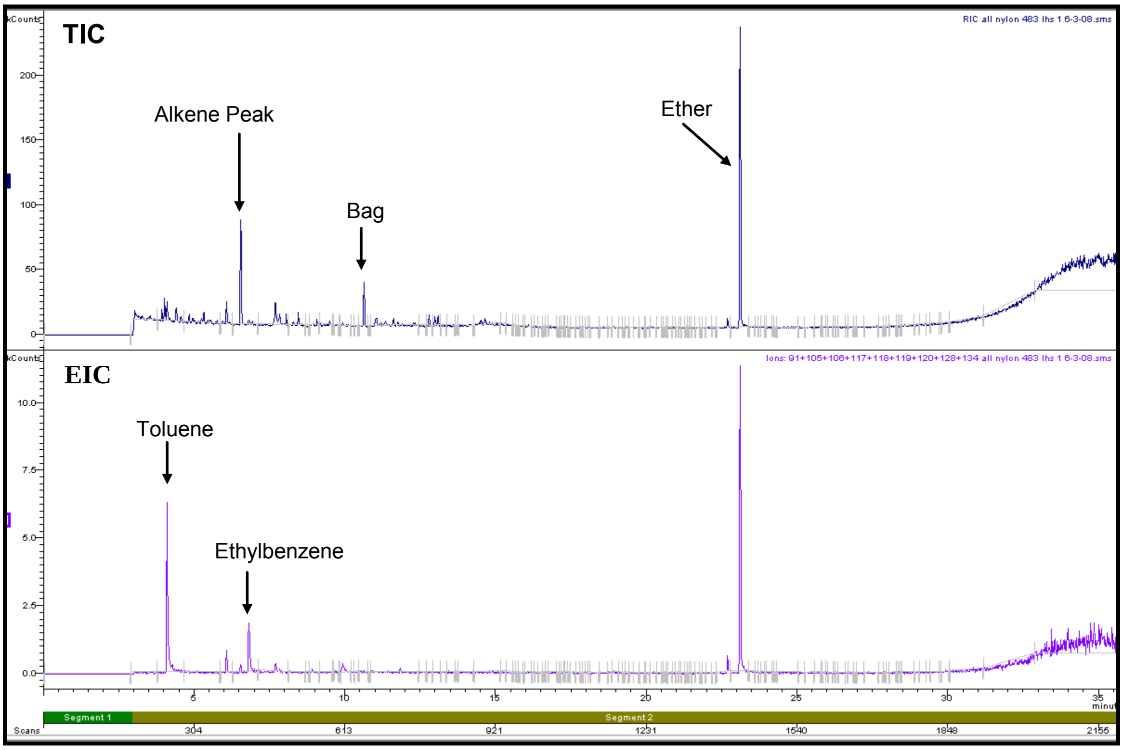


Figure 4.17(a): Total Ion Chromatogram and Extracted Ion Chromatogram of Left Side of the Nylon Carpet after Furnace Burn at 483ºC (Refer to Section 2.5.1 for GC/MS conditions)

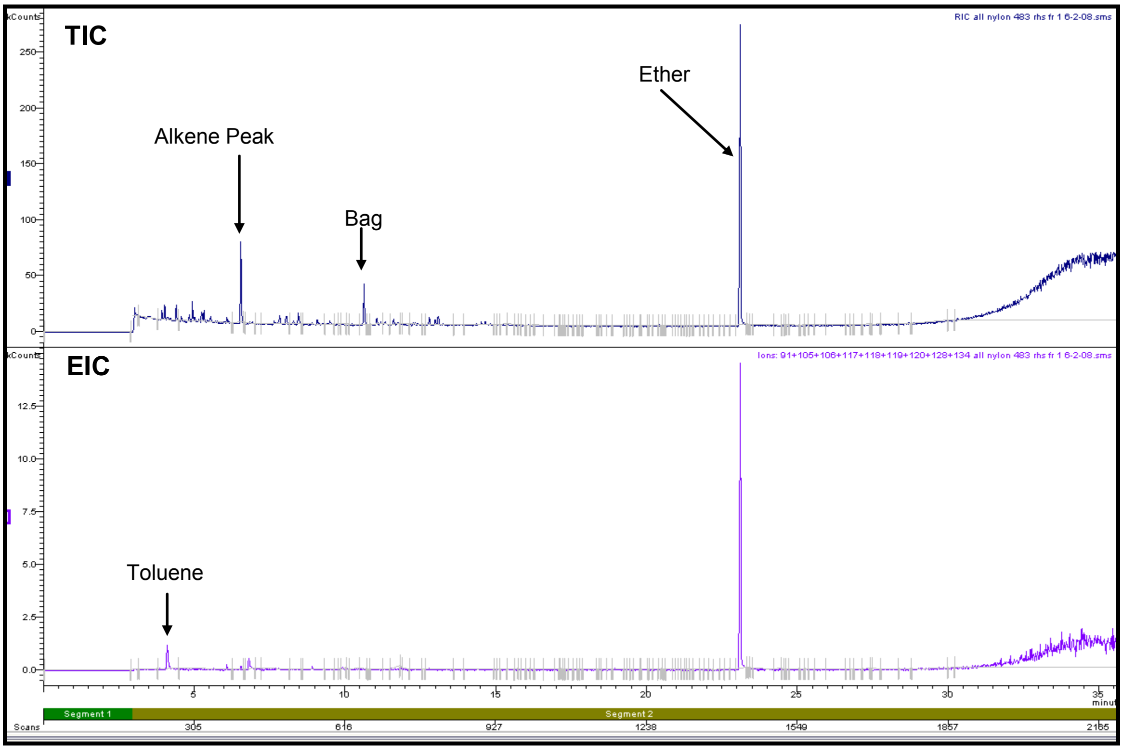


Figure 4.17(b): Total Ion Chromatogram and Extracted Ion Chromatogram of the Right Side-Front of the Nylon Carpet after Furnace Burn at 483ºC (Refer to Section 2.5.1 for GC/MS conditions)

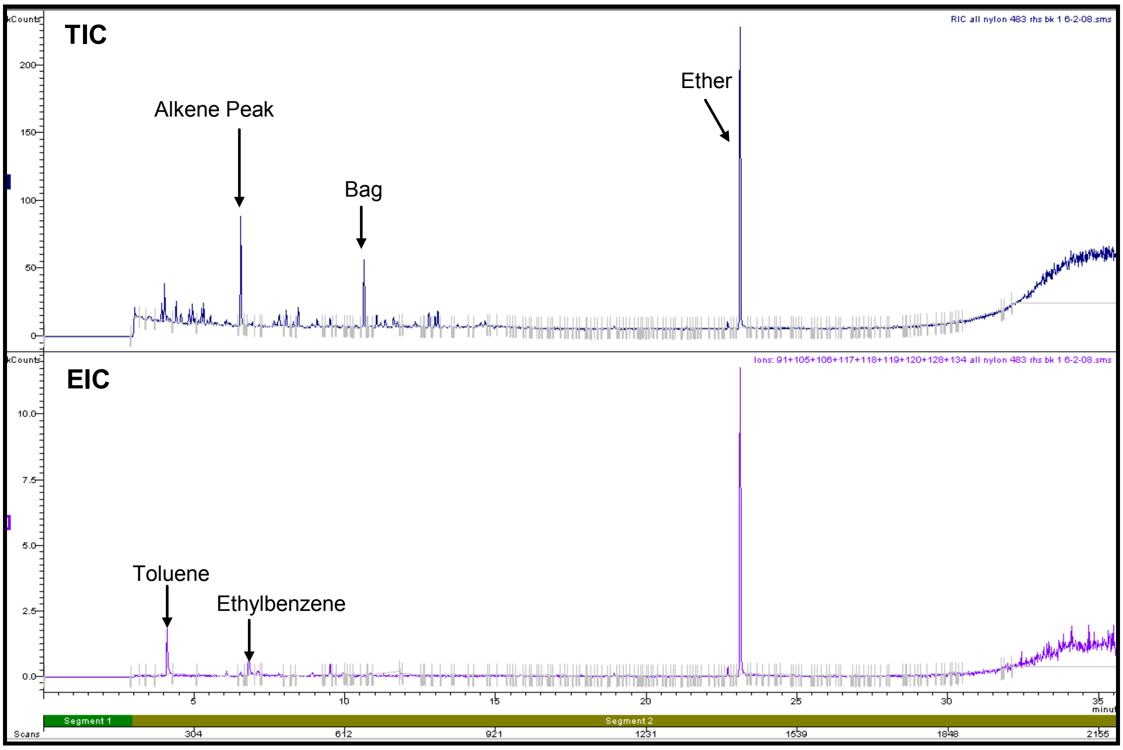


Figure 4.17(c): Total Ion Chromatogram and Extracted Ion Chromatogram of Right Side-Back of the Nylon Carpet after Furnace Burn at 483ºC (Refer to Section 2.5.1 for GC/MS conditions)

The nylon carpet pieces burnt in the furnace at 483°C show that the piece on the left side of the furnace had undergone extensive burning and two target compounds, toluene and ethylbenzene, were recovered. The total ion chromatogram shows that the abundance of these two compounds was low as it was just above baseline and the abundance in the extracted ion chromatogram was at levels less than those in the limit for pattern comparison standards (see Section 3.2). The burnt carpet from the back of the right side of the furnace which had undergone considerably less burning also produced these same two target compounds but in even lower amounts (not present in the total ion chromatogram and just above baseline in the extracted ion chromatogram) for a similar sample size. The carpet piece placed at the front on the right side of the furnace appeared to have burnt more than the piece collected from the back however only toluene was able to be recovered in even lower amounts than the other two swatches (again not present in the target compound chromatogram and just above baseline in the extracted ion chromatogram). Similar to the large room fires, these results again suggest that extent of burning has little bearing on levels of volatile organic compounds recovered because there are negligible levels present in the burnt substrate as they are consumed or otherwise lost during the burning process. Interestingly, the large room fire conducted in room 3 (see Section 4.3.4) where the nylon carpet was also extensively burnt also produced the same two target compounds (Figure 4.13) and furthermore the abundances of these two compounds are comparable for both burning tests and this may not be surprising given that the sample sizes were similar (90cm x 40cm in the large room fires and approximately 1m x 0.5m in the furnace).

The total ion chromatograms in Figures 4.17(a-c) also show a peak at 6.56 minutes. This compound was not a target compound but retention time and MS matching confirm it was recovered in a number of the burning tests including pyrolysis GC/MS. Given this fact the recovery of this compound may be an indicator of interferences coming from the burning of carpets and foam. Preliminary MS studies indicate this compound is an alkene however due to time restraints the nature of this compound was not pursued in this study and shall be the subject of further work in our laboratories. In Figures 4.17(a-c) and in other total ion chromatograms in the remainder of this chapter, the unidentified peak at 6.56 minutes shall be labelled as the ‘alkene peak’.

For the test burn at 433°C the most heavily burnt carpet piece, located on the left side at the front of the furnace, was the only piece to produce any target compounds. The total ion chromatogram and extracted ion chromatogram are presented in Figure 4.18.

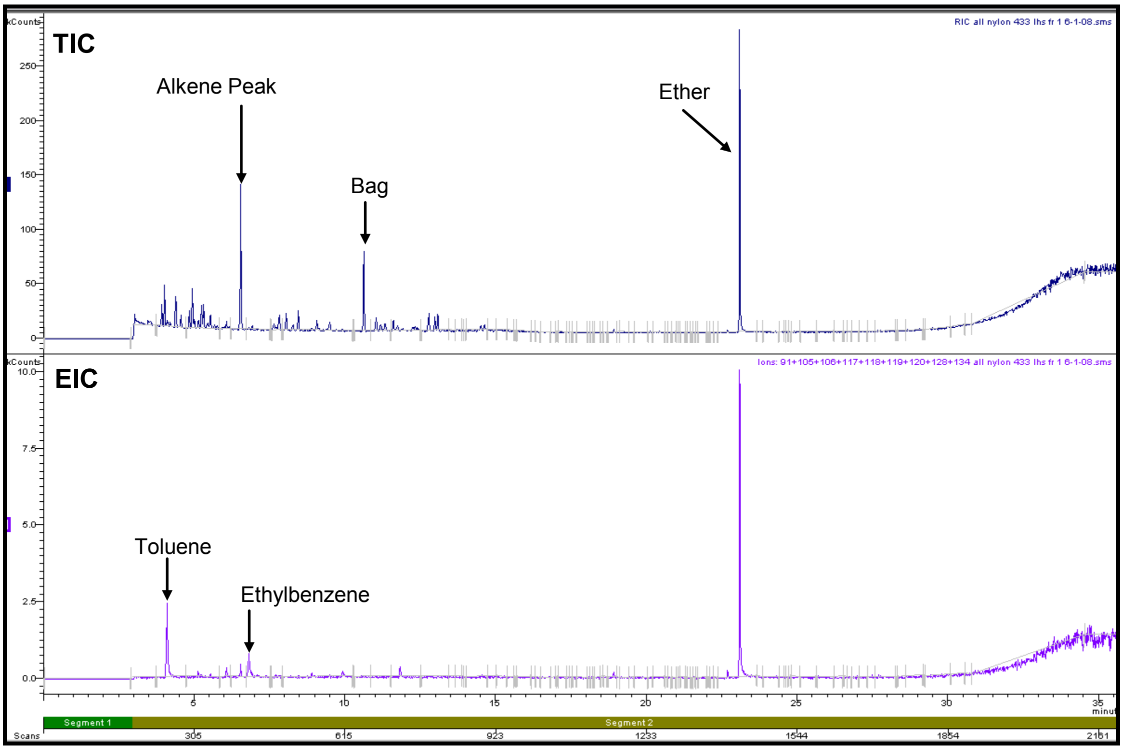


Figure 4.18: Total Ion Chromatogram and Extracted Ion Chromatogram of the Left Side-Front of the Nylon Carpet after Furnace Burn at 433ºC (Refer to Section 2.5.1 for GC/MS conditions)

Similar to the nylon carpet burnt at 483ºC the two target compounds recovered in very low abundances were toluene and ethylbenzene. The total ion chromatogram shows that the abundance of these two compounds was low as it was just above baseline and the abundance in the extracted ion chromatogram was at levels less than those in the limit for pattern comparison standards. No target compounds were recovered from the other three pieces of carpet burnt in the furnace at 483°C. There were also no target compounds recovered from the nylon carpet burnt in the furnace at 433°C.

4.4.2 Furnace Burns for Polypropylene Carpet

The first furnace fire conducted was stopped at 570ºC, which is the ignition temperature of the polypropylene carpet[62]. Another two burns were subsequently performed at 100ºC and 200ºC below the ignition temperature (shown in Table 4.3). Figure 4.19 shows a photo of the carpet when the furnace doors were open at the ignition temperature of polypropylene. Figure 4.20(a-b) shows a photo of the carpet when the furnace doors were opened after burning at 470ºC and after extinguishment, respectively. Figure 4.21 (a-b) shows a photo of the carpet when the furnace doors were open after burning at 370ºC and after extinguishment.

Figure 4.19: Polypropylene Carpet when Doors were Opened after Furnace Burn at 570ºC

Figure 4.20(a): Polypropylene Carpet when Doors were Opened after Furnace Burn at 470ºC

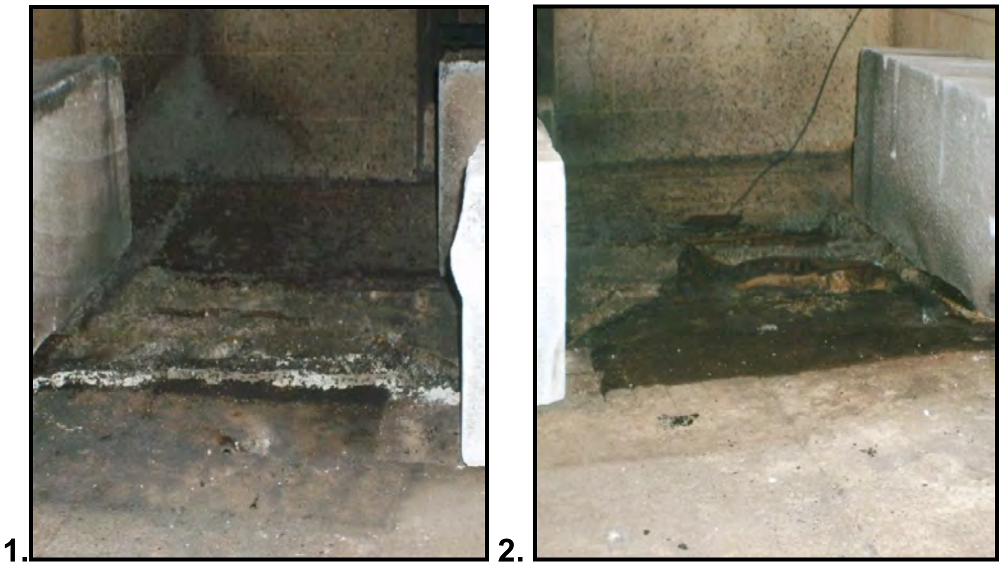


Figure 4.20(b): Polypropylene Carpet after Extinguishment following the Furnace Burn at 470ºC 1. Left Side and 2. Right Side of the Furnace

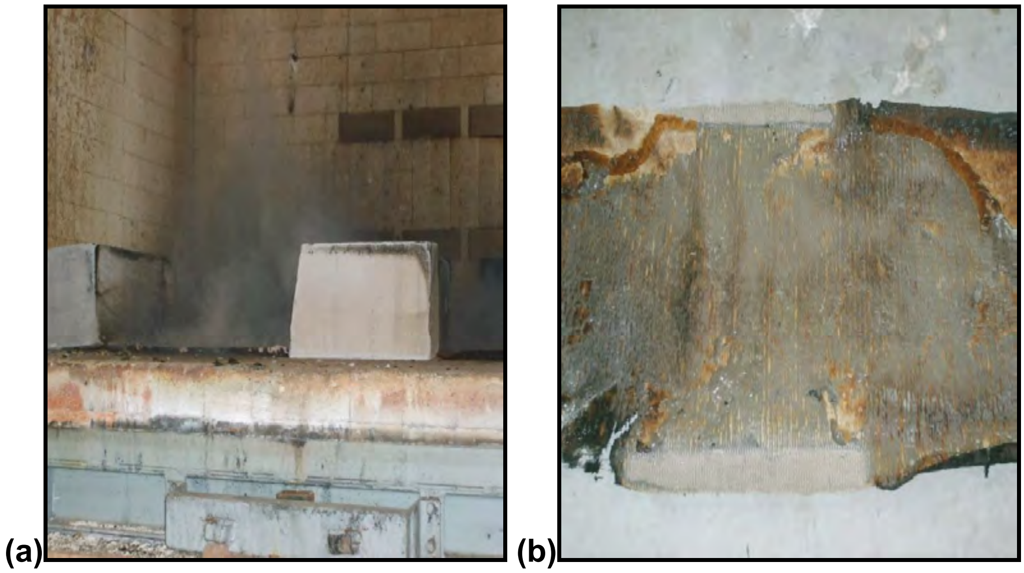


Figure 4.21: Polypropylene Carpet after Furnace Burn at 370ºC (a) When Doors were Opened (b) After Burning

After stopping the furnace and opening the doors at 570°C and 470ºC the carpet was alight and had to be extinguished with water. After extinguishment, it was observed that the polypropylene carpet, in both instances, had undergone extensive burning. Upon inspection of the carpet swatch burnt in the furnace at 370°C, it appeared as though the hessian had ignited but the polypropylene fibres appeared to have only melted (Figure 4.21(b)).

The burnt polypropylene carpet samples were allowed to cool then cut into pieces. These pieces were then collected and analysed as described in Section 2.4 and 2.5.1. Table 4.5 lists the pieces of polypropylene carpet, the area of the furnace they occupied, their extent of burning and the petrol target compounds recovered.

Table 4.5: Observations and Target Compounds Recovered from Furnace Fire Experiments for Polypropylene Carpet

Temperature (°C)	**Area of Furnace where Sample was Collected**	**Observations**	**Target Compounds Recovered**
570	Left Side	Extensively burnt, including backing. Carbonised residue remaining.	-
	Right Side	Extensively burnt, including backing. Carbonised residue remaining.	-
470	Left Side & Right Side	Extensively burnt, including backing. Carbonised residue remaining.	Toluene, Ethylbenzene
370	Left Side	Fibres melted and the backing had burnt around the edges.	Toluene
	Right Side	Fibres melted and the backing was still completely intact.	-

No target compounds were recovered from the polypropylene carpet burnt in the furnace at 570°C. Two target compounds, toluene and ethylbenzene, were recovered from the residue collected from the carpet burnt in the furnace at 470ºC. These are shown in the total ion chromatogram and extracted ion chromatogram presented in Figure 4.22.

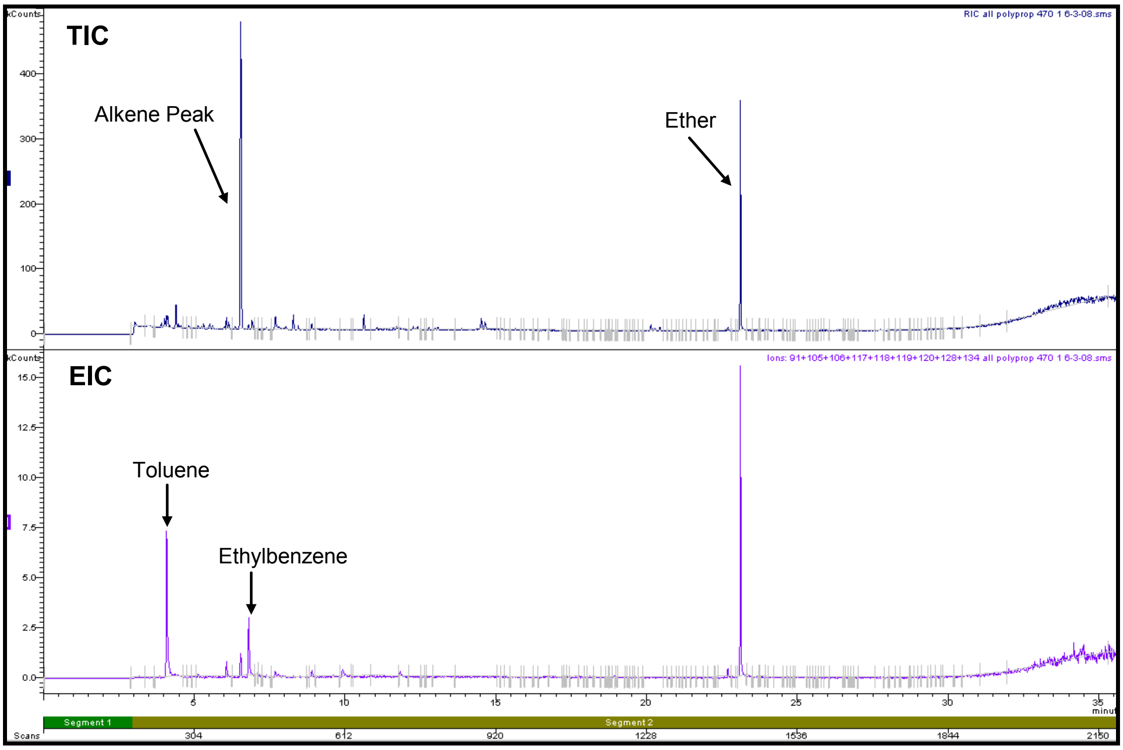


Figure 4.22: Total Ion Chromatogram and Extracted Ion Chromatogram of the Polypropylene Carpet after Furnace Burn at 470ºC (Refer to Section 2.5.1 for GC/MS conditions)

Although the carpet had undergone extensive burning, the extracted ion chromatogram shows that the two target compounds were recovered in amounts that are less than those in the limit for pattern comparison standards (the total ion chromatogram shows that the abundance of toluene and ethylbenzene were just above baseline and the abundance in the extracted ion chromatogram was also quite low).

The polypropylene carpet burnt in the furnace at 370ºC was collected in two parts. The carpet piece collected from the left side of the furnace burnt slightly more than the piece situated on the right side of the furnace. The piece on the left side produced one target compound, identified as toluene, in negligible levels. The total ion chromatogram and extracted ion chromatogram is presented in Figure 4.23

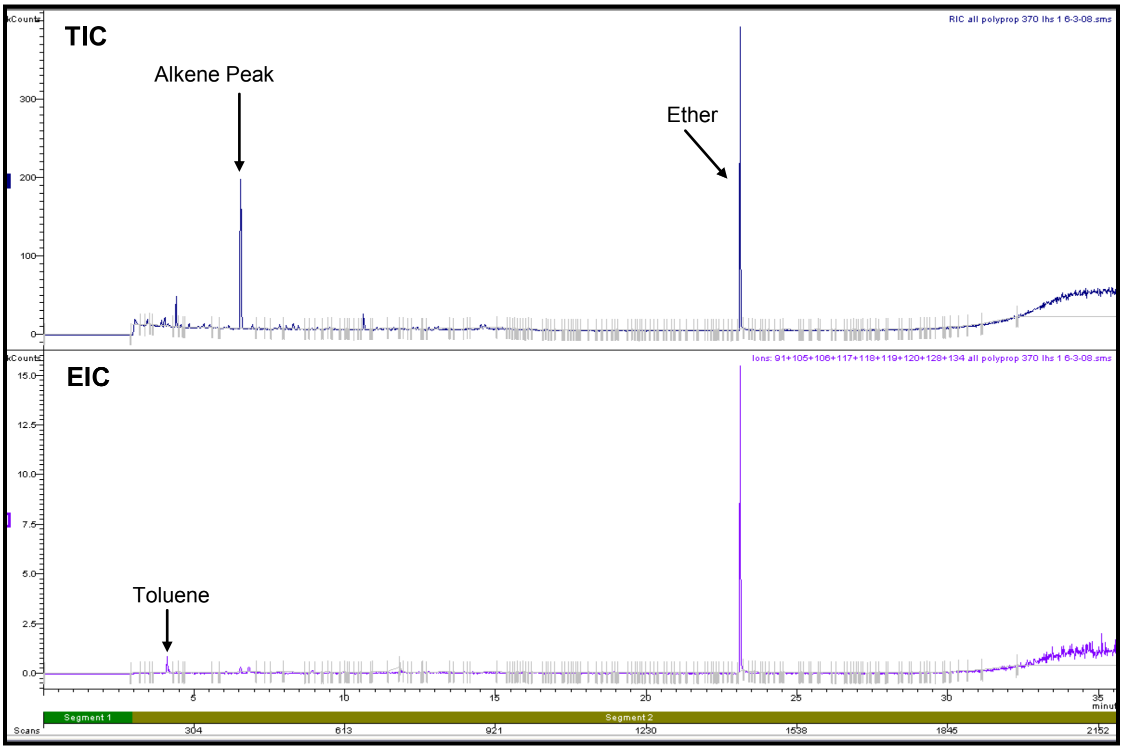


Figure 4.23: Total Ion Chromatogram and Extracted Ion Chromatogram of the Left Side of the Polypropylene Carpet after Furnace Burn at 370ºC (Refer to Section 2.5.1 for GC/MS conditions)

4.4.3 FURNACE BURNS FOR WOOL CARPET

The first furnace burn conducted on the wool carpet was stopped at 230ºC, which is the ignition temperature for wool[62]. As minimal burning occurred at this temperature, another two burns were subsequently performed at 50ºC and 100ºC above this ignition temperature (shown in Table 4.3). Figures 4.24 to 4.26 show the photos of the carpet after the three burns at the different temperatures.

The carpet swatch burnt in the furnace at 230°C appeared to have had only singed fibres with slight burning around the edges of the backing. Burning at 280ºC appeared to not make much difference again with only noticeable singeing of the fibres. At 330ºC however, although the carpet swatch remained intact, the wool fibres appeared singed in some areas and burnt in others. The burnt fibres were burnt to such an extent that when touched they disintegrated leaving a carbonised residue.

Figure 4.24: Wool Carpet after the Furnace Burn at 230ºC

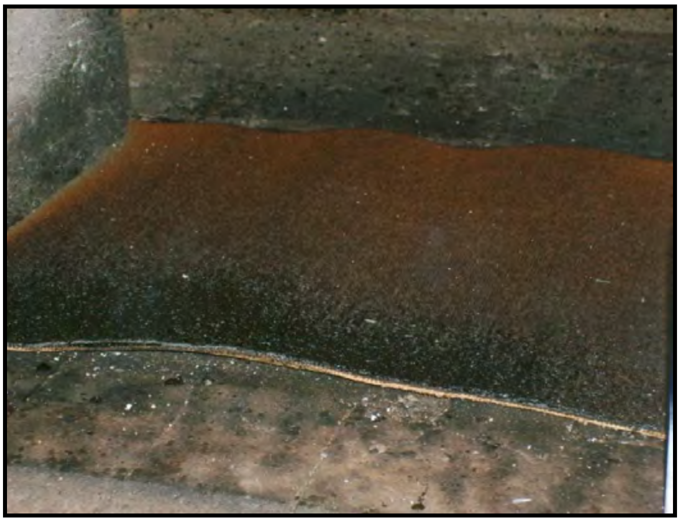


Figure 4.25: Wool Carpet after the Furnace Burn at 280ºC

Figure 4.26: Wool Carpet after the Furnace Burn at 330ºC

The burnt wool carpet samples were allowed to cool then cut into pieces. These pieces were then collected and analysed as described in Section 2.4 and 2.5.1. Table 4.6 lists the pieces of wool carpet, the area of the furnace they occupied, their extent of burnings and petrol target compounds recovered.

As seen in Table 4.6, no petrol target compounds were able to be recovered from any of the pieces of wool carpet burnt at these temperatures. Given that toluene was recovered from wool carpet burnt in the large scale room fires it was also expected to be recovered in the furnace fires. But overall these wool results are consistent with the other large scale room fires and furnace fire results and show that these burnt substrates have negligible levels of volatile organic compounds remaining and the levels remaining have little bearing on the extent of burning because volatile organic compounds are consumed or otherwise lost during the burning process in these open fire situations.

Table 4.6: Observations and Target Compounds Recovered from Furnace Fire Experiments for Wool Carpet

Temperature (°C)	**Area of Furnace where Sample was Collected**	**Observations**	**Target Compounds Recovered**
230	Left Side-Front	Fibres had singed but no burning.	-
	Left Side-Back	Fibres had singed but no burning.	-
	Right Side-Front	Fibres had singed but no burning.	-
	Right Side-Back	Fibres had singed but no burning.	-
280	Left Side	Fibres singed and the backing had burnt around the edges.	-
	Right Side	Fibres singed and the backing had burnt around the edges.	-
330	Left Side	Fibres had carbonised in some areas and the backing was burnt around the edges.	-
	Right Side	Fibres singed but not completely carbonised and the backing had burnt around the edges.	-

4.4.4 SUMMARY

Furnace fires did allow carpet samples (sizes typical of those collected in a real fire investigation scenario) with varying extents of burning to be collected, where various sections of carpet showed extensive burning (where only a carbonised residue remained) and others only melted fibres. Extremely low levels of toluene and/or ethylbenzene were recovered from the various samples and the results indicated that the extent of burning had little bearing on the levels of target compounds recovered but rather negligible levels are present in the burnt substrates because they are consumed or otherwise lost during burning in an open fire situation. Furnace fire results are consistent with results from the large room fires and support the contention that the low levels of toluene and/or ethylbenzene present and hence recovered would not interfere with a petrol identification.

4.5 SMALL CAN FIRES

Small can fires have been conducted by a number of researchers to determine the volatile organic compounds produced from burning different household materials; however each experiment is carried out slightly differently[3, 117, 141]. For example, Stauffer placed samples in an open (no lid) quart (0.95 L) paint can and burnt the samples by holding a propane torch to the sample to assist with the burning. Volatile organic compounds were subsequently collected on a charcoal strip placed in the can. He allowed the substrate to burn freely for approximately 2 minutes or until two thirds of the substrate had charred. Where the substrates could not sustain a flame, the propane torch was continuously held to the sample. The fires were then extinguished using either a fine spray of water or by depriving the fire of oxygen by sealing the can with the lid. Recovery of volatiles was conducted after the can was vented for an hour and involved desorption of volatile organic compounds trapped on a charcoal strip with carbon disulfide followed by GC/MS analysis. Stauffer found that the most encountered volatile organic compounds produced by the burning of carpets, by this method, included benzaldehyde, styrene, toluene, ethylbenzene, naphthalene, acetophenone,

C_{12} branched alkenes, C_{15} branched alkenes, phenyl ethyne, α- methylstyrene and C_9 branched alkenes[3].

Keto and Wineman on the other hand, conducted small can fires in 1 gallon (3.8 L) metal paint cans which were sealed with a lid containing a small vent hole (6mm in diameter) on top. The can containing the substrate was placed on a Meker burner and allowed to burn until heavy smoke was observed escaping from the vent hole and recovery of volatile organic compounds involved adsorption onto a charcoal tube followed by desorption using carbon disulfide. In order to evaluate the ability to extract useable target compound chromatograms from highly contaminated ignitable liquid samples, Keto and Wineman spiked the residues from the samples burnt in the small can fires with weathered ignitable liquids at levels adjusted so that the ignitable liquids chromatographic pattern would be obscured. They found that the presence of the petroleum pattern in the total ion chromatograms was not obvious; however the target compound chromatograms left little doubt as to their presence. The results from this study found that the target compound chromatograms for fresh and weathered petrol samples are sufficiently specific to allow their identification in high background arson samples[117, 153].

Bertsch also conducted small can fires using 1 gallon (3.8L) metal paint cans which he placed on a Bunsen burner. He allowed some of the samples of carpet and carpet padding to undergo extensive burning and extinguished some with water and some by oxygen starvation. Bertsch recovered volatile organic compounds from all samples using passive headspace and carbon disulfide extraction. He analysed his data using target compounds which he considered to be primary indicators of highly evaporated petrol. These compounds included the C_2-C_5 alkylbenzenes and 2-methylnaphthalene isomers. He found that although some ignitable liquid type compounds, particularly aromatic compounds, can be generated by burning the carpet and carpet padding, petrol can still be recognised[141].

Using the information from the previous research, further work on small can fires was conducted in this study with the aim to develop a laboratory test method for the burning of substrate comparison sample. Of particular interest was the effect of the volatile organic compounds recovered from the small can fire experiments when the following parameters were investigated:

- The effect of having the lid on or off the can.
- The effect of type of extinguishment.
- Determination of location of volatile organic compounds within the can after burning.
- The orientation of the sample within the can.
- The effect of burning time.

The initial investigations were conducted using nylon carpet and these findings are presented in the following section concluding with a small can test fire protocol for the burning of nylon carpet which was then applied to the other carpet and foam samples investigated in this study. A final test protocol for the burning of carpet and foam substrate comparison sample is then described in the final chapter.

In order to ensure the burning of the can itself did not produce any volatile organic compounds that are themselves petrol target compounds, or that co-elute with or contain ions similar to target compounds, a ‘can blank’ was conducted. This involved placing an empty can on the burner and allowing it to burn for approximately 2 minutes. After cooling, the inside of the can appeared to have considerable burning on the bottom, the sides of the can had discoloured and there was some bubbling evidenced around the joins. The total ion chromatogram and extracted ion chromatogram are shown in Figure 4.27 and even though a number of volatile organic compounds were recovered in the total ion chromatogram, the extracted ion chromatogram shows no petrol target compounds were recovered.

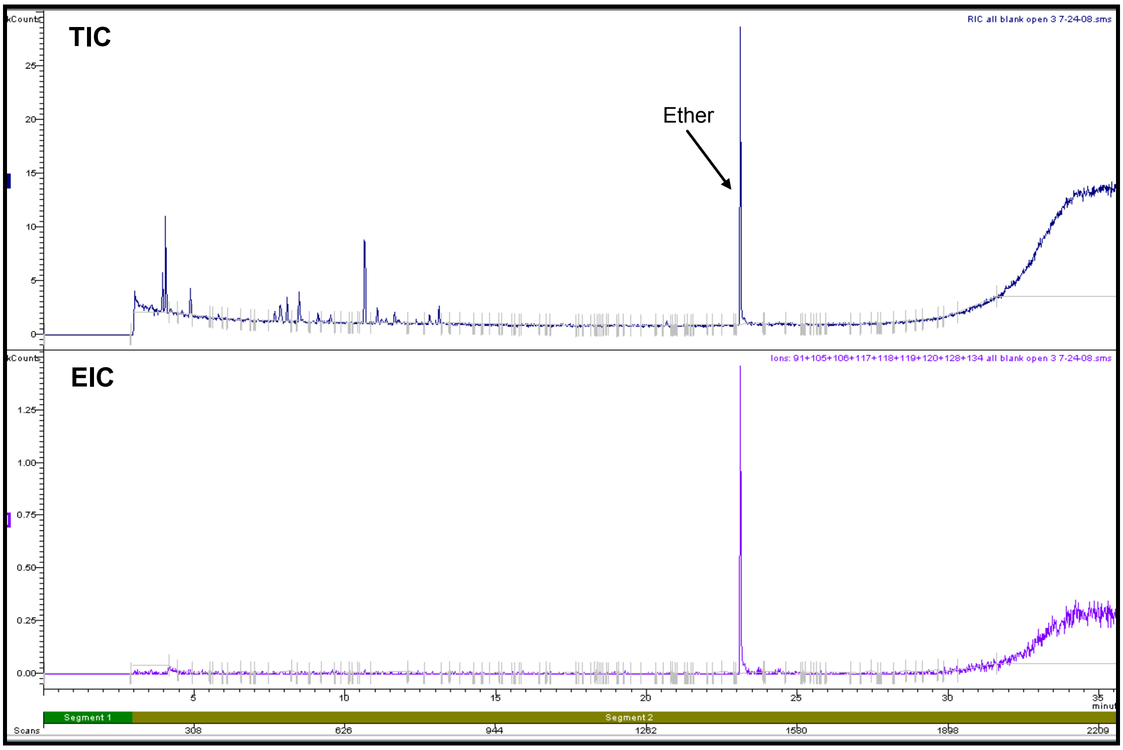


Figure 4.27: Total Ion Chromatogram and Extracted Ion Chromatogram of 'Can Blank' (Refer to Section 2.5.1 for GC/MS conditions)

4.5.1 SMALL CAN FIRES WITH LID OFF THE CAN

Initial small can fires were based on a method similar to the one used by Stauffer where burning in small cans occurs with no lid[3]. For these small can fire experiments recovery of volatile organic compounds was performed by placing the charcoal tube inside the can and placing the entire can with the sample into an evidence bag as shown in Figure 4.28. The recovery and GC/MS analysis was then performed as described in Sections 2.4 and 2.5.1, respectively.

Figure 4.28: Can containing Charcoal Tube in Evidence Bag

For the initial experiment, a piece of nylon carpet (10cm x 10cm in size) was placed in a 1L metal paint can and a butane gas stove lighter was used to try to ignite the carpet. After numerous attempts it was noted that the backing of the carpet would ignite easily, however the flame would self-extinguish prior to the carpet fibres burning regardless of whether or not the lighter flame was continuously held to the sample.

The next trial was conducted in the same manner described above, however a more powerful ignition source was utilised. A piezo ignition micro torch (butane) which has a high temperature (1300ºC) flame was used and once again the carpet samples failed to ignite easily and sustain a flame.

In an attempt to burn the carpet a three ring burner connected to a liquefied petroleum gas (LPG) cylinder was used and this proved to be successful. The carpet swatch utilised in this initial experiment was cut in a disc shape so it could fit flat on the bottom of the can, as shown in Figure 4.29, thus allowing the entire swatch to be exposed to radiant heat. Once the can got hot enough, the carpet began to fold and shortly after copious amounts of smoke was emitted from the can. The backing then ignited and shortly thereafter again the nylon ignited. The carpet was then extinguished approximately 2 minutes after being placed on the burner by spraying a small volume of water into the can.

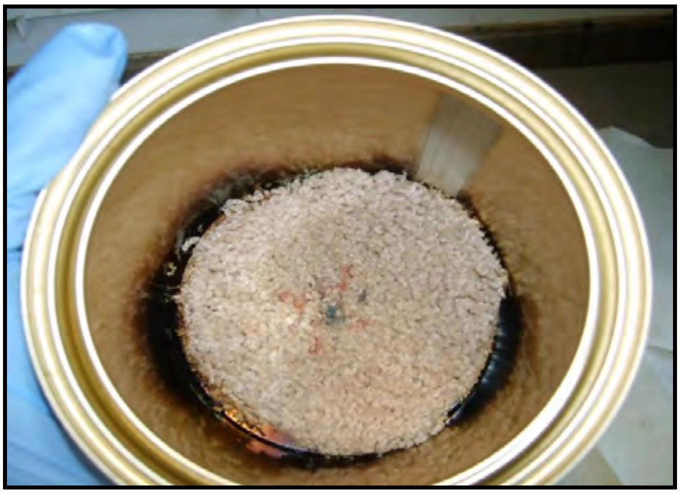


Figure 4.29: Nylon Carpet Cut to Fit Flat in the Bottom of the Can

Visual inspection of the can contents showed that the carpet had burnt to approximately three quarters of its original size, with the majority of heavy burning occurring around the edges, see Figure 4.30. A small piece of hessian remained intact as it had been protected from the burning by the nylon which had melted and collected in that area.

Figure 4.30: Nylon Carpet after Burning for approximately 2 minutes

Analysis of this sample resulted in very low levels of toluene and ethylbenzene being recovered. The total ion chromatogram and extracted ion chromatogram are shown in Figure 4.31 where these peaks are not present in the total ion chromatogram and just above baseline in the extracted ion chromatogram. These results are consistent with the results obtained from the large scale room fires and furnace fires where low levels of toluene and ethylbenzene were also recovered.

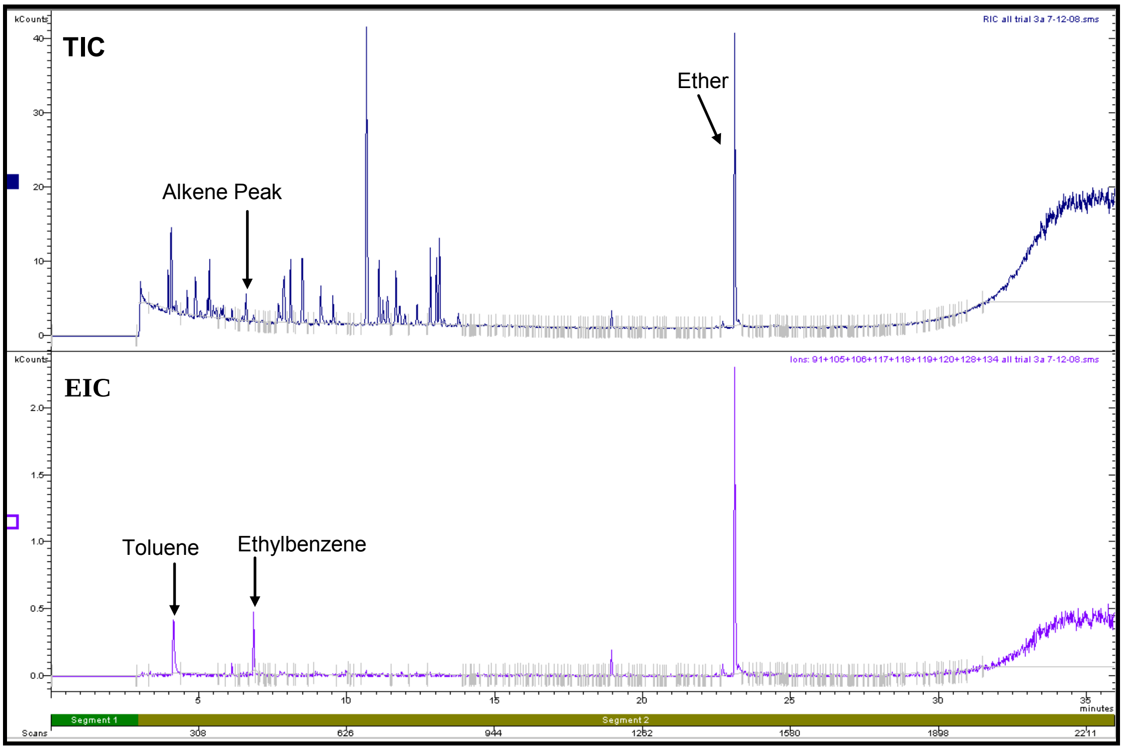


Figure 4.31: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon burnt in a Small Can with Lid Off (Refer to Section 2.5.1 for GC/MS conditions)

4.5.2 EFFECT OF EXTINGUISHMENT

In order to avoid wetting the sample the next small can fire was extinguished by immersing the can in a bucket of cold water (carefully so as to ensure no water entered the can). Again, the carpet was cut in a disc shape to fit into the bottom of the can and was placed in the can as shown in Figure 4.29. The can with lid off, was then placed on the burner and allowed to burn for approximately 2 minutes. It was noticed that soon after being placed on the burner, the carpet began to curl, shortly after copious amounts of smoke was emitted from the can. As the burning progressed the amount of smoke produced was such that the burning taking place in the can was no longer visible. After approximately 2 minutes the can was removed from the burner and immersed into the bucket of cold water to cool the can and stop any further burning.

Visual inspection of the can contents showed that the nylon carpet had been considerably burnt, with only a small piece remaining intact. The nylon had once again melted and collected in the centre of the carpet swatch thus protecting the backing in this area, whilst the rest of the backing had completely burnt away. Figure 4.32 shows the total ion chromatogram and extracted ion chromatogram for this small can fire

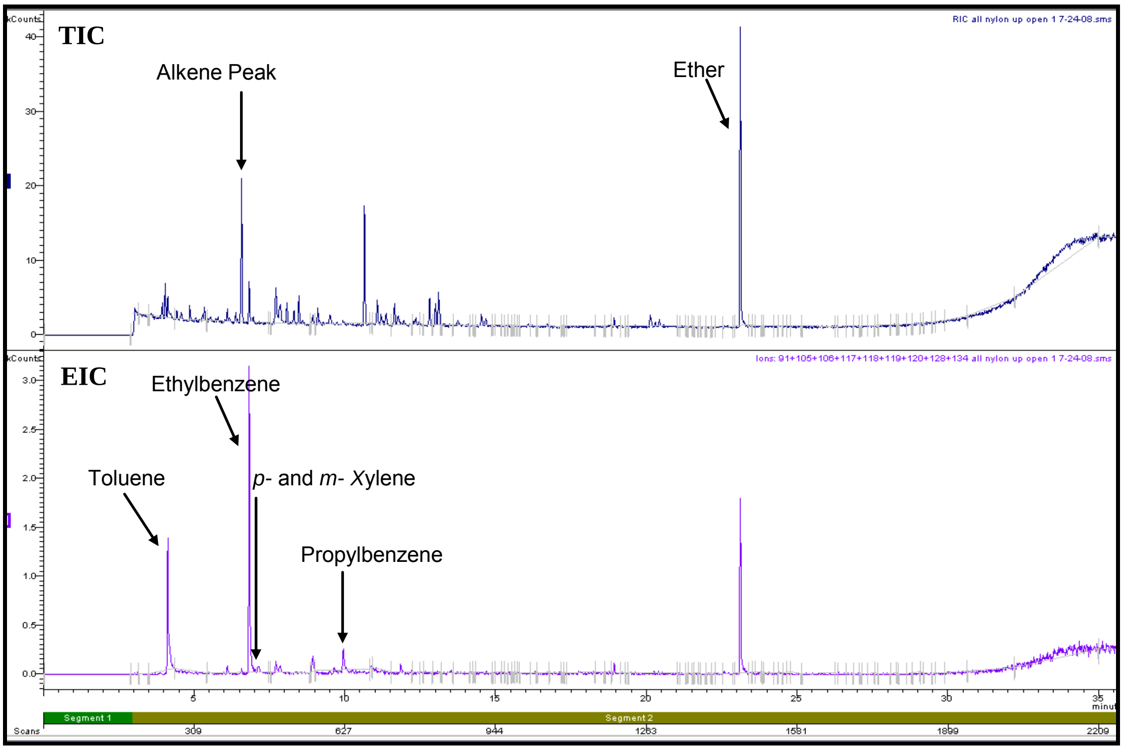


Figure 4.32: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Swatch burnt in a Small Can with Lid Off and Extinguished in a Bucket of Water (Refer to Section 2.5.1 for GC/MS conditions)

Like the previous small can fire (Figure 4.31), toluene and ethylbenzene were recovered but this time *p*- and *m*-xylene and propylbenzene were also recovered although in very low abundances. This was the first time that compounds other than toluene and ethylbenzene were recovered in this study. The other two compounds were recovered in such low levels (baseline levels) that it is unlikely that the method of extinguishment had any significant impact on the recovery of these volatile organic compounds.

Interestingly, Stauffer was able to recover a large number of volatile organic compounds in his small can fire experiments of nylon carpet with lid off[3].

Another observation made by Stauffer during his small can fire experiments was that when extinguishing the small can fires by placing the lid on the can and depriving the fire of oxygen, a greater amount of pyrolysis products are produced. His research showed that a sample extinguished in this manner produces up to 10 times the amount of volatile organic compounds compared to a sample extinguished with water. He also states that this method may generate even more volatile organic compounds than what is found in a real fire scenario[3, 139]. Keto and Wineman were also able to recover a number of target compounds from the burning of substrates in small can fires with lid on[117]. Therefore further studies with small can fires were conducted in a can with the lid on and are described in detail in the following section.

4.5.3 SMALL CAN FIRES WITH LID ON THE CAN

Small can fire experiments with the lid on were conducted using an adaptation of the method described by Keto and Wineman[117, 153]. The Meker burner was replaced with the three ring burner and a 1L metal paint can was used instead of the 3.8L metal can. As per Keto and Wineman's method a 6mm vent hole was pre-drilled into the lid of the can and the sample was placed into the can and sealed[117, 153]. The method of extinguishment was conducted in the same manner as previously described where the can was carefully immersed in a bucket of cold water so as to ensure that no water entered the can. Furthermore, after extinguishment the lid was opened and a charcoal tube was inserted into the can and lid placed back on. The entire can, including the lid was placed in an evidence bag. The recovery of volatile organic compounds was conducted as described in Section 2.4.

The initial experiment was a 'can blank' to determine if the can burnt with the lid on, produced any volatile organic compounds that are themselves petrol target compounds or that co-elute with or contain ions similar to target compounds. The lid, with the 6mm vent hole, was placed on the can and the can was placed on the burner for approximately 2 minutes and then immersed in a bucket of cold water to cool it down.

After extinguishment, it was observed that the underside of the lid had discoloured. Furthermore the inside of the can had turned a pink/brown in colour on the bottom. However, similar to the previous ‘can blank’ burn, no petrol target compounds were recovered as seen in the total ion chromatogram and extracted ion chromatogram presented in Figure 4.33.

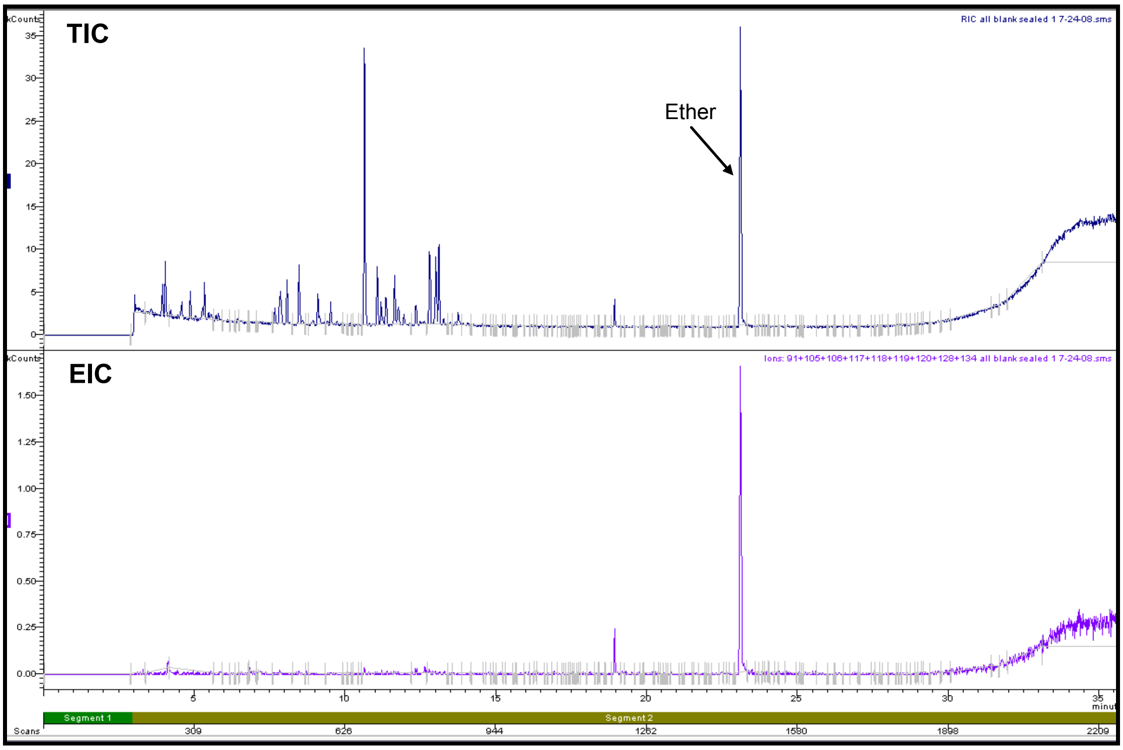


Figure 4.33: Total Ion Chromatogram and Extracted Ion Chromatogram of burnt ‘Can Blank with Lid On’ (Refer to Section 2.5.1 for GC/MS conditions)

The next small can fire experiment consisted of burning a swatch of nylon carpet in the can with lid on. The nylon carpet was cut in a disc shape and placed in the bottom of the can as shown in Figure 4.29. The lid, with the pre-drilled vent hole (see Figure 4.34) was securely placed on the can, which was then placed on the burner.

Figure 4.34: Pre-drilled Hole in lid placed on Can

After burning for approximately 1 to 1.5 minutes copious amounts of smoke was observed emitting from the vent hole. After 2 minutes the can was cooled and the lid was removed. Visual inspection of the underside of the lid showed that it had discoloured and was coated with a yellowish residue. The can contents showed that the nylon carpet had been considerably burnt, with only a small piece remaining intact. The nylon had once again melted and collected in the centre of the carpet swatch thus protecting the backing in this area, whilst the rest of the backing had completely burnt away. The total ion chromatogram and extracted ion chromatogram for this experiment are presented in Figure 4.35 and the target compound chromatogram is shown in Figure 4.36.

Of the nine petrol target compounds recovered, toluene and ethylbenzene were recovered in the greatest abundance and at levels approximately 10 times greater than the other target compounds. These results do agree with those obtained by Stauffer as well as Keto and Wineman in that placing the lid on the can does eventuate in greater amounts of volatile organic compounds being collected. However no compounds heavier than indane were able to be recovered when burning the sample of nylon carpet under these conditions. Both Stauffer and Keto and Wineman were able to recover much heavier compounds from their small can fire experiments where they burnt nylon carpet and nylon carpet with polyurethane underlay[3, 117]. Perhaps the nylon carpet used in this study was of a different composition (backing, glue etc) and subjected to different manufacturing processes than that used in the other studies. Another interesting observation is the presence of styrene in amounts now observable in the total ion chromatogram. This peak was not a target compound in this study but styrene has been identified as a compound produced by the burning of carpet by a number of researchers including Fernandes *et al*, Bertsch, DeHaan and Bonarius, Stauffer, Almirall and Furton and Lentini *et al* [3, 64, 111-113, 141].

This small can fire experiment shows that petrol target compounds can be recovered from nylon carpet when subjected to the burning conditions in a small can with lid on.

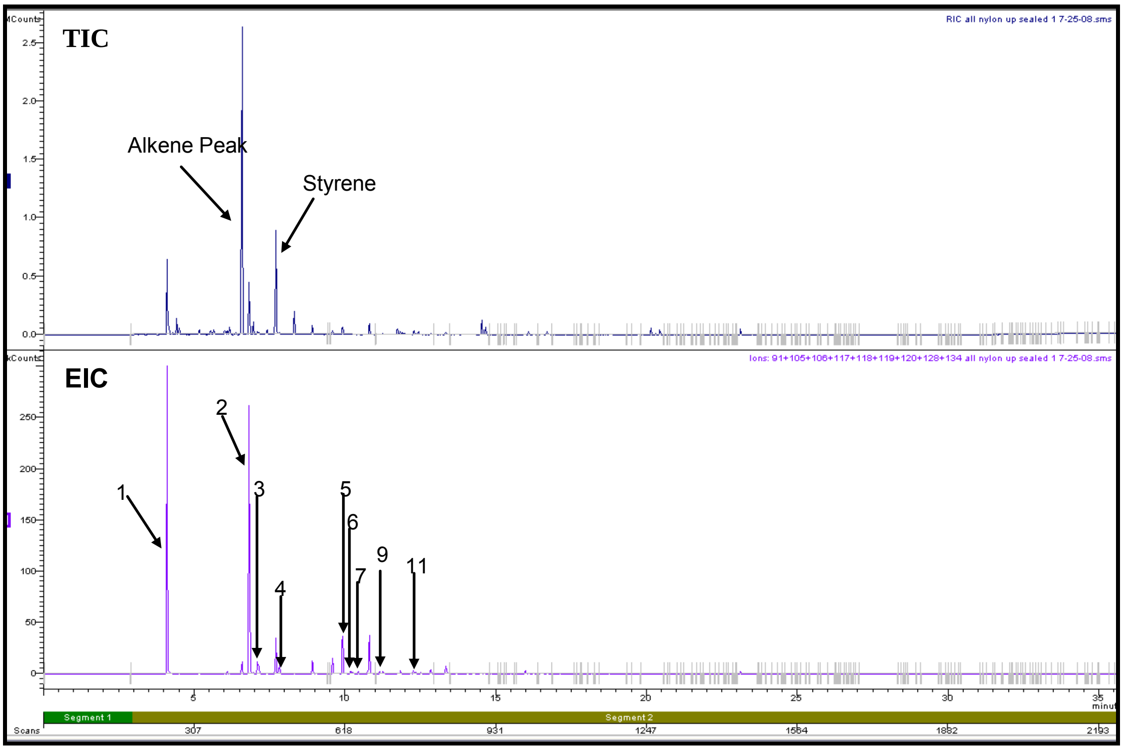


Figure 4.35: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Swatch placed in the Bottom of a Can burnt with Lid On (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p-* and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 9= 1,2,4-Trimethylbenzene, 11=Indane

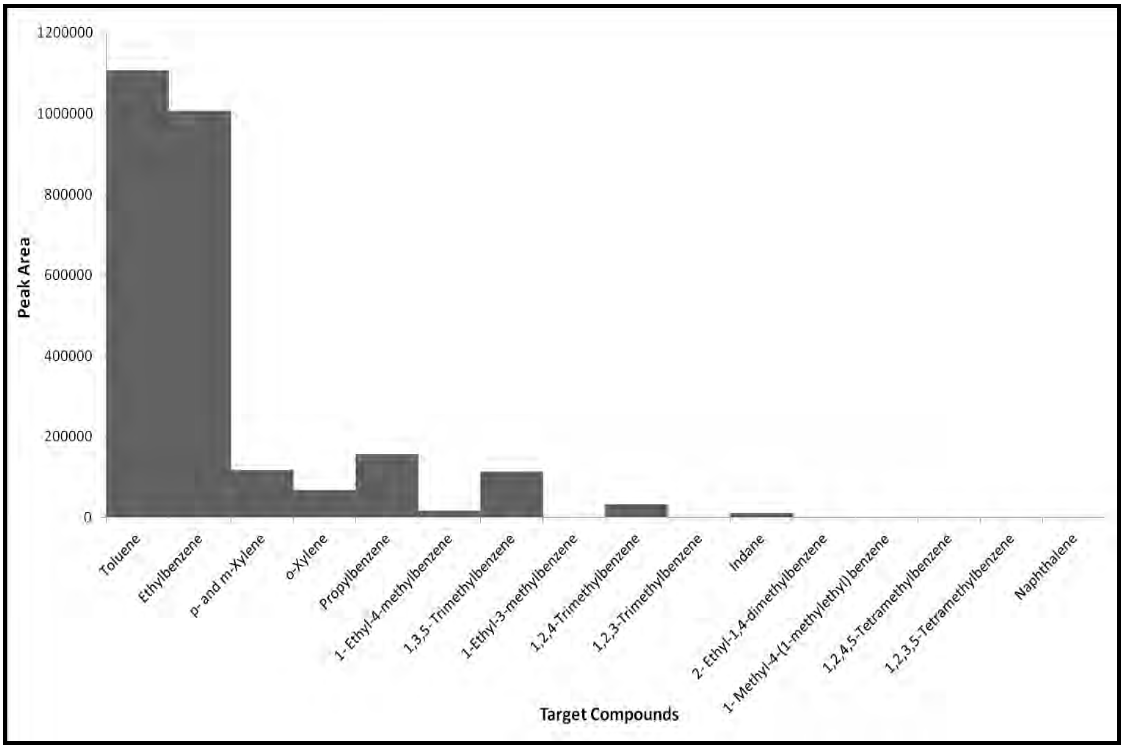


Figure 4.36: Target Compound Chromatogram of Nylon Swatch placed in the Bottom of a Can burnt with Lid On

4.5.4 DETERMINATION OF LOCATION OF VOLATILE ORGANIC COMPOUNDS WITHIN THE CAN AFTER BURNING

The result from the previous small can fire experiments show that leaving the lid on the can whilst burning the carpet has a great affect on the volatile organic compounds that can be recovered. The question generated from these results was where in the can, that is, on the lid, on the sides of the can, or in the carpet, were the volatile organic compounds located after the burn? Therefore another small can fire experiment was conducted similar to that above however this time the lid, carpet swatch and can were then placed in separate evidence bags and the recovery of volatile organic compounds, as described in Section 2.4, was conducted.

After the burning test visual inspection of the underside of the lid showed that it had discoloured and was coated with a yellowish residue. The nylon carpet swatch was still intact however it was considerably burnt and very brittle and on closer inspection it was evident that the fibres had melted. The sides of the can were observed to have also discoloured and there was a slight streaking pattern observed.

The total ion chromatograms and extracted ion chromatograms from the lid, nylon carpet and can are presented in Figures 4.37, 4.38 and 4.39 respectively.

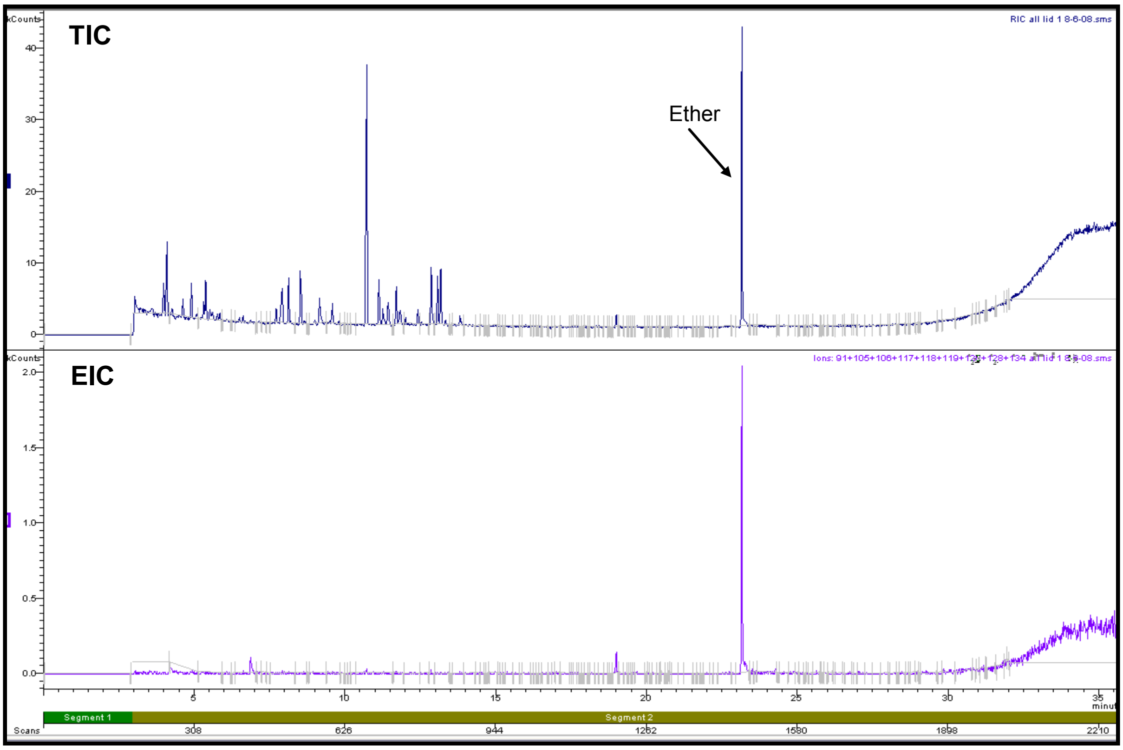


Figure 4.37: Total Ion Chromatogram and Extracted Ion Chromatogram of the Lid (Refer to Section 2.5.1 for GC/MS conditions)

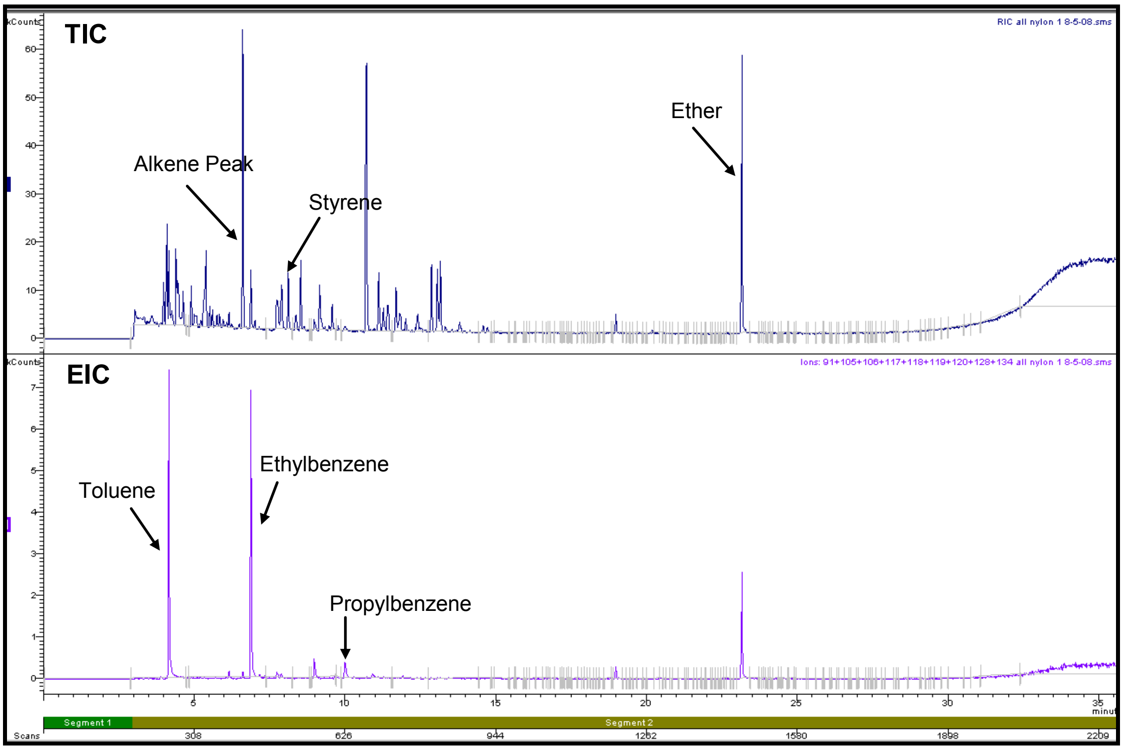


Figure 4.38: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Carpet (Refer to Section 2.5.1 for GC/MS conditions)

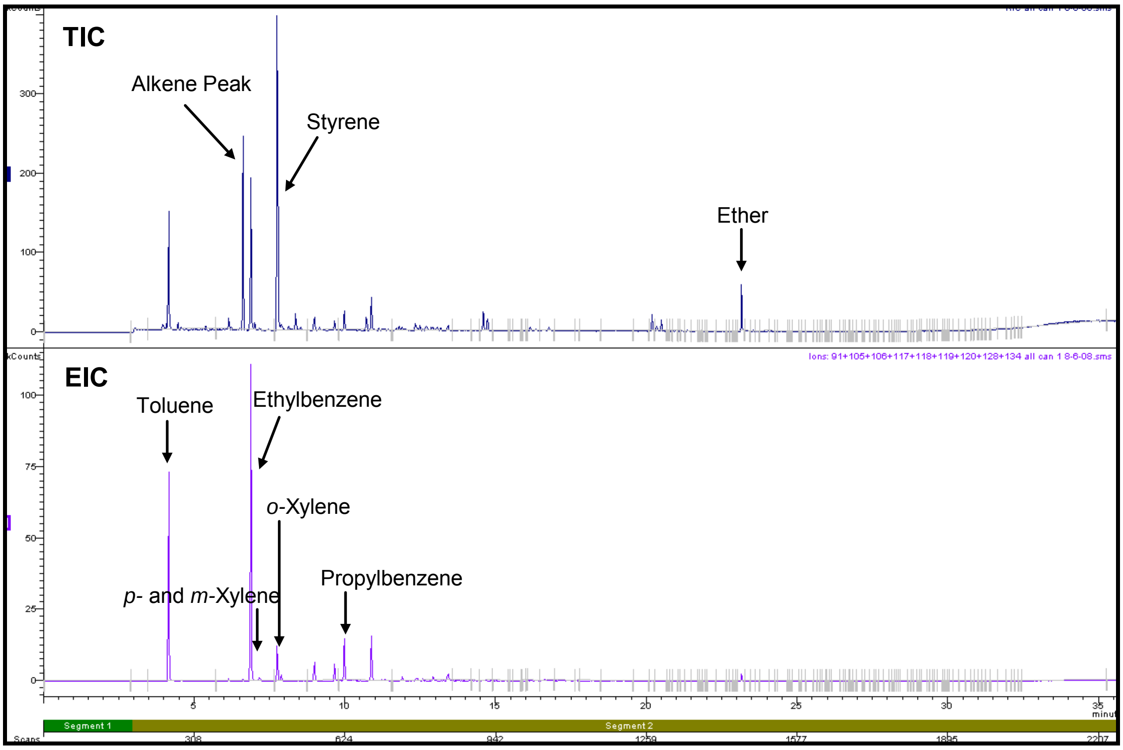


Figure 4.39: Total Ion Chromatogram and Extracted Ion Chromatogram of Can (Refer to Section 2.5.1 for GC/MS conditions)

The total ion chromatograms and extracted ion chromatograms for the lid, nylon carpet and can are very interesting and show that while no target compounds were recovered from the lid, 10 times more target compounds were recovered from the can than the burnt carpet sample, where the levels in the carpet are less than those in the limit for pattern comparison standards. This implies that when the sample is burnt the volatile organic compounds produced are trapped in the can, and when cooled they condense on the sides of the can. As described above, there was a residue observed as a streaking pattern on the sides of the can and the volatile organic compounds are more than likely contained within this residue. This result indicates that it is important that the entire can and its contents be sampled when recovering volatile organic compounds from these small can fire experiments. Sampling the burnt carpet itself will only result in very low abundances of volatile organic compounds.

The fact that low levels of volatile organic compounds remain in the burnt carpet is significant and this result further supports the findings from the large room fires and furnace fires in that negligible levels of volatile organic compounds remain in a burnt substrate because these are consumed or otherwise lost during the burning process.

Another interesting observation is that the unidentified alkene peak and styrene were also observed in the carpet and the can.

4.5.5 THE ORIENTATION OF THE SAMPLE WITHIN THE CAN

Two further experiments were conducted to determine what effect the orientation of the carpet swatch in the can had on the recovery of volatile organic compounds. Test burns were conducted as described above except in one can the carpet was placed with the fibres facing down and the other can consisted of a 10cm x 10cm nylon swatch being placed vertically in the can. The total ion chromatograms, extracted ion chromatograms and target compound chromatograms for these two experiments are shown in Appendix B. The results obtained are virtually identical to that of the experiment with the fibres facing up (see Figure 4.35). The presence or absence of the volatile organic compounds recovered in very low abundances, for example 1,2,4-trimethylbenzene was present when the fibres were facing up, could not be attributed to the orientation of the carpet. Therefore it can be concluded that the orientation of the carpet in the can had little bearing on the type and abundance of volatile organic compounds produced by the burning of the carpet and the remaining small can fire experiments were conducted with the carpet sample being placed in the bottom of the can with the fibres facing up.

4.5.6 THE EFFECT OF BURNING TIME

In the previous small can fire experiments the duration of the burn from when the can was placed on the burner until extinguishment was approximately 2 minutes. The next set of experiments investigated the effect of burning time of the type and abundance of target compounds recovered.

The length of burning time for the nylon carpet ranged from 30 seconds to 5 minutes, increasing by 30 second intervals, with a further two burns being conducted at 7.5 and 10 minutes. Appendix C lists details of each of these burns including photos, total ion chromatograms, extracted ion chromatograms and target compound chromatograms. This information is tabulated and presented in Table 4.7 below.

Table 4.7: Observations and Target Compounds recovered from Small Can Fire Experiments for Nylon Carpet

Burn Time (min)	**Visual Observations**	**Target Compounds Recovered**
0.5	Not much burning of the carpet occurred. The carpet swatch exhibited slight charring on the back of the carpet swatch and very minimal burning around the edges. The bottom of the can showed evidence of burning.	Toluene, *p*- and *m*-Xylene
1	The underside of the lid had undergone some slight discolouration as did the inside of the can. The carpet was burnt around the edges and the hessian on the back was blackened. The middle section of the nylon fibres remained unburnt.	Toluene, Ethylbenzene, *p*- and *m*-Xylene
1.5	The underside of the lid and the inside of the can both discoloured slightly. The carpet swatch remained its original size but was slightly burnt around the edges. The fibres were singed and the hessian on the back was blackened but still intact.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, Propylbenzene
2	The underside of the lid and the inside of the can were discoloured. The carpet swatch remained its original size however the fibres melted around the edge of the carpet. Towards the middle of the carpet, only the tips of the fibres were burnt but actual bunches of fibres were still evident. The hessian was also quite burnt.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene

Table 4.7: Observations and Target Compounds recovered from Small Can Fire Experiments for Nylon Carpet *(continued)*

Burn Time (min)	**Visual Observations**	**Target Compounds Recovered**
2.5	The underside of the lid showed slight discolouration and the sides of the can also showed some streaking. The nylon carpet sample remained intact but was extremely brittle and on closer inspection it became evident that the fibres had melted but some still retained their original shape.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, Indane
3	The underside of the lid was coated with a thick residue and the inside of the can showed considerable streaking down the sides. The carpet swatch was slightly smaller than its original size. The nylon fibres had completely melted and the hessian was blackened but still intact. The sample was extremely thin and quite brittle.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-methyl-4-ethylbenzene, Indane
3.5	The underside of the lid had a thick coating of residue on it. The sample was only slightly smaller than the original but was extremely brittle and a piece snapped off when it was removed from the can. On closer inspection it was evident that the nylon fibres had completely melted and tiny bubbles were present on the top. The hessian was intact but blackened.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
4	The underside of the lid had a thick layer of a burnt residue on it and the inside of the can had obvious streaking down the sides. The sample was recovered from this burn in pieces and it was found to be paper thin, extremely brittle and it appeared that most of the nylon had melted off the backing and all that remained was some hessian with a thin layer of nylon.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene

Table 4.7: Observations and Target Compounds recovered from Small Can Fire Experiments for Nylon Carpet *(continued)*

Burn Time (min)	**Visual Observations**	**Target Compounds Recovered**
4.5	The sample was considerably burnt. The nylon melted to a thin layer covering some of the hessian which was also blackened and burnt. The sample was approximately three quarters of its original size and had bits broken off and some parts were so badly burnt they had turned to charcoal. There was residue on the underside of the lid and a streaking pattern in the can.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
5	The sample was so burnt it was broken in tiny pieces. On closer inspection, there was almost no nylon left however what was left formed a thin layer over the hessian protecting it from burning. The lid and the sides of the can once again show the condensed residues.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
7.5	Only the backing of the carpet was left intact, however when touched it disintegrated. The underside of the lid had a thick, bubbled layer of residue condensed on it and the sides of the can had considerable streaking.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene, 1-ethyl-3-methylbenzene, 1,2,4- Trimethylbenzene and Indane
10	The underside of the lid and the sides of the can being covered with a considerable amount of residue. The sample of carpet was extremely thin and brittle and only small pieces remained, the sample was so fragile when it was touched it disintegrated.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene, 1-ethyl-3-methylbenzene, 1,2,4- Trimethylbenzene and Indane

In order to compare the target compounds produced and abundances of these at the various burn times, the peak area from the extracted ion chromatogram of each of the target compounds was plotted as a ratio with the butylated hydroxytoluene peak (referred to as the ‘Ether’ peak in the total ion chromatograms) versus burn time. Only one batch of diethyl ether was used in this study to prepare all standards and samples for GC and when examining the butylated hydroxytoluene peak in these chromatograms retention time reproducibility was less than 1% and peak area reproducibility showed RSD ranging from 5 to 8.8%. This confirmed that the 'Ether' peak could be used as an internal standard. This approach allowed a more quantitative comparison between the data at each burn time. This plot is shown below in Figure 4.40.

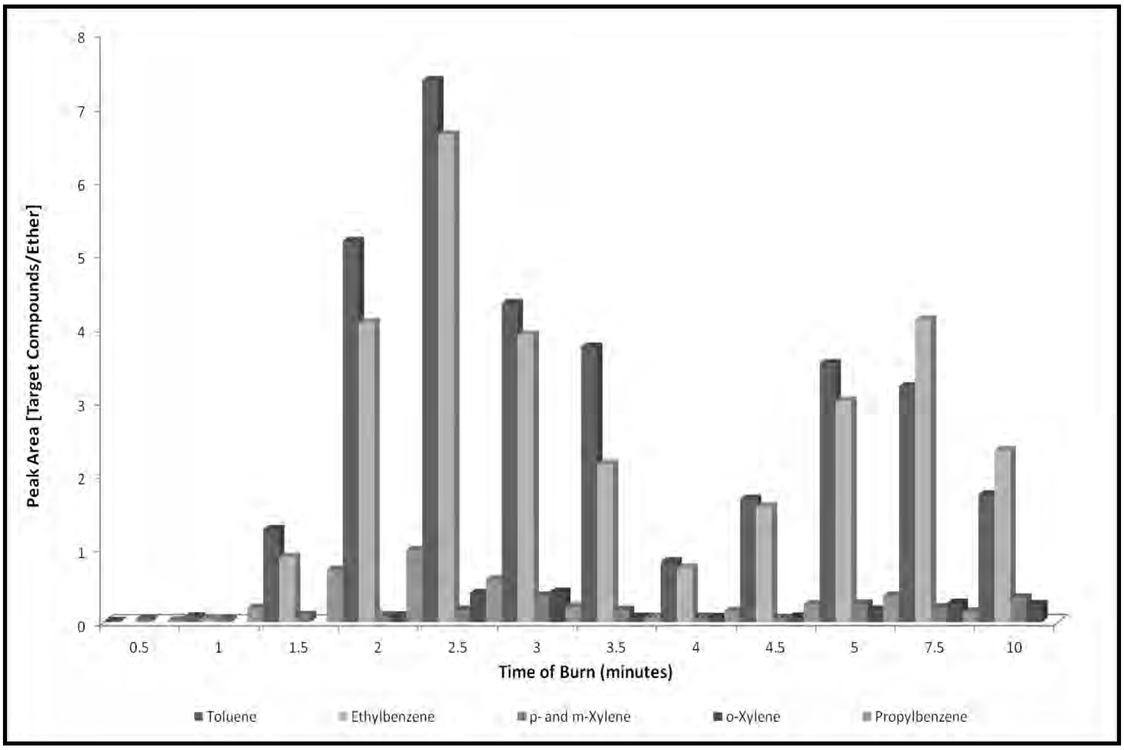


Figure 4.40: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time

Similar to the previous small can fire results toluene and ethylbenzene (the dark and light grey columns, respectively in Figure 4.40) were recovered in the greatest abundances compared to the other target compounds. These two compounds were recovered in their greatest abundance in the 2.5 minute burn. After burning for 4 minutes the levels of these two compounds recovered were at the lowest and then as burning time increases the amounts recovered once again started to increase. Other compounds such as *o*-xylene and propylbenzene exhibited a similar trend.

The burning time experiments show that the target compounds are recovered in their greatest abundance after 2.5 minutes of burning however the greatest number of target compounds were observable after 7.5 minutes of burning. Burning for 2.5 minutes produced five target compounds whereas burning for 7.5 minutes produced 10 target compounds. It must be remembered that the aromatics besides toluene and ethylbenzene were always recovered in very low abundances. As can be seen in Figure 4.41 for the 7.5 and 10 minute burn times, even though other target compounds were recovered, these were recovered in small amounts when compared to the toluene and ethylbenzene peaks. Based on these results the small can test fires for nylon carpet indicate a burn time of 2.5 minutes would be adequate as the carpet has undergone sufficient burning whereas excessive burning (longer than 5 minutes) results in the carpet being almost completed carbonised.

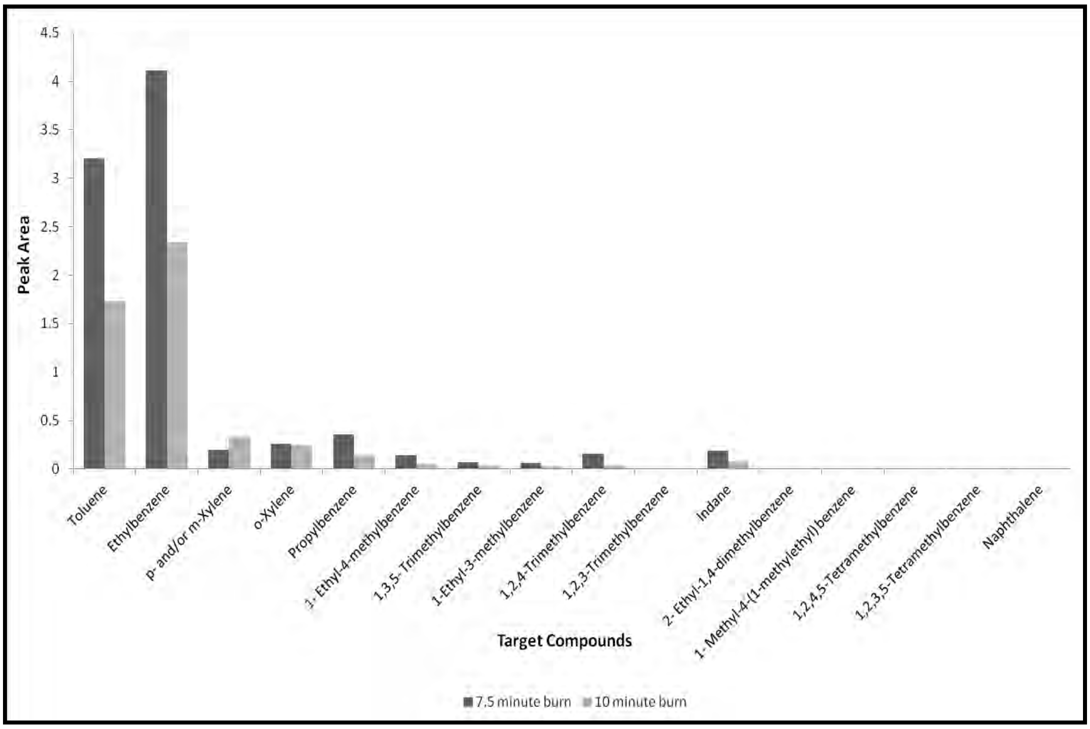


Figure 4.41: Graph of peak area of Target Compounds recovered when burning Nylon Carpet for 7.5 and 10 minutes in a Small Can plotted as a Ratio with Butylated Hydroxytoluene

he protocol developed for nylon carpet was next applied to the other carpets to see if burn time was a critical factor when burning other types of carpet and foam.

4.5.6.1 Polypropylene, Wool and 50-50 Polypropylene-Wool Carpet

The length of burning time for the polypropylene, wool and the 50-50 polypropylene-wool carpet was conducted for 2.5, 5, 7.5 and 10 minutes. Appendix D lists details of each of these burns including photos, total ion chromatograms, extracted ion chromatograms and target compound chromatograms. This information is tabulated and presented in Tables 4.8, 4.9 and 4.10, respectively.

Table 4.8: Observations and Target Compounds recovered from Small Can Fire Experiments for Polypropylene Carpet

Burn Time (min)	Visual Observations	Target Compounds Recovered
2.5	The underside of the lid had discoloured. The top of the sample showed that the polypropylene had melted and the hessian appeared to have been protected by the molten polypropylene and had only blackened. The sides and bottom of the can showed some discolouration but no considerable streaking.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
5	The polypropylene carpet was considerably burnt but still intact. On closer inspection, the fibres had almost burnt completely leaving the hessian layer intact but extremely burnt. The underside of the lid showed considerable discolouration, whilst the sides of the can showed slight streaking.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
7.5	The backing of the carpet was the only part of the carpet left intact, however it was extremely fragile and when touched disintegrated. The underside of the lid had a thick, bubbled layer of residue condensed on it and the sides of the can had considerable streaking.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1,3,5-Trimethylbenzene
10	The top and underside of the lid discoloured. The sides of the can had a considerable amount of streaking. The sample of carpet was extremely thin and brittle but still intact and the polypropylene was completely burnt.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene

Table 4.9: Observations and Target Compounds recovered from Small Can Fire Experiments for Wool Carpet

Burn Time (min)	**Visual Observations**	**Target Compounds Recovered**
2.5	The top of the lid showed no discolouration however the underside of the lid appeared to be speckled with residue. The wool sample was stuck to the inside of the can and was unable to be removed. However, it appeared as if the wool fibres had only been singed. The inside of the can had discoloured slightly.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
5	The wool carpet sample was considerably burnt but still intact. This sample had stuck to the bottom of the can and unable to be removed for closer examination. However, it was observed that the top of the lid had slightly discoloured and the underside of the lid had a considerable amount of residue on it. The sides of the can showed some streaking.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene
7.5	The carpet stuck to the bottom of the can and when an attempt was made to remove the swatch it disintegrated. The top of the lid discoloured particularly around the vent hole whilst the underside of the lid had a thick layer of residue and considerable streaking was also observed on the sides of the can.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene
10	The top and underside of the lid discoloured and the underside was almost completely covered in a thick residue. The sides of the can had a considerable amount of streaking. The sample of carpet remained the same size and intact however it was very fragile as it had burnt through to the hessian.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene

Table 4.10: Observations and Target Compounds recovered from Small Can Fire Experiments for 50-50 Polypropylene-Wool Carpet

Burn Time (min)	Visual Observations	Target Compounds Recovered
2.5	The underside of the lid discoloured as did the sides of the can, which also showed some slight streaking. The sample remained intact but the fibres had melted in the centre of the swatch and there was some burning evident around the edges.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene
5	The 50-50 polypropylene-wool blended carpet sample was considerably burnt but still intact. On closer inspection, the carpet fibres had almost burnt completely leaving a very burnt hessian layer that was very fragile when touched. The top and underside of the lid showed considerable discolouration, with the underside of the lid also showing a burnt residue on it. The inside of the can had also discoloured and it appeared that there was also some streaking on the sides of the can.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene,
7.5	The sample was intact, however when touched it disintegrated. The fibres had the appearance similar to heavily burnt wool and were very rough and crumbly. The underside of the lid had a thick, bubbled layer of residue condensed on it and the sides of the can also had considerable streaking. The top side of the lid also changed colour going from white to a brown/black and residue was also evident.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene,
10	The top of the lid turned a beige/black colour with a dark brown residue. The underside of the lid was also discoloured and coated in a thick residue. The inside of the can had a considerable amount of streaking. The sample of carpet was extremely thin and brittle but still intact and there was only patches of the burnt wool textured fibres left, however when touched they disintegrated.	Toluene, Ethylbenzene, *p*- and *m*-Xylene, *o*-Xylene, Propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5- Trimethylbenzene, 1,2,4- Trimethylbenzene

Interestingly, similar target compounds were recovered from all the carpet samples and again toluene and ethylbenzene were recovered in much greater abundances than the other aromatic target compounds. Figures 4.42 to 4.49 show the total ion chromatograms, extracted ion chromatograms and target compound chromatograms for the nylon, polypropylene, wool and the 50-50 polypropylene-wool carpet burnt in the small can for 2.5 minutes.

Based on the target compound chromatograms of the carpets burnt for 2.5 minutes, the abundances of toluene and ethylbenzene are again more than 10 times the amount of the other aromatic target compounds recovered for polypropylene, wool and 50-50 polypropylene-wool carpet.

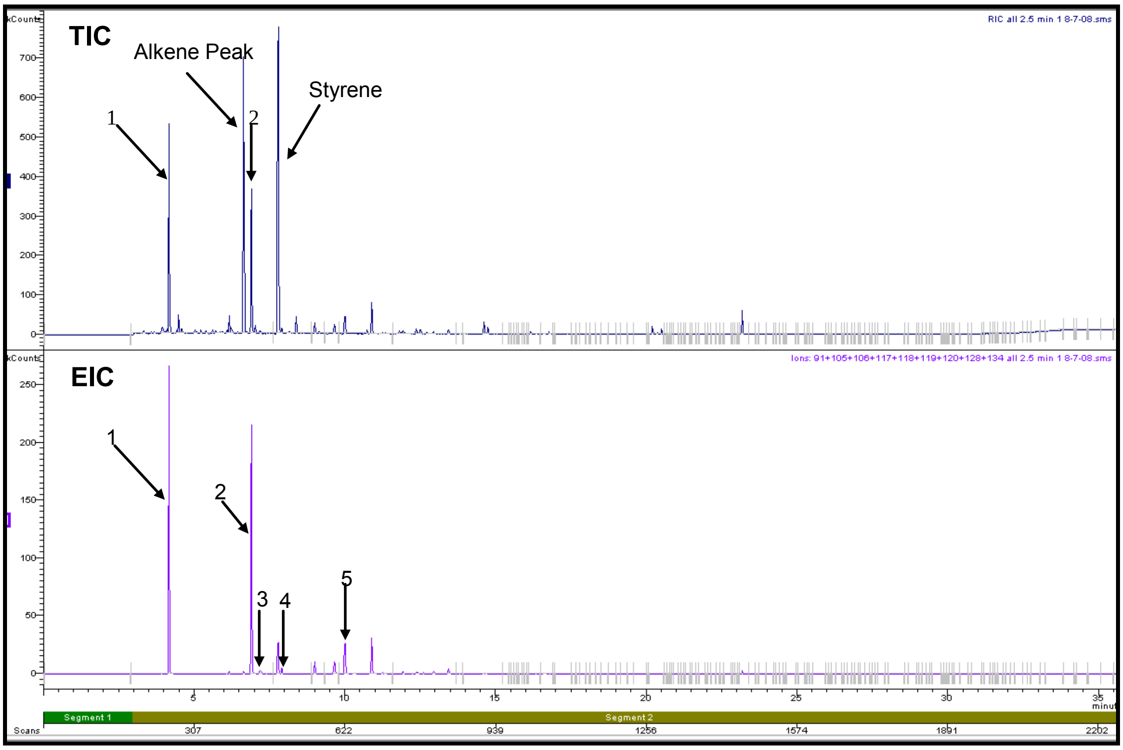


Figure 4.42: Total Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 2.5 minutes (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

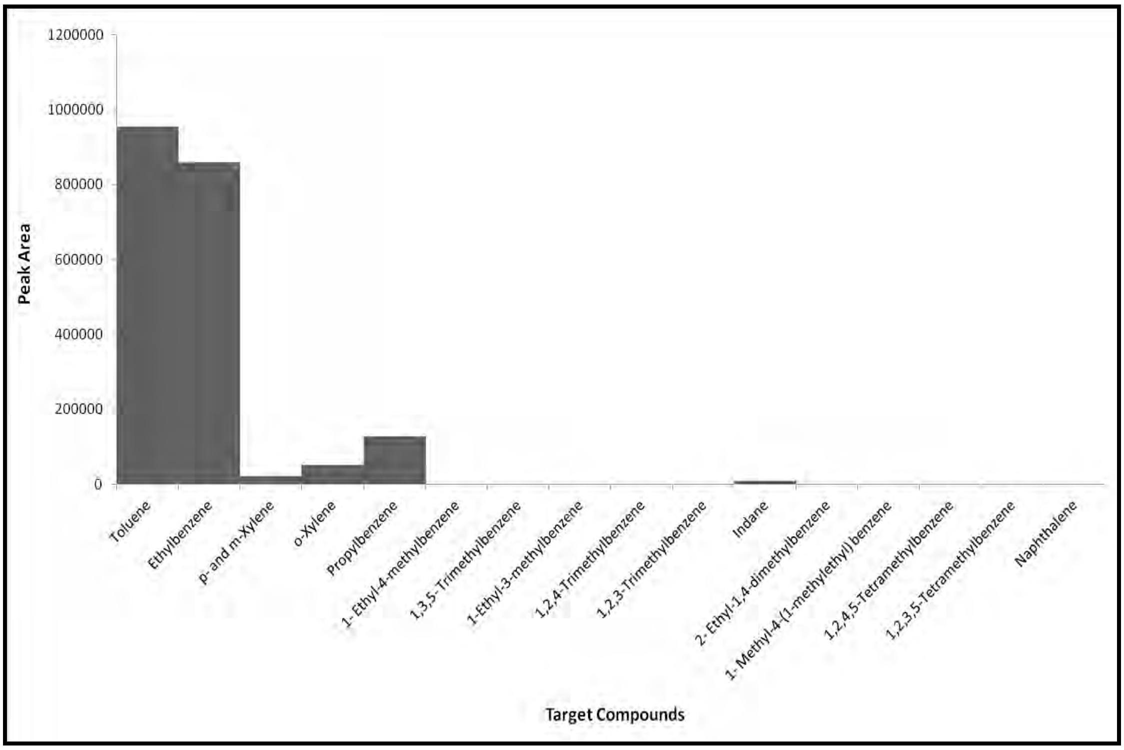


Figure 4.43: Target Compound Chromatogram of a Nylon Carpet swatch burnt in a Can with Lid On for 2.5 minutes

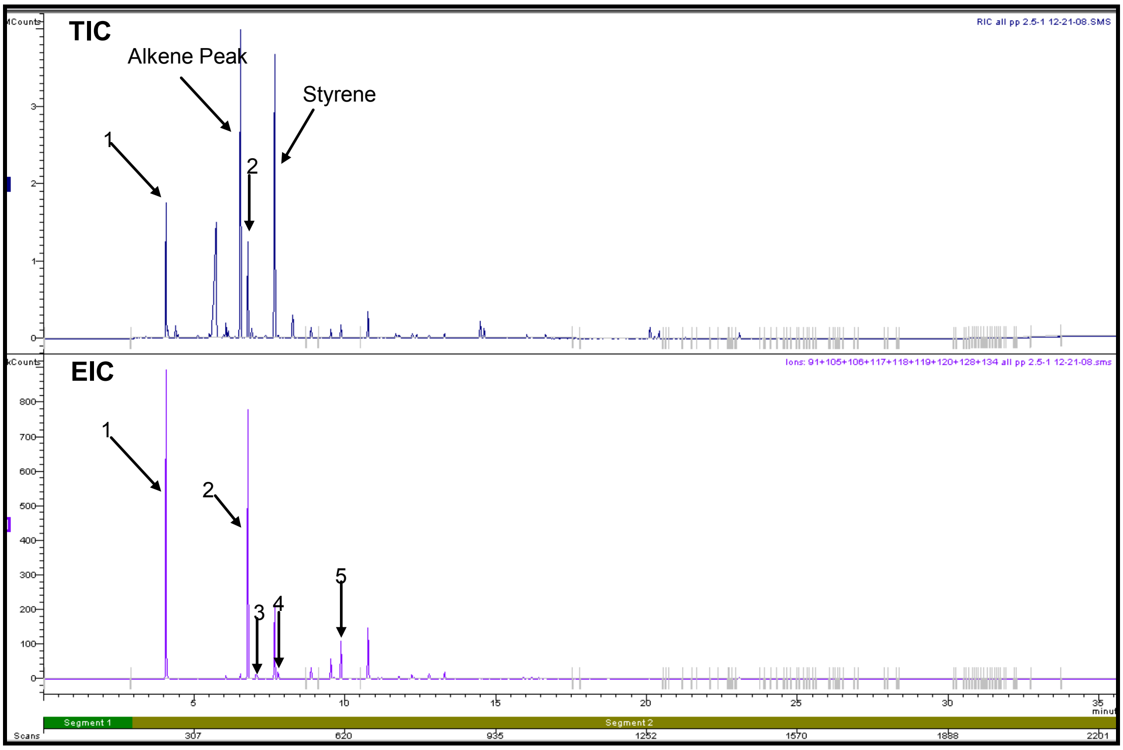


Figure 4.44: Total Ion Chromatogram and Extracted Ion Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 2.5 minutes (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

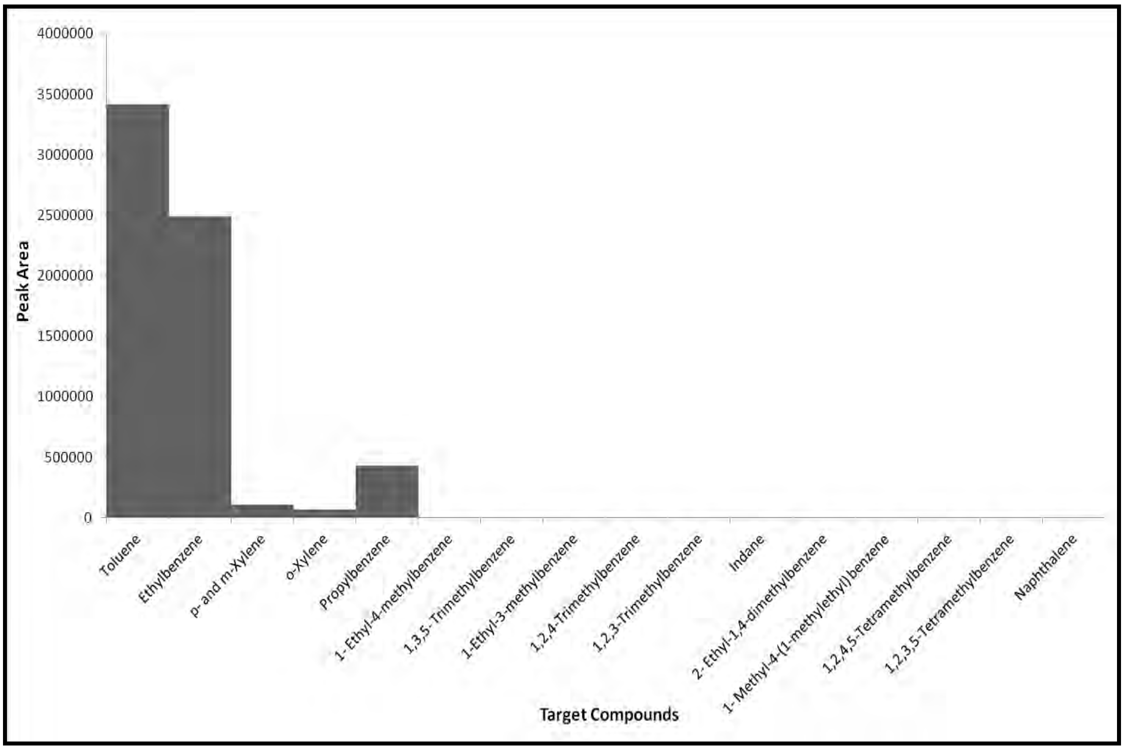


Figure 4.45: Target Compound Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

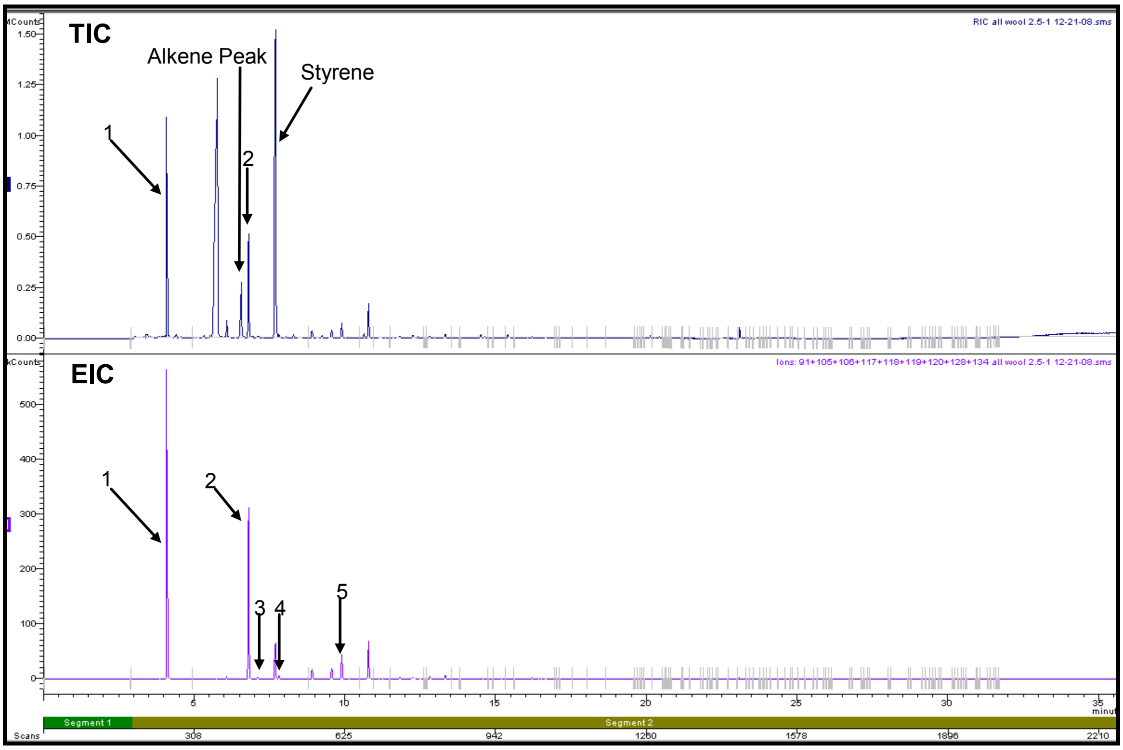


Figure 4.46: Total Ion Chromatogram and Extracted Ion Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

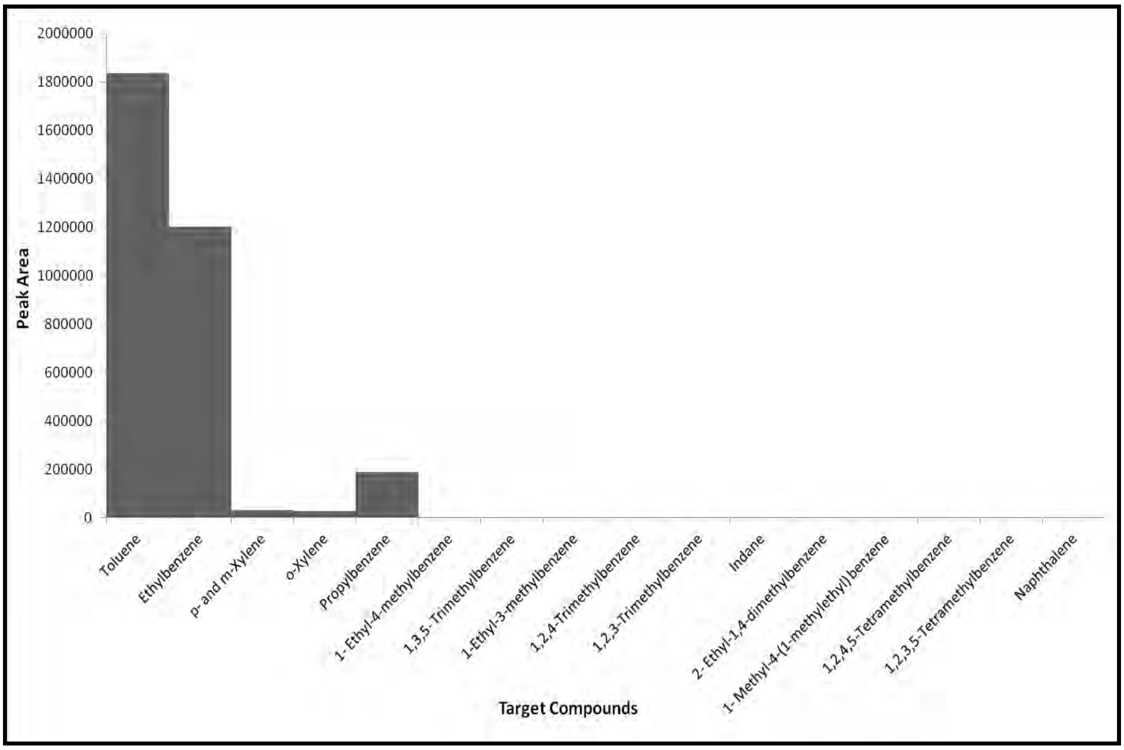


Figure 4.47: Target Compound Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

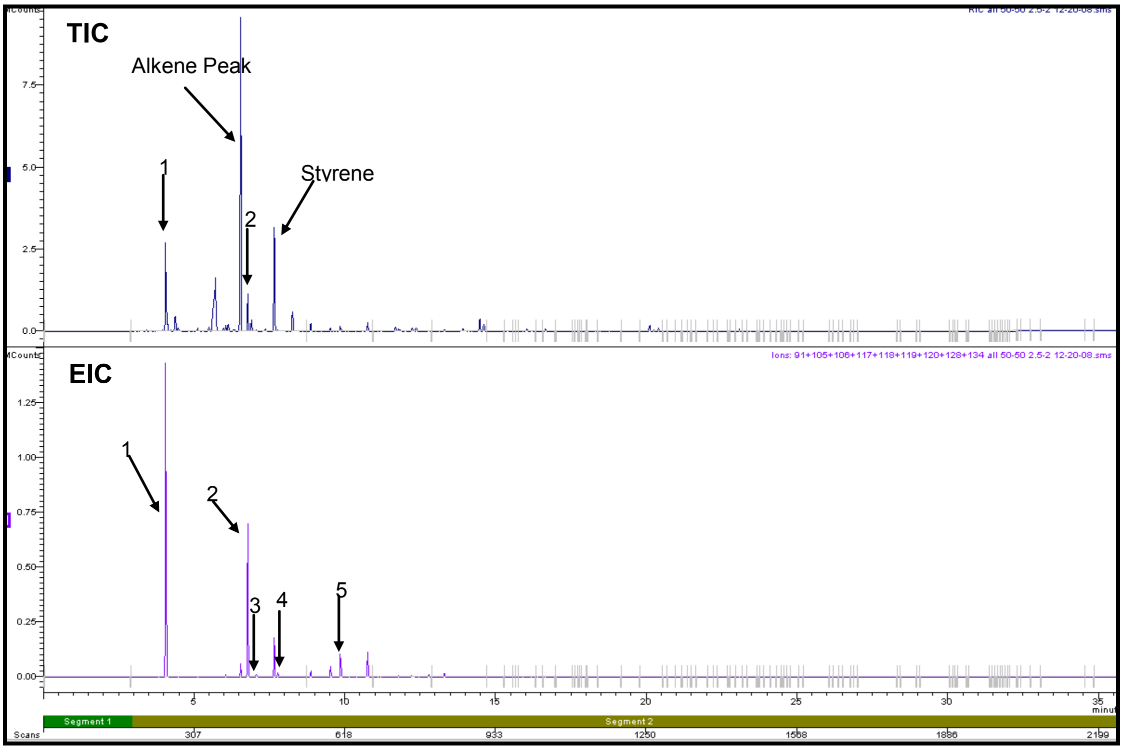


Figure 4.48: Total Ion Chromatogram and Extracted Ion Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes (Refer to Section 2.5.1 for GC/MS conditions)

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=propylbenzene

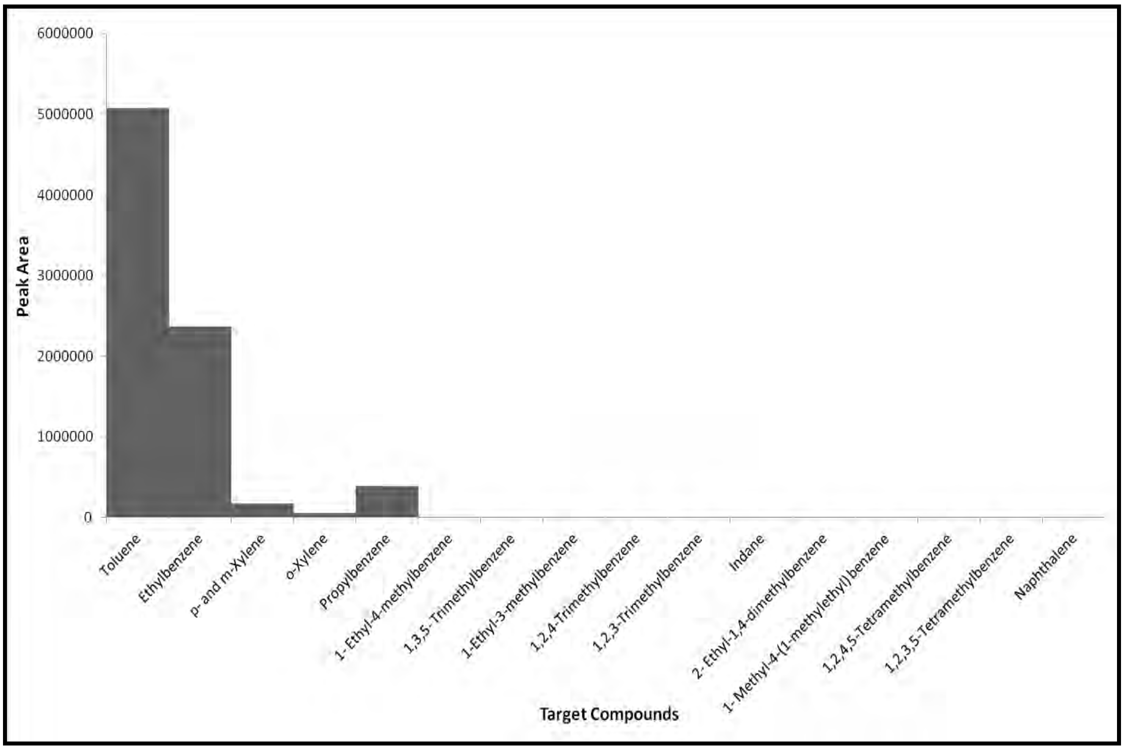


Figure 4.49: Target Compound Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

Figures 4.50 to 4.53 shows the peak area of each of the target compounds recovered plotted as a ratio with the butylated hydroxytoluene versus burn time for the nylon, polypropylene, wool and the polypropylene-wool blended carpet, respectively. Nylon results at these four burn times are also shown in Figure 4.50 to allow for visual comparison with the other carpet types.

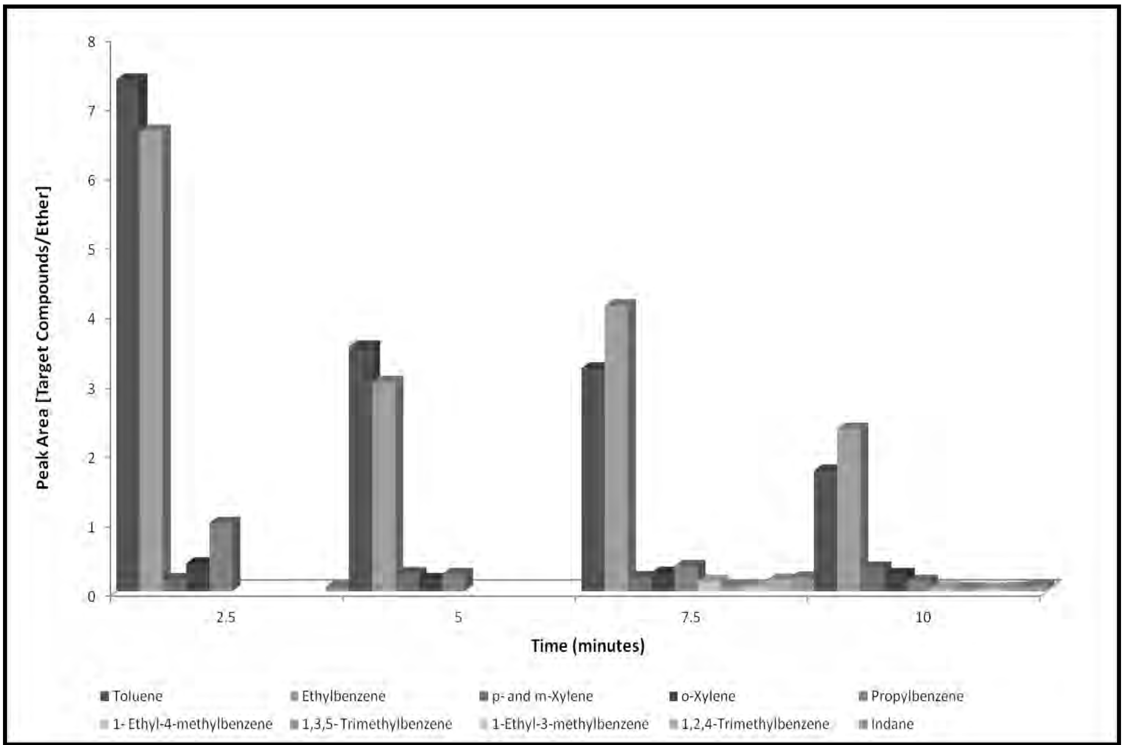


Figure 4.50: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for Nylon Carpet

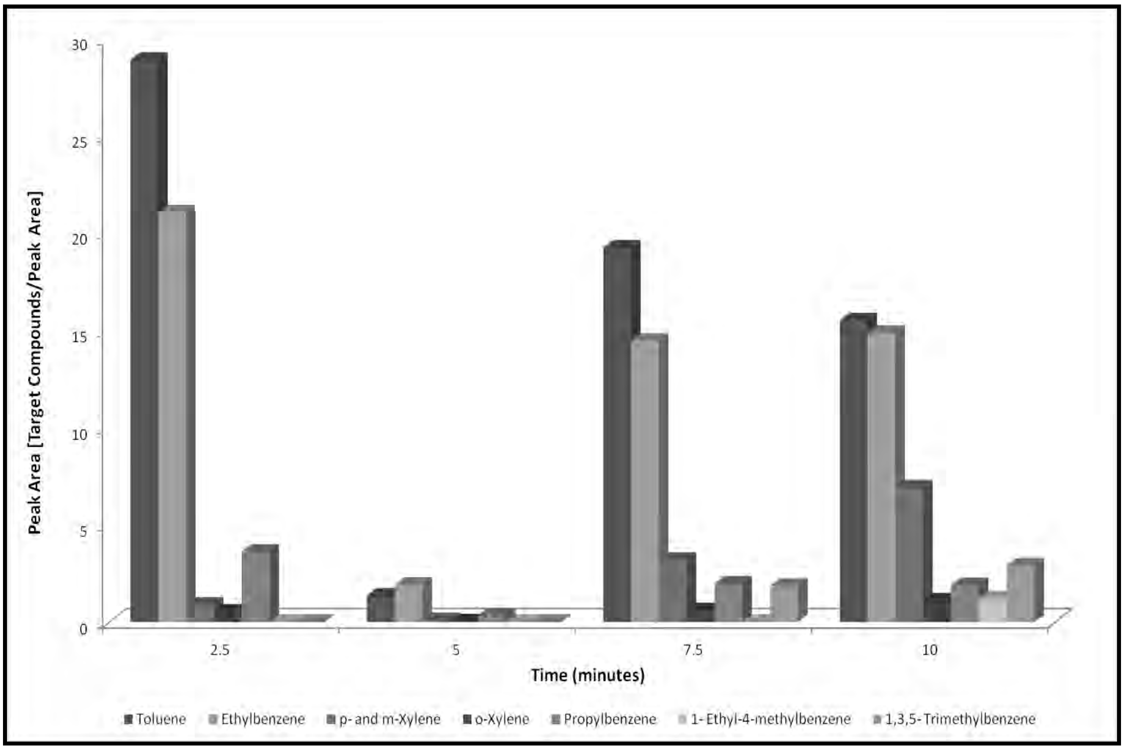


Figure 4.51: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for Polypropylene Carpet

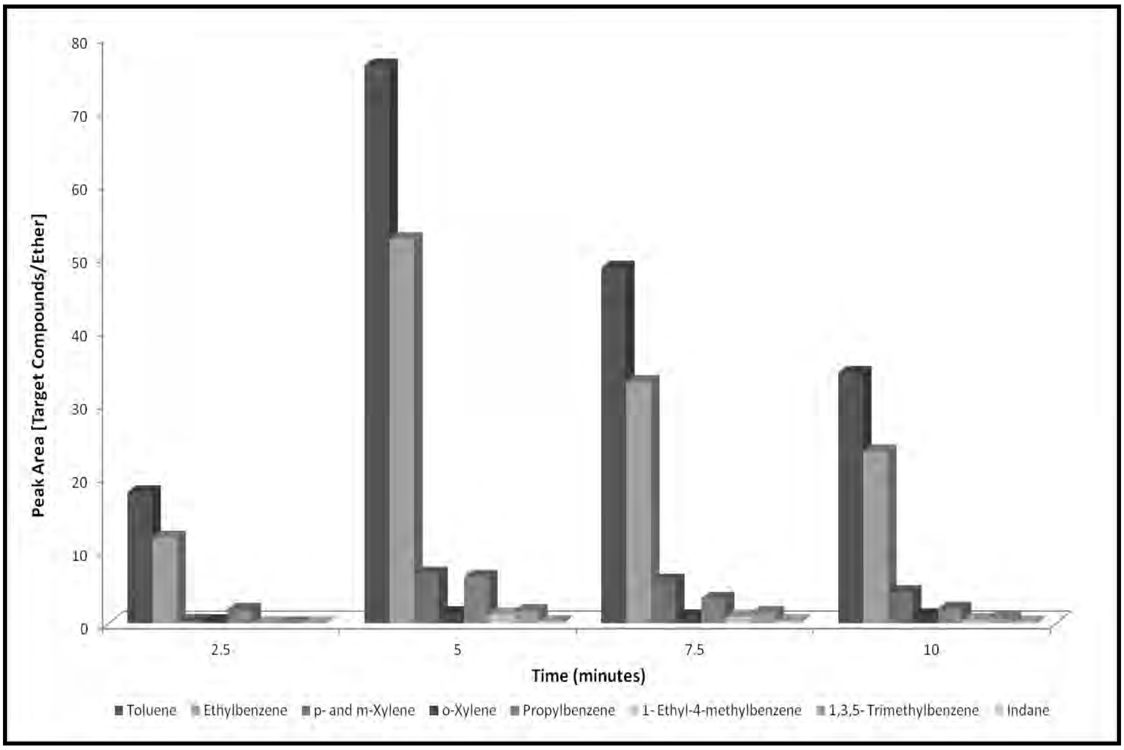


Figure 4.52: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for Wool Carpet

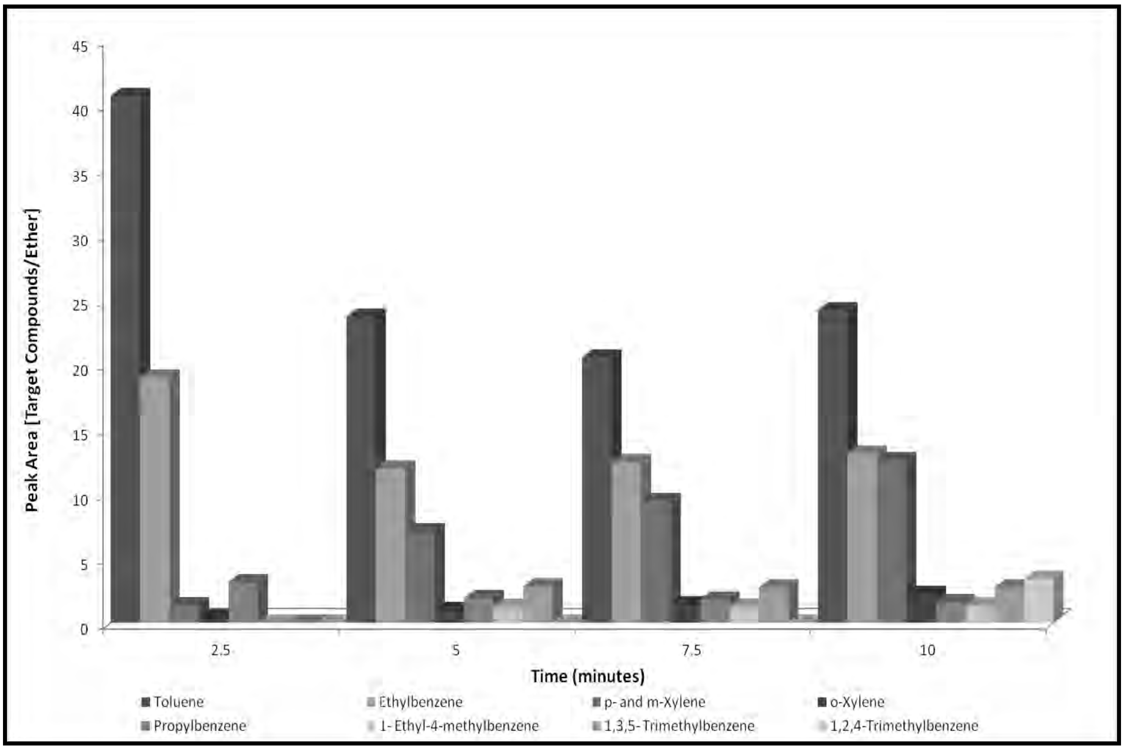


Figure 4.53: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for 50-50 Polypropylene-Wool Carpet

Observations from the comparison of results from Figures 4.50 to 4.53 are listed below:

- The number and types of compounds recovered are similar.
- Toluene and ethylbenzene were again present in the greatest abundances. *P*- and *m*-xylene could also be recovered in abundances comparable to toluene and ethylbenzene in the longer burn times for polypropylene and 50-50 polypropylene-wool.
- The synthetic carpets produced maximum levels of target compounds after burning for approximately 2.5 minutes whereas the wool carpet took slightly longer to achieve the maximum levels of target compounds (approximately 5 minutes). Further burning results in the carpet being almost completed carbonised.
- Burning of nylon carpet produced the lowest abundance of target compounds recovered.
- Again the alkene peak and styrene are present in the total ion chromatograms (See total ion chromatograms in Appendix D).

Burning trends from the burning time experiments for all the carpet showed that a burning time of 2.5 minutes would allow sufficient levels of the important target compounds to be recovered. This is further highlighted in Figure 4.54 below where the target compounds recovered and their abundances for each carpet are shown. Similar graphs for the 5, 7.5 and 10 minute burns are shown in Appendix E.

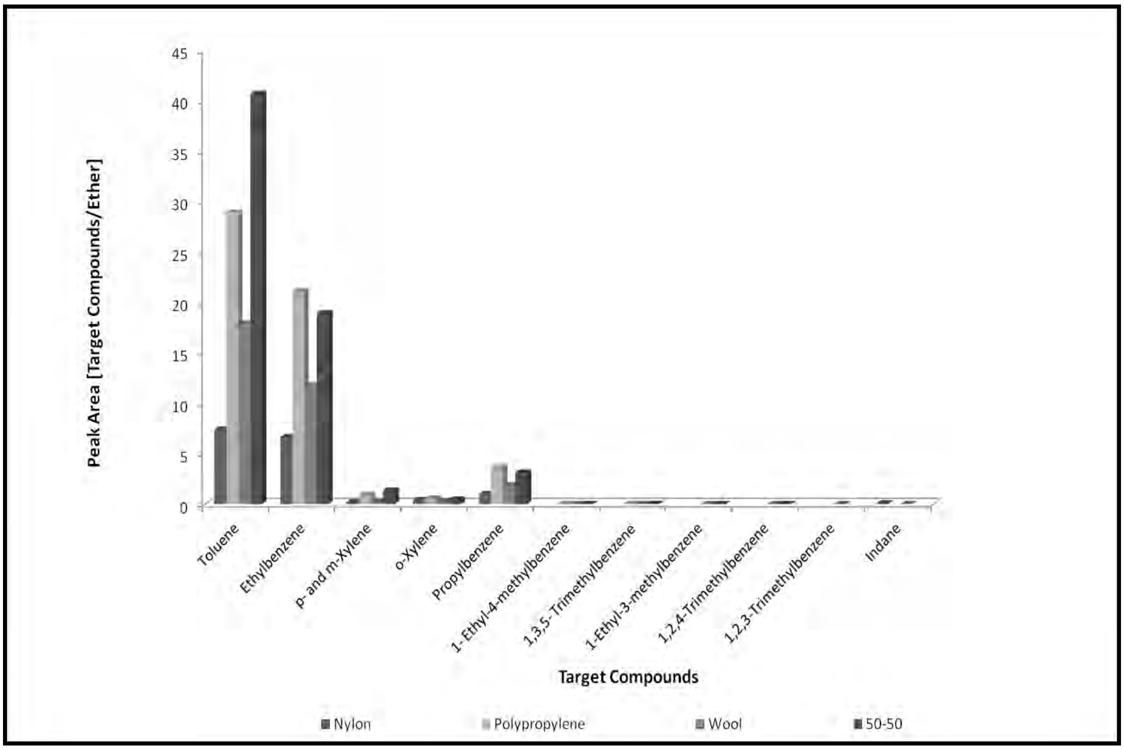


Figure 4.54: Target Compound Chromatogram for all Carpets when Burnt in the Small Can with Lid On for 2.5 minutes

4.5.6.2 Furniture Foam and Underlay

Like the carpet samples, the underlay was cut to fit flat in the bottom of the can. The furniture foam samples were cut into a disc of the same circumference as the can with a height of approximately 3cm and placed in the bottom of the can. Burning times for the foam samples were also conducted for the four time periods used for the carpet samples, these being 2.5, 5, 7.5 and 10 minutes. Appendix F lists details of each of these burns including photos, total ion chromatograms, extracted ion chromatograms and target compound chromatograms. This information is tabulated and presented in Tables 4.11 and 4.12 for the foam and underlay, respectively.

Table 4.11: Observations and Target Compounds recovered from Small Can Fire Experiments for Foam Carpet

Burn Time (min)	**Visual Observations**	**Target Compounds Recovered**
2.5	The underside of the lid had discoloured and had a burnt residue on it. The consistency of the foam after burning was very airy and fragile and fell apart when touched. The bottom of the can appeared to have also burnt, whilst the sides had a burnt residue on them.	Toluene
5	The top of the lid had discoloured around the vent hole, whilst the underside of the lid and the sides of the can had a residue (streaked) on them. Although the sample appeared to be more burnt than after the 2.5 minute small can fire, it still had a very light, airy and fragile texture.	Toluene, Ethylbenzene, *p- and m-Xylene*
7.5	The top of the lid had discoloured, particularly around the vent hole. Similar to the previous two burns the underside of the lid appeared to be coated with a solidified residue as did the sides of the can. The foam sample was extremely fragile and it was observed that the inside of the can contained a burnt residue (appeared to be tiny pieces of foam) on the bottom and along the sides.	Toluene, Ethylbenzene, *p- and m-Xylene*, *o-*Xylene
10	The top of the lid had discoloured, particularly around the vent hole. The underside of the lid and inside the can had the same type of residue as seen in the previous small can fire experiments. Furthermore the inside of the can had little solidified bubbles or shards of residue around the sides and the sample was extremely fragile that it disintegrated when touched.	Toluene, Ethylbenzene, *p- and m-Xylene*, *o-*Xylene

Table 4.12: Observations and Target Compounds recovered from Small Can Fire Experiments for Underlay Carpet

Burn Time (min)	Visual Observations	Target Compounds Recovered
2.5	The lid had discoloured slightly, particularly around the vent hole, whilst the underside of the lid was coated with a thick residue. The sides of the can were heavily streaked. The sample appeared to have melted and stuck to the bottom of the can and felt very rough when touched.	Toluene, Ethylbenzene, *p- and m-Xylene*, Propylbenzene, 1-ethyl-4-methylbenzene
5	The lid had discoloured slightly, particularly around the vent hole, whilst the underside of the lid appeared to have been coated with a thick residue. The sides of the can appeared to be heavily streaked and had solidified balls at the end of the streaks. The sample appeared to have melted and stuck to the bottom of the can.	Toluene, Ethylbenzene, *p- and m-Xylene*, *o-*Xylene, Propylbenzene, 1-ethyl-4-methylbenzene
7.5	The lid of the can had discoloured and turned brown with some blackening around the vent hole whilst the underside of the lid was coated with a thick layer of residue, similar to the 2.5 and 5 minute burns. Again similar to the 5 minute burn, the sides of the can showed some evidence of streaking, with large solidified droplets forming at the bottom of the streaks. There appeared to be no sample left after this can fire.	Toluene, Ethylbenzene, *p- and m-Xylene*, *o-*Xylene, Propylbenzene, 1-ethyl-4-methylbenzene
10	The lid of the can had discoloured considerably, turning a dark shade of brown whilst the underside of the lid was coated with a thick layer of residue which appeared burnt. Again similar to the previous fires, the sides of the can showed some evidence of streaking, with large solidified droplets forming at the bottom of the streaks. There appeared to be no sample left after this can fire.	Toluene, Ethylbenzene, *p- and m-Xylene*, *o-*Xylene, Propylbenzene, 1-ethyl-4-methylbenzene

Interestingly, similar target compounds to the carpet samples were recovered from the foam and underlay samples however burning trends were not similar. Burning trends are shown in Figures 4.55 and 4.56 where the extracted ion chromatogram peak area of each of the target compounds is plotted as a ratio with the butylated hydroxytoluene versus burn time for the furniture foam and underlay, respectively.

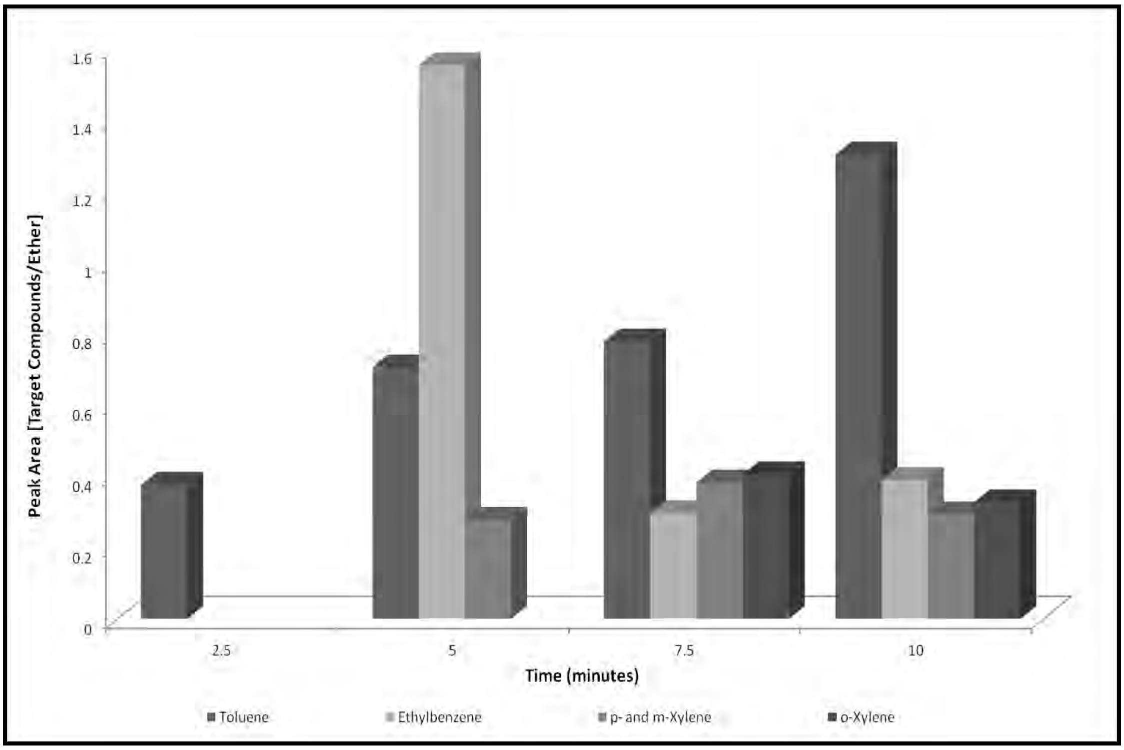


Figure 4.55: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for Furniture Foam

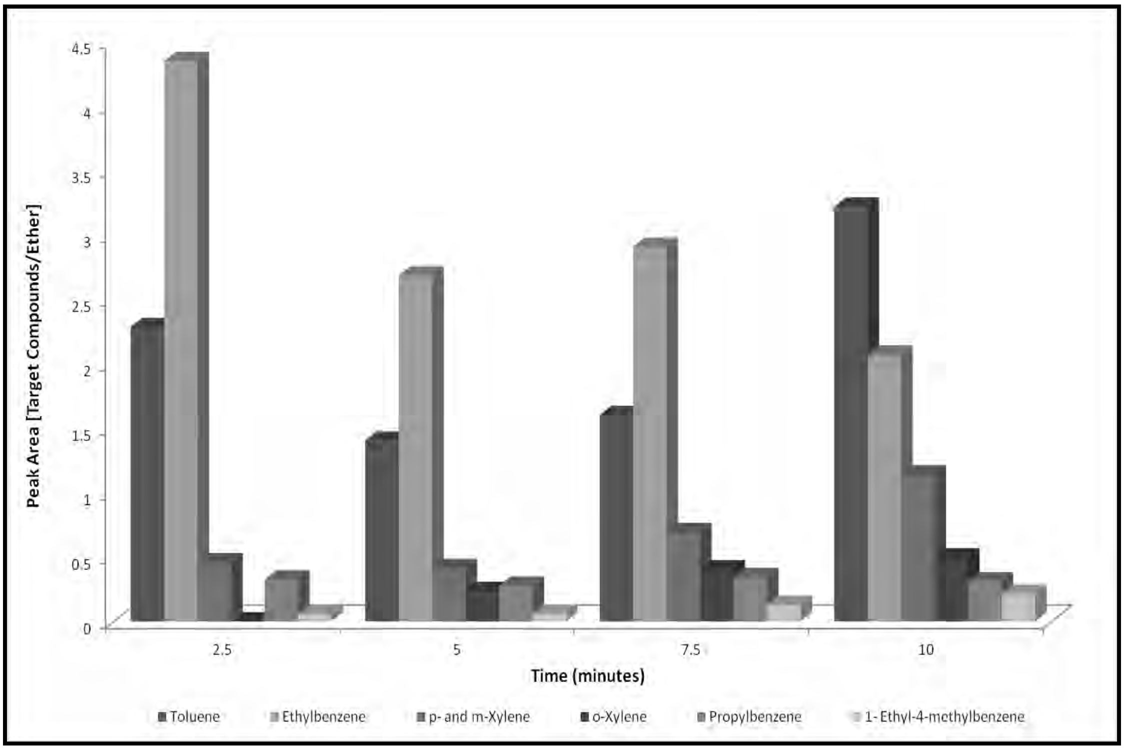


Figure 4.56: Graph of Peak Area of Target Compounds with Butylated Hydroxytoluene vs. Burn Time for Underlay

Observations from the comparison of results from Figures 4.55 and 4.56 are listed below:

- The number and types of compounds recovered are similar to those recovered from the carpets. However the underlay produced more target compounds than the furniture foam for similar burn times.
- For the furniture foam, toluene was the most abundant at all burn times except 5 minutes with comparable levels of ethylbenzene, *p*- and *m*-xylene and *o*-xylene being recovered in the longer burn times.
- Toluene and ethylbenzene were present in the greatest abundance for the underlay. *P*- and *m*-xylene could also be recovered in greater abundances in the longer burn times.
- Burning foam samples for 7.5 minutes would allow sufficient levels of target compounds to be recovered.

Burning trends from the burning time experiments for foam samples showed that a burning time of 7.5 minutes would allow sufficient levels of the important target compounds to be recovered. This is further highlighted in Figure 4.57 below where the target compounds recovered and their abundances for the foam are shown. Similar graphs for the 5, 7.5 and 10 minute burns are shown in Appendix G.

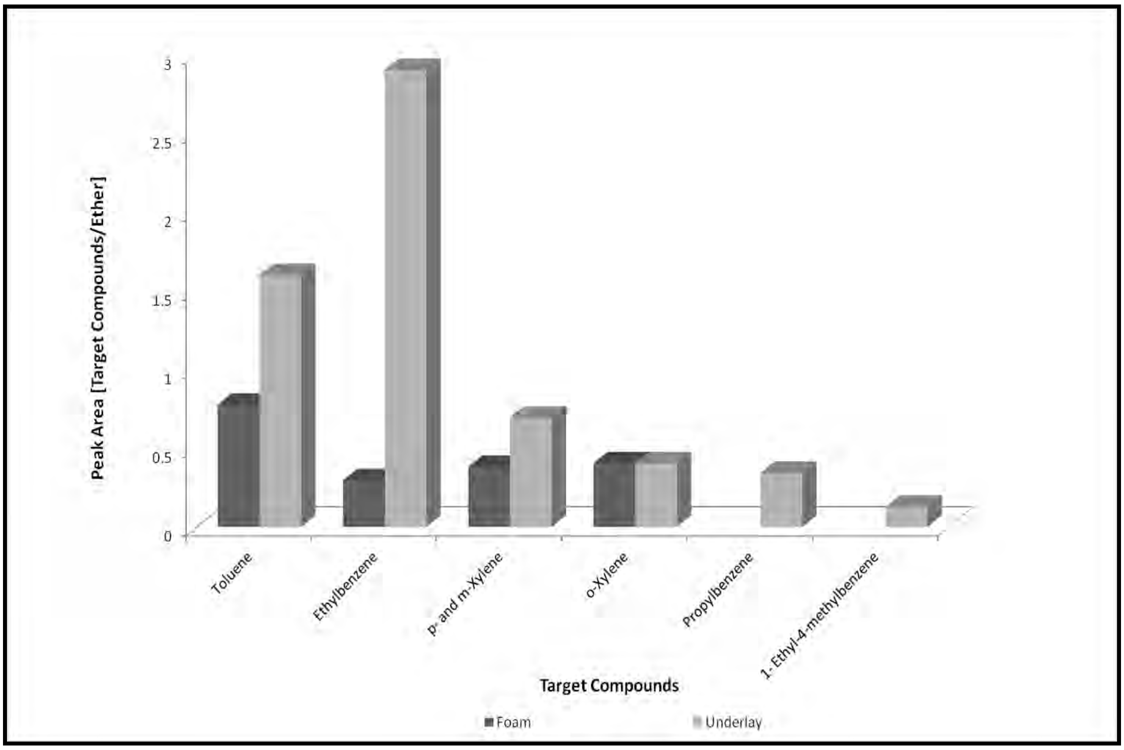


Figure 4.57: Target Compound Chromatogram for Furniture Foam and Underlay burnt in a Small Can with Lid On for 7.5 minutes

4.5.7 SUMMARY

Work on small can fires showed that when burning nylon carpet in a can with lid off very low levels of toluene and ethylbenzene were able to be recovered, whereas burning with lid on allowed these same two compounds to be recovered in abundances more than 100 times greater along with smaller abundances of other aromatic target compounds. These results are consistent with burning tests conducted by Fernandes *et* al whereby trace levels of toluene was recovered from burnt carpet samples[113] Whether extinguishing by spraying with water or immersing the can in a bucket of cold water had no effect on the types of target compounds recovered nor did the orientation of the carpet within the can. When determining the location of the volatile organic compounds within the can after burning, of particular interest was the finding that most of the target compounds were present on the sides of the can with no target compounds recovered from the lid and very low abundances recovered from the burnt carpet itself. This result suggests that the volatile organic compounds present in the can condense onto the sides of the can when the burning is stopped by immersing the can in a bucket of cold water.

Burning trends from the burning time experiments for the carpet and foam samples showed that although the types and relative abundances of the various target compounds recovered were similar, burning trends were different, where a 2.5 minute burn for carpet and a 7.5 minute burn for foam would allow sufficient levels of the important target compounds to be recovered.

Interestingly, in the case of the majority of carpet samples the total ion chromatograms would also contain the unidentified alkene peak and styrene.

It must be remembered that the burning conditions in a can with lid on are not indicative of that in a real fire but the information provided by the small can fire experiments may be useful as a method for analysing substrate comparison samples. Small can fire experiments are a simple and quick method to obtain further information regarding volatile organic compounds produced by the thermal degradation of carpet and foam. How the results from the small can fire experiments can be used for target compound analysis in arson investigation will be discussed in the conclusion.

4.6 PYROLYSIS GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

Pyrolysis GC/MS was also used to study the types of volatile organic compounds produced when the carpet and foam samples underwent thermal degradation in the inert atmosphere of a micro-furnace pyrolyser. The temperatures for the pyrolysis experiments were determined by the large scale room fires conducted with the CFA in Fiskville and described in Section 3.5. These results showed that the maximum temperature occurred at flashover and this was at approximately 900°C and therefore this was the maximum pyrolysis temperature used. In order to investigate the effect of temperature on pyrolysis products produced, three other temperatures were investigated; these included 750°C, 600°C and 450°C. Temperatures below

450°C were not investigated as lower temperatures resulted in blockage of the pyrolyser transfer tube into the GC, probably as a result of condensation of the pyrolysed sample in the transfer tube. Pyrolysis GC/MS conditions are described in Section 2.5.2.

The following sections present the results of the pyrolysis experiments for the carpet and foam samples. Due to the requirement of extremely small samples for pyrolysis, it was not feasible to pyrolyse the carpet sample as a whole and therefore the carpet sample components were pyrolysed individually. Hence the carpet fibres were pyrolysed on their own, as were the components which make up the carpet backing, including the hessian, the plastic and the adhesive. These components are shown in the schematic of the carpet shown in Figure 4.58. It was still necessary to ensure samples were small enough so as not to overload the GC/MS signal. Further details on pyrolysis sampling are given in Sections 2.5.2.3 and 3.4.1.

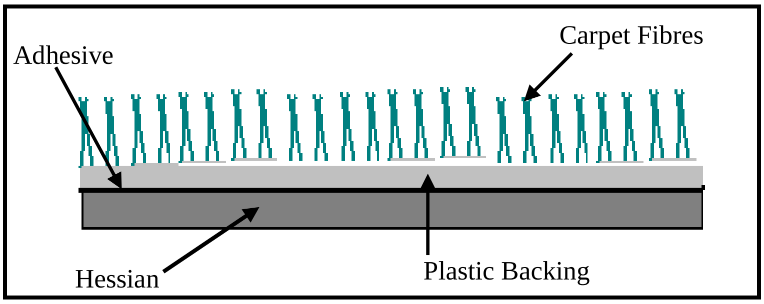


Figure 4.58: Cross Section of Carpet

Pyrolysis experiments were conducted on the following samples, nylon, polypropylene, wool and 50-50 polypropylene-wool carpet fibres, hessian, plastic and glue taken from the carpet backing, foam and underlay. All total ion chromatograms, extracted ion chromatograms and target compound chromatograms produced are shown in Appendix H. Appendix I shows tables summarising the target compounds produced for each sample at the various pyrolysis temperatures and Appendix J shows graphs that compare target compounds recovered. Table 4.13 shows all the target compounds produced from the combined pyrolysis experiments. Pyrolysis was able to produce 15 of the 16 target compound chromatograms chosen in this study, where the only target compound not found was 1,2,3,4-Tetramethylbenzene.

Table 4.13: Target Compounds Recovered from the Combined Pyrolysis Experiments

Target Compounds Recovered
Toluene
Ethylbenzene
p- and *m*-xylene
o-xylene
Propylbenzene
1-Ethyl-4-methylbenzene
1,3,5-Trimethylbenzene
1-Ethyl-3-methylbenzene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
Indane
2-Ethyl-1,4-dimethylbenzene
1-Methyl-2-(1-methylethyl)benzene
1,2,4,5-Tetramethylbenzene
Naphthalene

From the abundance of pyrolysis data generated, the following general conclusions can be drawn:

- For all carpet fibres, hessian and plastic backing a number of aromatics were produced, where toluene was usually the most abundant followed by other C_2 and C_3 alkylbenzenes. These points are demonstrated in Figure 4.59 which shows the target compound chromatogram generated at 750°C and incorporates all the carpet fibres and carpet components and Figure 4.60 which shows the foam and underlay.
- The adhesive for the carpet behaved differently to the other carpet components but still either toluene or ethylbenzene was the most abundant aromatic produced, this is shown in Figure 4.61 where ethylbenzene was the most abundant and in Figure 4.62 where toluene was the most abundant. Figure 4.63 also shows that at 900°C naphthalene was produced in abundances similar to toluene

.

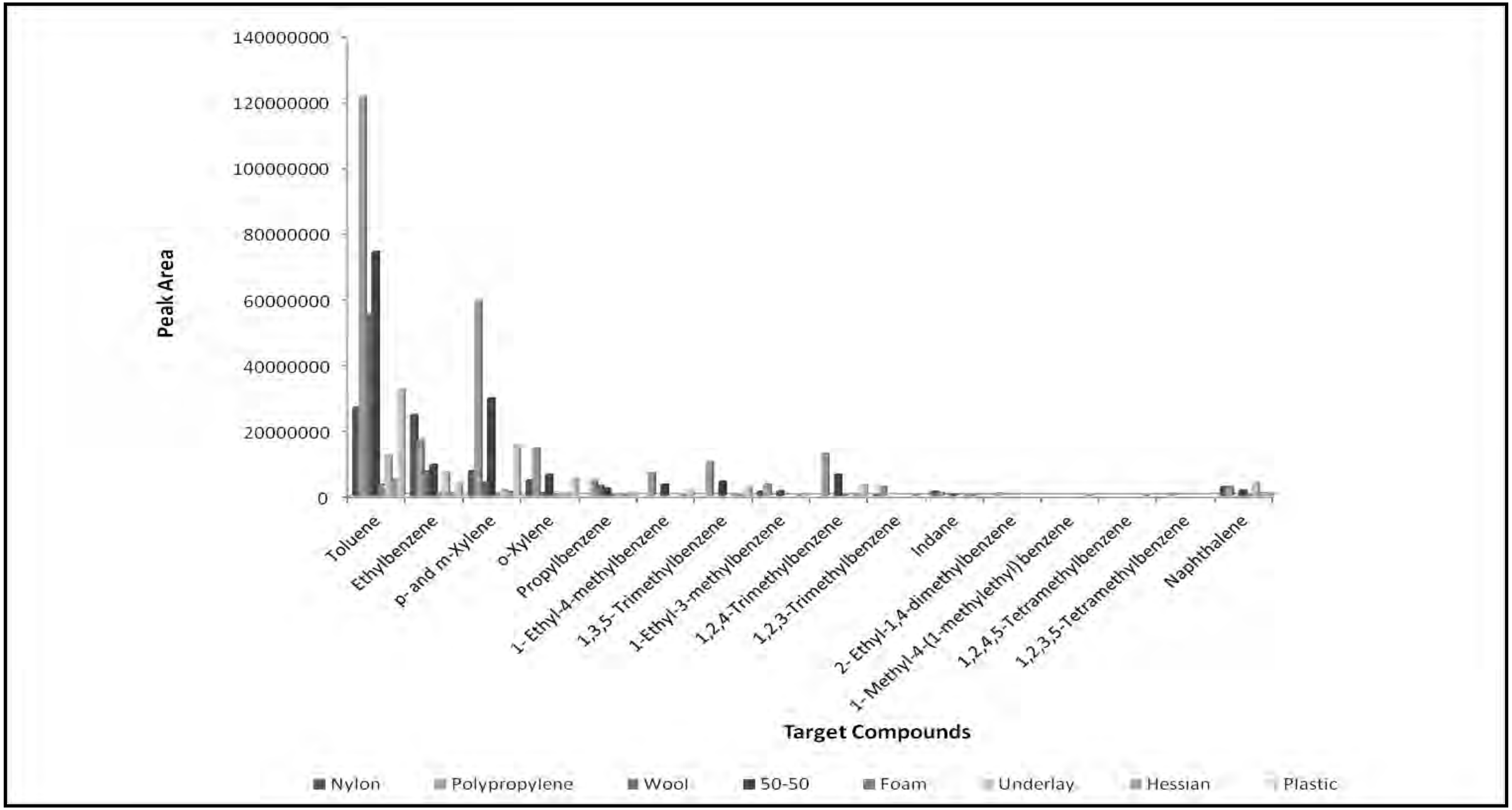


Figure 4.59: Target Compound Chromatograms incorporating Carpet Fibres and Carpet Backing Components Pyrolysed 750°C

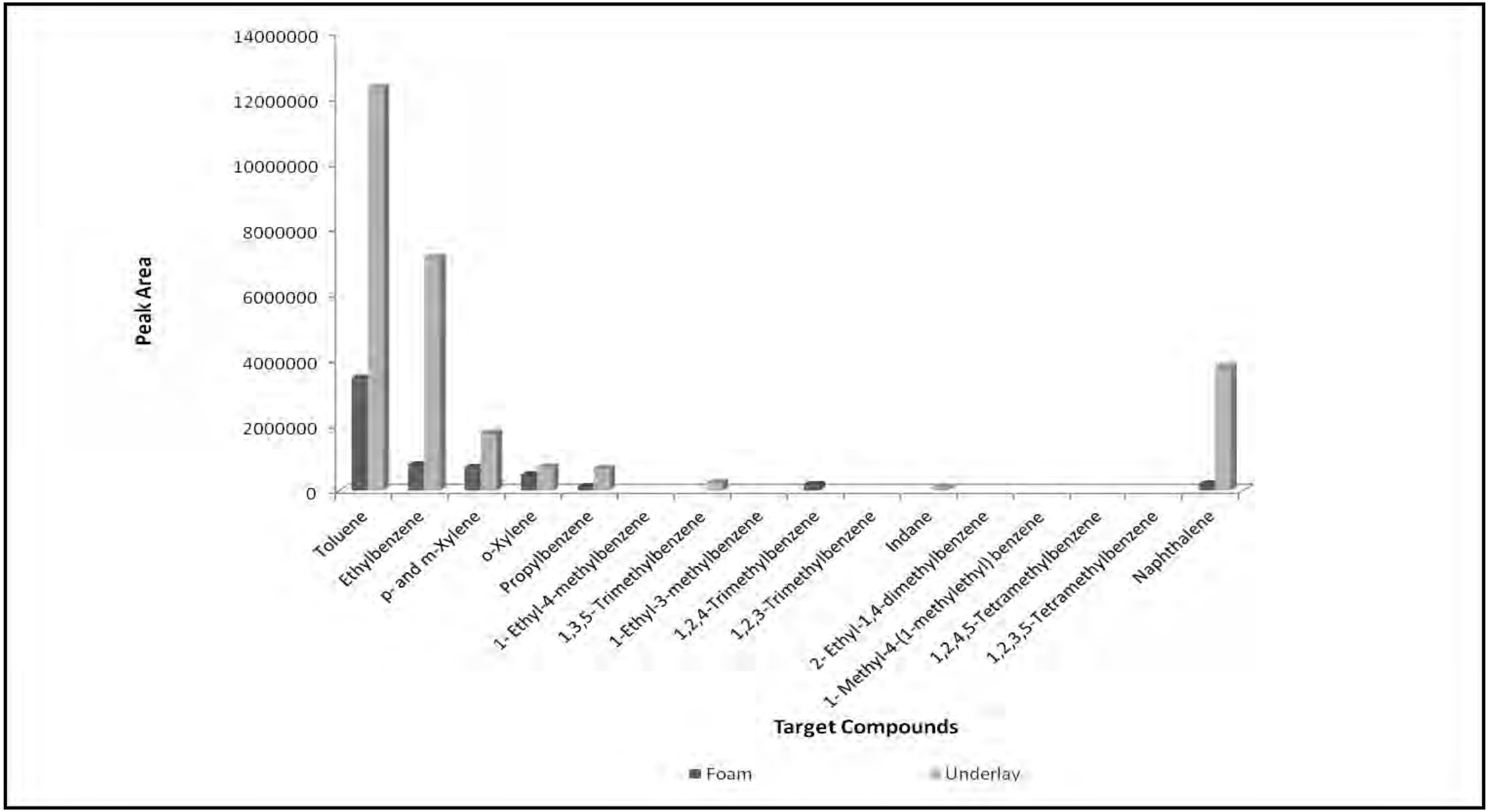


Figure 4.60: Target Compound Chromatograms incorporating Foam and Underlay Pyrolysed at 750°C

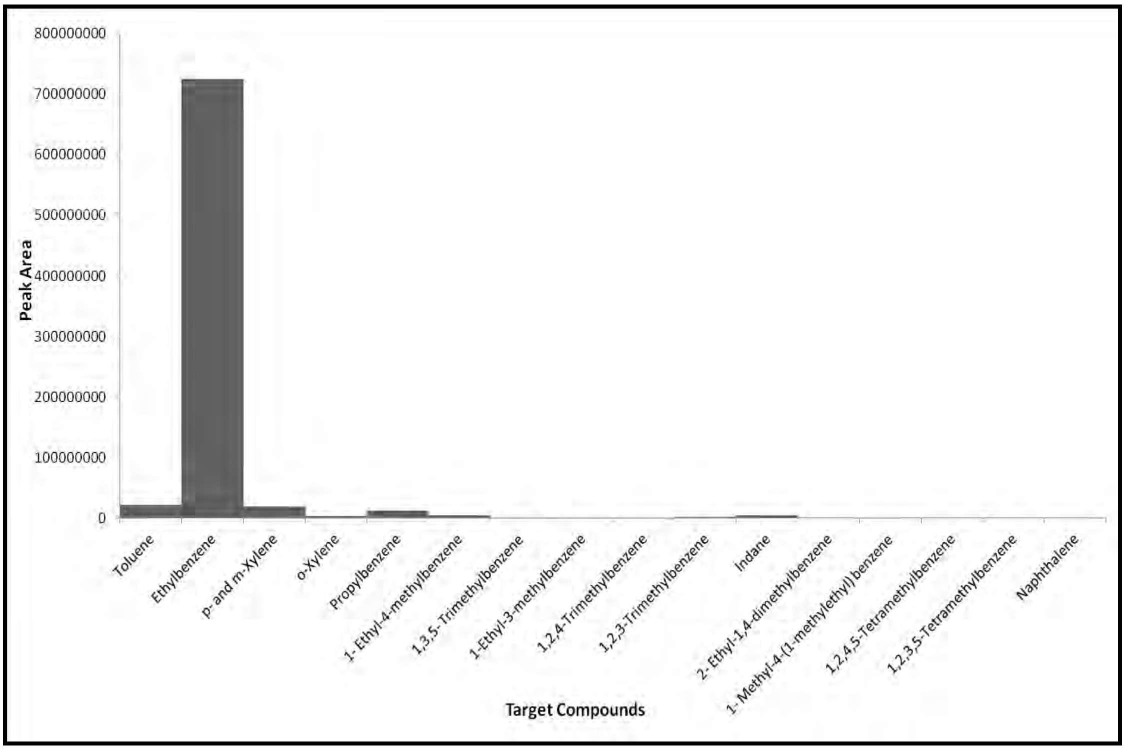


Figure 4.61: Target Compound Chromatogram for Adhesive Pyrolysed at 750°C

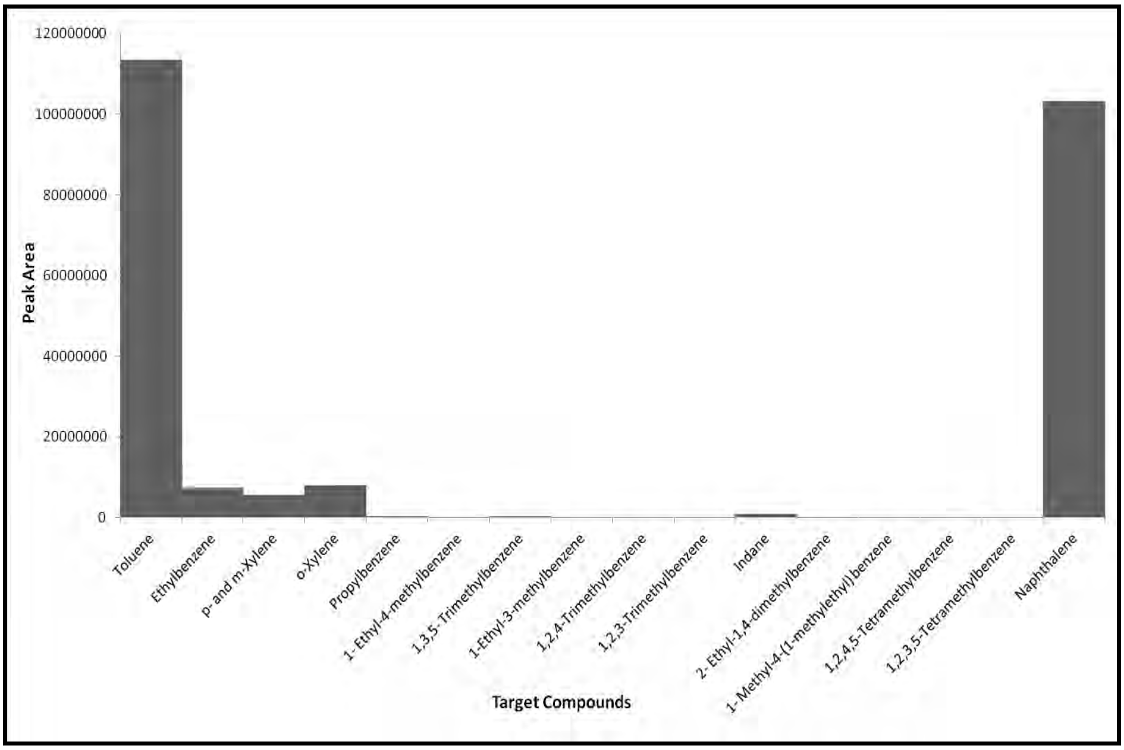


Figure 4.62: Target Compound Chromatogram for Adhesive Pyrolysed at900°C

- Naphthalene was produced for the majority of pyrolysis experiments. This is demonstrated in Figure 4.63 which shows the target compound chromatogram generated at 900°C and incorporates all the carpet fibres and carpet components and Figure 4.64 which shows the foam and underlay.
- Target compounds recovered vary with pyrolysis temperature for all samples, usually target compounds produced at 900°C and 750°C are similar with significantly fewer compounds produced at 600°C and virtually no pyrolysis at 450°C. This conclusion is obvious given that less thermal degradation will occur at lower temperatures. These points are demonstrated in Figures 4.65 and 4.66 which show the target compound chromatogram generated at 600°C and 450°C and incorporates all the carpet fibres and carpet backing components.
- The alkene peak identified in the furnace fire experiments (Section 4.4.1) and styrene was also produced in all samples. This is shown in Figure 4.67.

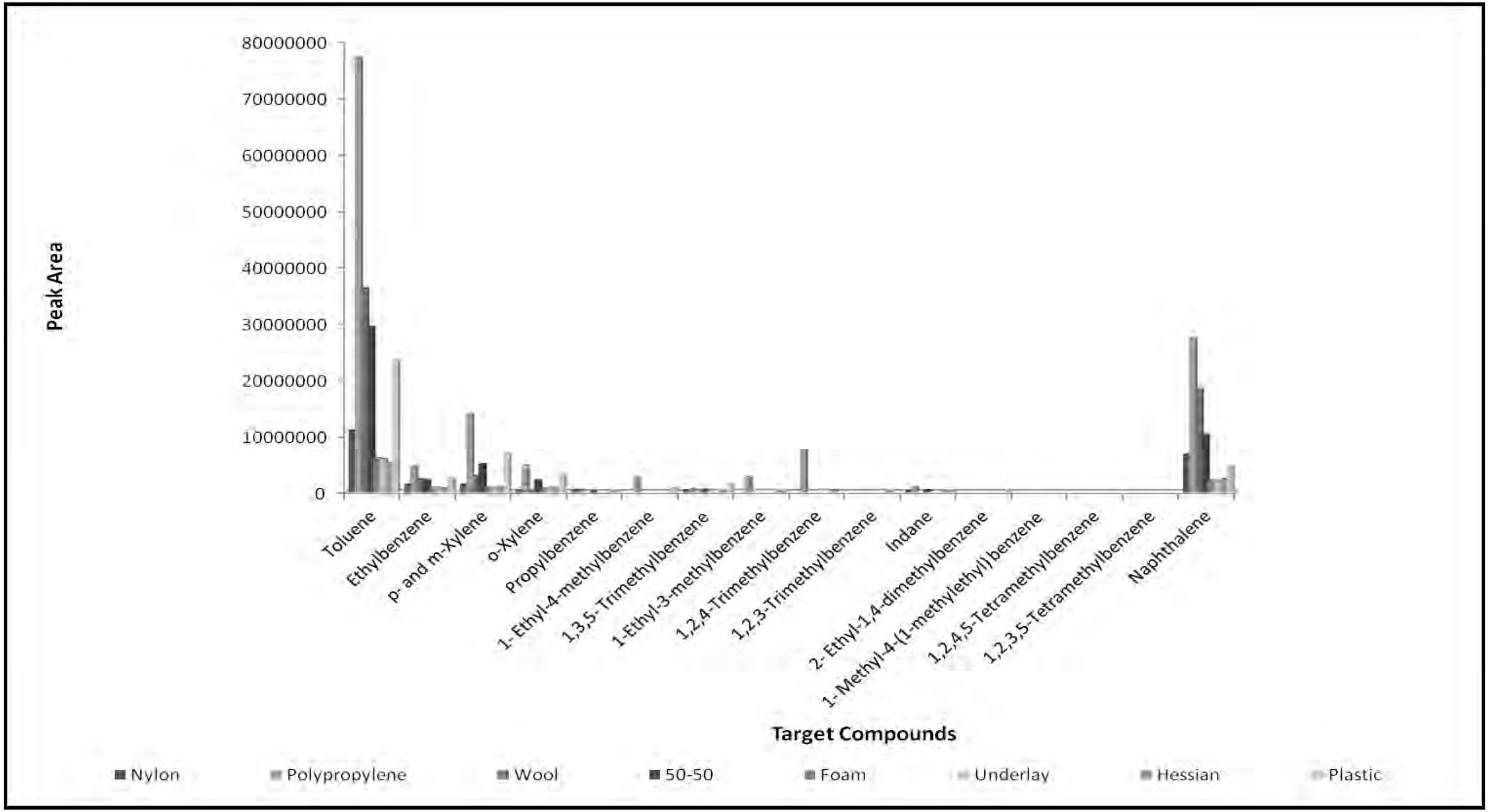


Figure 4.63: Target Compound Chromatograms incorporating Carpet Fibres and Carpet Backing Components Pyrolysed at 900°C

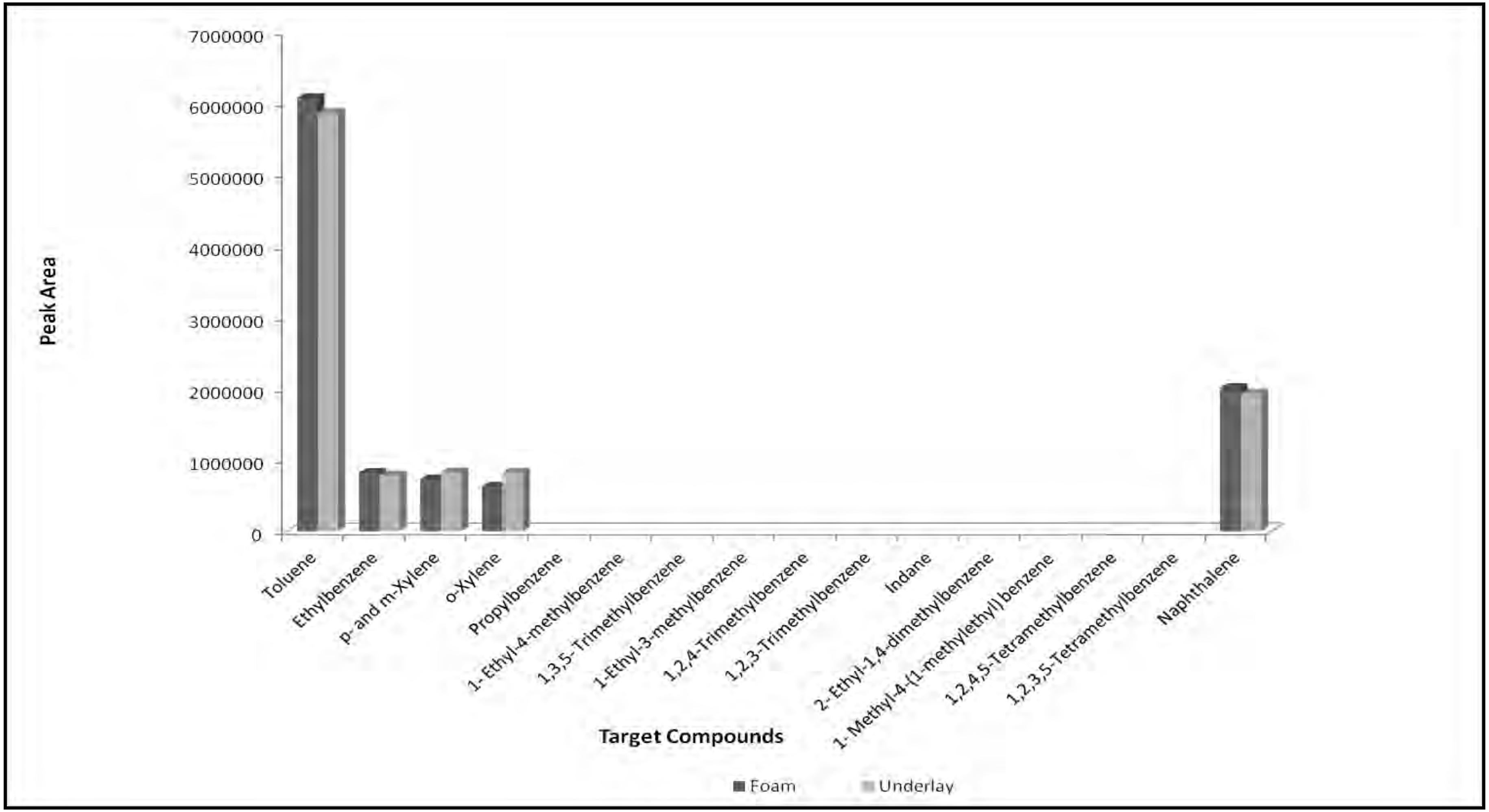


Figure 4.64: Target Compound Chromatograms incorporating Foam and Underlay Pyrolysed at 900°C

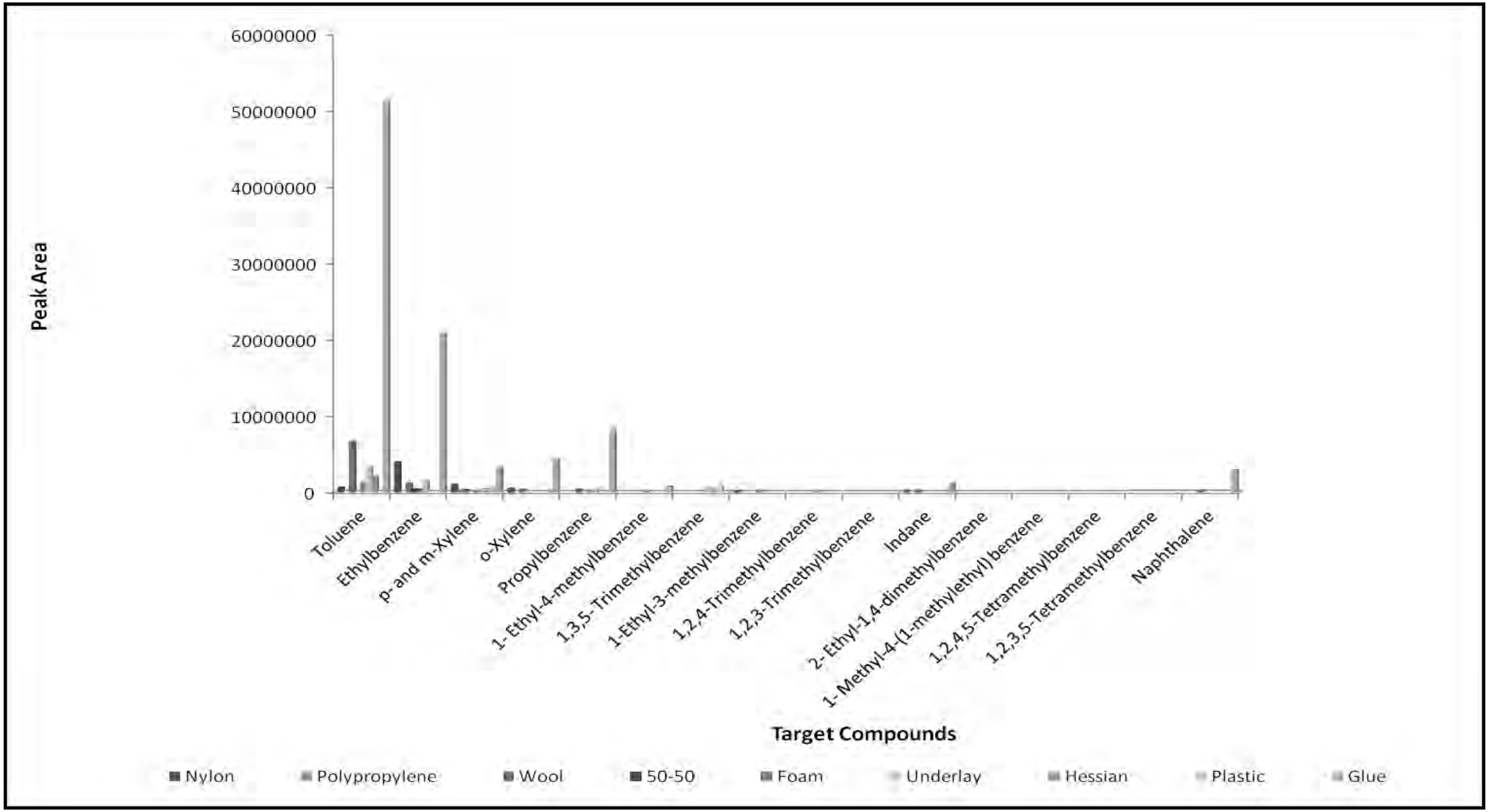


Figure 4.65: Target Compound Chromatograms incorporating Carpet Fibres and Carpet Backing Components Pyrolysed at 600°C

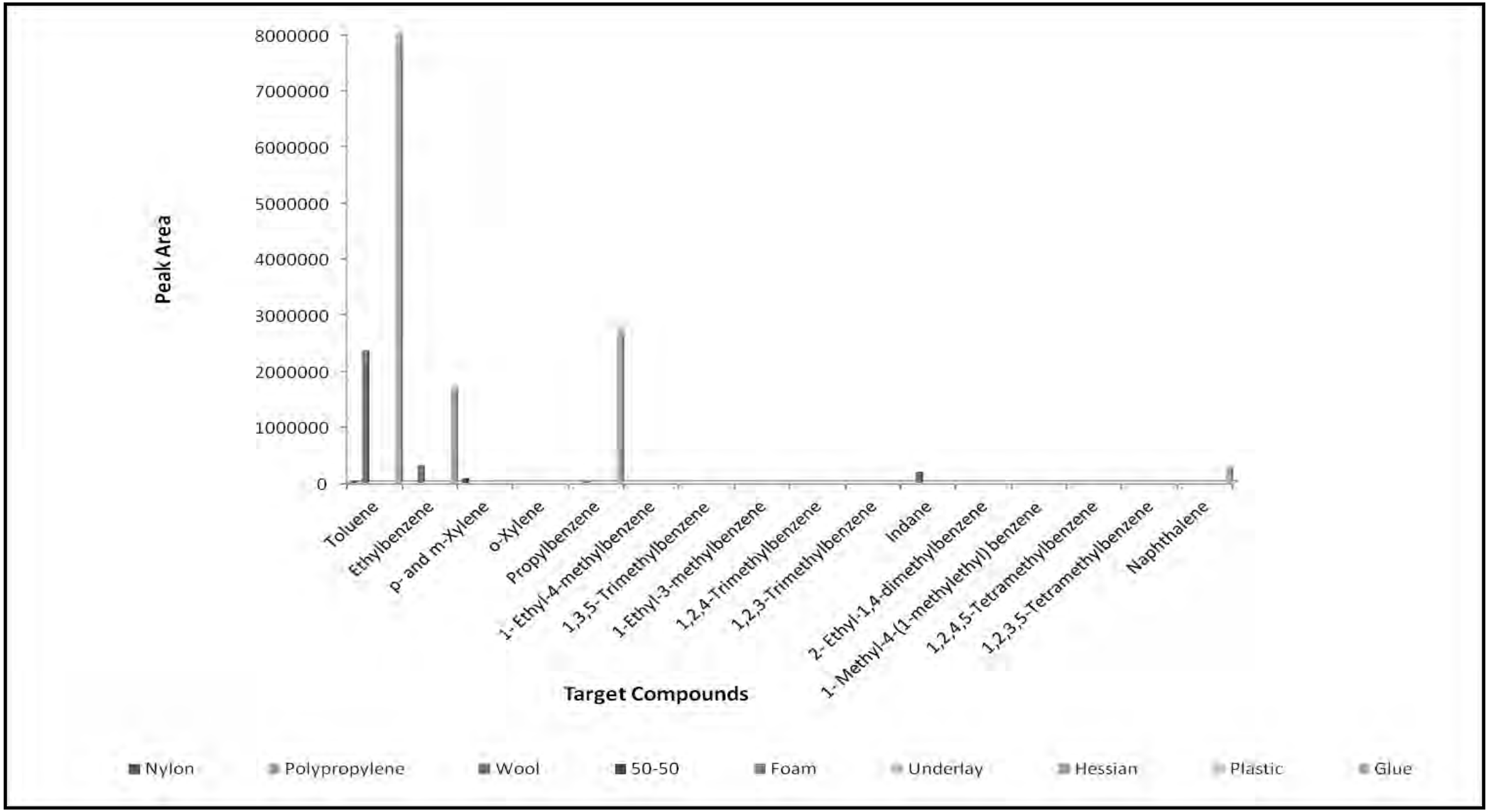


Figure 4.66: Target Compound Chromatograms incorporating Carpet Fibres and Carpet Backing Components Pyrolysed at 450°C

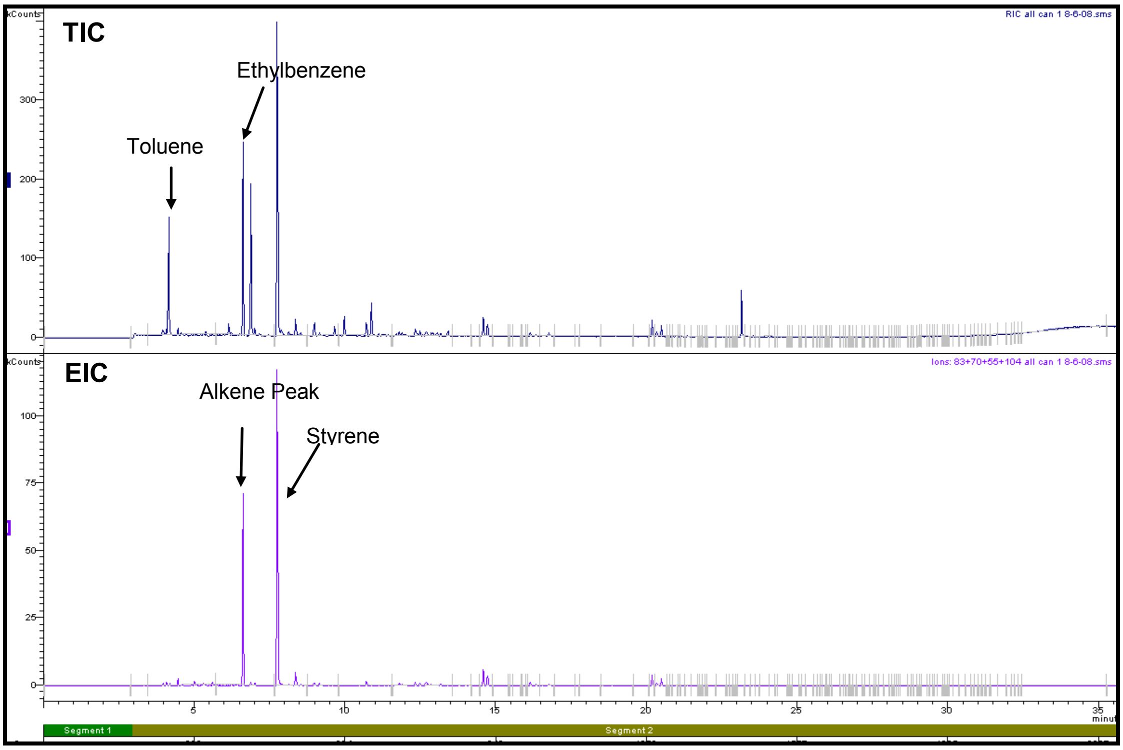


Figure 4.67: Total Ion Chromatogram and Extracted Ion Chromatogram showing Alkene Peak and Styrene (Refer to Section 2.5.1 for GC/MS conditions)

4.6.1 SUMMARY

Pyrolysis experiments showed that the target compounds similar to those obtained from the other burning tests are produced. This is interesting given that the thermal degradation occurring in the pyrolyser unit that is heating in an inert atmosphere, is different to the burning conditions in the large rooms, furnace or small can fires. In all fire experiments including pyrolysis, aromatic target compounds are produced, with toluene and ethylbenzene usually produced in greater abundances followed by lower abundances of other C_2 and C_3 alkylbenzenes. Naphthalene was only produced in pyrolysis experiments and this compound was not recovered in any of the other fire experiments.

Pyrolysis GC/MS data cannot be directly compared with the results from other burning tests but like the small can fires it can provide further information regarding volatile organic compounds produced by the thermal degradation of carpet and foam. How the results from the pyrolysis GC/MS experiments can be used for target compound analysis in arson investigation will be discussed in the conclusion .

5. CONCLUSION AND FURTHER WORK

The burning tests conducted on carpet and foam in this study showed that all but one of the 16 target compounds identified as important petrol target compounds can either be recovered from the fire tests or produced via pyrolysis. The only target compound not found was 1,2,3,4-Tetramethylbenzene. Table 5.1 below summarises these findings.

Table 5.1: Petrol Target Compounds Recovered from each Burning Test and Produced by Pyrolysis GC/MS

Petrol Target Compound	Large Scale Fires	Furnace Fires	Small Can Fires	Pyrolysis GC/MS
Toluene	X	X	X	X
Ethylbenzene	X	X	X	X
p- and *m*-Xylene			X	X
o-Xylene			X	X
Propylbenzene			X	X
1-Ethyl-4-methylbenzene			X	X
1,3,5-Trimethylbenzene			X	X
1-Ethyl-2-methylbenzene			X	X
1,2,4-Trimethylbenzene			X	X
1,2,3-Trimethylbenzene				X
Indane			X	X
2-Ethyl-1,4-dimethylbenzene				X
1-Methyl-2-(1-methylethyl)benzene				X
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				X
Naphthalene				X

***X indicates compound is present*

Applying the results from the burning tests to arson investigation is not straightforward and the way in which the results are applied to a real fire situation needs to be carefully considered. Results from large scale room fires, where burning conditions are those encountered in a real fire and furnace fires, which best represent simulated fire scenarios, can perhaps be better related to what may be found in a real fire situation compared to small can fires and pyrolysis experiments where burning conditions are not representative of a real fire.

In the large room and furnace fires, burning conditions and sample sizes best represented those encountered in a typical fire and the findings were significant even though very low levels of toluene and/or ethylbenzene were recovered. Results showed that extent of burning had little bearing on levels of volatile organic compounds that could be recovered from the burnt substrates because there are negligible levels of these burning products present as they are mostly consumed or otherwise lost during the burning process. The levels of toluene and/or ethylbenzene recovered were below the limit for pattern comparison, which is far below the range in which fire investigation scientists would work and as such it is unlikely that at these levels interferences from the burning of carpet and foam would interfere with petrol identification. Even at the limits for pattern comparison interference is unlikely. A hypothetical situation is shown below in Figure 5.1. Here the pattern shown in dark grey is that of a petrol standard (2μl of 50% evaporated petrol headspace standard) which represents the pattern obtained from petrol recovered from fire debris at the limit for pattern comparison and this is superimposed with the pattern shown in light grey (nylon carpet burnt in room 3 of the large scale room fires) which represents the contribution from interferences produced by the burning of carpet and foam in the fire debris.

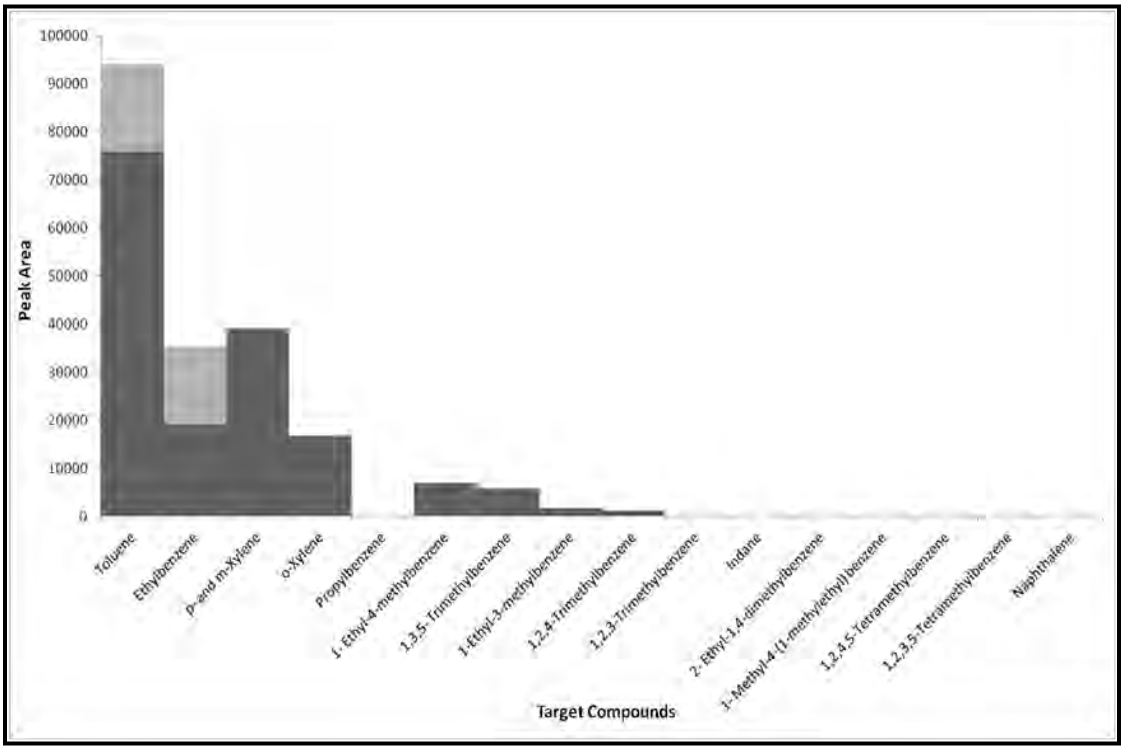


Figure 5.1: Hypothetical Target Compound Chromatogram of Fire Debris containing Petrol Residue (dark grey) superimposed with Interferences from Carpet and Foam (light grey)

As can be seen the petrol pattern is still observable with only a slight increase in the toluene and ethylbenzene peaks. For greater levels of petrol residues recovered any interfering contributions from the burning or carpet and foam at the low levels found in this study would not interfere with a petrol target compound chromatogram.

The implications of the large room and furnace fire results for fire investigation using target compound analysis is that it would be unlikely to encounter interferences from the burning of carpet and foam that would hinder a petrol identification. Furthermore, the burning and analysis of substrate comparison samples to determine interfering products for these substrates may not be warranted.

The results of the small can fires with lid on and pyrolysis experiments do allow volatile organic compound profiles from the thermal degradation of these substrates to be collected. Considering that the burning conditions in these tests are not representative of those encountered in a typical fire, the volatile organic compound profiles would still be useful in investigating potential interfering products. The GC/MS data obtained from the small can fire experiments and pyrolysis GC/MS can provide information to fire investigators and assist in their understanding and awareness of not just the types of volatile organic compounds but also the patterns of volatile organic compounds that these substrates produce when thermally degraded. Useful information on the types of volatile organic compounds was obtained from the total ion chromatogram and pattern information was obtained from the extracted ion chromatogram and target compound chromatogram, respectively and this information is used below to suggest possible indicators of potential interferences from the burning of carpet and foam in identifying petrol in arson investigation.

- Small can fire and pyrolysis target compound chromatogram profiles showed that toluene and ethylbenzene were usually recovered in the greatest abundance followed by lower levels of C_2 and C_3 alkylbenzenes and even lower levels of other aromatics. This type of interfering pattern may result in a petrol target compound chromatogram being skewed towards the toluene, ethylbenzene and to a lesser extent other C_2 and C_3 alkylbenzenes. A hypothetical situation is shown in Figure 5.2. Here the pattern shown in dark grey is that of a petrol standard (10μl of 50% evaporated petrol headspace standard) which represents the pattern obtained from petrol recovered from fire debris and this is superimposed with the pattern shown in light grey (nylon carpet burnt in a small can with lid on for 2.5 minutes) which represents the contribution from interferences produced by the burning of carpet and foam in the fire debris. As can be seen the petrol pattern is heavily skewed towards toluene and ethylbenzene, this would distort the ratios of target compounds, which is the basis of pattern comparison using GC/MS and target compound chromatograms. Even though ratios are distorted this may hinder a direct comparison to a petrol standard, however knowing the important target compounds of petrol and the recognisable pattern that it produces and being aware of the potential interferences identified in this study, these interferences would be easily recognised and a petrol identification could not be excluded. One way to be able to better compare target compound chromatograms such as the one in Figure 5.2 to petrol standards is to remove the toluene and ethylbenzene from the target compound chromatograms, resulting in a sample target compound chromatogram where the ratios would better match those of a petrol standard. It should be noted that in this example the contribution represents an extreme case, because as shown in this study when burning in a small can with lid on more volatile organic compounds and in greater abundances are recovered. In a more realistic situation the contributions could be significantly less given that, as was shown in this study, less volatile organic compounds are present in the burnt substrate in an open fire situation.

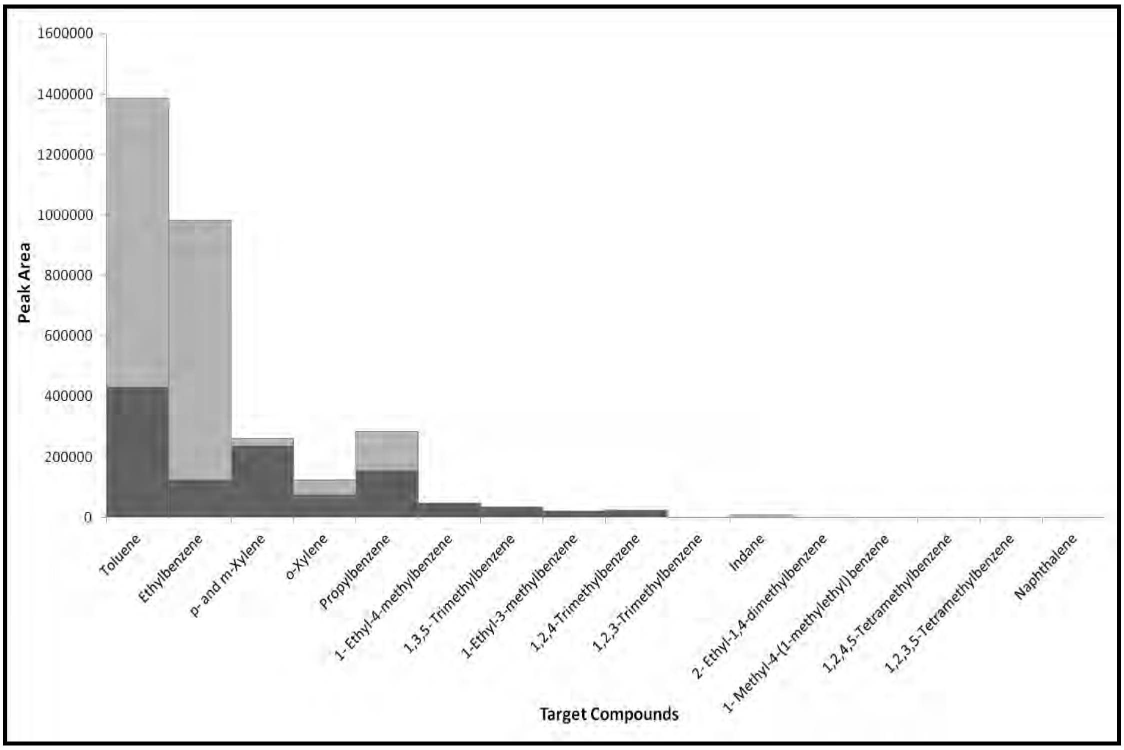


Figure 5.2: Hypothetical Target Compound Chromatogram of Fire Debris containing Petrol Residue (dark grey) superimposed with Interferences from Carpet and Foam (light grey)

- A second hypothetical situation is shown in Figure 5.3. Here the pattern shown in dark grey is that of a highly evaporated petrol standard (10μl of 95% evaporated petrol headspace standard) which represents the pattern obtained from petrol recovered from fire debris and this is superimposed with the pattern shown in light grey (nylon carpet burnt in a small can with lid on for 2.5 minutes) which represents the contribution from interferences produced by the burning of carpet and foam in the fire debris. As can be seen the petrol pattern is heavily skewed towards toluene and ethylbenzene, this would distort the ratios of target compounds, which is the basis of pattern comparison using GC/MS and target compound chromatogram. In this case those important heavier petrol target compounds are present in a recognisable pattern and skewing towards toluene and ethylbenzene is easily recognised and a petrol identification cannot be excluded. Like the previous example, if toluene and ethylbenzene were removed from the target compound chromatogram, the ratios of the sample target compounds would better match those from a petrol standard. Also like the previous example, the scenario proposed represents an extreme case of interference.

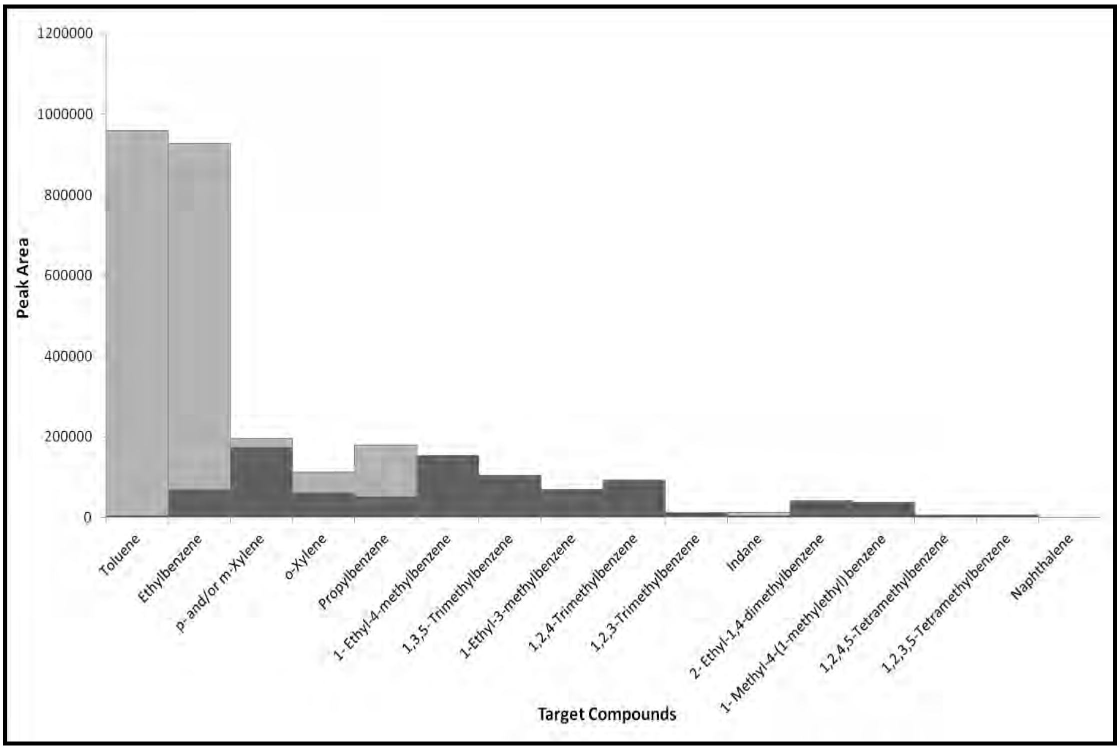
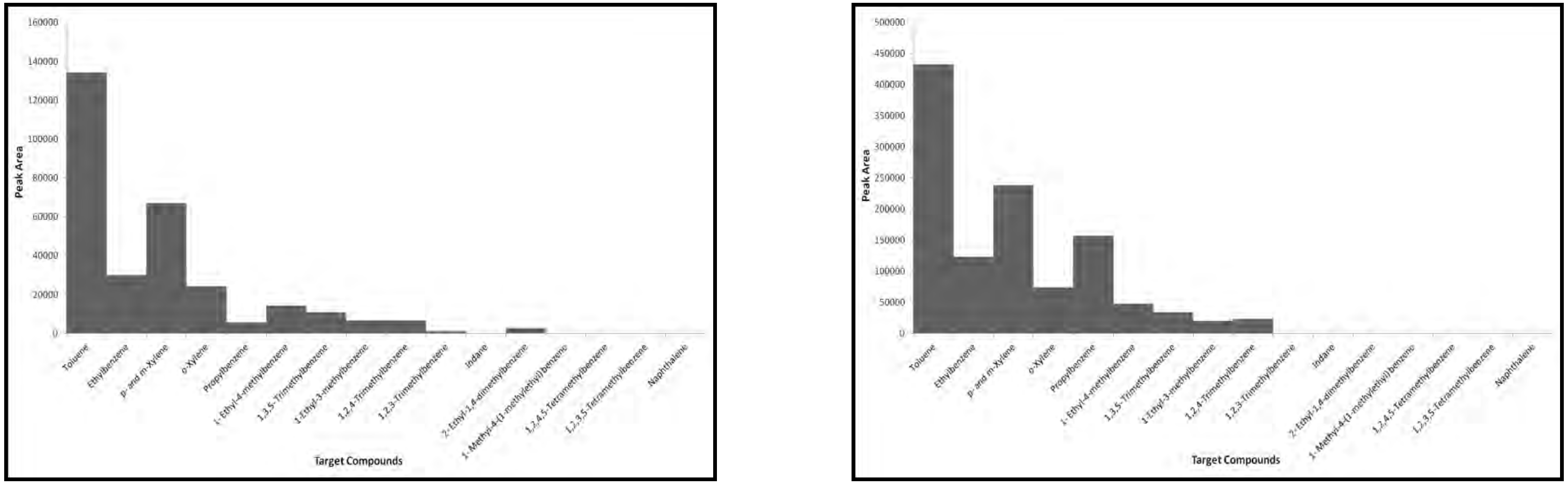


Figure 5.3: Hypothetical Target Compound Chromatogram of Fire Debris containing Heavily Evaporated Petrol Residue (dark grey) superimposed with Interferences from Carpet and Foam (light grey)

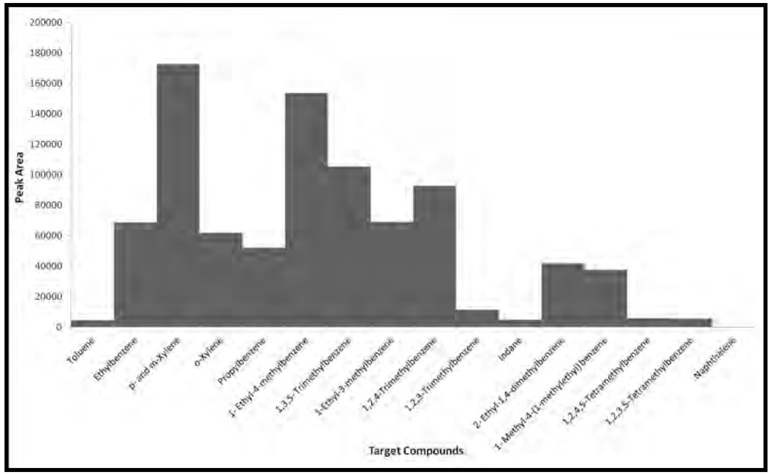
- The unidentified alkene peak and styrene were also a common feature present in the total ion chromatogram of the furnace, small can and pyrolysis burning tests. Since these two compounds are produced in the furnace tests, where burning conditions better represent those in a real fire, it follows that the presence of these two compounds in a fire residue total ion chromatogram may be indicative that there is contribution from the burning of these substrates. In this study naphthalene was only produced from the pyrolysis experiments and this suggests that naphthalene would not be a source of interference in a real fire situation.

The results of this study showed that for fire debris containing no ignitable liquid but containing contributions from the burning of carpet and foam a false identification of petrol is most unlikely to be made. Using the method for analysing substrate comparison samples (presented below), when comparing target compound chromatograms of carpet substrates burnt in a small can with lid on for 2.5 minutes and foam for 7.5 minutes, these target compound chromatograms in no way resemble those from the headspace petrol standards. Figure 5.4 shows the target compound chromatograms of the petrol standards at various evaporation states and Figure 5.5 shows the target compound chromatograms for the burnt carpet and foam samples.

As can be seen a false identification of petrol is unlikely to be made because fire residues containing contributions from carpet and foam do not display characteristic petrol target compound chromatograms that is distinctive petrol patterns with the appropriate target compound ratios. Even if contributions from carpet and foam underlay are combined (as these two substrates are usually present together), as shown in Figure 5.6, again a false identification of petrol should not be made for the same reasons above.

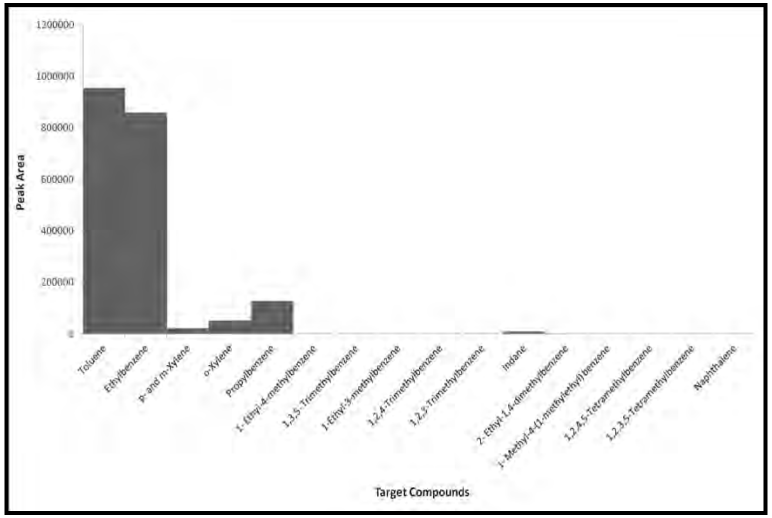


Unevaporated Petrol **50% Evaporated Petrol**

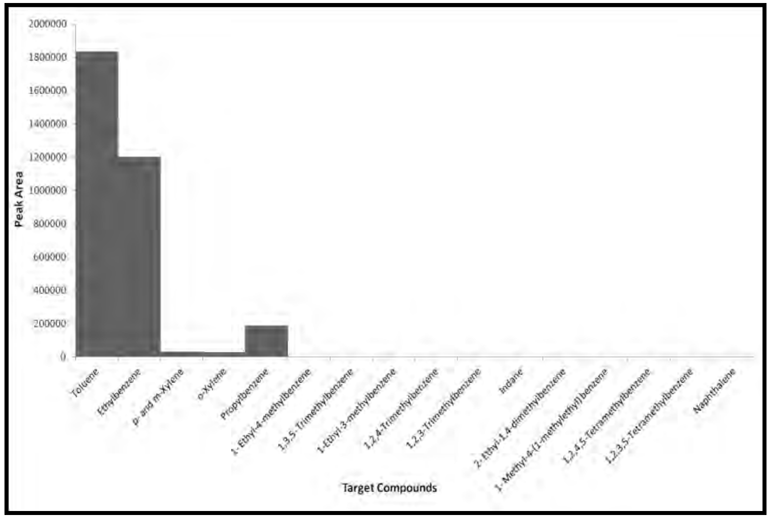


95% Evaporated Petrol

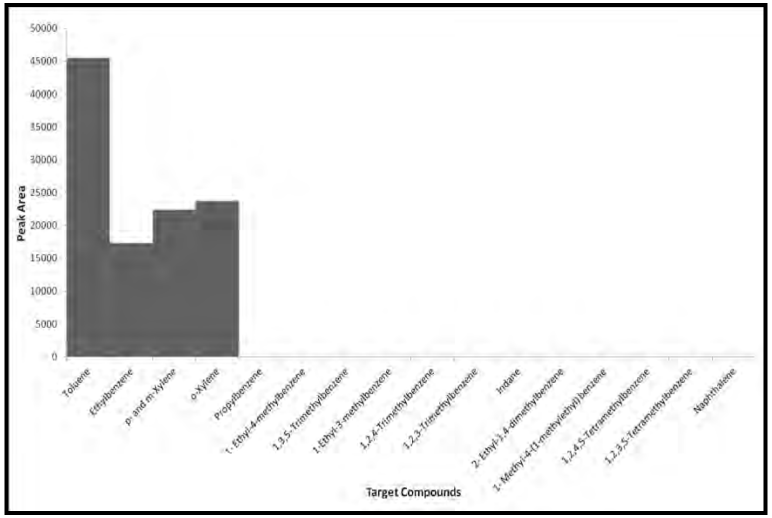
Figure 5.4: Target Compound Chromatograms of 10μL Headspace Petrol Standards



Target Compound chromatogram of a nylon carpet swatch burnt for 2.5 minutes in a can



Target Compound Chromatogram of a wool carpet swatch burnt for 2.5 minutes in a can



Target Compound Chromatogram of a foam swatch burnt for 7.5 minutes in a can

Figure 5.5: Target Compound Chromatograms of Nylon, Wool and Foam Burnt in a Small Can with Lid On

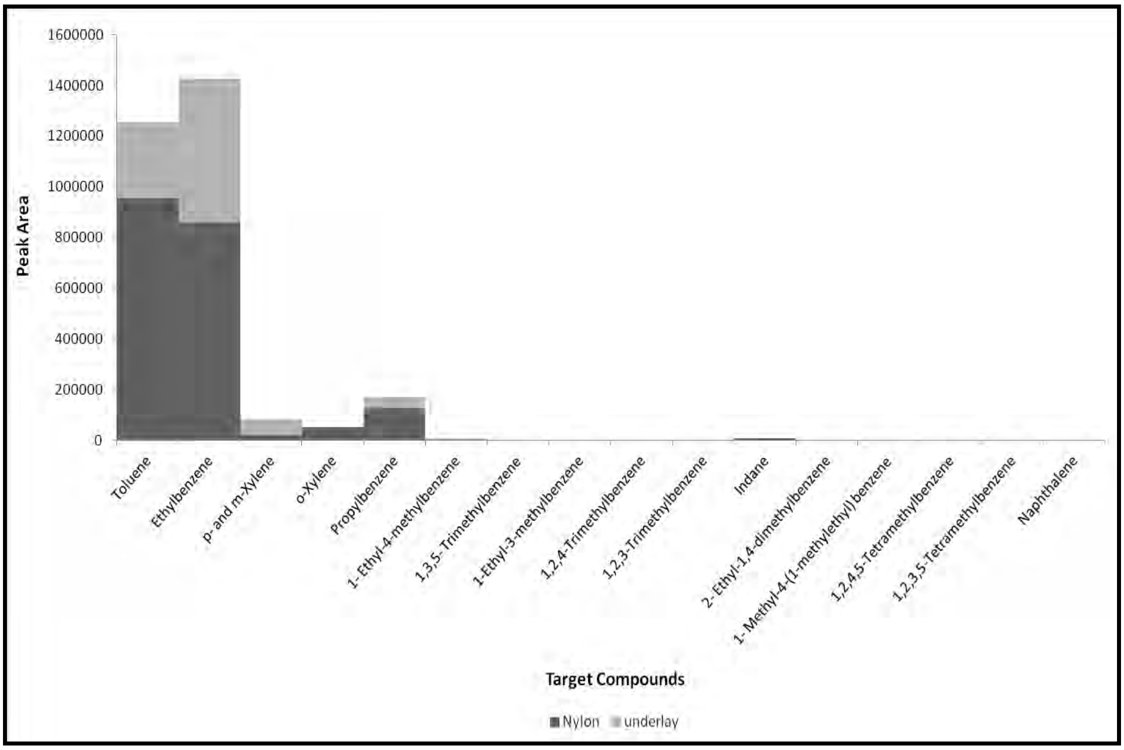


Figure 5.6: Target Compound Chromatogram of Nylon Carpet superimposed with Underlay burnt in a Small Can with Lid On for 2.5 minutes

It should be noted that when comparing all petrol standard target compound chromatograms, including both liquid and headspace at all evaporation states and dilutions, to all burning tests including pyrolysis GC/MS, the same conclusion is arrived at. Standard petrol target compound chromatograms are distinctly different to those produced by the burning of carpet and foam and a false identification of petrol is unlikely.

Overall the results of this study suggest that it would be unlikely to encounter interferences from the burning of carpet or foam when analysing fire debris for the presence of petrol. Firstly, the large room and furnace fires show that negligible levels of volatile organic compounds remain in the burnt substrates; secondly, small can and pyrolysis results indicate that it is difficult to confuse a petrol target compound chromatogram with that of a burnt substrate. Additionally, if there was contribution to a petrol target compound chromatogram from burnt substrates then there may be recognisable indicators such as skewing towards toluene and ethylbenzene as well as the presence of the unidentified alkene peak and styrene in the total ion chromatogram.

In extending the results of this study to other ignitable liquids besides petrol the potential for interference from the burning of carpet and foam maybe significant for more volatile ignitable liquids that contain toluene and ethylbenzene.

Some of the petrol target compounds chosen for this study are also target compounds listed for heavier classes of ignitable liquids (ASTM Standard E1618-01), for example kerosene and automotive diesel fuel, in particular the trimethylbenzenes and tetramethylbenzenes[78]. In this study when recovered, they were always recovered in extremely low abundances and their potential to interfere in target compound chromatogram pattern comparison when these heavier ignitable liquids are used is minimal. This implies that for these heavier ignitable liquids, which are more likely to be encountered in a real fire situation, the potential for interference from the burning of carpet and foam would be much less.

Where petrol is identified in arson investigation the likelihood of interferences from the burning of these materials is extremely low and therefore the analysis of substrate comparison samples for this purpose may not be necessary.

Small can fires are a simple and quick laboratory method for analysing substrate comparison samples when the fire investigation scientist deems it necessary, as these can provide a fire investigator with further information as to potential interferences from burning substrates. However, this information needs to be used cautiously given that the burning conditions in the can are different to the burning conditions of a real fire.

This study demonstrates it is important to conduct small can fires with lid on as this allows sufficient levels of volatile organic compounds to be recovered. Importantly, the entire can and its contents should be sampled when recovering volatile organic compounds as the bulk (10 times more) of the volatile organic compounds are present in the can and not on the lid or sample. From the small can fire experiments a protocol for burning carpet and foam samples is proposed below:

- Carpet or foam samples are cut to fit flat in the bottom of the 1L metal paint can. Carpet samples are placed in the can with the fibres facing up.
- The lid of the can with a 6mm (diameter) pre- drilled hole is placed on the can and sealed.
- The can, with the lid on, is placed on a three ring burner connected to an LPG cylinder. For carpet the can is removed after 2.5 minutes of burning and after 7.5 minutes for foam.
- To extinguish the fire or cool down the can, the can is removed from the burner and immersed into a bucket of cold water, ensuring that no water gets in the can.
- The lid is then pried open slightly so that a charcoal tube can be placed in the can.
- The can (including the can, lid and sample) is placed in an evidence bag and sealed.
- Recovery of volatile organic compounds can then be performed as described in Section 2.4.
- It may be necessary to conduct a ‘can black’ that is a can burnt with no sample to ensure that no interfering volatile organic compounds are produced by the burning of the can.

An obvious aim of further work following on from this study is to extend the investigation to other ignitable liquids to see what the likelihood of interferences from the burning of the various substrates may have on identifying these ignitable liquids in arson investigation. Other ignitable liquids include different petrols, such as high ethanol petrols, low toluene and low xylene petrols as well as different fuels such as diesel and kerosene. As was shown in this study, the Australian petrol did not contain the list of target compounds as specified by the ASTM Standard method (E1618-01), highlighting the difference between the petrol used in this study and that used to generate the list of target compounds in the ASTM standard. There may be a need for different countries to determine what target compounds are specific for the fuel sources relevant to their region, to the extent that even variability of fuel sources in the same region may need to be considered.

Another natural extension to this study is the investigation of other domestic and commercial substrates submitted as fire debris samples to the laboratory such as fabrics, vinyl flooring, plastics, wood and paper to name a few. Other substrates could also include those from other fire scenarios such as automobiles.

The results in this study showed that if interferences from substrates where petrol is suspected did occur, the target compound chromatograms of the ignitable liquid residue would be skewed towards the lighter end of the chromatogram. It would be advantageous to examine a number of real fire debris samples where the fire investigation scientists believe there is accelerant to see if this skewing is observed.

Other work could include characterisation of the unidentified alkene peak that was present in a number of the burning test total ion chromatograms, as this compound may provide an indication of interferences from the burning of carpet and foam. Similar to potential skewing in ignitable liquid residue chromatograms it would be advantageous to analyse real fire debris samples to see if this alkene peak is observed.

The application of the findings from this study to fire investigation overseas could also be investigated, in particular by running both national and international collaborative trials using the protocol suggested for the burning of substrate comparison samples. This could ultimately lead to the development of an international standard method for the burning of substrate comparison samples.

With the small can fires, the levels of target compounds produced at the different burn times showed some interesting trends and further work is required to better understand how these time dependent profiles occur and develop.

6. REFERENCES

1. DeHaan, J. D., *Kirk's Fire Investigation*. 5th ed.; Prentice Hall: New Jersey, 2002.

2. Sheppard, D. T., Fire Dynamics. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 1-32.

3. Stauffer, E. Identification and Characterization of Interfering Products in Fire Debris Analysis. Florida International University, Miami, 2001.

4. De Vos , B. J. Gas Chromatography Coupled With Ion Trap Mass Spectrometry (GC-MS and GC-MS-MS) for Arson Debris Analysis. University of Pretoria, Pretoria, 2005.

5. Cafe, T.; Stern, W., Is it an Acciddental Fire or Arson? *Chemistry in Australia* April, 1989.

6. Ashe, B. S. W.; McAneney, A. J.; Pittman, A. J., Total Cost of Fire in Australia. *Journal of Risk Research* **2009,** *12* (2), 121-136.

7. Lane, B., *The Encyclopedia of Forensic Science*. BCA Publishing: UK, 1992.

8. Drabsch, T., *Arson: briefing paper 2/2003*. Sydney: NSW Parliament: 2003.

9. Saferstein, R., *Criminalistic: An Introduction to Forensic Science*. 8th ed.; Prentice Hall: USA, 2004.

10. Noon, R., *Engineering Analysis of Fires and Explosions*. CRC Press: USA, 1995.

11. Saferstein, R., *Forensic Science Handbook*. Prentice Hall: USA, 1982.

12. Yingyu, L.; Yanyan, C.; Hao, S.; Dong, L., Study on Fire Residues in Pure Cotton Fabric Combustion. *Advanced Materials Research* **2012,** *391-391*, 1479-1482.

13. Armstrong, A.; Babrauskas, V.; Holmes, D. L.; Martin, C.; Powell, R.; Riggs, S.; Young, L. D., The Evaluation of the Extent of Transporting or "Tracking" an Identifiable Ignitable Liquid (Gasoline) Throughout Fire Scenes During the Investigative Process. *Journal of Forensic Sciences* **2004,** *49* (4), 741-748.

14. Barshick, S.-A., Analysis of Accelerants and Fire Debris Using Aroma Detection Technology. *Journal of Forensic Sciences* **1998,** *43* (2), 284-293.

15. Furton, K. G.; Harper, R. J.; Perr, J. M.; Almirall, J. R., Optimization of Biological and Instrumental Detection of Explosives and Ignitable Liquid Residues including Canines, SPME/ITMS and GC/MS. *Proceedings of SPIE, the International Society for Optical Engineering* **2003,** *5071*, 183-192.

16. Sandercock, P. M. L., Fire Investigation and Ignitable Liquid Residue Analysis - A Review: 2001-2007. *Forensic Science International* **2008,** *176*, 93-110.

17. Sanagi, M. M.; Basri, R. S.; Miskam, M.; Ibrahim, W. A. W.; Ahmad, U. K.; Y., A.-E. H., Headspace Single Drop Microextraction for the Analysis of Fire Accelerants in fire Debris Samples. *Analytical Letters* **2010,** *43*, 2257-2266.

18. Darrer, M.; Jacquemet-Papilloud, J.; Delemont, O., Gasoline on Hands: Preliminary Study on Collection and Persistence. *Forensic Science International* **2008,** *175*, 171-178.

19. Hine, G. A., Fire Scene Investigation: An Introduction for Chemists. In *Analysis and Interpretation of Fire Scene Evidence* Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 33 - 74.

20. Ren, Q.; Bertsch, W., A Comprehensive Sample Preparation Scheme for Accelerants in Suspect Arson Cases. *Journal of Forensic Sciences* **1999,** *44* (3), 504-515.

21. Maguire, C., Fires from causes other than electrical malfunctions:theory and case studies. In *Fire Investigation*, Daeid, N. N., Ed. CRC Press LLC: Florida, 2004; pp 13-60.

22. Aernecke, M. J.; Walt, D. R., Detection and Classification of Ignitable Liquid Residues Using a Fluorescence-Based Vapor-Sensitive Microsphere Array. *Journal of Forensic Sciences* **2010,** *55* (1), 178-184.

23. Almirall, J. R.; Furton, K. G., New Developments in Sampling and Sample Preparation for Forensic Analysis. In *Wilson and Wilson's Comprehensive Analytical Chemistry*, Pawliszyn, J., Ed. Elsevier Science: 2002; pp 919-938.

24. Baechler, S.; Comment, S.; Delemont, O., Extraction and Concentration of Vapors from Fire Debris for Forensic Purposes: Evaluation of the Use of Radiello Passive Air Sampler. *Talanta* **2010,** *82*, 1247-1253.

25. Borusiewicz, R.; Zadora, G.; Zieba-Palus, J., Application of Head-Space Analysis with Passive Adsorption for Forensic Purposes in the Automated Thermal Desorption-Gas Chromatography-Mass Spectrometry. *Chromatographia* **2004,** *60*, S133-S142.

26. Cavanagh, K.; Du Pasquier, E.; Lennard, C., Background Interference from Car Carpets - The Evidential Value of Petrol Residues in Cases of Suspected Vehicle Arson. *Forensic Science International* **2002,** *125*, 22-36.

27. ASTM E1618-97 Standard Guide for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography - Mass Spectrometry. In *ASTM* West Conshohocken, PA, 1997.

28. ASTM E1387-95 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography. In *Annual Book of ASTM Standards*, ASTM, Ed. West Conshohocken, PA, 1995.

29. Sigman, M. E.; Williams, M. R., Covariance Mapping in the Analysis of Ignitable Liquids by Gas Chromatography/Mass Spectrometry. *Analytical Chemistry* **2006,** *78*, 1713-1718.

30. Steffen, A.; Pawliszyn, J., Determination of Liquid Accelerants in Arson Suspected Fire Debris using Headspace Solid-Phase Microextraction. *Analytical Communications* **1996,** *33* (4), 129-131.

31. Tranthim-Fryer, D. J.; DeHaan, J. D., Canine Accelerant Detectors and Problems with Carpet Pyrolysis Products. *Science & Justice* **1997,** *37*, 39-46.

32. Baerncopf, J. M.; McGuffin, V. L.; Smith, R. W., Association of Ignitable Liquid Residues to Neat Ignitable Liquids in the Presence of Matrix Interferences Using Chemometric Procedures. *Journal of Forensic Sciences* **2011,** *56* (1), 70-81.

33. Barnes, A. T.; Dolan, J. A.; Kuk, R. J.; Siegel, J. A., Comparison of Gasolines using Gas Chromatography-Mass Spectrometry and Target Ion Response. *Journal of Forensic Sciences* **2004,** *49* (5), 1018-1023.

34. Bodle, E. S.; Hardy, J. K., Multivariate Pattern Recognition of Petroleum-Based Accelerants by Solid-Phase Microextraction Gas Chromatography with Flame Ionization Detection. *Analytica Chimica Acta* **2007,** *589*, 247-254.

35. Frysinger, G. S.; Gaines, R. B., Forensic Analysis of Ignitable Liquids in Fire Debris by Comprehensive Two-Dimensional Gas Chromatography. *Journal of Forensic Sciences* **2002,** *47* (3), 471-482.

36. Lu, Y.; Harrington, P. B., Forensic Application of Gas Chromatography-Differential Mobility Spectrometry with Two-Way Classification of Ignitable Liquids from Fire Debris. *Analytical Chemistry* **2007,** *79* (17), 6752-6759.

37. Monfreda, M.; Gregori, A., Differentiation of Unevaporated Gasoline Samples According to Their Brands, by SPME-GC-MS and Multivariate Statistical Analysis. *Journal of Forensic Sciences* **2011,** *56* (2), 372-380.

38. Rella, R.; Sturaro, A.; Parvoli, G.; Ferrara, D.; Doretti, L. Accelerant Identification in Fire Debris by TCT-GC-MS, p. 603-609. (accessed May 2012).

39. Rodgers, R. P.; Blumer, E. N.; Freitas, M. A.; Marshall, A. G., Compositional Analysis for Identification of Arson Accelerants by Electron

Ionization Fourier Transform Ion Cyclotron Resonance High-Resolution Mass Spectrometry. *Journal of Forensic Sciences* **2001,** *46* (2), 268-279.

40. Touron, P.; Malaquin, P.; Gardebas, D.; Nicolai, J.-P., Semi-Automatic Analysis of Fire Debris. *Forensic Science International* **2000,** *110*, 7-18.

41. What is Arson? Australian Government: Australian Institute of Criminology: 2004; Vol. 1.

42. Bertsch, W., Chemical Analysis of Fire Debris; Was it Arson? *Analytical Chemistry* **1996,** *68*, 541A.

43. Bertsch, W.; Zhang, Q.-W., Sample Preparation for the Chemical Analysis of Debris in Suspect Arson Cases. *Analytica Chimica Acta* **1990,** *236*, 183-195.

44. Daeid, N. N., An Introduction to Fires and Fire Investigation. In *Fire Investigation*, Daeid, N. N., Ed. CRC Press LLC: Florida, 2004; pp 1 - 12.

45. Pert, A. D.; Baron, M. G.; Birkett, J. W., Review of Analytical Techniques for Arson Residues. *Journal of Forensic Sciences* **2006,** *51* (5), 1033-1049.

46. Higgins, K. M.; Higgins, M. K.; Oakes, C. L.; Bracerman, S. F., High-Speed Extraction of Accelerants from Arson Debris. *Journal of Forensic Sciences* **1984,** *29* (3).

47. Olenick, S. M.; Klassen, M. S.; Roby, R. J.; Ma, T.; Torero, J. L., The Behaviour of Liquid Fuel on Carpet (Porous Media): A Case for the Inclusion of Science in Fire Investigation. *Fire Technology* **2010,** *46*, 843-852.

48. Koussiafes, P. M., The Interpretation of Data Generated from Fire Debris Examination: Report Writing and Testimony. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 193-228.

49. Stauffer, E., Sources of Interference in Fire Debris Analysis. In *Fire Investigation*, Daeid, N. N., Ed. CRC Press LLC: Florida, 2004; pp 191- 226.

50. Sauers, D. G., The Effects of Forced Air Flow and Oxygen Concentration on Flammability, Smoke Density, and Pyrolytic Toxicity. *Journal of Fire and Flammability* **1976,** *7*, 181-199.

51. Moldoveanu, S. C., *Analytical Pyrolysis of Natural Organic Polymers*. 1st ed.; Elsevier: Amsterdam, 1998; Vol. 20.

52. Schaffer, M. A.; Marchildon, E. K.; McAuley, K. B.; Cunningham, M. F., Thermal Nonoxidative Degradation of Nylon 6,6. *Journal of Macromolecular Science - Reviews in Macromolecular Chemistry & Physics* **2000,** *C40* (4), 233-272.

53. Drysdale, D., *An Introduction to Fire Dynamics*. John Wiley and Sons Ltd: U.K, 1985.

54. Kelly, R. L.; Martz, R. M., Accelerant Identification in Fire Debris by GC/MS Techniques. *Journal of Forensic Science* **1984,** *29* (3), 714-722

55. Furton, K. G.; Harper, R. J., Detection of Ignitable Liquid Residues in Fire Scenes: Accelerant Detection Canine (ADC) Teams and Other Field Tests. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 75 - 96.

56. White, P., *Crime Scene to Court: The Essentials of Forensic Science*. Royal Society of Chemistry: UK, 2002.

57. Frontela, L.; Pozas, J. A.; Picabea, L., A Comparison of Extraction and Adsorption Methods for the Recovery of Accelerants from Arson Debris. *Forensic Science International* **1995,** *125*, 22 - 36.

58. Stauffer, E.; Dolan, J. A.; Newman, R. T., Chapter 5: Detection of Ignitable Liquid residues at Fire Scenes. In *Fire Debris Analysis*, Elsevier: USA, 2008.

59. Kelleher, J., Chief Fire Investigation Scientists, VPFSC. Sferopoulos, R., Ed. 2011.

60. Jackowski, J. P., The Incidence of Ignitable Liquid Residues in Fire Debris as Determined by a Sensitive and Comprehensive Analytical Scheme. *Journal of Forensic Science* **1997,** *42* (5), 828 - 832.

61. Lang, T.; Dixon, B. M., The Possible Contamination of Fire Scenes by the Use of Positive Pressure Ventilation Fans. *Journal of the Canadian Society of Forensic Science* **2000,** *33* (2), 55-60.

62. Cafe, T., Sampling Debris at the Fire Scene. In *2nd Australian Arson Fraud Seminar*, Sydney, Australia, 1990.

63. Massey, D.; Du Pasquier, E.; Lennard, C., Solvent Desorption of Charcoal Strips (DFLEX) in the Analysis of Fire Debris Samples: Replacement of Carbon Disulfide. *Journal of the Canadian Society of Forensic Science* **2002,** *35* (4), 195-207.

64. Lentini, J. J.; Dolan, J. A.; Cherry, C., The Petroleum- Laced Background. *Journal of Forensic Science* **2000,** *45* (5), 968-989

65. Chasteen, C. E., Essential Tools for the Analytical Laboratory: Facilities, Equipment, and Standard Operating Procedures. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 97 - 136.

66. Williams, M. R.; Sigman, M. E., Performance Testing of Commercial Containers for Collection and Storage of Fire debris Evidence. *Journal of Forensic Sciences* **2007,** *52* (3), 579-585.

67. Kocisko, M. J., Absorption of Ignitable Liquids into Polyethylene/ Polyvinylidine Dichloride Bags. *Journal of Forensic Sciences* **2001,** *46* (2), 356-362.

68. Mann, D. C., Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparisons in Casework. *Journal of Forensic Science* **1987,** *32* (3), 828 - 832.

69. ASTM E1388-95 Standard Practise for Sampling of Headspace Vapours from Fire Debris Samples. In *ASTM* West Conshohocken, PA, 1995.

70. Kwon, M.; Hong, S.; Choi, H., Sampling of Highly Volatile Accelerants at the Fire Scene. *Canadian Society of Forensic Science* **2003,** *36* (4), 197-205.

71. ASTM E1413-95 Standard Practise for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration. In *ASTM* West Conshohocken, PA, 1995.

72. Smith, R. M., Before the Injection - Modern Methods of Sample Preparation for Separation Techniques *Journal of Chromatography A* **2003,** *1000*, 3-27.

73. Ueta, I.; Saito, Y.; Teraoka, K.; Matsuura, H.; Fujimura, K.; Jinno, K., Novel Fire Investigation Technique Using Needle Extraction in Gas Chromatography. *Analytical Sciences* **2010,** *26*, 1127-1132.

74. ASTM E1412-95 Standard Practise for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration. In *ASTM*, West Conshohocken, PA, 1995.

75. Lentini, J. J.; Armstrong, A., Comparison of the Eluting Efficiency of Carbon Disulfide with Diethyl Ether: The Case for Laboratory Safety. *Journal of Forensic Sciences* **1997,** *42* (2), 307-311.

76. Dietz, W. R., Improved Charcoal Packaging for Accelerant Recovery by Passive Diffusion. *Journal of Forensic Sciences* **1991,** *36* (1), 111-121.

77. Dolan, J. A., Recent Advances in the Applications of Forensic Science to Fire Debris Analysis. *Analytical and Bioanalytical Chemistry* **2003,** *376*, 1168-1171.

78. ASTM E 1618-01 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography - Mass Spectrometry. In *ASTM* West Conshohocken, PA, 2001

79. Ren, Q.; Bertsch, W., Sample Preparation for the Analysis of Water Soluble Accelerants in Fire Debris. *Journal of Canadian Society of Forensic Science* **2000,** *33* (1), 7-12.

80. Newman, R. T.; Dietz, W. R.; Lothridge, K., The Use of Activated Charcoal Strips for Fire Debris Extractions by Passive Diffusion. Part 1: The Effects of Time, Temperature, Strip Size, and Sample Concentration. *Journal of Forensic Sciences* **1996,** *41* (3), 361-370.

81. Mindrup, R., Rapid, Sensitive Detection of Gasoline in Fire Debris using SPME/Capillary GC. *Supelco* **1998,** *17* (4), 3.

82. Tranthim-Fryer, D. J., The Application of a Simple and Inexpensive Modified Carbon Wire Adsorption/ Solvent Extraction Technique to the Analysis of Accelerants and Volatile Organic Compounds in Arson Debris. *Journal of Forensic Sciences* **1990,** *35* (2), 271-280.

83. Almirall, J. R.; Wang, J.; Lothridge, K.; Furton, K. G., The Detection and Analysis of Ignitable Liquid Residues extracted from Human Skin using SPME/GC. *Journal of Forensic Sciences* **2000,** *45* (2), 453-461.

84. Bozalongo, R.; Carrillo, J. D.; Torroba, M. A. F.; Tena, M. T., Analysis of French and American Oak Chips with Different Toasting Degrees by Headspace Solid-Phase Microextraction-Gas Chromatography-Mass Spectrometry. *Journal of Chromatography A* **2007,** *1173*, 10-17.

85. Lai, H.; Guerra, P.; Joshi, M.; Almirall, J. R., Analysis of Volatile Components of Drugs and Explosives by Solid Phase Microextyraction-Ion Mobility Spectrometry. *Journal of Separation Science* **2008,** *31*, 402-412.

86. Lee, X.-P.; Kumazawa, T.; Kondo, K.; Furuta, S.; Sato, K., Improved Extraction of Thinner Components from Human Body Fluids by Headspace Solid-Phase Microextraction with a Carboxen/ Polydimethylsiloxane-Coated Fiber. *Legal Medicine* **1999,** *1*, 231-237.

87. ASTM E1385-95 Standard Practise for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Steam Distillation. In *ASTM* West Conshohocken, PA, 1995.

88. Furton, K. G.; Almirall, J. R.; Bi, M.; Wang, J.; Wu, L., Application of Solid-Phase Microextraction to the Recovery of Explosives and Ignitable Liquid Residues from Forensic Specimens. *Journal of Chromatography A* **2000,** *885*, 419-432.

89. Jain, A.; Verma, K. K., Recent Advances in Applications of Single-Drop Microextraction: A Review. *Analytica Chimica Acta* **2011,** *706*, 37-65.

90. Furton, K. G.; Wang, J.; Hsu, Y.-L.; Walton, J.; Almirall, J. R., The Use of Solid-Phase Microextraction-Gas Chromatography in Forensic Analysis. *Journal of Chromatographic Science* **2000,** *38* (7), 297-306.

91. Shojania, S.; McComb, M. E.; Oleschik, R. D.; Perreault, H.; Gesser, H. D.; Chow, A., Qualitative Analysis of Complex Mixtures of VOCs using the Inside Needle Capillary Adsorption Trap. *Canadian Journal of Chemistry* **1999,** *77* (11), 1716-1727.

92. Tranthim-Fryer, D. J.; Hansson, R. C.; Norman, K. W., Headspace/ Solid-Phase Microextraction/ Gas Chromatography - Mass Spectrometry: A Screening Technique for the Recovery and Identification of Volatile Organic Compounds (VOC's) in Postmortem Blood and Viscera Samples*. *Journal of Forensic Sciences* **2001,** *46* (4), 934-946.

93. Wu, C.-H.; Chen, C.-L.; Huang, C.-T.; Lee, M.-R.; Huang, C.-M., Identification of Gasoline Soot in Suspect Arson Cases by Using Headspace Solid Phase Microextraction - GC/MS. *Analytical Letters* **2004,** *37* (7), 1373-1384.

94. Furton, K. G.; Almirall, J. R.; Bruna, J. C., A Novel Method for the Analysis of Gasoline from Fire Debris using Headspace Solid-Phase Microextraction. *Journal of Forensic Sciences* **1996,** *41* (1), 12-22.

95. Yoshida, H.; Kaneko, T.; Suzuki, S., A Solid-phase Microextraction Method for the Detection of Ignitable Liquids in Fire Debris. *Journal of Forensic Sciences* **2008,** *53* (3), 668-676.

96. Almirall, J. R.; Bruna, J.; Furton, K. G., The Recovery of Accelerants in Aqueous Samples from Fire Debris using Solid-Phase Microextraction (SPME). *Science & Justice* **1996,** *36* (4), 283-287.

97. Kaneko, T.; Nakada, M., Forensic Application of the Solid-Phase Microextraction Method to the Analysis of Gasoline and Kerosine. *Kagaku Keisatsu Kenkysusto Hokoku, Hokagaku-hen* **1995,** *48* (3), 107-111.

98. Harris, A. C.; Wheeler, J. F., GC-MS of Ignitable Liquids using Solvent-Desorbed SPME for Automated Analysis. *Journal of Forensic Sciences* **2003,** *48* (1), 41-46.

99. Lloyd, J. A.; Edmiston, P. L., Preferential Extraction of Hydrocarbons from Fire Debris Samples by Solid Phase Microextraction. *Journal of Forensic Sciences* **2003,** *48* (1), 1-5.

100. ASTM E 1386-95 Standard Practise for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction. In *ASTM* West Conshohocken, PA, 1995.

101. Yip, I. H.; Clair, E. G., A Rapid Analysis of Accelerants in Fire Debris. *Canadian Society of Forensic Science Journal* **1976,** *9* (2).

102. Brackett, J. W., Separation of Flammable Material of Petroleum Origin from Evidence submitted in Cases involving Fires and Suspected Arson. *Journal of Criminal Law, Criminology and Police Science* **1955,** *46*, 554.

103. Woycheshin, S.; DeHaan, J. D., An Evaluation of Some Distillation Techniques. *Arson Analysis Newsletter* **1978,** *2* (5), 1-16.

104. Dolan, J. A., Analytical Methods for the Detection and Characterization of Ignitable Liquid Residues from Fire Debris. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 137-164.

105. Stauffer, E., Concept of Pyrolysis for Fire debris analysts. *Science & Justice* **2003**
43 (1), 29-40.

106. Nowicki, J., An Accelerant Classification Scheme Based on Analysis by GC/MS. *Journal of Forensic Science* **1990,** *35* (5), 1064-1086.

107. O'Donnell, J. F., Interferences from Backgrounds in Accelerant Residue Analysis. *The Fire and Arson Investigator* **1989,** *39* (4), 25-27.

108. Keto, R. O., GC/MS Data Interpretation for Petroleum Distillate Identification in Contaminated Arson Debris. *Journal of Forensic Science* **1995,** *40* (3), 412-423.

109. Almirall, J. R.; Furton, K. G., *Analysis and Interpretation of Fire Scene Evidence*. CRC Press: 2004.

110. Alaska Scientific Crime Detection Laboratory - Fire Debris Analysis Manual. Safety, S. o. A. D. o. P., Ed. Fire Debris Supervisor: 2012; Vol. FD2012 R0.

111. Almirall, J. R.; Furton, K. G., Characterization of Background and Pyrolysis products that may interfere with the forensic analysis of fire debris. *Journal of Analytical and Applied Pyrolysis* **2004,** *71*, 51-67.

112. DeHaan, J. D.; Bonarius, K., Pyrolysis Products of Structure Fires. *Journal of the Forensic Science Society* **1988**
28 (1), 229 - 309.

113. Fernandes, M. S.; Lau, C. M.; Wong, W. C., The Effect of Volatile Residues in Burnt Household Items on the Detection of Fire Accelerants. *Science & Justice* **2002,** *42* (1), 7-15.

114. Clodfelter, R. W.; Hueske, E. E., A Comparison of Decomposition Products from Selected Burned Materials with Common Arson Accelerants. *Journal of Forensic Science* **1977,** *22* (1), 116 -118.

115. Gilbert, M., The Use of Individual Extracted Ion Profile vs. Summed Ion Profiles in Fire Debris Analysis. *Journal of Forensic Science* **1998,** *43* (4), 871-876.

116. Smith, R. M., Arson Analysis by Mass Chromatography. *Analytical Chemistry* **1982,** *54* (13), 1399A - 1409A.

117. Keto, R. O.; Wineman, P. L., Detection of Petroleum- Based Accelerants in Fire Debris by Target Compound GC/MS. *Analytical Chemistry* **1991,** *63*.

118. Tan, B.; Hardy, J. K.; Snavely, R. E., Accelerant Classification by Gas Chromatography/ Mass Spectrometry and Multivariate Pattern Recognition. *Analytica Chimica Acta* **2000,** *422*, 37-46.

119. Warnke, M. M.; Erickson, A., E., Simplex Optimization of Headspace-Enrichment Conditions of Residual Petroleum Distillates Used by Arsonists. *Journal of Chemical Education* **2005,** *82* (7), 1082-1085.

120. Koussiafes, P.; Bertsch, W., Profile Matching for the Analysis of Accelerants in Suspected Arson Cases. *Journal of Chromatographic Science* **1993,** *31*, 137-144.

121. Stauffer, E.; Dolan, J. A.; Newman, R. T., Chapter 9: Interpretation of Data Obtained from Neat Ignitable Liquids. In *Fire Debris Analysis*, Elsevier: USA, 2008.

122. Hupp, A. M.; Marshall, L. J.; Campbell, D. I.; Waddell-Smith, R.; McGuffin, V. L., Chemometric Analysis of Diesel Fuel for Forensic and Environmental Analysis. *Analytica Chimica Acta* **2008,** *606*, 159-171.

123. Harynuk, J. J.; Paulina de la Mata, A.; Sinkov, N. A., Application of Chemometrics to the Interpretation of Analytical Separations Data. In *Chemometrics in Practical Applications*, Varmuza, K., Ed. Intech: USA, 2012.

124. Sandercock, P. M. L.; Du Pasquier, E., Chemical Fingerprinting of Unevaporated Automotive Gasoline Samples. *Forensic Science International* **2003,** *134* (1), 1-10.

125. Sandercock, P. M. L.; Du Pasquier, E., Chemical Fingerprinting of Gasoline: 2. Comparison of Unevaporated and Evaporated Automotive and Gasoling Samples. *Forensic Science International* **2004,** *140* (1), 43-59.

126. Sandercock, P. M. L.; Du Pasquier, E., Chemical Fingerprinting of Gasoline: 3. Comparison of Unevaporated and Evaporated Gasoline Samples from Australia and New Zealand. *Forensic Science International* **2004,** *140* (1), 71-77.

127. Sigman, M. E.; Williams, M. R.; Ivy, R. G., Individualization of Gasoline Samples by Covariance Mapping and Gas Chromatography/Mass Spectrometry. *Analytical Chemistry* **2007,** *79*, 3462-3468.

128. Newman, R., Interpretation of Laboratory Data. In *Fire Investigation*, Daeid, N. N., Ed. CRC Press LLC: Florida, 2004; pp 155-190.

129. Howard, J.; McKague, A. B., A Fire Investigation Involving Combustion of Carpet Material. *Journal of Forensic Science* **1984,** *29* (3), 919-922.

130. Lennard, C. J.; Tristan Rochaix, V.; Margot, P., A GC-MS Database of Target Compound Chromatograms for the Identification of Arson Accelerants. *Science & Justice* **1995,** *1*, 19-30.

131. Newman, R., ASTM Approach to Fire Debris Analysis. In *Analysis and Interpretation of Fire Scene Evidence*, Almirall, J. R.; Furton, K. G., Eds. CRC Press LLC: Florida, 2004; pp 165-192.

132. Brettell, T. A., Forensic Science Applications of Gas Chromatography. In *Modern Practise of Gas Chromatography*, 4th ed.; Grob, R. L.; Barry, E. F., Eds. John Wiley & Sons, Inc.: USA, 2004; pp 883-967.

133. CDS Analytical, I. *Degradation Mechanism- Random Scission*.

134. Wampler, T., *Applied Pyrolysis Handbook*. Marcel Dekker, Inc.: New York, 1995.

135. Pielichowski, K.; Njuguna, J., *Thermal Degradation of Polymeric Materials*. Rapra Technology Limited: UK, 2005.

136. CDS Analytical, I. *Degradation Mechanism - Side Group Elimination*.

137. CDS Analytical, I. *Degradation Mechanisms - Depolymerization*.

138. Thomas, C. L., Arson Debris Control Samples. *Fire and Arson Investigator* **1978,** *28* (3), 23-25.

139. Stauffer, E.; Dolan, J. A.; Newman, R. T., *Fire Debris Analysis*. Elsevier Inc: USA, 2008.

140. Ettling, B. V.; Adams, M. F., The Study of Accelerant Residues in Fire Remains. *Journal of Forensic Science* **1968,** *13* (1), 76-89.

141. Bertsch, W., Volatiles from Carpet: A Source of Frequent Misinterpretation in Arson Analysis. *Journal of Chromatography A* **1994,** *674*, 329-333.

142. Borusiewicz, R.; Zieba-Palus, J.; Zadora, G., The Influence of the Type of Accelerant, Type of Burned Material, Time of Burning and Availability of Air on the Possibility of Detection of Accelerant Traces. *Forensic Science International* **2006,** *160*, 115-126.

143. Godfrey Hirst carpets: Fibre/Carpet Types. http://www.godfreyhirst.com/fibre-carpet-types.html (accessed August, 2008).

144. Carpet Backing Composition. Sferopoulos, R., Ed. Melbourne, 2007.

145. Dunlop Foams: Comfort that Lasts - Speciality Foams. http://www.dunlopfoams.com.au/Our-Products/Specialty-Foams.asp#Re-bond (accessed August, 2008).

146. Sack, R., Technical Manager, Dunlop Foam. Sferopoulos, R.; Caridi, D. D., Eds. 2007.

147. Goodman, S., Kimwipes – The benefits of delicate task wipes. 26 January 2012 ed.; 2012.

148. Solid Sampling Kit for the SGE Pyrojector II: Quantitative Analysis of Solid Samples by Pyrolysis. (accessed March 2009).

149. Temperature Measurement Designers Guide. Thermo Electric Co., I., Ed. Thermo express: USA, 1993.

150. Singh, H.; Jain, A. K., Ignition, Combustion, Toxicity, and Fire Retardancy of Polyurethane Foams: A Comprehensive Review. *Journal of Applied Polymer Science* **2009,** *111*, 1115-1143.

151. B.C, L.; Paabo, M.; Fultz, M. L.; Bailey, C. S., Generation of Hydrogen Cyanide from Flexible Polyurethane Foam Decomposed under Different Combustion Conditions. *Fire and Materials* **1985,** *9* (3), 125-134.

152. Australian Standard: Methods for fire tests on building materials, components and structures. Part 4: Fire-resistance test of elements of construction AS 1530.4—2005. SAI Global: 2005.

153. Wineman, P. L.; Keto, R. O., Target-Compound Method foer the Analysis of Accelerant Residues in Fire Debris. *Analytica Chimica Acta* **1994,** *288*, 91-110.

154. Sferopoulos, R. Differentiation of Petrols in Arson Investigation. Victoria University, 2004.

155. Kirkbride, K. P.; Tungol, M. W., Chapter 8: Infrared Microspectroscopy of Fibres. In *Forensic Examination of Fibres*, 2nd ed.; Robertson, J.; Grieve, M., Eds. CRC Press: Boca Raton, Florida, 1999.

156. Goodpaster, J. V.; Liszewski, E. A., Forensic Analysis of Dyed Textile Fibers. *Analytical and Bioanalytical Chemistry* **2009,** *394*, 2009-2018.

157. David, S. K.; Pailthorpe, M. T., Chapter 1: Classification of Textile Fibres: Production, Structure and Properties. In *Forensic Examination of Fibres*, 2nd ed.; Robertson, J.; Grieve, M., Eds. CRC Press: Boca Raton, Florida, 1999.

158. Braun, E.; Levin, B. C., Nylons: A Review of the Literature on Products of Combustion and Toxicity. *Fire and Materials* **1987,** *11*, 71-88.

159. Wool Fibre. http://www.woolinnovation.com.au/Education/Student_information/Wool_fibre/page__2157.aspx
(accessed 26 June 2008).

APPENDICES

APPENDIX A

STEAM DISTILLATION

Steam distillation was conducted, as per the ASTM D1385-95 ‘Standard Practise for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Steam Distillation’, at the VPFSC laboratories. The apparatus is shown in Figures A1.1 (a-e).

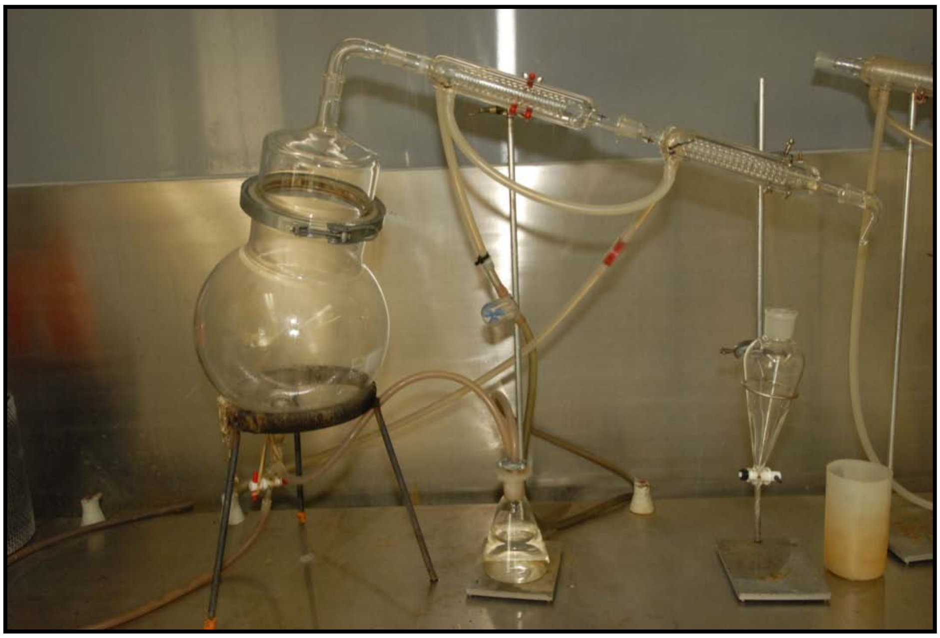


Figure A1.1(a): Steam Distillation set up at VPFSC Laboratories

Figure A1.1(b): Steam Distillation set up at VPFSC Laboratories with Sample of Burnt Nylon Carpet

Figure A1.1(c): Steam Distillation set up at VPFSC Laboratories with Sample of Burnt Nylon Carpet, During Distillation

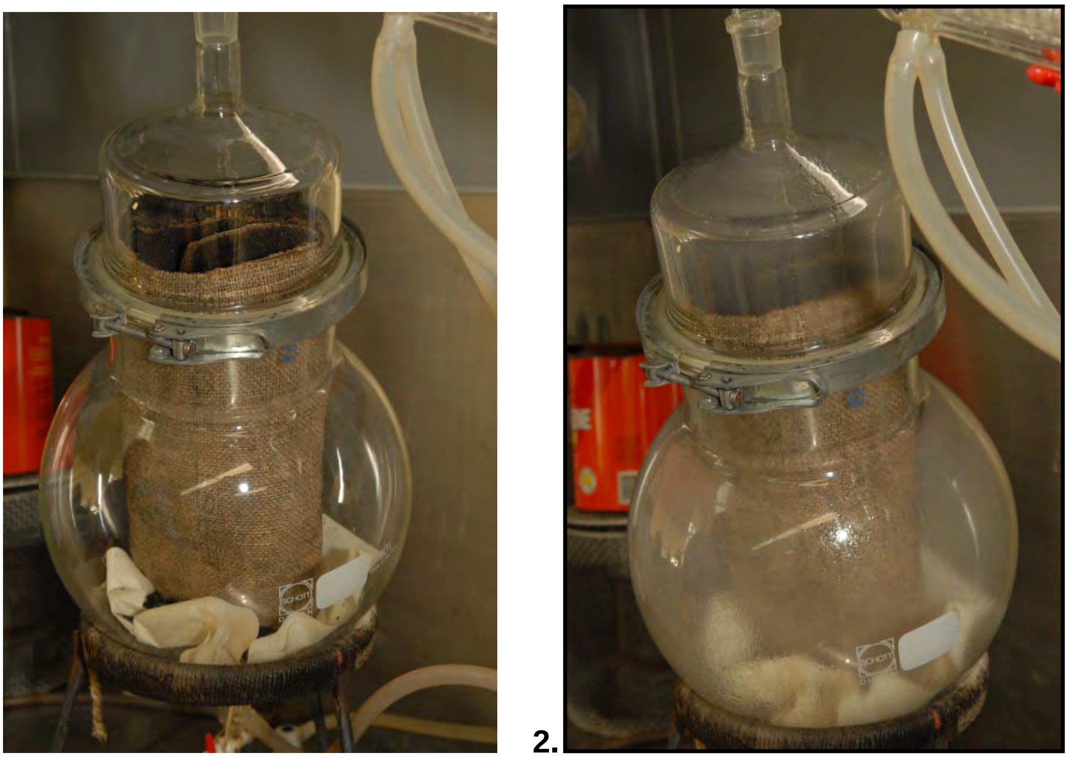


Figure A1.1(d): Sample of Nylon 1. Before Distillation and 2. During Distillation

Figure A1.1(e): Condensation of Steam and Volatiles in Separatory Funnel

Figures A1.2 (a-f) shows the total ion chromatograms and extracted ion chromatograms for the carpet and foam samples burnt in room 1 and ignitable liquid residues recovered by steam distillation. The extracted ion chromatograms s show that all the samples except foam produced no interfering target compounds. The furniture foam produced a target compound at 4.12 minutes which was identified as toluene.

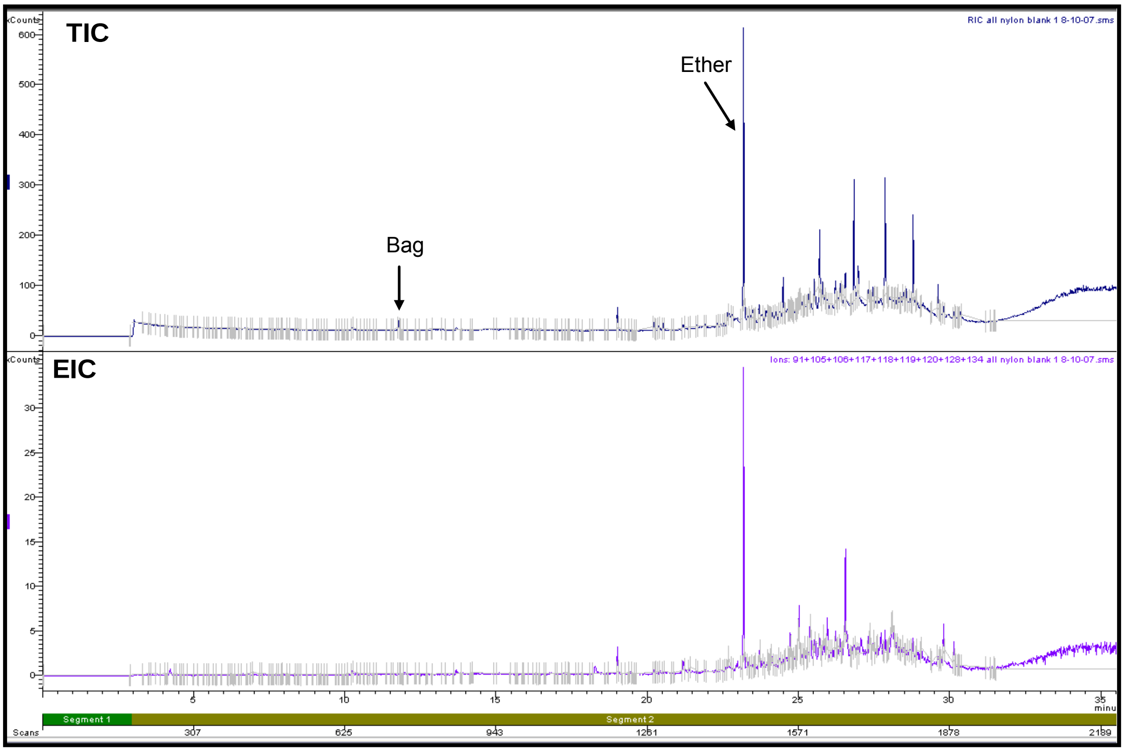


Figure A1.2(a): Target Ion Chromatogram and Extracted Ion Chromatogram of Nylon Carpet burnt in Room 1

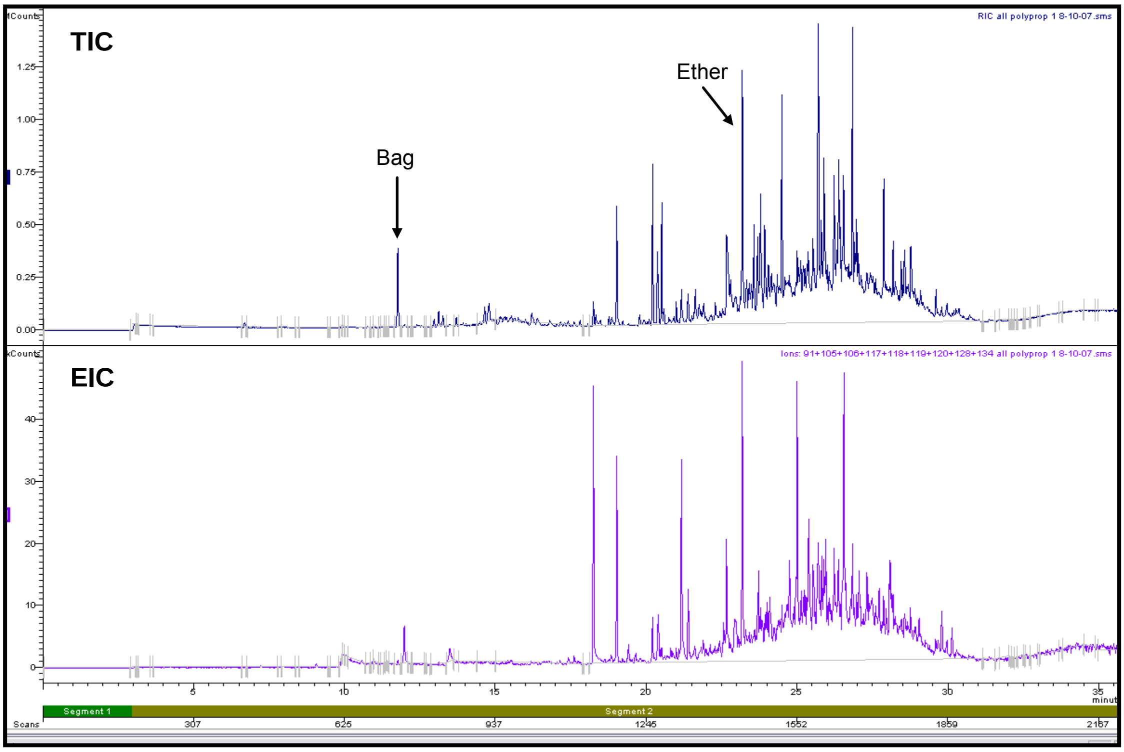


Figure A1.2(b): Target Ion Chromatogram and Extracted Ion Chromatogram of Polypropylene Carpet burnt in Room 1

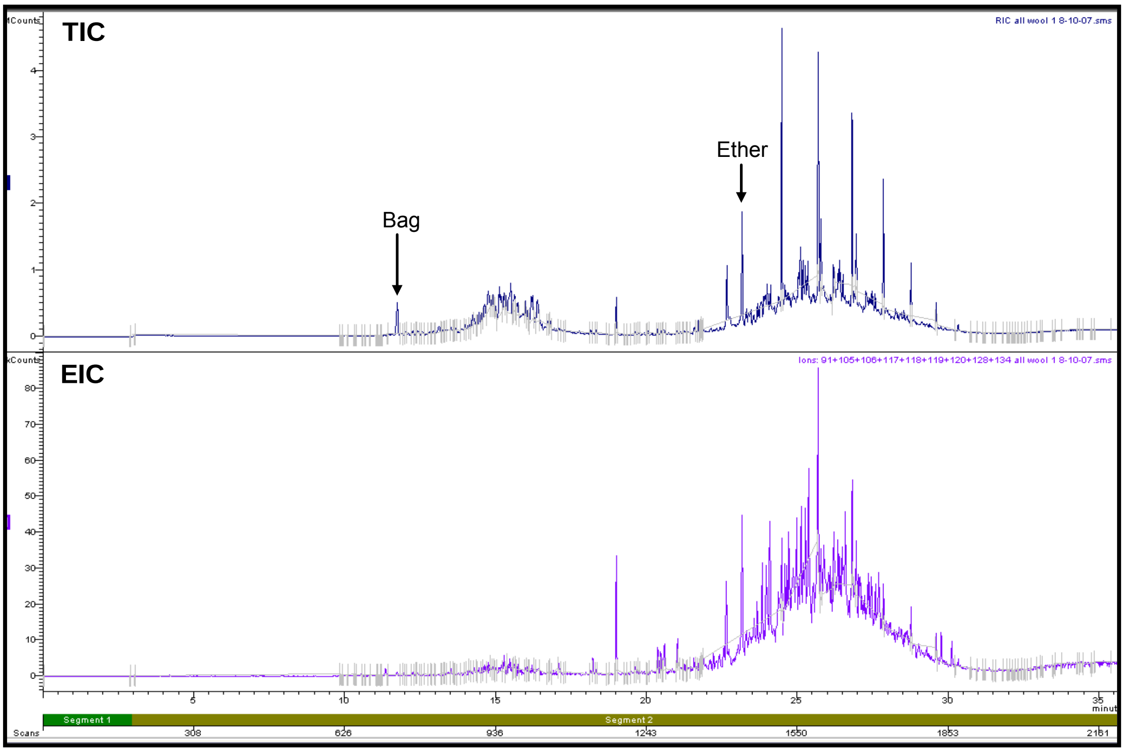


Figure A1.2(c): Target Ion Chromatogram and Extracted Ion Chromatogram of Wool Carpet burnt in Room 1

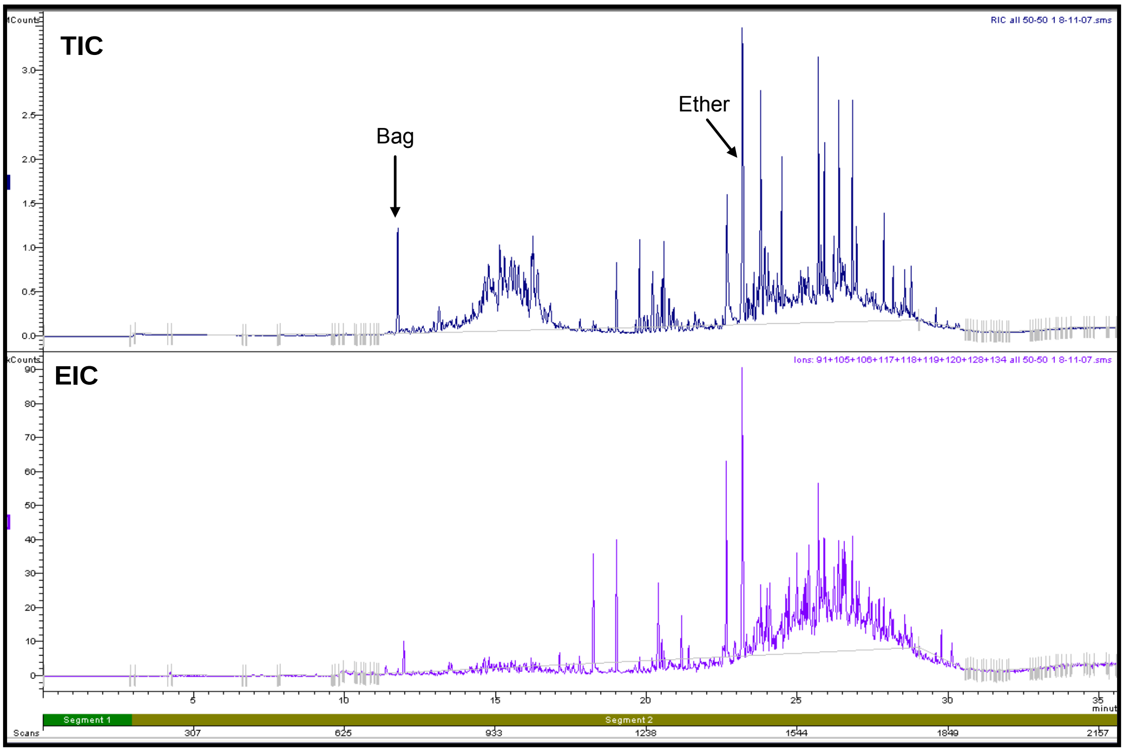


Figure A1.2(d): Target Ion Chromatogram and Extracted Ion Chromatogram of 50-50 Polypropylene-Wool Carpet burnt in Room 1

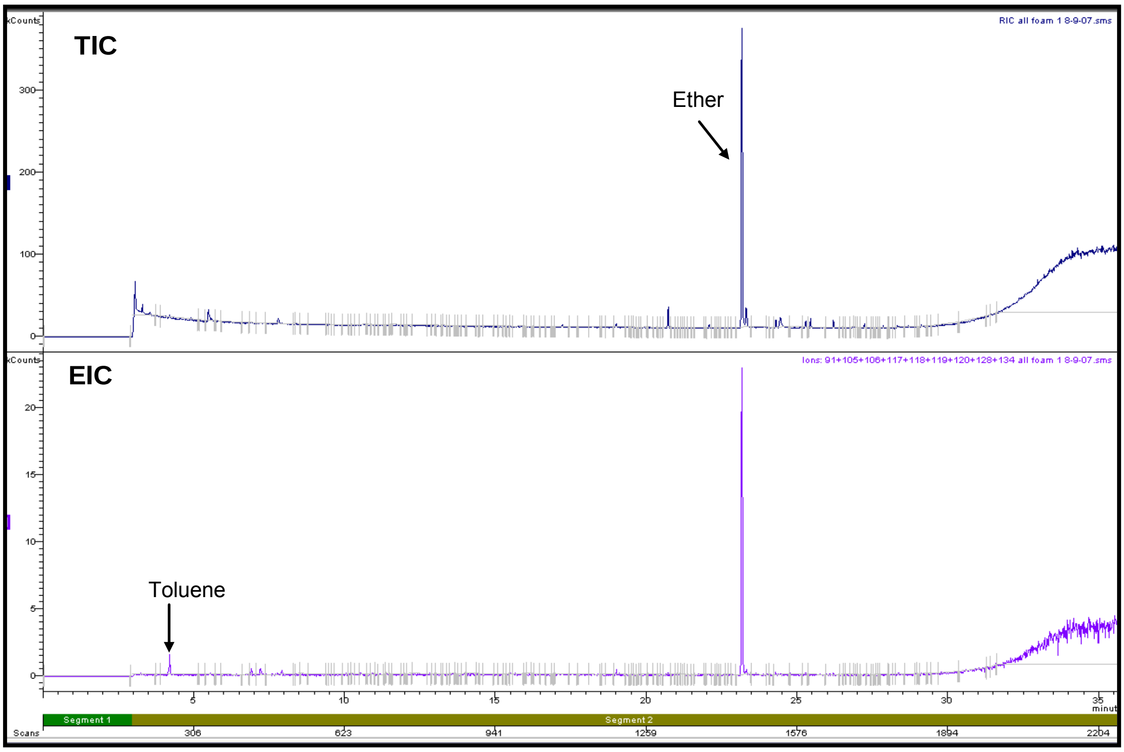


Figure A1.2(e): Target Ion Chromatogram and Extracted Ion Chromatogram of Foam burnt in Room 1

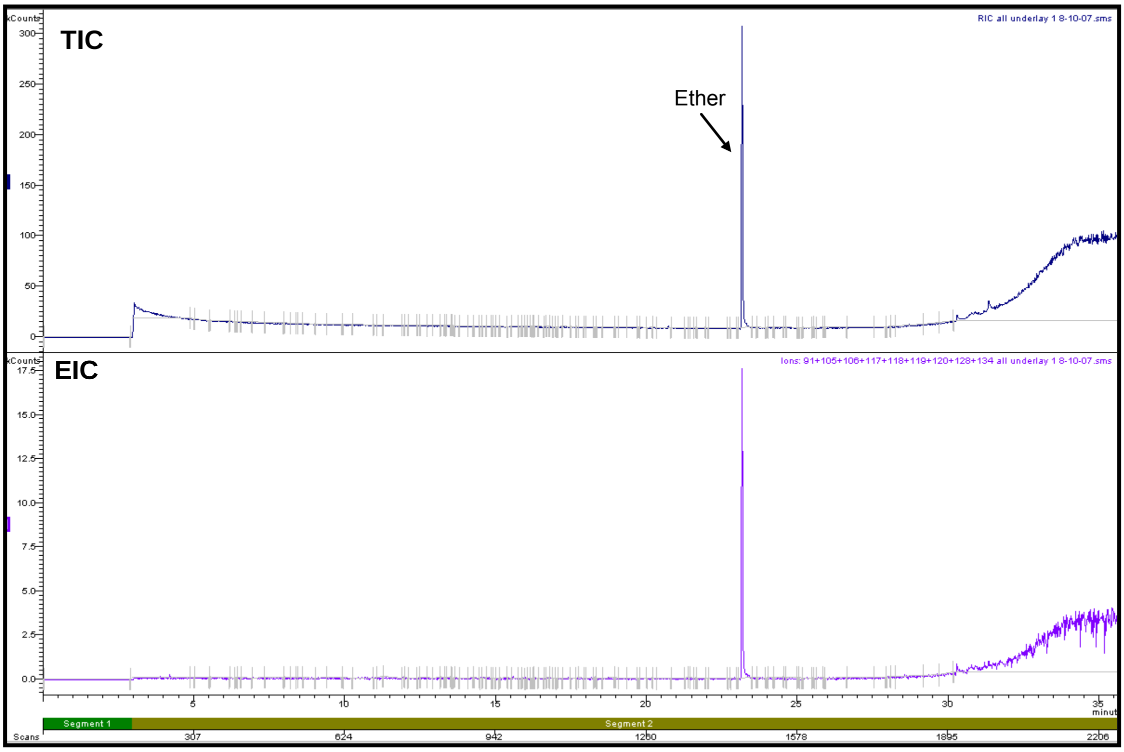


Figure A1.2(e): Target Ion Chromatogram and Extracted Ion Chromatogram of Underlay burnt in Room 1

APPENDIX B

ORIENTATION OF NYLON CARPET FIBRES

Fibres Facing Down

The total ion chromatogram, extracted ion chromatogram and target compound chromatogram for the nylon carpet burnt in the small can with fibres facing down are presented in Figures B1.1 and B1.2, respectively. Toluene and ethylbenzene were recovered in the greatest abundance, as well as a number of other aromatics including *p*- and *m*-*x*ylene and *o*- xylene, propylbenzene, 1-ethyl-4-methylbenzene and 1,3,5-trimethylbenzene.

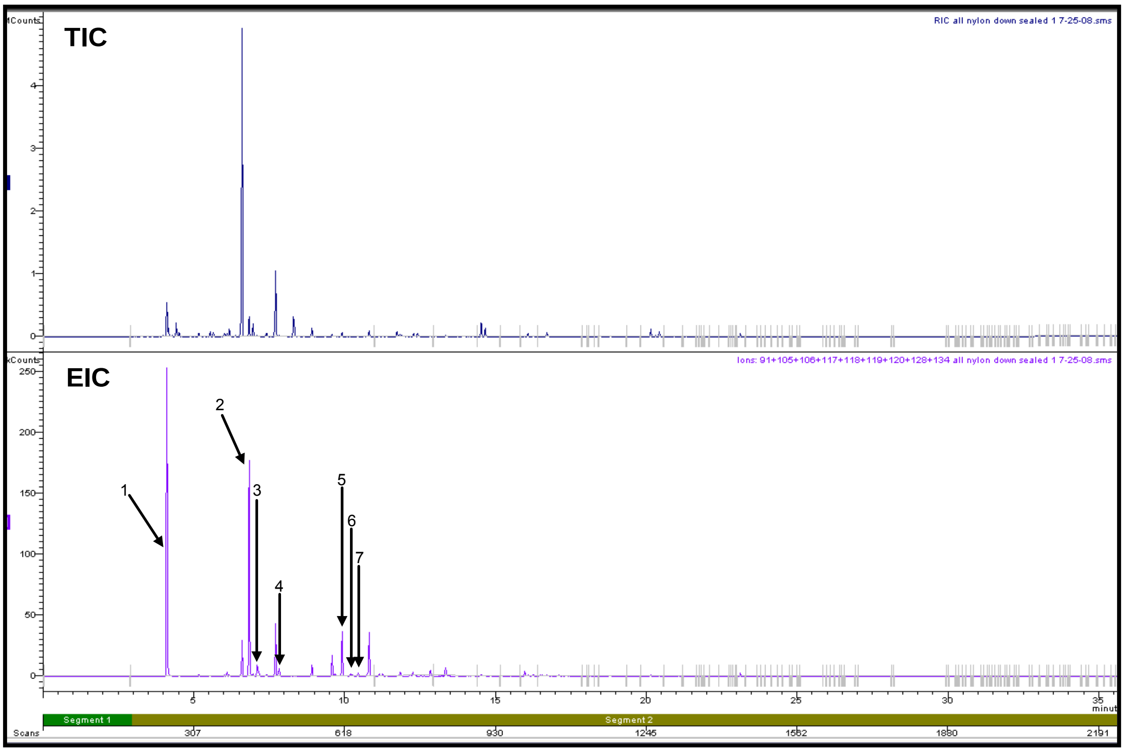


Figure B1.1: Target Ion Chromatogram and Extracted Ion Chromatogram of Nylon Swatch placed Face Down in the Bottom of a Can burnt with Lid On

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene

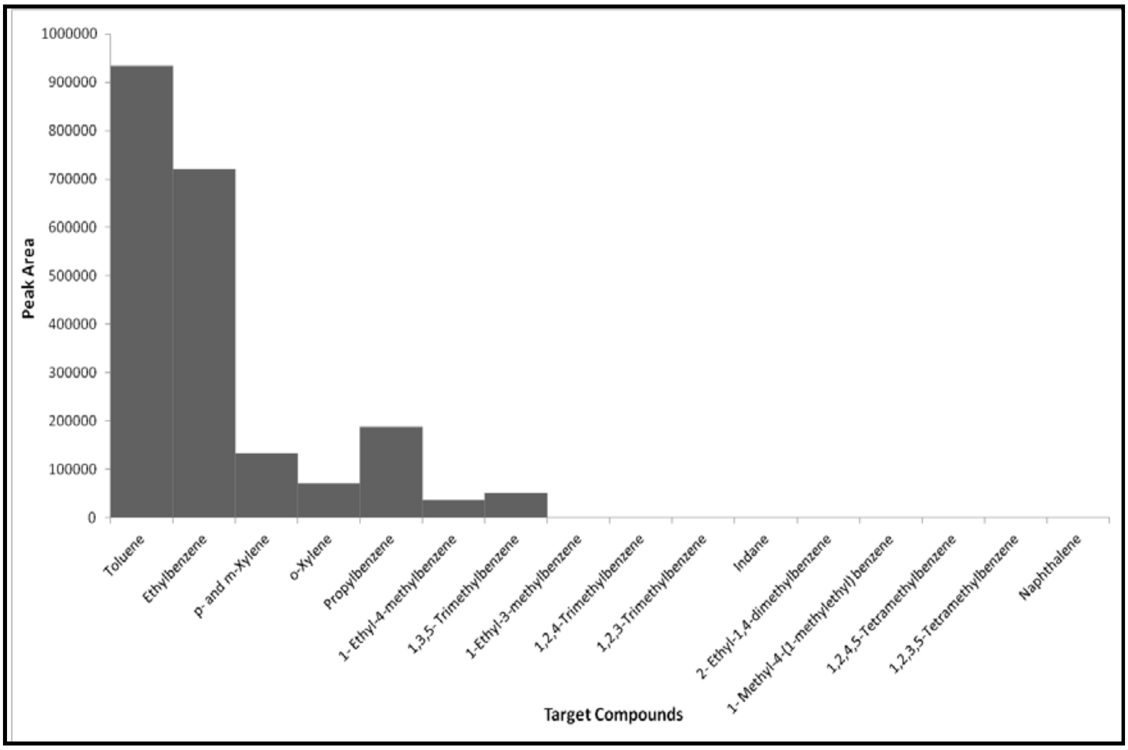


Figure B1.2: Target Compound Chromatogram of Nylon Swatch placed Face Down in the Bottom of a Can burnt with Lid On

Carpet Sample on Side

The total ion chromatogram, extracted ion chromatogram and target compound chromatogram for the 10cm x 10cm nylon swatch placed vertically in the can and burnt with the lid on is shown in Figure B1.3 and B1.4, respectively. Toluene and ethylbenzene, as well as a number of other aromatics including *p-* and *m-x*ylene and *o-* xylene, propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene and indane were recovered.

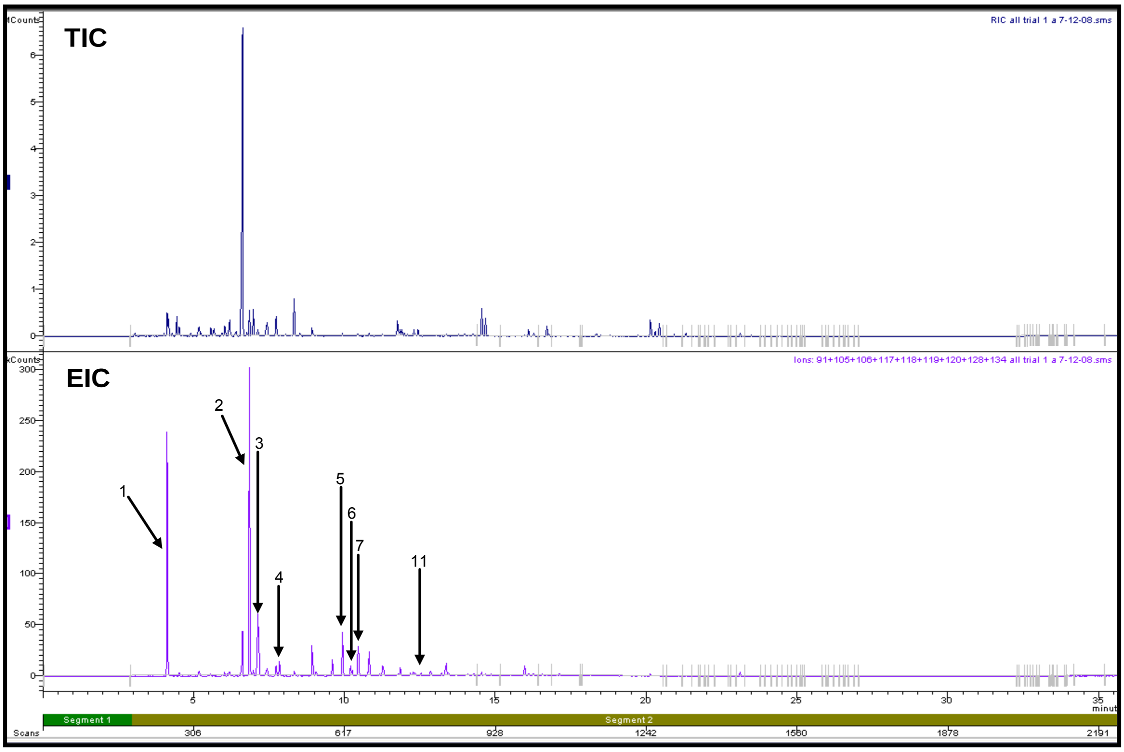


Figure B1.3: Target Ion Chromatogram and Extracted Ion Chromatogram of Nylon (10cm x10cm swatch) burnt in a Can with Lid On

Key: 1= Toluene, 2=Ethylbenzene, 3= *p-* and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene, 11= Indane

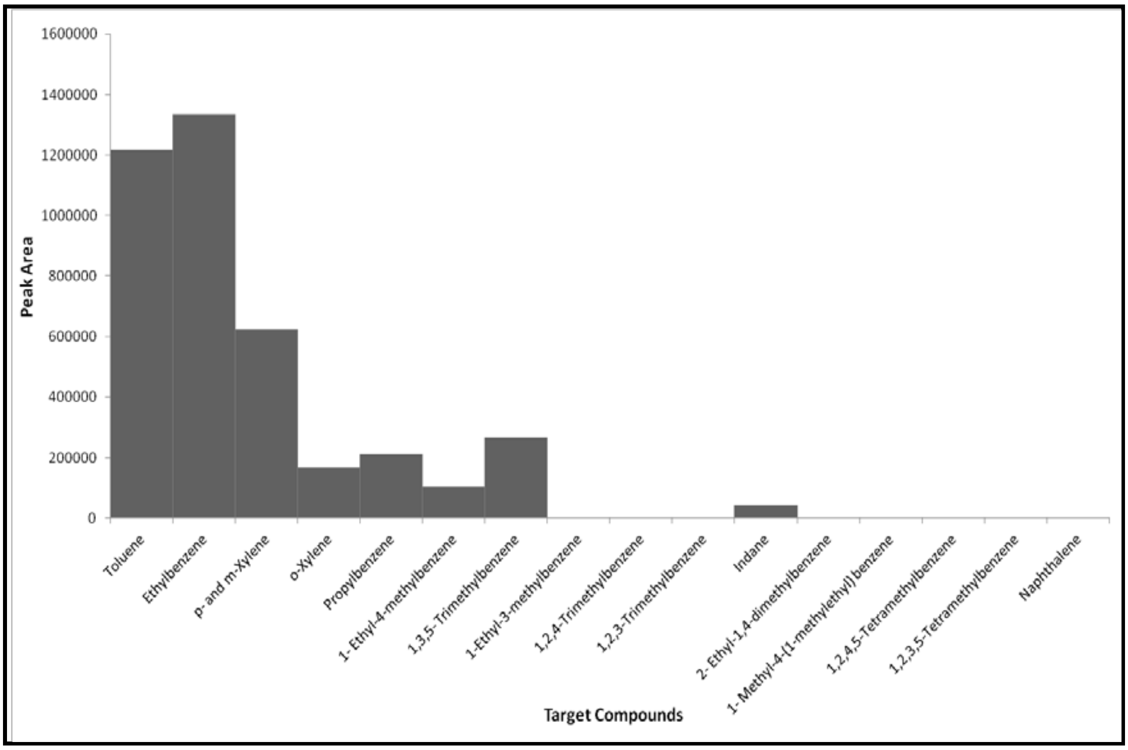


Figure B1.4: Target Compound Chromatogram of Nylon (10cm x10cm swatch) burnt in a Can with Lid On

APPENDIX C

BURNING TIME EXPERIMENTS FOR NYLON CARPET

30 second burn

Pictures of the samples after the 30 second burn are presented in Figure C1.1 (a-c)

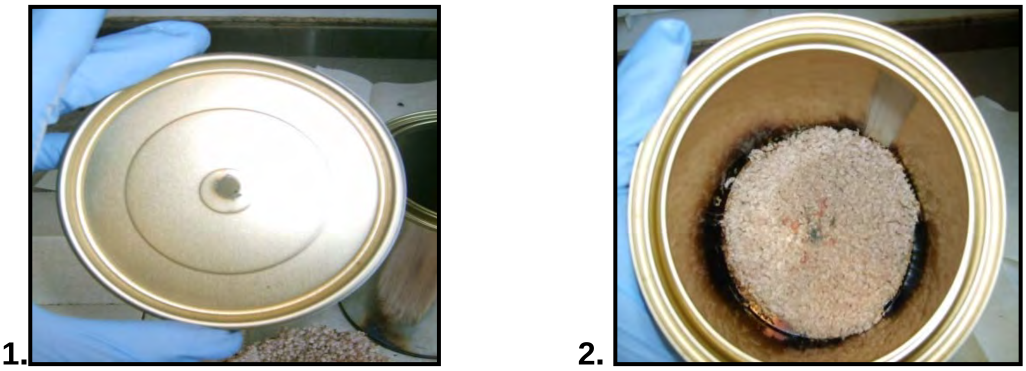


Figure C1.1 (a): 1. Underside of Lid and 2. Nylon Carpet in Bottom of Can after Burning

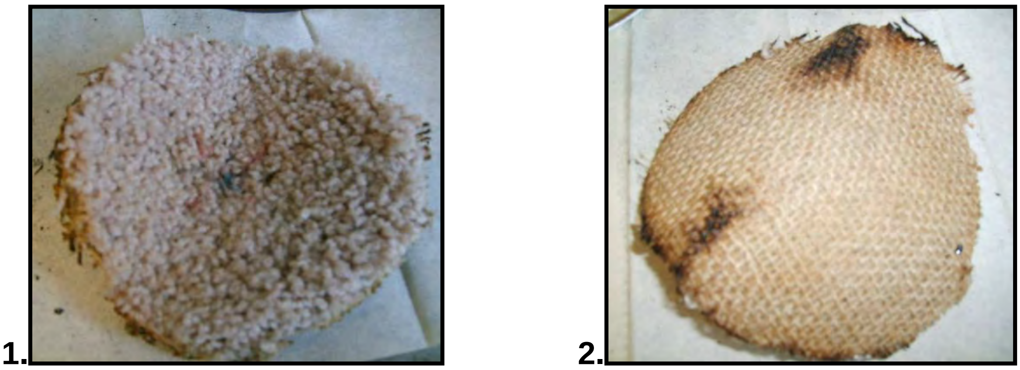


Figure C1.1 (b): 1. Top and 2. Underside of Sample after Burning

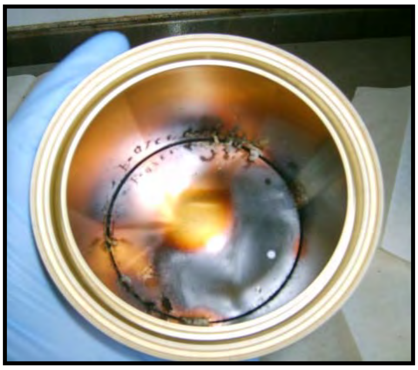


Figure C1.1 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the carpet swatch burnt in the can for 30 seconds can be seen in Figure C1.2. The EIC shows two target compounds were able to be recovered and were identified as toluene and *p*- and *m*-*x*ylene.

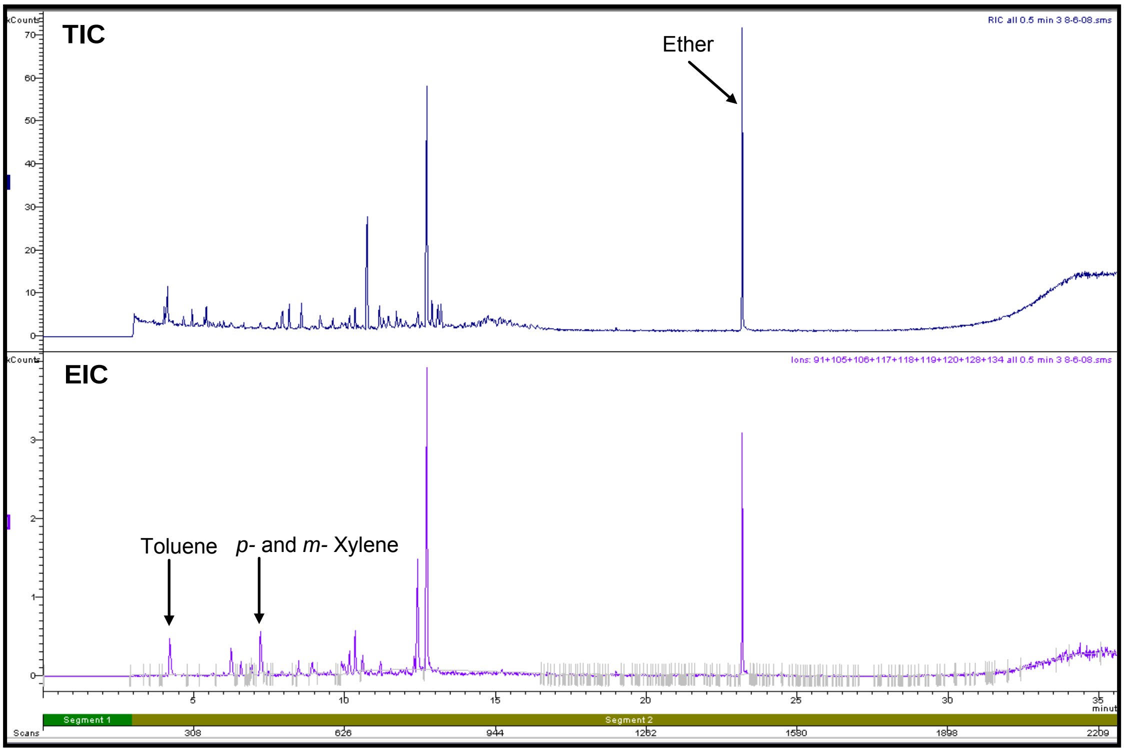


Figure C1.2: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 30 Seconds

1 minute burn

Pictures of the samples after the 1 minute burn are presented in Figure C1.3 (a-b)

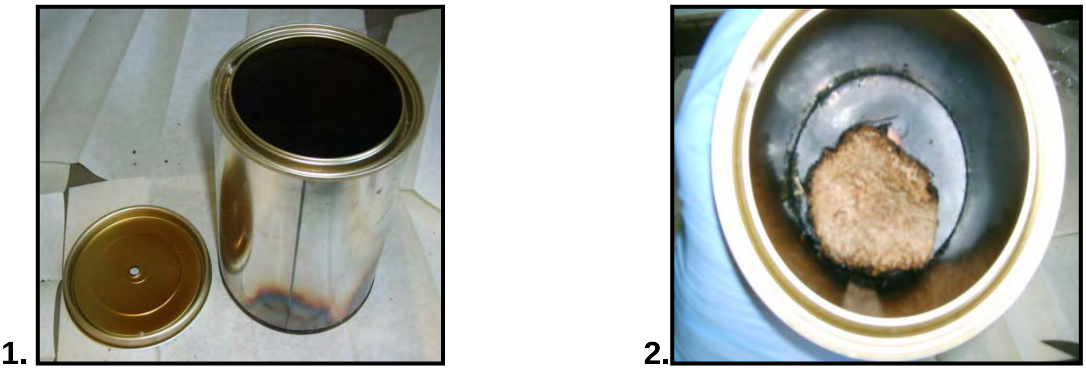


Figure C1.3 (a): 1. Open can and 2. Sample in can after burning

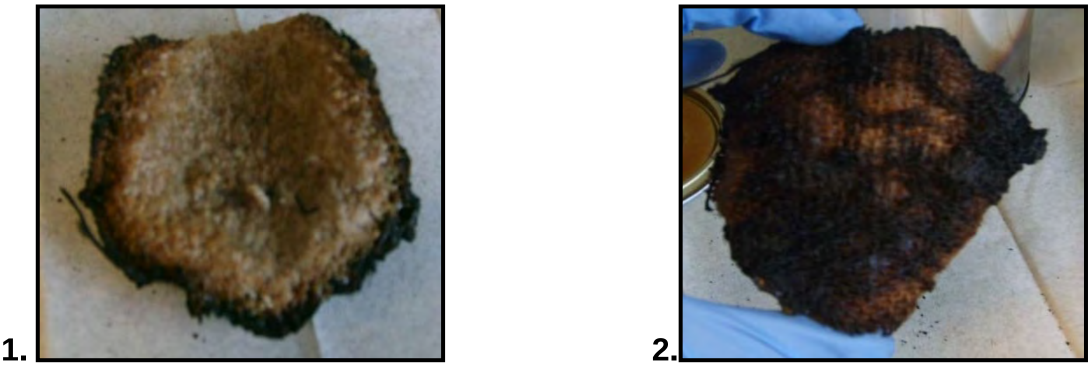


Figure C1.3 (b): 1. Top and 2. Underside of sample after burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet burnt for 1 minute can be seen in Figure C1.4. The extracted ion chromatogram shows three target compounds were recovered and identified as toluene, ethylbenzene and *p-* and *m-x*ylene.

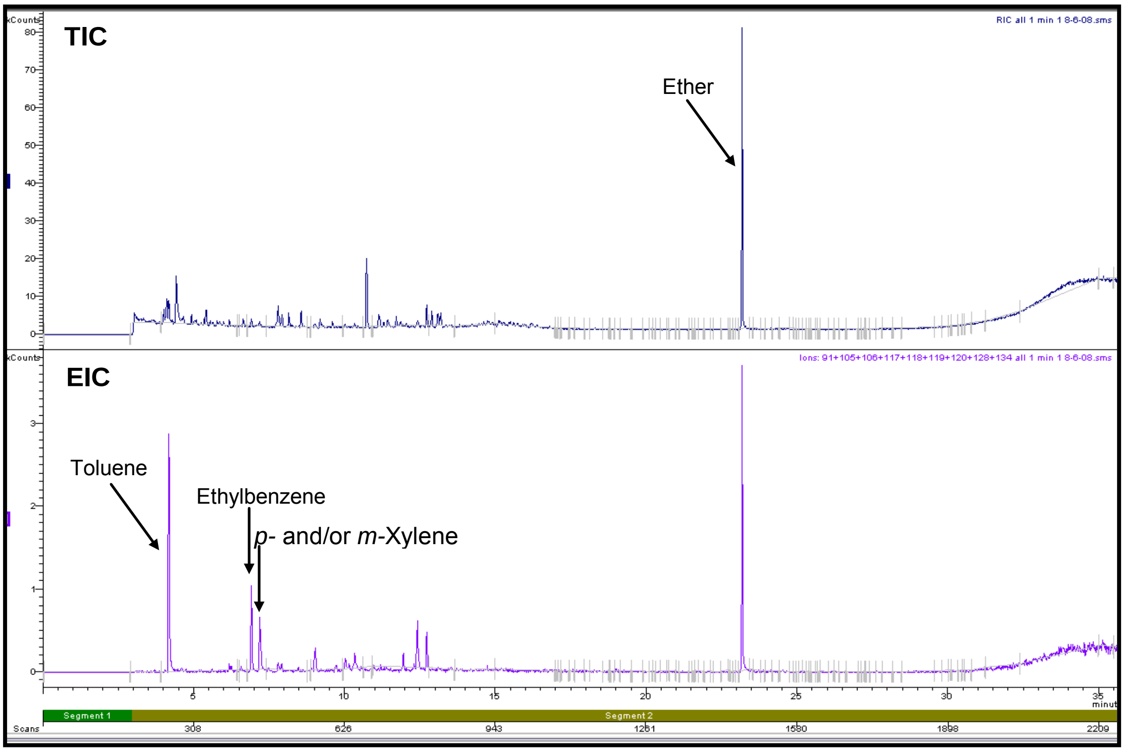


Figure C1.4: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 1 minute

1.5 minute burn

Pictures of the samples after the 1.5 minute burn are presented in Figure C1.5 (a-c)

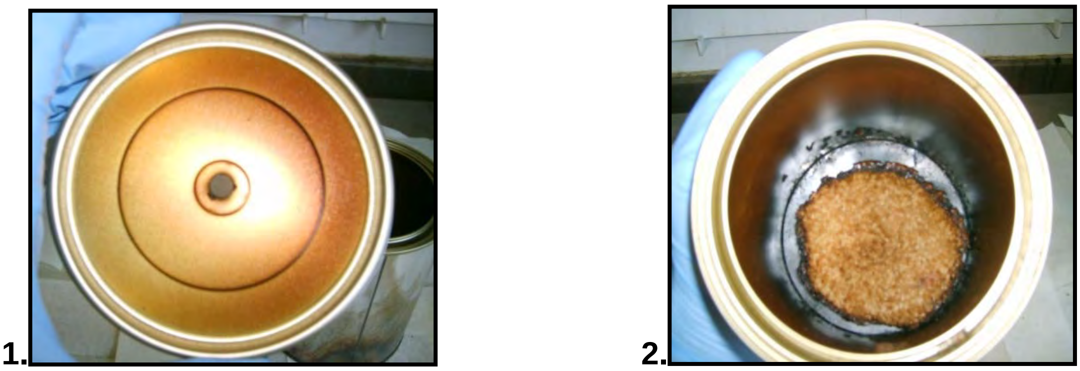


Figure C1.5 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

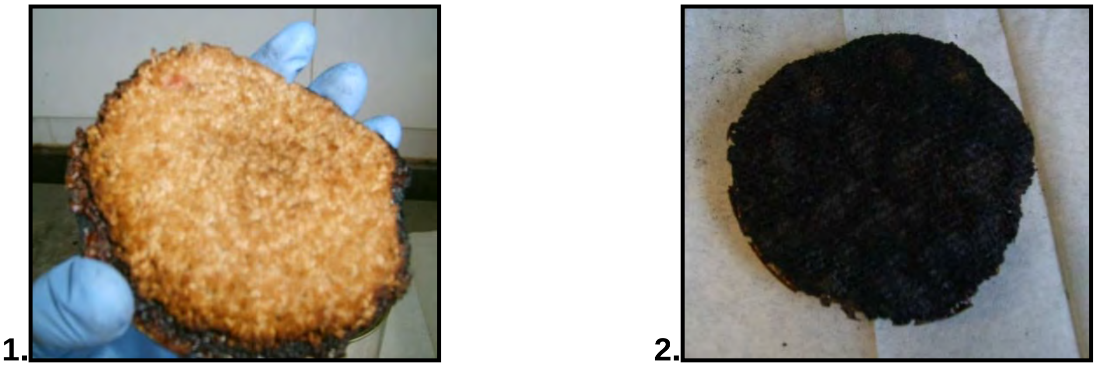


Figure C1.5 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.5 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet swatch burnt in a can for 1.5 minutes is presented in Figure C1.6. The extracted ion chromatogram shows four target compounds were able to be recovered and were identified as toluene, ethylbenzene, *p*- and *m*-*x*ylene and propylbenzene.

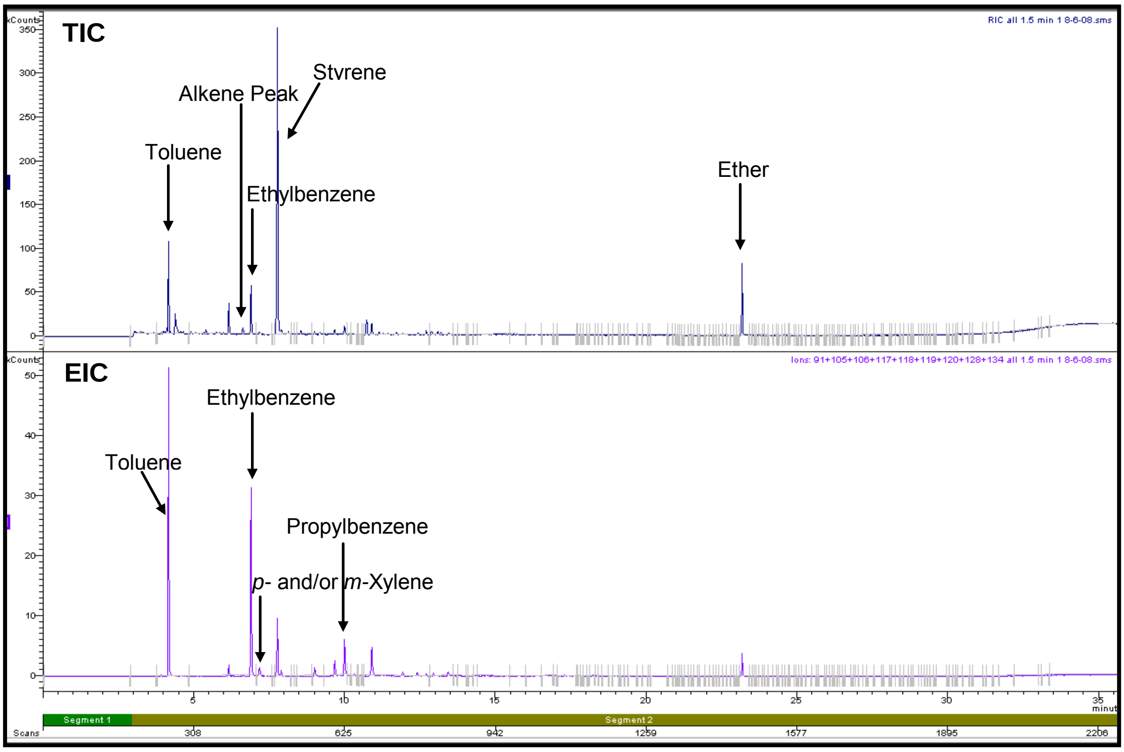


Figure C1.6: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 1.5 minutes

2 minute burn

Pictures of the samples after the 2 minute burn are presented in Figure C1.7 (a-c).

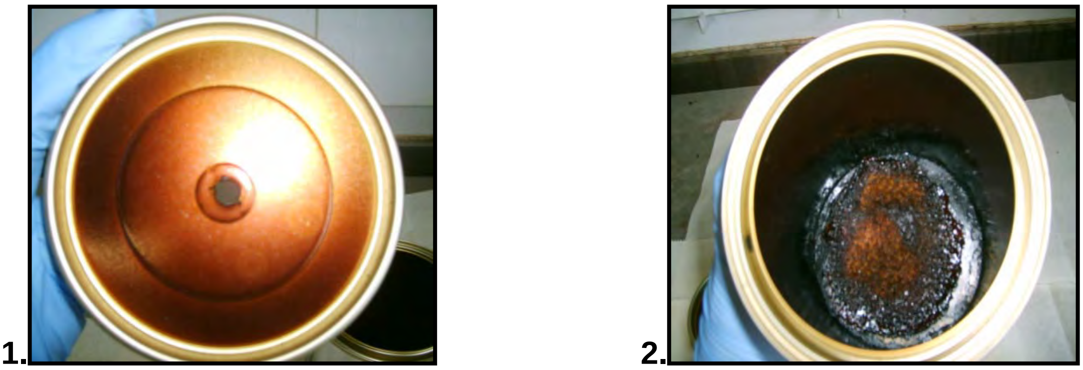


Figure C1.7 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

1. 

2. 

Figure C1.7 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.7 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet swatch burnt in a can for 2 minutes is presented in Figure C1.8. The extracted ion chromatogram shows five target compounds were able to be recovered and were identified as toluene, ethylbenzene, *p*- and *m*-xylene, *o*-xylene and propylbenzene.

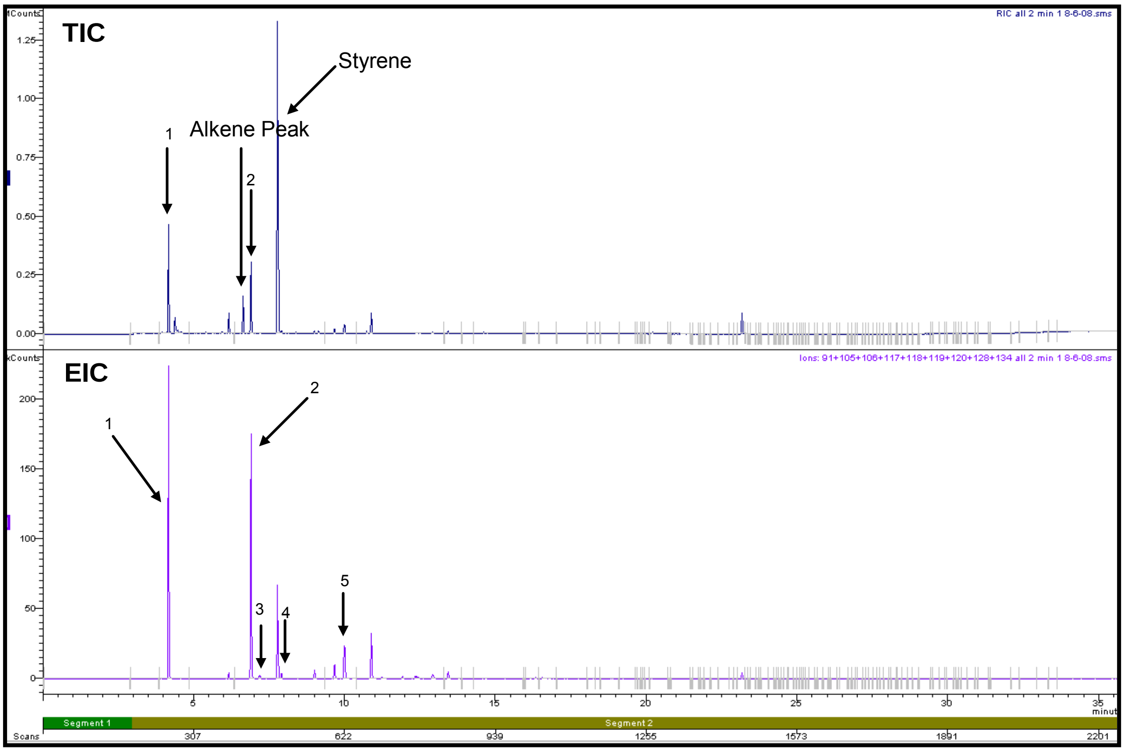


Figure C1.8: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 2 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

2.5 minute burn

Pictures of the samples after the 2.5 minute burn are presented in Figure C1.9 (a-c).

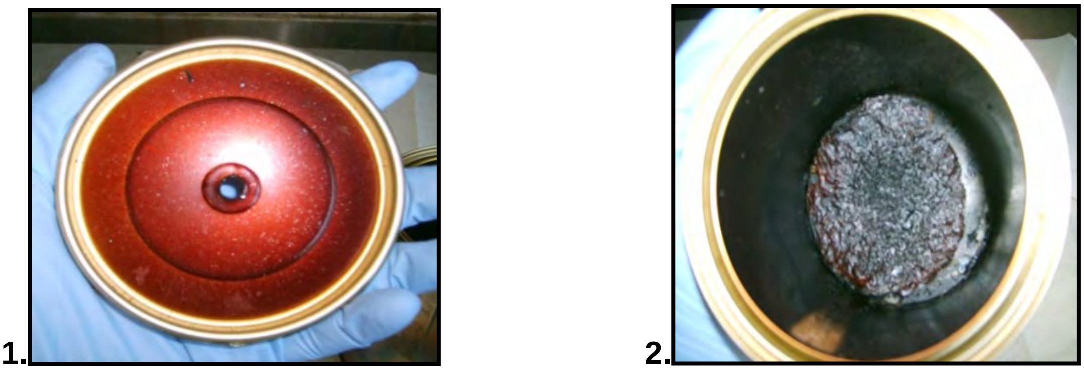


Figure C1.9 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

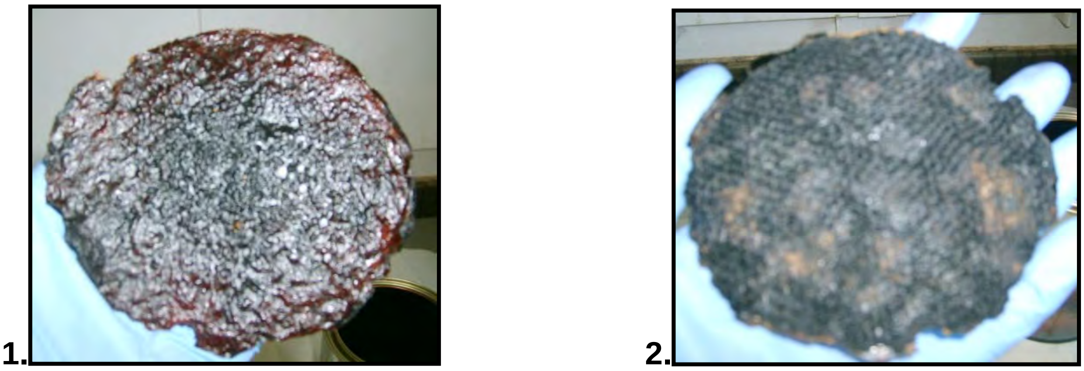


Figure C1.9 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.9 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet swatch burnt in a can for 2 minutes is presented in Figure C1.10. The extracted ion chromatogram again shows five target compounds were able to be recovered and were identified as toluene, ethylbenzene, *p*- and *m*-xylene, *o*-xylene and propylbenzene.

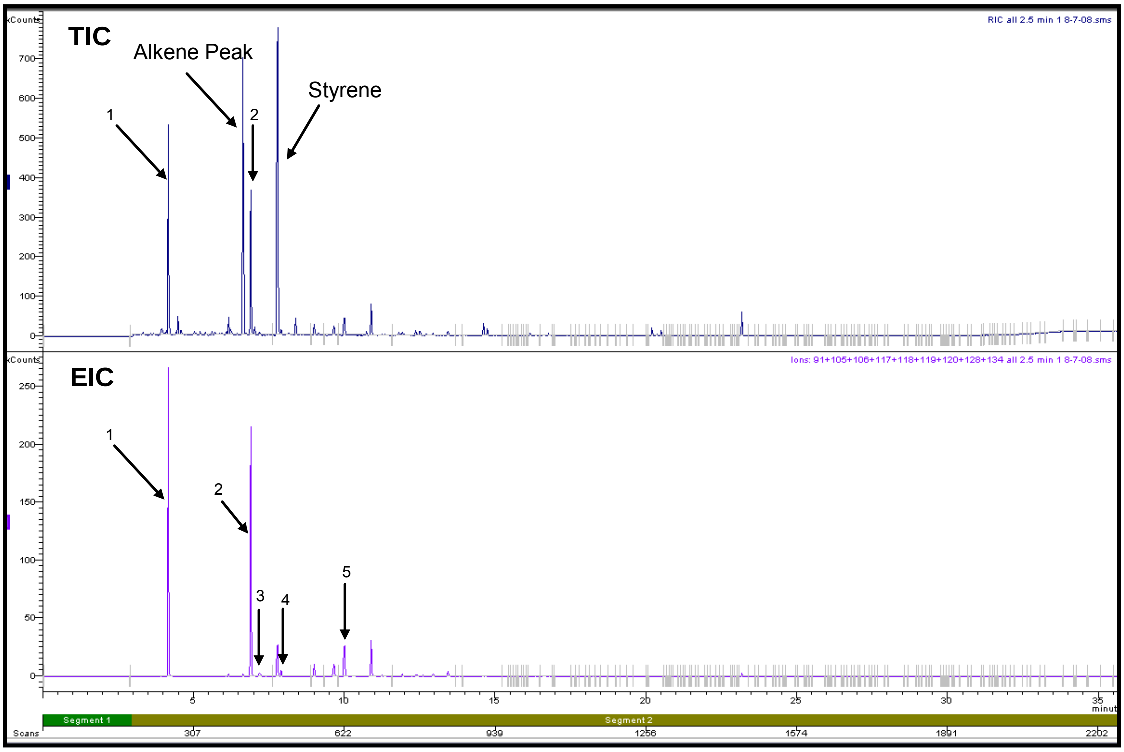


Figure C1.10: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=propylbenzene

3 minute burn

Pictures of the samples after the 3 minute burn are presented in Figure C1.11 (a-c).

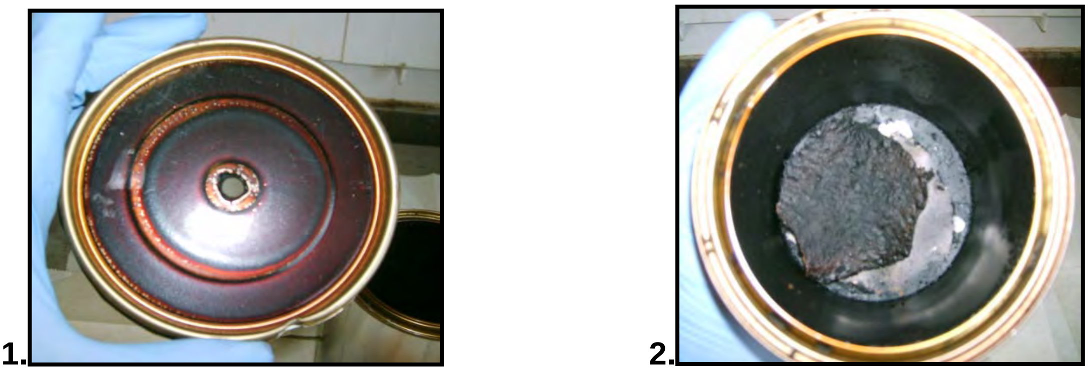


Figure C1.11 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

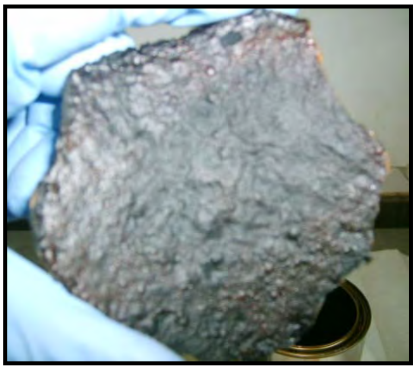
1.  2. 

Figure C1.11 (b): 1. Top and 2. Underside of Sample after Burning

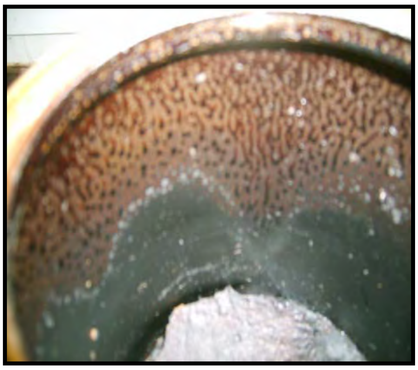


Figure C1.11(c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet burnt in the small can for 3 minutes can be seen in Figure C1.12. There were two abundant peaks recovered in the extracted ion chromatogram which were identified as toluene and ethylbenzene. A number of other TCs, identified as *p*- and *m*-xylene, *o*-xylene, propylbenzene, 1-methyl-4-ethylbenzene and indane were also recovered from this sample. The seven target compounds recovered are presented in the target compound chromatogram in Figure C1.13.

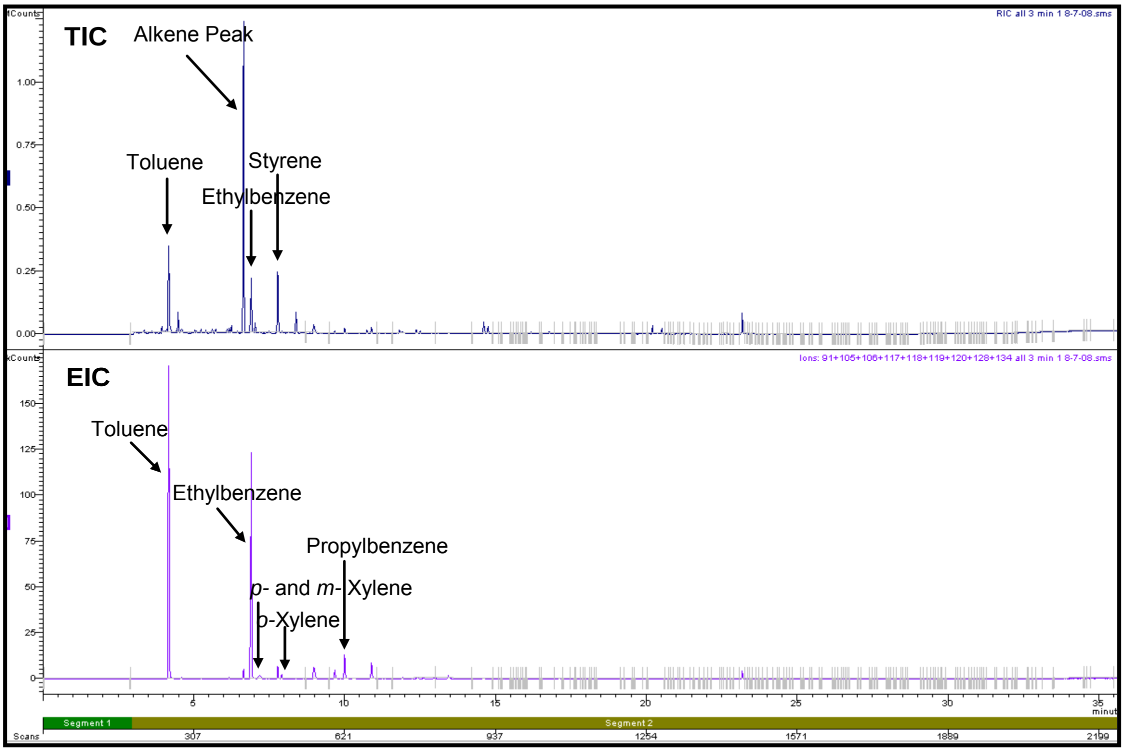


Figure C1.12: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 3 minutes

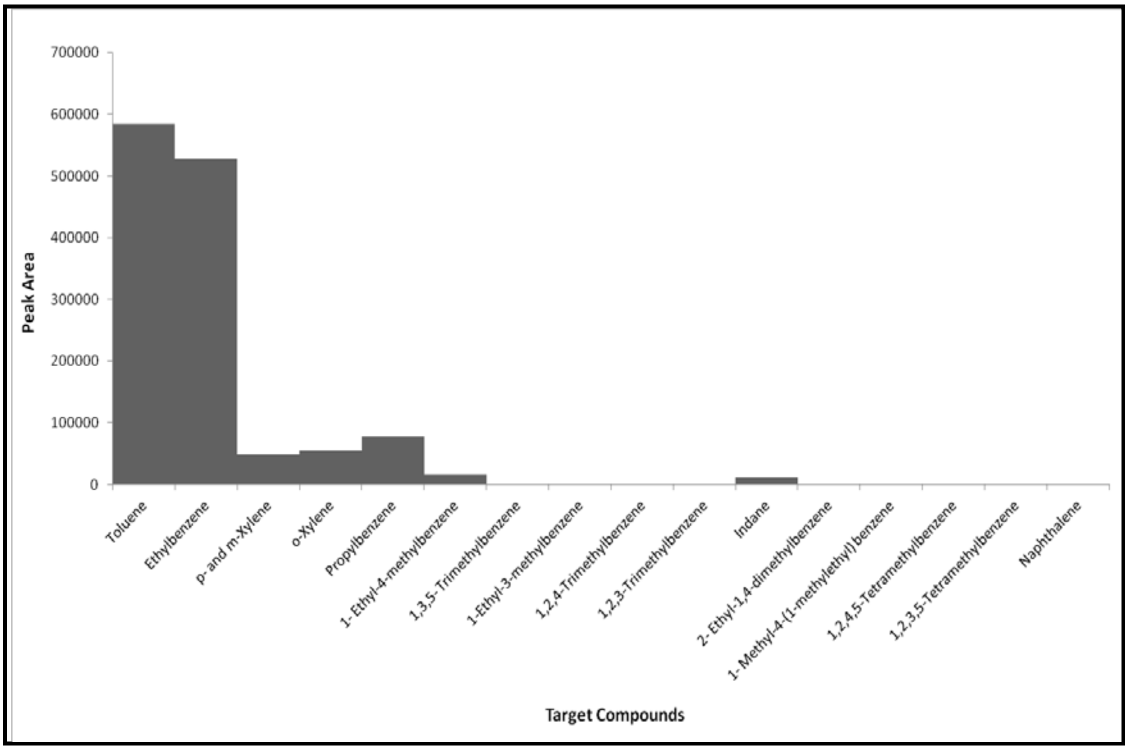


Figure C1.13: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 3 minutes

3.5 minute burn

Pictures of the samples after the 3.5 minute burn are presented in Figure C1.14 (a-c).

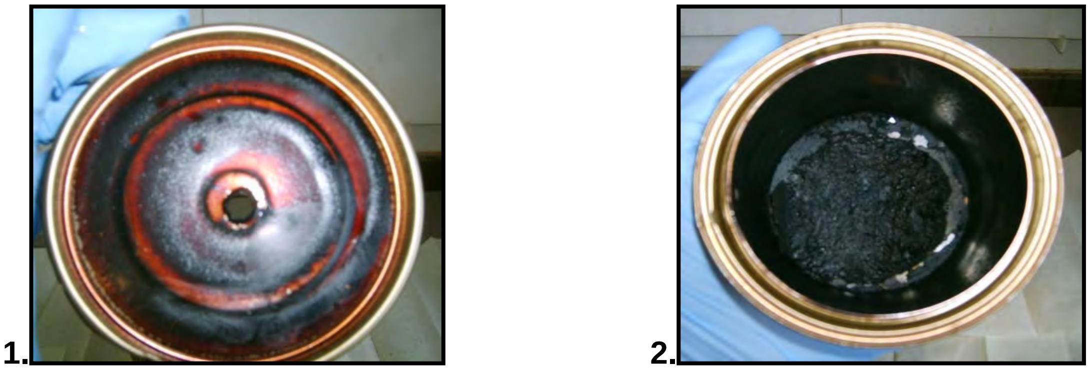


Figure C1.14 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

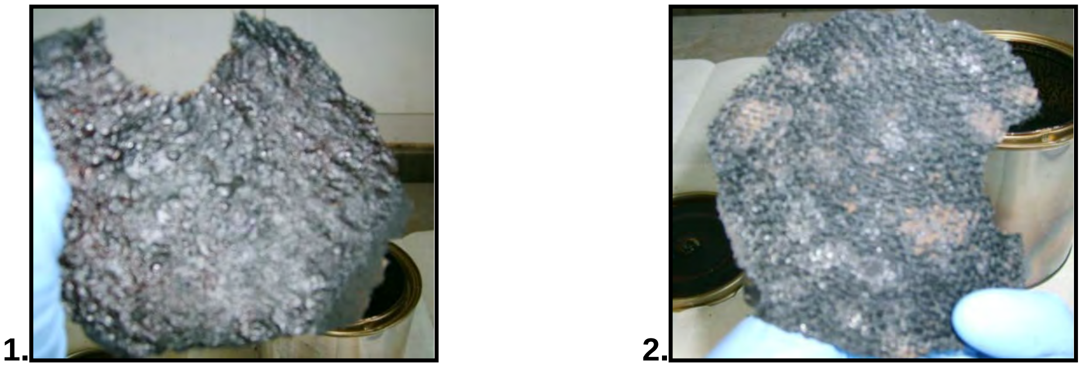


Figure C1.14 (b): 1. Top and 2. Underside of Sample after Burning

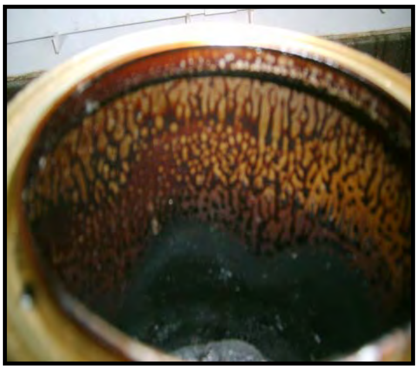


Figure C1.14 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon burnt in a small can for 3.5 minutes can be seen in Figure C1.15. The extrcated ion chromatogram shows that toluene and ethylbenzene were recovered from the burning of this nylon swatch. *P*- and *m*-xylene, *o*-xylene and propylbenzene were also recovered. The target compound chromatogram for these recovered compounds are presented in Figure C1.16.

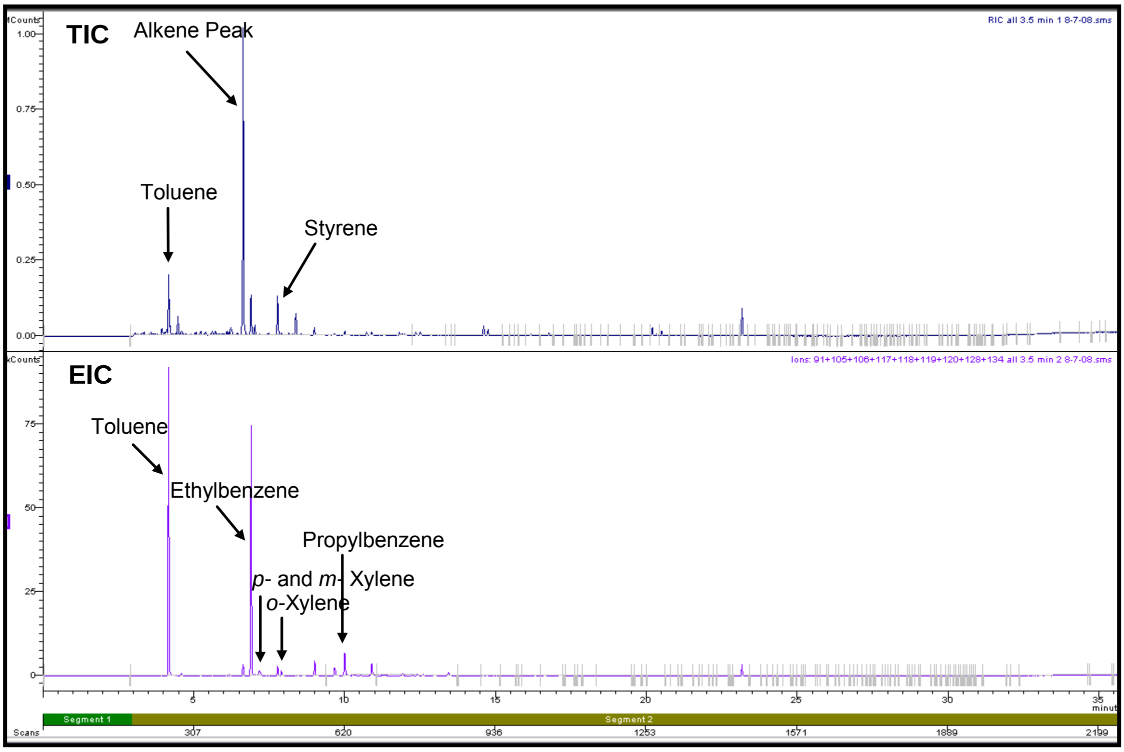


Figure C1.15: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 3.5 minutes

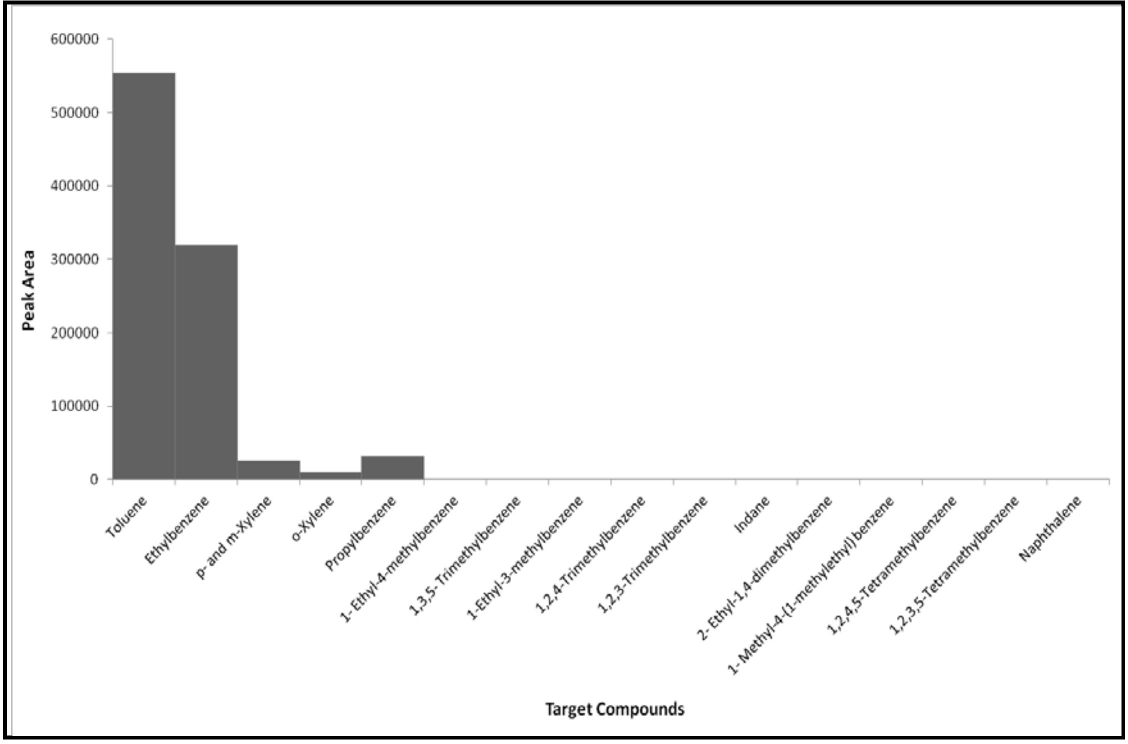


Figure C1.16: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 3.5 minutes

4 minute burn

Pictures of the samples after the 4 minute burn are presented in Figure C1.17 (a-c).

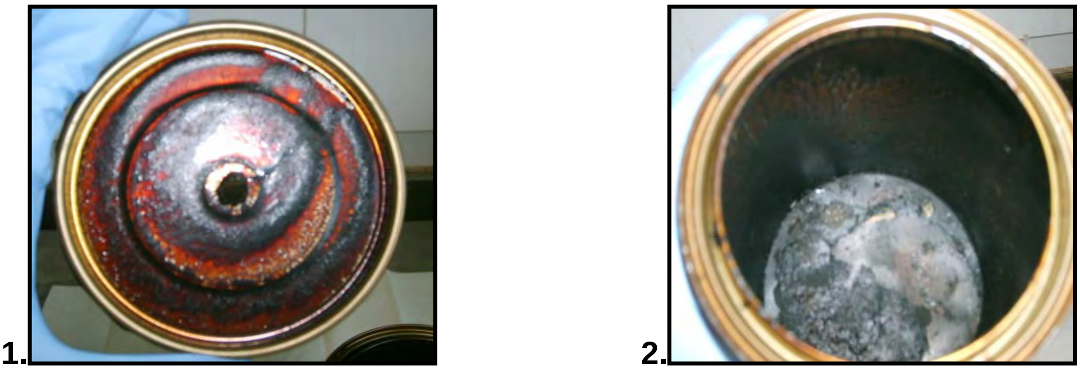
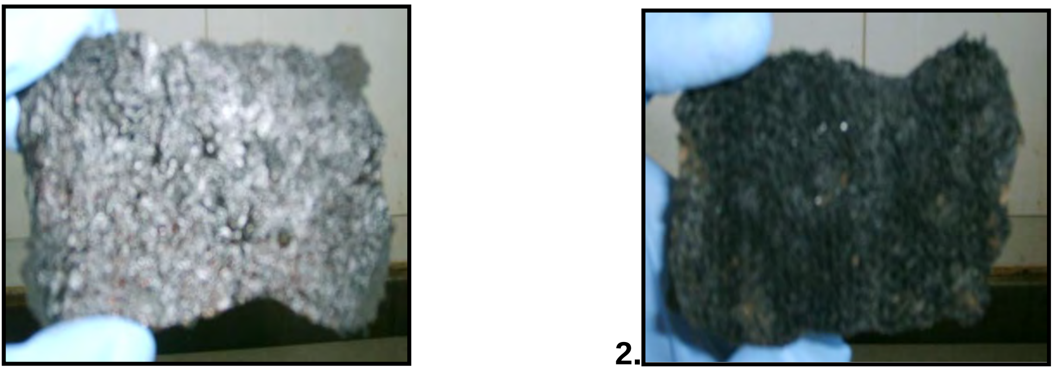


Figure C1.17 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning



1. 2.

Figure C1.17 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.17 (c): Inside of Can after Burning

The TIC and EIC for this can fire can be seen in Figure C1.18.

Similar to the total ion chromatogram for the 3.5 minute burn, the most predominate peak was the alkene peak. The extracted ion chromatogram shows that toluene and ethylbenzene were recovered from the burning of this nylon swatch. *P*- and *m*-xylene, *o*-xylene and propylbenzene were again recovered and the target compound chromatogram for these recovered compounds are presented in Figure C1.19.

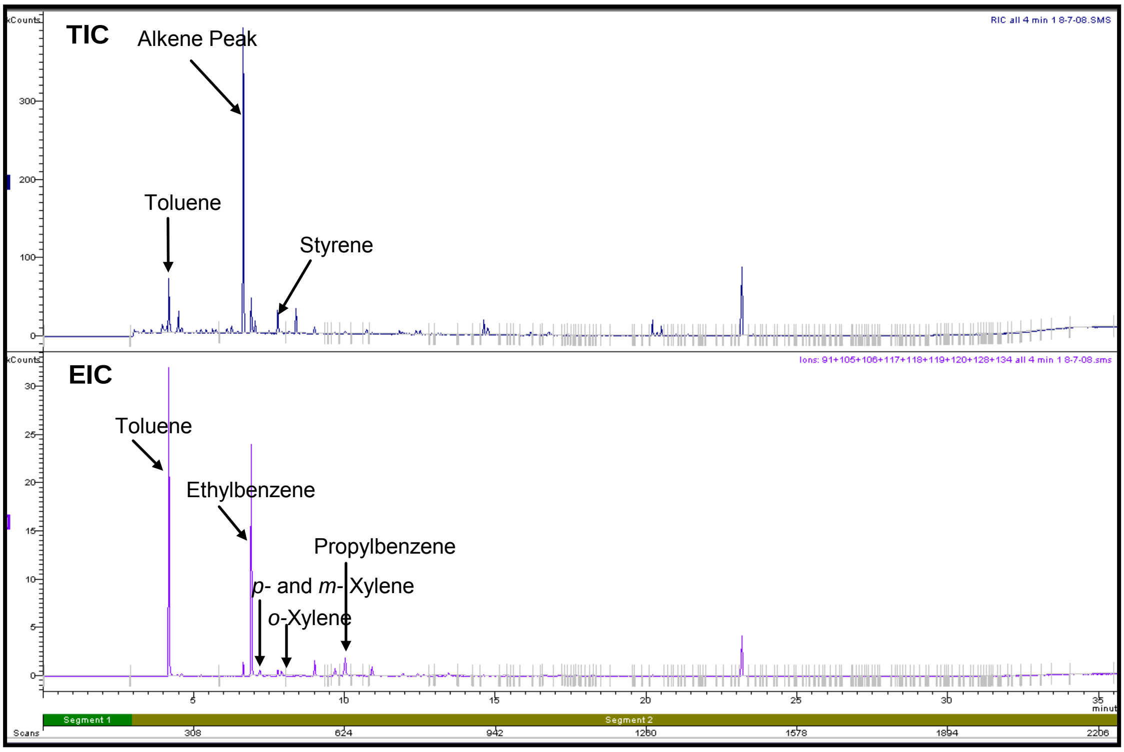


Figure C1.18: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 4 minutes

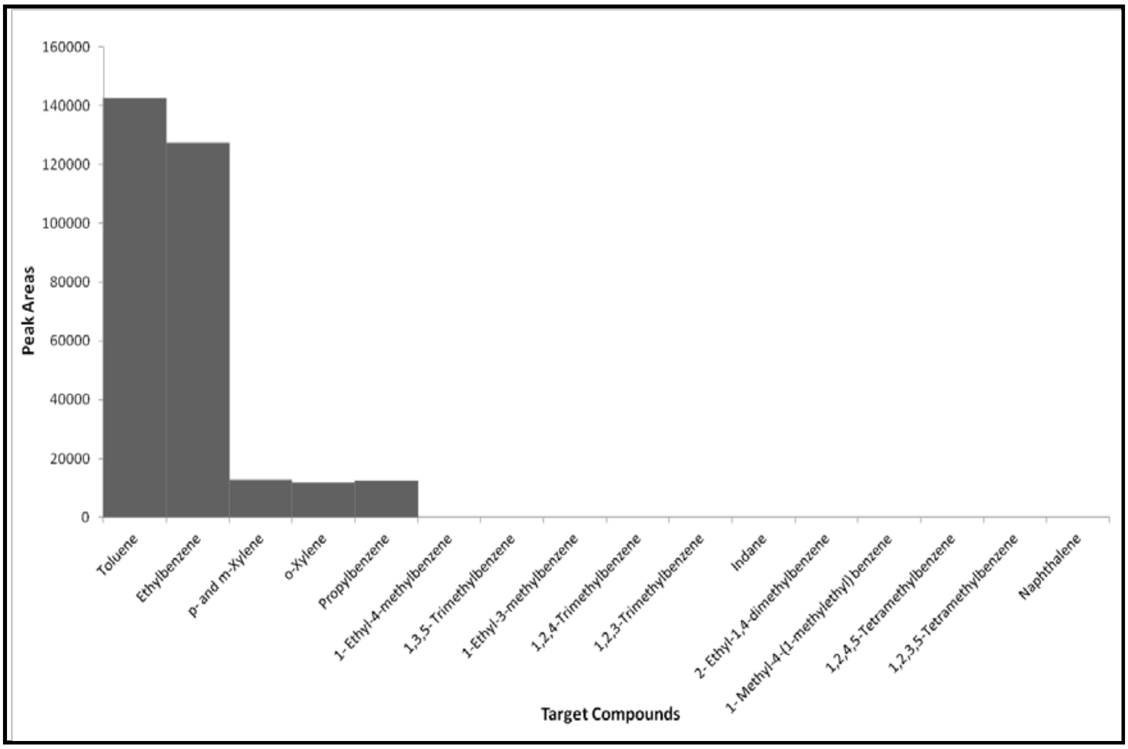


Figure C1.19: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 4 minutes

4.5 minute burn

Pictures of the samples after the 4.5 minute burn are presented in Figure C1.20 (a-c).

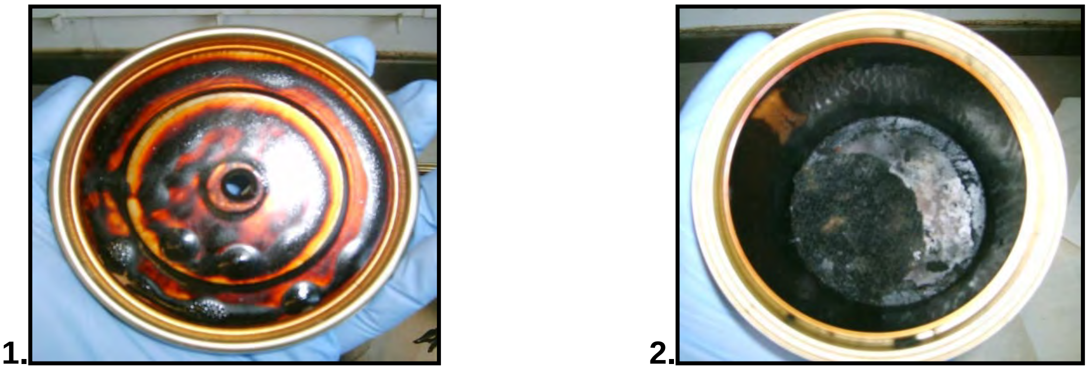


Figure C1.20 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

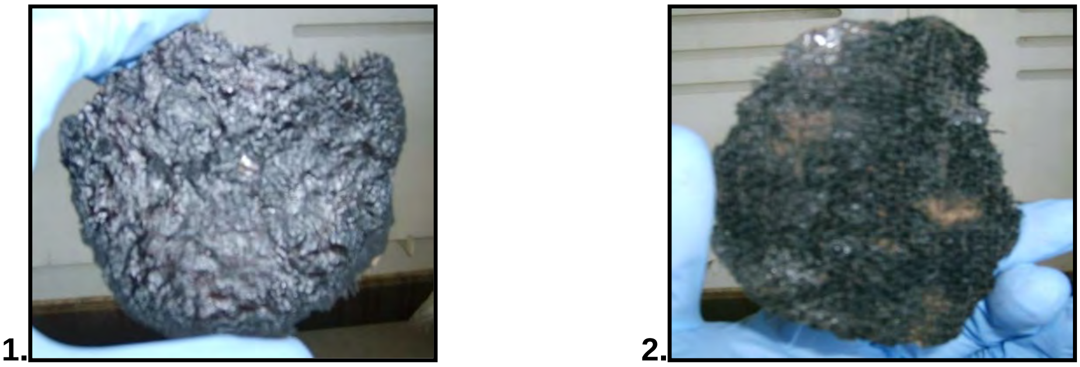


Figure C1.20 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.20 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this sample can be seen in Figure C1.21. Similar to the total ion chromatograms for the previous few burns, the most abundant peak was the alkene peak. The extracted ion chromatogram shows that toluene and ethylbenzene were recovered from the burning of this nylon swatch. *P*- and *m*-xylene, *o*-xylene and propylbenzene were again recovered. The target compound chromatogram for these recovered compounds are presented in Figure C1.22.

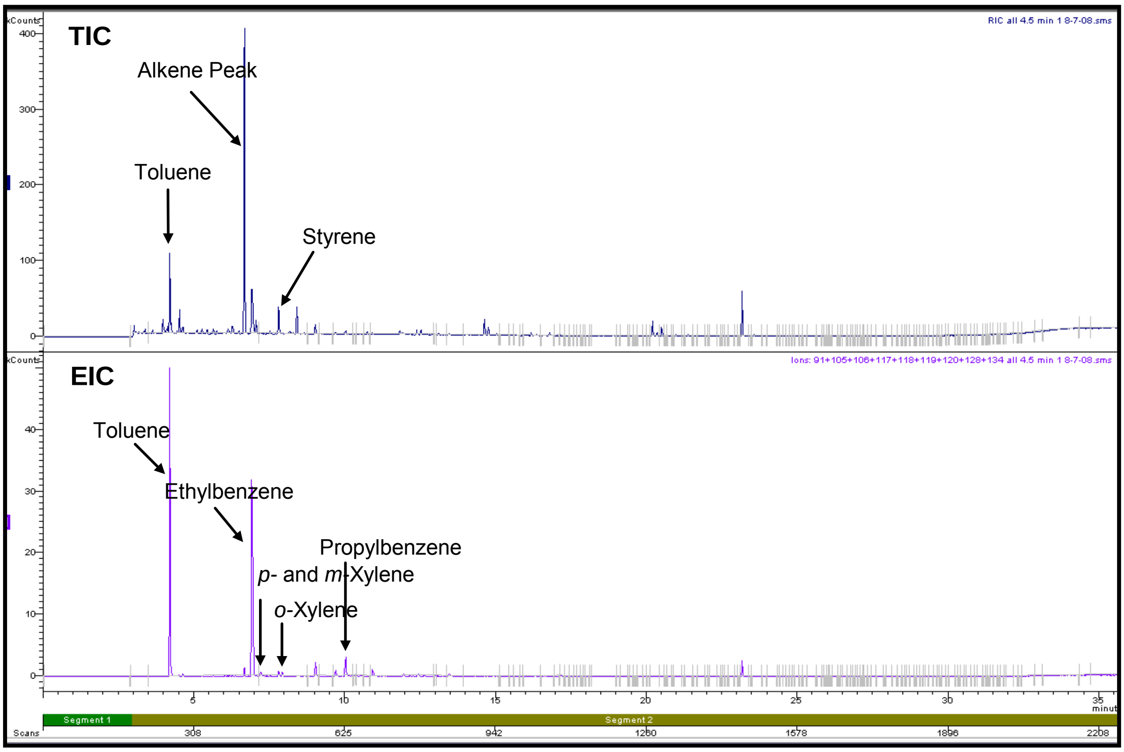


Figure C1.21: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 4.5 minutes

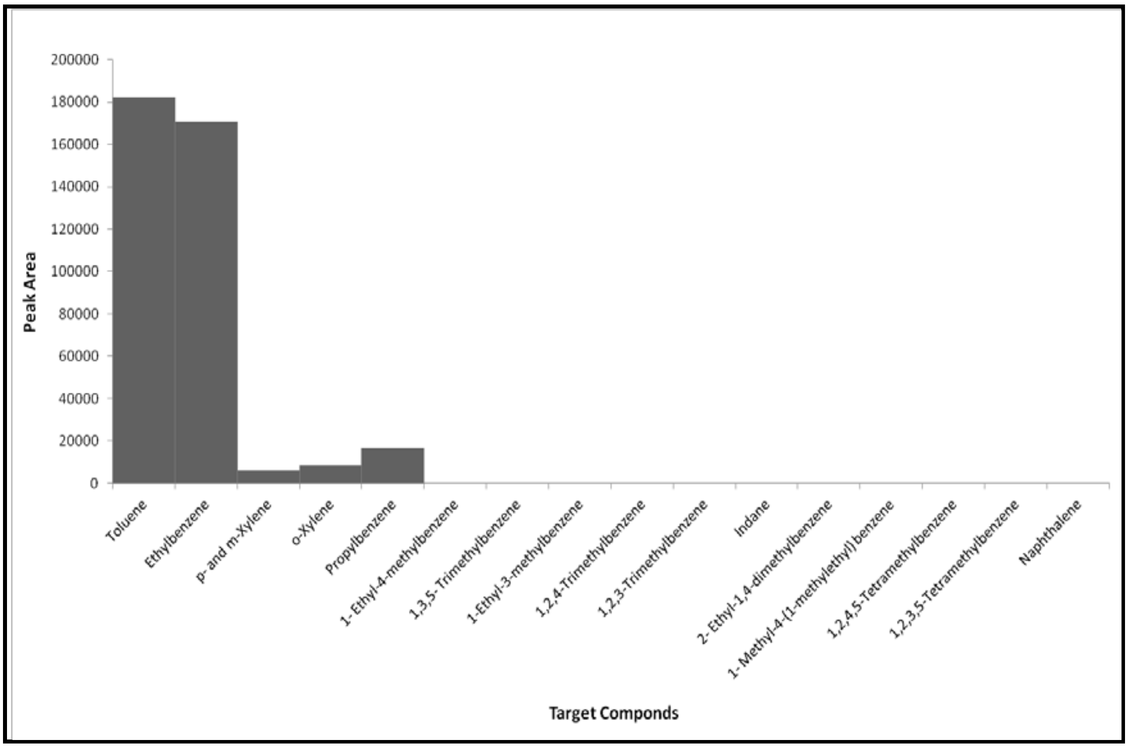
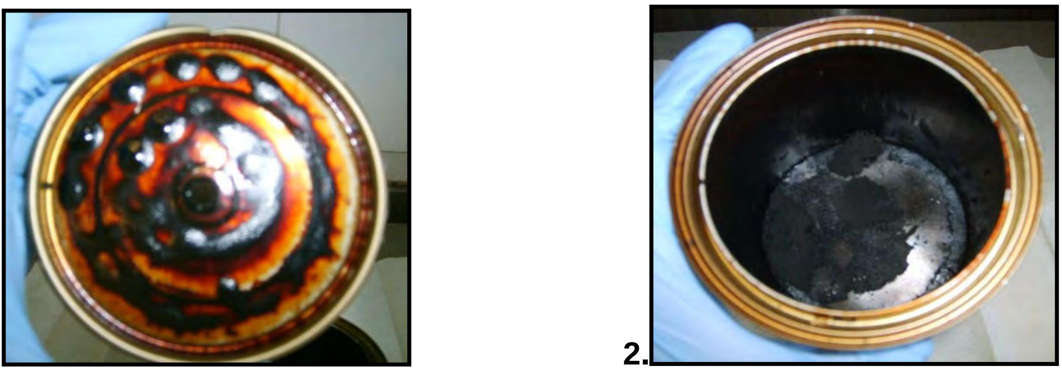


Figure C1.22: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 4.5 minutes

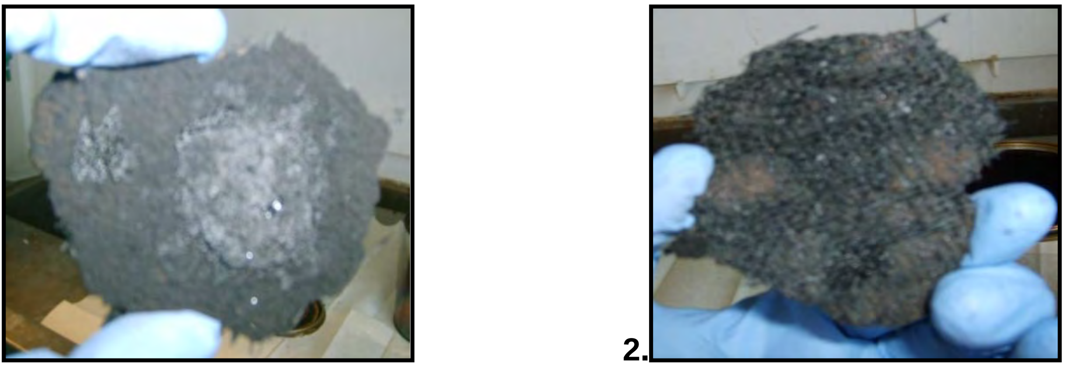
5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure C1.23 (a-c).



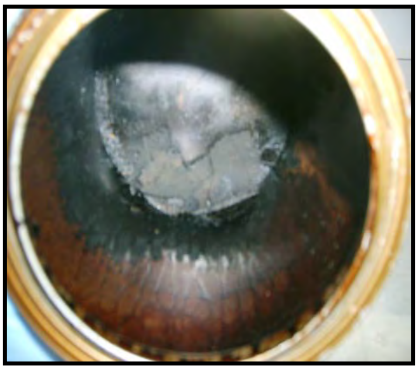
1. **2.**

Figure C1.23 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning



1. 2.

Figure C1.23 (b): 1. Top and 2. Underside of Sample after Burning



FigureC1.23 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram is shown in Figure C1.24. The most abundant compounds in the extracted ion chromatogram are toluene and ethylbenzene, *p*- and *m*-xylene, *o*-xylene and propylbenzene were also able to be recovered. The target compound chromatogram is presented in Figure C1.25.

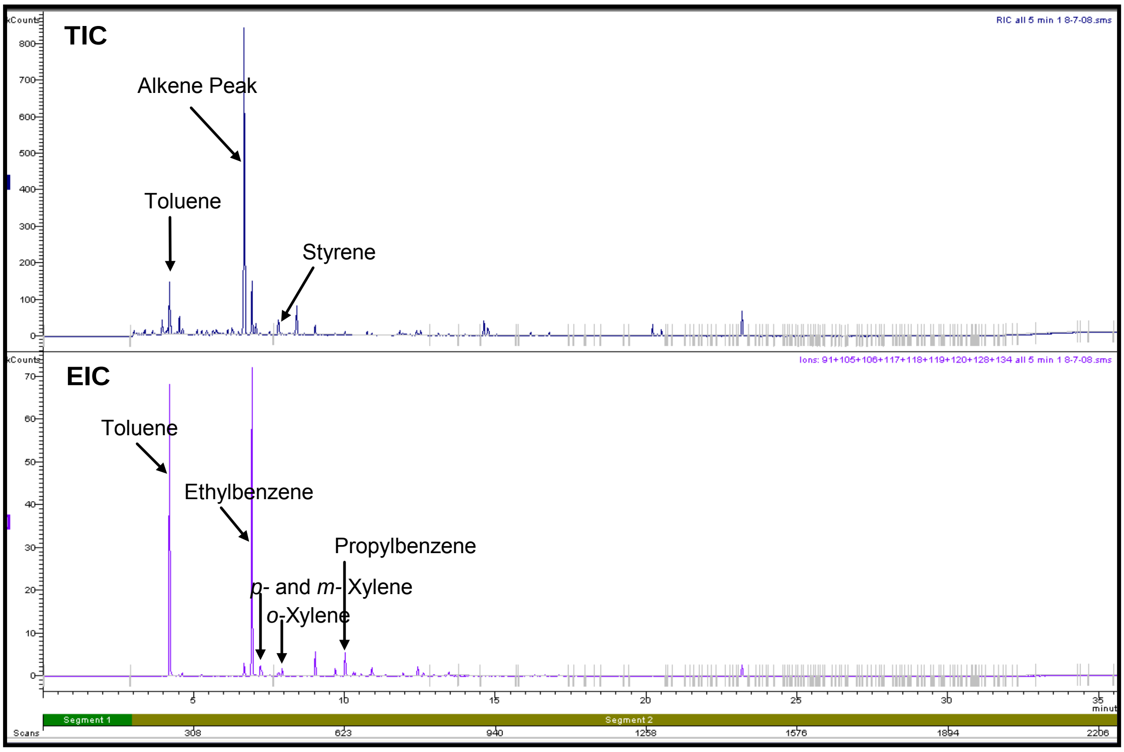


Figure C1.24: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 5 minutes

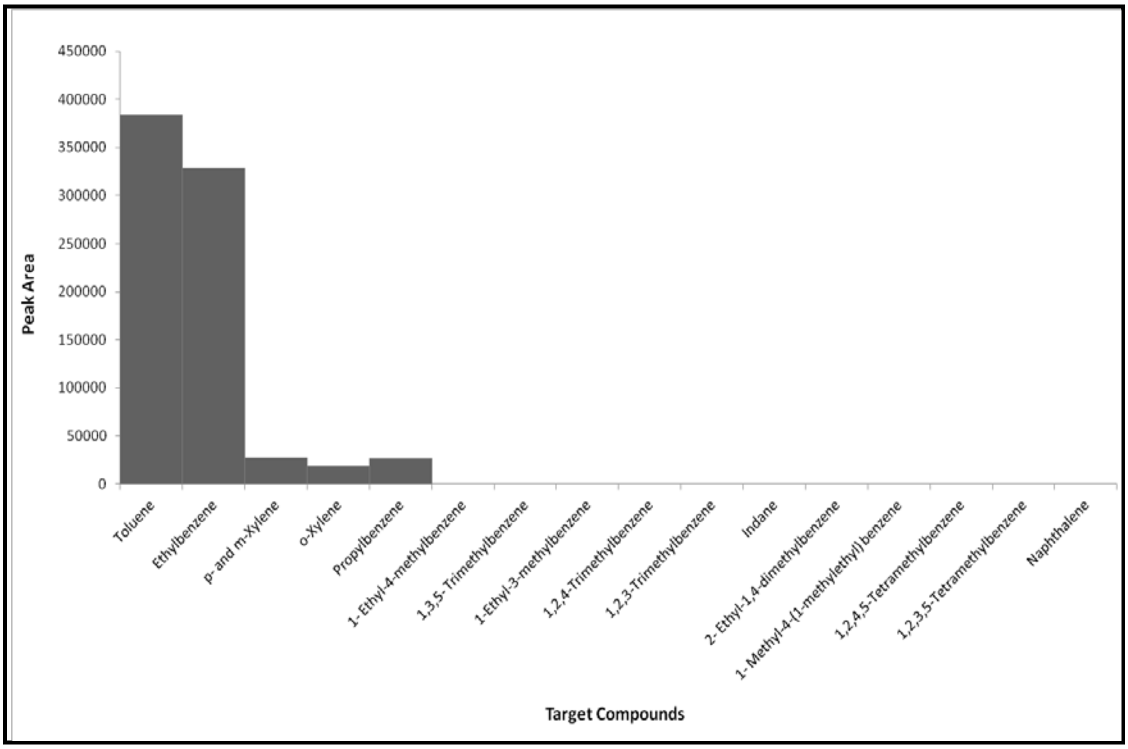


Figure C1.25: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure C1.26 (a-c).

Figure C1.26 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

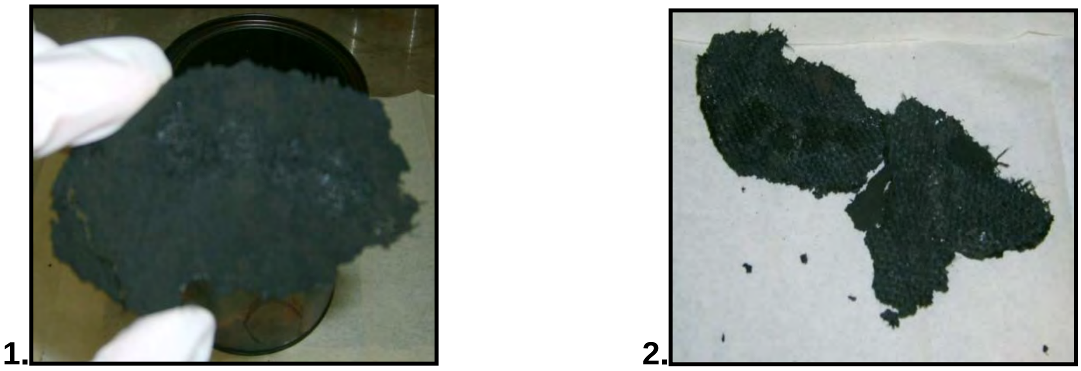


Figure C1.26 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.26 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the nylon carpet burnt in a small can for 7.5 minutes can be seen in Figures C1.27. Similar to the previous fires, the most abundant target compounds, present in both the total ion chromatogram and extracted ion chromatogram are toluene and ethylbenzene. The other target compounds recovered are presented in the target compound chromatograms (Figure C1.28).

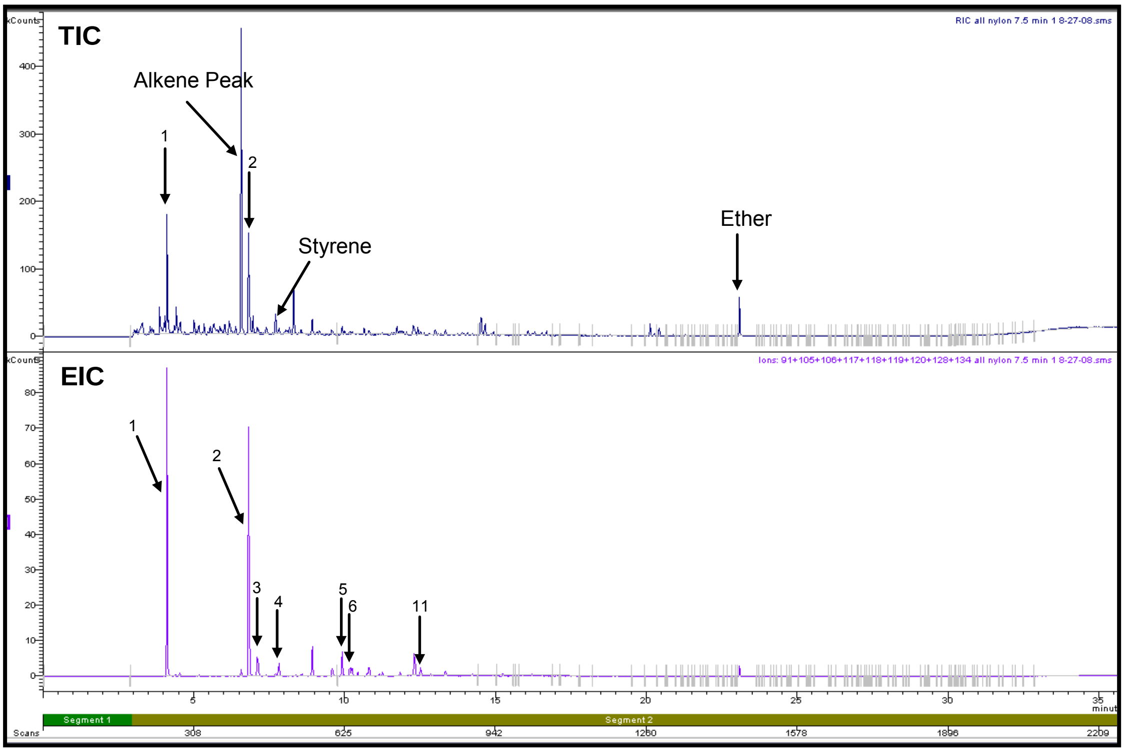


Figure C1.27: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6=1-Ethyl-4-methylbenzene, 11= Indane

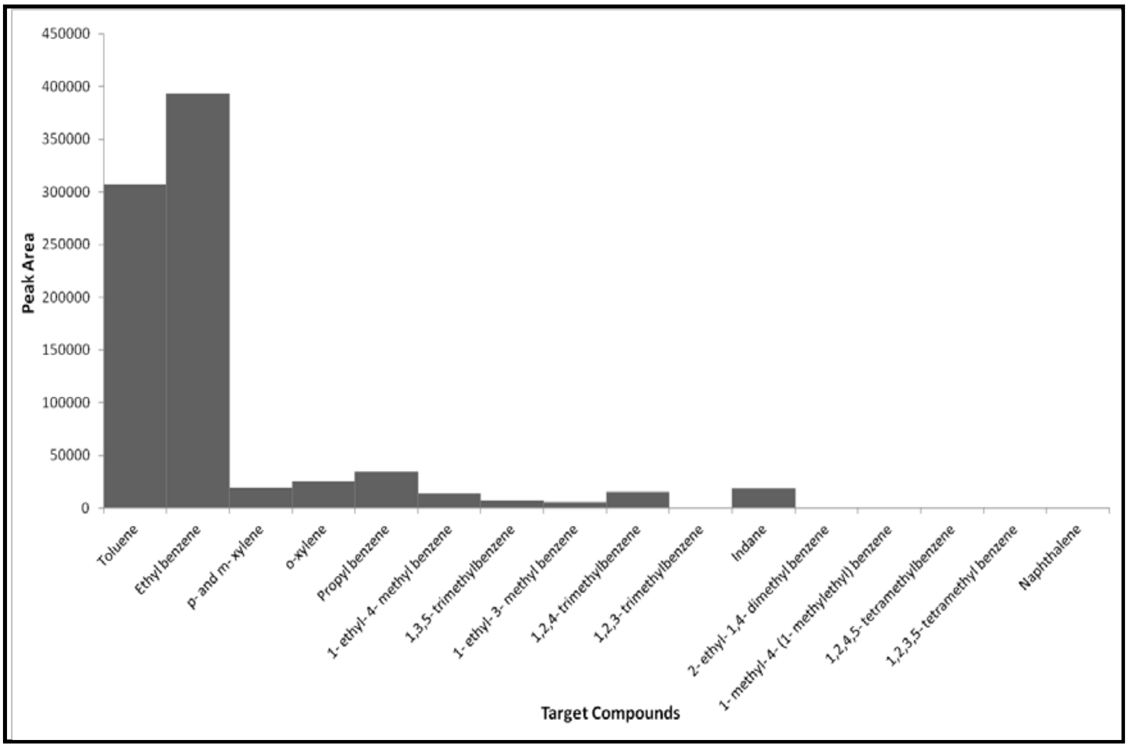


Figure C1.28: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

10 minute burn

Pictures of the samples after the 10 minute burn are presented in Figure C1.29 (a-c).

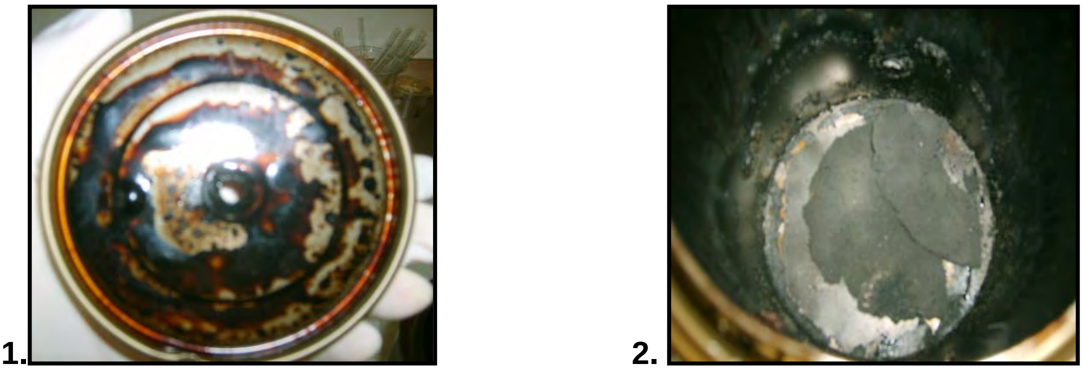


Figure C1.29 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

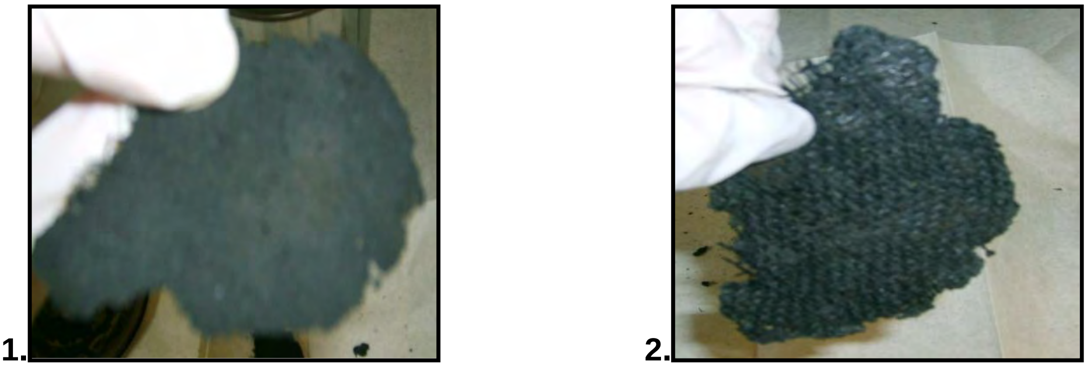


Figure C1.29 (b): 1. Top and 2. Underside of Sample after Burning

Figure C1.29 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this small can fire is presented in Figure C1.30. Toluene and ethylbenzene were the most abundant peaks recovered in the extracted ion chromatogram. The target compound chromatogram is presented in Figure C1.31.

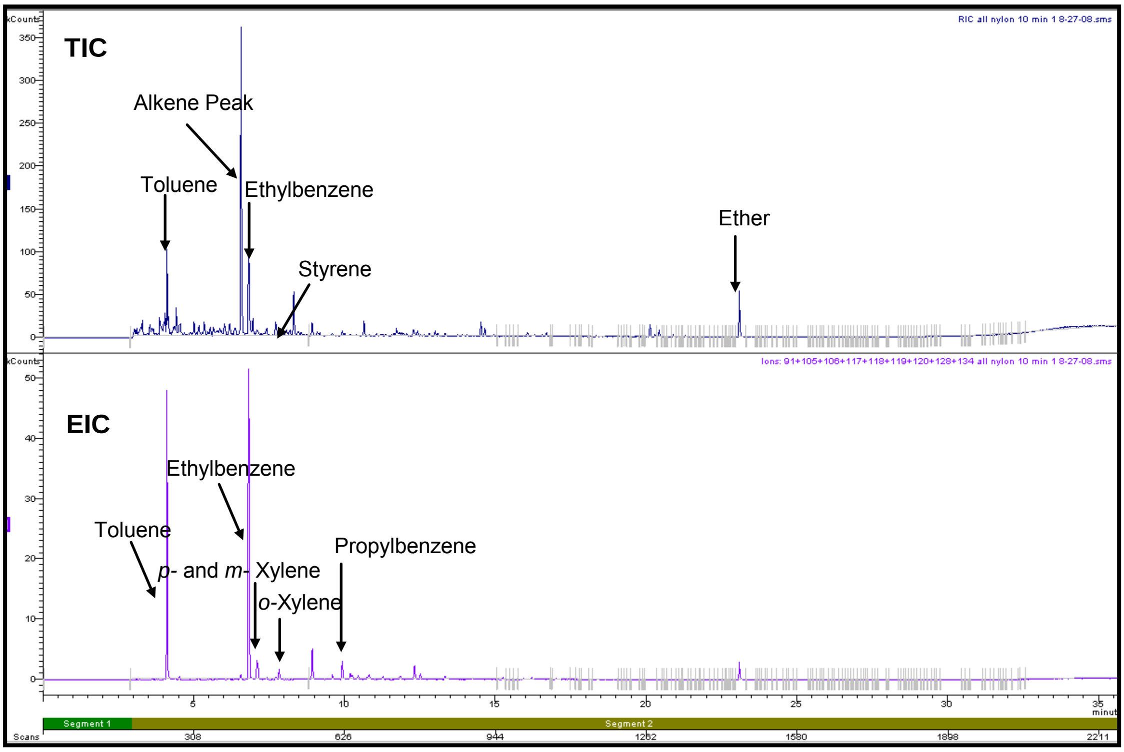


Figure C1.30: Target Ion Chromatogram and Extracted Ion Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 10 minutes

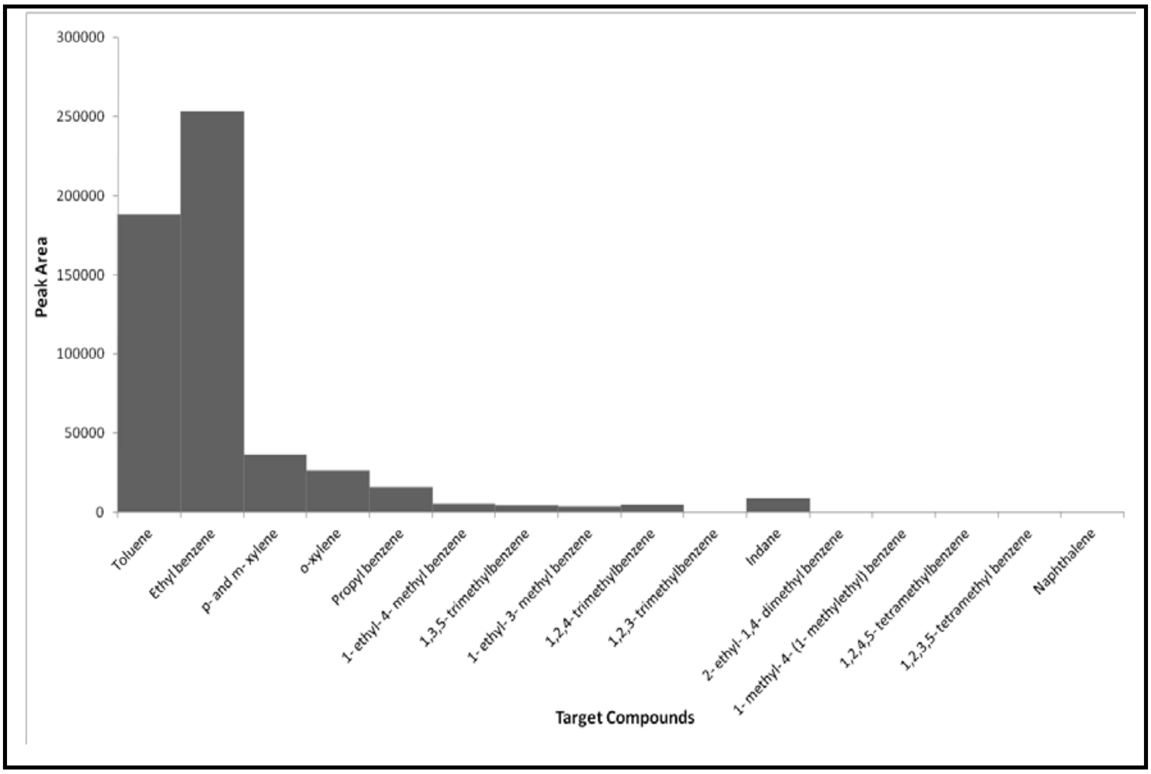


Figure C1.31: Target Compound Chromatogram of a Nylon Carpet Swatch burnt in a Can with Lid On for 10 minutes

APPENDIX D

BURNING TIME EXPERIMENTS FOR POLYPROPYLENE, WOOL AND 50-50 POLYPROPYLENE-WOOL CARPET

Based on the results from the nylon carpet small can fire experiments, a series of burns were conducted to determine the effect of burning time on polypropylene, wool and 50-50 polypropylene-wool carpet and therefore the production and recovery of petrol target compounds. The carpet was burnt for 2.5, 5, 7.5 and 10 minutes.

Polypropylene Carpet

2.5 minute burn

Pictures of the samples after the 2.5 minute burn are presented in Figure D1.1 (a-c).

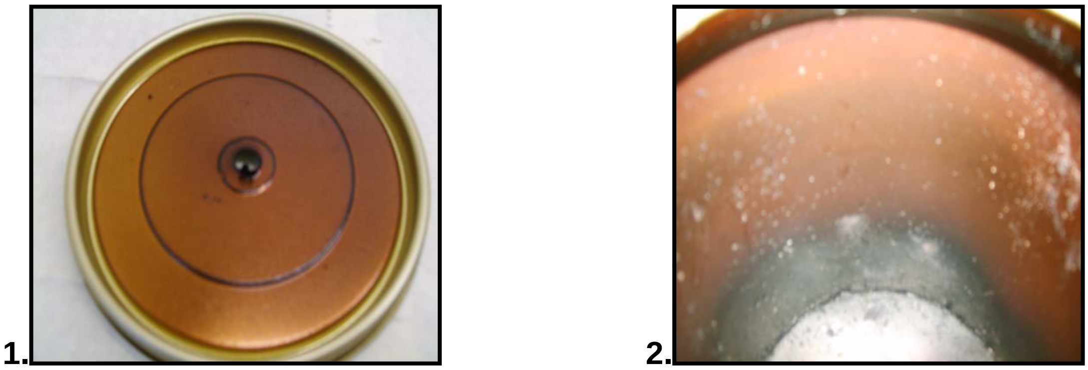


Figure D1.1 (a): 1. Underside of Lid and 2. Side of Can after Burning

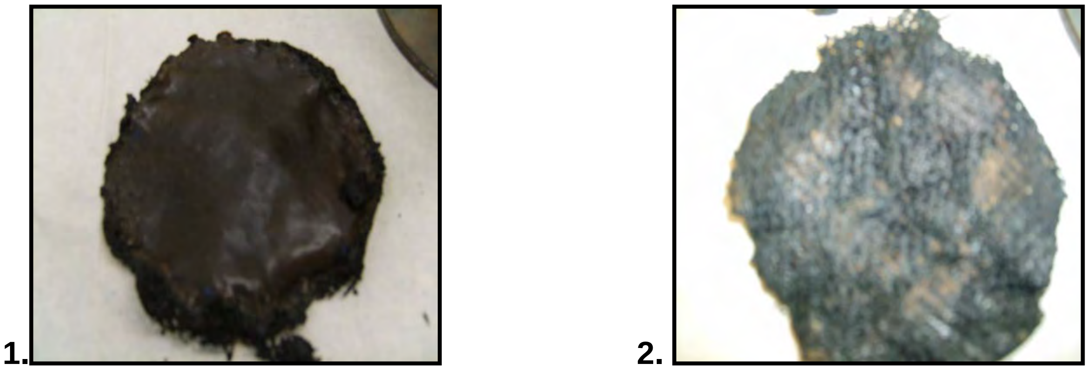


Figure D1.1 (b): 1. Top and 2. Underside of Sample after Burning

Figure D1.1 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the polypropylene carpet burnt in a small can for 2.5 minutes is presented in Figure D1.2. The extracted ion chromatogram shows five target compounds were able to be recovered and they were identified as toluene, ethylbenzene, *p*- and *m*-xylene, *o*-xylene and propylbenzene (Figure D1.2). The target compound chromatogram is presented in Figure D1.3.

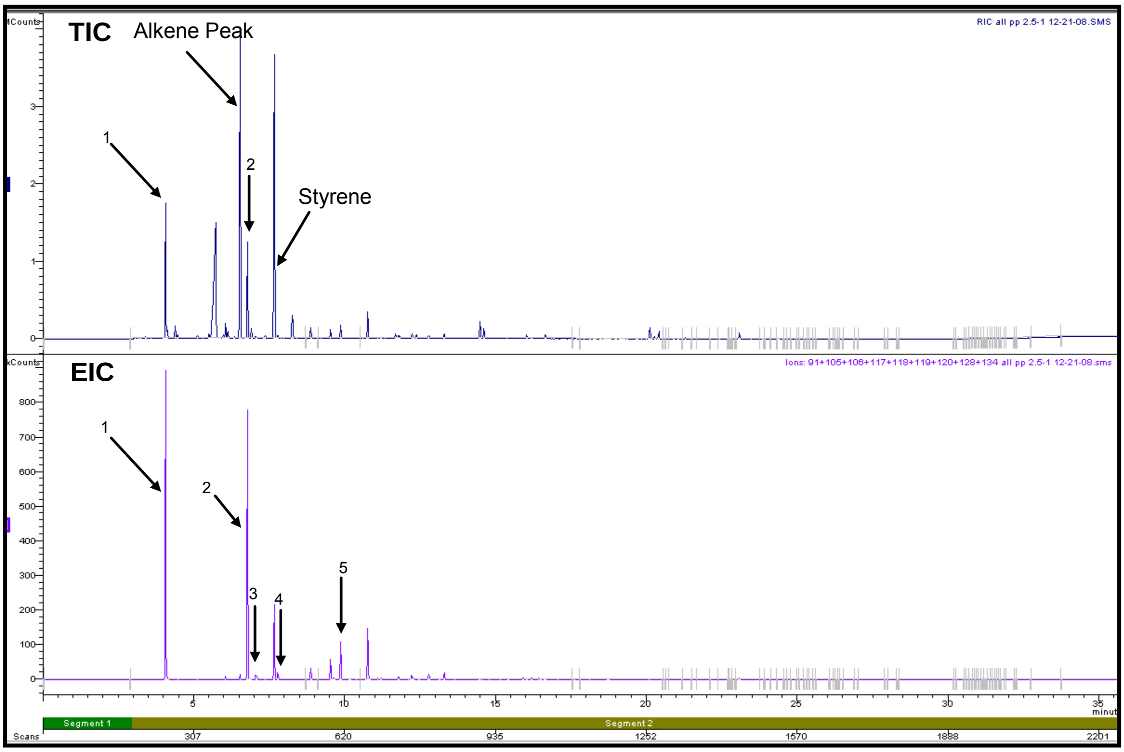


Figure D1.2: Total Ion Chromatogram and Extracted Ion Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

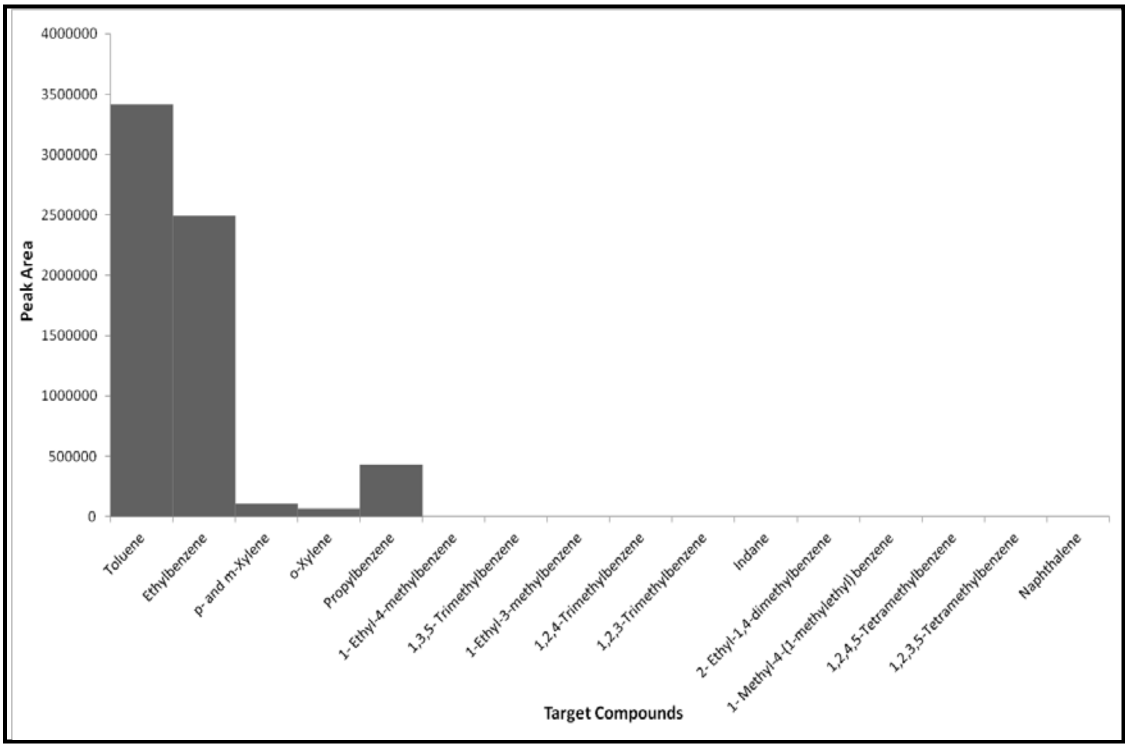


Figure D1.3: Target Compound Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure D1.4 (a-c).

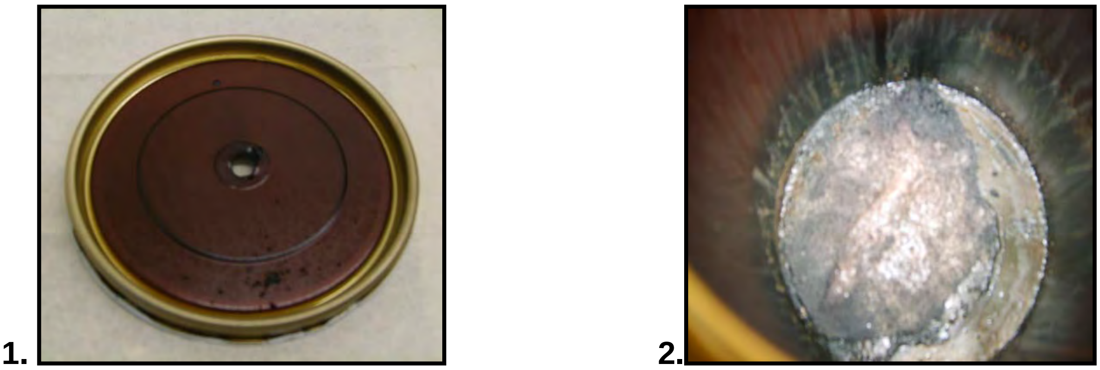


Figure D1.4 (a): 1. Underside of Lid and 2. Sample in Bottom of Can after Burning

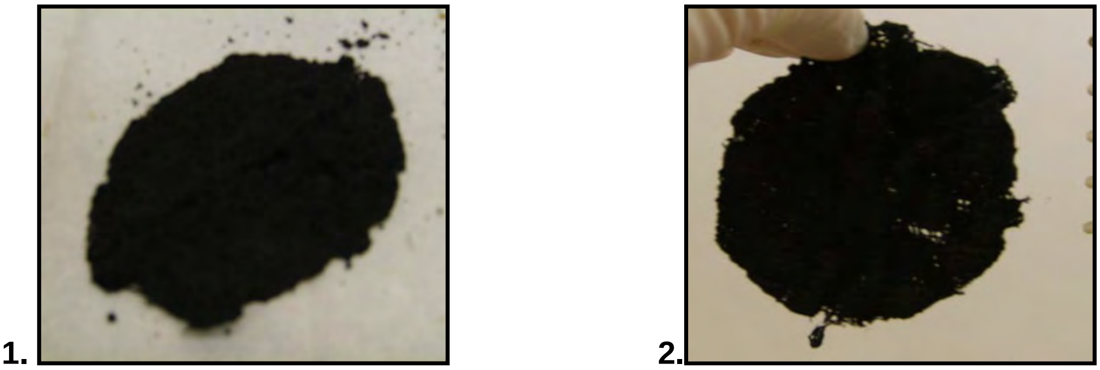


Figure D1.4 (b): 1. Top and 2. Underside of Sample after Burning

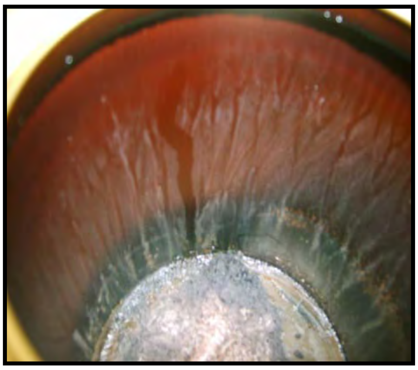


Figure D1.4 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram is shown in Figure D1.5. The most abundant peaks in the extracted ion chromatogram were toluene and ethylbenzene. However *p*- and *m*-xylene, *o*-xylene and propylbenzene were also able to be recovered and the target compound chromatogram is presented in Figure D1.6.

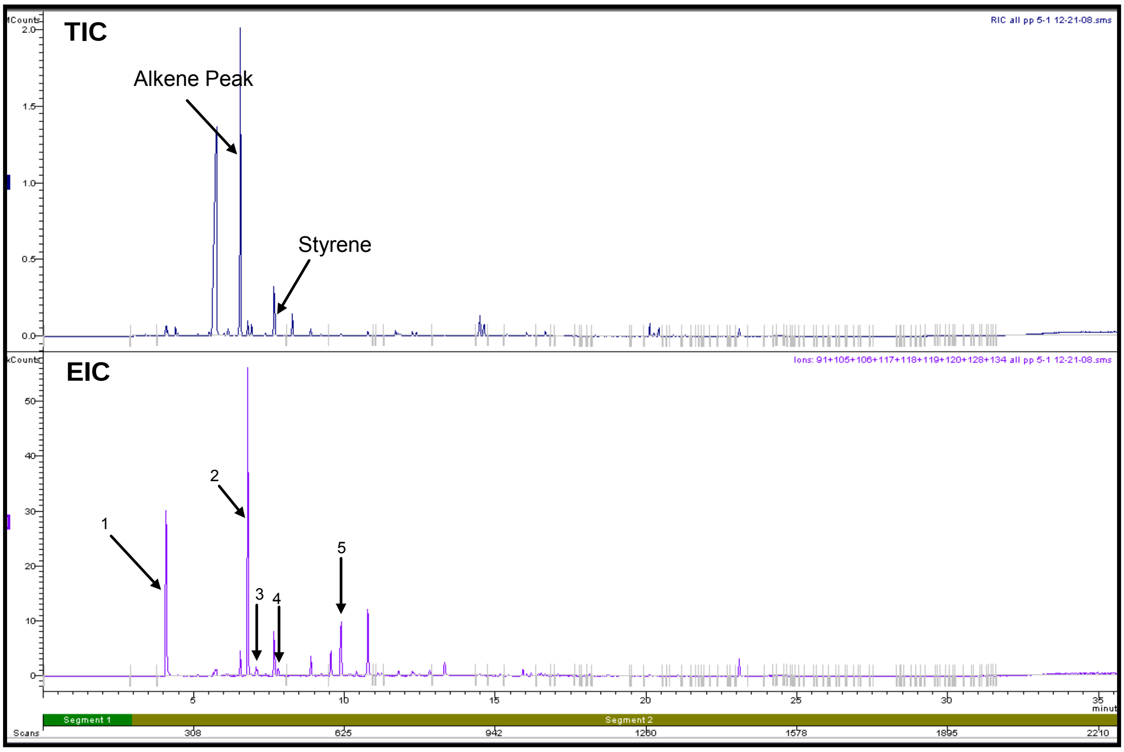


Figure D1.5: Total Ion Chromatogram and Extracted Ion Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=propylbenzene

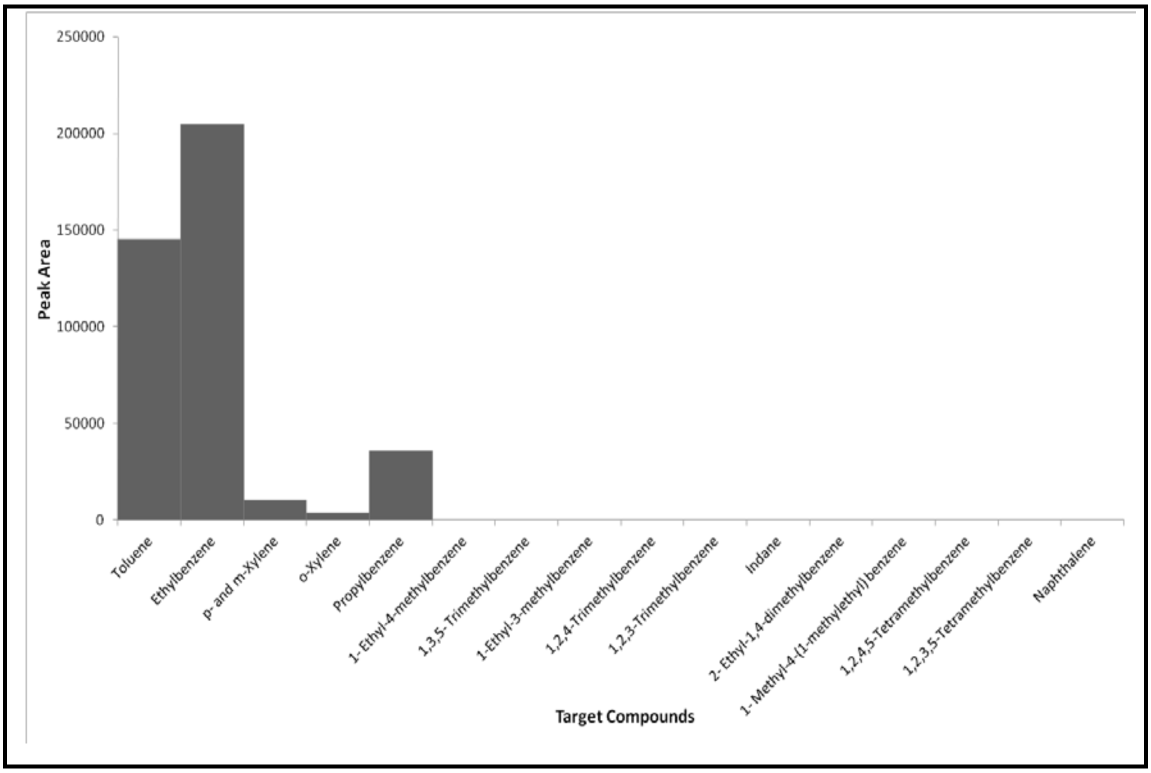


Figure D1.6: Target Compound Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure D1.7 (a-c).

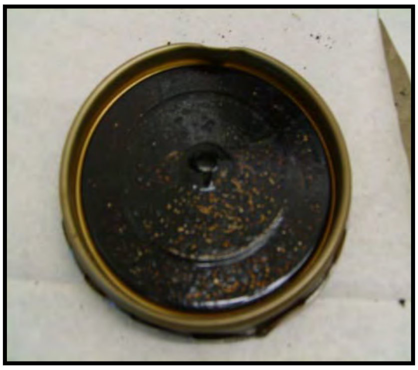


Figure D1.7 (a): Underside of Lid

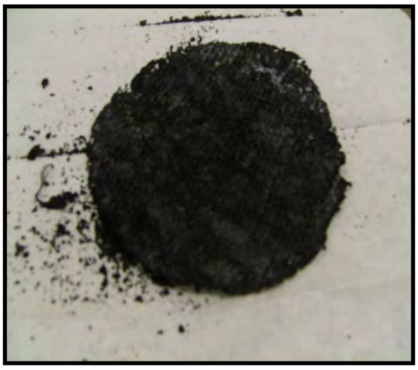


Figure D1.7 (b): Underside of Sample after Burning

Figure D1.7 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the polypropylene carpet burnt in a small can for 7.5 minutes can be seen in

Figures D1.8. A number of target compounds were identified in the extracted ion chromatogram with the toluene and ethylbenzene being the most abundant. *P*- and *m*- *x*ylene, *o*-xylene, propylbenzene and 1, 3,5-trimethylbenzene were also recovered and the target compound chromatogram is presented in Figure D1.9.

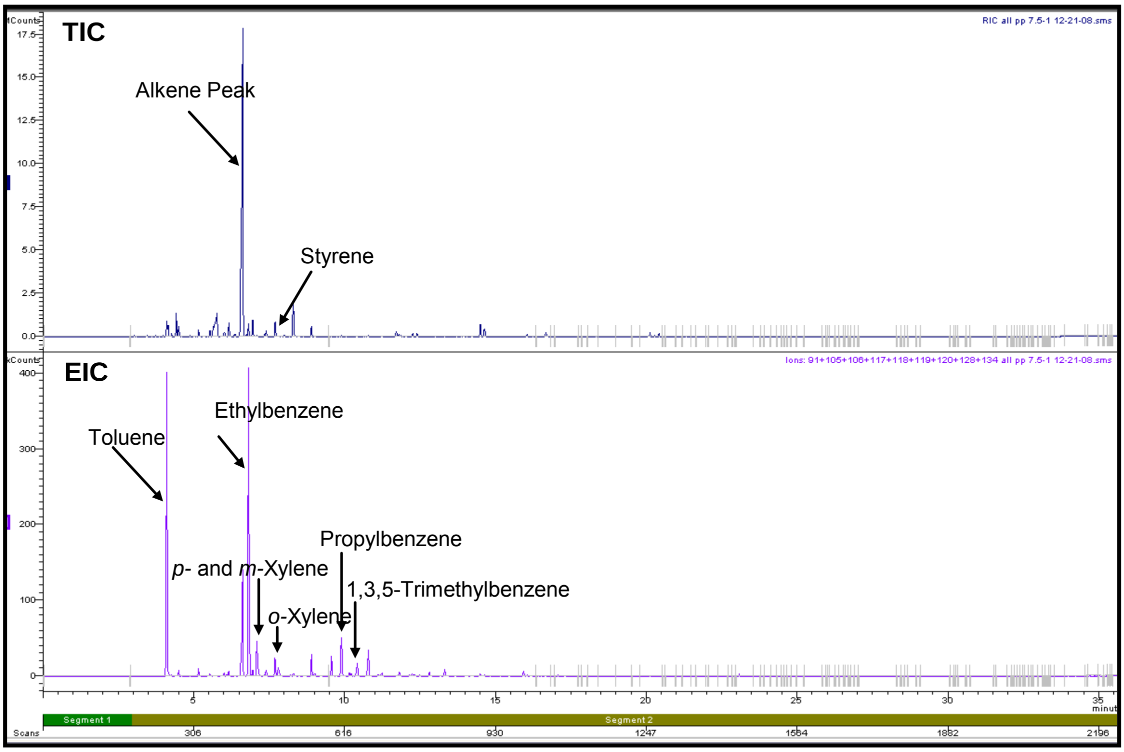


Figure D1.8: Total Ion Chromatogram and Extracted Ion Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

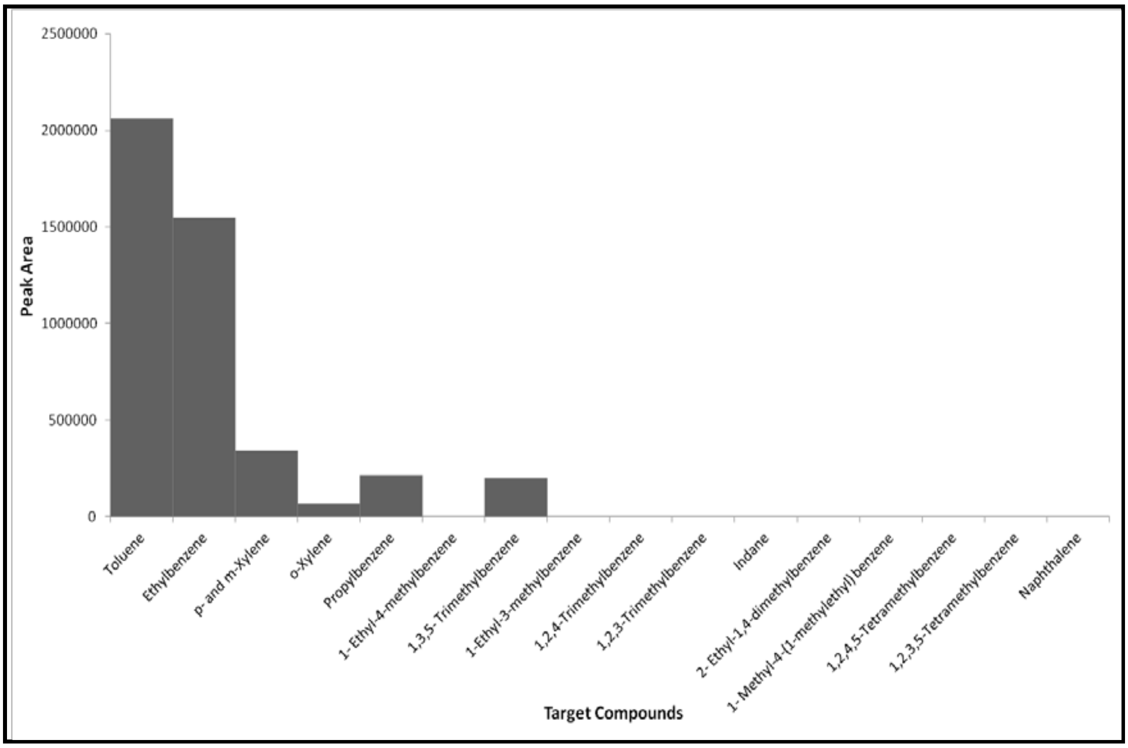


Figure D1.9: Target Compound Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

10 minute burn

Pictures of the polypropylene after the 10 minute burn are presented in Figure D1.10 (a-c).

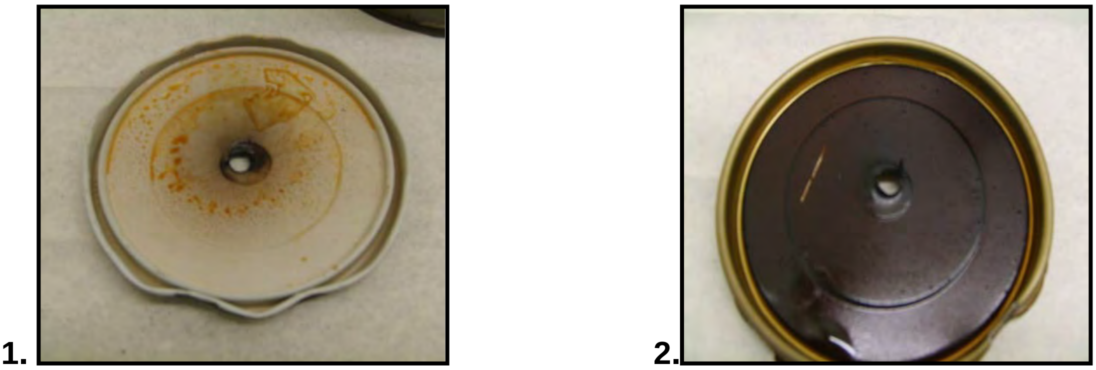


Figure D1.10 (a): 1. Top of lid and 2. Underside of Lid after Burning

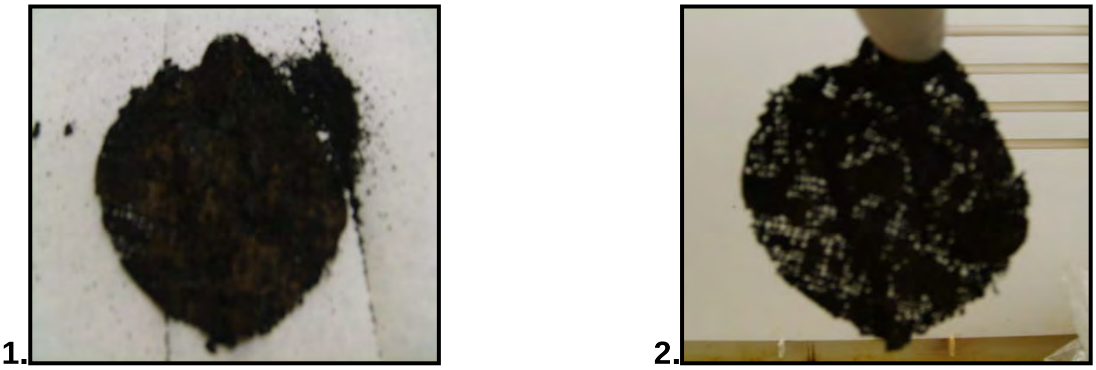


Figure D1.10 (b): 1. Top and 2. Underside of Sample after Burning

Figure D1.10 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this small can fire is presented in Figure D1.11. Toluene and ethylbenzene were the most abundant peaks recovered in the extracted ion chromatogram. The target compound chromatogram is presented in Figure D1.12.

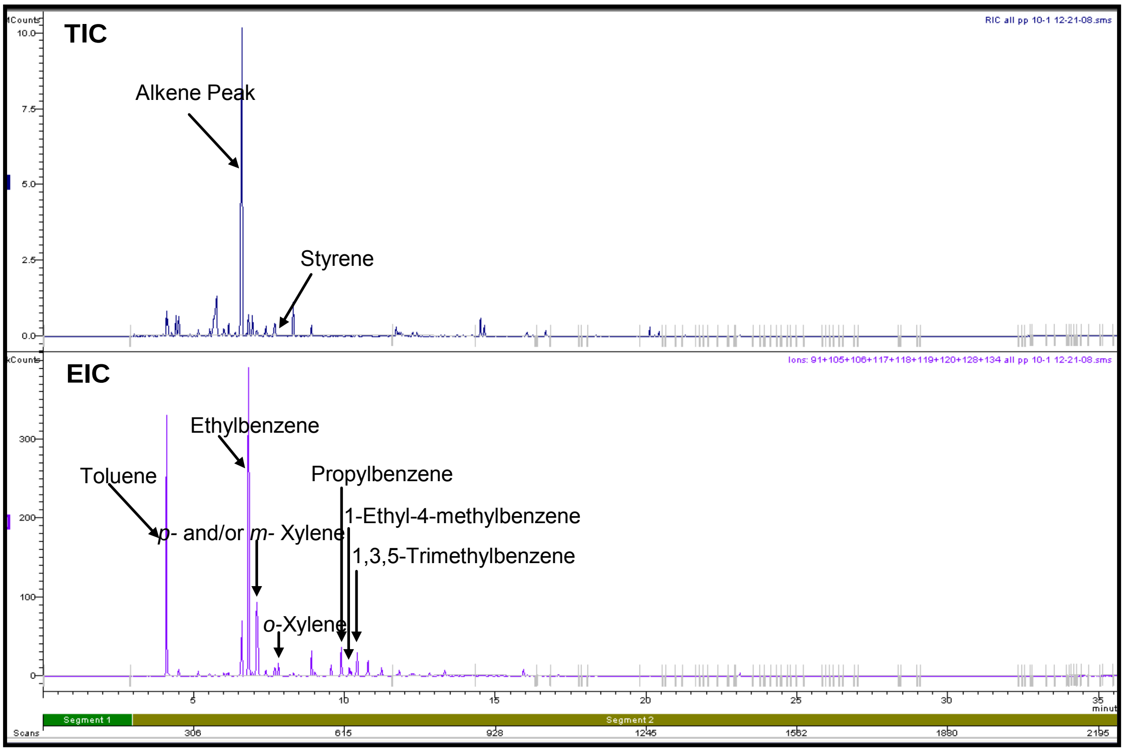


Figure D1.11: Total Ion Chromatogram and Extracted Ion Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 10 minutes

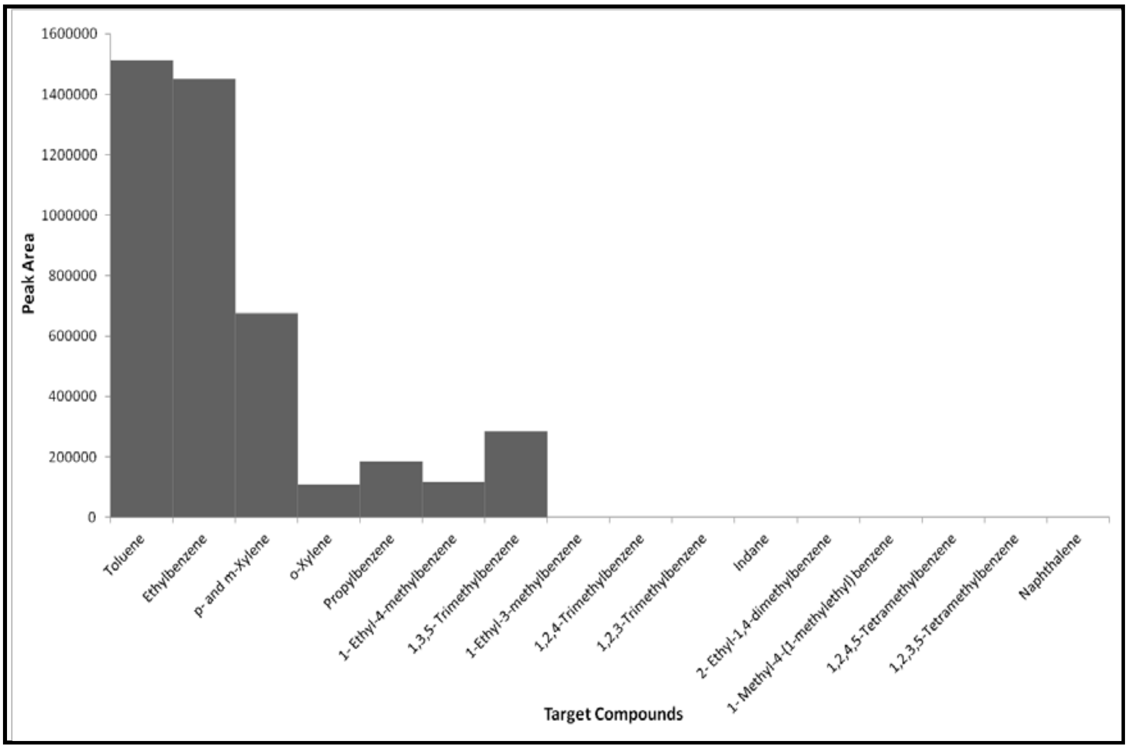


Figure D1.12: Target Compound Chromatogram of a Polypropylene Carpet Swatch burnt in a Can with Lid On for 10 minutes

Wool Carpet

Similar to the polypropylene carpet, the wool carpet was burnt over a range of times including 2.5, 5, 7.5 and 10 minutes.

2.5 minute burn

Pictures of the samples after the 2.5 minute burn are presented in Figure D2.1 (a-b).

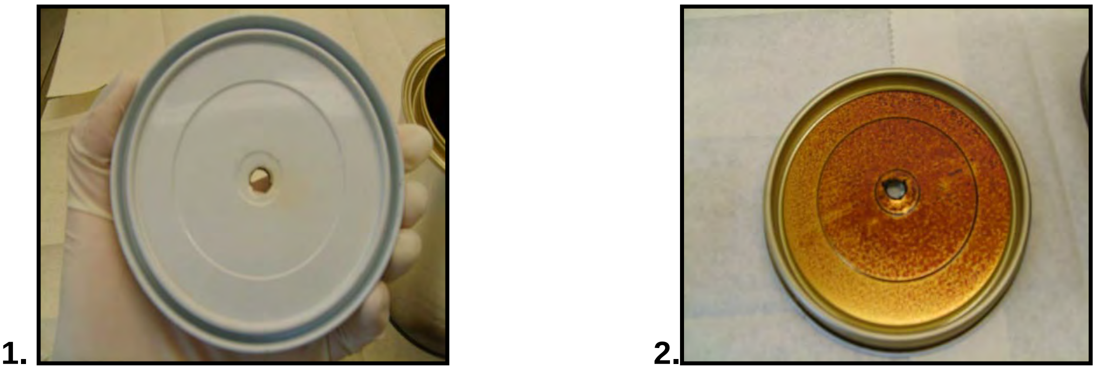


Figure D2.1 (a): 1. Top and 2. Underside of Lid after Burning

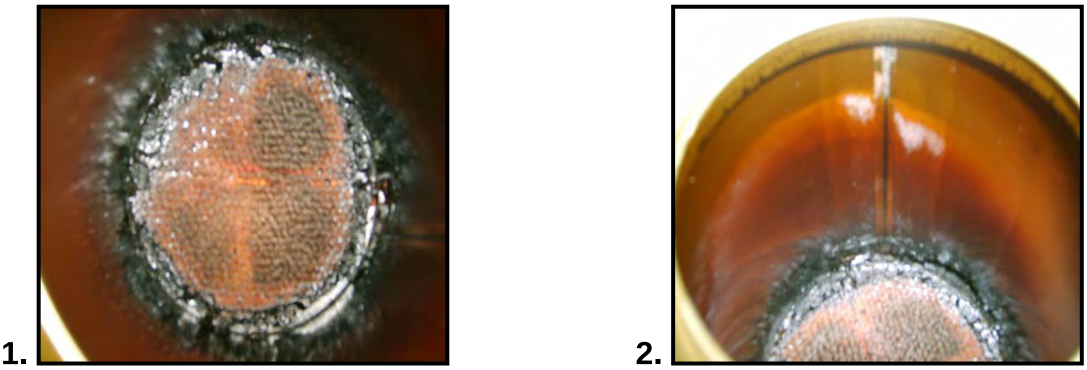


Figure D2.1 (b): 1. Top of Sample and 2. Side of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the wool carpet burnt in a small can for 2.5 minutes is presented in Figure D2.2. The extracted ion chromatogram shows five target compounds were able to be recovered and they were identified as toluene, ethylbenzene, *p*- and *m*-*x*ylene, *o*-xylene and propylbenzene. The target compound chromatogram is presented in Figure D2.3.

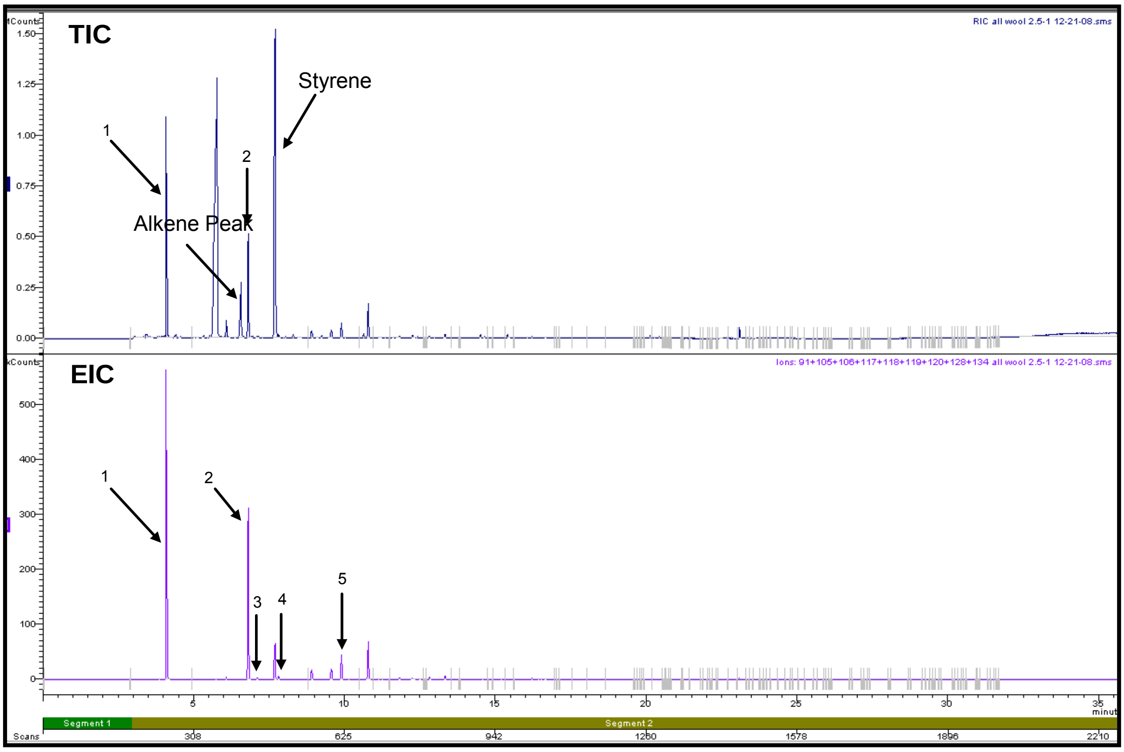


Figure D2.2: Total Ion Chromatogram and Extracted Ion Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene

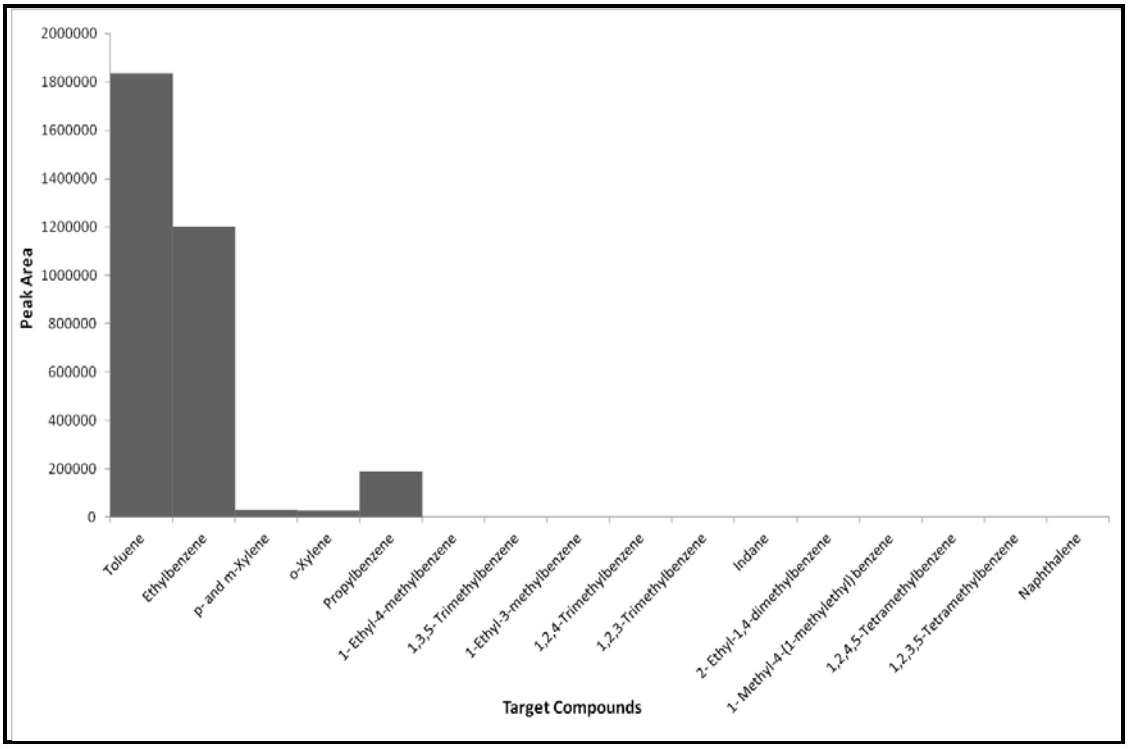


Figure D2.3: Target Compound Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure D2.4 (a-b).

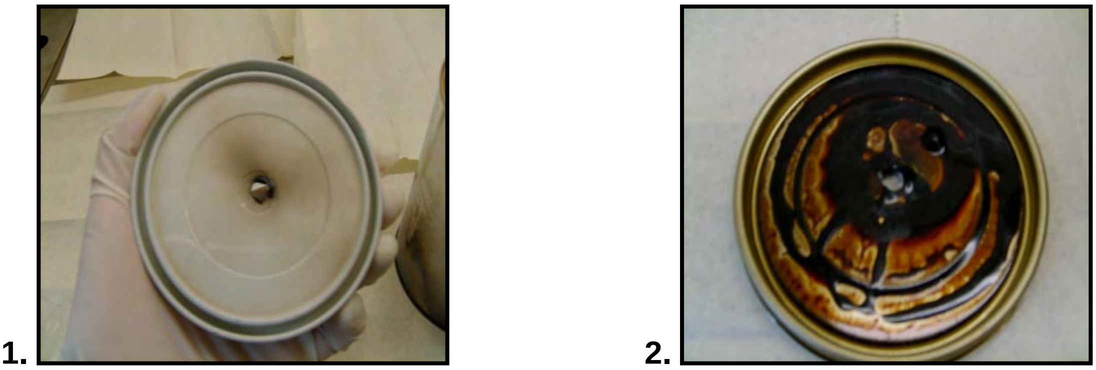


Figure D2.4 (a): 1. Top and 2. Underside of Lid after Burning

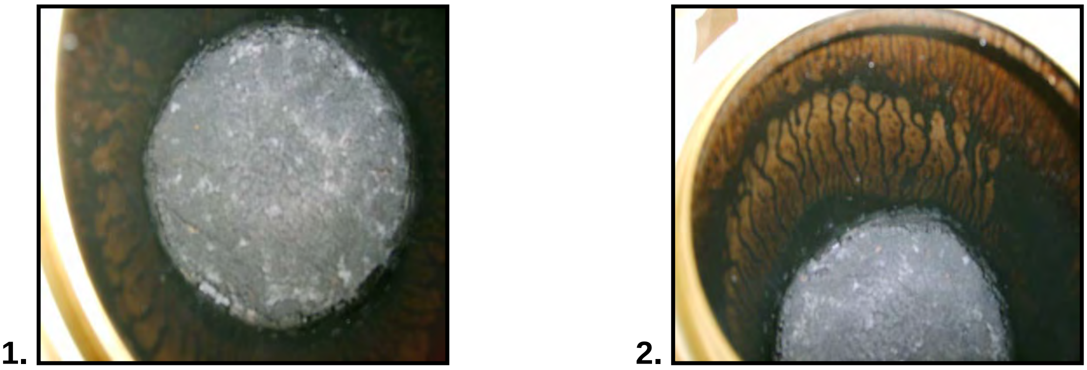


Figure D2.4 (b): 1. Top of Sample and 2. Side of Can after Burning

The total ion chromatogram and extracted ion chromatogram is shown in Figure D2.5. The most abundant peaks in the extracted ion chromatogram were toluene and ethylbenzene however *p*- and *m*-xylene, *o*-xylene and propylbenzene were also able to be recovered. The petrol target compounds recovered from the burning of wool in the small can for 5 minutes are presented in the target compound chromatogram in Figure D2.6.

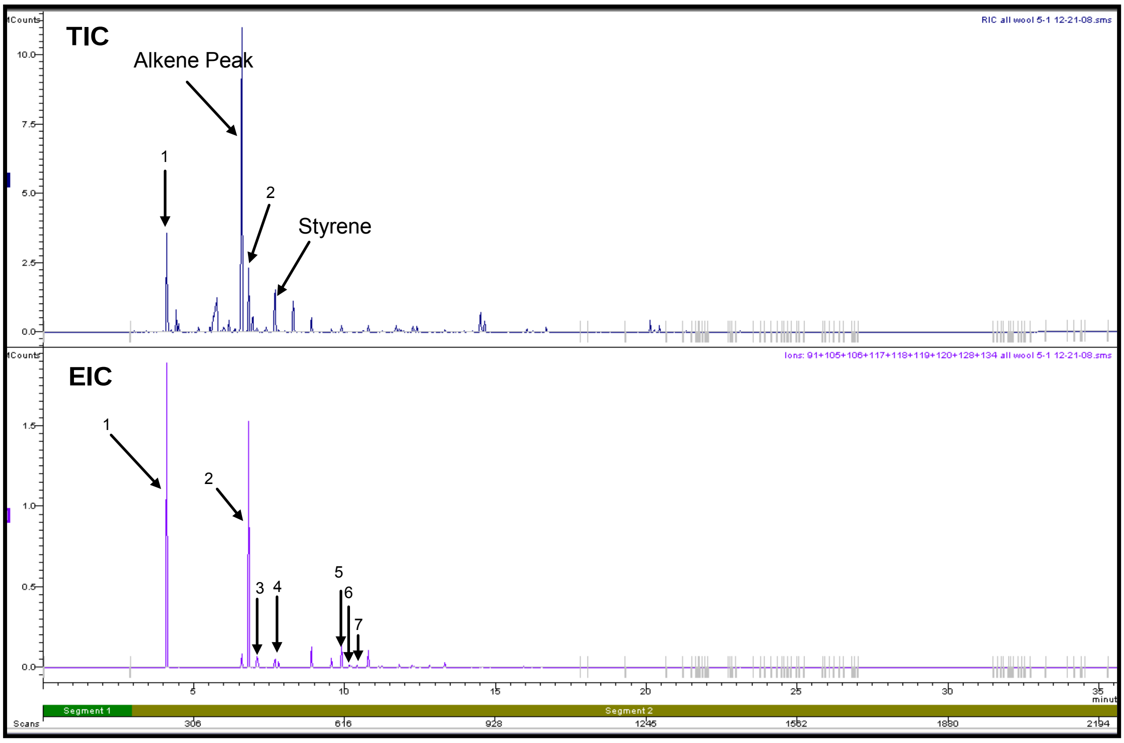


Figure D2.5: Total Ion Chromatogram and Extracted Ion Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 5 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene

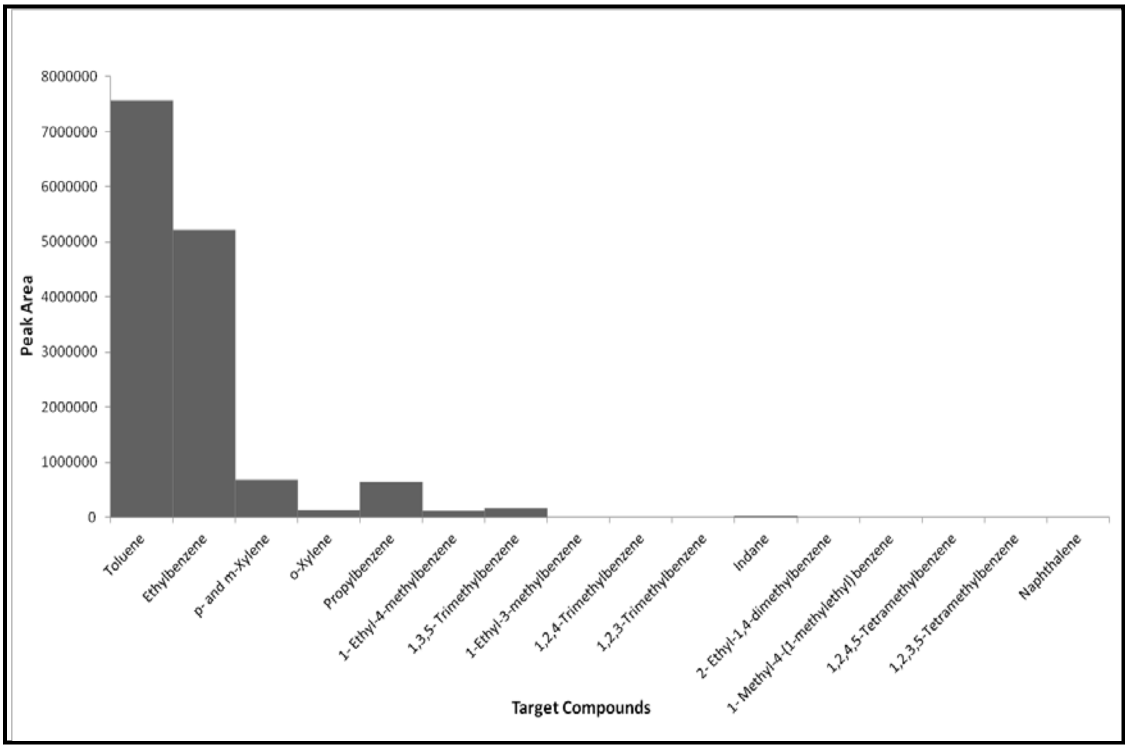


Figure D2.6: Target Compound Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure D2.7 (a-b).

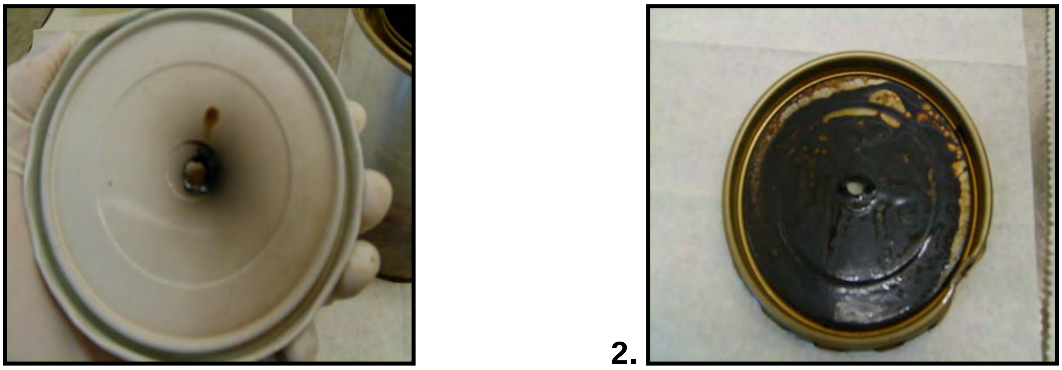

1. **2.**

Figure D2.7 (a): 1. Top and 2. Underside of Lid after Burning

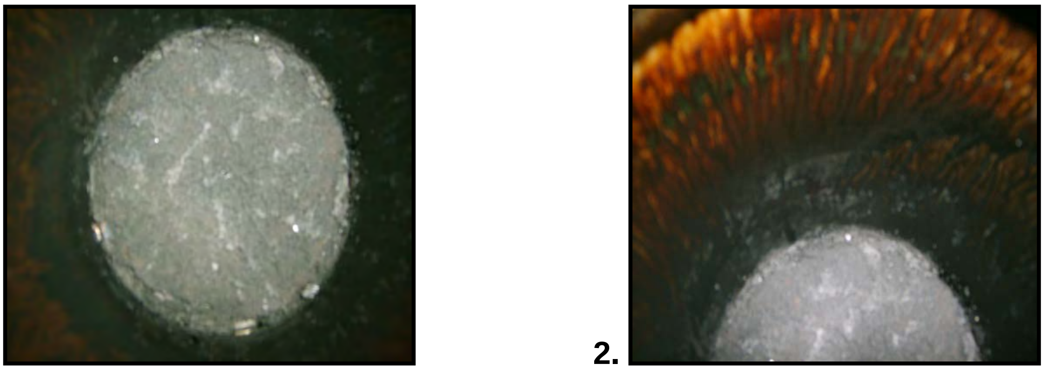

1. **2.**

Figure D2.7 (b): 1. Top of Sample and 2. Side of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the wool carpet burnt in a small can for 7.5 minutes can be seen in Figures D2.8. Toluene and ethylbenzene were the most abundant peaks recovered in the extracted ion chromatogram. The target compound chromatogram is presented in Figure D2.9.

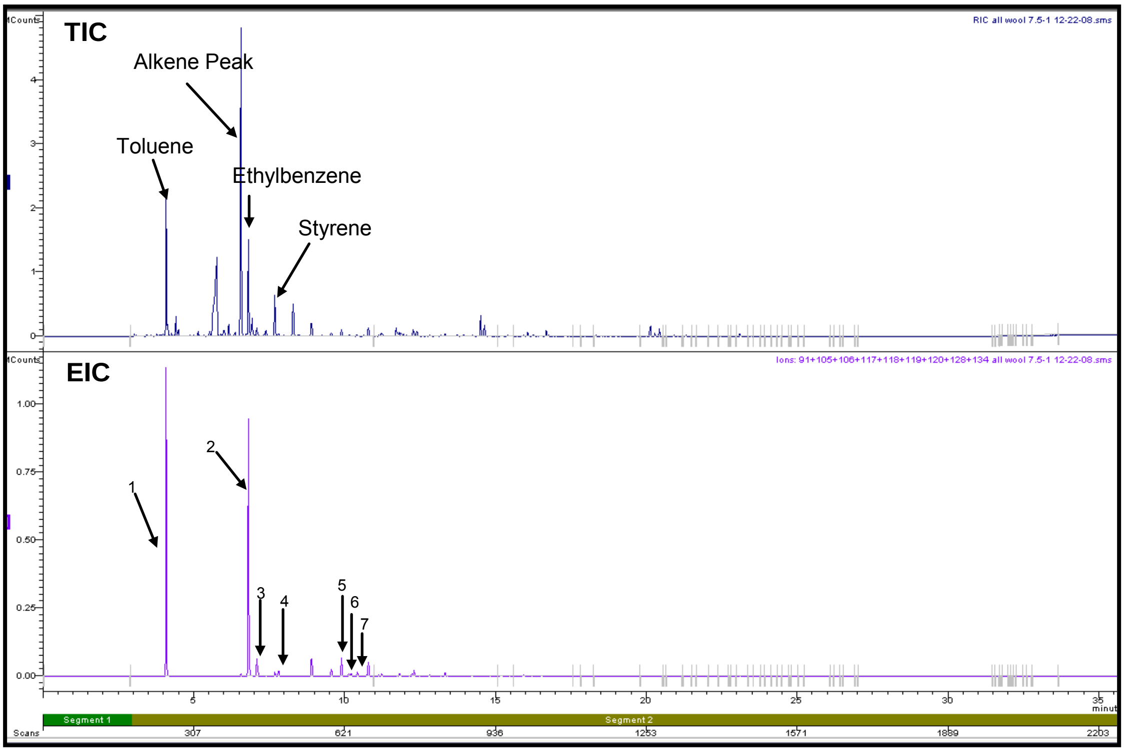


Figure D2.8: Total Ion Chromatogram and Extracted Ion Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3 *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene

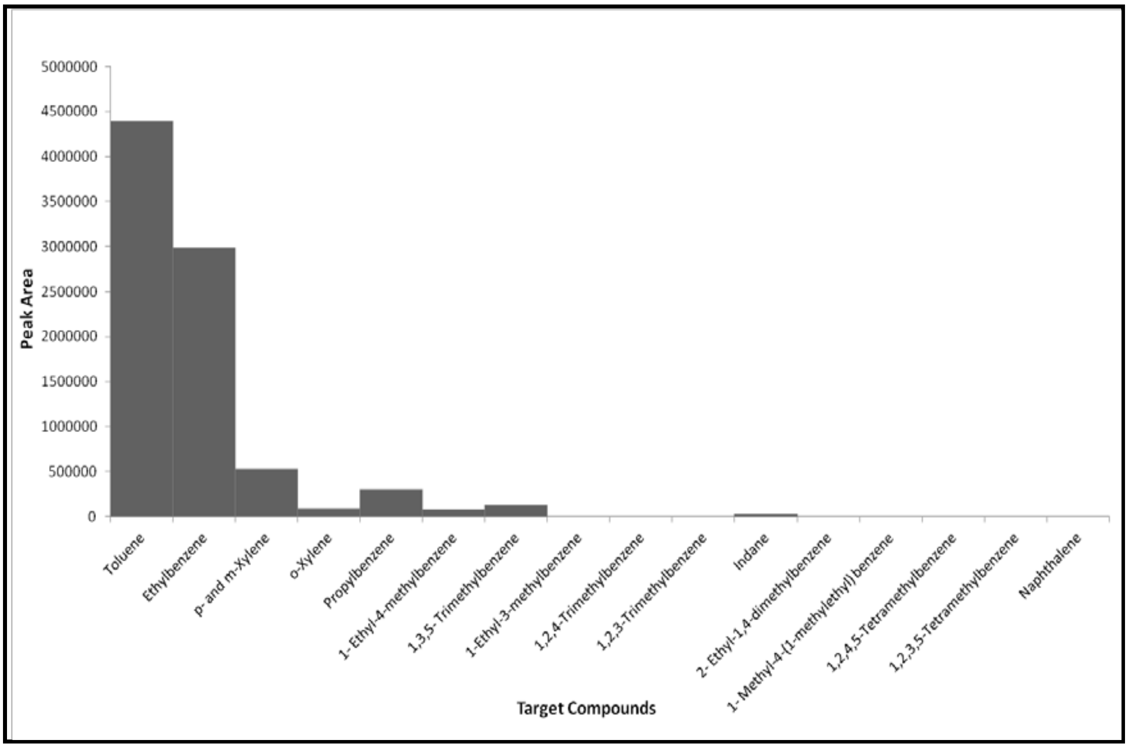


Figure D2.9: Target Compound Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

10 minute burn

A final 10 minute burn was conducted to determine the volatile organic compounds produced after a longer burn. Pictures of the samples after the 10 minute burn are presented in Figure D2.10 (a-b).

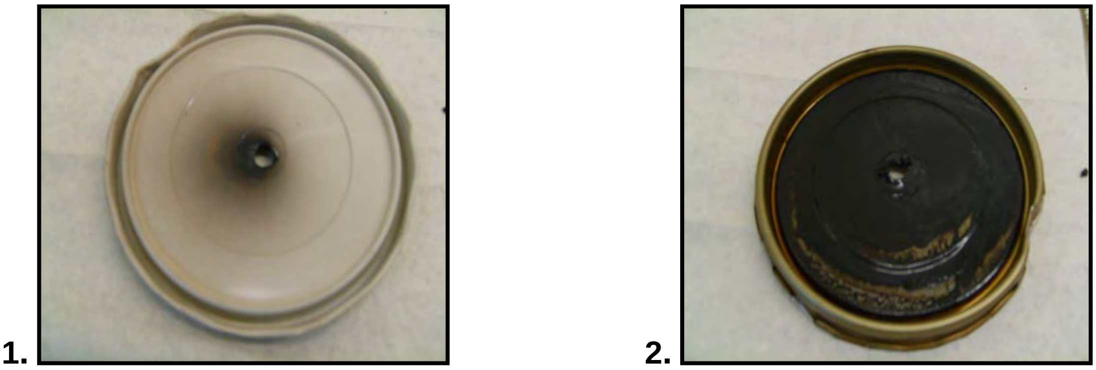


Figure D2.10 (a): 1. Top of Lid and 2. Underside of Lid after Burning

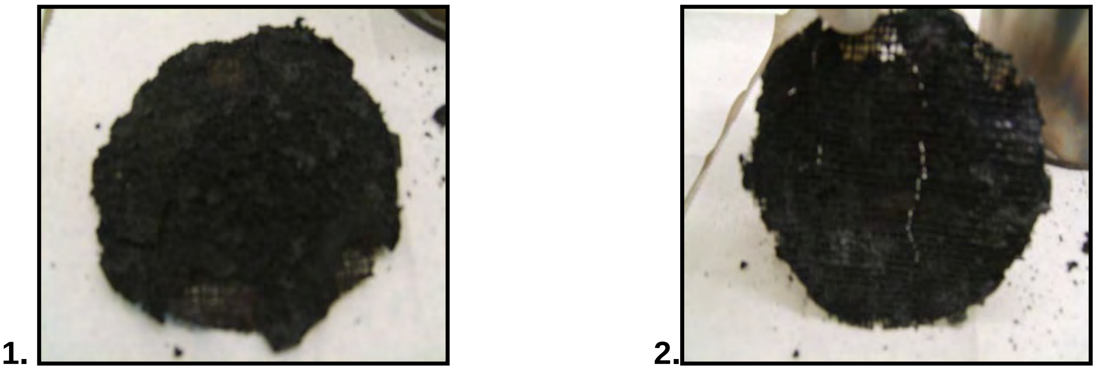


Figure D2.10 (b): 1. Top and 2. Underside of Sample after Burning

Figure D2.10 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this small can fire is presented in Figure D2.11. Toluene and ethylbenzene were the most abundant peaks recovered in the extracted ion chromatogram. The target compound chromatogram for the 10 minute can fire is presented in Figure D2.12.

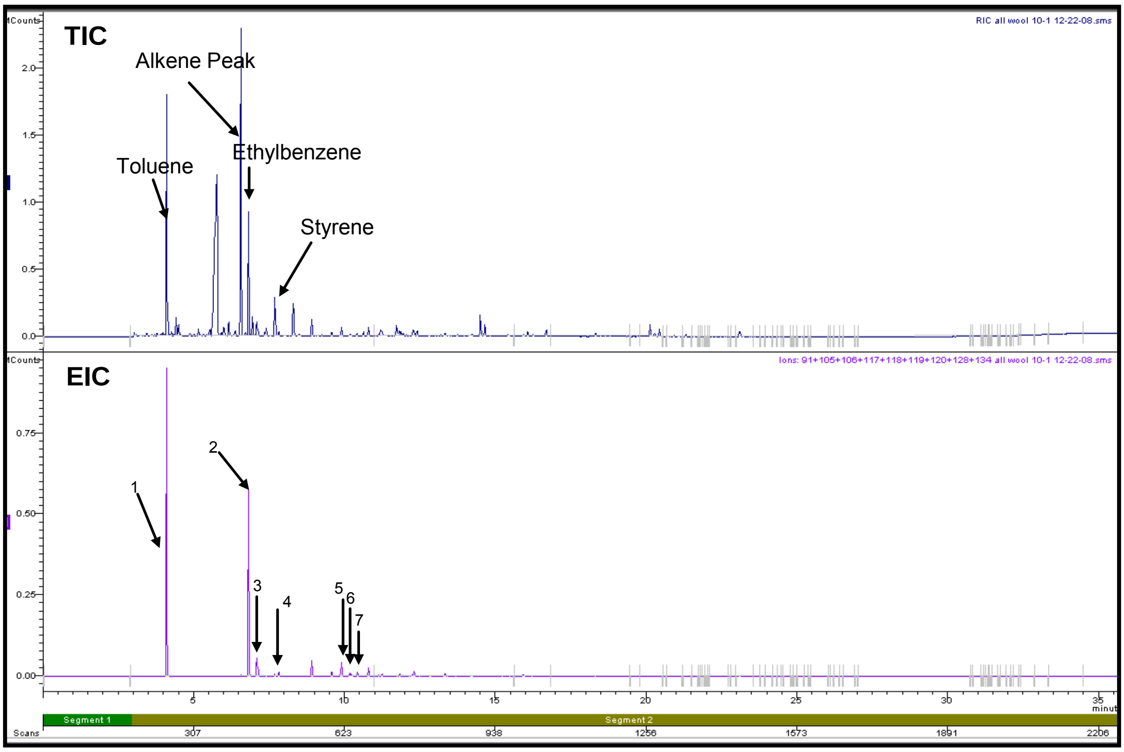


Figure D2.11: Total Ion Chromatogram and Extracted Ion Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 10 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene

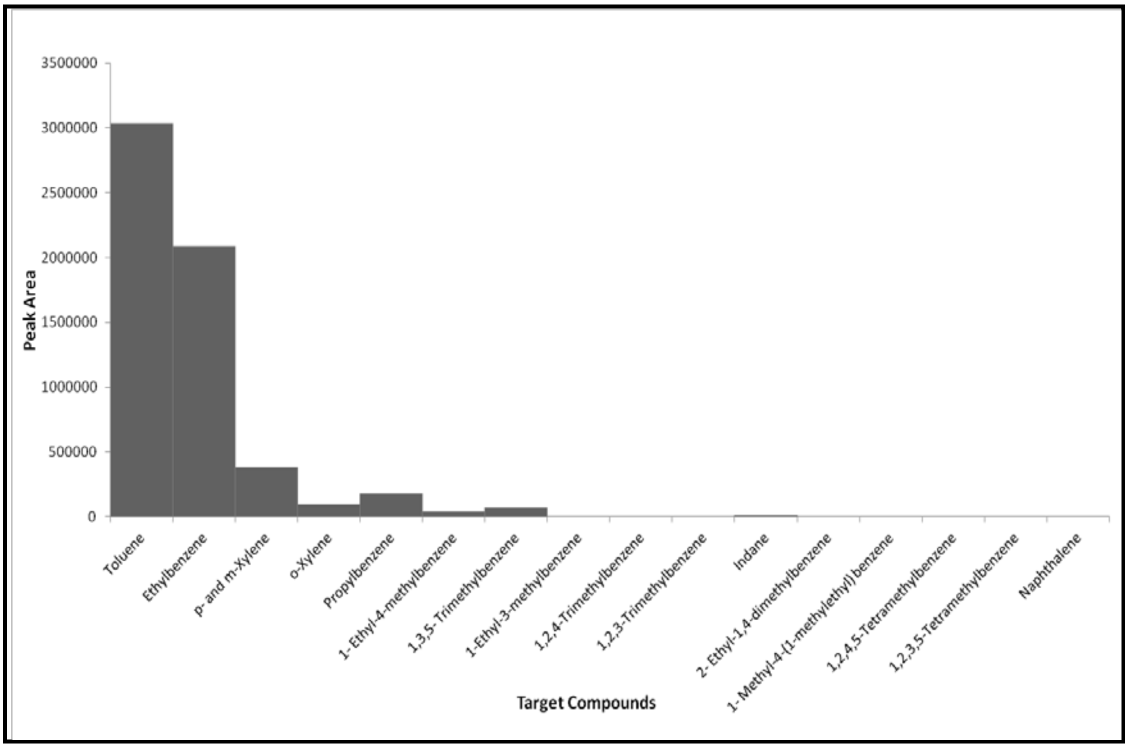
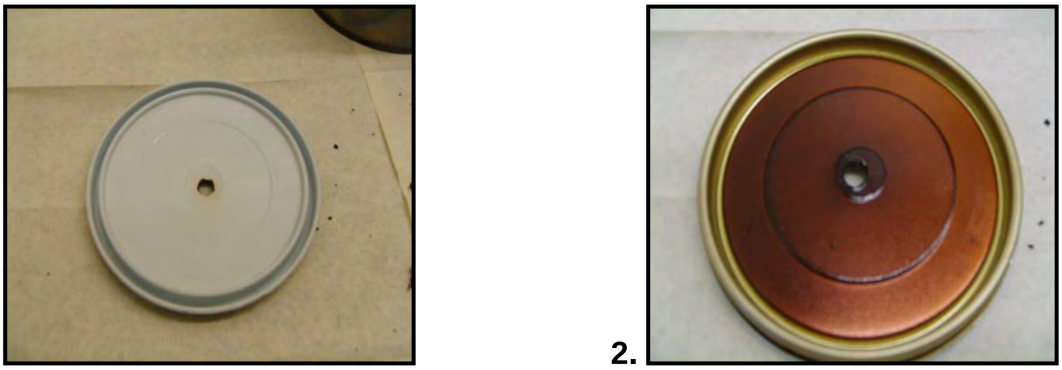


Figure D2.12: Target Compound Chromatogram of a Wool Carpet Swatch burnt in a Can with Lid On for 10 minutes

50-50 Polypropylene-wool Carpet

2.5 minute burn

Pictures of the samples after the 2.5 minute burn are presented in Figure D3.1 (a-b).



1. **2.**

Figure D3.1 (a): 1. Top and 2. Underside of Lid after Burning

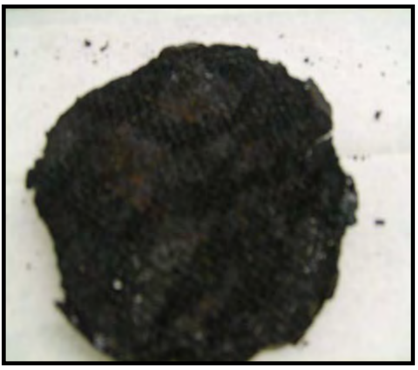
1.  2. 

Figure D3.1 (b): 1. Top and 2. Underside of Sample after Burning

Figure D3.1 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the 50-50 polypropylene-wool carpet burnt in a small can for 2.5 minutes, is presented in Figure D3.2. The extracted ion chromatogram shows five target compounds were able to be recovered and they were identified as toluene, ethylbenzene, *p*- and *m*-xylene, *o*-xylene and propylbenzene. The target compound chromatogram is presented in Figure D3.3.

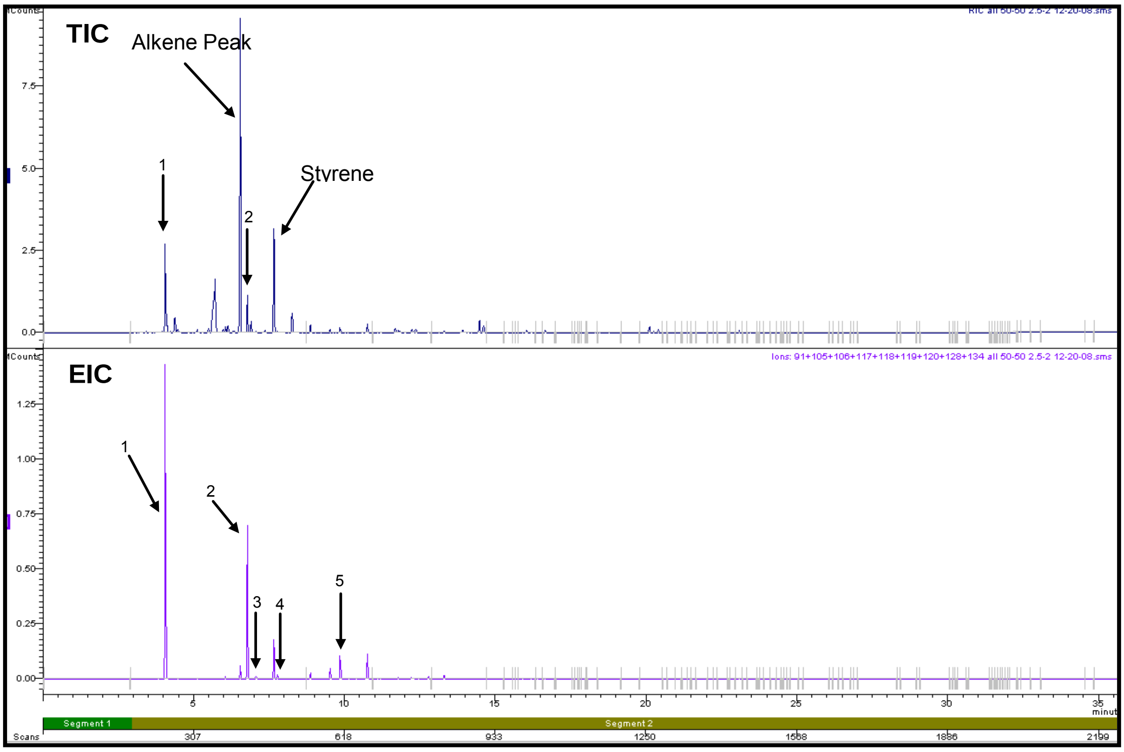


Figure D3.2: Total Ion Chromatogram and Extracted Ion Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=propylbenzene

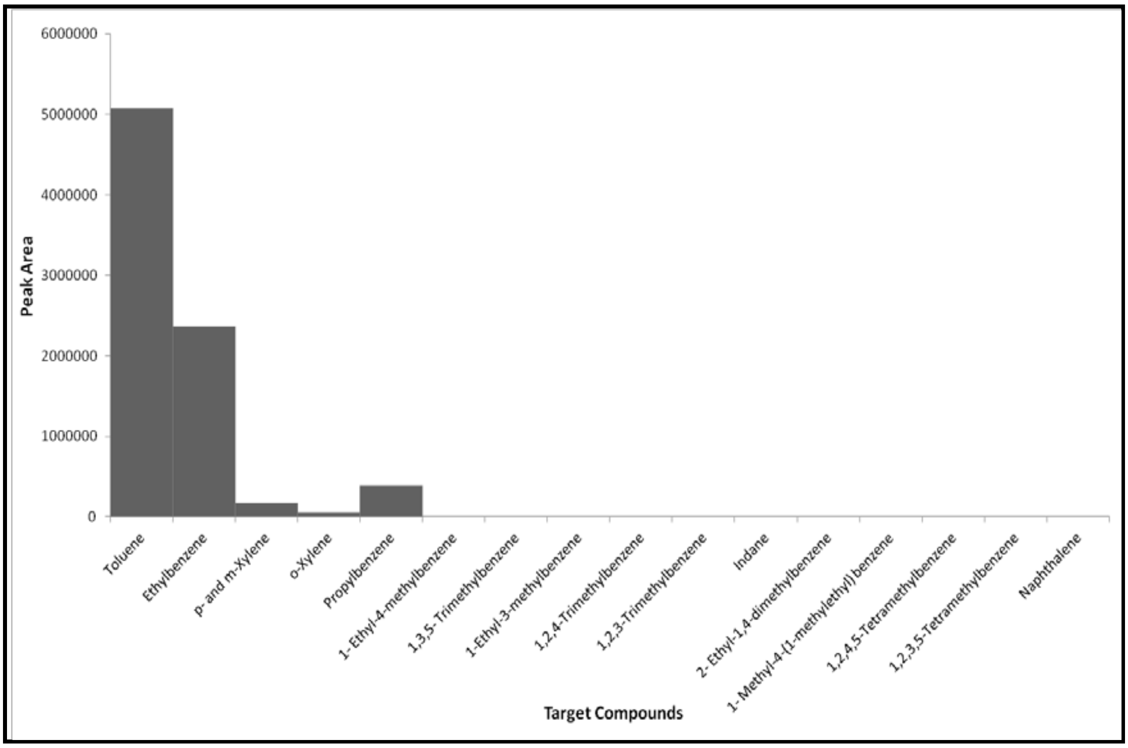


Figure D3.3: Target Compound Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure D3.4 (a-b).

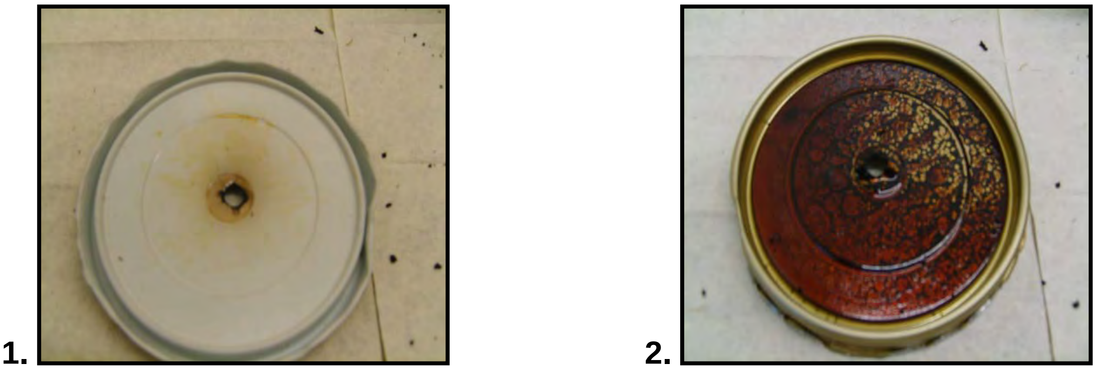


Figure D3.4 (a): 1. Top and 2. Underside of Lid after Burning

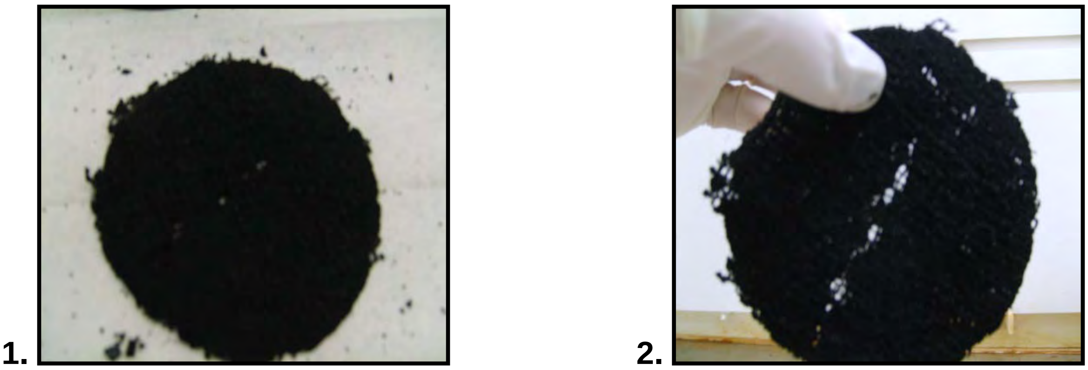


Figure D3.4 (b): 1. Top of Sample and 2. Side of Can after Burning

Figure D3.4 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram is shown in Figure D3.5. The extracted ion chromatogram showed the characteristic toluene, ethylbenzene and xylene peak pattern which is quite distinctive for petrol. On closer inspection, a few other target compound were also able to be recovered and these include propylbenzene, 1-ethyl-4-methylbenzene and 1,3,5-trimethylbenzene. These recovered target compounds are presented in the target compound chromatogram in Figure D3.6.

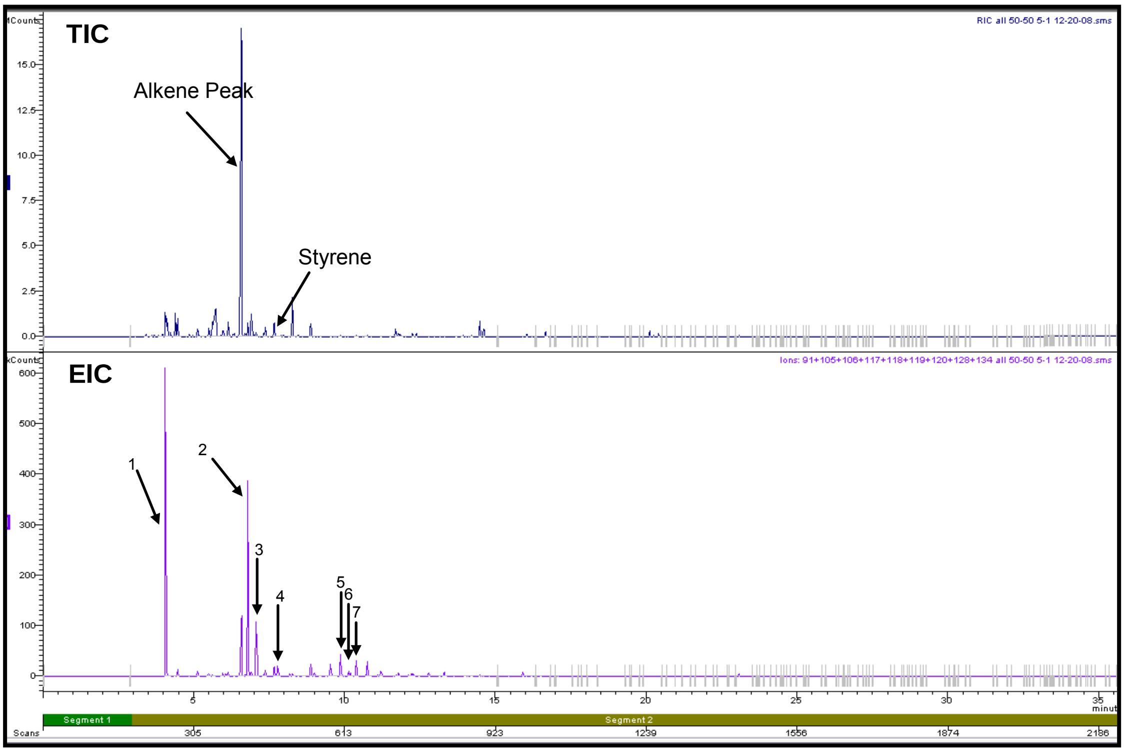


Figure D3.5: Total Ion Chromatogram and Extracted Ion Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 5 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene

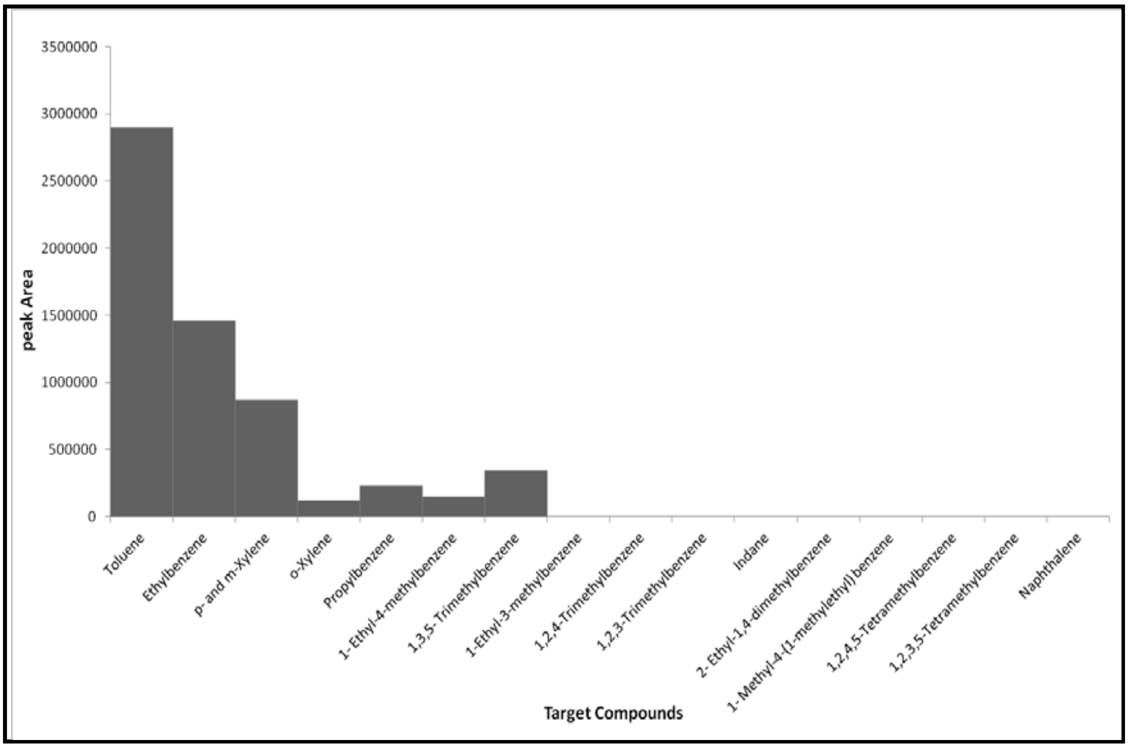


Figure D3.6: Target Compound Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 2.5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure D3.7 (a-b).

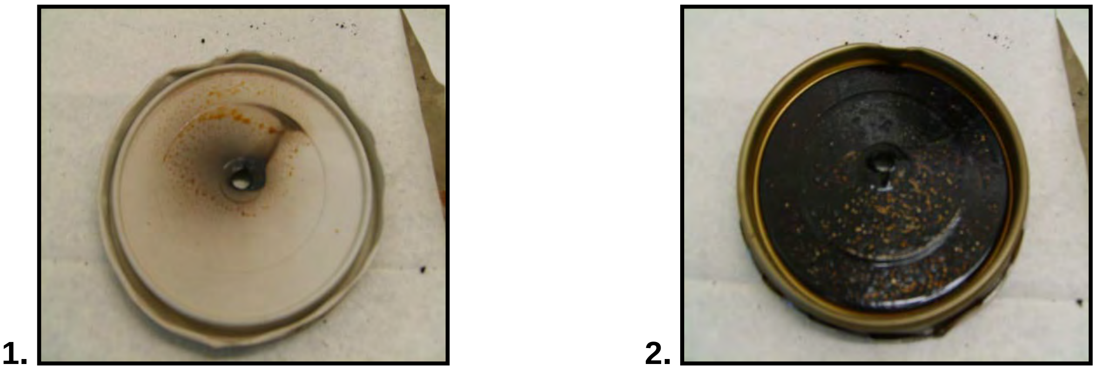


Figure D3.7 (a): 1. Top and 2. Underside of Lid after Burning

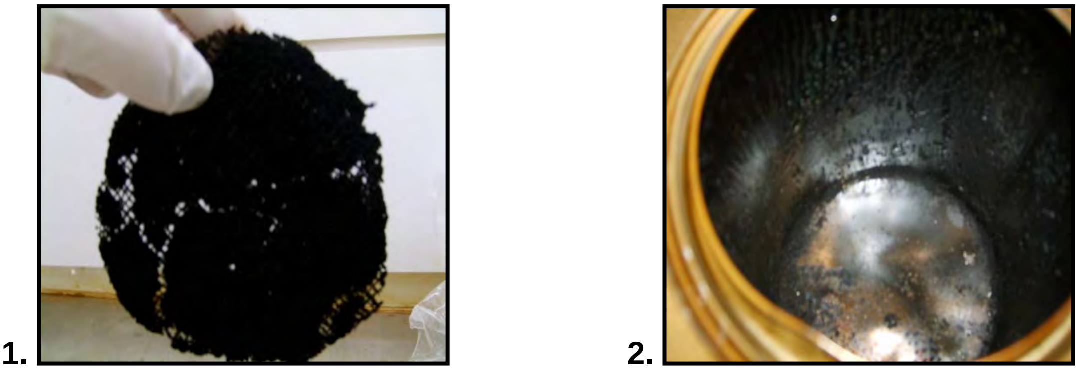

1. 2.

Figure D3.7 (b): 1. Underside of Sample and 2. Side of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the 50-50 polypropylene-wool blended carpet burnt in a small can for 7.5 minutes can be seen in Figures D3.8. The EIC showed toluene, ethylbenzene, *p*- and *m*-*x*ylene, *o*-xylene, propylbenzene, 1-ethyl-4-methylbenzene and 1,3,5-trimethylbenzene were able to be recovered. These recovered target compounds are presented in the target compound chromatogram in Figure D3.9.

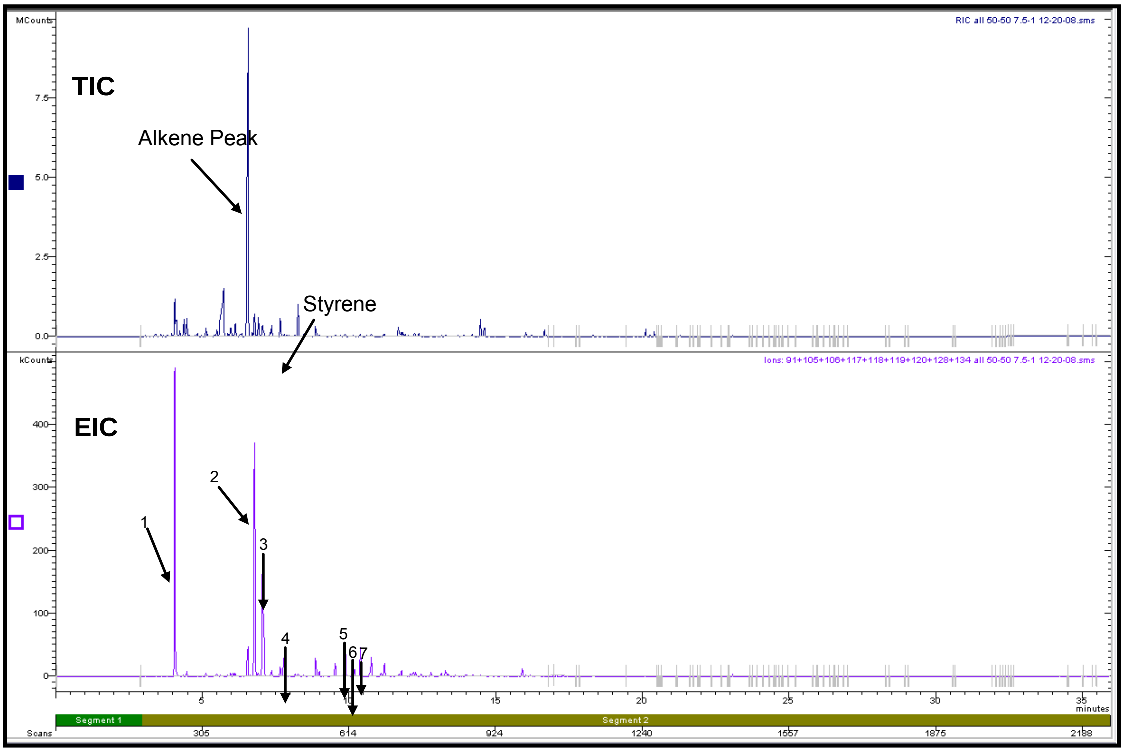


Figure D3.8: Total Ion Chromatogram and Extracted Ion Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 7.5 minutes Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene

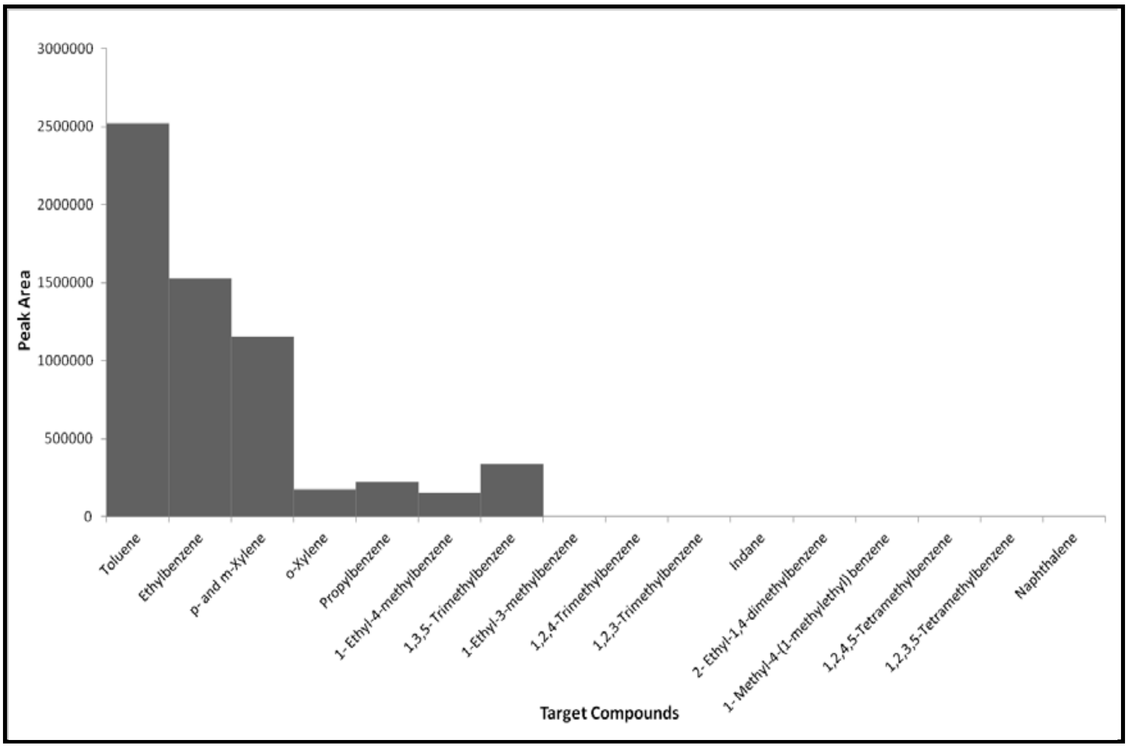
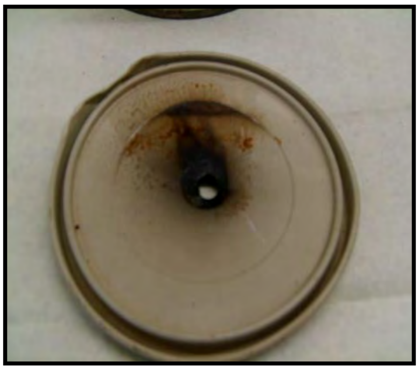


Figure D3.9: Target Compound Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 7.5 minutes

10 minute burn

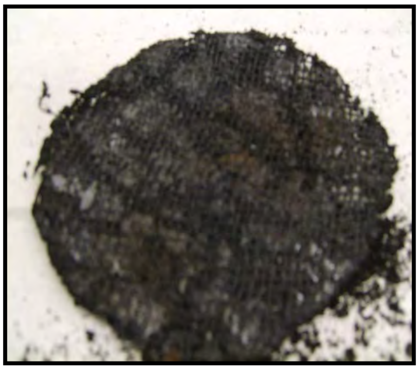
The final small can fire conducted to determine the effect of burning time on the recovery of target compounds from the blended carpet sample was a 10 minute burn. The pictures from this burn are presented in Figures D3.10 (a-b).

1.



2.

Figure D3.10 (a): 1. Top of Lid and 2. Underside of Lid after Burning

1. 

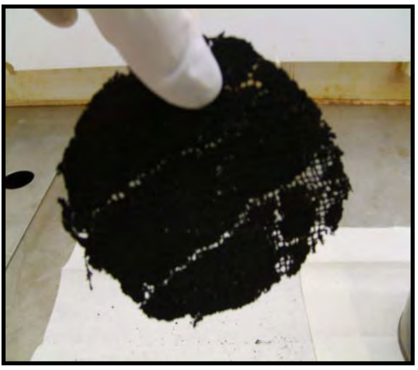
2. 

Figure D3.10 (b): 1. Top and 2. Underside of Sample after Burning

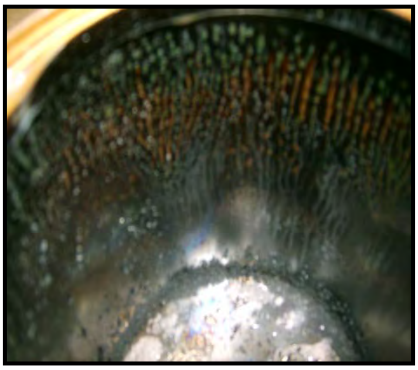
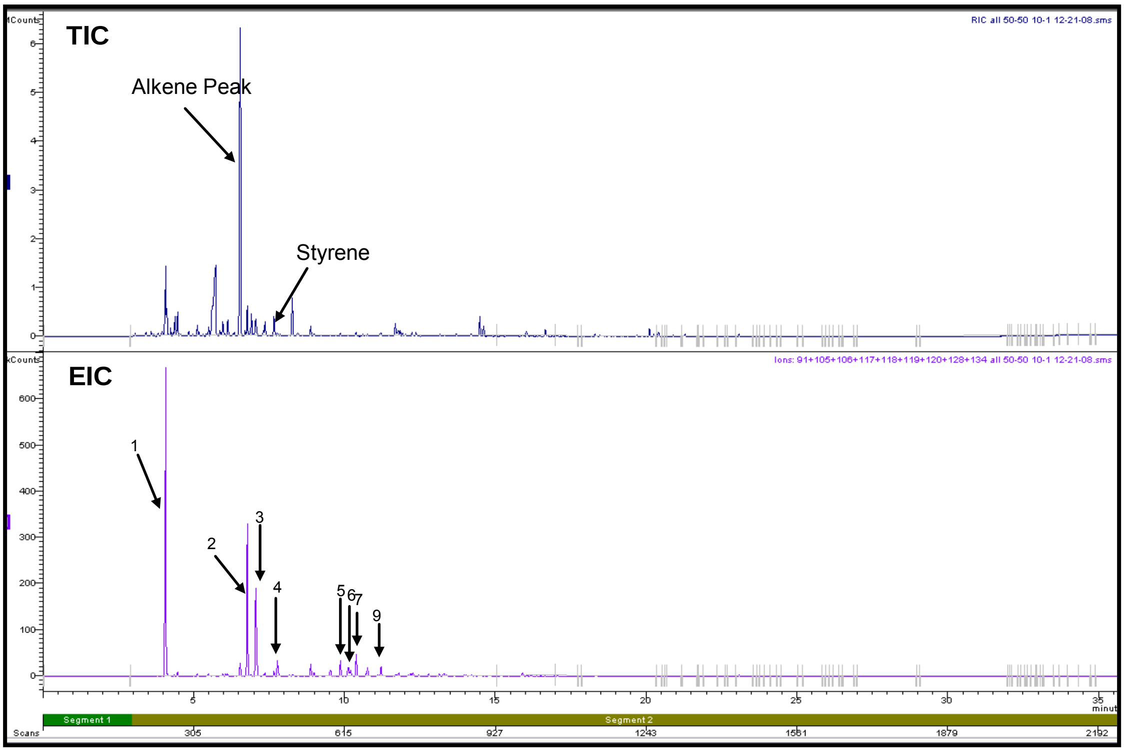


Figure D3.10 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this small can fire is presented in Figure D3.11. The extracted ion chromatogram showed that toluene, ethylbenzene and *p*- and *m*-xylene and *o*-xylene were recovered in abundance. However, on closer inspection, a few other target compound were also able to be recovered and these include propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene. These recovered target compounds are presented in the target compound chromatogram in Figure D3.12.



FigureD3.11: Total Ion Chromatogram and Extracted Ion Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 10 minutes

Key: 1= Toluene, 2= Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 9=1,2,4-Trimethylbenzene

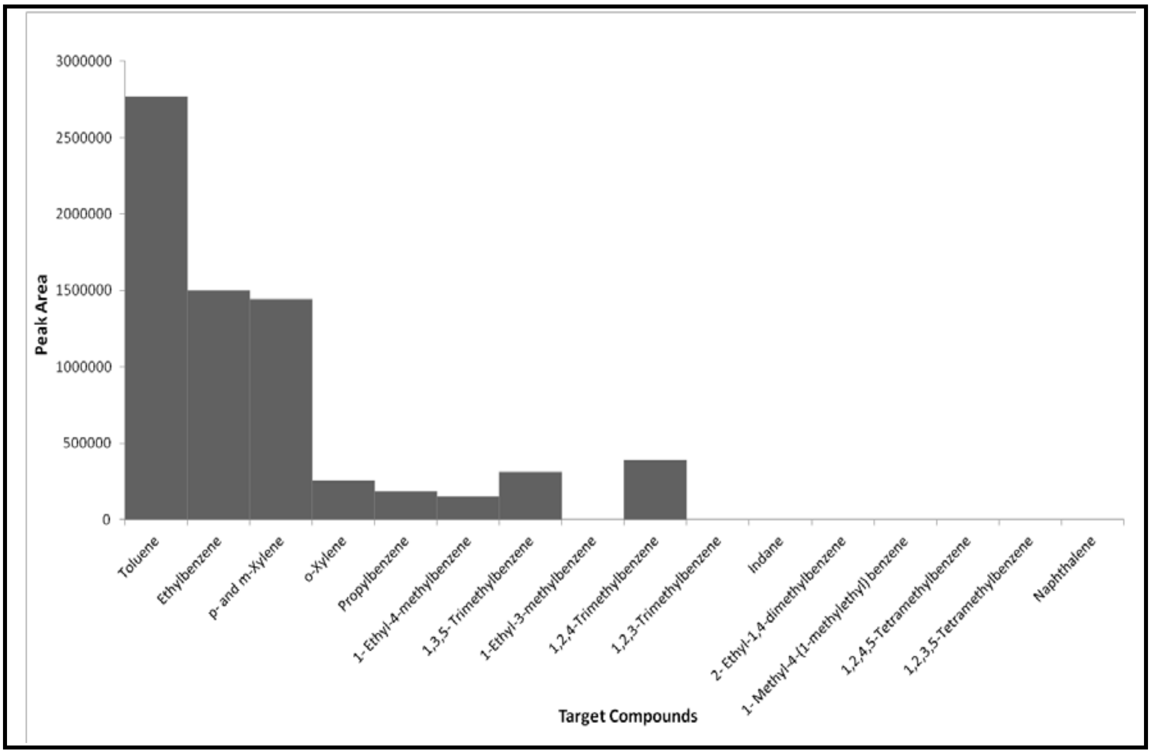
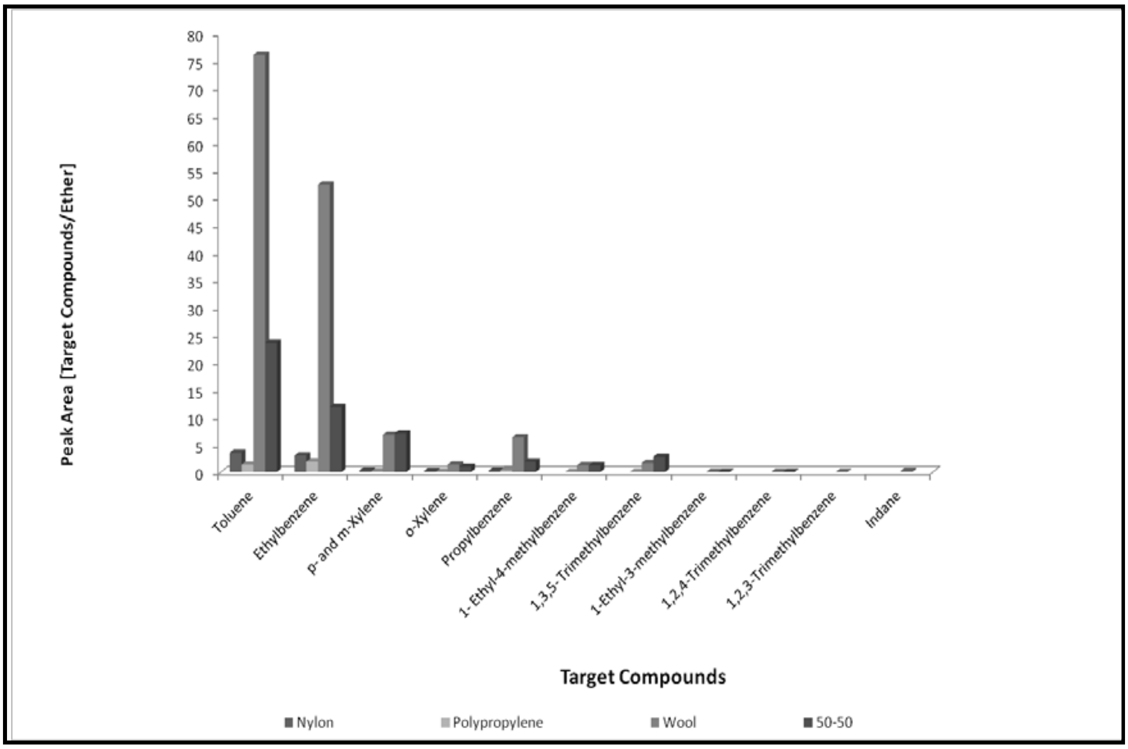


Figure D3.12: Target Compound Chromatogram of a 50-50 Polypropylene-Wool Carpet Swatch burnt in a Can with Lid On for 10 minutes

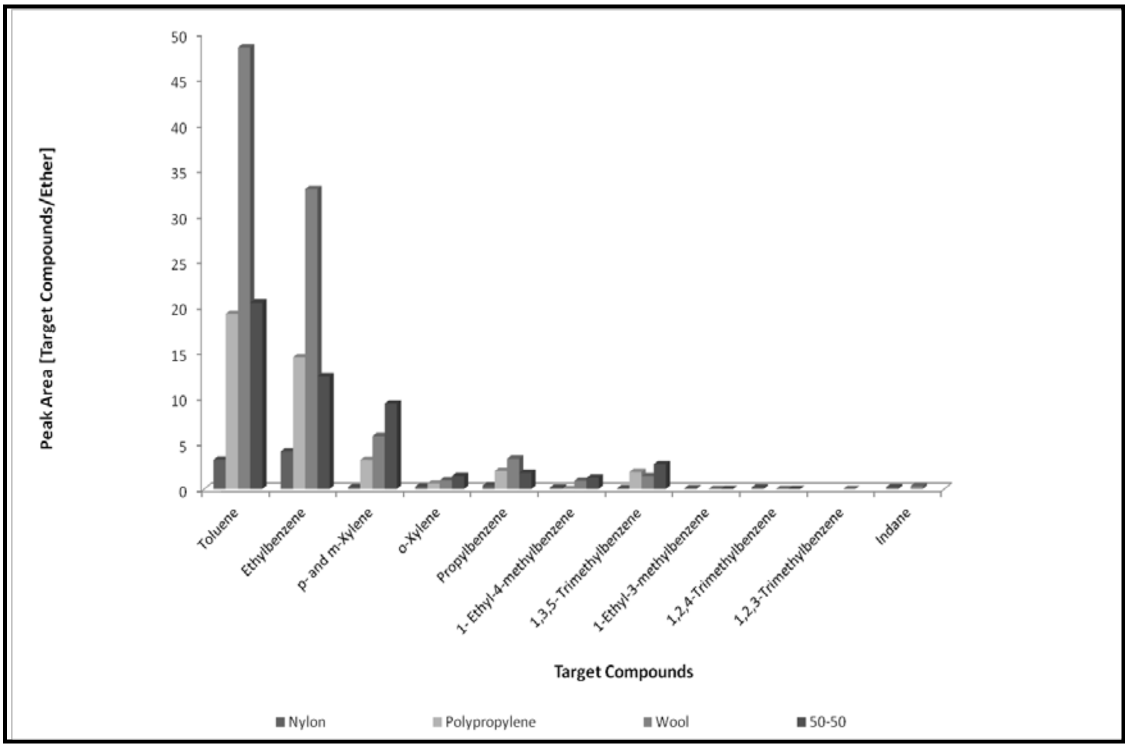
APPENDIX E

COMPARISON OF TARGET COMPOUNDS RECOVERED FOR ALL CARPETS BURNT IN SMALL CAN FIRES

Figures E1.1 to E1.3 below show a comparison of the target compounds recovered and their abundances for each of the carpets for the 5, 7.5 and 10 minute burns.



Figures E1.1: Target Compound Chromatogram for all Carpets when Burnt in the Small Can with Lid On for 5 minutes



Figures E1.2: Target Compound Chromatogram for all Carpets when Burnt in the Small Can with Lid On for 7.5 minutes

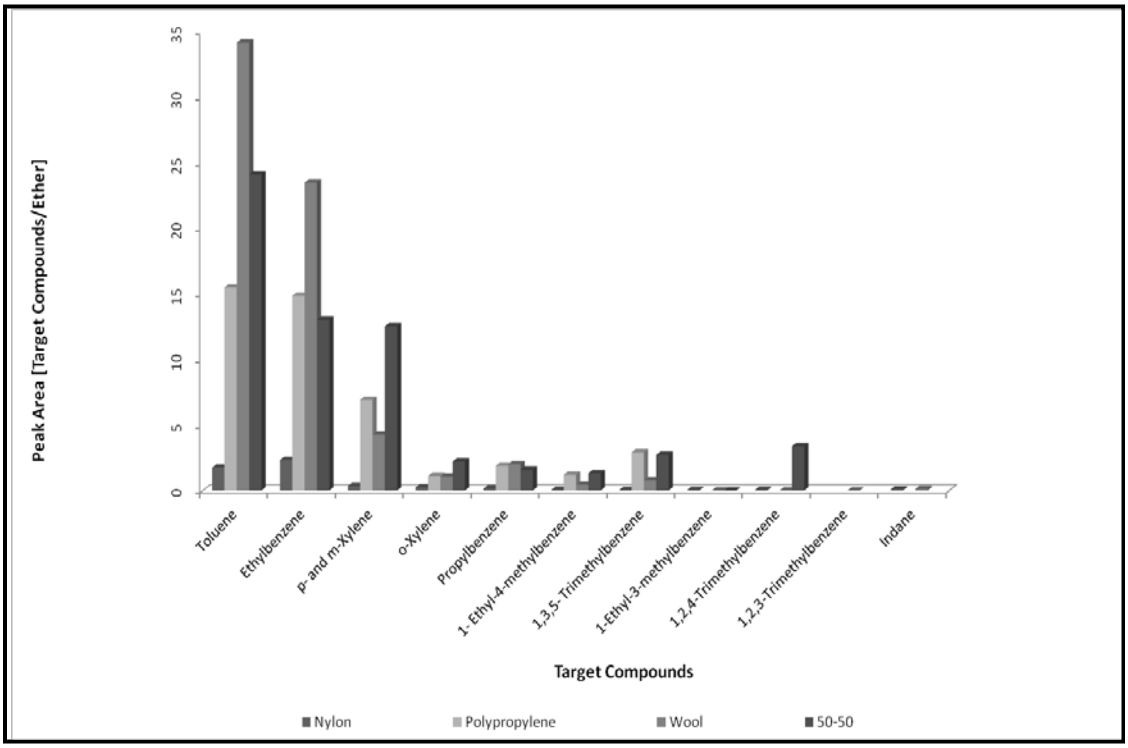


Figure E1.3: Target Compound Chromatogram for all Carpets when Burnt in the Small Can with Lid On for 10 minutes

APPENDIX F

BURNING TIME EXPERIMENTS FOR FURNITURE FOAM AND UNDERLAY

Furniture Foam

Similar to the carpets, foam was burnt over a range of times including 2.5, 5, 7.5 and 10 minutes.

2.5 minute burn

Pictures of the samples after the 2.5 minute burn are presented in Figure F1.1 (a-c).

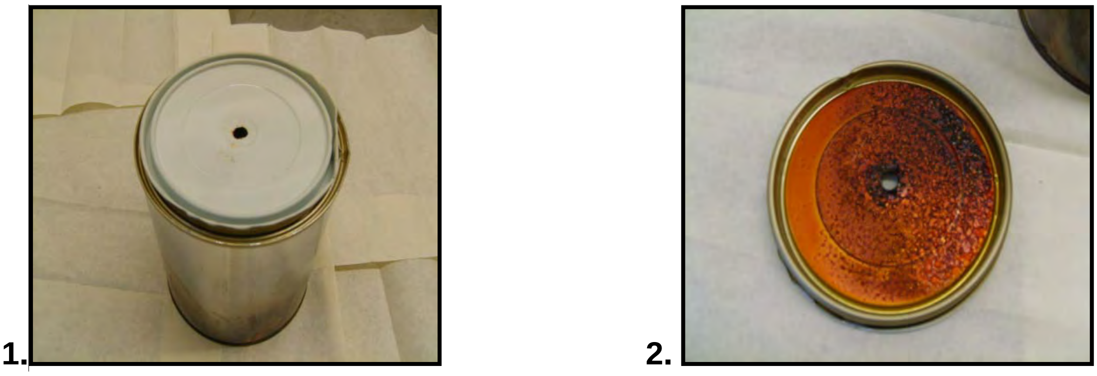


Figure F1.1 (a): 1. Top and 2. Underside of Lid after Burning

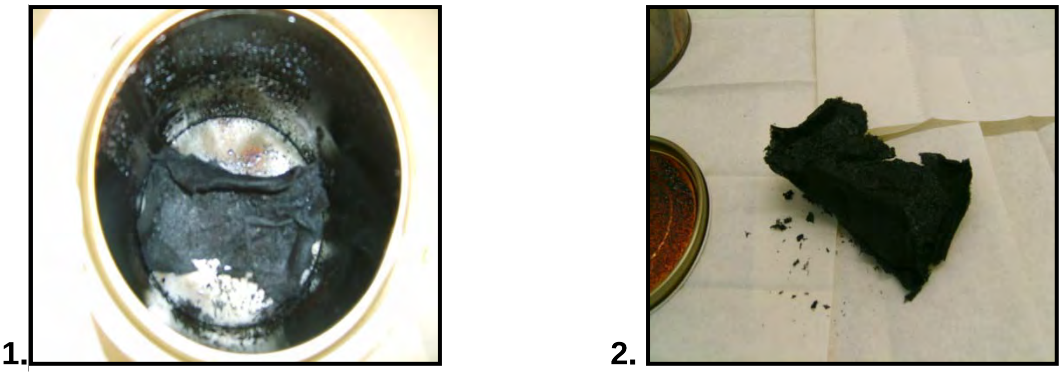


Figure F1.1 (b): 1. Sample in Can 2. Sample after Burning

Figure F1.1 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram produced from the burning of this sample is presented in Figure F1.2. Toluene was the only target compound identified in this extracted ion chromatogram.

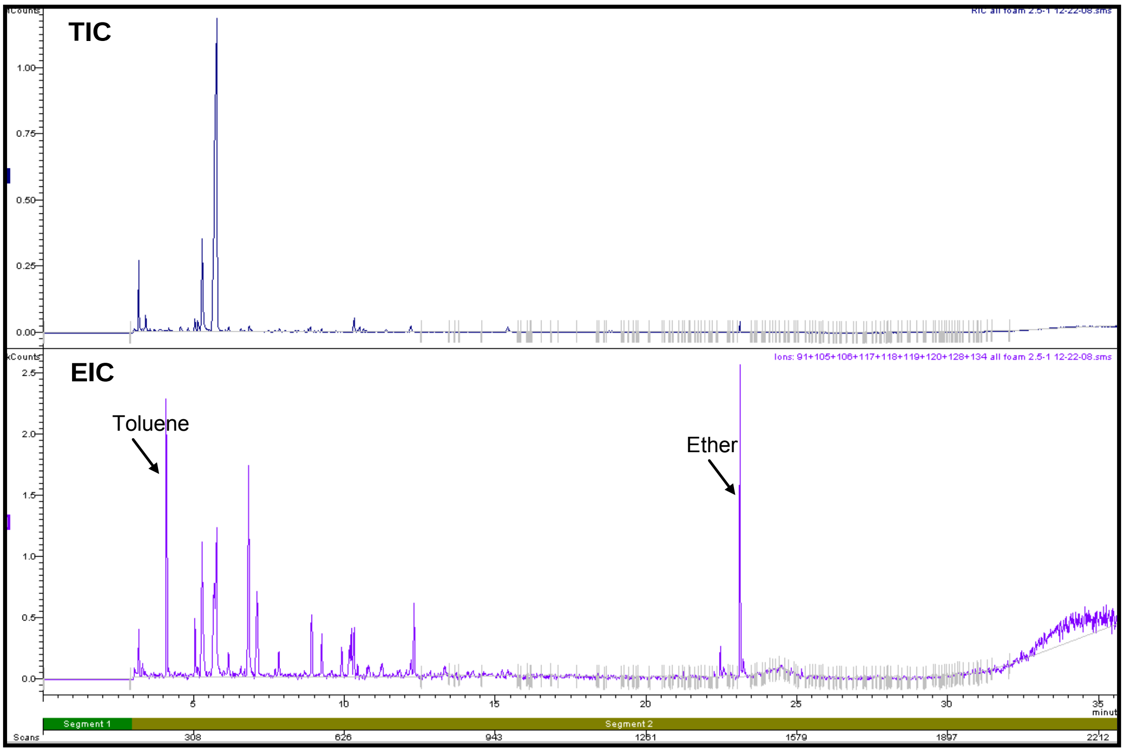


Figure F1.2: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Burnt in a Can with Lid On for 2.5 minutes

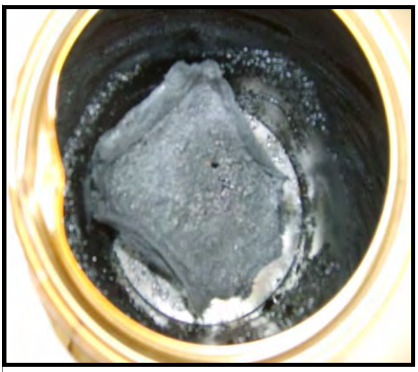
5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure F1.3 (a-c).

1. 

2. 

Figure F1.3 (a): 1. Top and 2. Underside of Lid after Burning

1. 

2. 

Figure F1.3 (b): 1. Sample in Can 2. Sample after Burning

Figure F1.3 (c): Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the foam sample burnt in the small can for 5 minutes is presented in Figure F1.4. Toluene, ethylbenzene and *p*- and *m*-xylene were the only target compounds were identified in this extracted ion chromatogram. The target compound chromatogram is presented in Figure F1.5.

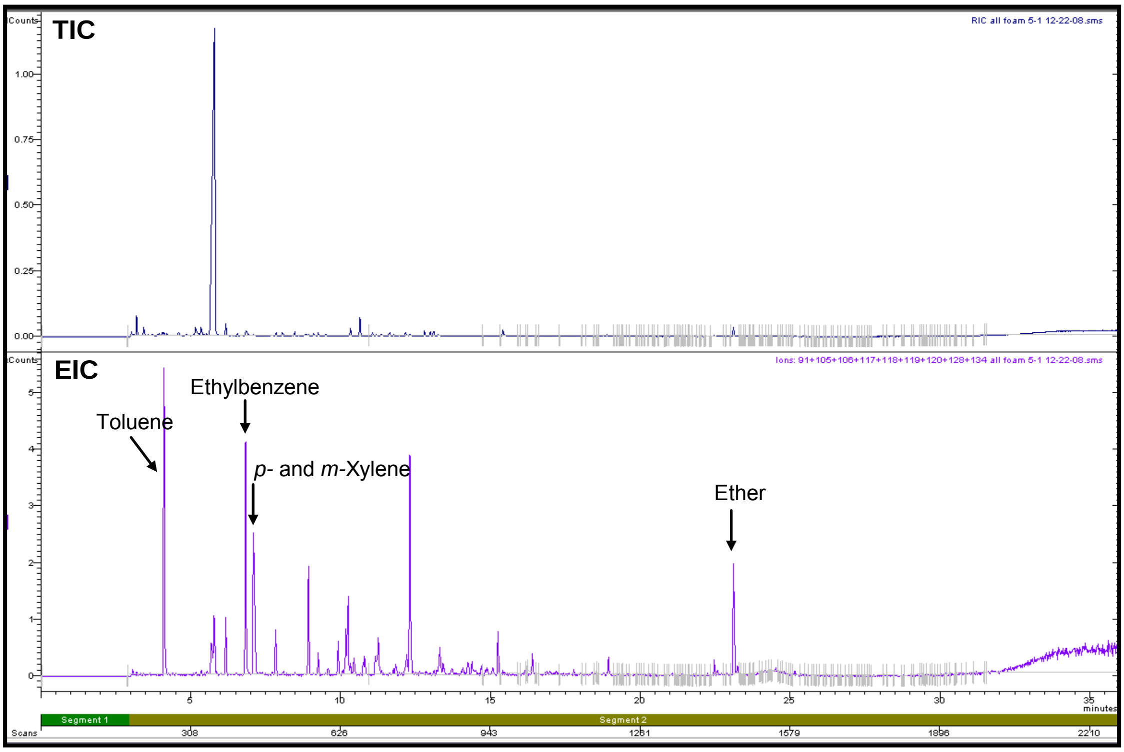


Figure F1.4: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Burnt in a Can with Lid On for 5 minutes

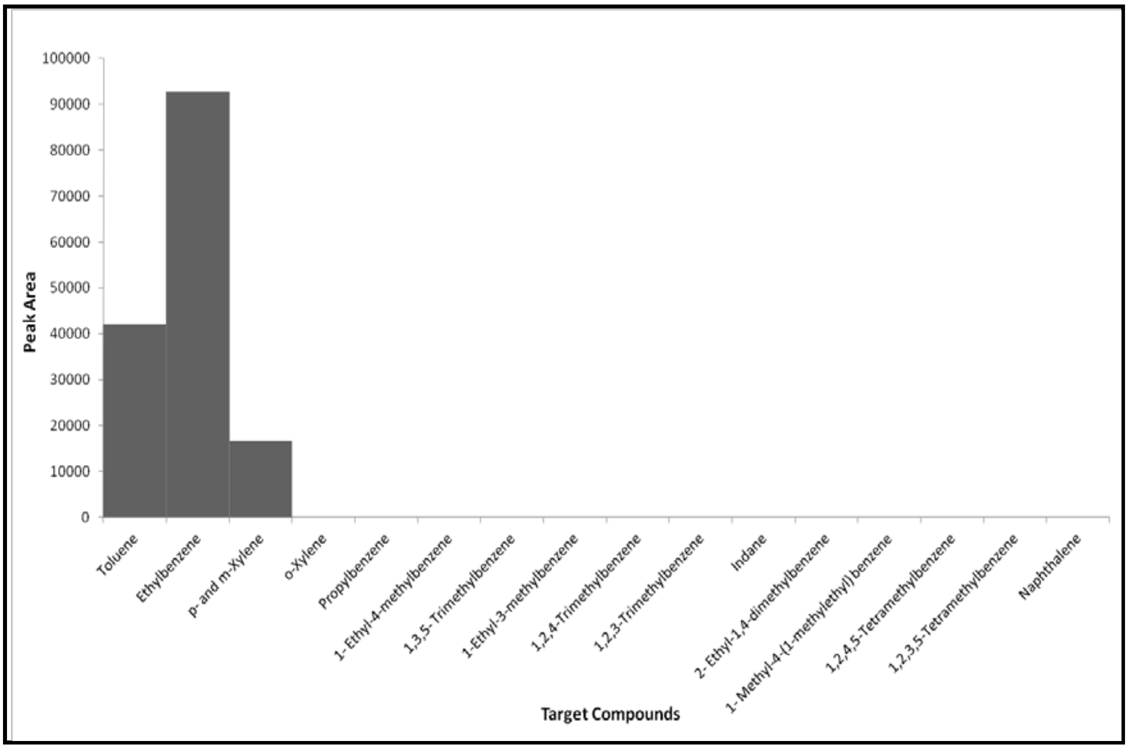


Figure F1.5: Target Compound Chromatogram of Foam Burnt in a Can with Lid On for 5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure F1.6 (a-b).

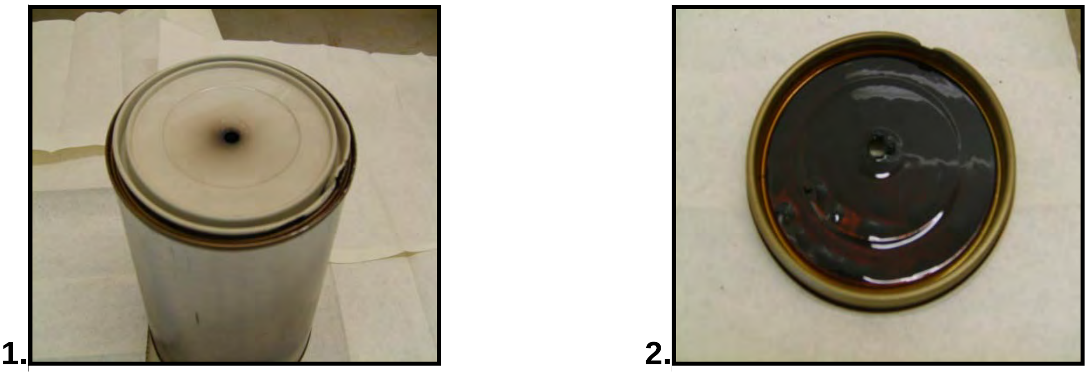


Figure F1.6 (a): 1. Top and 2. Underside of Lid after Burning

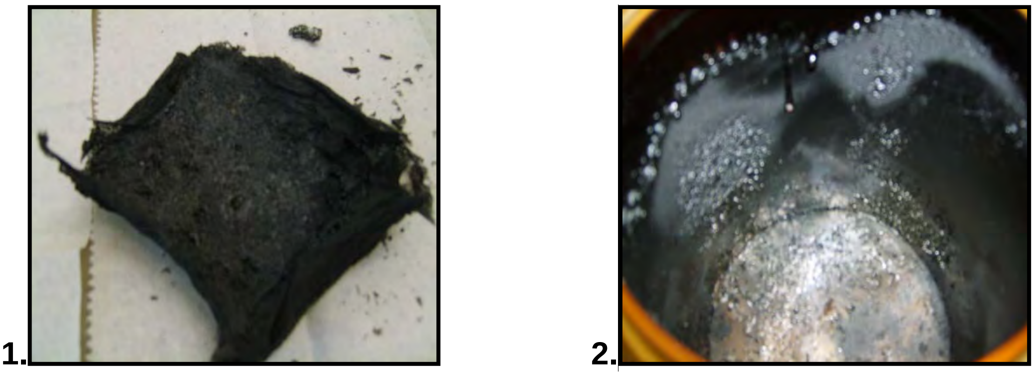


Figure F1.6 (b): 1. Sample after Burning 2. Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram are presented in Figure F1.7. Toluene, ethylbenzene, *p*- and *m*-xylene and *o*-xylene were the four target compounds identified in this extracted ion chromatogram. The target compound chromatogram is presented in Figure F1.8.

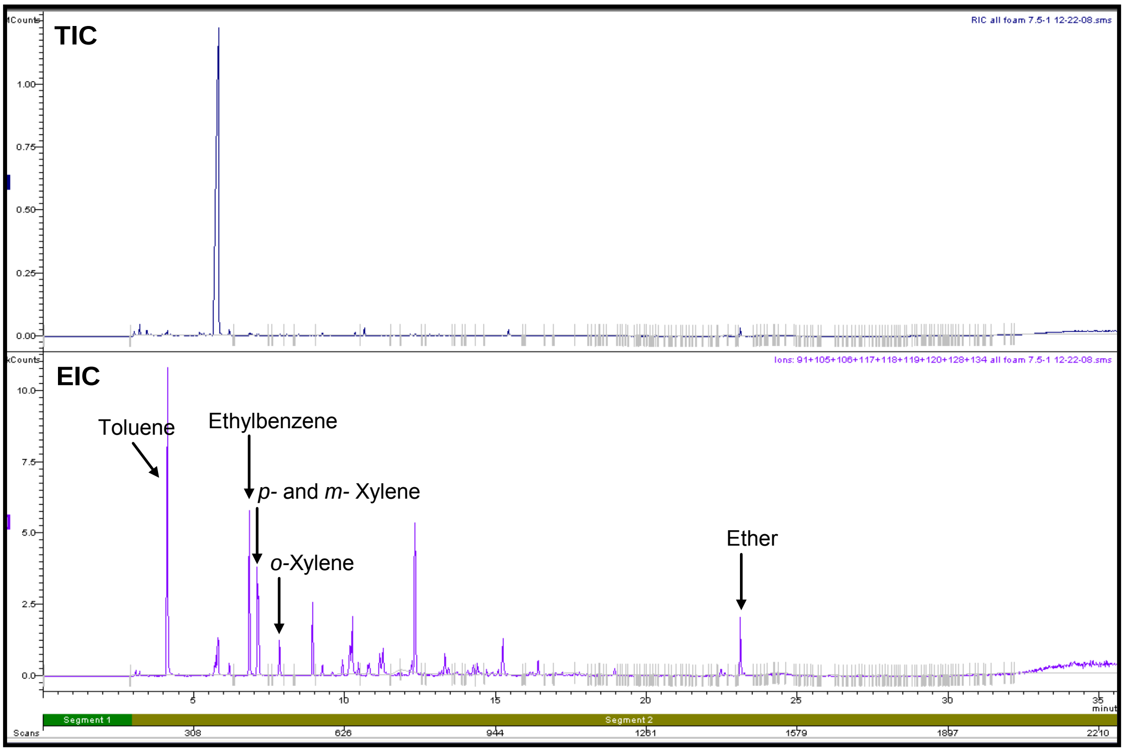


Figure F1.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Burnt in a Can with Lid On for 7.5 minutes

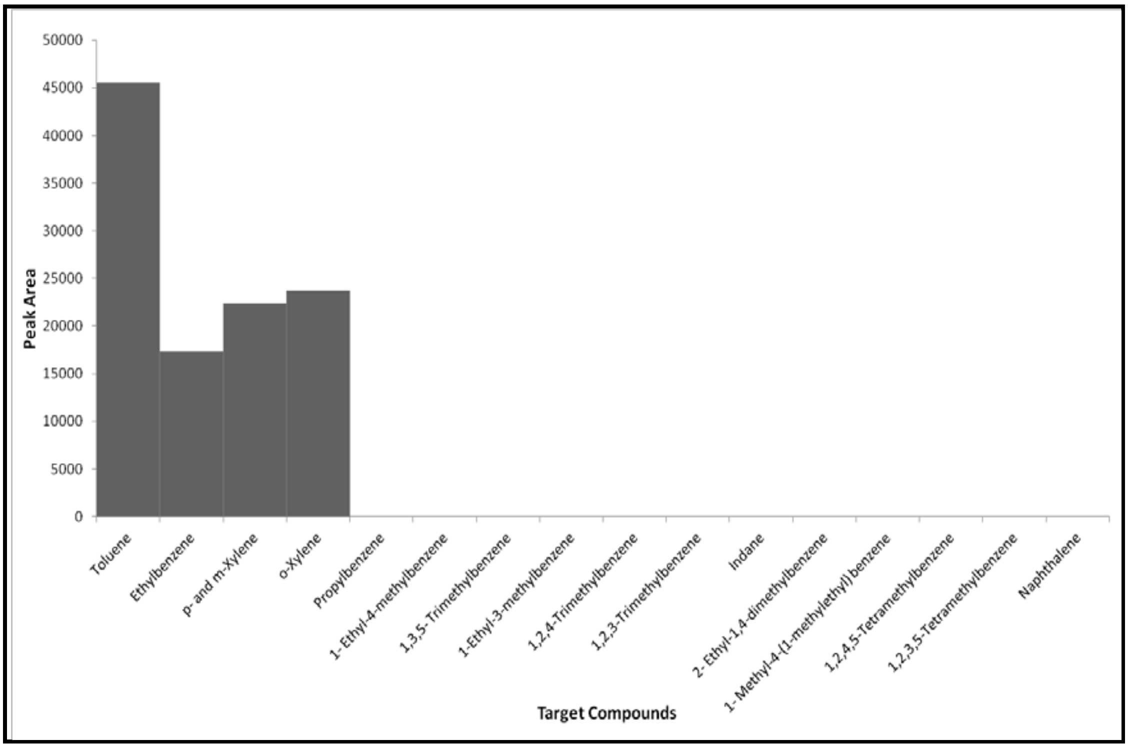


Figure F1.8: Target Compound Chromatogram of Foam Burnt in a Can with Lid On for 7.5 minutes

10 minute burn

Pictures of the samples after the 10 minute burn are presented in Figure F1.9 (a-b).

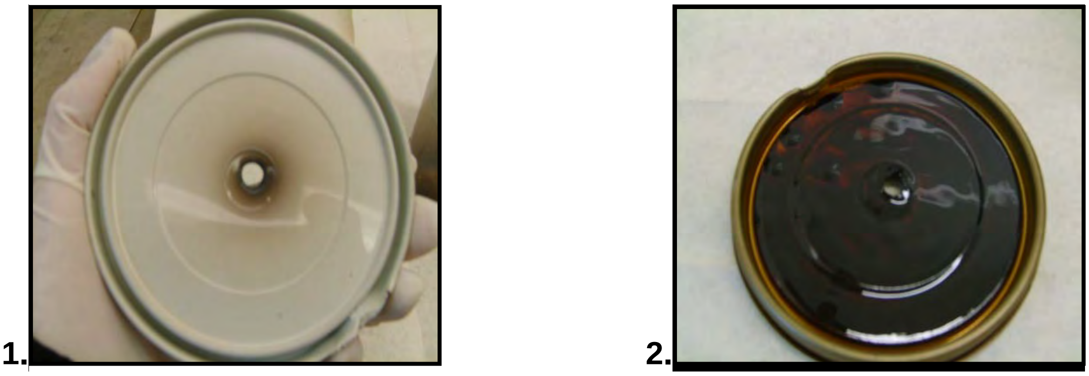


Figure F1.9 (a): 1. Top and 2. Underside of Lid after Burning

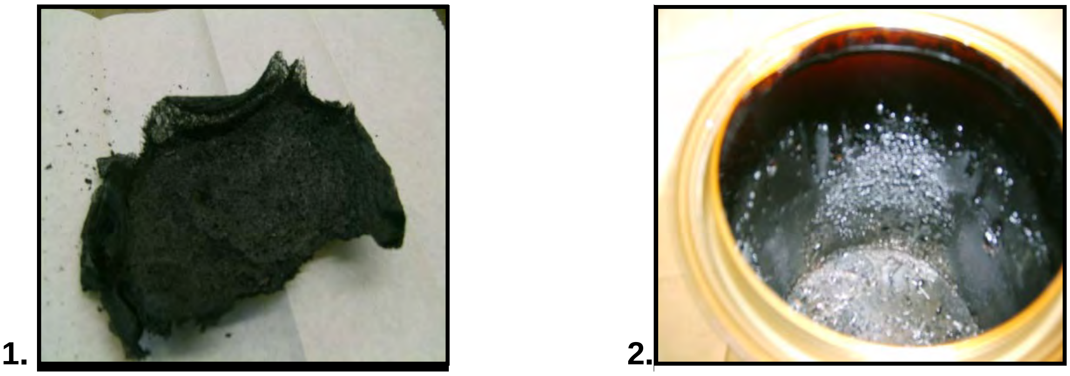


Figure F1.9 (b): 1. Sample after Burning 2. Inside of Can after Burning

The total ion chromatogram and extracted ion chromatogram produced by this burn is presented in Figure F1.10. Similar to the total ion chromatogram and extracted ion chromatogram produced from the 7.5 minute small can fire, the 10 minute can fire only produced four target compounds identified as toluene, ethylbenzene, *p*- and *m*-xylene and *o*-xylene. The target compound chromatogram is presented in Figure F1.11.

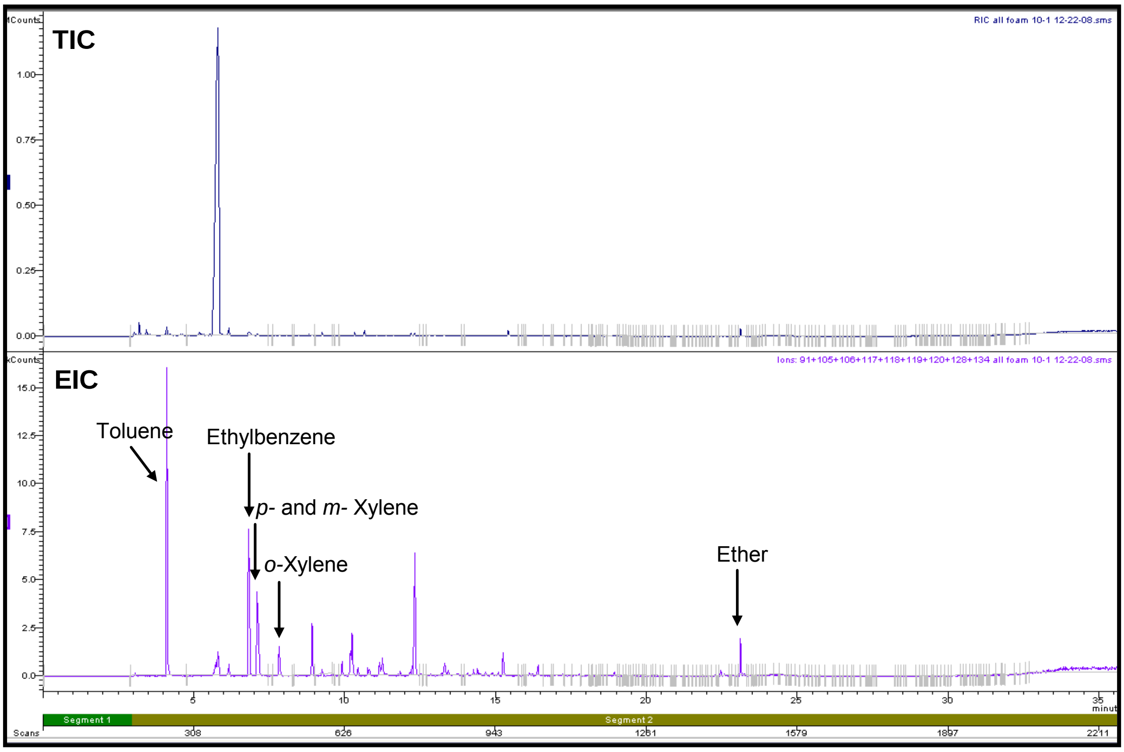


Figure F1.10: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Burnt in a Can with Lid On for 10 minutes

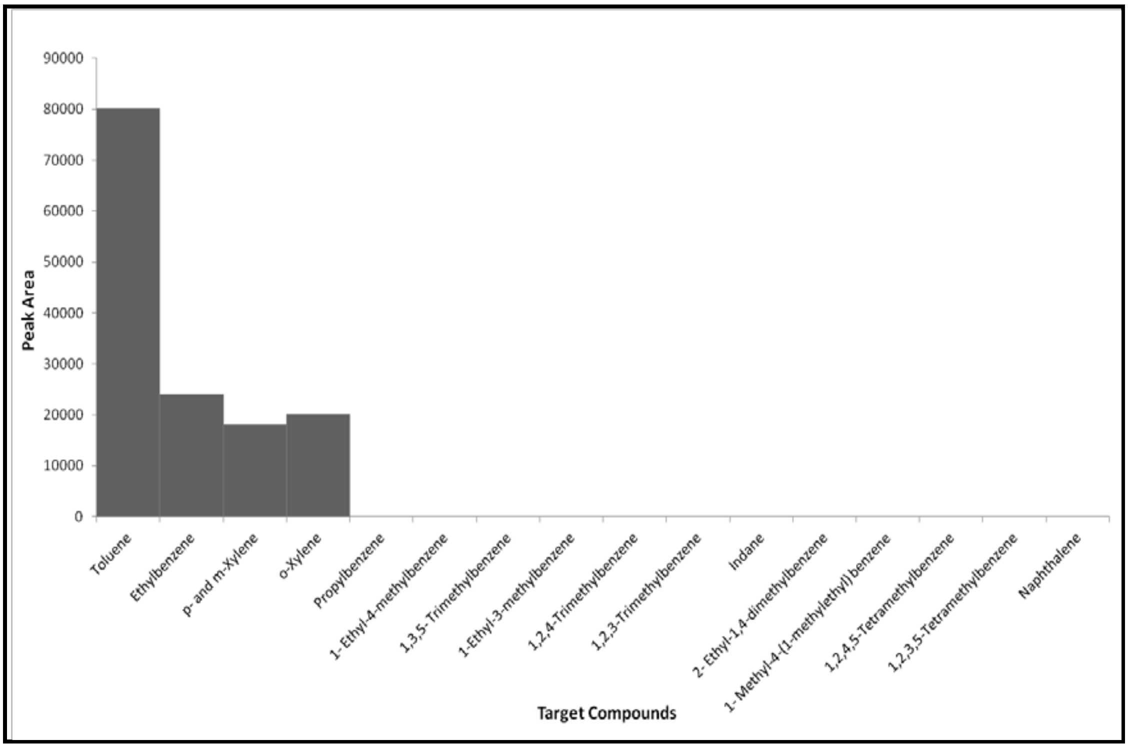


Figure F1.11: Target Compound Chromatogram of Foam Burnt in a Can with Lid On for 10 minutes

Underlay

2.5 minute burn

Pictures of the underlay samples after the 2.5 minute burn are presented in Figure F2.1 (a-b).

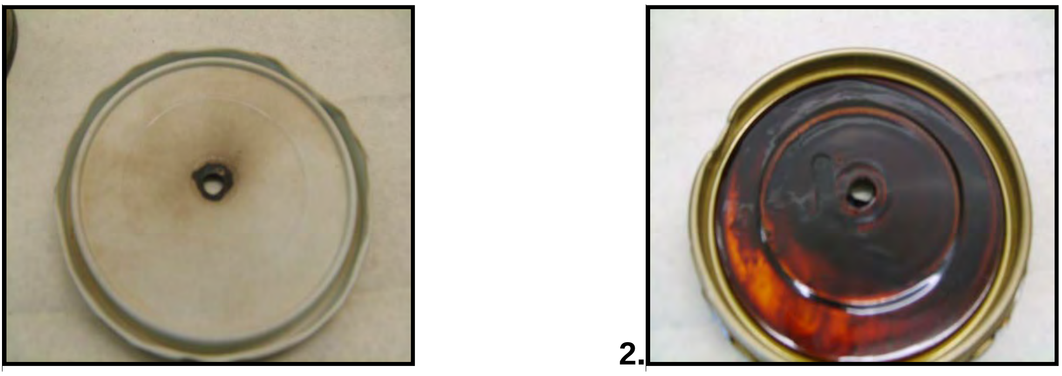


Figure F2.1 (a): 1. Top and 2. Underside of Lid after Burning

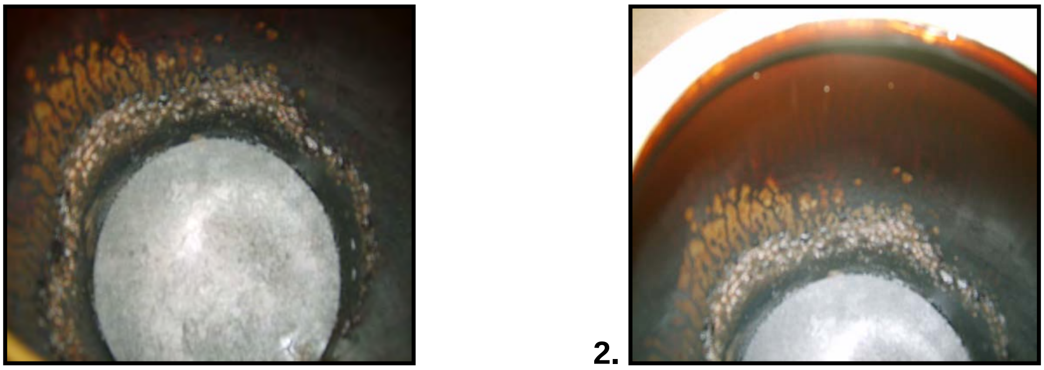


Figure F2.1 (b): 1. Bottom and 2. Sides of Can after Burning

The total ion chromatogram and extracted ion chromatogram for the underlay burnt in the small can for 2.5 minutes is presented in Figure F2.2. A number of target compounds were present in the extracted ion chromatogram with toluene and ethylbenzene being the most abundant. The other compounds recovered are presented in the target compound chromatogram in Figure F2.3.

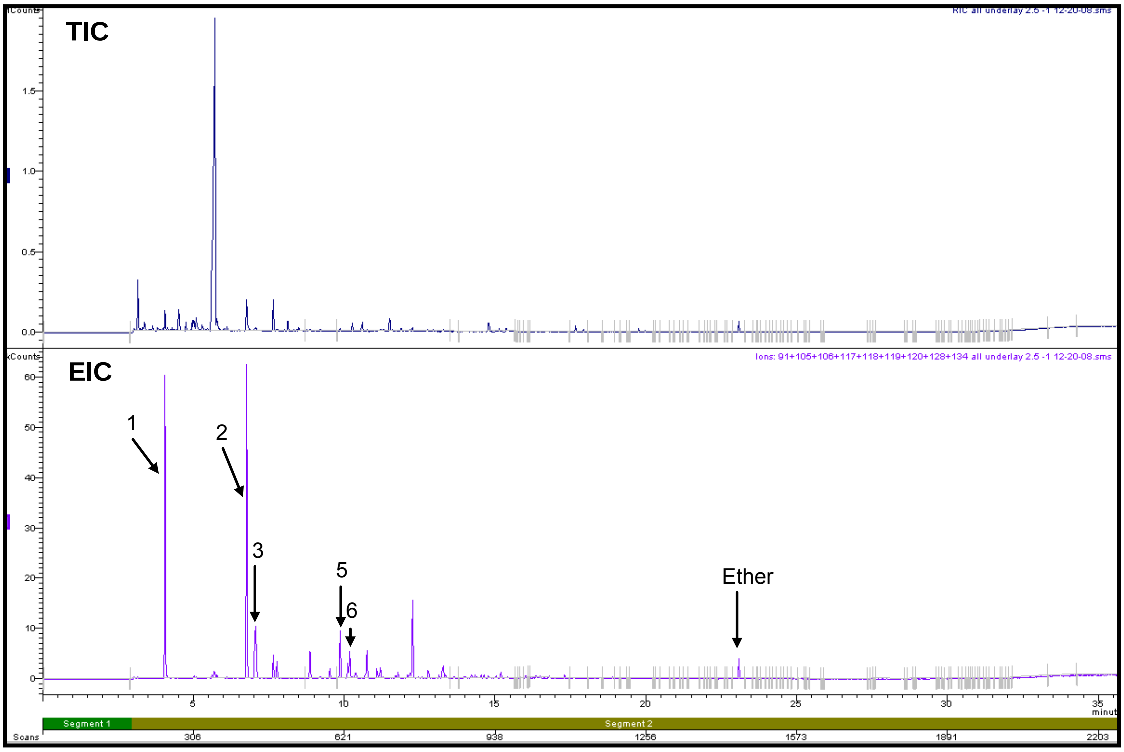


Figure F2.2: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Burnt in a Can with Lid On for 2.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3 *p*- and *m*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene

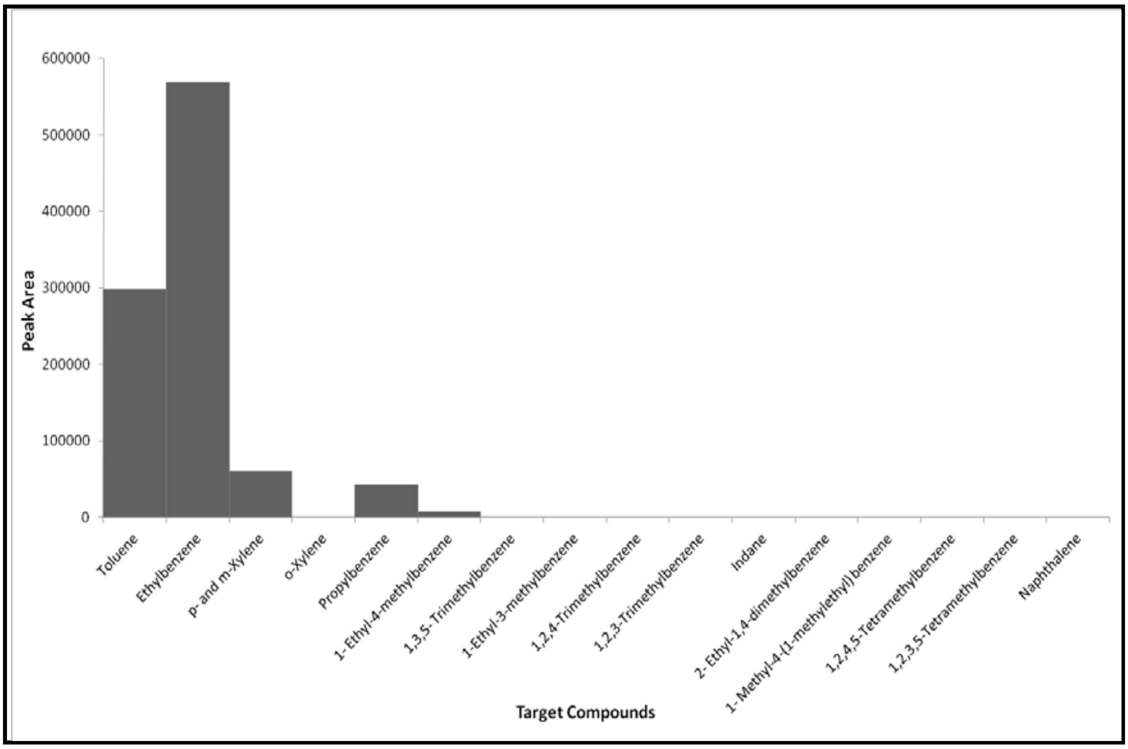


Figure F2.3: Target Compound Chromatogram of Underlay Burnt in a Can with Lid On for 2.5 minutes

5 minute burn

Pictures of the samples after the 5 minute burn are presented in Figure F2.6 (a-b).

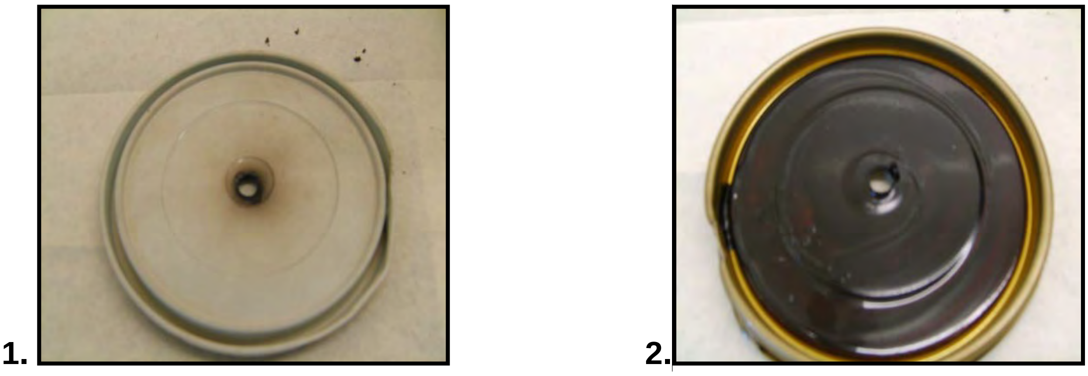


Figure F2.6 (a): 1. Top and 2. Underside of Lid after Burning

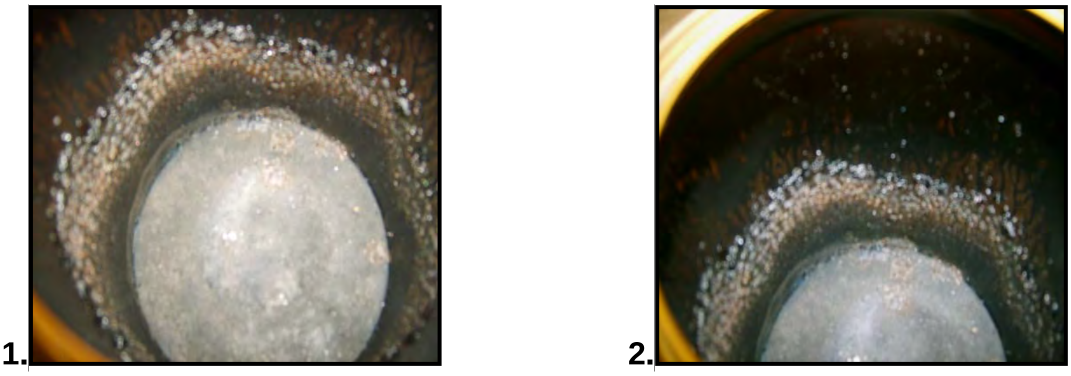


Figure F2.6 (b): 1. Bottom and 2. Sides of Can after Burning

The total ion chromatogram and extracted ion chromatogram for this sample is presented in Figure F2.7. A number of target compounds were present in the extracted ion chromatogram with toluene and ethylbenzene being the most abundant. The other compounds recovered are presented in the target compound chromatogram in Figure F2.8.

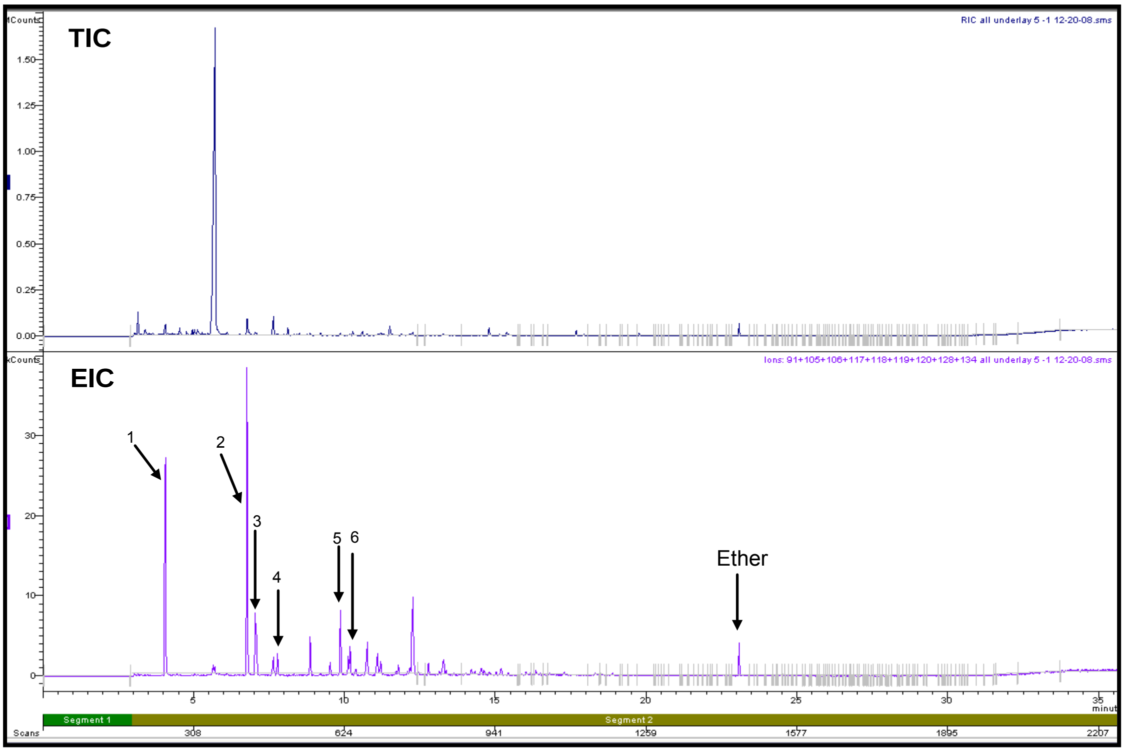


Figure F2.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Burnt in a Can with Lid On for 5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene

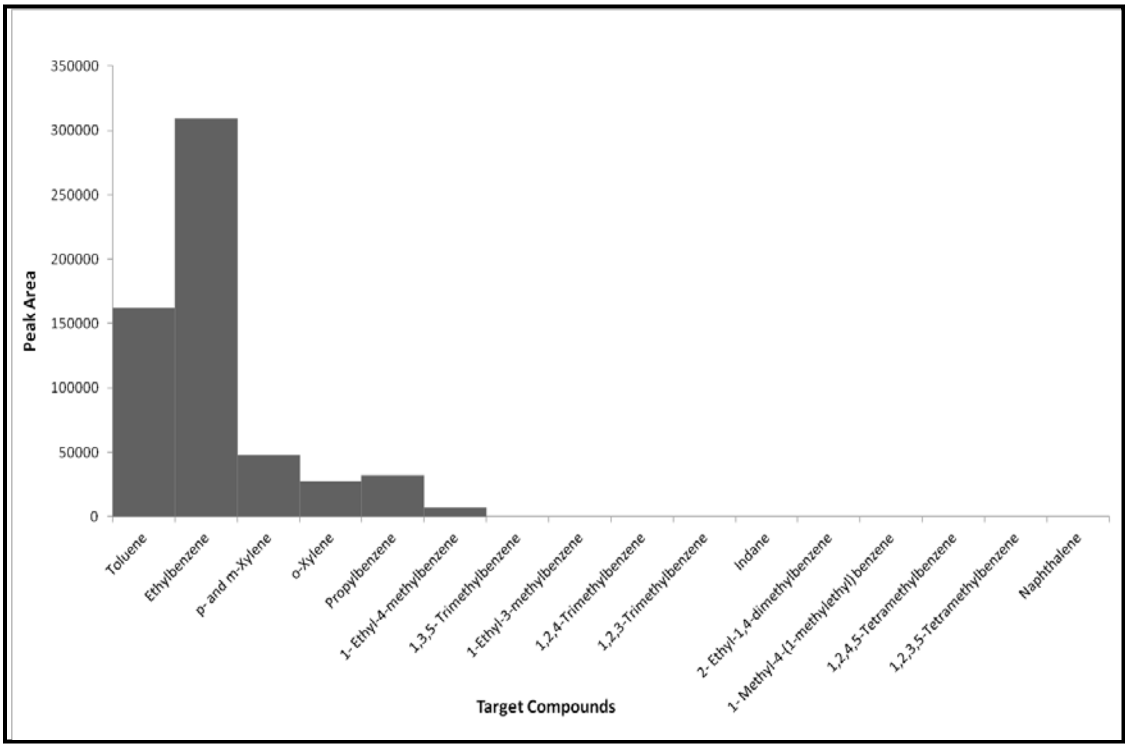


Figure F2.8: Target Compound Chromatogram of Underlay Burnt in a Can with Lid On for 5 minutes

7.5 minute burn

Pictures of the samples after the 7.5 minute burn are presented in Figure F2.9 (a-b).

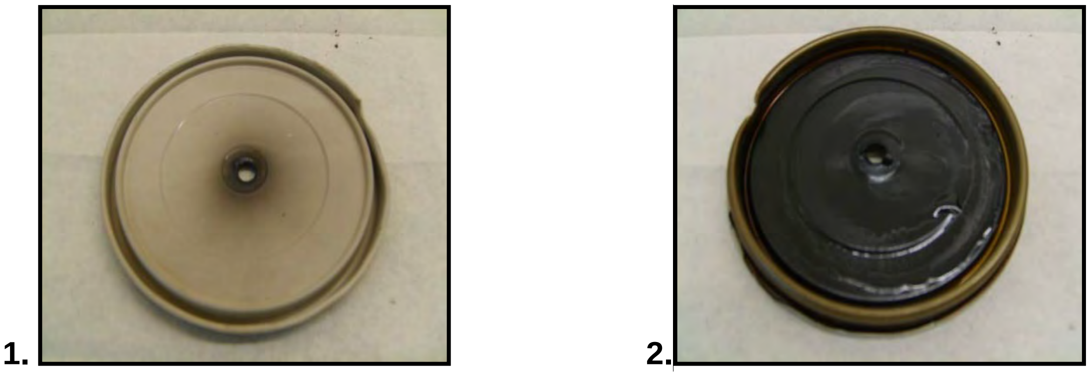


Figure F2.9 (a): 1. Top and 2. Underside of Lid after Burning

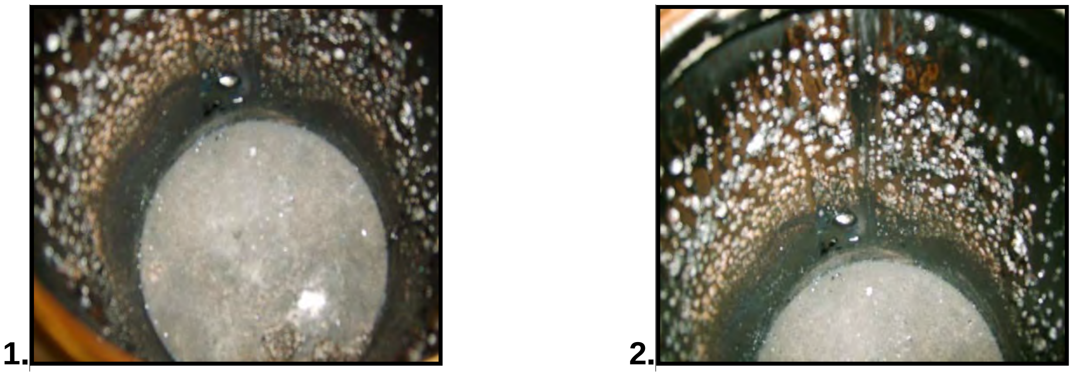


Figure F2.9 (b): 1. Bottom and 2. Sides of Can after Burning

The total ion chromatogram andextracted ion chromatogram are presented in Figure F2.10. Toluene and ethylbenzene were recovered in the greatest abundance and the other compounds recovered are shown in the target compound chromatogram in Figure F2.11.

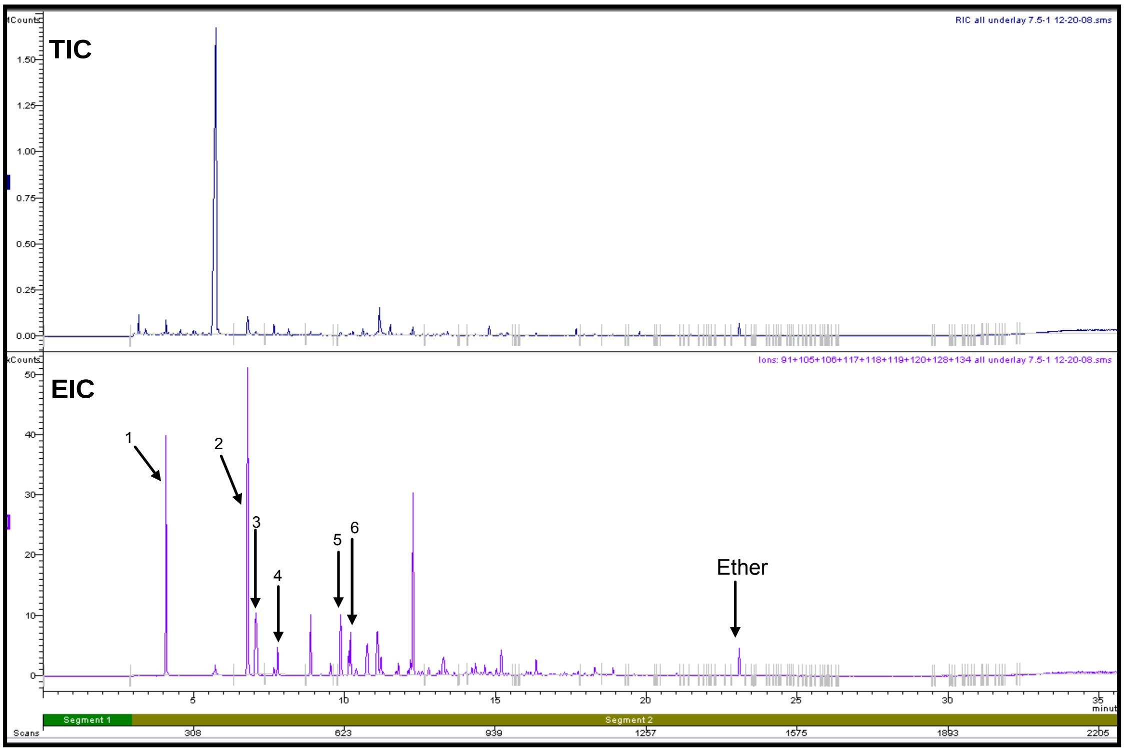


Figure F2.10: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Burnt in a Can with Lid On for 7.5 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*-Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene

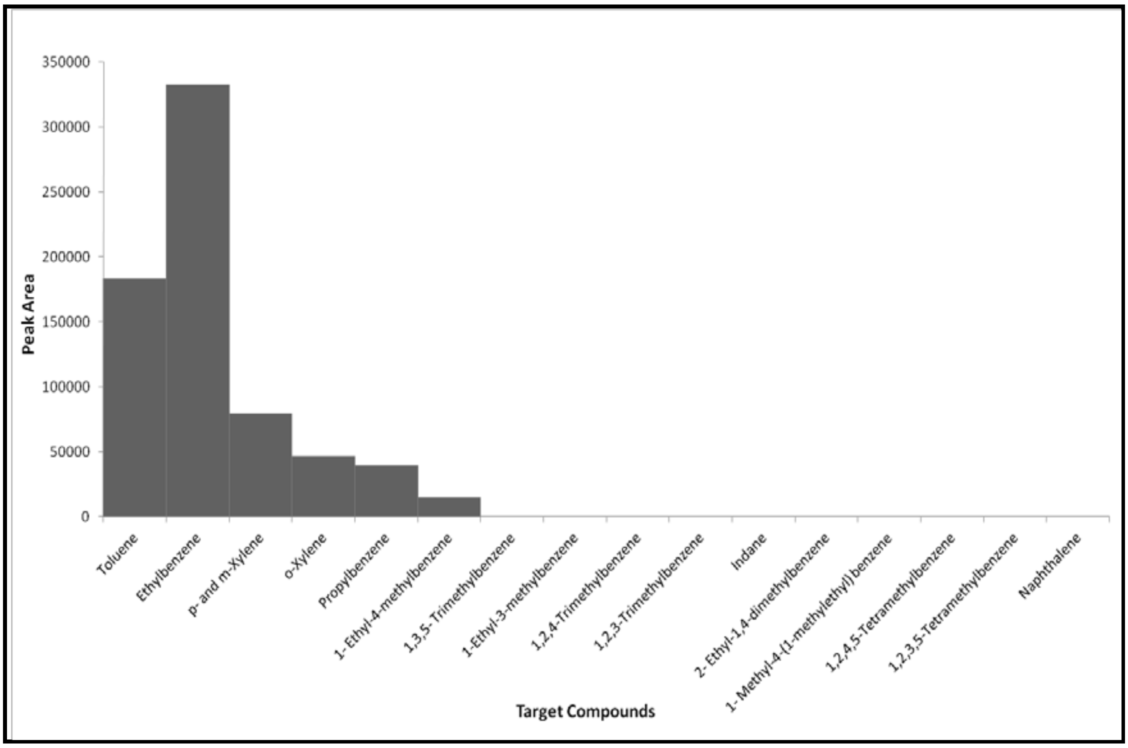


Figure F2.11: Target Compound Chromatogram of Underlay Burnt in a Can with Lid On for 7.5 minutes

10 minute burn

Pictures of the samples after the 10 minute burn are presented in Figure F2.12 (a-b).

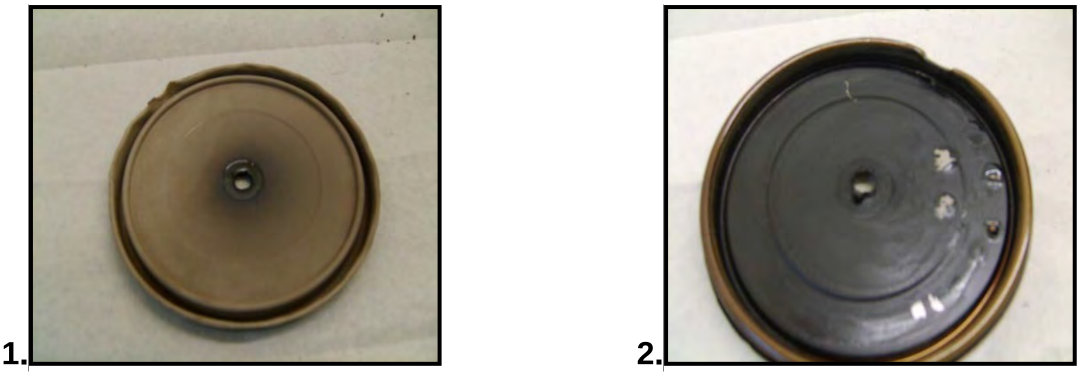


Figure F2.12 (a): 1. Top and 2. Underside of Lid after Burning

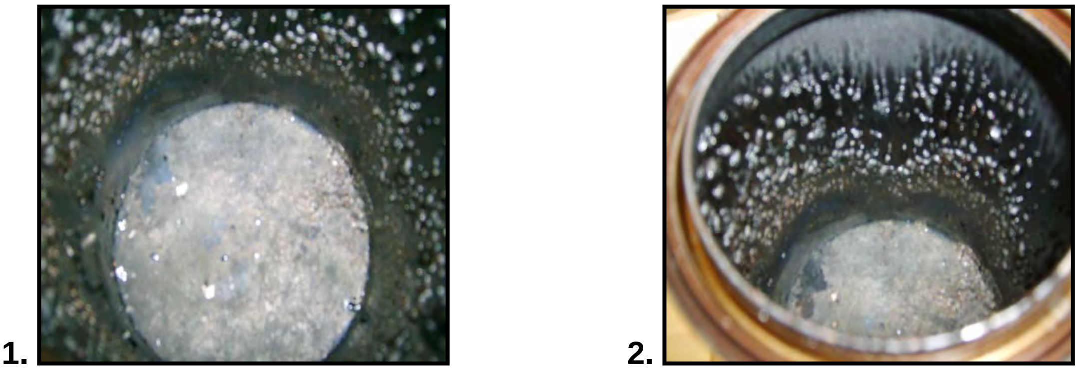


Figure F2.12 (b): 1. Bottom and 2. Sides of Can after Burning

The total ion chromatogram and extracted ion chromatogram are presented in Figure F2.13. Toluene, ethylbenzene, *p*- and *m*-xylene, *o*-xylene, propylbenzene and 1-Ethyl-4-methylbenzene were the six target compounds identified in this extracted ion chromatogram. The target compound chromatogram is presented in Figure F2.14.

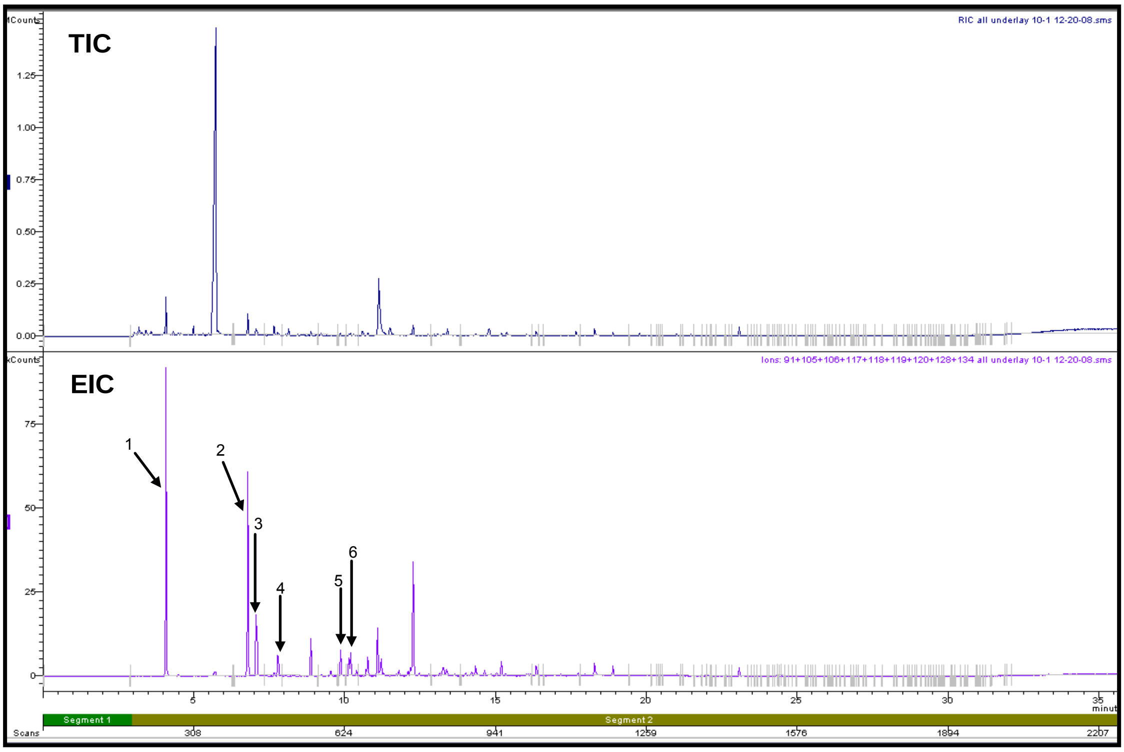


Figure F2.13: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Burnt in a Can with Lid On for 10 minutes

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene

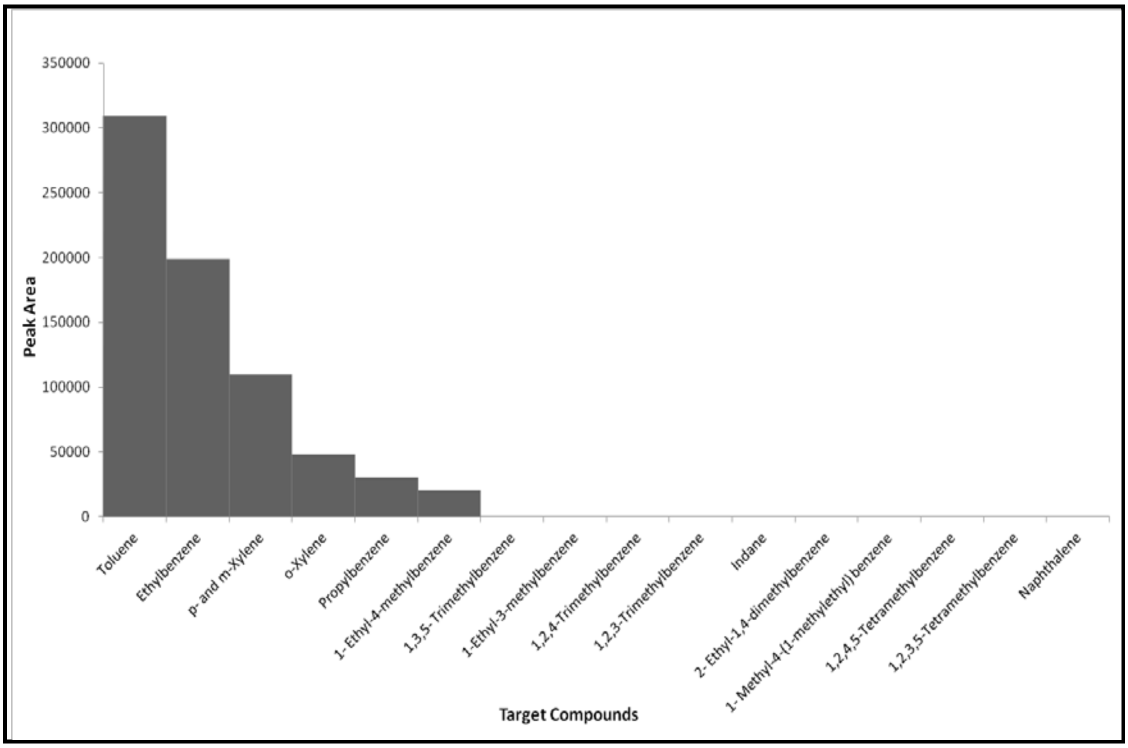


Figure F2.14: Target Compound Chromatogram of Underlay Burnt in a Can with Lid On for 10 minutes

APPENDIX G

COMPARISON OF TARGET COMPOUNDS RECOVERED FOR FOAM AND UNDERLAY BURNT IN SMALL CAN FIRES

Figures G1.1 to G1.3 below show a comparison of the target compounds recovered and their abundances for the foam and underlay burnt for the 2.5, 5 and 10 minutes in the small can fires.

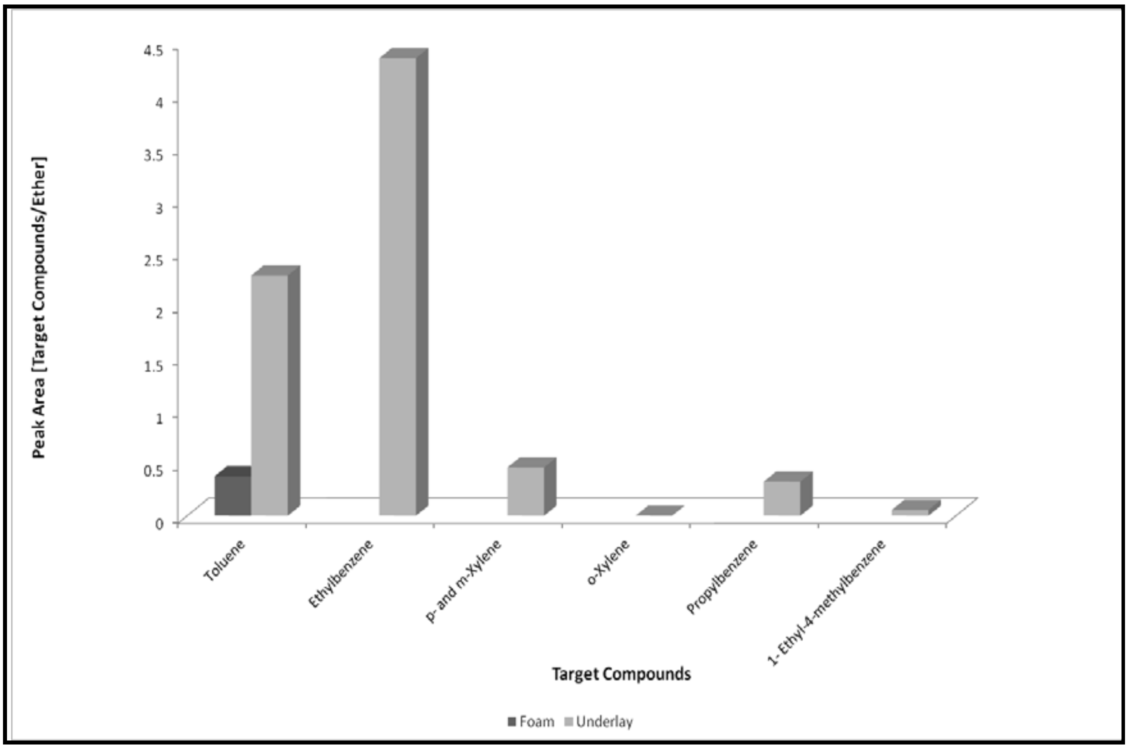


Figure G1.1: Target Compound Chromatogram for Foam and Underlay when Burnt in the Small Can with Lid On for 2.5 minutes

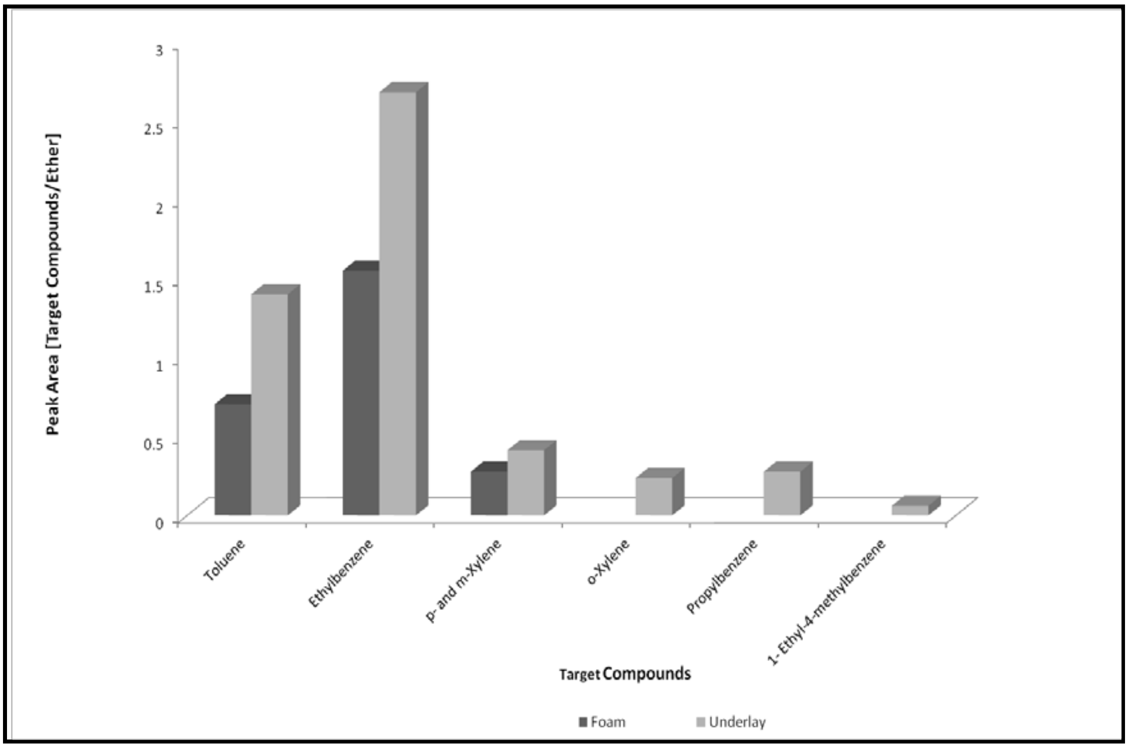


Figure G1.2: Target Compound Chromatogram for Foam and Underlay when Burnt in the Small Can with Lid On for 5 minutes

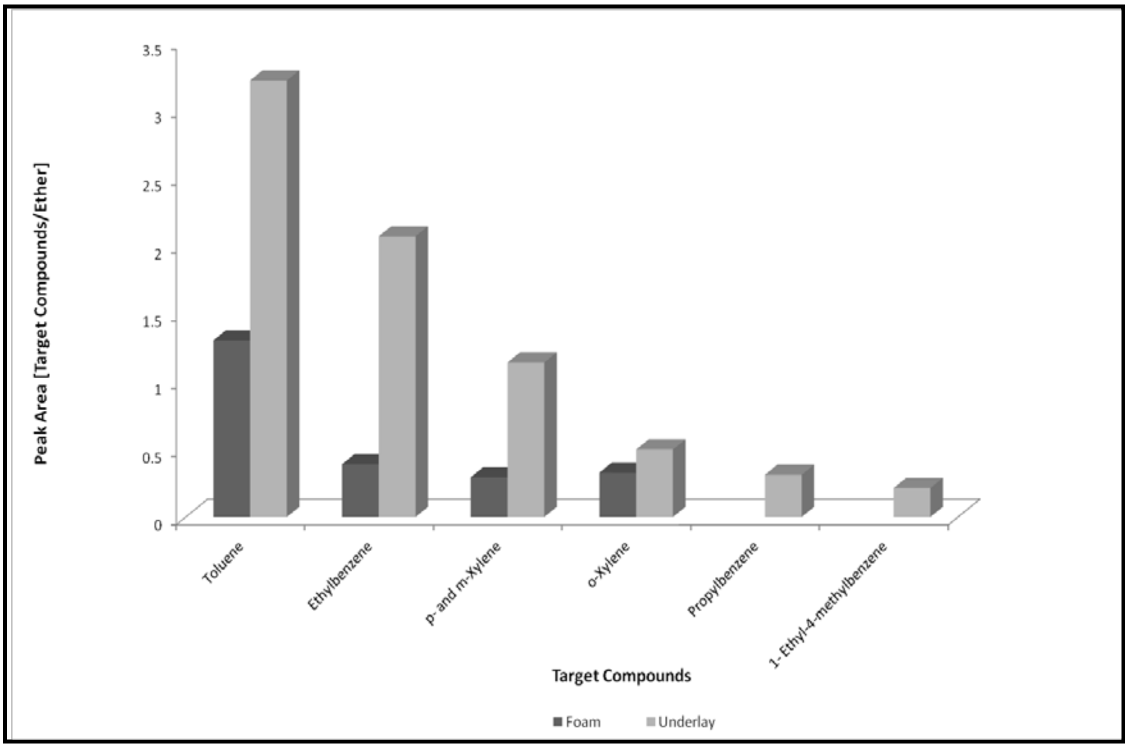


Figure G1.3: Target Compound Chromatogram for Foam and Underlay when Burnt in the Small Can with Lid On for 10 minutes

APPENDIX H

PYROLYSIS GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

Pyrolysis experiments were conducted on the nylon, polypropylene, wool and 50-50 polypropylene-wool carpet fibres and components of the carpet backing including hessian, plastic and adhesive, foam and underlay. Pyrolysis experiments for all samples were conducted at 900°C, 750°C, 600°C and 450°C.

NYLON CARPET

Pyrolysis at 900ºC

The total ion chromatogram and extracted ion chromatogram of the nylon carpet fibre pyrolysed at 900°C is shown in Figure H1.1. Toluene is produced in the greatest abundance and other aromatics produced in smaller amounts include ethylbenzene, *p*- and *m*- *x*ylene and *o*-xylene, propylbenzene, 1,3,5-trimethylbenzene and indane. Styrene was also identified in the total ion chromatogram. The target compound chromatogram is show in Figure H1.2.

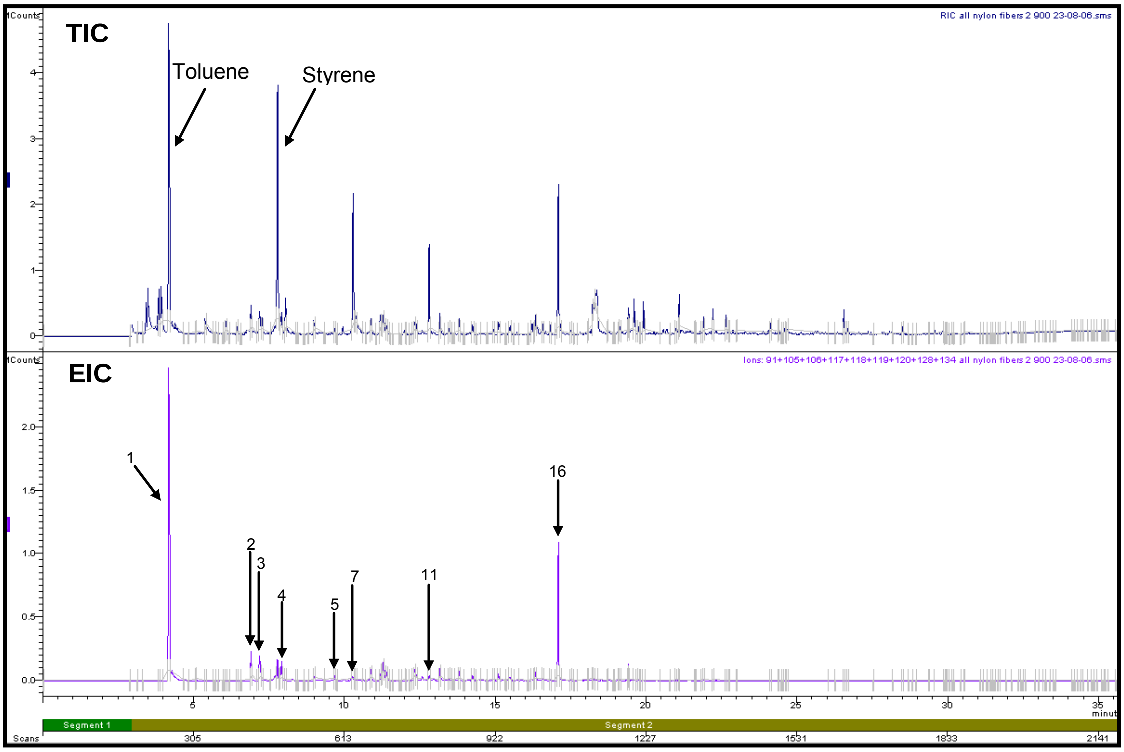


Figure H1.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Fibres Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 7 = 1,3,5-Trimethylbenzene, 11= Indane, 16= Naphthalene

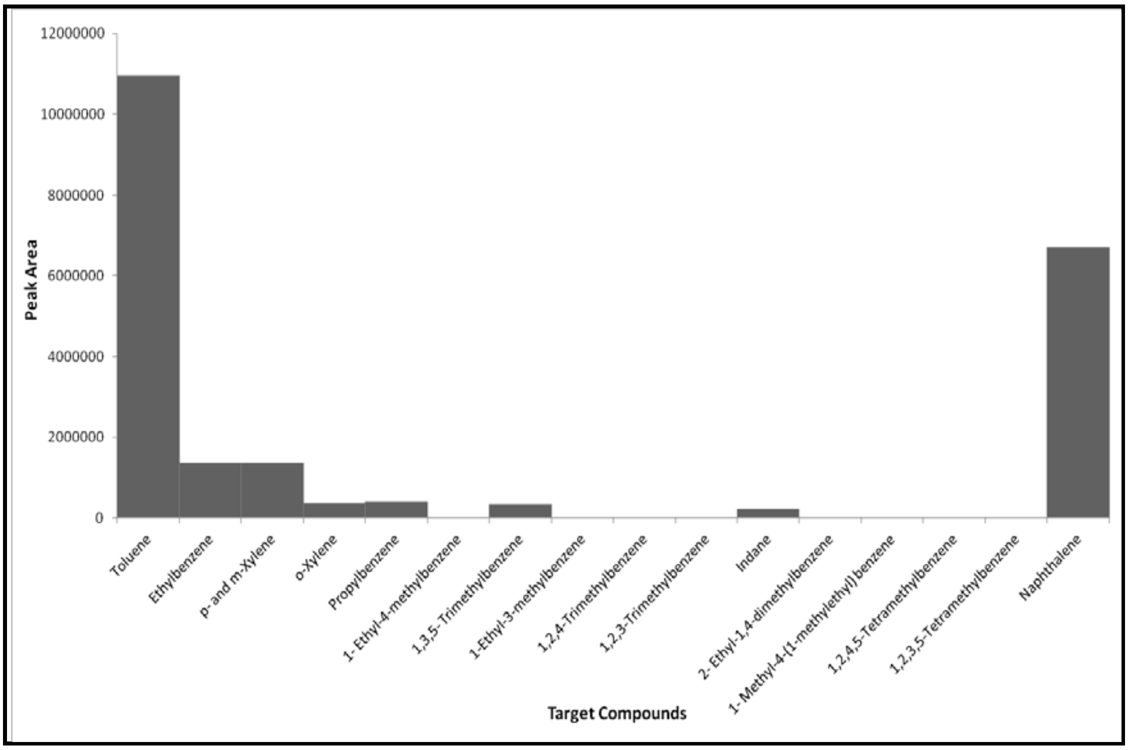


Figure H1.2: Target Compound Chromatogram of Nylon Fibres Pyrolysed at 900ºC

Pyrolysis at 750ºC

The total ion chromatogram and extracted ion chromatogram for nylon fibres pyrolysed at 750ºC can be seen in Figure H1.3. A number of target compounds were identified in the extracted ion chromatogram, these include toluene, ethylbenzene, *p*- and *m*- *x*ylene and *o*- xylene, 1-ethyl-3-methylbenzene, 1,2,3- trimethylbenzene, indane and naphthalene. The target compound chromatogram is presented in Figure H1.4.

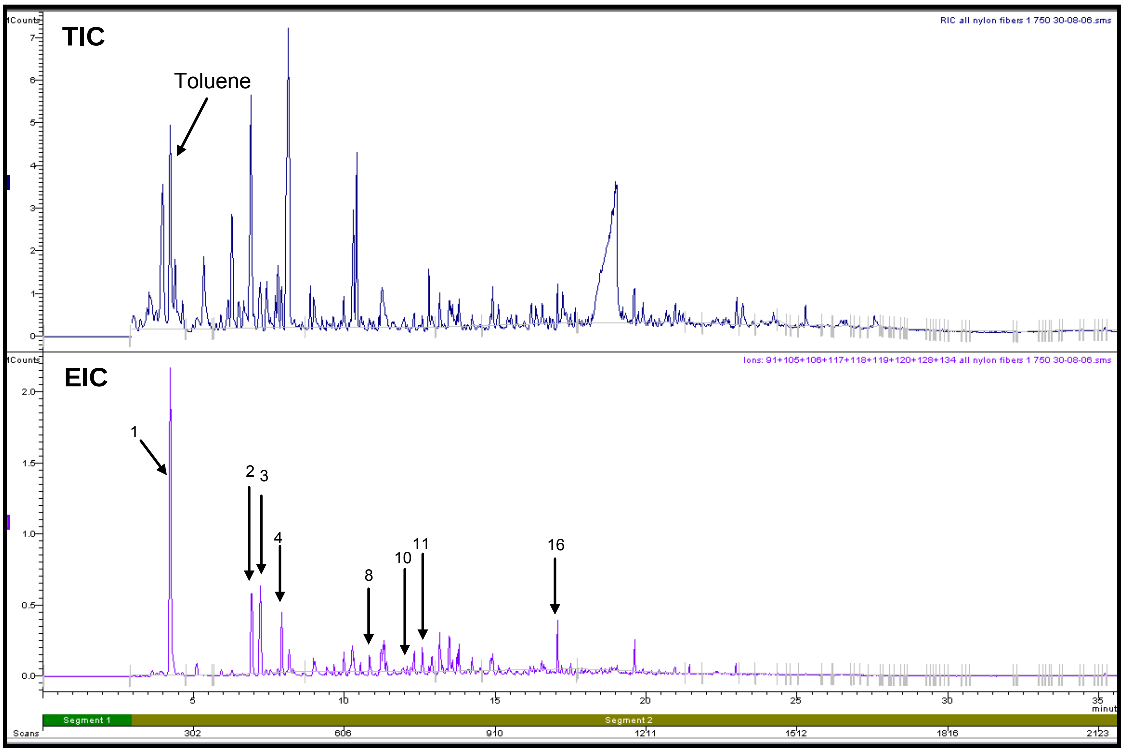


Figure H1.3: Total Ion Chromatogram and Extracted Ion Chromatogram Nylon Fibres Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 8= 1-Ethyl-3-methylbernzene, 10 = 1,2,3-Trimethylbenzene, 11= Indane, 16= Naphthalene

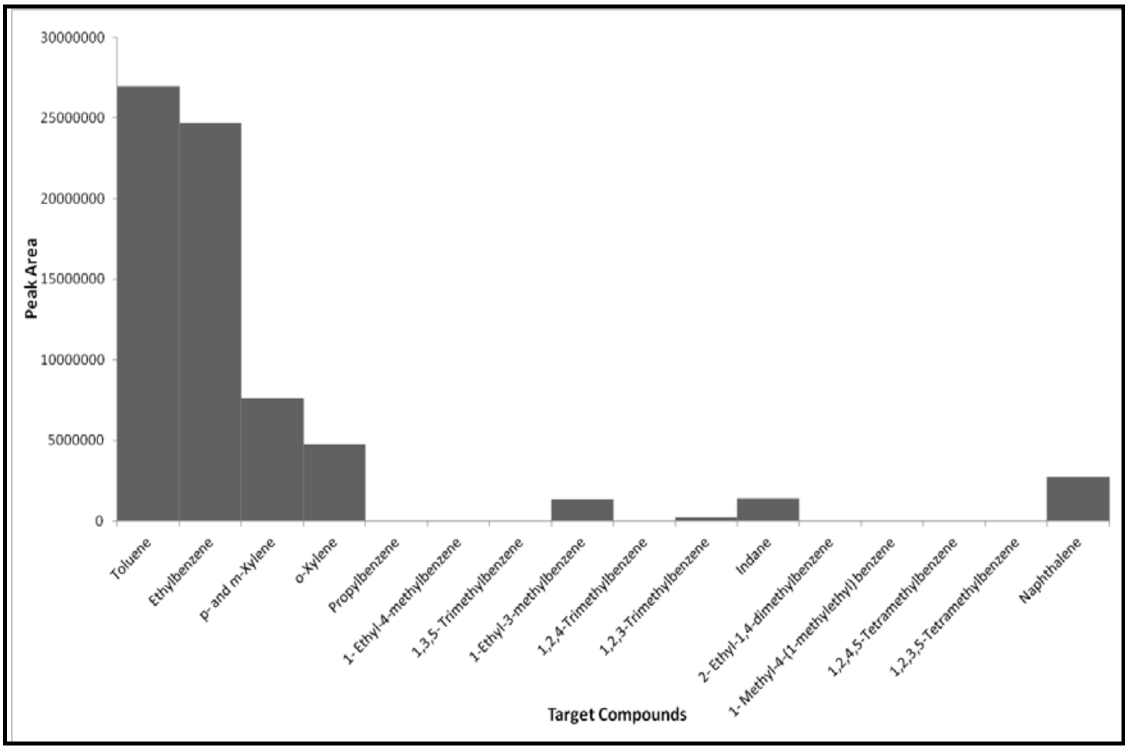


Figure H1.4: Target Compound Chromatogram of Nylon Fibres Pyrolysed at 750ºC

Pyrolysis at 600ºC

Nylon fibres pyrolysed at 600ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H1.5. The nylon fibres pyrolysed at 600ºC do not produce as many of the volatile products compared with nylon fibres pyrolysed at the higher temperatures. The extracted ion chromatogram is quite convoluted with none of the petrol target compounds being obvious. However, as seen in the target compound chromatogram shown in Figure H1.6, a n umber of target compounds were able to be recovered and were identified as toluene, ethylbenzene, *p-* and *m- x*ylene and *o-* xylene, 1-ethyl-3-methylbenzene and indane.

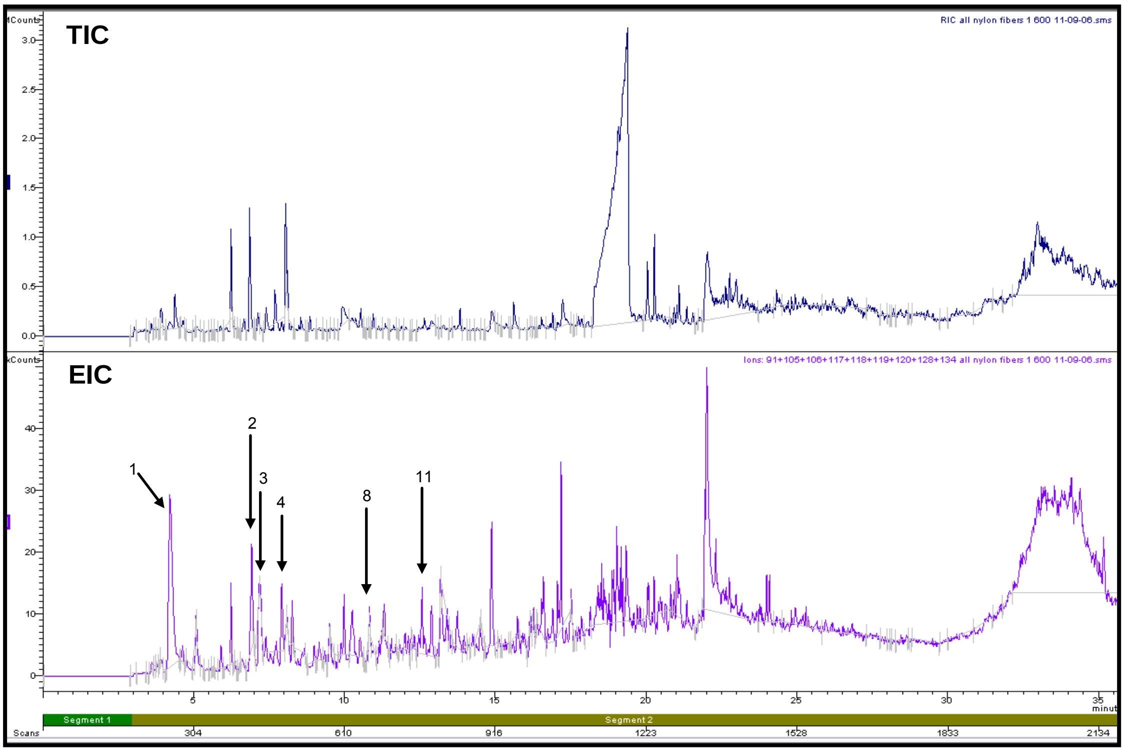


Figure H1.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Fibres Pyrolysed at 600ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 8= 1-Ethyl-3-methylbernzene, 11= Indane

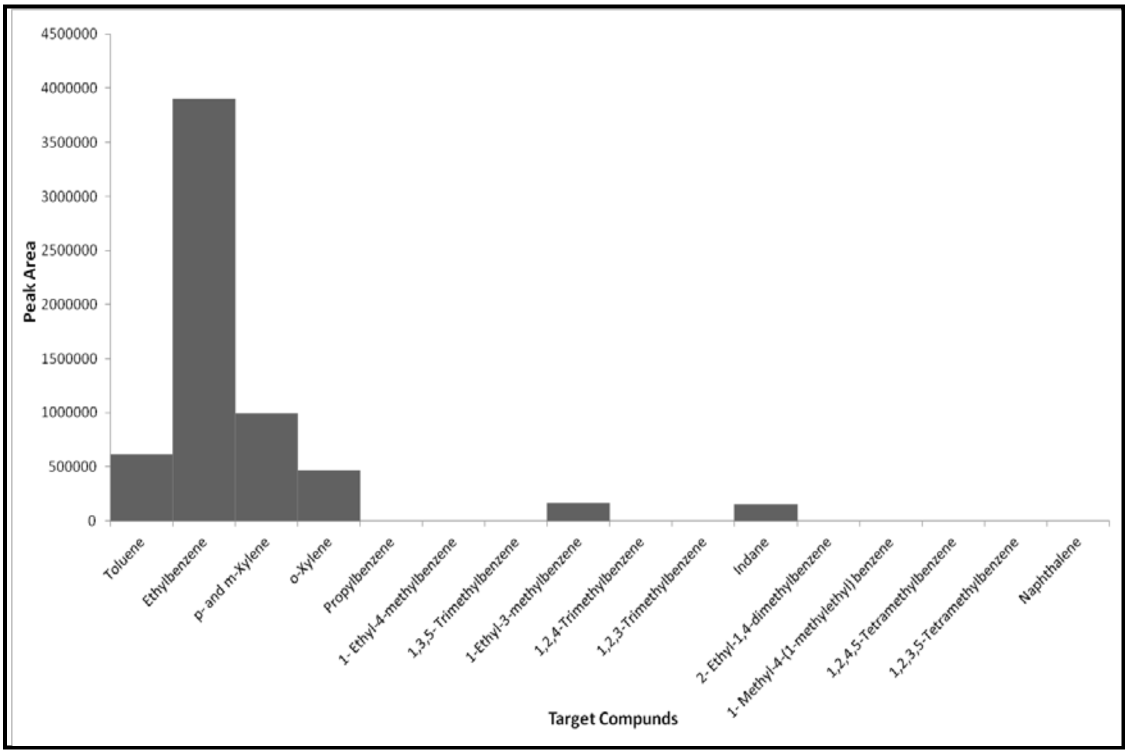


Figure H1.6: Target Compound Chromatograms of Nylon Fibres Pyrolysed at 600ºC

Pyrolysis at 450ºC

Nylon fibres pyrolysed at 450ºC produce the total ion chromatogram and extracted ion chromatogram shown in Figure H1.7. Nylon pyrolysed at 450ºC does not produce many volatile organic compounds, thus indicating that at this temperature not much thermal degradation is occurring. However, toluene and *p*- and *m*- *x*ylene were identified in the EIC.

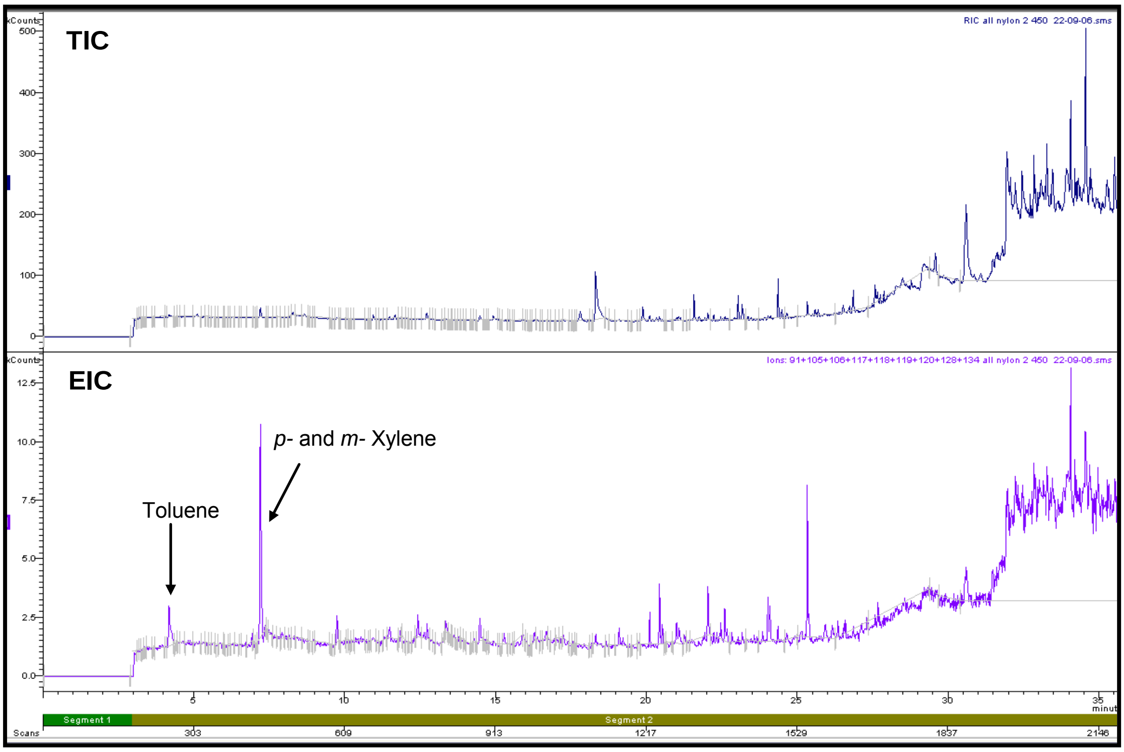


Figure H1.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Nylon Fibres Pyrolysed at 450ºC

HESSIAN CARPET BACKING

Pyrolysis at 900ºC

Figure H2.1 shows the total ion chromatogram and extracted ion chromatogram for the hessian carpet backing pyrolysed at 900ºC. Toluene is the target compound produced in the greatest abundance followed by naphthalene. Other aromatics recovered in smaller amounts include ethylbenzene, *p*- and *m*- xylene and *o*-xylene. The target compound chromatogram is show in Figure H2.2.

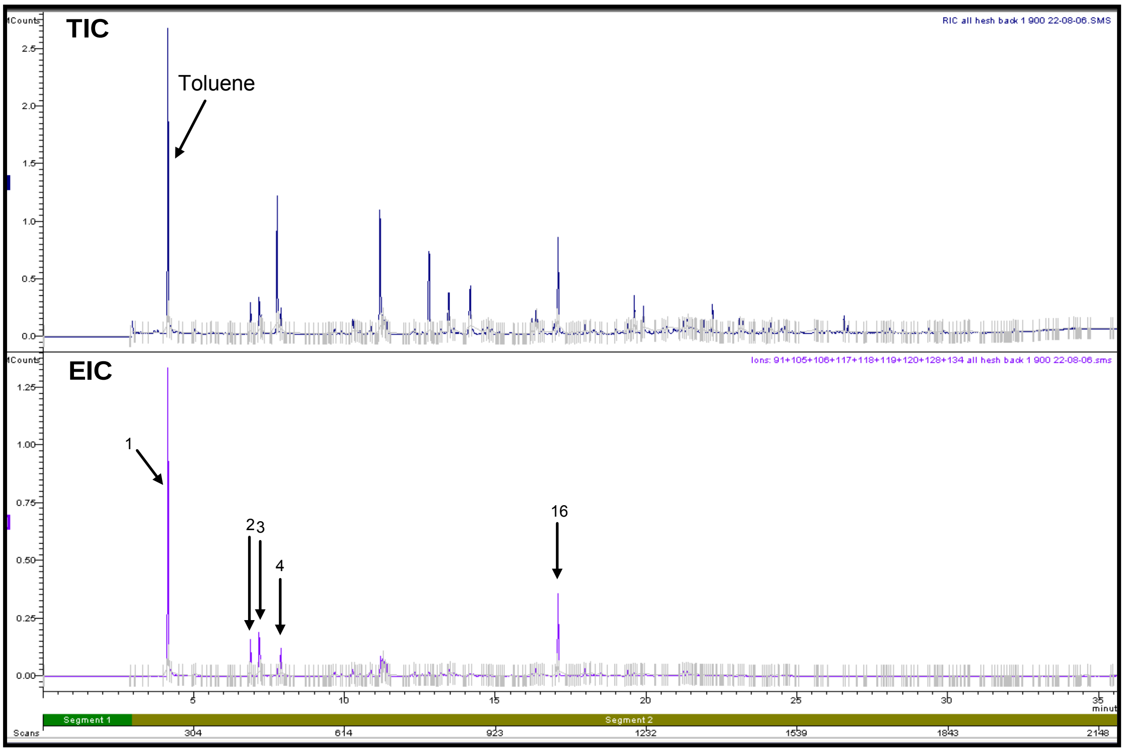


Figure H2.1: Total Ion Chromatogram and Extracted Ion Chromatograms of Hessian Carpet Backing Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 16= Naphthalene

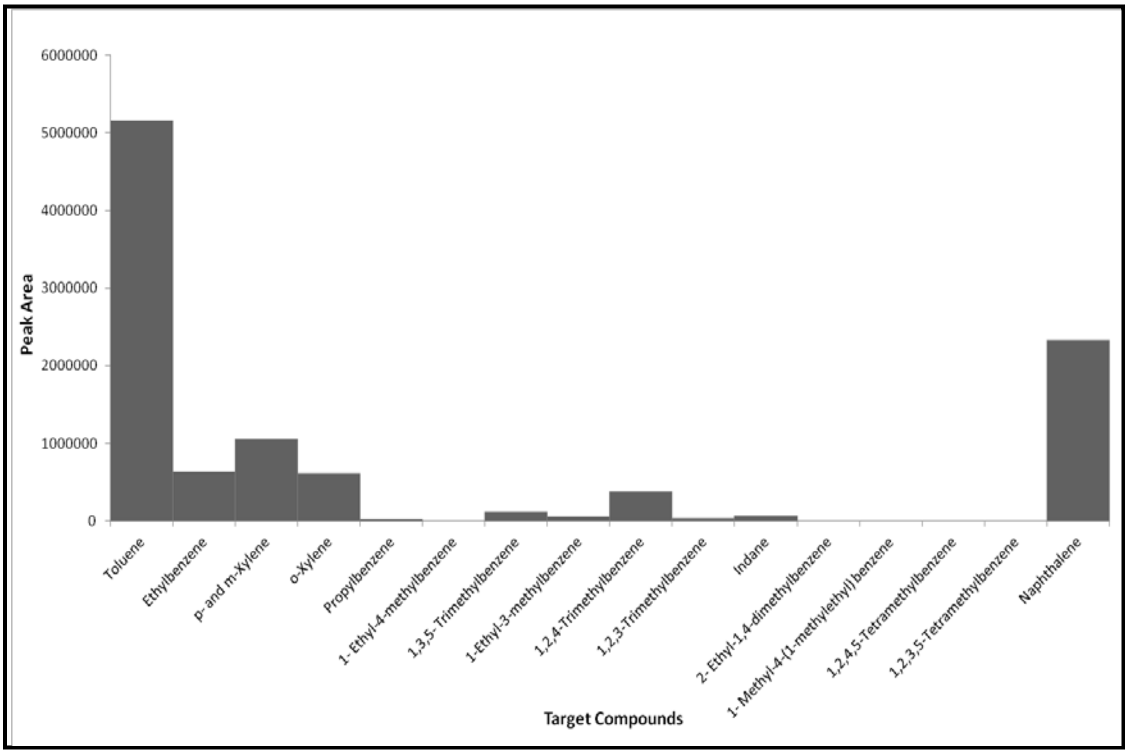


Figure H2.2: Target Compound Chromatogram of Hessian Carpet Backing Pyrolysed at 900ºC

Pyrolysis at 750ºC

The total ion chromatogram and extracted ion chromatogram for hessian carpet backing pyrolysed at 750ºC can be seen in Figure H2.3. Pyrolysis of the hessian carpet backing at 750ºC produced more target compounds than when pyrolysed at 900ºC. Of the 13 target compounds recovered, toluene was again recovered in the greatest abundance. The target compound chromatogram is shown in Figure H2.4.

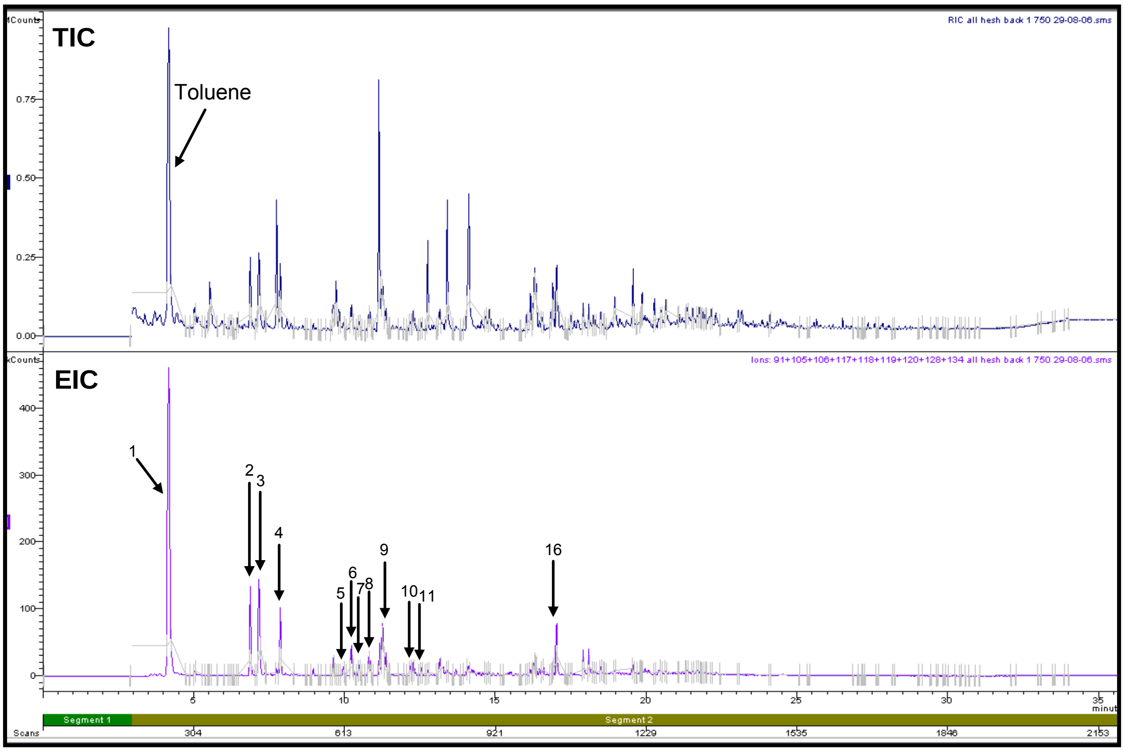


Figure H2.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Hessian Carpet Backing Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4- Trimethylbenzene, 10= 1,2,3-Trimethylbenzene, 11= Indane, 16= Naphthalene

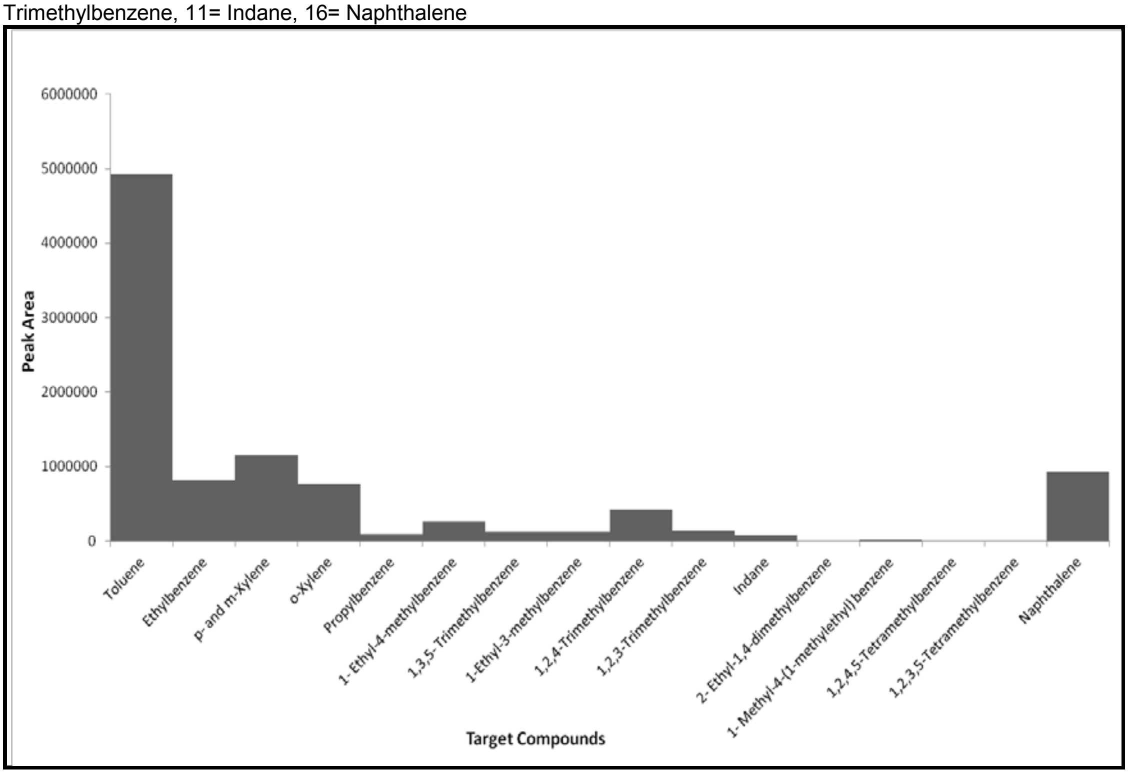


Figure H2.4: Target Compound Chromatogram of Hessian Carpet Backing Pyrolysed at 750ºC

Pyrolysis at 600ºC

The total ion chromatogram and extracted ion chromatogram for hessian carpet backing pyrolysed at 600ºC can be seen in Figure H2.5. Pyrolysis at 600ºC resulted in three target compounds being recovered, the target compound chromatogram is shown in Figure H2.6.

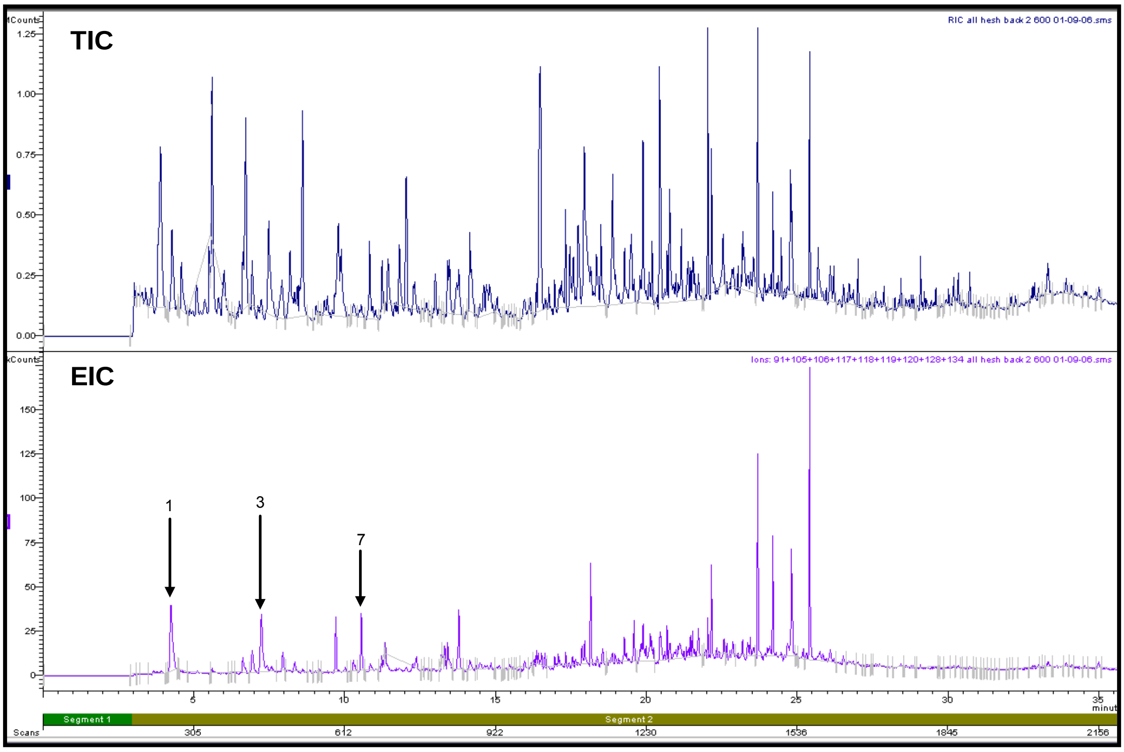


Figure H2.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Hessian Carpet Backing Pyrolysed at 600ºC

Key: 1= Toluene, 3= *p*- and *m*- Xylene, 7= 1,3,5- Trimethylbenzene

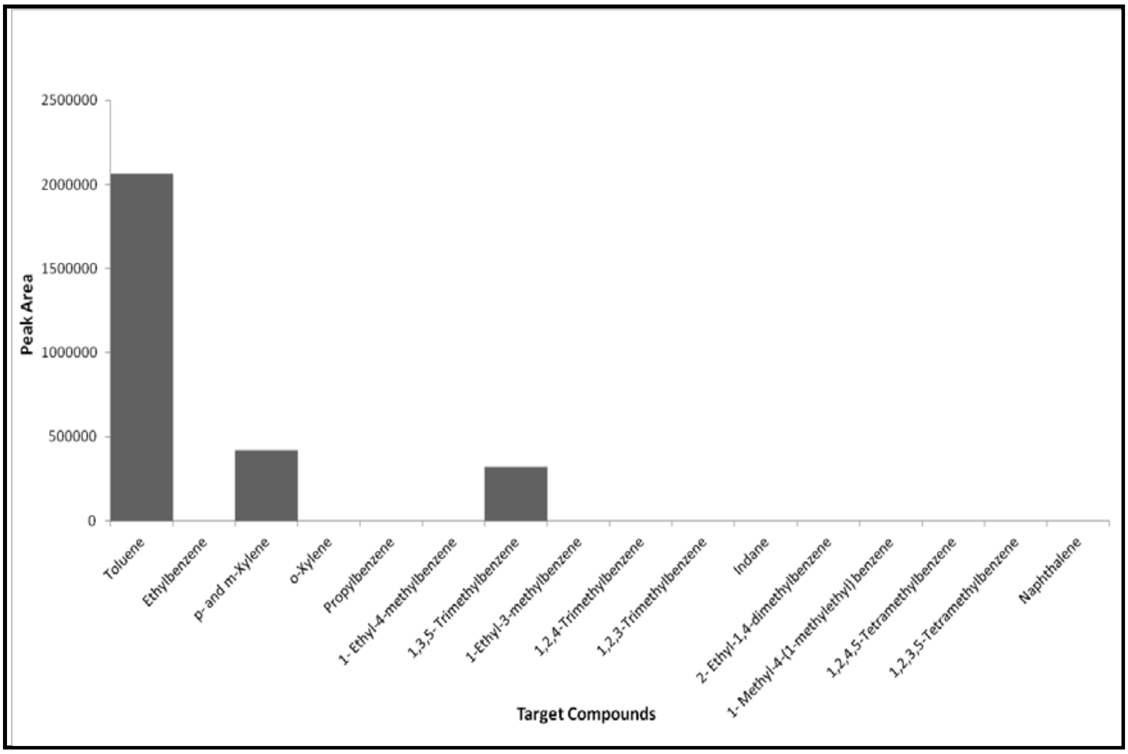


Figure H2.6: Target Compound Chromatogram of Hessian Carpet Backing Pyrolysed at 600ºC

Pyrolysis at 450ºC

The total ion chromatogram and extracted ion chromatogram for hessian carpet backing pyrolysed at 450ºC, shown in Figure H2.7, resulted in no target compounds being produced.

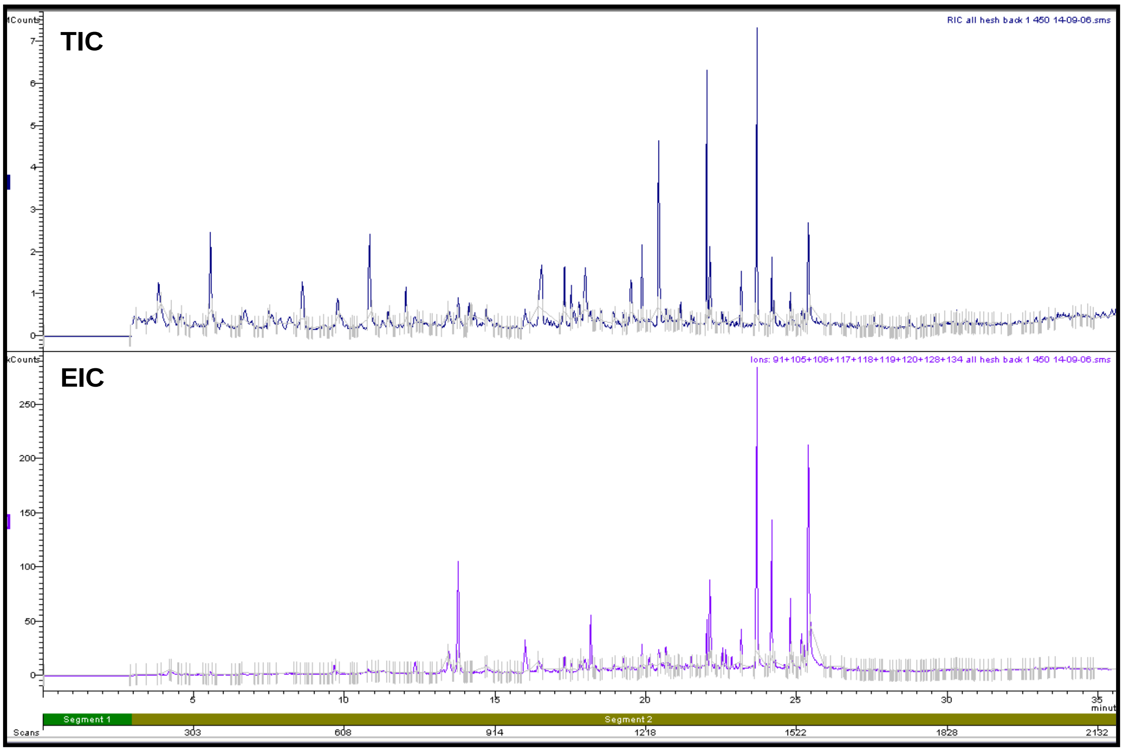


Figure H2.7: Total Ion Chromatohgram and Extracted Ion Chromatogram of Hessian Carpet Backing Pyrolysed at 450ºC

PLASTIC FROM CARPET BACKING

Pyrolysis at 900ºC

Figure H3.1 shows the total ion chromatogram and extracted ion chromatogram for the plastic carpet backing pyrolysed at 900ºC. Toluene is recovered in the greatest abundance whilst the other target compounds were recovered in smaller amounts. The target compound chromatogram is shown in Figure H3.2.

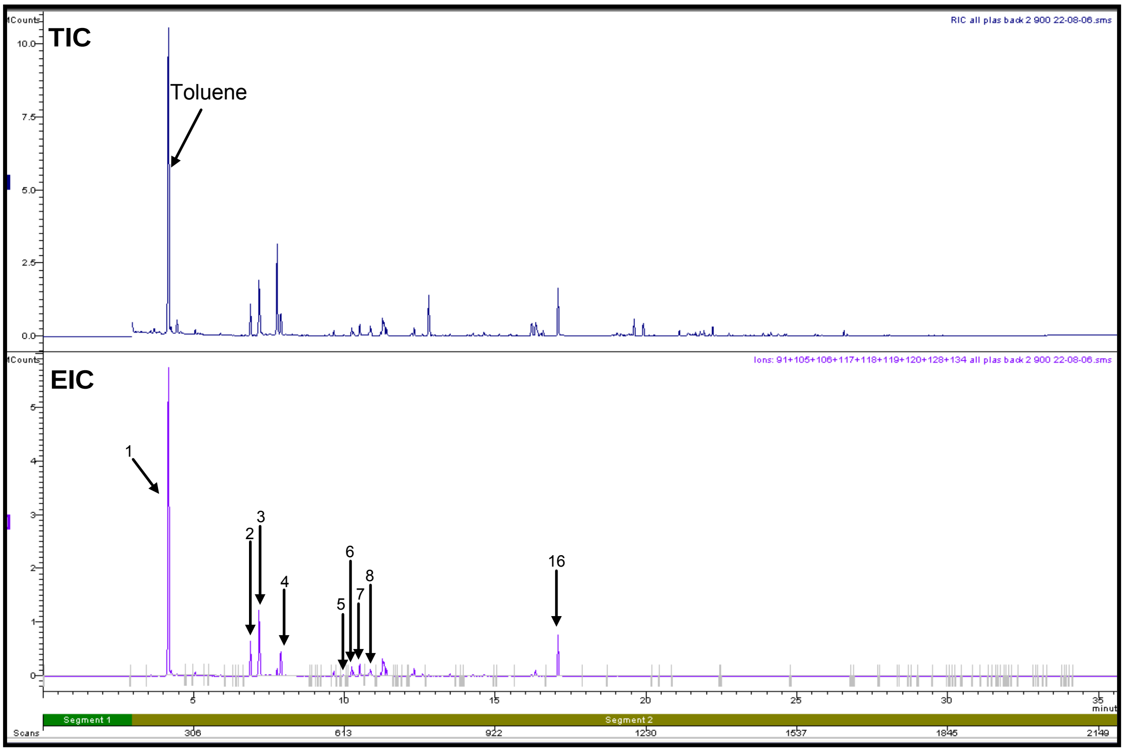


Figure H3.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Plastic Carpet Backing Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 16= Naphthalene

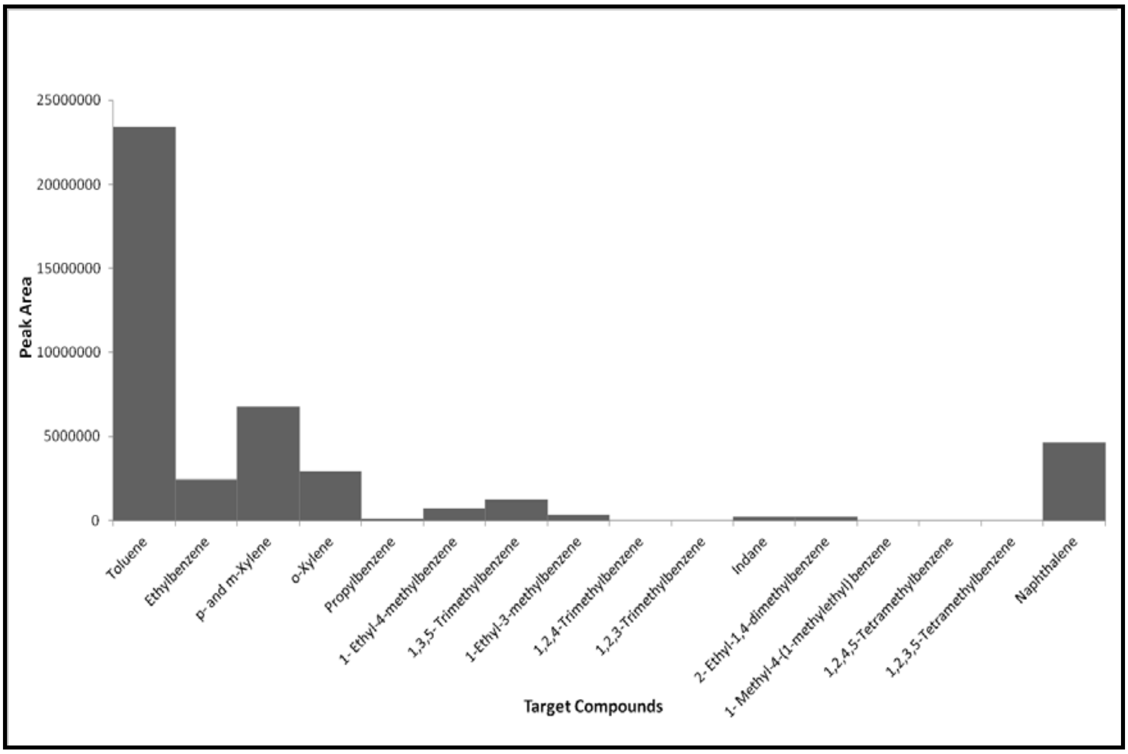


Figure H3.2: Target Compound Chromatogram of Plastic Carpet Backing Pyrolysed at 900ºC

Pyrolysis at 750ºC

Figure H3.3 shows the total ion chromatogram and extracted ion chromatogram for the plastic carpet backing pyrolysed at 750ºC. The target compound chromatogram is shown in Figure H3.4. Pyrolysis at 750ºC produces 10 of the 16 target compounds, with toluene being present in the greatest abundance.

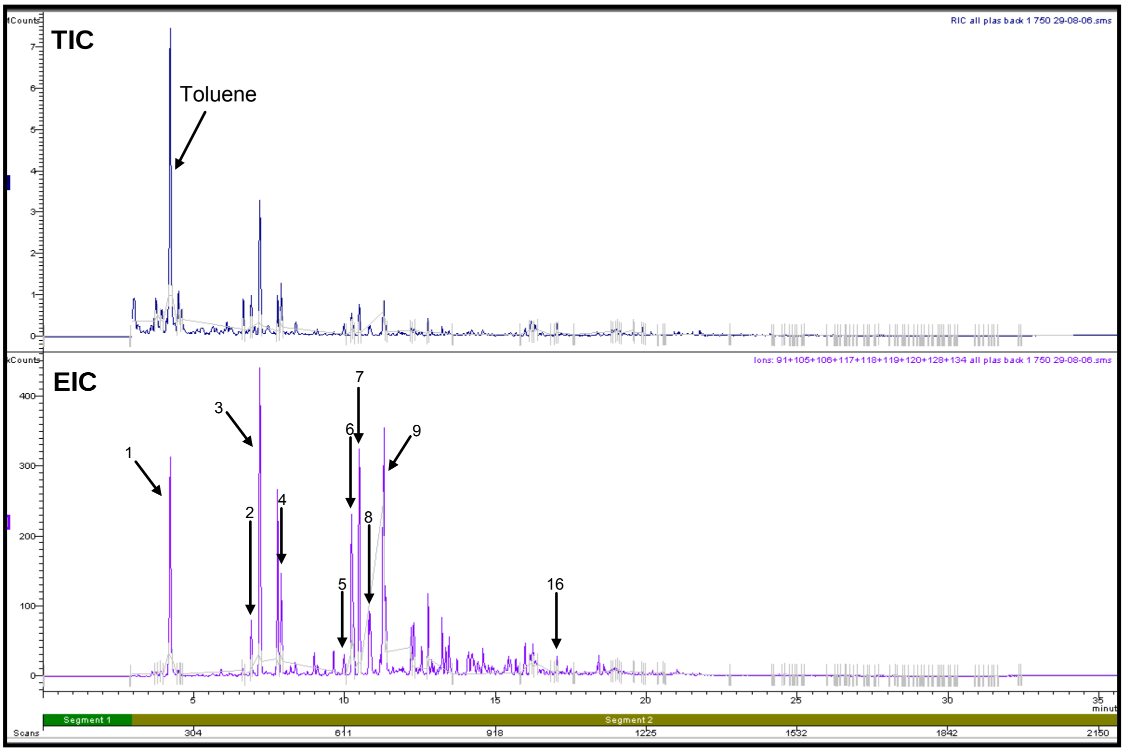


Figure H3.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Plastic Carpet Backing Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene, 8= 1-Ethyl-3-methylbenzene, 9= 1,2,4- Trimethylbenzene, 16= Naphthalene

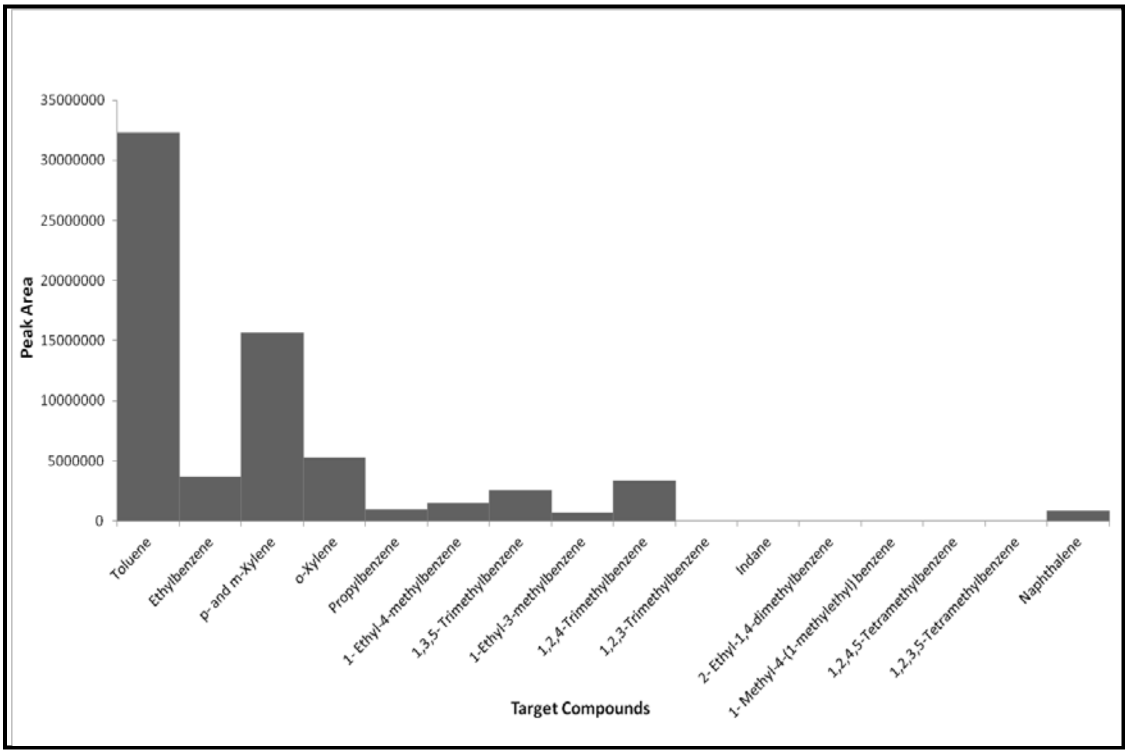


Figure H3.4: Target Compound Chromatogram of Plastic Carpet Backing Pyrolysed at 750ºC

Pyrolysis at 600ºC

Figure H3.5 shows the total ion chromatogram and extracted ion chromatogram for the plastic carpet backing pyrolysed at 600ºC. Pyrolysis at 600ºC resulted in only three target compounds being produced, including *p*- and *m*-xylene and *o*- xylene and 1,3,5- Trimethylbenzene. Interestingly at this temperature toluene and ethylbenzene were not produced. The target compound chromatogram is presented in Figure H3.6.

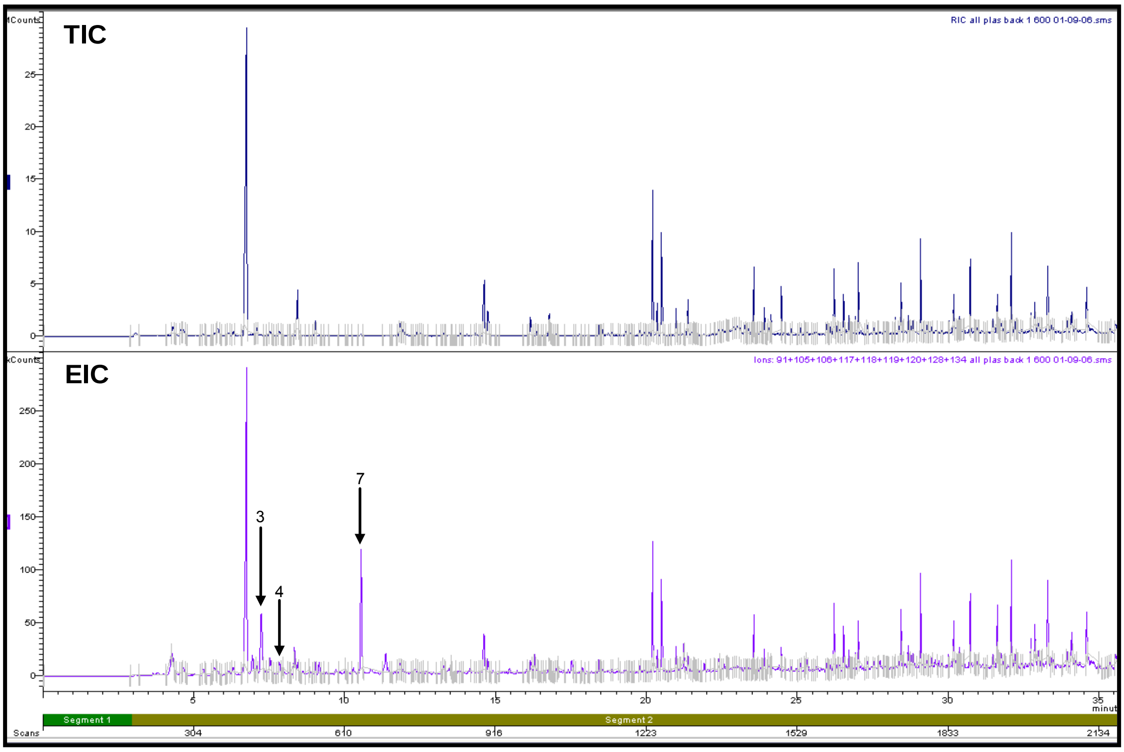


Figure H3.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Plastic Carpet Backing Pyrolysed at 600ºC

Key: 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 7= 1,3,5- Trimethylbenzene

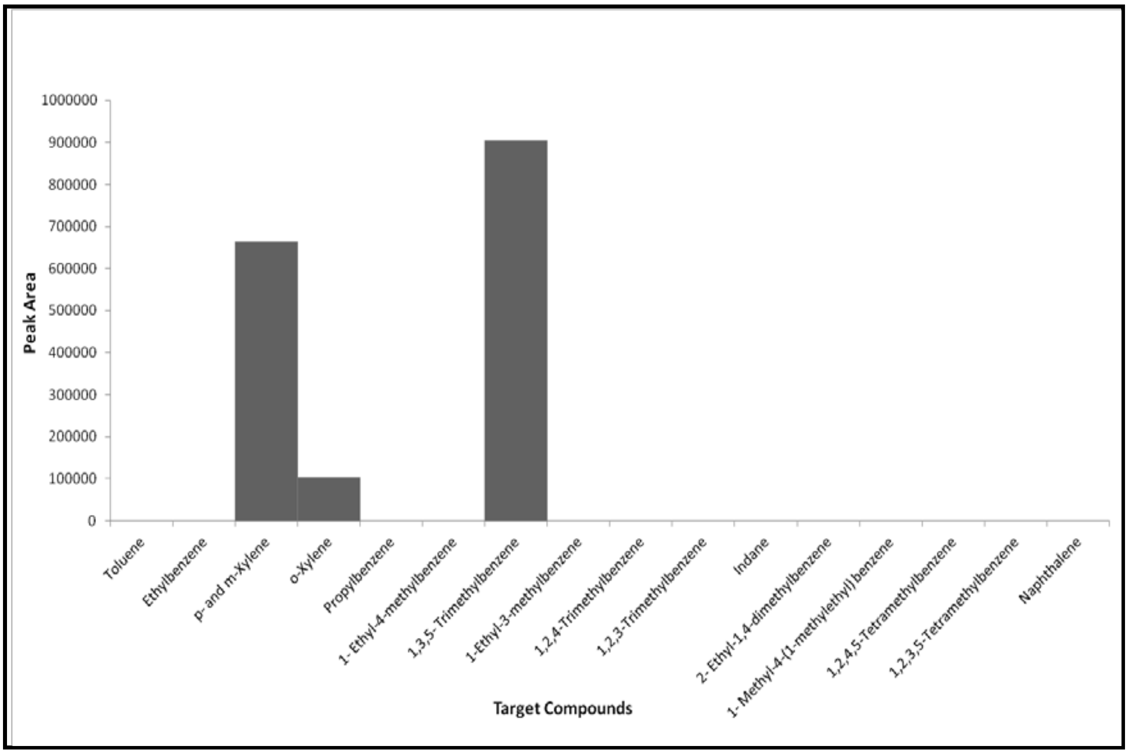


Figure H3.6: Target Compound Chromatogram of Plastic Carpet Backing Pyrolysed at 600ºC

Pyrolysis at 450ºC

Figure H3.7 shows the total ion chromatogram and extracted ion chromatogram for the plastic carpet backing pyrolysed at 450ºC. Pyrolysis at this temperature resulted in no target compounds being produced.

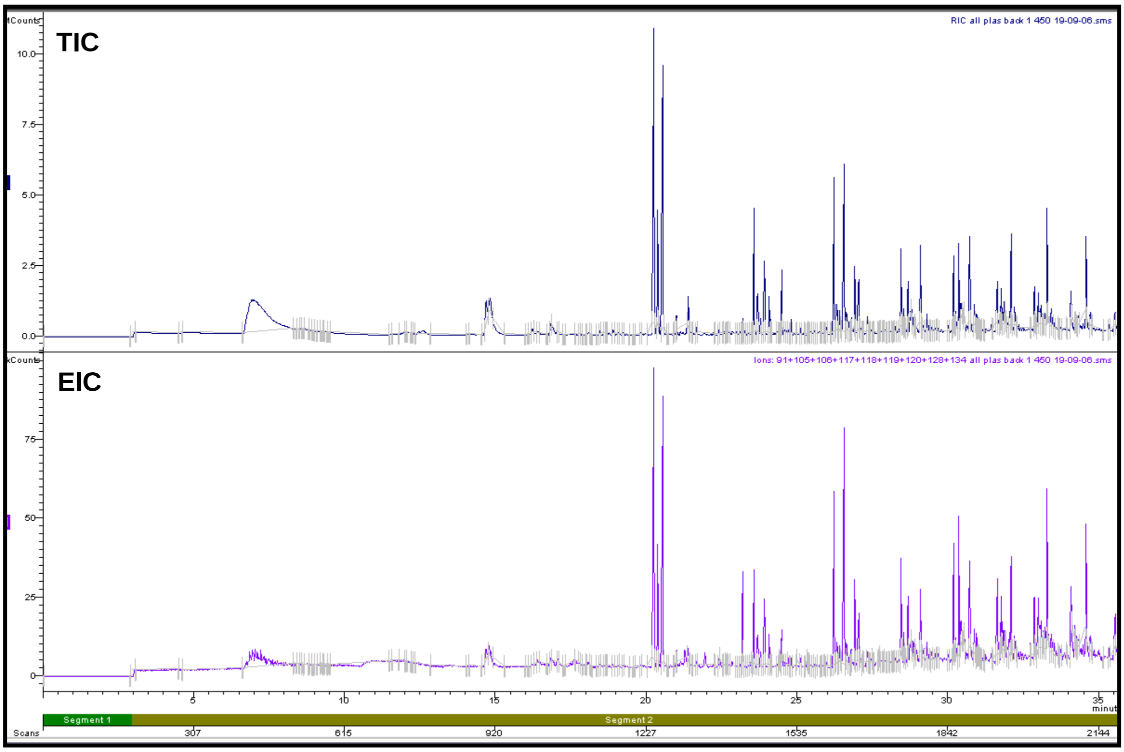


Figure H3.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Plastic Carpet Backing Pyrolysed at 450ºC

ADHESIVE FROM CARPET BACKING

Pyrolysis at 900ºC

Figure H4.1 shows the total ion chromatogram and extracted ion chromatogram for the adhesive from the carpet backing pyrolysed at 900ºC. Toluene and naphthalene were produced in the greatest abundance whilst ethylbenzene, *p*- and *m*-xylene and *o*- xylene were produced in lesser amounts. The target compound chromatogram is presented in FigureH4.2.

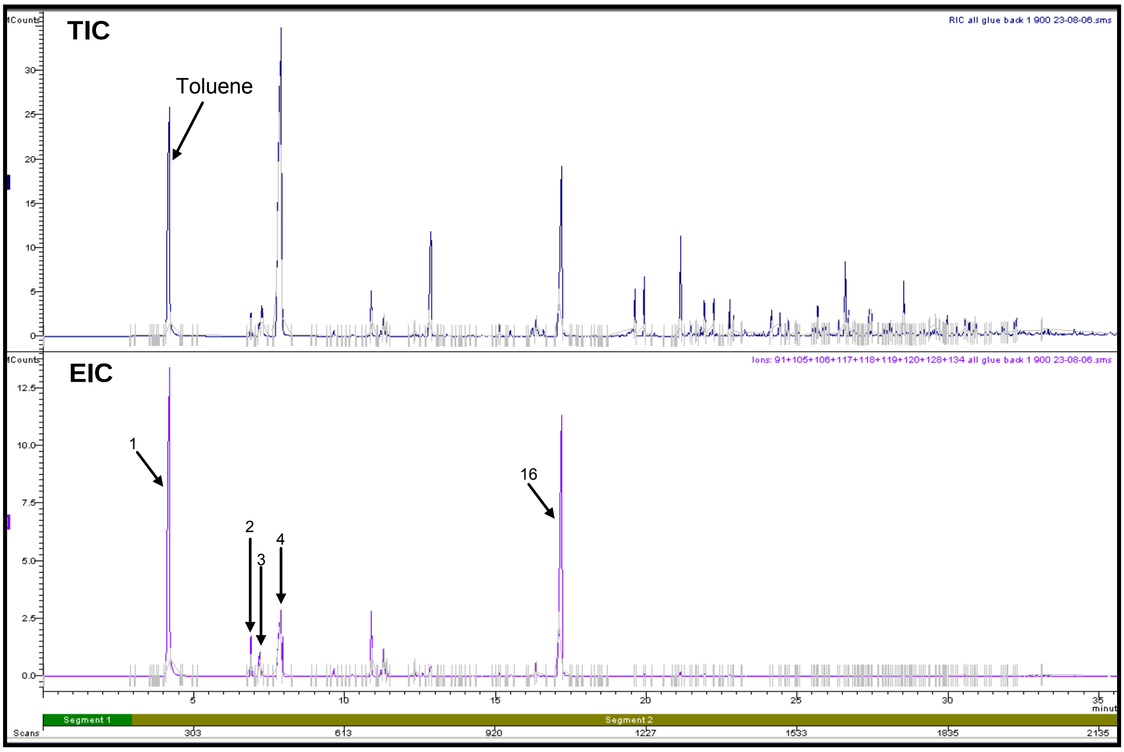


Figure H4.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Adhesive from Carpet Backing Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 16= Naphthalene

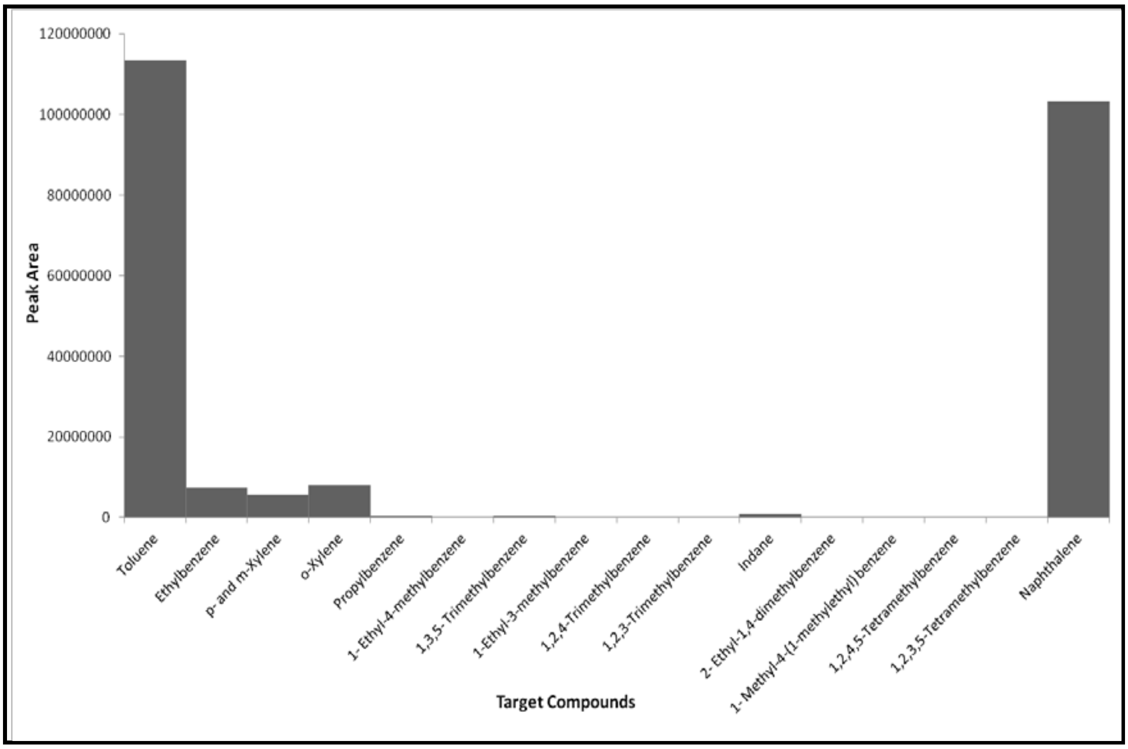


Figure H4.2: Target Compound Chromatogram of Adhesive from Carpet Backing Pyrolysed at 900ºC

Pyrolysis at 750ºC

Figure H4.3 shows the total ion chromatogram and extracted ion chromatogram for the adhesive from the carpet backing pyrolysed at 750ºC. The target compound chromatogram is shown in Figure H4.4. The most abundant target compound produced when the adhesive was pyrolysed at 750ºC was ethylbenzene, toluene, *p*- and *m*- *x*ylene, propylbenzene and 1-ethyl-4-methylbenzene were produced in significantly lesser amounts.

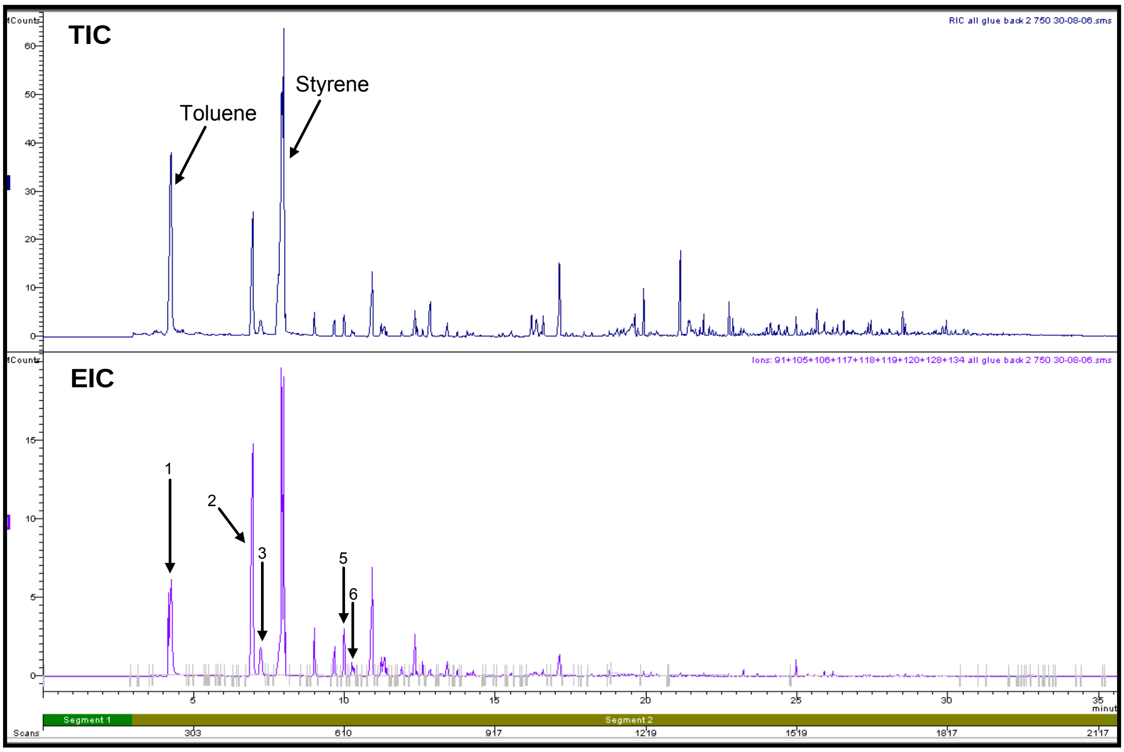


Figure H4.3: Total Ion Chromatogram and Extracted Ion Chromatogram Adhesive from Carpet Backing Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene

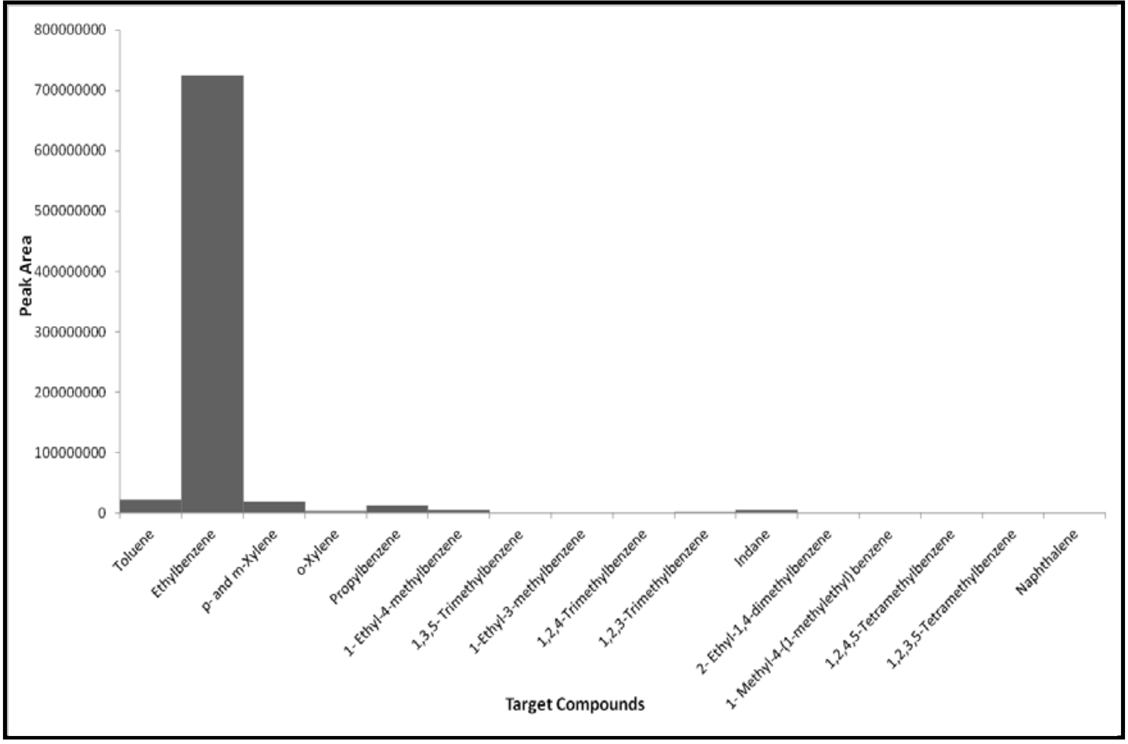


Figure H4.4: Target Compound Chromatogram of Adhesive from Carpet Backing Pyrolysed at 750ºC

Pyrolysis at 600ºC

Figure H4.5 shows the total ion chromatogram and extracted ion chromatogram for the adhesive from the carpet backing pyrolysed at 600ºC. Eight of the 16 target compounds were produced when the adhesive from the carpet backing was pyrolysed at this temperature. As seen in the target compound chromatogram (Figure H4.6) toluene and ethylbenzene were produced in the greatest abundance, whilst the other target compounds were produced in smaller amounts.

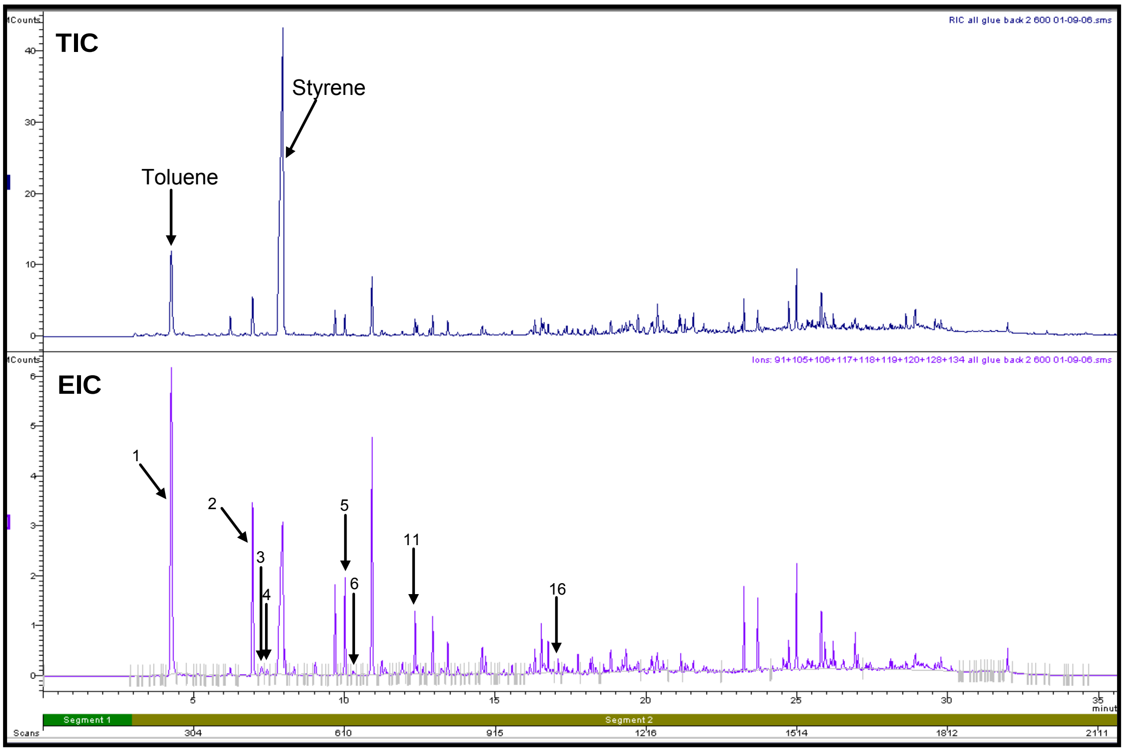


Figure H4.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Adhesive from Carpet Backing Pyrolysed at 600ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 11= Indane, 16= Naphthalene

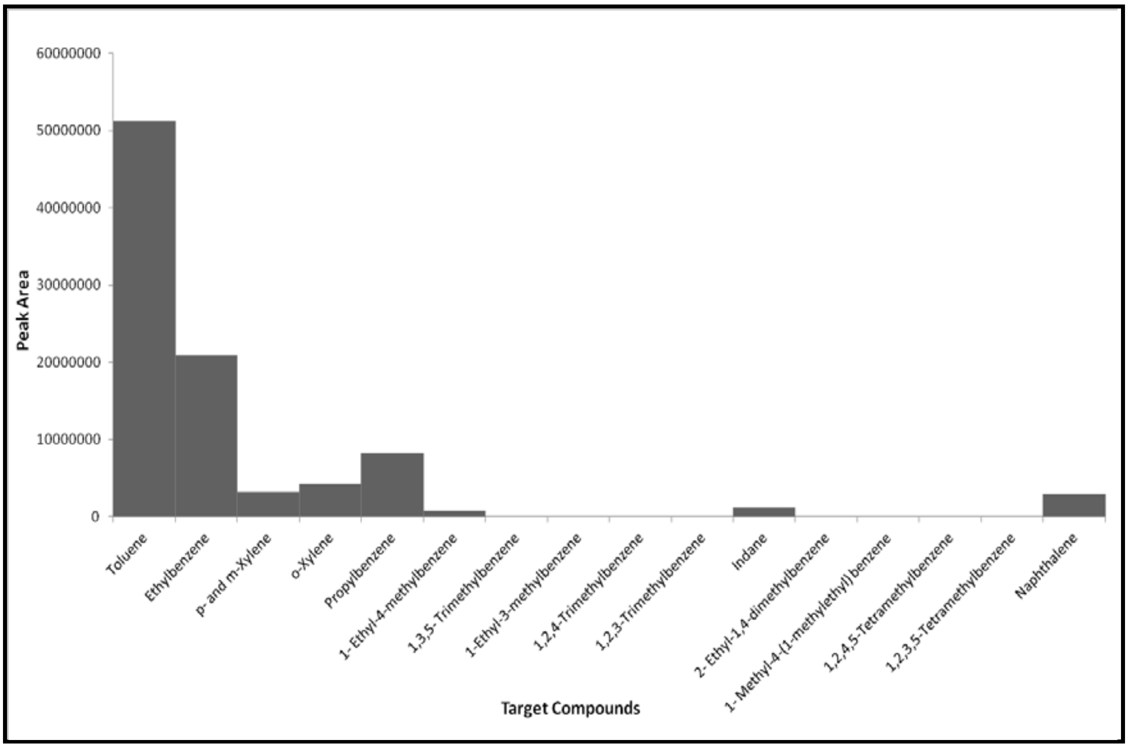


Figure H4.6: Target Compound Chromatogram of Adhesive from Carpet Backing Pyrolysed at 600ºC

Pyrolysis at 450ºC

Figure H4.7 shows the total ion chromatogram and extracted ion chromatogram for the adhesive from the carpet backing pyrolysed at 450ºC. Four target compounds were produced at this temperature, including toluene, ethylbenzene, propylbenzene and naphthalene. The target compound chromatogram is presented in Figure H4.8.

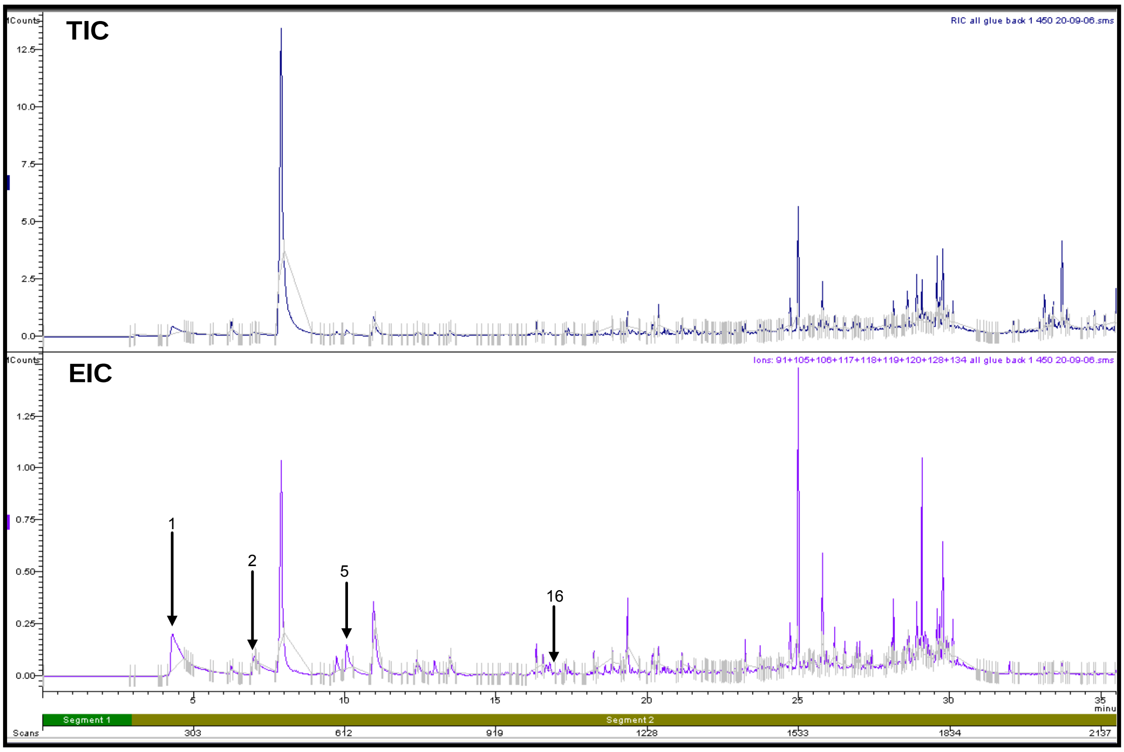


Figure H4.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Adhesive from Carpet Backing Pyrolysed at 450ºC

Key: 1= Toluene, 2=Ethylbenzene, 5=Propylbenzene, 16= Naphthalene

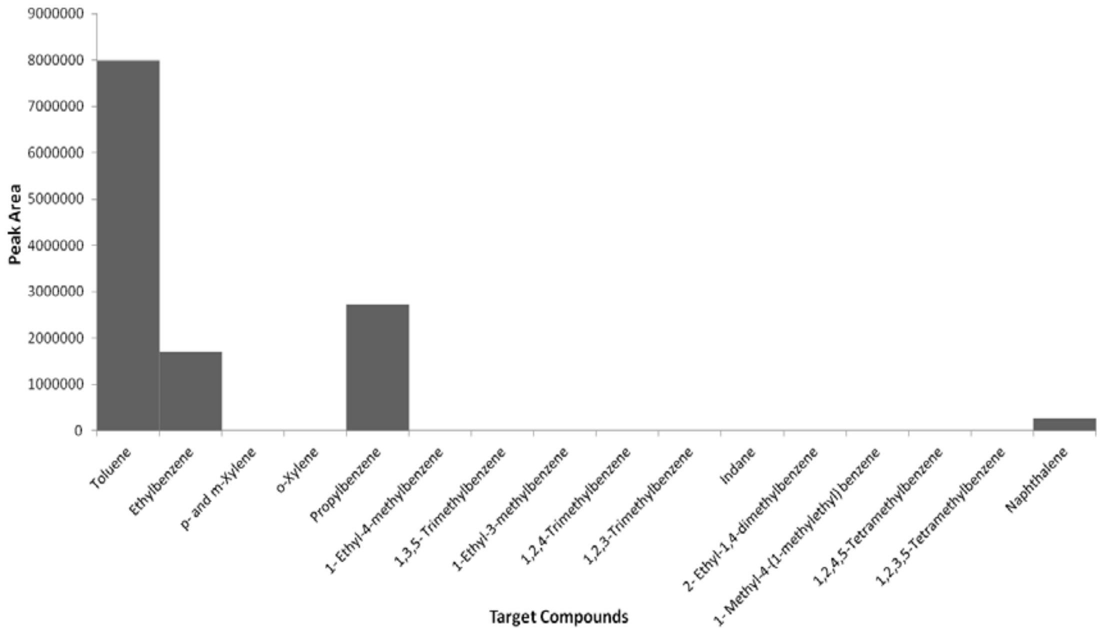


Figure H4.8: Target Compound Chromatogram of Adhesive from Carpet Backing Pyrolysed at 450ºC

POLYPROPYLENE CARPET FIBRES

Pyrolysis at 900ºC

Polypropylene fibres were initially pyrolysed at 900ºC. The total ion chromatogram and extracted ion chromatogram are presented in Figure H5.1. The most abundant peak in the total ion chromatogram and extracted ion chromatogram for the polypropylene fibres pyrolysed at this temperature was identified as toluene. Styrene was also identified in the total ion chromatogram however in the extracted ion chromatogram the other most abundant compound produced was naphthalene. On closer inspection, a number of other target compounds were able to be recovered from this sample, including ethylbenzene, *p-* and *m-* *x*ylene and *o*-xylene, propylbenzene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene, 1-ethyl-3-methylbenzene, 1,2,4-trimethylbenzene and indane were also able to be extracted. The target compound chromatogram is presented in Figure H5.2.

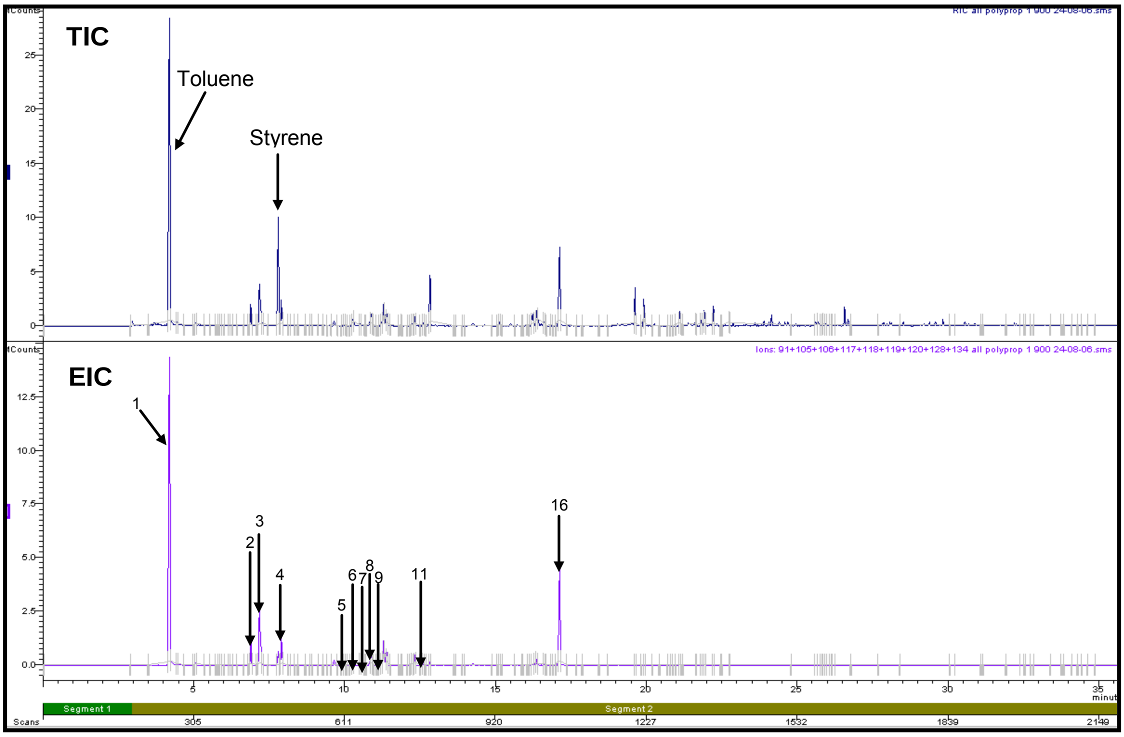


Figure H5.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Polypropylene Fibres Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5= Propylbenzene, 6= 1-Ethyl-4-methylbenzene, 7= 1,3,5-Trimethylbenzene, 8= 1-Ethyl-3-methylbernzene, 9= 1,2,4-Trimethylbenzene, 11= Indane, 16= Naphthalene

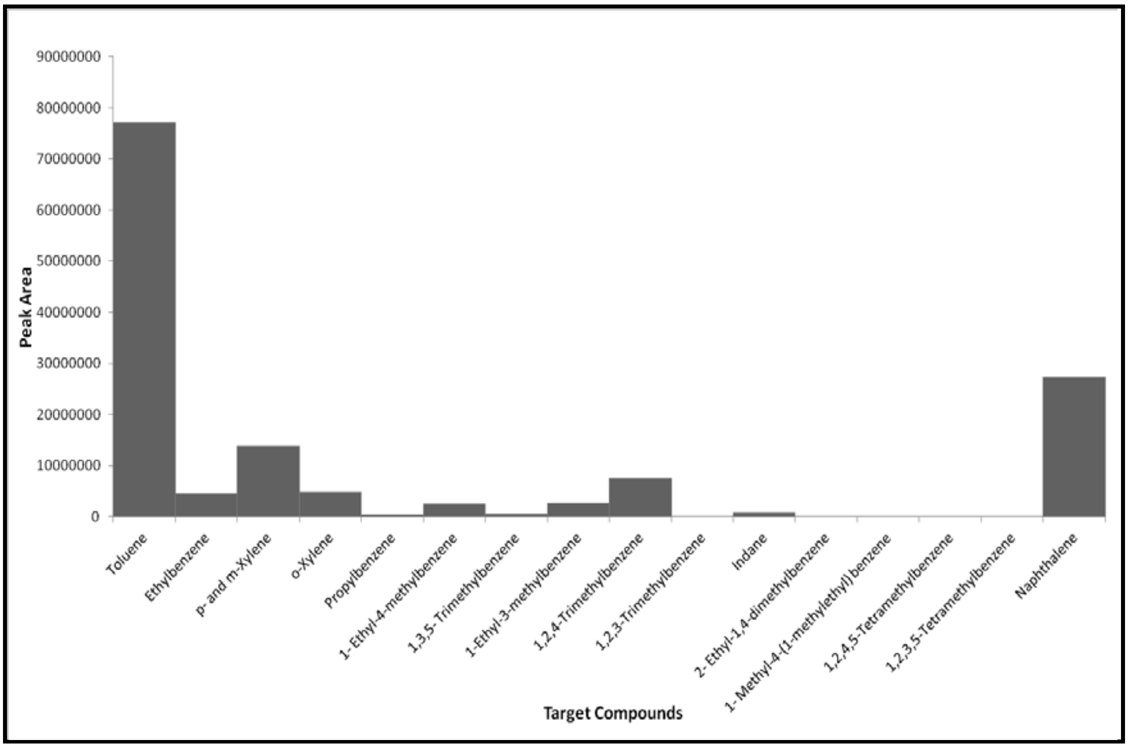


Figure H5.2: Target Compound Chromatogram of Polypropylene Fibres Pyrolysed at 900ºC

Pyrolysis at 750ºC

The total ion chromatogram and extracted ion chromatogram for polypropylene fibres pyrolysed at 750ºC can be seen in Figure H5.3. The extracted ion chromatogram shows that a number of petrol target compounds were produced. These were identified as toluene, ethylbenzene, *p*- and *m*-*x*ylene, *o*-xylene, propylbenzene, 1-ethyl-4-methylbenzene and 1,3,5-trimethylbenzene. On closer inspection, other target compounds were also identified and are presented in Figure H5.4.

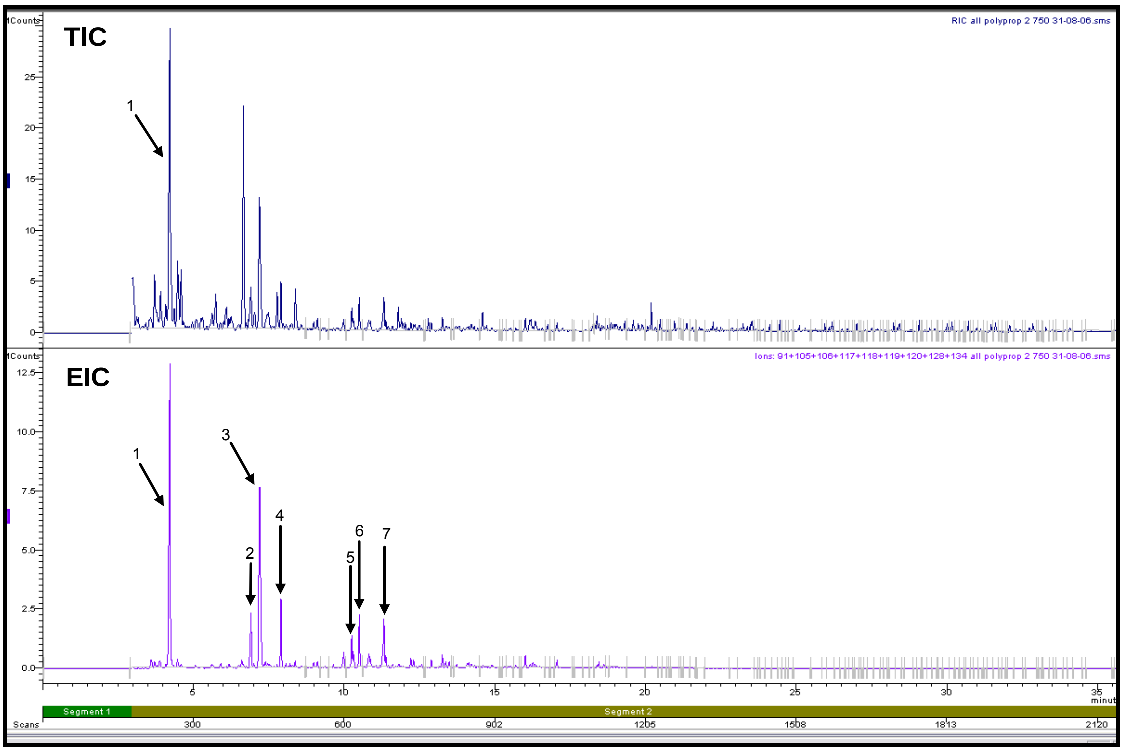


Figure H5.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Polypropylene Fibres Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene, 7= 1,3,5- Trimethylbenzene

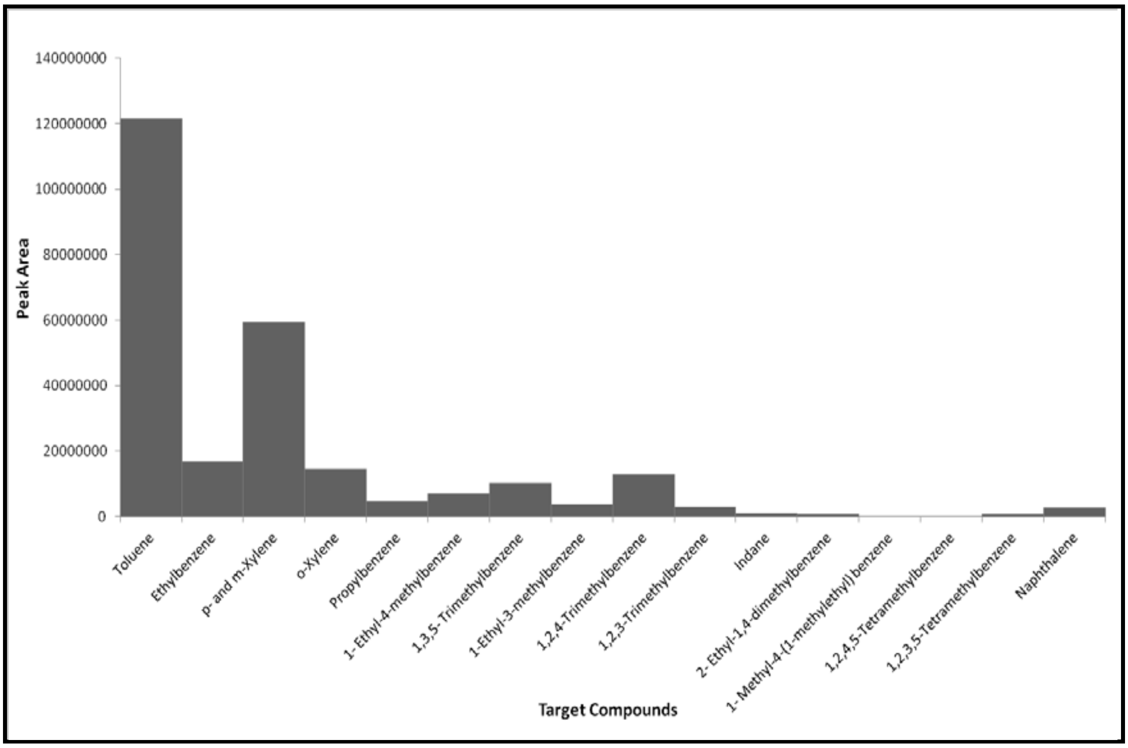


Figure H5.4: Target Compound Chromatogram of Polypropylene Fibres Pyrolysed at 750ºC

Pyrolysis at 600ºC

Polypropylene fibres pyrolysed at 600ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H5.5. As seen in Figure H5.5, polypropylene fibres pyrolysed at 600ºC do not produce as many of the volatile products as compared with the polypropylene fibres pyrolysed at 900ºC and 750ºC.

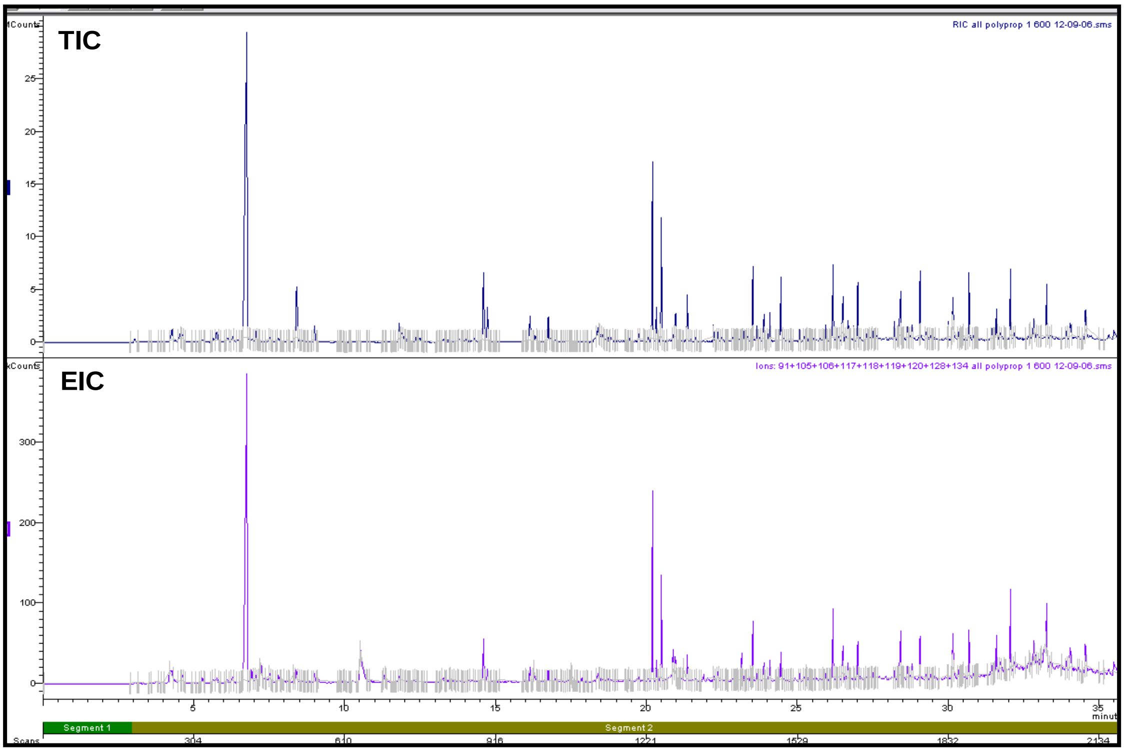


Figure H5.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Polypropylene Fibres Pyrolysed at 600ºC

Pyrolysis at 450ºC

Polypropylene fibres pyrolysed at 450ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H5.6. Polypropylene fibres pyrolysed at 450ºC do not produce many volatile products, thus indicating that at this temperature not much thermal degradation is occurring. As a result no petrol target compounds were produced.

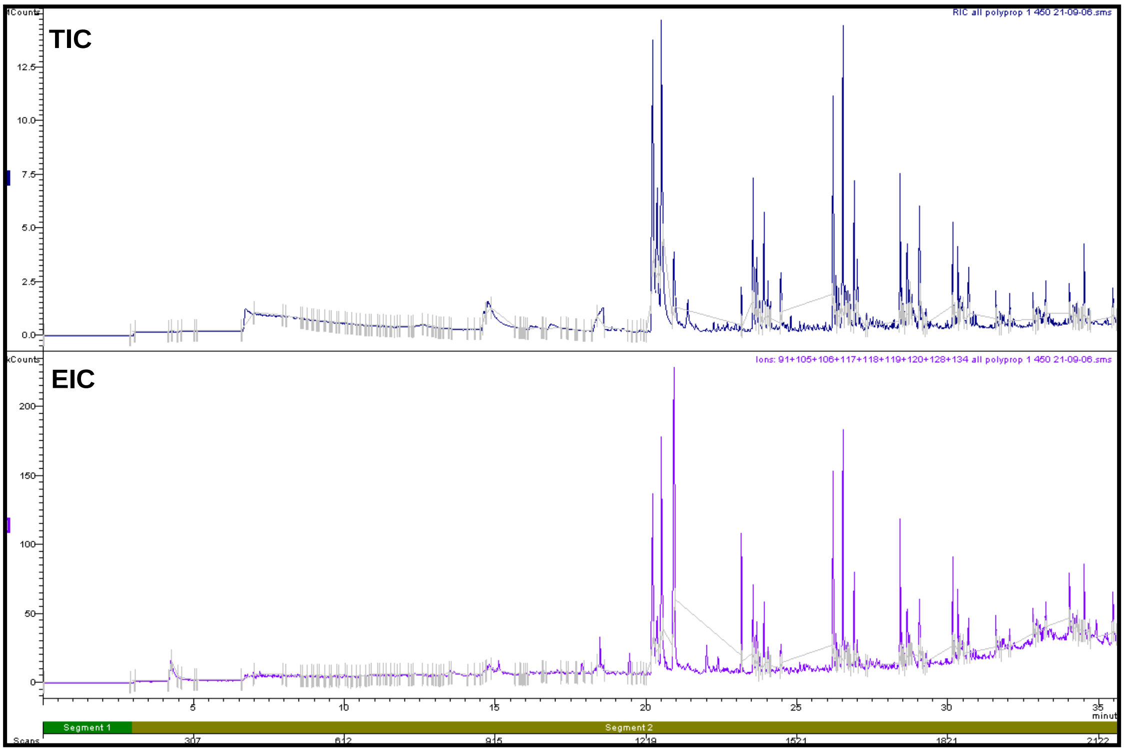


Figure H5.6: Total Ion Chromatogram and Extracted Ion Chromatogram of Polypropylene Fibres Pyrolysed at 450ºC

PYROLYSIS OF WOOL CARPET

Pyrolysis at 900ºC

Wool fibres were initially pyrolysed at 900ºC. The total ion chromatogram and extracted ion chromatogram is presented in Figure H6.1. Toluene and naphthalene were the only observable target compounds in the total ion chromatogram. However in the extracted ion chromatogram, ethylbenzene and *p*- and *m*- *x*ylene were also able to be identified and are presented in the target compound chromatogram in Figure H6.2.

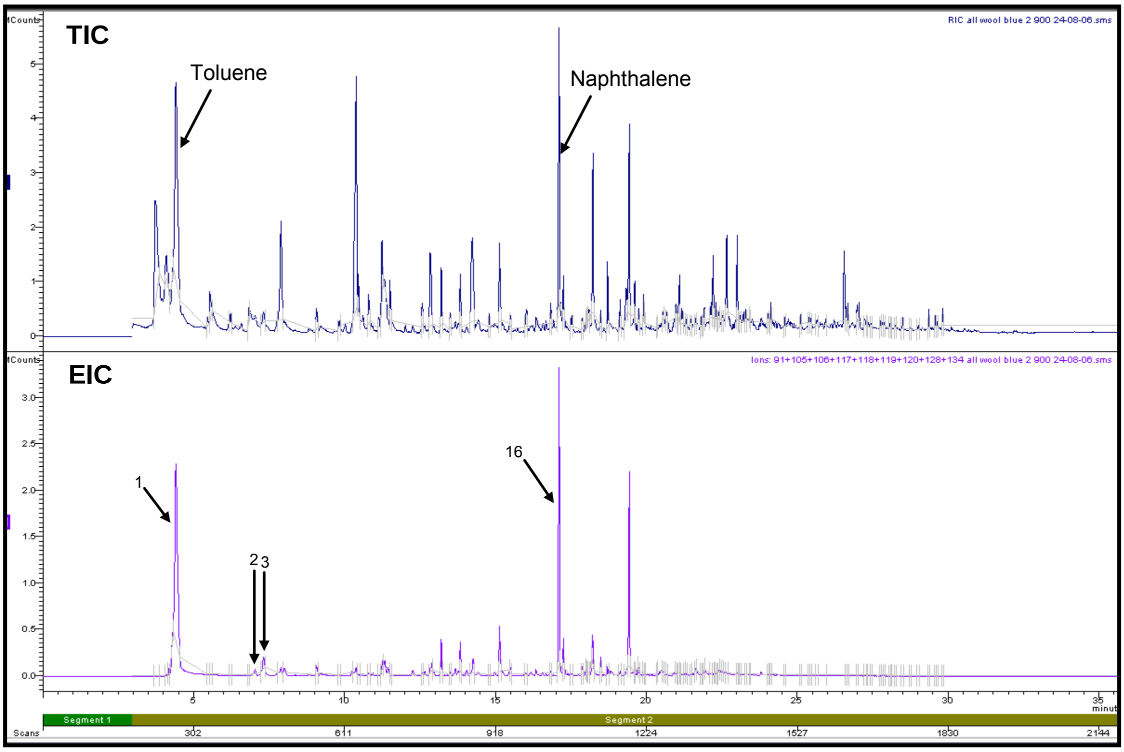


Figure H6.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Wool Fibres Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 16= Naphthalene

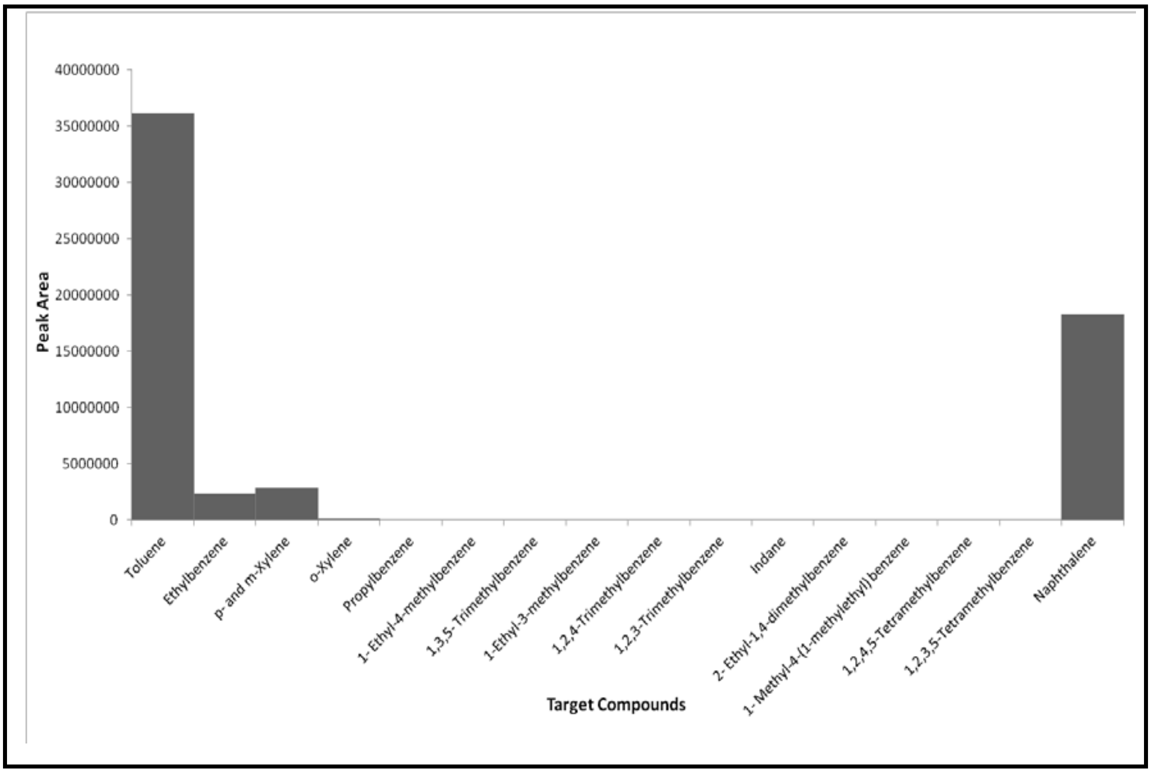


Figure H6.2: Target Compound Chromatogram of Wool Fibres Pyrolysed at 900ºC

Pyrolysis at 750ºC

The total ion chromatogram and extracted ion chromatogram for wool pyrolysed at 750ºC is shown in Figure H6.3. The most abundant peak in both the total ion chromatogram and extracted ion chromatogram was identified as toluene. Ethylbenzene, *p*- and *m*- *x*ylene and *o*-xylene and propylbenzene were also produced and identified. The target compound chromatogram is presented in Figure H6.4.

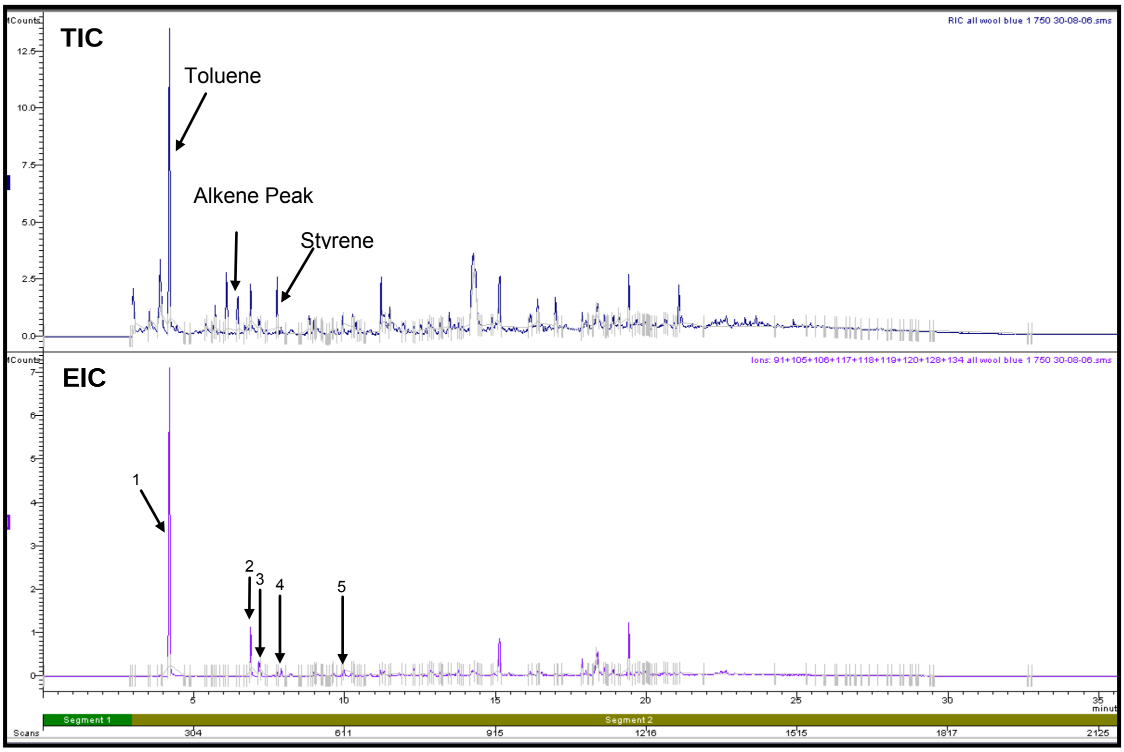


Figure H6.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Wool Fibres Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5= Propylbenzene

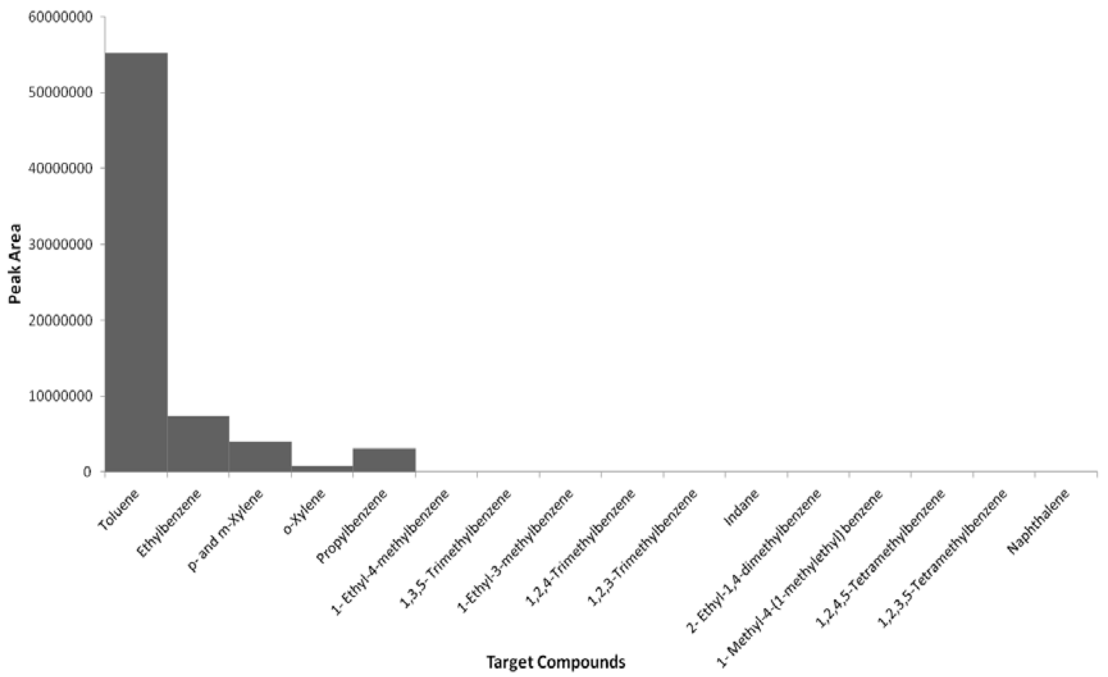


Figure H6.4: Target Compound Chromatogram of Wool Fibres Pyrolysed at 750ºC

Pyrolysis at 600ºC

The total ion chromatogram and extracted ion chromatogram for wool pyrolysed at 600ºC is shown in Figure H6.5. The most abundant target compound present in the extracted ion chromatogram was identified as toluene however ethylbenzene, *p*- and *m*- *x*ylene and *o*-xylene, propylbenzene, indane and naphthalene were also identified and are present in the target compound chromatogram in Figure H6.6.

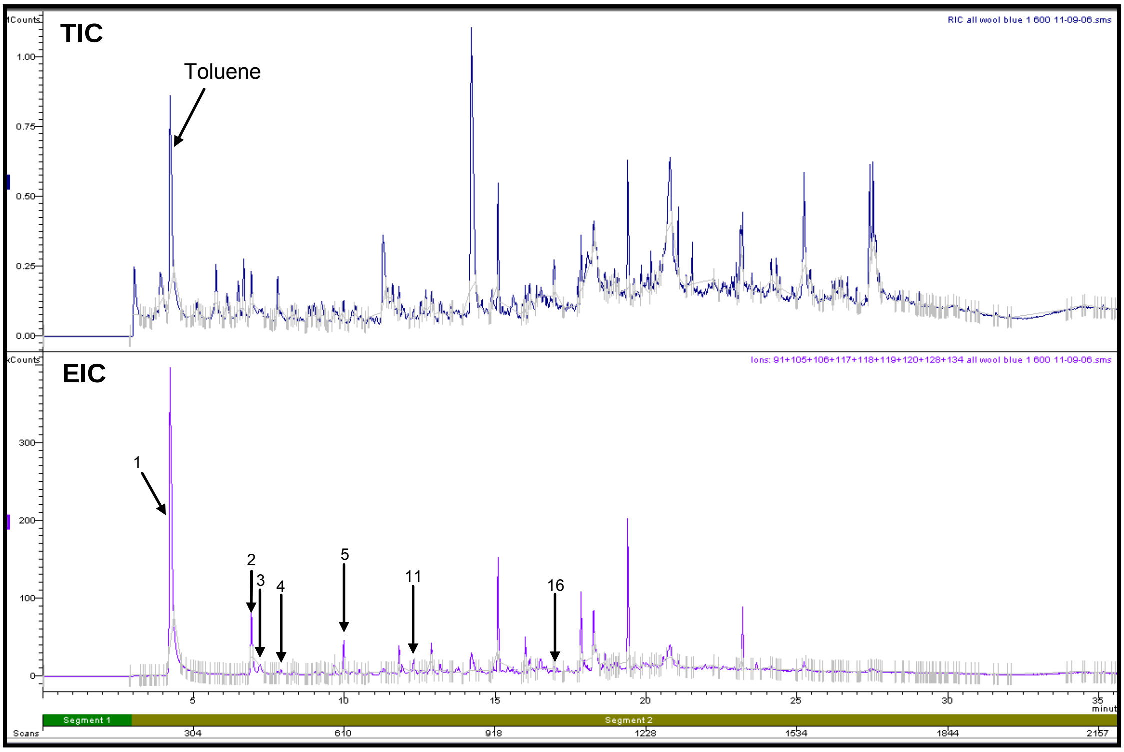


Figure H6.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Wool Fibres Pyrolysed at 600ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5= Propylbenzene, 11= Indane, 16= Naphthalene

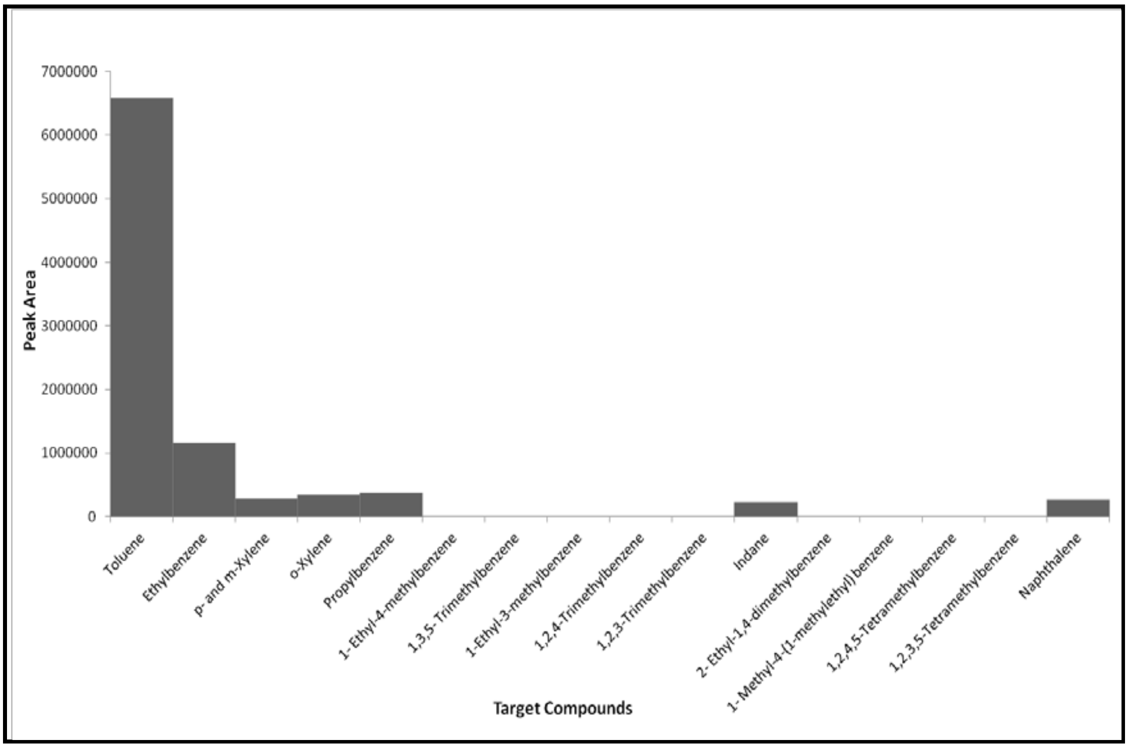


Figure H6.6: Target Compound Chromatogram of Wool Fibres Pyrolysed at 600ºC

Pyrolysis at 450ºC

The total ion chromatogram and extracted ion chromatogram for wool fibres pyrolysed at 450ºC is shown in Figure H6.7. Figure H6.7 shows that wool fibres pyrolysed at 450ºC do not produce many volatile products, thus indicating that at this temperature not much thermal degradation is occurring. However, toluene was still able to be identified in the extracted ion chromatogram.

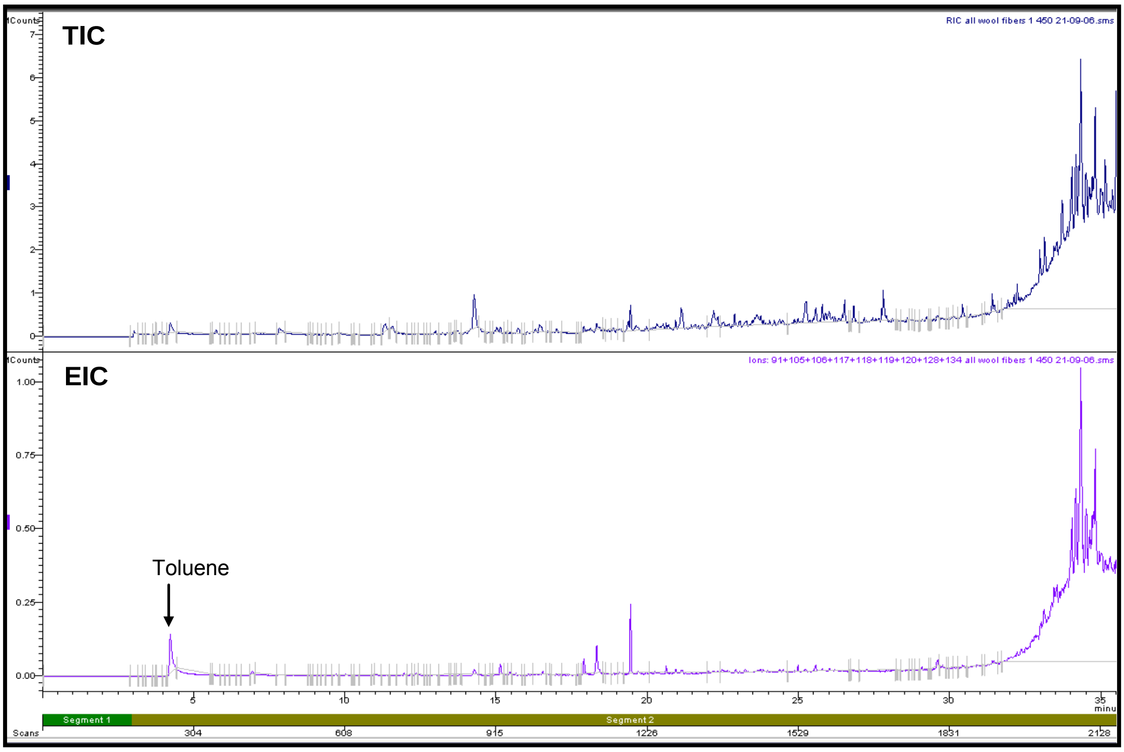


Figure H6.7: Total Ion Chromatogram and Extracted Ion Chromatogram of Wool Fibres Pyrolysed at 450ºC

50-50 POLYPROPYLENE-WOOL CARPET

Pyrolysis at 900ºC

The 50-50 blended fibres were initially pyrolysed at 900ºC. The total ion chromatogram and extracted ion chromatogram is presented in Figure H7.1. The most abundant peak in the total ion chromatogram and extracted ion chromatogram for the fibres pyrolysed at this temperature was identified as toluene. Styrene was also identified in the total ion chromatogram however in the extracted ion chromatogram the other abundant compound recovered was naphthalene. Similar to the polypropylene fibres, a number of other target compound were able to be recovered from this sample, including ethylbenzene, *p-* and *m-* *x*ylene and *o*-xylene, propylbenzene, 1,3,5-trimethylbenzene and indane were also able to be extracted. The target compound chromatogram is presented in Figure H7.2.

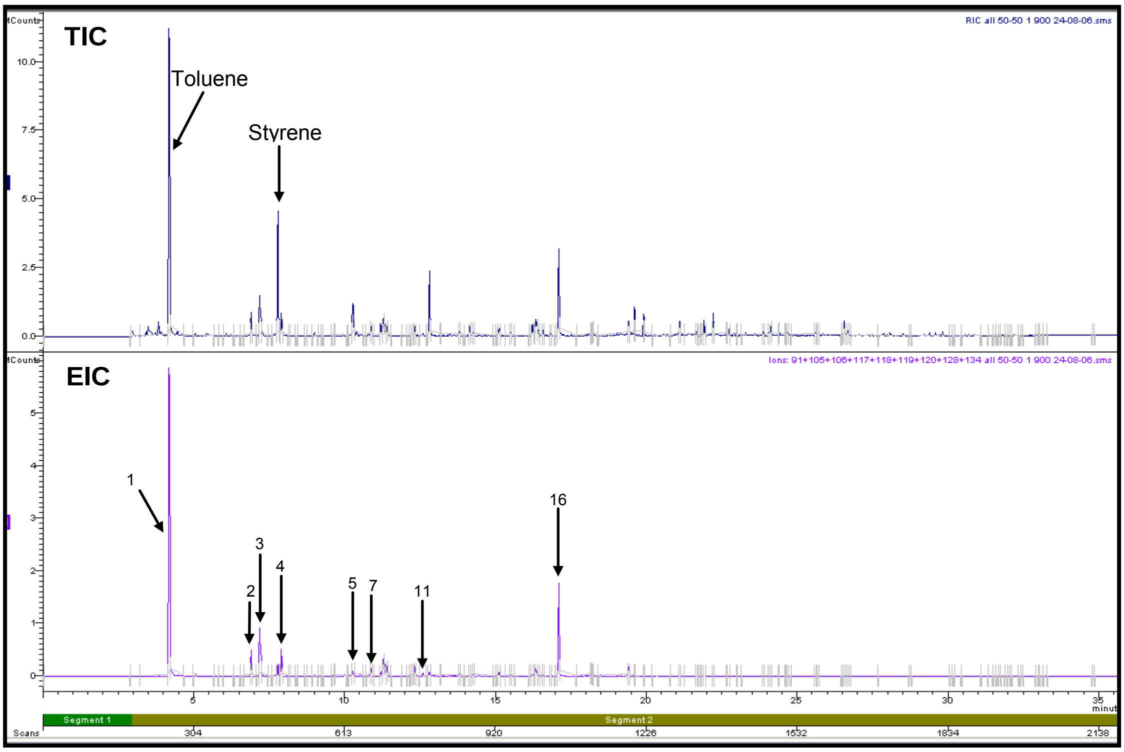


Figure H7.1: Total Ion Chromatogram and Extracted Ion Chromatogram of 50-50 Polypropylene-Wool Fibres Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p-* and *m-* Xylene, 4= *o*-Xylene, 5= Propylbenzene, 7= 1,3,5-Trimethylbenzene, 11= Indane, 16= Naphthalene

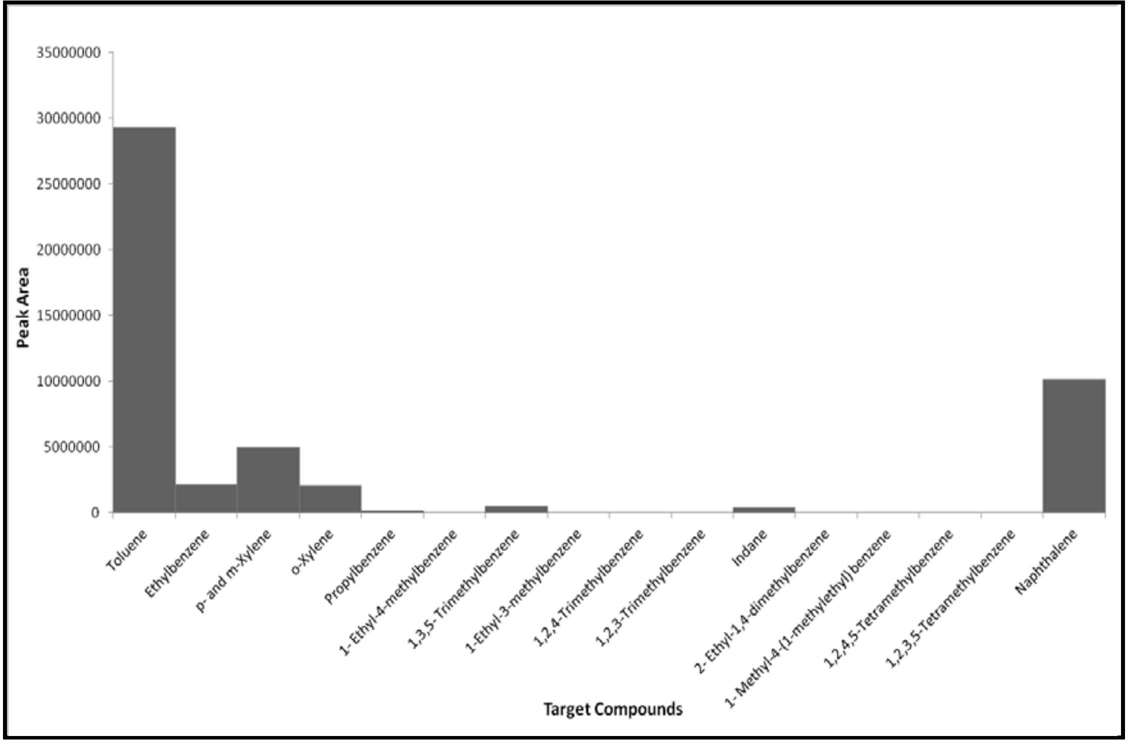


Figure H7.2: Target Compound Chromatogram of 50-50 Polypropylene-Wool Fibres Pyrolysed at 900ºC

Pyrolysis at 750ºC

The total ion chromatogram and extracted ion chromatogram for 50-50 polypropylene-wool pyrolysed at 750ºC can be seen in Figure H7.3. The extracted ion chromatogram produced a number of other petrol target compounds which were identified as toluene, ethylbenzene, *p*- and *m*- *x*ylene, *o*-xylene, propylbenzene, 1-ethyl-4-methylbenzene and 1,3,5-trimethylbenzene. On closer inspection, other target compounds were also identified and are presented in the target compound chromatogram in Figure H7.4.

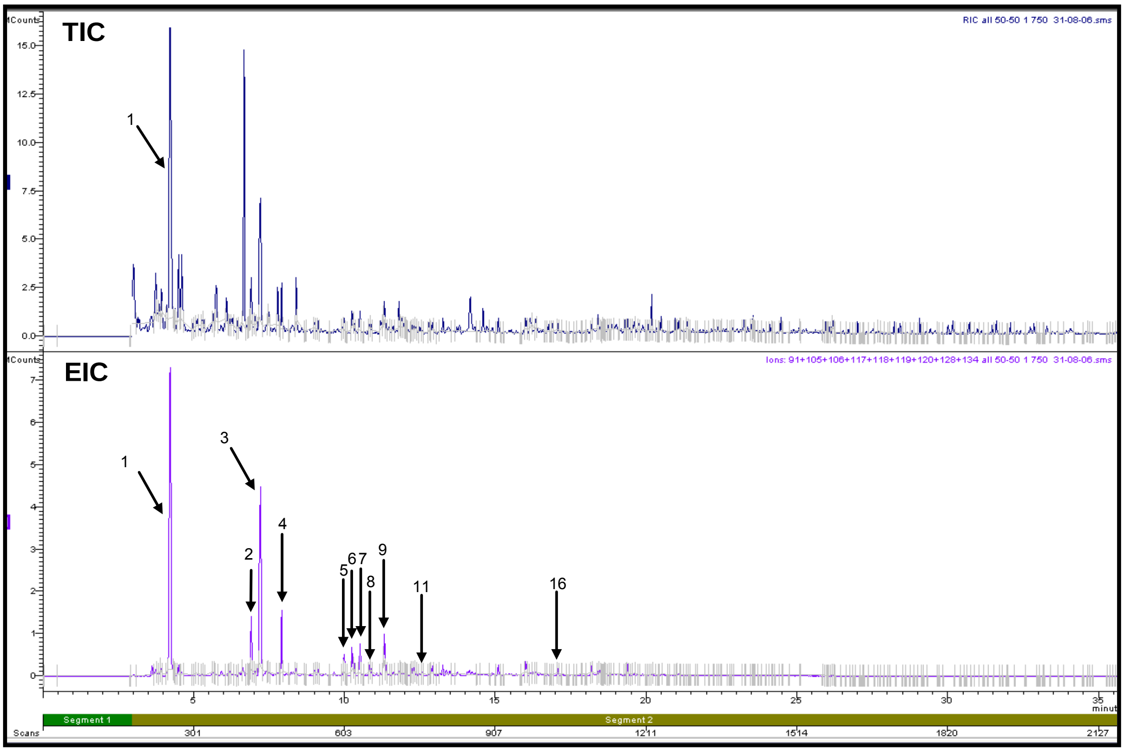


Figure H7.3: Total Ion Chromatogram and Extracted Ion Chromatogram of 50-50 Polypropylene-Wool Fibres Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 6 = 1-Ethyl-4-methylbenzene, 7= 1,3,5-trimethyl benzene, 8=1-Ethyl-3-methylbenzene, 9= 1,2,3-trimethyl benzene, 11= Indane, 16= Naphthalene

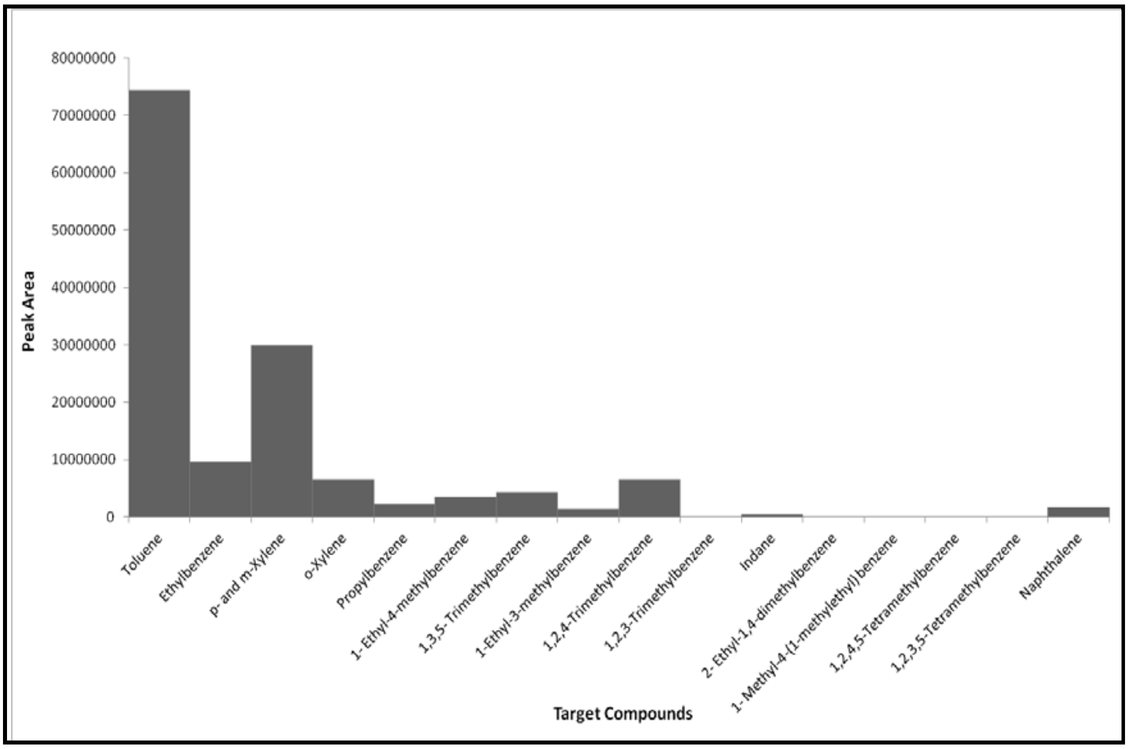


Figure H7.4: Target Compound Chromatogram of 50-50 Polypropylene-Wool Fibres Pyrolysed at 750ºC

Pyrolysis at 600ºC

The polypropylene-wool fibres pyrolysed at 600ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H7.5. The only target compound able to be identified was toluene.

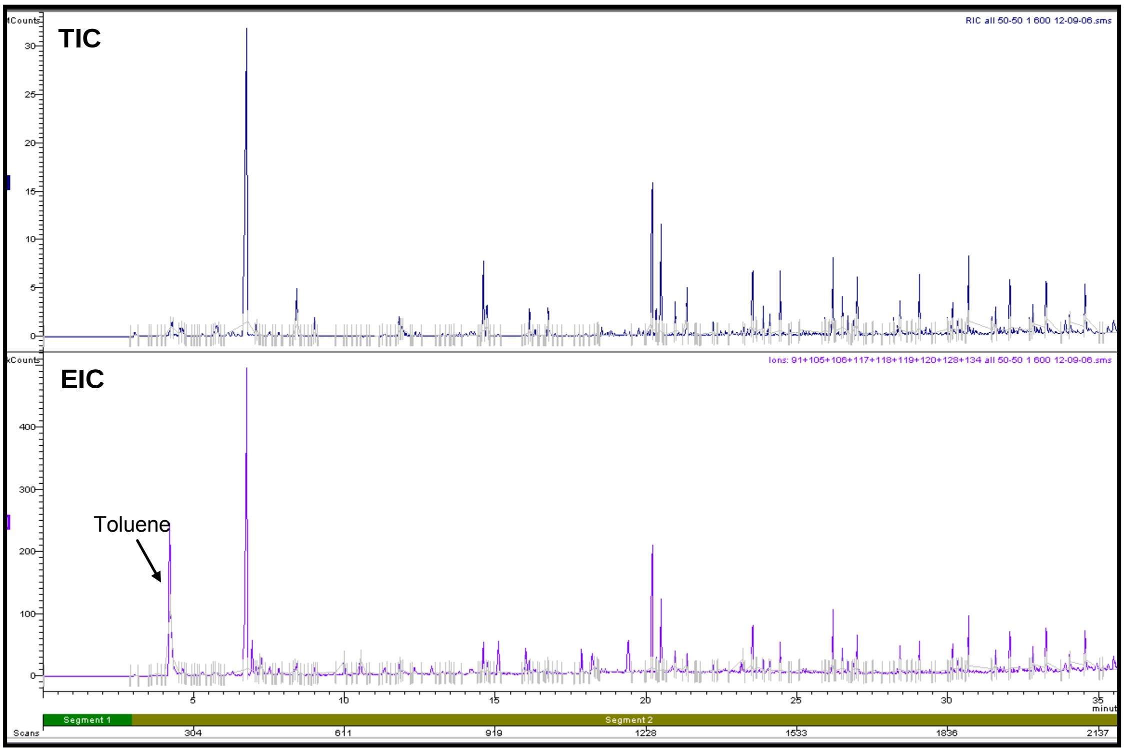


Figure H7.5: Total Ion Chromatogram and Extracted Ion Chromatogram of 50-50 Polypropylene-Wool Fibres Pyrolysed at 600ºC

Pyrolysis at 450ºC

The polypropylene-wool fibres pyrolysed at 450ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H7.6. No volatile products appeared evident in the total ion chromatogram, which indicates that not much thermal degradation is happening.

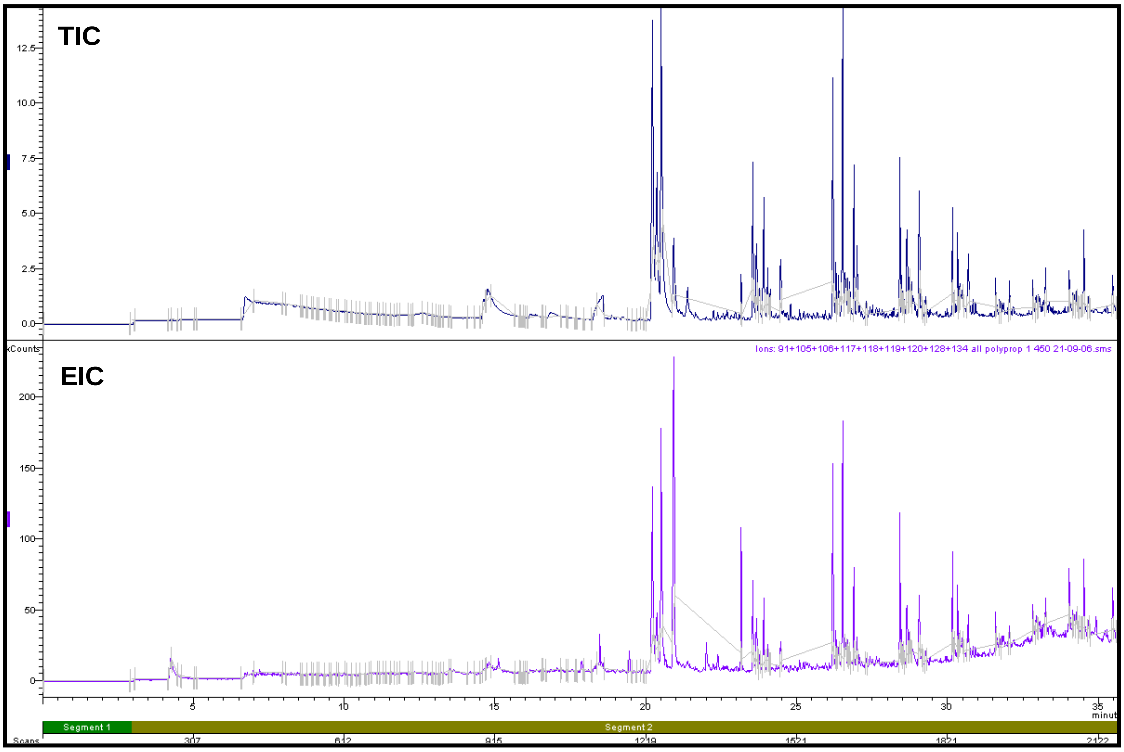


Figure H7.6: Total Ion Chromatogram and EIC of 50-50 Polypropylene-Wool Fibres Pyrolysed at 450ºC

FURNITURE FOAM

Pyrolysis at 900ºC

The furniture foam pyrolysed at 900ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H8.1. The target compounds produced when pyrolysing this sample were toluene, ethylbenzene, *p*- and *m*- xylene and *o*- xylene and naphthalene. The target compound chromatogram is presented in Figure H8.2.

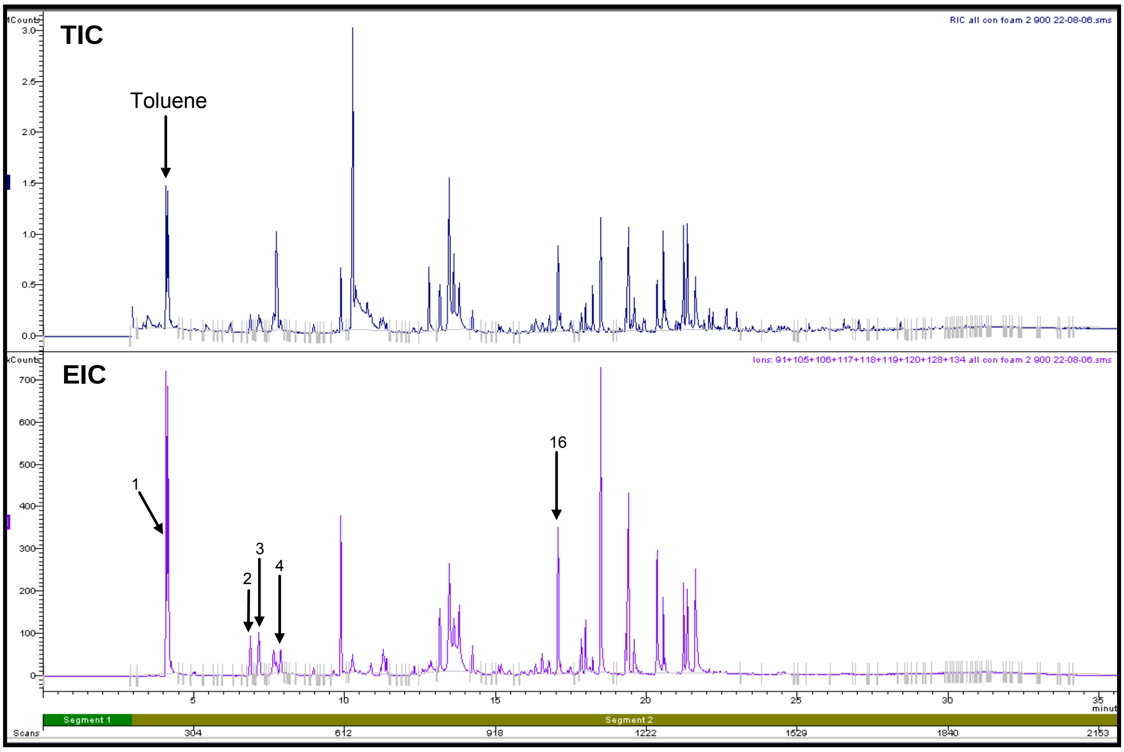


Figure H8.1: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 16= Naphthalene

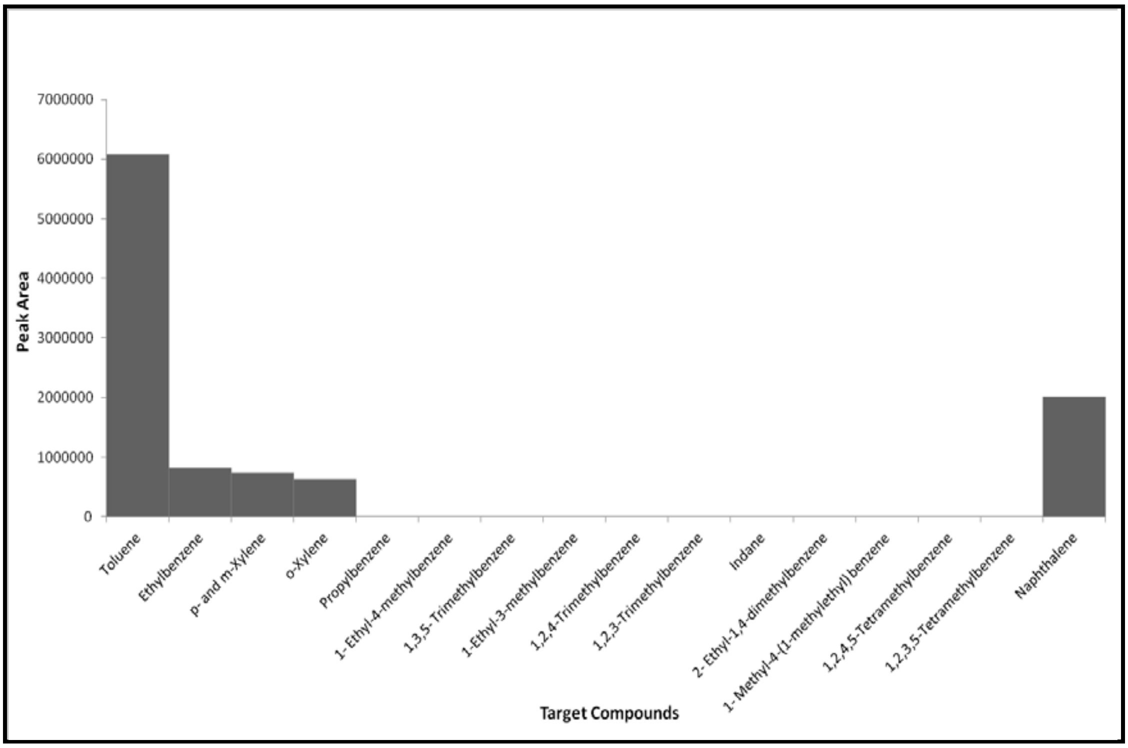


Figure H8.2: Target Compound Chromatogram of Foam Pyrolysed at 900ºC

Pyrolysis at 750ºC

The furniture foam pyrolysed at 750ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H8.3. A number of target compounds were produced by the pyrolysis of the foam at 750ºC including toluene, ethylbenzene, *p*- and *m*- xylene and *o*-xylene, propylbenzene, 1,2,4-trimethylbenzene and naphthalene. The target compound chromatograms is presented in Figure H8.4.

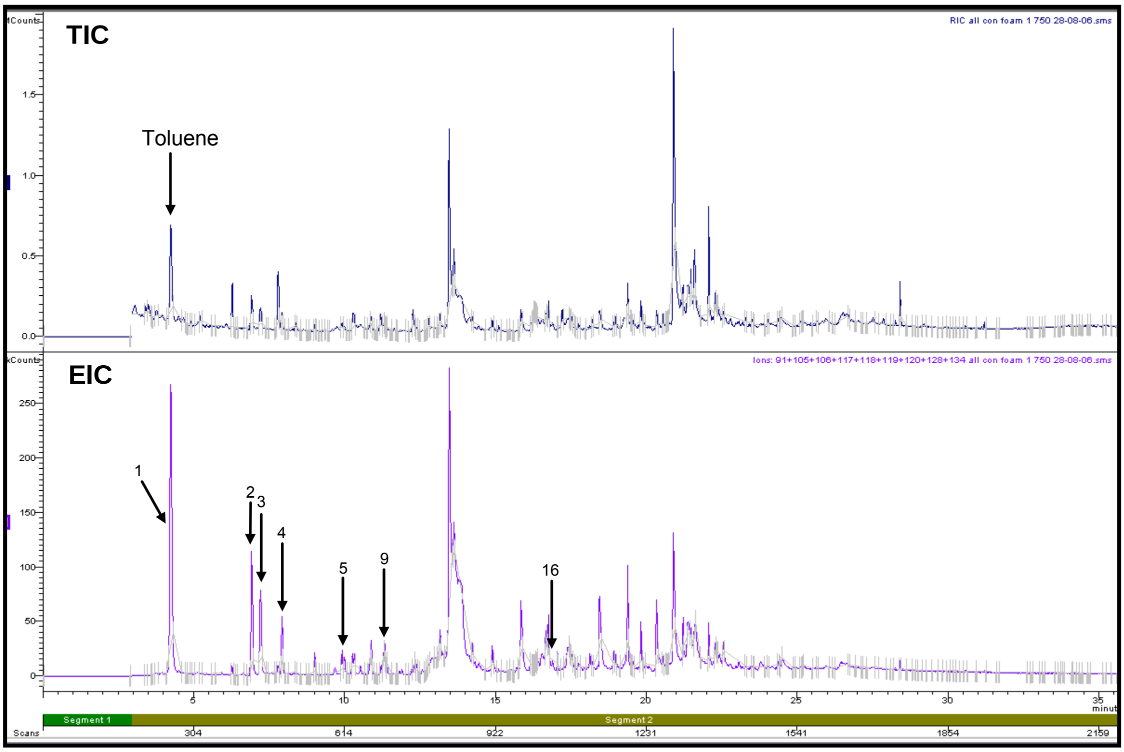


Figure H8.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 9= 1,2,3-trimethyl benzene, 16= Naphthalene

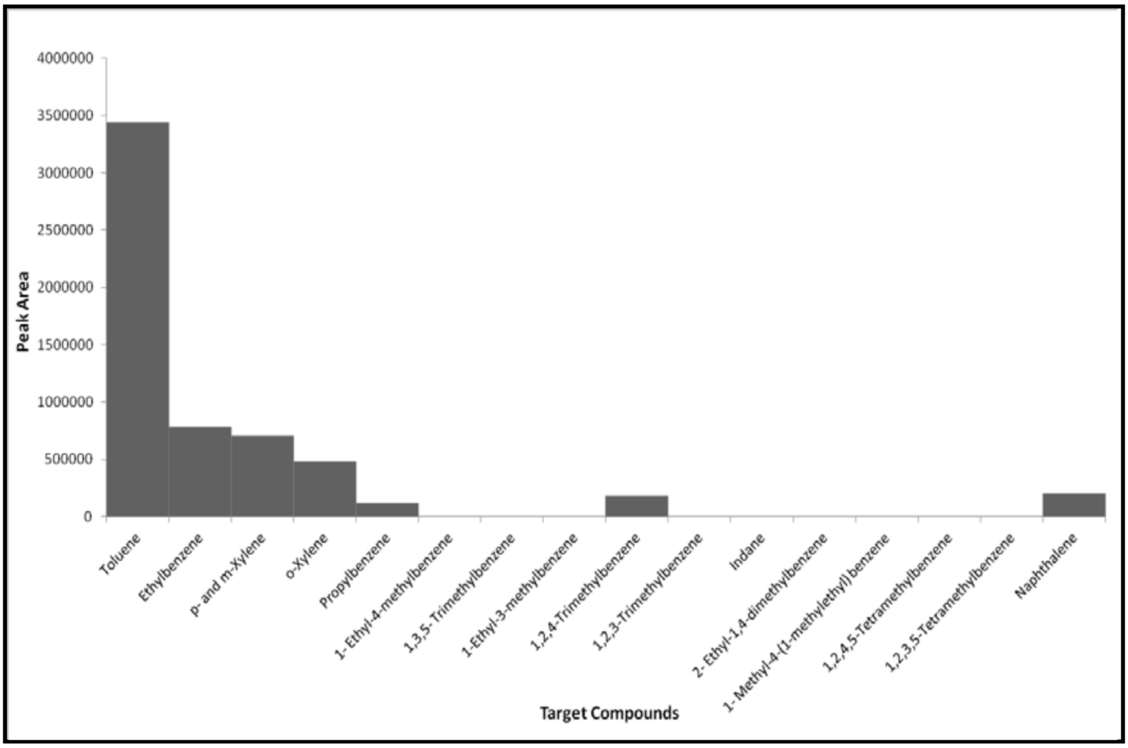


Figure H8.4: Target Compound Chromatogram of Foam Pyrolysed at 750ºC

Pyrolysis at 600ºC

The furniture foam pyrolysed at 600ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H8.5. The extracted ion chromatogram for the foam pyrolysed at 600ºC shows two major peaks present, which were not identified as target compounds.

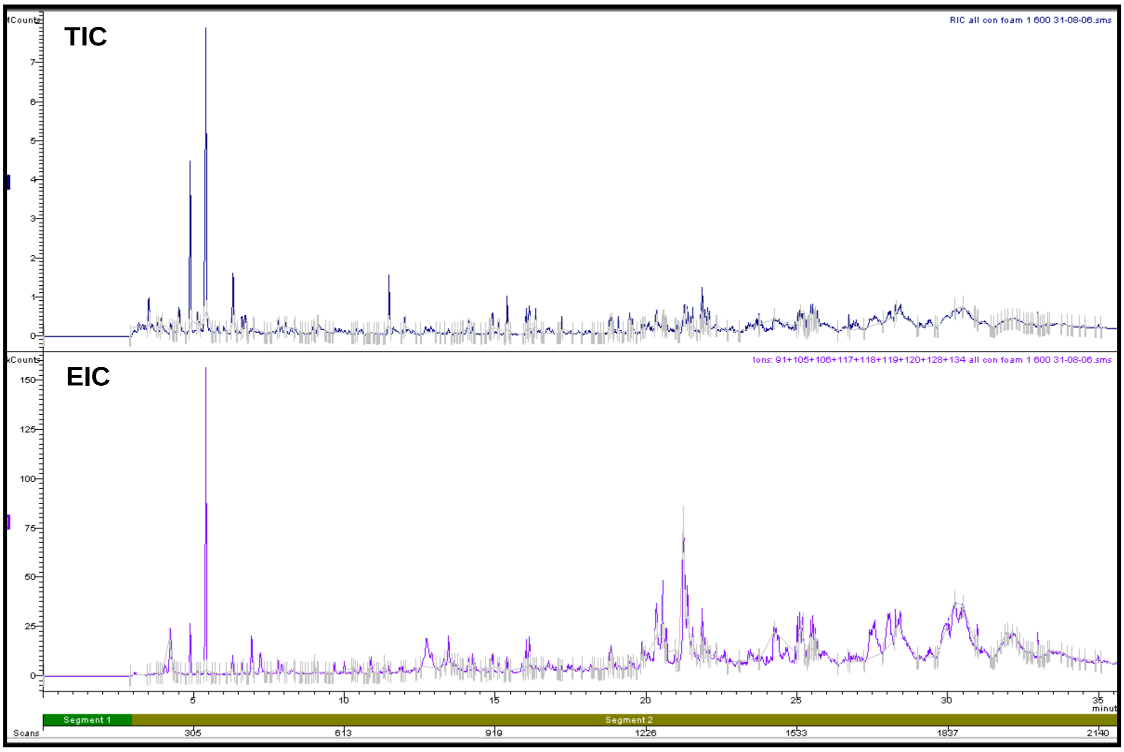


Figure H8.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Pyrolysed at 600ºC

Pyrolysis at 450ºC

The furniture foam pyrolysed at 450ºC produced no target compounds, the total ion chromatogram and extracted ion chromatogram is presented in Figure H8.6.

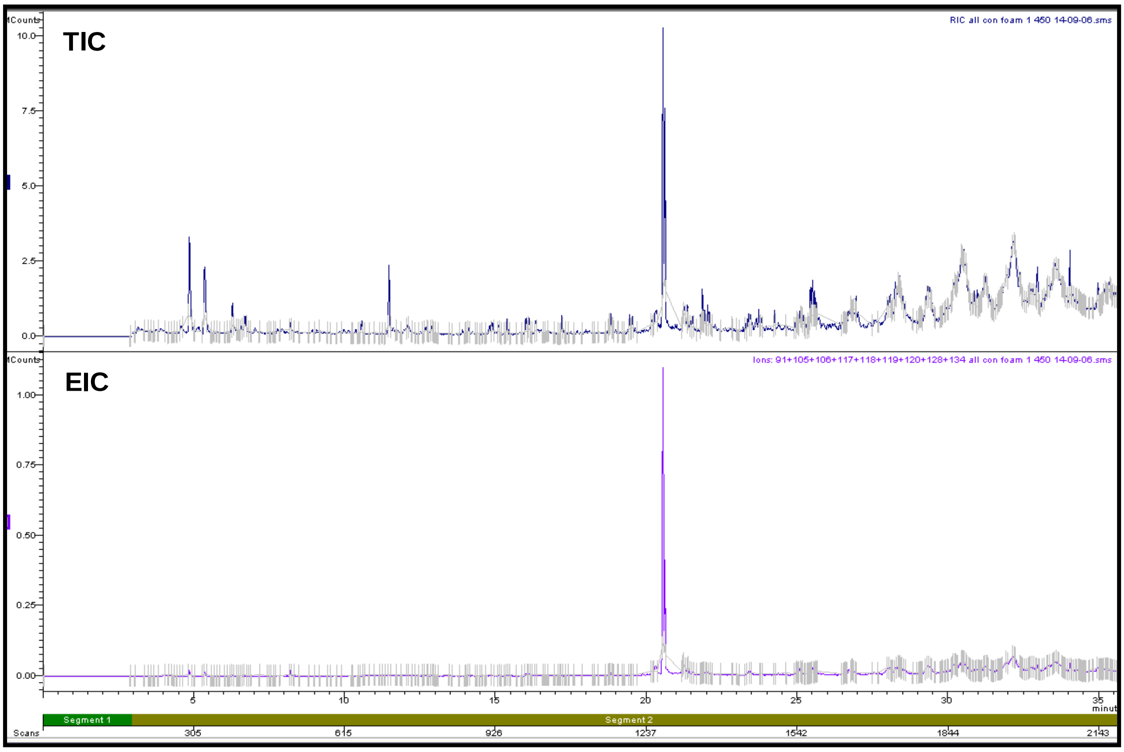


Figure H8.6: Total Ion Chromatogram and Extracted Ion Chromatogram of Foam Pyrolysed at 450ºC

UNDERLAY

Pyrolysis at 900ºC

The underlay pyrolysed at 900ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H9.1. The target compounds produced when pyrolysing this sample were toluene, ethylbenzene, *p*- and *m*-*x*ylene and *o*-xylene and naphthalene. The target compound chromatogram is presented in Figure H9.2.

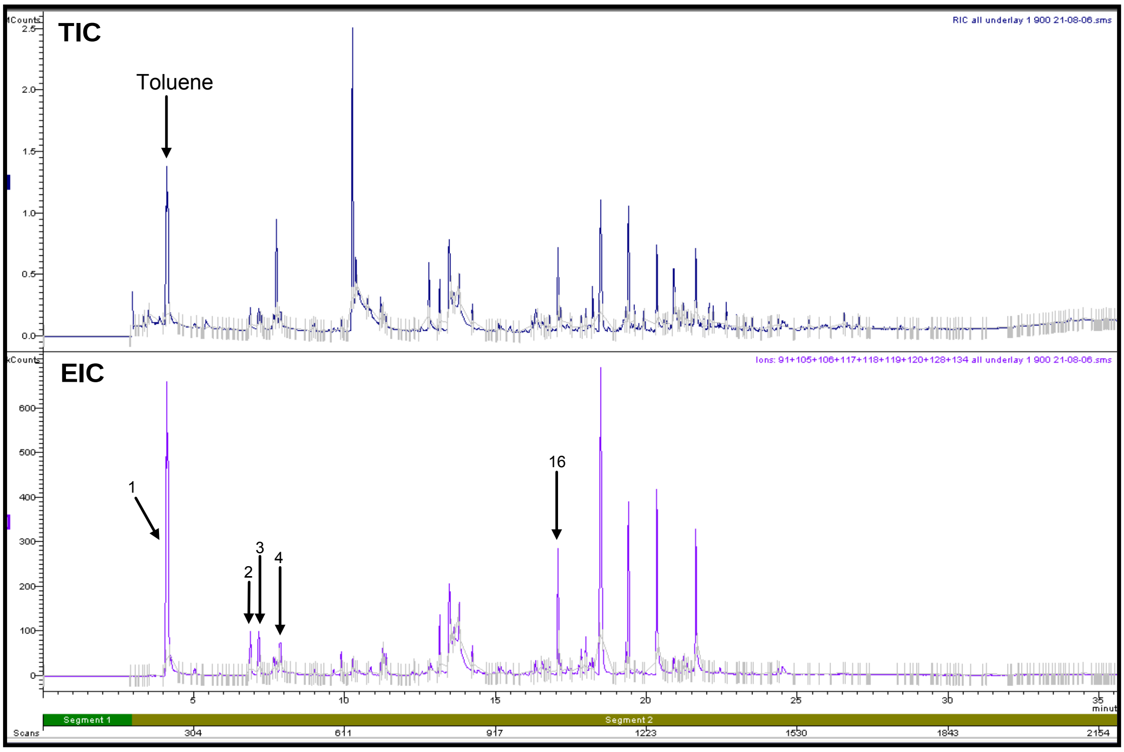


Figure H9.1: Total Ion Chromatogram and Extyracted Ion Chromatogram of Underlay Pyrolysed at 900ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 16= Naphthalene

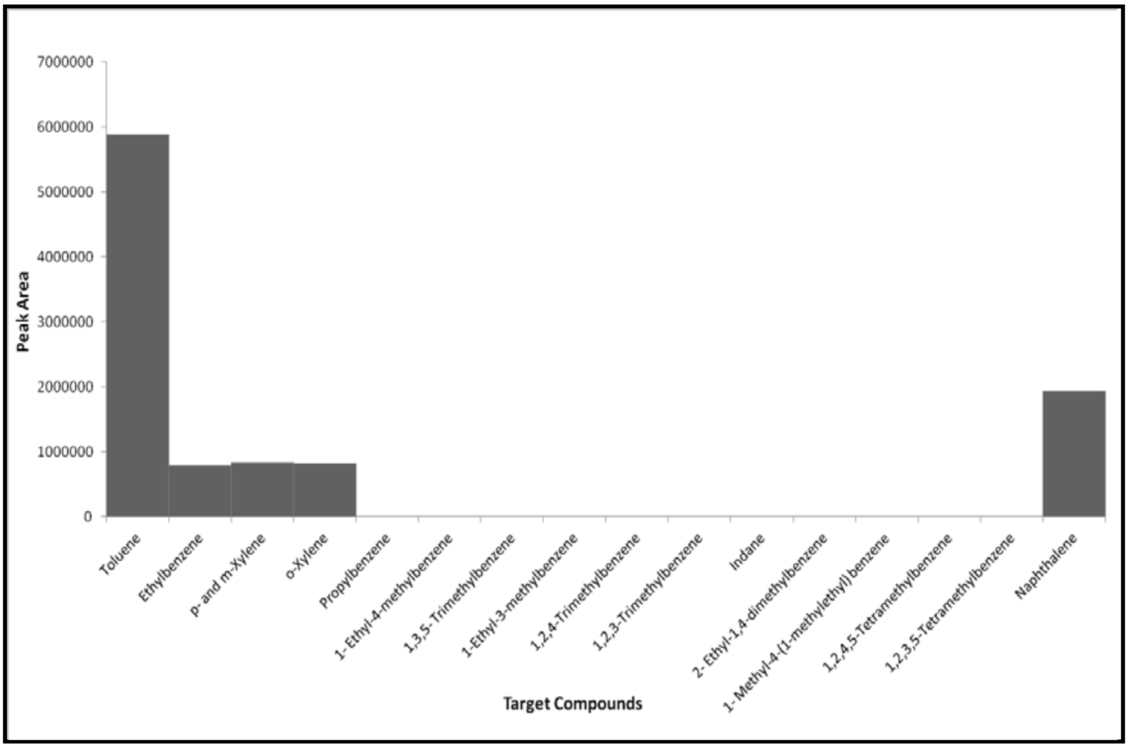


Figure H9.2: Target Compound Chromatogram of Underlay Pyrolysed at 900ºC

Pyrolysis at 750ºC

The underlay pyrolysed at 750ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H9.3. Once again, similar to the foam pyrolysed at 750ºC a number of target compounds were produced by the pyrolysis of the underlay including toluene, ethylbenzene, *p*- and *m*-*x*ylene and *o*-xylene, propylbenzene, 1,3,5-trimethylbenzene, indane and naphthalene. The target compound chromatogram is presented in Figure H9.4.

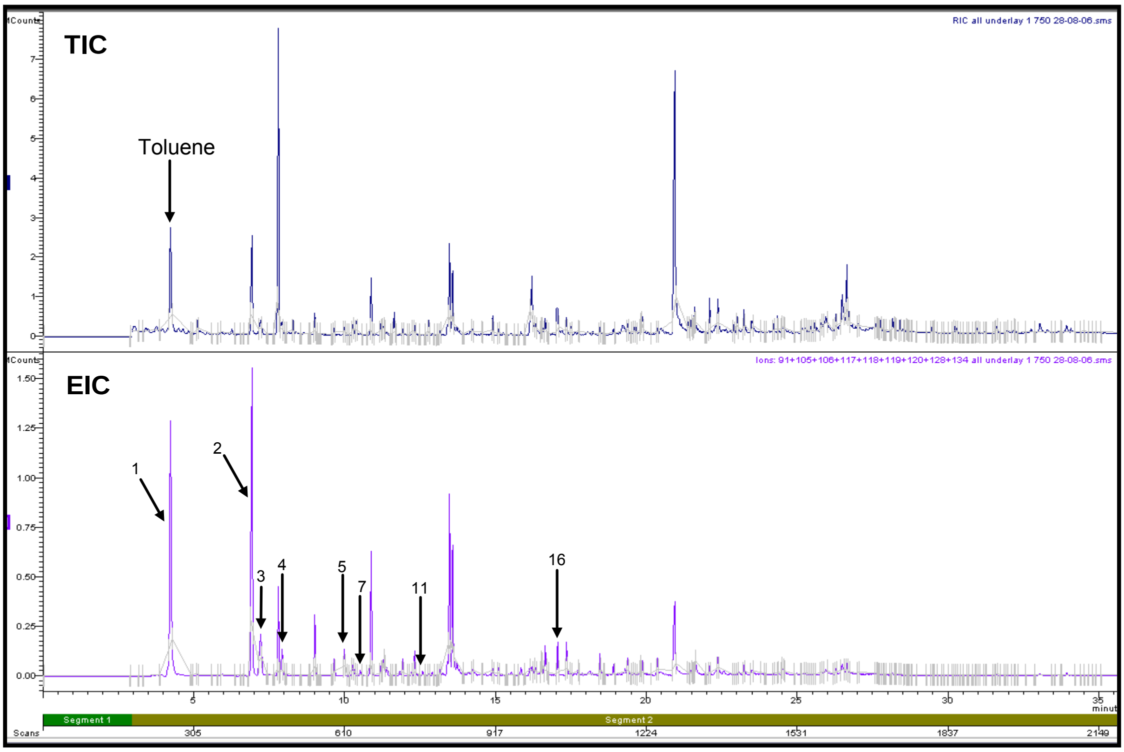


Figure H9.3: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Pyrolysed at 750ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 4= *o*-Xylene, 5=Propylbenzene, 7= 1,3,5-trimethyl benzene, 11= Indane, 16= Naphthalene

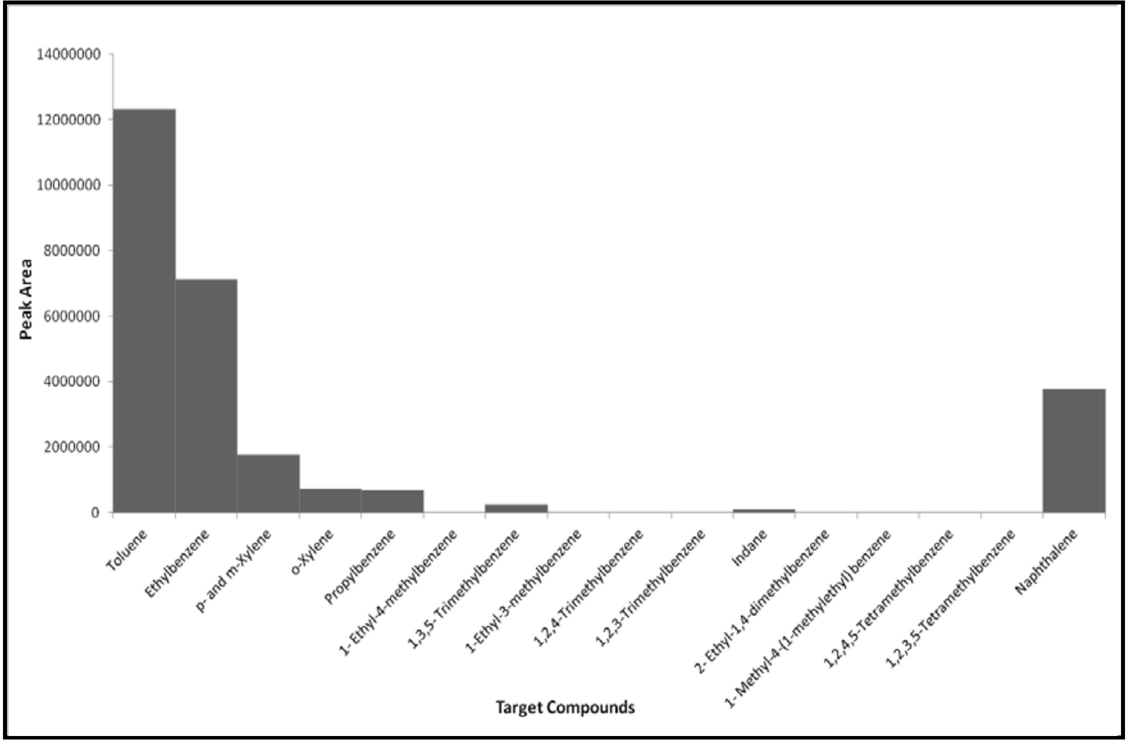


Figure H9.4: Target Compound Chromatogram of Underlay Pyrolysed at 750ºC

Pyrolysis at 600ºC

The underlay pyrolysed at 600ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H9.5. Only five of the 16 petrol target compounds were produced and were identified as toluene, ethylbenzene, *p*- and *m*- *x*ylene, propylbenzene and 1,3,5-trimethylbenzene. The target compound chromatogram is presented in Figure H9.6.

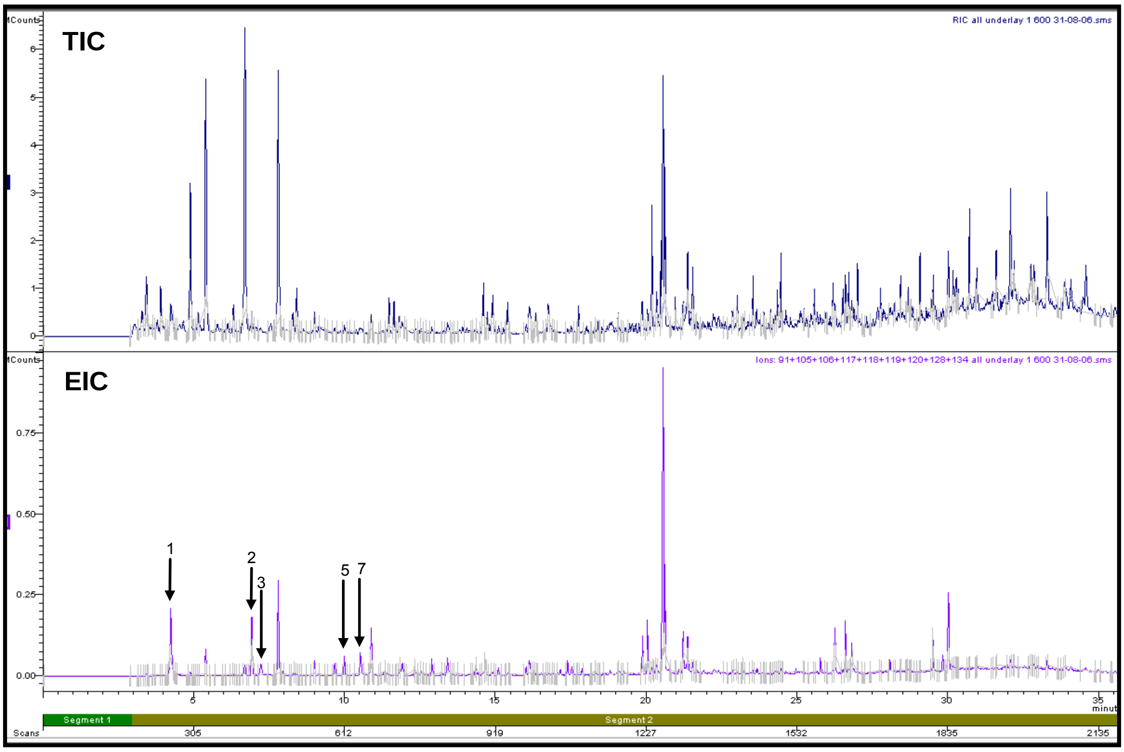


Figure H9.5: Total Ion Chromatogram and Extracted Ion Chromatogram of Underlay Pyrolysed at 600ºC

Key: 1= Toluene, 2=Ethylbenzene, 3= *p*- and *m*- Xylene, 5=Propylbenzene, 7= 1,3,5-trimethyl benzene

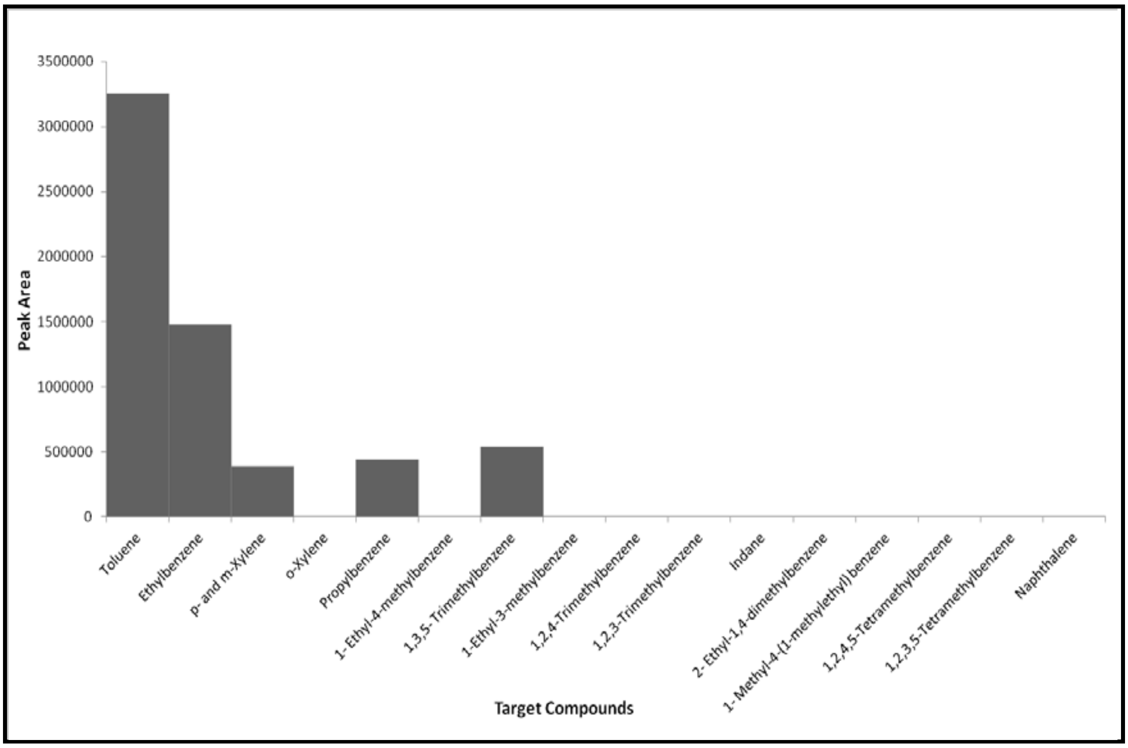


Figure H9.6: Target Compound Chromatogram of Underlay Pyrolysed at 600ºC

Pyrolysis at 450ºC

The underlay pyrolysed at 450ºC produced the total ion chromatogram and extracted ion chromatogram presented in Figure H9.7.

The extracted ion chromatogram for the underlay pyrolysed at 450ºC shows no target compounds were produced.

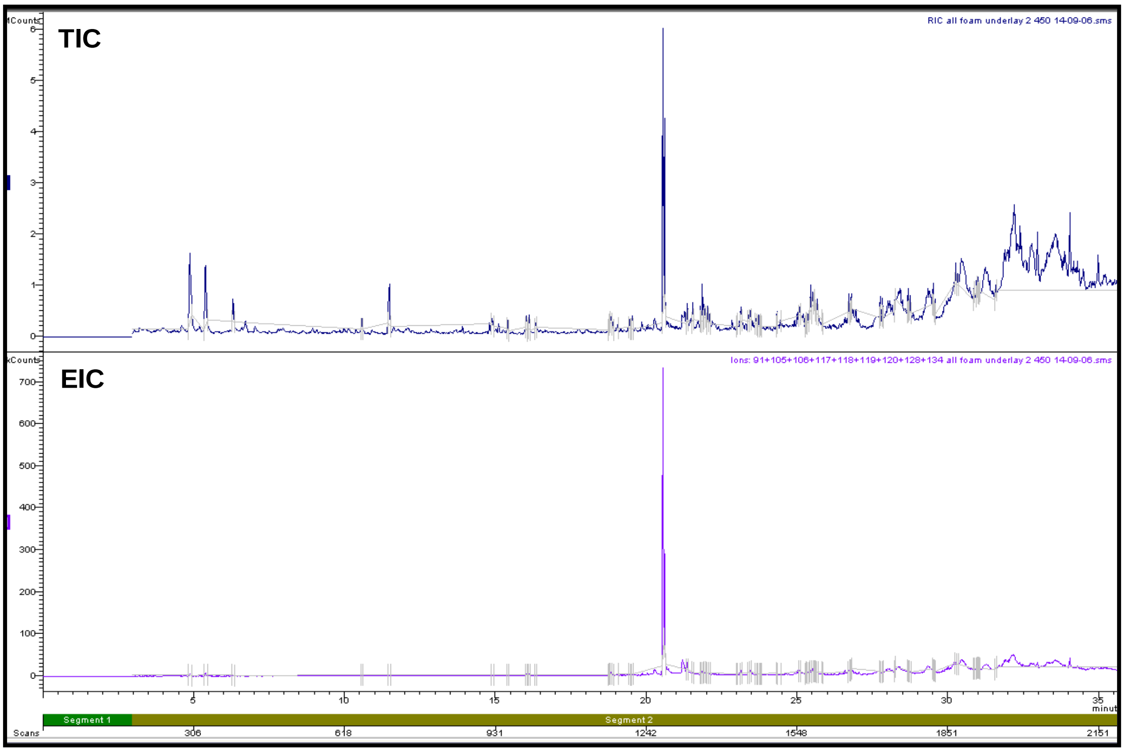


Figure H9.7: Total Ion Chromatogram and Extracted Ion Cjhromatogram of Underlay Pyrolysed at 450ºC

APPENDIX I

TARGET COMPOUNDS PRODUCED WHEN PYROLYSING CARPET FIBRES, CARPET BACKING COMPONENTS, FOAM AND UNDERLAY

Tables I1.1 to I1.9 shows the target compounds produced by pyrolysing the carpet fibres, carpet backing, foam and underlay as a function of temperature.

Table I1.1: Target Compounds Produced by Pyrolysing Nylon Carpet Fibres

Target Compounds	**900ºC**	**750ºC**	**600ºC**	**450ºC**
Toluene	X	X	X	X
Ethylbenzene	X	X	X	
p- and *m*- *x*ylene	X	X	X	X
o-xylene	X	X	X	
Propylbenzene	X			
1-Ethyl-4-methylbenzene				
1,3,5-Trimethylbenzene	X			
1-Ethyl-3-methylbenzene		X	X	
1,2,4-Trimethylbenzene				
1,2,3-Trimethylbenzene		X		
Indane	X	X	X	
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

\

Table I1.2: Target Compounds Produced by Pyrolysing Hessian from Carpet Backing

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X	X	
Ethylbenzene	X	X		
p- and *m-* xylene	X	X	X	
o-xylene	X	X		
Propylbenzene	X	X		
1-Ethyl-4-methylbenzene		X		
1,3,5-Trimethylbenzene	X	X	X	
1-Ethyl-3-methylbenzene	X	X		
1,2,4-Trimethylbenzene	X	X		
1,2,3-Trimethylbenzene	X	X		
Indane	X	X		
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene		X		
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

Table I1.3: Target Compounds Produced by Pyrolysing Plastic from Carpet Backing

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X		
Ethylbenzene	X	X		
p- and *m-* xylene	X	X	X	
o-xylene	X	X	X	
Propylbenzene	X	X		
1-Ethyl-4-methylbenzene	X	X		
1,3,5-Trimethylbenzene	X	X	X	
1-Ethyl-3-methylbenzene	X	X		
1,2,4-Trimethylbenzene		X		
1,2,3-Trimethylbenzene				
Indane	X			
2-Ethyl-1,4-dimethylbenzene	X			
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

Table I1.4: Target Compounds Produced by Pyrolysing Adhesive from Carpet Backing

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X	X	X
Ethylbenzene	X	X	X	X
p- and *m*- xylene	X	X	X	
o-xylene	X	X	X	
Propylbenzene		X	X	X
1-Ethyl-4-methylbenzene		X	X	
1,3,5-Trimethylbenzene	X			
1-Ethyl-3-methylbenzene				
1,2,4-Trimethylbenzene				
1,2,3-Trimethylbenzene				
Indane	X	X	X	
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X		X	

***X indicates compound is present*

Table I1.5: Target Compounds Produced by Pyrolysing Polypropylene Carpet Fibres

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X		
Ethylbenzene	X	X		
p- and *m*- xylene	X	X		
o-xylene	X	X		
Propylbenzene	X	X		
1-Ethyl-4-methylbenzene	X	X		
1,3,5-Trimethylbenzene	X	X		
1-Ethyl-3-methylbenzene	X	X		
1,2,4-Trimethylbenzene	X	X		
1,2,3-Trimethylbenzene		X		
Indane	X	X		
2-Ethyl-1,4-dimethylbenzene		X		
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene		X		
Naphthalene	X	X		

***X indicates compound is present*

Table I1.6: Target Compounds Produced by Pyrolysing Wool Carpet Fibres

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X	X	X
Ethylbenzene	X	X	X	
p- and *m*- xylene	X	X	X	
o-xylene		X	X	
Propylbenzene		X	X	
1-Ethyl-4-methylbenzene				
1,3,5-Trimethylbenzene				
1-Ethyl-3-methylbenzene				
1,2,4-Trimethylbenzene				
1,2,3-Trimethylbenzene				
Indane			X	
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X		X	

***X indicates compound is present*

Table I1.7: Target Compounds Produced by Pyrolysing 50-50 Polypropylene-Wool Carpet Fibres

Target Compounds	900ºC	750ºC	600ºC	450ºC
Toluene	X	X	X	
Ethylbenzene	X	X		
p- and *m*- xylene	X	X		
o-xylene	X	X		
Propylbenzene	X	X		
1-Ethyl-4-methylbenzene		X		
1,3,5-Trimethylbenzene	X	X		
1-Ethyl-3-methylbenzene		X		
1,2,4-Trimethylbenzene		X		
1,2,3-Trimethylbenzene				
Indane	X	X		
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

Table I1.8: Target Compounds Produced by Pyrolysing Foam

Target Compounds	**900ºC**	**750ºC**	**600ºC**	**450ºC**
Toluene	X	X		
Ethylbenzene	X	X		
p- and *m*- *x*ylene	X	X		
o-xylene	X	X		
Propylbenzene		X		
1-Ethyl-4-methylbenzene				
1,3,5-Trimethylbenzene				
1-Ethyl-3-methylbenzene				
1,2,4-Trimethylbenzene		X		
1,2,3-Trimethylbenzene				
Indane				
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

Table I1.9: Target Compounds Produced by Pyrolysing Underlay

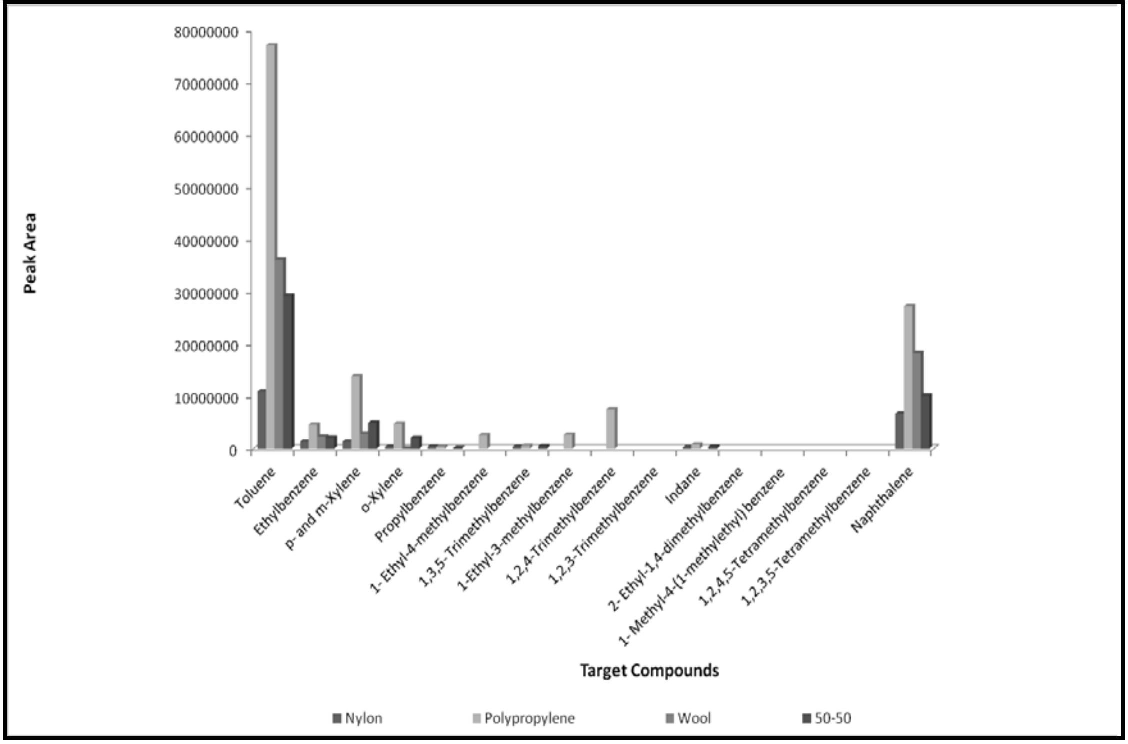
Target Compounds	**900ºC**	**750ºC**	**600ºC**	**450ºC**
Toluene	X	X	X	
Ethylbenzene	X	X	X	
p- and *m*- *x*ylene	X	X	X	
o-xylene	X	X		
Propylbenzene		X	X	
1-Ethyl-4-methylbenzene				
1,3,5-Trimethylbenzene		X	X	
1-Ethyl-3-methylbenzene				
1,2,4-Trimethylbenzene				
1,2,3-Trimethylbenzene				
Indane		X		
2-Ethyl-1,4-dimethylbenzene				
1-Methyl-2-(1-methylethyl)benzene				
1,2,3,4-Tetramethylbenzene				
1,2,4,5-Tetramethylbenzene				
Naphthalene	X	X		

***X indicates compound is present*

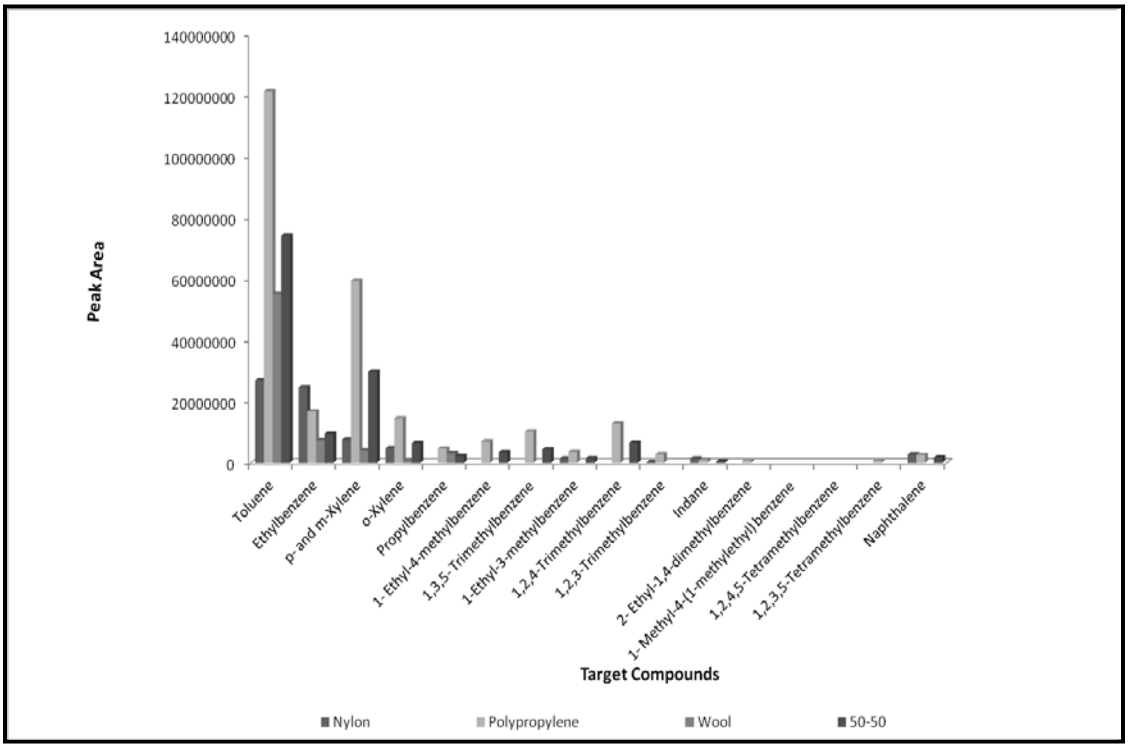
APPENDIX J

COMPARISONS OF Target Compounds S PRODUCED WHEN PYROLYSING CARPET FIBRES, CARPET BACKING COMPONENTS, FOAM AND UNDERLAY

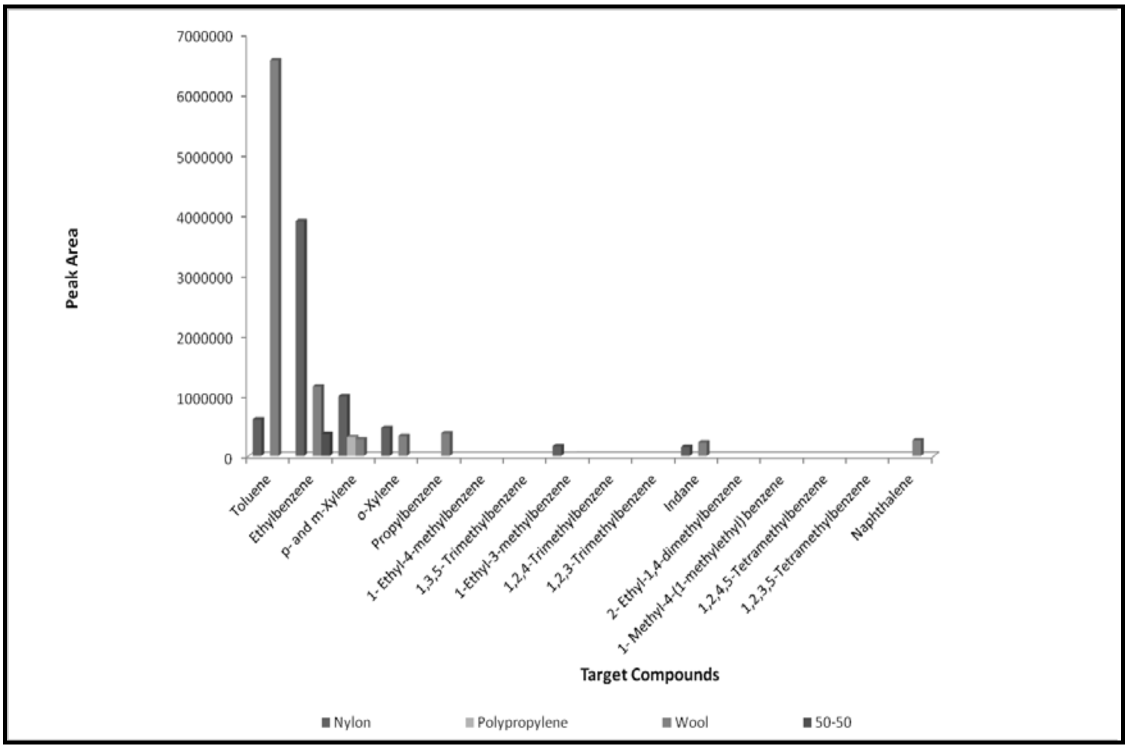
In order to compare the target compounds produced and abundances of these at the various pyrolysis temperatures, the extracted ion chromatogram peak area of each of the target compounds was plotted as a ratio with the butylated hydroxytoluene versus pyrolysis temperature. Figures J1.10 to J1.13 below show a comparison of the target compounds produced and their abundances for the carpet fibres pyrolysed at 900°C, 750°C, 600°C and 450°C.



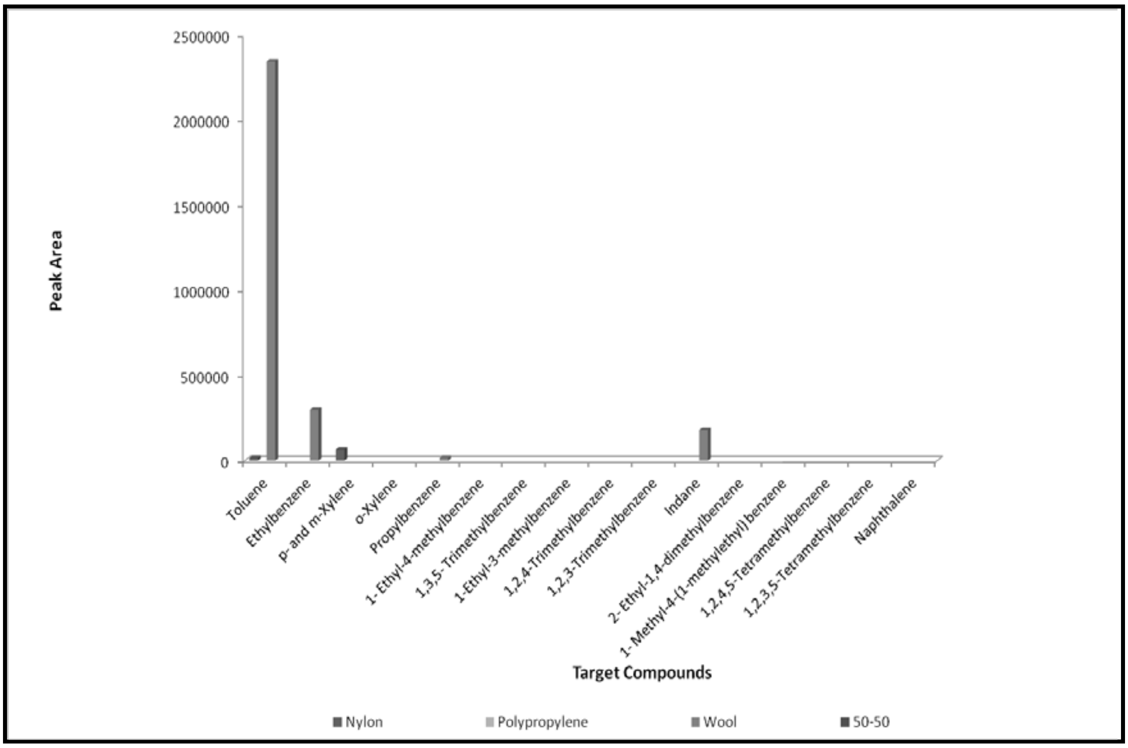
Figures J1.10: Target Compound Chromatogram for all Carpet Fibres pyrolysed at 900°C



Figures J1.11: Target Compound Chromatogram for all Carpet Fibres pyrolysed at 750°C

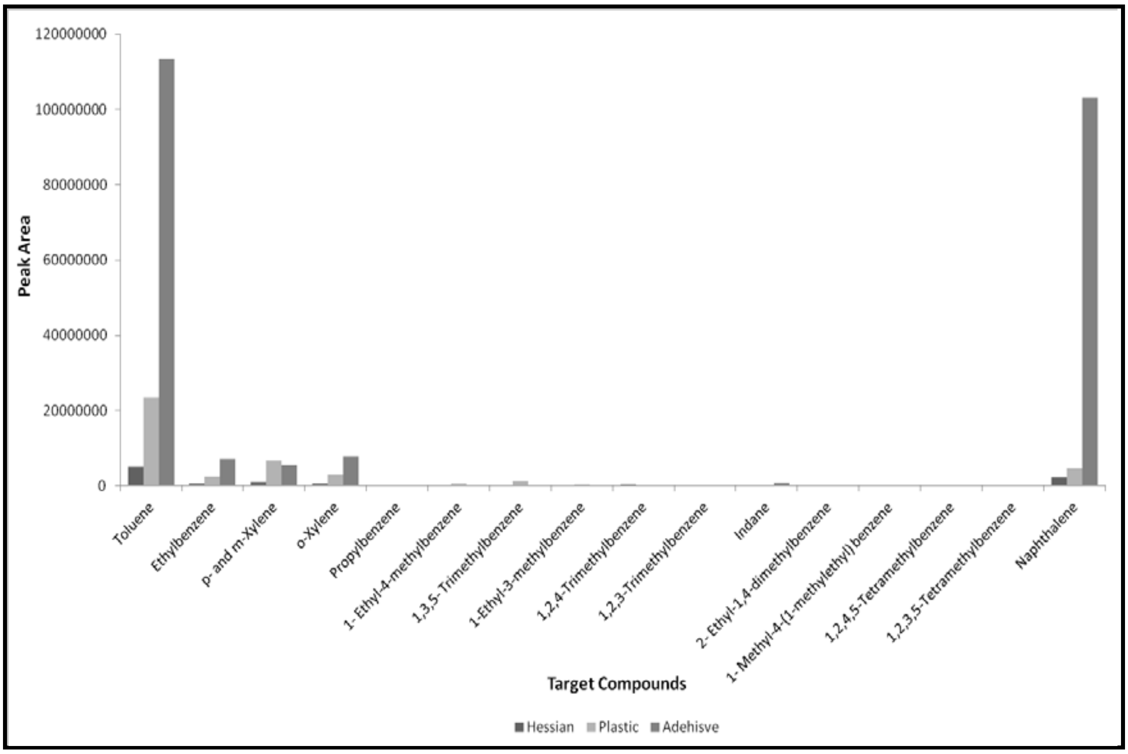


Figures J1.12: Target Compound Chromatogram for all Carpet Fibres pyrolysed at 600°C

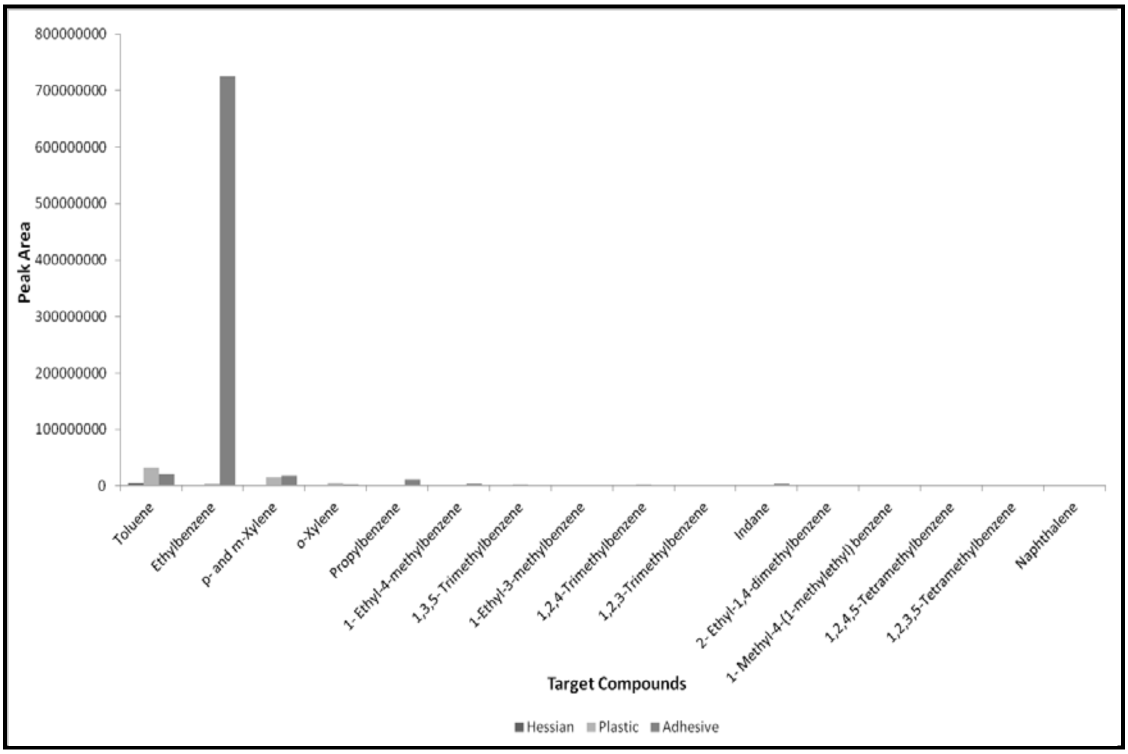


Figures J1.13: Target Compound Chromatogram for all Carpet Fibres pyrolysed at 450°C

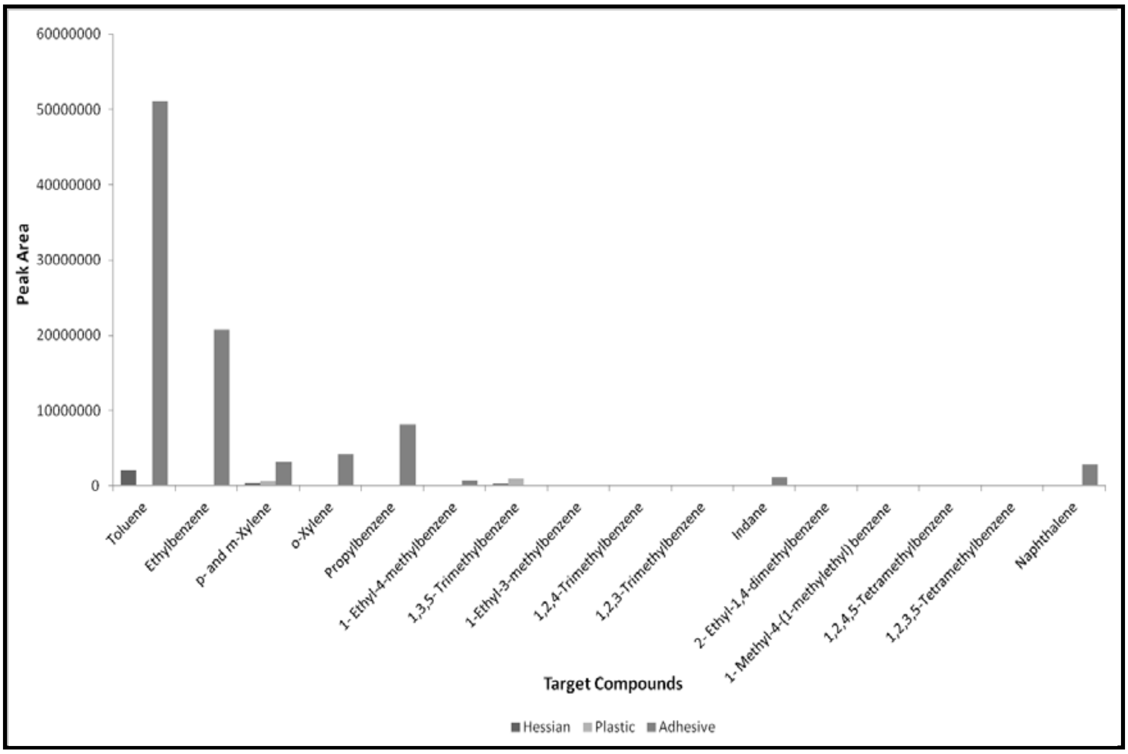
Figures J1.14 to J1.17 below show a comparison of the target compounds produced and their abundances for the carpet backing components pyrolysed at 900°C, 750°C, 600°C and 450°C.



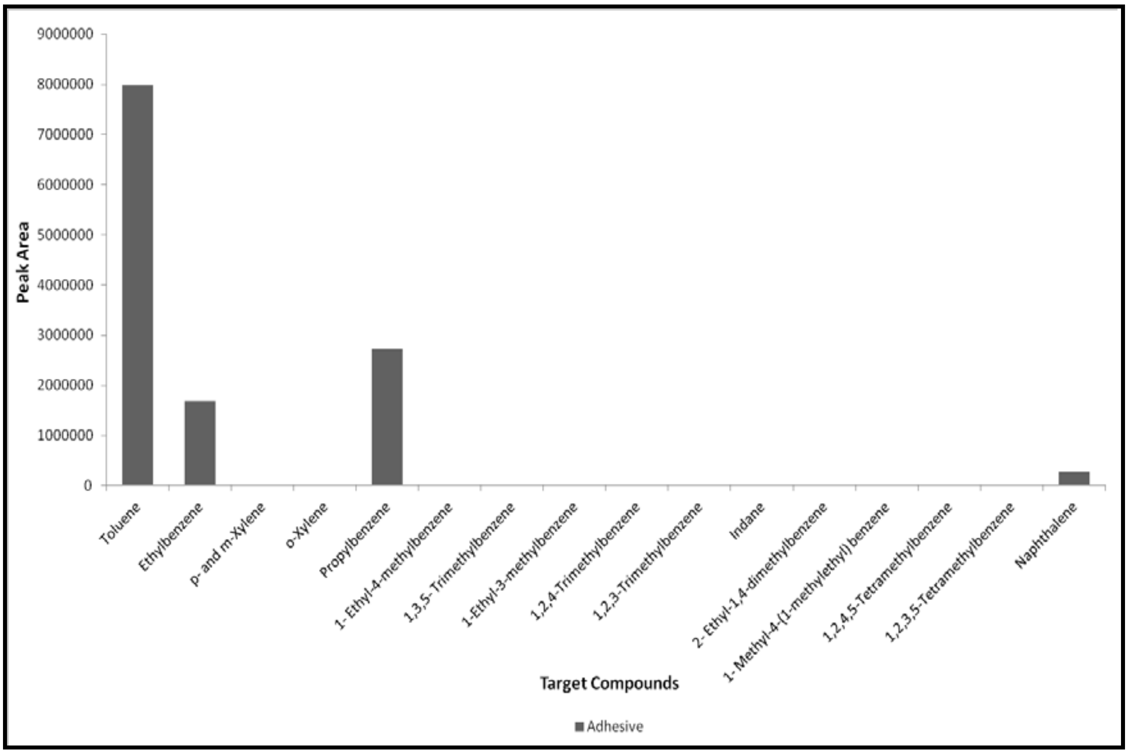
Figures J1.14: Target Compound Chromatogram for Carpet Backing Components pyrolysed at 900°C



Figures J1.15: Target Compound Chromatogram for Carpet Backing Components pyrolysed at 750°C

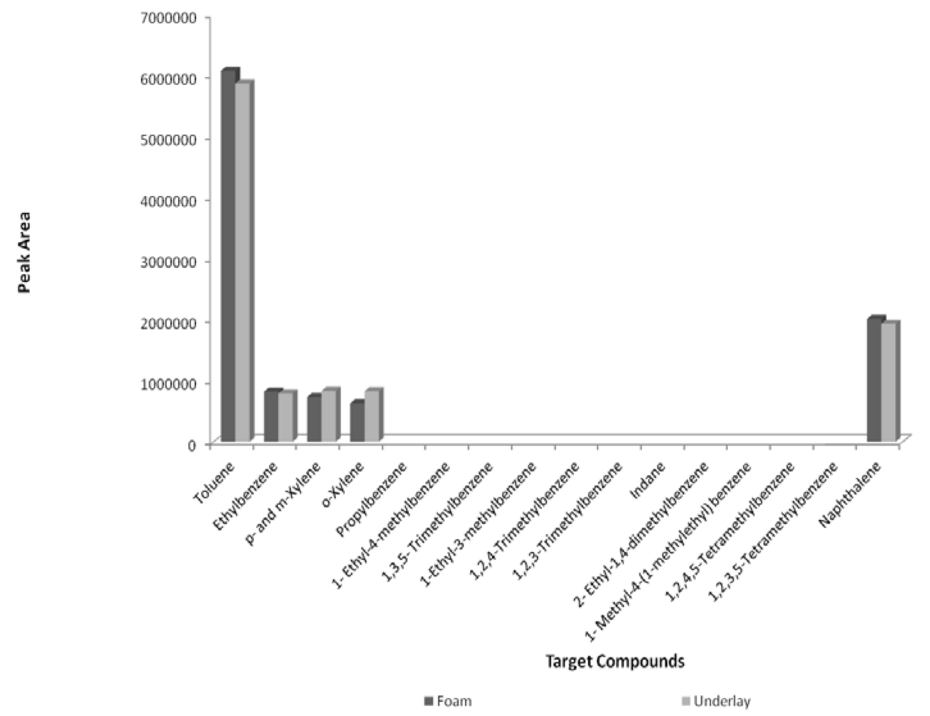


Figures J1.16: Target Compound Chromatogram for Carpet Backing Components pyrolysed at 600°C

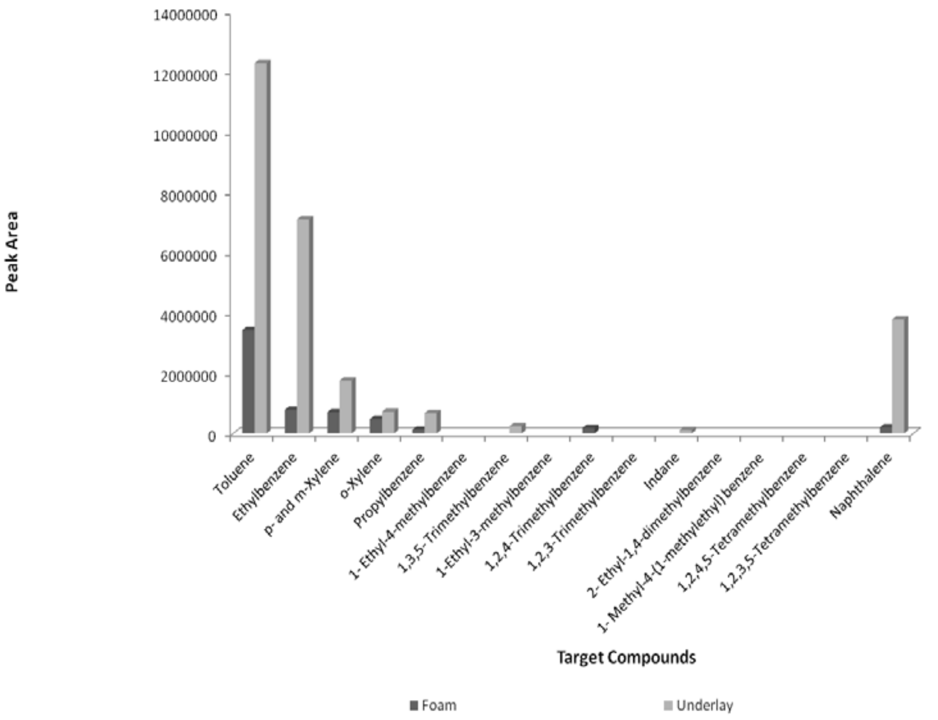


Figures J1.17: Target Compound Chromatogram for Carpet Backing Components pyrolysed at 450°C

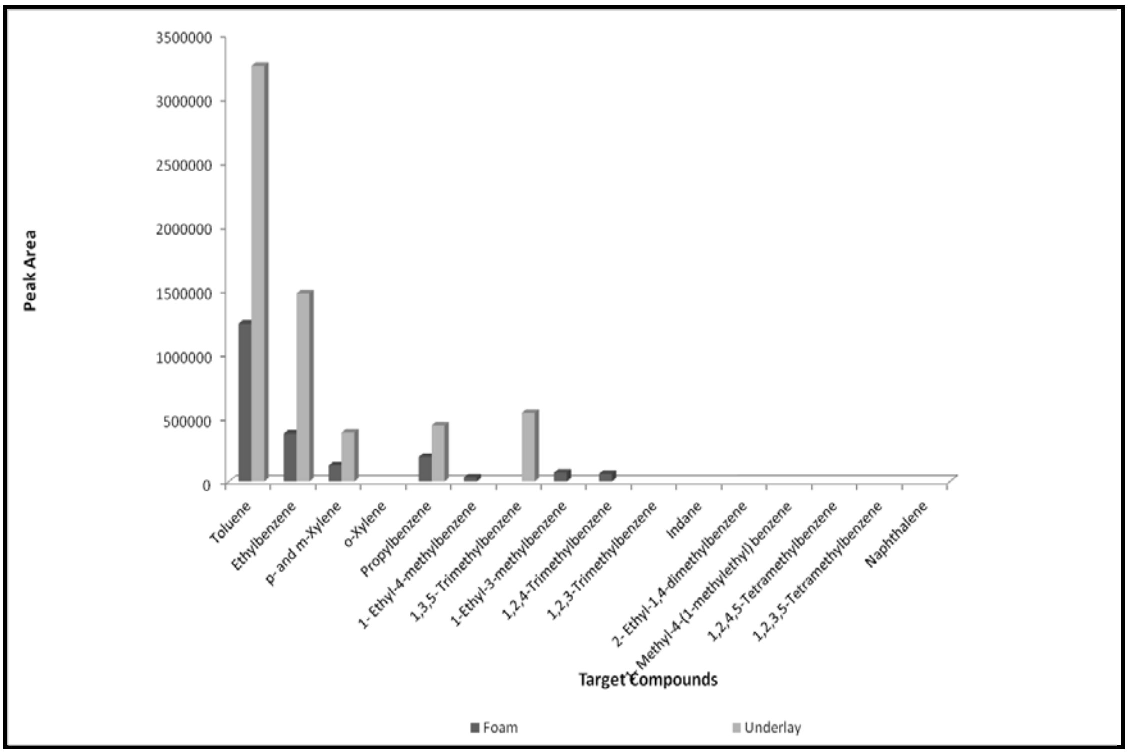
Figures J1.18 to J1.21 below show a comparison of the target compounds produced and their abundances for the foam and underlay pyrolysed at 900°C, 750°C and 600°C.



Figures J1.18: Target Compound Chromatogram for Foam and Underlay pyrolysed at 900°C



Figures J1.19: Target Compound Chromatogram for Foam and Underlay pyrolysed at 750°C



Figures J1.20: Target Compound Chromatogram for Foam and Underlay pyrolysed at 600°C

APPENDIX K

ABSTRACT FOR KEYNOTE ADDRESS

THE GCMS ANALYSIS OF FIRE DEBRIS FOR IGNITABLE LIQUID RESIDUES CONTAINING INTERFERENCES FROM FLOORING AND FURNITURE PADDING MATERIAL

Rodi Sferopoulos[1], Domenico CaridH1, John Kelleher[2], Jim Pearson[2] and Nicole Harvey[3]

[1]School of Molecular Sciences, Victoria University, PO Box 14428, Melbourne, Victoria, 8001

[2]Forensic Services Department, Victoria Police Forensic Services Centre, Forensic Drive, Macleod, Victoria, 3085

[3]Country Fire Authority, 8 Lakeside Drive, Burwood East, Victoria, 3151

Many common household materials, such as floor coverings and furniture padding materials are of petrochemical origin and when exposed to heat can decompose to produce volatile hydrocarbons. These thermal decomposition products may interfere with the identification of ignitable liquid residues in fire debris. Currently, the best way to obtain breakdown products is to subject substrate comparison samples to test burning back at the laboratory. However, there is no standard guideline available for how this test burning should be conducted. In this work common carpets and foam have been subjected to thermal degradation using pyrolysis, small-scale fires in a 1 L paint can, burning in a 8 m^3 furnace and large-scale fires in 9 m^2 concrete bunkers fitted out as a nor mal house rooms. The volatile decomposition products were then analysed by gas chromatography- mass spectrometry. This information will be used to develop guidelines for the analysis of substrate comparison samples and help fire investigators to better interpret fire residues that may contain interferences from flooring and furniture material.