UNIVERSITY OF CANBERRA

Bachelor of Applied Science (Honours)

Application of a Next-Generation Portable Gas Chromatograph-Mass Spectrometer for the On-Site Analysis of Ignitable Liquid Residues

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Honours Thesis

A thesis submitted in partial fulfilment of the requirements of the degree of Bachelor of Applied Science (Honours) at the University of Canberra.

26 November 2013

Abstract

When a fire has been deliberately lit as an act of arson, a liquid accelerant is often used to intensify the blaze. Ignitable liquid residues can be left behind at the scene after the fire has been extinguished. These residues are valuable items of evidence which can indicate, in a court of law, that the fire may have been set with malicious intent. Current procedures dictate that items of fire debris thought to contain ignitable liquids residues must be collected at the scene and sent to the laboratory for confirmatory analysis. This process can take several days at its quickest and many months at its longest, depending on the caseload of the laboratory.

Performing such analyses at the scene of the fire can help guide investigators much more effectively than waiting for laboratory results. Fast analysis on-site can also be utilised to screen potential fire debris samples as a quality control measure before they are submitted to the laboratory. This study aimed to evaluate the TRIDION-9 portable gas chromatograph-mass spectrometer instrument for the purpose of on-site fire debris analysis. The TRIDION-9 is the latest iteration in portable gas chromatograph-mass spectrometer instrumentation developed by Torion Technologies, Incorporated (American Fork, Utah, USA).

A variety of substrate matrices and ignitable liquids were analysed using the TRIDION-9. Seven substrates were chosen to represent surfaces common in residential dwellings. These were nylon carpet, polypropylene carpet, wool carpet, rubber carpet underlay, foam carpet underlay, raw pine wood and polyurethane. Seven ignitable liquids were examined, including unleaded petroleum, diesel fuel, kerosene and mineral turpentine. Unleaded petroleum was sampled at various levels of weathering (evaporation). These levels were neat (unevaporated), 70%, 90% and 97% weathered. Substrates were burned before being spiked with 0.1 μL of ignitable liquid. Sampling was performed via passive headspace solid phase microextraction, followed by immediate analysis using the TRIDION-9. Operational samples were also gathered from a realistic burn scenario and analysed on-site.

The TRIDION-9 was used to positively identify 38 of 49 ignitable liquid samples on burned substrates. Four samples produced inconclusive results, but correctly suggested that ignitable liquids were present in the samples. Seven samples could not be identified using TRIDION-9 data. Operational samples were obtained from a real fire scene. The

TRIDION-9 positively identified ignitable liquid residues in 9 of 11 operational samples. Two samples did not produce positive results due to sampling issues.

The results of this study show that the TRIDION-9 is well-suited to field-based fire debris analysis applications as a presumptive testing tool. The TRIDION-9 is easy to use and operates effectively in a field environment. Result quality is excellent, rivalling the sensitivity of traditional laboratory-based instrumentation. However, specialised training is required in the use and maintenance of the system.

Keywords: forensic science, fire debris analysis, arson, portable instrumentation, gas chromatography-mass spectrometry, TRIDION-9.

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Acknowledgements

This research project relied on the contributions of a large number of friends and colleagues. First and foremost, I must thank my primary supervisor, Chris Lennard, for his support. Administration of this project involved a number of organisations (spanning two countries!) and Chris's willingness to act as a conduit between them all made this research possible.

This project was truly international in scope, and my next thanks must go to the team at Torion Technologies, Inc. in Utah for inviting me to attend an advanced TRIDION-9 troubleshooting and maintenance course. The experience I gained with the instrument while in Utah proved invaluable over the course of the year. In particular, I owe many thanks to Chuck Sadowski for offering his expertise over the phone and assisting in troubleshooting the instrument while halfway across the globe.

Thanks must also go to my secondary supervisors, each of which contributed to the outcome of this project. Laura Bowen and Phillipa Nolan (Australian Federal Police) assisted with data analysis and interpretation. I give special thanks to Joel Walton and Phillip Etienne (Fire and Rescue New South Wales) for inviting me to participate in the Gilgandra research burn exercise. Their friendliness and helpfulness was much appreciated. I would also like to thank canine handler Timothy Garrett for his handling of accelerant detection canine Sheba.

The National Centre for Forensic Studies provided a welcoming learning environment over the course of the year. Research sometimes feels like a lonely endeavour; inclusion into a group of like-minded students and staff in the NCFS was a great motivator.

Finally, I would like to thank my partner, Fiona, for her support. Her patience was endless during the course of the year. I am extremely lucky to have such an understanding partner and thank her dearly.

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Abbreviations and Acronyms

ADC	Accelerant detection canine
ASTM	American Society for Testing and Materials
DVB	Divinylbenzene (adsorbent)
EIP	Extraction ion profile (software output) or; Extracted ion profiling (technique)
CWA	Chemical warfare agent
GC	Gas chromatograph (instrument) or; Gas chromatography (technique) or; Gas chromatogram (instrument output)
GC-MS	Gas chromatograph-mass spectrometer (instrument) or; Gas chromatography-mass spectrometry (technique)
HPD	Heavy petroleum distillate
ILR	Ignitable liquid residue
LTM	Low thermal mass (gas chromatograph column)
MPD	Medium petroleum distillate
MS	Mass spectrometer (instrument) or; Mass spectrometry (technique) or; Mass spectrum (instrument output)
NFPA	National Fire Protection Association
NFSTC	National Forensic Science Technology Center
PDMS	Polydimethylsiloxane (SPME fibre adsorbent)
PV	Performance Validation
SOP	Standard operating procedure
SPME	Solid phase microextraction
SVOC	Semi-volatile organic compound
TIC	Total ion chromatogram
TIC	Toxic industrial compound
VOC	Volatile organic compound

1. Introduction

1.1: Arson and ignitable liquid residues

The presence of an accelerant at a fire indicates an act of arson may have taken place as opposed to an accidental blaze (Hess & Orthmann, 2010). An accelerant can be defined as any material used to start or speed up a fire's progression (Bertsch & Ren, 2000). Arson, on the other hand, is the wilful or malicious burning of property, especially with criminal or fraudulent intent (Merriam-Webster, 2013). Arson is considered one of the easiest crimes to commit, yet one of the hardest to investigate (Pert, et al., 2006). Evidentially, the presence of ignitable liquid residues[1] (ILR) at a fire scene suggests that there was premeditated intent (*mens rea*) to damage property, which constitutes a criminal offense (Crimes Act 1900 (ACT) s. 117 (Austl.)).

Flammable liquids are common accelerants as they are volatile and easy to ignite (Dolan, 2003). Petroleum (gasoline) is the most common due to its widespread availability (Stauffer, et al., 2008). Other ignitable liquids are used as accelerants less commonly, such as lighter fluids and kerosene (Lennard, et al., 1995). If a liquid accelerant was used to propagate a fire, examination of the scene relies on the fact that unburned ILR will still exist as a result of incomplete combustion. It is this unburned ILR that is sampled and analysed in the laboratory for use in court as evidence (Saferstein, 2007).

Ignitable liquids encompass a large number of mixtures with varied chemical compositions. Such a large variance elicited the American Society for Testing and Materials (now ASTM International) to establish a classification system that could be used as a guide for the identification of these liquids. The ASTM classification scheme relies on gas chromatograph data, including carbon number range and ion profile abundances (particularly aromatic, alkane and polynuclear ion profiles) to classify samples (Stauffer & Lentini, 2003). Generally, ignitable liquids can be classified as petroleum (derived from crude oil) or non-petroleum products (derived from other sources) (Newman, 2004).

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[1] Throughout this review, the term 'ignitable liquid residue' (ILR), is used to refer to samples of liquid accelerants that are gathered at the fire scene. The term 'accelerant', while widely used, implies a crime has been committed. Since this review focuses on portable instrumentation used for presumptive testing, ILR is a more apt term since ignitable liquids are common around the home and workplace, and their presence at a fire scene does not automatically indicate malicious intent. Use of the term 'accelerant' is only appropriate after the sample has undergone confirmatory testing. Moreover, it must be proven that the liquid was intentionally deployed to accelerate a fire before it can accurately be called an accelerant for court purposes.

Petroleum products are created via the distillation of crude oil into separate fractions (Australian Institute of Petroleum, n.d.). These fractions are then further treated depending on their intended use. Petroleum products are composed primarily of hydrocarbons; saturated molecules consisting of carbon and hydrogen. Additives are common to adjust the odour, taste and colour of the final mixture and impurities may also be present.

The process of identifying ILR from sample collection to laboratory analysis is a cumbersome process. Firstly, ILR must be located within the fire scene in order to be sampled. Fire scene examiners can use several techniques to achieve this (see Section 1.4: Techniques for the detection of ignitable liquid residue). Fire scene examiners are only called to the scene after the fire has been extinguished and the scene has been declared safe. This can be many hours after the fire was initially set. Second, a sample must be collected and packaged. This usually involves collecting a small amount of scene debris which is thought to contain ILR. The sample is then placed into a container before it is taken away from the scene. In Australia, acts of arson are investigated by the police (Brogan, 2009). The exhibit may spend several hours in transit before it arrives at the police station exhibit store. Fire debris can remain here for hours to months before it is forwarded to the laboratory. The debris is then examined at the convenience of the laboratory, which can take some time depending on casework priorities.

Confirmatory laboratory identification of ILR is also a lengthy procedure. Laboratories use a process consisting of sample assessment, sample preparation (extraction), instrumental analysis and data interpretation (Newman, 2004). Sample extraction can be the longest of these steps, depending on the extraction method chosen. Extraction via the use of activated charcoal (the most popular technique) takes approximately sixteen hours and generally requires the debris to be heated in an oven (ASTM International, 2000). The extracted sample must then be prepared for injection into a gas chromatograph-mass spectrometer (GC-MS), typically via solvent extraction, which can involve hazardous solvents. Run times vary depending on instrument operating parameters, though analysis times of 20 to 60 minutes are common for fire debris (Stauffer, et al., 2008). Finally, the results must be interpreted and compared to reference standards before the sample can be conclusively reported as an ignitable liquid. Several days of report writing may follow before the results are finally known to the investigating officer.

1.2: Gas chromatography-mass spectrometry

Chromatography is a physical separation technique that passes an analyte over a stationary phase using a mobile phase (International Union of Pure and Applied Chemistry, 1987). In gas chromatography (GC), the mobile phase is an inert gas such as helium. Samples are inserted into the injection port of the GC and vaporised before being forced through the column by the carrier gas. Based on the mass of the compounds passing through the column, some will be slowed as they enter and exit the stationary phase (partitioning). Lighter compounds will have their movement retarded less than heavier compounds. The time it takes each compound to elute from the column is its retention time. This data is recorded in the form of peaks on a chromatogram. After eluting from the GC column, the sample enters the mass spectrometer (MS). In electron impact mass spectrometry, analyte molecules are bombarded in the ionisation chamber by a high-energy electron source (Clench & Tetler, 2000). The electron source is typically a heated tungsten filament (Busch, 2000). Molecules in the analyte will fragment from the resulting ionisation (hard ionisation). These mass fragments are then detected and converted into an electrical signal that creates a peak on a mass spectrum. The analyst exploits GC chromatograms for pattern matching between reference liquids and fire debris samples, while MS spectra assist with target compound identification.

Combining results from several analytical techniques (i.e. GC and MS) when attempting to identify compounds is advantageous (Arnold, et al., 2000). While MS alone can be used to identify a compound, its effectiveness is greatly reduced as the complexity of the mixture being analysed increases (Contreras, et al., 2008). On the other hand, GC can separate compounds with great resolution, but cannot identify them. Combining GC with MS (hyphenating), therefore, allows for confirmatory identifications to be made with a greater degree of certainty than by using each technique on its own (orthogonal testing).

GC-MS is the gold standard for structural chemical identification in the laboratory (Tilstone, et al., 2006) and has become a standard technique for the analysis of fire debris (ASTM International, 2010). GC-MS is the only technique that can provide unambiguous identification of organic compounds in complex mixtures (Robbat Jr., et al., 1999) and allows for thorough, orthogonal testing due to the selectivity, sensitivity, and universal applicability of mass spectrometry (Blain, et al., 2004). Laboratory testing of fire debris for ILR is the most important hypothesis test in an arson investigation. Paradoxically, when these tests are performed in the laboratory, they are completely removed from the context of the fire scene. While ASTM standards emphasise using fire debris analysis (FDA) to support fire scene examiner opinions on fire origin, these opinions are inconsequential to the forensic chemist in the laboratory who uses the ASTM standards. Portable instrumentation allows analysis to be performed in the context of the investigation where the results are relevant and useful.

1.3: The need for portable instrumentation

Currently, the results of ILR analyses cannot be used for intelligence purposes because by the time results are known, the police investigation has concluded. Identification of evidence traces directly at the scene can contribute to an effective intelligence-led policing strategy (Ribaux, et al., 2010). Forensic science begins at the crime scene with the recognition and collection of samples (Kelty, et al., 2011), such as fire debris. It is these items of trace evidence that ultimately drive criminal investigations by connecting a suspect to the scene. On-site evidence analysis makes this link between crime scene and policing outcomes direct and instantaneous. Examples of the benefits of a rapid forensic response have previously been outlined (Ribaux, et al., 2012). Unlike laboratory instrumentation, portable instrumentation can provide real-time, actionable data to investigating officers. This data can then be used when search warrants are executed and suspects are questioned, well before laboratory analysis results are known. Portable instrumentation can also benefit the fire scene examiner by allowing them to test fire cause and origin hypotheses as they arise. Investigators with an underdeveloped scientific approach to examinations have been known to arrive at incorrect conclusions (Ogle, 2000), some of which have been documented to end in tragedy (Carpenter, et al., 2006). The use of portable instrumentation as decision-making aids has previously been recommended (Overton, et al., 1996).

In terms of FDA, the hypothesis that often concerns the scene examiner is typically: "does this debris contain an ignitable liquid?" The ability to test such hypotheses at the scene has the potential to end the laboratory backlog phenomenon as described by Ribaux et al. (2012). Samples can be pre-screed before they are packaged; ensuring the laboratory only gets high quality samples. In this way, field-based testing can reduce laboratory workloads while maintaining high-quality forensic outcomes. This duality is represented particularly well by portable GC-MS, which can satisfy the security-related intelligence requirements of police investigators ("what accelerant is it?"), as well as the evidence requirements of the laboratory (sample screening) (Ribaux, et al., 2012). However, it is important to remember that field-based tests are designed to guide, rather than instruct, the investigator (Almog, 2006). They complement, rather than replace, laboratory techniques.

The need for accurate, portable field instruments in a forensic context has been recognised previously. Almog (2006) called upon the need for diagnostic field tests as a way to deal with dissipating evidence. This is a pertinent issue when analysing fire debris. The residues of flammable liquids will not stay trapped in debris for long periods of time due to their volatility. Sometimes, their traces vanish completely before collection, making a confirmatory laboratory result difficult to attain. The need for portable tests was also recognised as a need by the U.S. National Institute of Justice, who asserted that affordable, reliable and portable technology was a significant need of the forensic science community (National Institute of Justice, 1999). Almog (2006), in relative agreement with Sparkman (2000), summarises the benefits of diagnostic field tests as such:

- They do not require scientists;
- They can be conducted anywhere;
- They can be applied before the evidence has deteriorated;
- They are relatively inexpensive;
- They enable the elimination of a large number of suspects in a short time.

The most important of these factors is portability. If field-portable tests cannot be applied at certain locations then the field test has been rendered useless. Particularly important to forensic field tests is the reduced potential for sample contamination during collection (Hutchinson, et al., 2008), a characteristic that is imperative when trace amounts of sample are being analysed.

1.4: Techniques for the detection of ignitable liquid residue

ILR detection is the first stage of FDA. Several field-based techniques already exist for this purpose. Accelerant detection canines (ADCs) have been deployed as biological detectors for ILR for decades. The principle behind their use relies on the fact that a canine's olfactory organ is much more developed a human's (Downey, 1991). ADCs have been used with success all over the world (Tranthim-Fryer & DeHaan, 1997). However, canine efficacy is affected by individual canine ability, training, mood and other factors. Canine alerts should be acted upon with caution as a result of these variables (Kurz, et al., 1994), which introduce reliability issues in court concerning the use of canines as detectors (Katz

& Midkiff, 1998). The National Fire Protection Association (NFPA) has issued guidelines that state canine alerts should not be used as evidence without laboratory confirmation (National Fire Protection Association, 2011).

Electronic noses (sniffers) are a means of mechanical ILR detection. Electrochemical and catalytic bead sensor devices are common. Electrochemical sensors produce an electric current when a target molecule and regent interact, whereas catalytic sensors combust gases onto a catalyst bead, producing a signal (Furton & Harper, 2004). Various mechanical device configurations have proven to be useful (Conner, et al., 2006). However, a large number of false positive alerts are associated with the use of electronic noses since the specificity of these devices is poor (Furton & Harper, 2004). Moreover, some sniffers are sensitive to environmental changes and require a constant operating environment to ensure consistency of results, which is unrealistic at a fire scene (Barshick, 1998).

More sensitive on-scene ILR detection can be achieved with portable GC units. A study by Casamento et al. (2005) evaluated a single device and found it to be inefficient at detecting accelerants due to column contamination, poor sensitivity, problems with result reproducibility and limited portability. Likewise, a study by Klinteberg and Wistedt (1998) evaluated a portable GC and concluded that it had poor sensitivity to common ignitable liquids, was impractical to use and cost-ineffective. Portable GC systems have been available for some time that can detect volatile organic compounds (VOCs) (Jia, et al., 2000; Koziel, et al., 1999). However, they lack specificity when compared to ADCs, and are less cost-effective than electronic noses. As technology moves towards bringing fully-fledged GC-MS instrumentation to the field, it is likely that portable GC will become unpopular.

1.5: Field-portable gas chromatography-mass spectrometry in the forensic sciences

An industry of analytical instrumentation geared towards operation in harsh environments has flourished as a result of advancements in portable GC-MS (The Harsh-Environment Mass Spectrometry Society, Inc., 2011). However, portable GC-MS technology was only making modest advancements at the turn of the century (Meuzelaar, et al., 2000). At that point in time, few field-portable GC-MS systems were truly portable. Most were vehicle-borne mobile laboratory setups or small 'towable' instruments rather than hand-portable devices. Meuzelaar et al. (2000) proposed that the goal of any portable GC-MS system should be mobility, speed and simplicity. Traditionally, the development of portable GC-MS systems has been slow compared to laboratory-based instrumentation due to resignations on behalf of commercial manufacturers (Meuzelaar, 2001). Difficulty in satisfying performance requirements, funding availability and technological feasibility made portable instrument development unappealing ten years ago. GC-MS instrumentation was too bulky, power hungry and fragile for mass market appeal and commercialisation (Eckenrode, 2001). At the 12th Sanibel Conference on Mass Spectrometry in 2000, Dr. Jochen Franzen claimed that there was simply no market for miniaturised MS instrumentation. The main reason suggested for this lack of market share was the unwillingness of laboratory chemists to give up their role to field-based technicians (Sparkman, 2000). Instrumentation would have to progress to a point where non-scientific personnel would trust them. This reliability is important, since it may be the duty of a crime scene examiner, rather than a trained chemist, to operate portable instrumentation at the scene.

In spite of this, it was suggested that an accurate, handheld GC-MS system would be commercially available by 2010 (Meuzelaar, et al., 2000) and that the field of portable mass spectrometry was on the cusp of developing multiple novel devices (Meuzelaar, 2001). Recent developments in GC-MS technology have proven this prediction correct. The advent of low-thermal mass (LTM) GC columns and lightweight batteries has had a significant impact on instrument portability and operational utility (Stevenson, 2012). These innovations have legitimised commercial interest in field-portable GC-MS technology, encouraging the development of novel portable GC-MS instrumentation. In addition to general requirements for diagnostic field tests, a portable GC-MS system has supplementary requirements that are relevant to the analysis of forensic specimens. Wahl et al. (2003), Sloan et al. (2001) and Smith et al. (2005) suggest that these requirements are:

- Small size;
- Robust analytical ability;
- Limited power usage;
- Minimal consumables;
- Rapid analysis and turnaround time.

Evidence collection at the scene and field analysis can proceed more confidently when portable instrumentation is used to screen samples prior to collection (Eckenrode, 2001). The ability to sample multiple media (gas, solid and liquid) is also a requirement, as the forensic examiner cannot know in advance what materials will require sampling (Wahl, et al., 2003). Sampling methods must therefore be robust, such that any sample matrix can be analysed.

1.6: Miniaturised gas chromatograph-mass spectrometer technology

A portable GC-MS system which implements the above criteria has been developed – the TRIDION-9™ gas chromatograph-toroidal ion trap mass spectrometer. The TRIDION-9 is engineered by Torion Technologies Incorporated (American Fork, Utah, USA) and is marketed as the world's smallest person-portable GC-MS (Torion Technologies, Inc., 2012). The trade-off between instrument size and sensitivity has traditionally been limiting (Sloan, et al., 2001), but the TRIDION-9 can detect analytes in the parts per billion (ppb) range. The system weighs 14.5 kilograms and is completely self-contained (Figure 1). Features of the instrument include an LTM GC with high-speed temperature programming and a miniaturised toroidal ion trap mass spectrometer. The mass spectrometer can detect ion fragments in a nominal mass resolution range of 45-500 atomic mass units. Samples are injected into the instrument using a novel CUSTODION SPME (solid phase microextraction) syringe (Figure 2). Data processing (i.e. peak deconvolution and compound identification) is performed by on-board software. Results can be exported to the CHROMION software package for further analysis. The TRIDION-9 can perform up to 150 runs using a high-purity helium carrier gas canister, and can run for two and a half hours using a rechargeable lithium ion battery (Torion Technologies, Inc., 2012). Results are displayed on a 5.7-inch colour LCD touchscreen and the instrument can be operated using its keypad or a stylus.

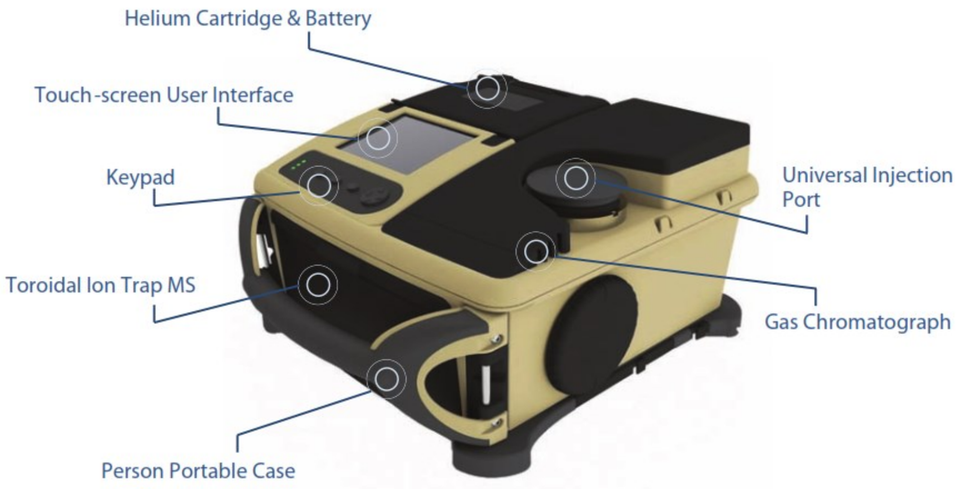

Figure 1: The TRIDION-9 GC-MS instrument. Image courtesy of Torion Technologies, Inc.

Figure 2: The CUSTODION SPME syringe. Image courtesy of Torion Technologies, Inc.

Instrument start-up and column cool down with the TRIDION-9 take only a few minutes, and sample analysis (depending on operating parameters) is typically a couple of minutes. This leads to high data turnaround times and increases the cost effectiveness of field sampling, which is otherwise compromised by waiting for laboratory analyses (Robbat Jr., 1998). It was previously asserted that there must be a compromise in the field between timely results and completeness (accuracy and precision) (Ribaux, et al., 2012). The TRIDION-9 offers both, in the form of chromatographic data and mass spectra. Typically, analysis bottlenecks due to long sample preparation and clean-up times pose a problem for field analysis (Robbat Jr., et al., 1999). Use of a pre-concentration device can also increase analysis time (Makas & Troshkov, 2004). The TRIDION-9's CUSTODION SPME syringe allows sample extraction to be performed in a single step. Fast sample preparation methods such as this are important for developing portable GC analysers (Harris, 2003).

The toroidal ion trap mass analyser is the most significant advance in mass analyser technology incorporated into the TRIDION-9 (Figure 3, Figure 4). The miniature radio frequency mass analyser was first reported in literature by Lammert et al. (2001), where the theory behind a toroid (donut) shaped mass analyser was discussed. Significant difficulties were reported with the first prototype due to the introduction of high-order, nonlinear fields which were responsible for poor mass resolution, poor sensitivity and erratic ion ejection. Unit mass resolution performance was achieved by making the toroidal ion trap analyser asymmetrical and increasing detector end cap separation.

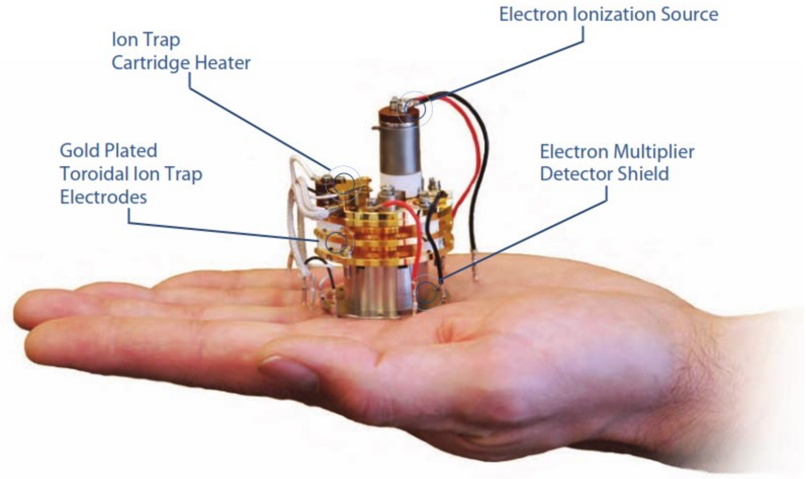

Figure 3: The toroidal ion trap, shown with a hand for scale. Image courtesy of Torion Technologies, Inc.

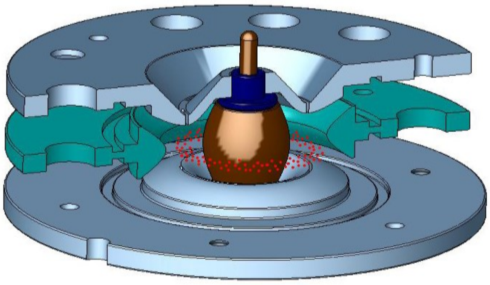

Figure 4: Internal schematic of the toroidal ion trap, showing trapped ions in red. Image courtesy of Torion Technologies, Inc.

A more advanced prototype of the same analyser was also reported (Lammert, et al., 2006). The authors described the ease of miniaturising ion trap mass analysers due to their simple components and the small number of ion optics. Benefits of small-size ion trap analysers include the ability to perform multiple stages of MS in a single mass analyser, less stringent pumping requirements and lower power requirements (Lammert, et al., 2006). Specific to the toroidal ion trap's shape is also a significant increase in trapping capacity compared to conventional quadrupole mass analysers (Lammert, et al., 2001).

There are two significant barriers preventing further miniaturisation of this type of mass analyser (Lammert, et al., 2006). The first of these is space change. Space charge refers to the effects of ion-ion repulsion which occur when a large number of ions are stored in a small volume such as an ion trap (Busch, 2004). This reduces mass resolution and induces peak shifting, thus controlling space charge is difficult in miniature ion traps. The second problem is due to limitations of fabrication technology. TRIDION-9 trap electrode dimensions are at the current limits of machining capabilities (Lammert, et al., 2006), thus smaller traps cannot be accurately manufactured. Further efforts at miniaturising mass analysers must therefore focus on developing new trap geometries or machining methods. Other trap geometries have been explored, though they do not lend themselves as well to miniaturisation.

The majority of efforts at making GC-MS systems truly portable have focused on miniaturising the GC column or mass analyser. However, few research groups have miniaturised associated components including electronics, consumables and vacuum systems (Contreras, et al., 2008). Miniaturisation of these components was raised as an issue more than ten years ago (Syage, et al., 2001; Badman & Cooks, 2000). Some research groups have managed to miniaturise self-contained mass spectrometers (Diaz, et al., 2001; Gao, et al., 2006), though these do not have the same analytical capabilities of GC-MS.

Reducing power requirements and analysis time is the key to making effective portable GC-MS systems (Contreras, et al., 2008). The only portable alternative to standard capillary GC which satisfies both these criteria is microchip-based GC. However, chip-based GC does not have the same separation power (Lambertus, et al., 2004) as capillary GC and is unsuitable for forensic purposes. The TRIDION-9 utilises a resistively heated LTM GC column, providing high heating and cooling efficiency at a fast speed (Figure 5). The narrow diameter column makes system construction inherently simpler (Smith, 2012). The TRIDION-9's LTM column is mounted on a circuit board where it is interfaced with the injection port and a cooling fan (Figure 6) As column flow rate is limited, the capillary column can be interfaced directly with the detector instead of requiring a separate transfer line. The low capacity of the column also limits the amount of analyte passed into the injector, preventing trap overloading.

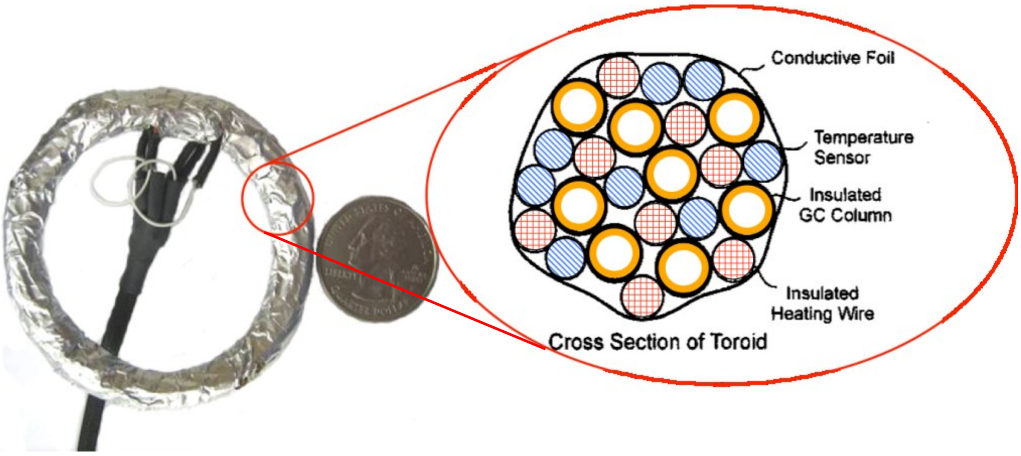

Figure 5: The resistively heated low thermal mass capillary column bundle used in the TRIDION-9. Image courtesy of Torion Technologies, Inc.

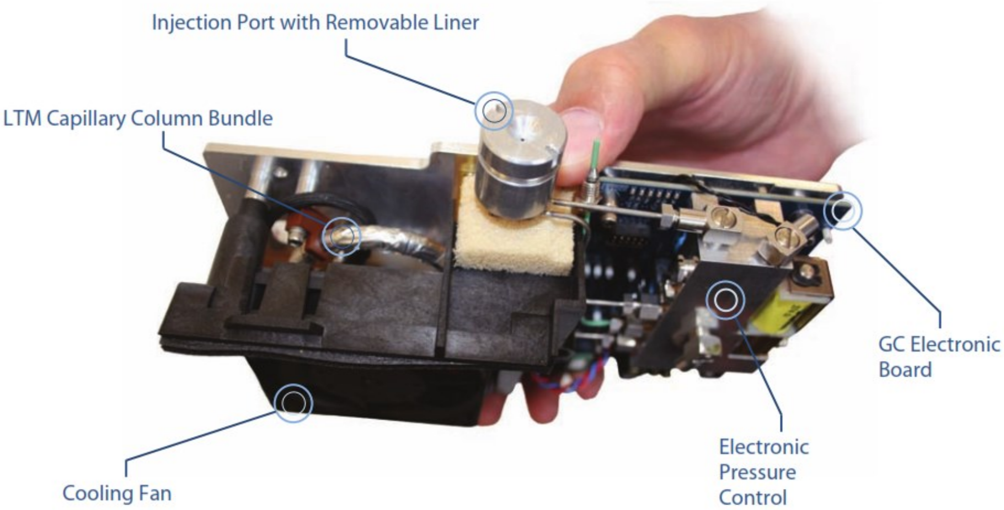

Figure 6: The LTM capillary column bundle and associated componentry. Image courtesy of Torion Technologies, Inc.

LTM technology is advantageous because it can be used in conjunction with any capillary column, is compatible with a wide range of temperature programs, has a fast cool-down rate and low power requirements (Sloan, et al., 2001). Problems using resistive heating to analyse complex samples have been reported (van Deursen, et al., 1999). However, these results are contradicted by Smith et al. (2005), who claimed resistive heating allowed for rapid identification of high-concern chemical agents. The superiority of resistive heating compared to conventional convection heating for field applications is well-supported by literature (Overton, et al., 1996; MacDonald & Wheeler, 1998; Jain & Phillips, 1995; Stearns, et al., 2008). However, the most significant advantage of resistive heating for field applications is the reduction in system size and power usage (Wang, et al., 2012).

MS vacuum pump systems are difficult to miniaturise due to their power requirements. First-generation portable equipment often utilised non-evaporative getter (NEG) pump designs, but these are undesirable for field portable instruments. First, the direct inlet of carrier gases quickly uses up the pumping capability of the NEG. Second, resolution may decrease as analytes diffusing through the membrane that separates the vacuum region and the GC column (Smith, et al., 2011). The TRIDION-9 uses a dual-stage vacuum system employing diaphragm roughing and turbo molecular pumps to sustain the vacuum required for analysis (Torion Technologies, Inc., 2012).

1.7: The GUARDION-7 gas chromatograph-mass spectrometer

The TRIDION-9 has a long development history. In 2008, Torion Technologies released the GUARDION-7, the first of their portable GC-MS range. A small literature base exists which describes the analytical capabilities of the GUARDION-7. Contreras et al. (2008) devised trials in which GUARDION-7 detection limits were determined to be in the low picogram range (200 picograms of methyl salicylate was detected). Compounds in aqueous solutions of n-butylbenzene and naphthalene were detected at concentrations as low as 100 ppt. The GUARDION-7 was able to achieve better than unit mass resolution in a range up to 220 m/z.

Twenty-five volatile organic compounds (VOCs), ranging from 1,1-dichlorothylene to 1,2-dichlorobenzene were detected in water samples in a total of seventy seconds using the GUARDION-7 (Bowerbank, et al., 2009). Water samples were spiked with twenty-five target compounds at concentrations of 0.04 μg/μL and sampled for five seconds using headspace SPME. All target compounds were detected by the GUARDION-7, including two co-eluting compounds that were resolved by on-board deconvolution algorithms.

In another study, the GUARDION-7 was able to reliably detect six chemical warfare agents (CWAs): VX[2], sulphur mustard, nitrogen mustard, tabun, sarin and soman (Bowerbank, et al., 2009). These agents were prepared at concentrations of 100 μg/mL in isopropyl alcohol and were sampled by SPME immersion. CWA simulants, by-products and precursors were also sampled at concentrations ranging from trace to neat. All target compounds were successfully detected.

Four trihalomethane (THM) compounds (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were detected in drinking water samples using the GUARDION-7 at concentrations of 500, 100, 20 and 10 ppb (Later, et al., 2008). Positive detections were reported for concentrations of 10 and 100 ppb, though no results were reported for higher concentration levels of 20 and 500 ppb.

Thirty-seven VOCs, ranging from trichlorofluoromethane to naphthalene, were detected after extraction from soil using water and the addition of salt (Torion Technologies Inc., 2009). Several compounds that co-eluted were identified by GUARDION-7 deconvolution software. Five compounds (2-hexanone, acetone, bromomethane, chloroethane, chloromethane) were not detected as they were too volatile for accurate sampling. It is

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[2] O-ethyl S-(2-diisopropylaminoethyl) methyl phosphonothiolate.

possible these compounds were lost during extraction, lost through improper handling, or did not adsorb onto the SPME fibre.

Several VOC and semi-volatile organic compounds (SVOCs) in samples of cocoa beans were identified by the GUARDION-7 (Bowerbank, et al., 2009). The names of these compounds and at what concentrations they were detected were not clear. In a similar study, VOCs and SVOCs from essential oils such as sandalwood, frankincense and corn mint were profiled using the GUARDION-7 (Bowerbank, et al., 2010). Differentiation of similar products according to their source was possible due to differences in volatile compound signatures.

The presence of TICs in mixtures was qualified using the GUARDION-7 and compared to material safety data sheet (MSDS) listings (Smith, et al., 2011). Many manufacturers do not list exactly what compounds are in their products, using ambiguous terms such as 'petroleum distillates' or 'naphtha'. Two samples of contact cement and one type of paint thinner were examined. The GUARDION-7 confirmed that n-hexane was not present in one of the contact cement samples, even though it was listed on the MSDS. The GUARDION-7 was also able to resolve three substituted benzene isomers present in the paint thinner sample, only one of which was listed on the MSDS.

Detection of extremely degraded VX CWA samples was successful using the GUARDION-7 (Smith, et al., 2011). VX often produces degradation products (i.e. pseudomolecular ions) that create substandard mass spectra with transmission quadrupole MS. Analysis of heat-degraded VX samples using the GUARDION-7 produced recognisable degradation products. These were identifiable through detection of related pseudomolecular ions, created by self-chemical ionisation.

Most of the aforementioned studies focus on testing a similar set of compounds. Many of these compounds are components in Torion's CALION Performance Validation (PV) mixture, which are specifically chosen for their ease of detection. This allows them to be used as benchmarks for mass calibration operations on the GUARDION-7. GUARDION-7 literature focuses very deliberately on the detection of CWAs and toxic industrial compounds (TICs) and most of these studies are derived from application briefs produced by the manufacturer, Torion. A report by the National Forensic Science Technology Center (NFSTC) provides an independent evaluation of the GUARDION-7 from an operational perspective.

The NFSTC report (Grates, 2009) highlights the strengths of the GUARDION-7 including its true portability, ability to perform in harsh environments, fast power-up time (3-4 minutes compared to other comparable instruments which take at least 25 minutes), and ease of sampling. Some criticisms were made of the GUARDION-7. These include irregularly shaped total ion chromatogram (TIC) peaks and the inability to change between methods on the instrument. These issues have been resolved with Torion's newest instrument, the TRIDION-9. TICs produced by the TRIDION-9 are comparable to those of a laboratory system and the instrument software now allows the user to change methods directly from the instrument. Grates (2009) reported issues with running out of storage space on the GUARDION-7's Compact Flash (CF) card, but this can be resolved by using a high-capacity card.

A research project conducted at the University of Canberra raised concerns regarding the operational capabilities of the GUARDION-7 (Brust, 2009). The aim of this study was to evaluate the GUARDION-7's ability to detect a range of organic explosives and illicit drugs. Two GC columns were evaluated: an MXT-5 and DB-1, as well as several sampling techniques. Only two out of eight explosive compounds could be detected using the GUARDION-7: TNT (trinitrotoluene) and TATP (triacetone triperoxide). Drug analysis proved to be more successful, with eleven out of fourteen substances positively identified. Three sampling methods were evaluated in the study: SPME, direct injection and coiled wire filament (CWF) sampling. SPME, using a 65μm PDMS/DVB fibre, was the most effective sampling technique.

Maintenance issues with the GUARDION-7 proved troublesome. Technical problems with the MS detector were common, requiring the replacement of parts and instrument cleaning at intervals unacceptable for an instrument designed for field use. For this reason, the GUARDION-7 could not be recommended for explosives and illicit compound detection.

1.8: The TRIDION-9 gas chromatograph-mass spectrometer

Most studies that examine the most recent of Torion's GC-MS systems, the TRIDION-9, are repeats of previous studies undergone by the GUARDION-7. In a recreation of a previous study using the GUARDION-7, the TRIDION-9 was able to resolve thirty-seven VOCs from a soil sample within three minutes (Wirth, et al., 2012). Analytes in this study were extracted from soil samples at concentrations of 15,000 µg/kg to 2,400 µg/kg, and were added to a salt and water solution before sampling by SPME. Target analytes were identified with the TRIDION-9's on-board library. Several extra target compounds appear to have been detected in the TRIDION-9 trials compared to the previous GUARDION-7 study. However, five compounds that originally could not be detected by the GUARDION-7 do not appear in the new list of target compounds, suggesting they were still undetectable.

Another iteration of a previous study with the GUARDION-7 aimed to detect four trihalomethane compounds in water using the TRIDION-9 (Wirth, et al., 2012). This study employed the same methodology as was used with the GUARDION-7, and reported the same results. As was the case previously, no reasons were given for the apparent inability of the instrument to detect all four THMs at concentrations of 20 and 500 ppb.

The use of the TRIDION-9 as a tool for sampling VOCs and SVOCs to obtain actionable data has also been investigated (Sadowski, et al., 2012). The TRIDION-9 was used to detect two compounds (trichloroethylene and perchloroethylene) at concentrations of 44 and 117 ppb, respectively. These analytes were detected in less than forty seconds by the TRIDION-9. No sampling parameters were provided.

Another study also explored the utility of the TRIDION-9 in providing actionable data at the scene (Wirth, et al., 2012). The TRIDION-9's ability to detect and quantitate volatile oligomers of halogenated compressor oil at a manufacturing facility was investigated. The study concluded that the TRIDION-9 was effective at detecting contaminants in samples of oil.

A recent report illustrated the TRIDION-9's sensitivity by successfully detecting seven target compounds at a concentration of 1 ppb in air (Sadowski, et al., 2013). The authors noted that at such trace levels, contaminant versus sample identification is difficult, giving the example of Tedlar™ bag contaminants being identified by the TRIDION-9. Such sensitivity rivals that of laboratory GC-MS, though it should be noted that sampling times for these trials was one hour. Long sampling times will ensure that low analyte concentrations are detected, but similar sampling parameters are unlikely to be utilised in a field context.

A related study involving the sampling of air contaminants was conducted in the same year, using a sampling time of only five minutes (Sadowski, et al., 2013). This study examined the presence of toluene, xylenes, styrene and benzene derivatives detected in air samples by the TRIDION-9. Some of these compounds are important target compounds for the purposes of FDA, while styrene is a common pyrolysis product. The PDMS/DVB SPME fibre used for this study proved effective at capturing these compounds.

The most recently published TRIDION-9 article describes its sensitivity in detecting geosmin in samples of water at the parts per trillion level (Richter, et al., 2013). This is the first study to introduce new sampling technology including the FUZION™ thermal desorption module and CLAIRION™ air pump for use with the TRIDION-9. Geosmin was detected at levels of 1 ppt in a creek and river sample, and a higher concentration of 2.5 ppt in a lake water sample.

In a similar vein to Brust's evaluation of the GUARDION-7 (2009), another University of Canberra research project was performed which evaluated an early prototype of the TRIDION-9 (Campbell, 2012). Campbell's study optimised parameters for explosive sample detection using the TRIDION-9. Campbell also analysed illicit drug samples as well as hydrocarbons as a proof of concept.

Three explosive compounds were detected (TNT, TATP, PETN) and only one (RDX) remaining undetected. Only four drug compounds could be identified (methadone, cocaine, amphetamine, methamphetamine), and four remained undetectable. Two drugs gave inconclusive results. Hydrocarbon analysis proved promising as all hydrocarbons (hexane, dodecane, o-xylene, kerosene and petrol) chromatographed well, with good mass spectral agreement.

Campbell et al. (2012) discovered a number of issues relating to instrument ruggedness and portability. Both the ion trap heater and the gas inlet valve malfunctioned after the instrument was relocated. Helium canisters only allowed for 20-30 analyses before they were depleted; a marked difference compared to the 100-150 analyses claimed possible by the manufacturer. Moreover, the battery only provided sufficient power for 20 analyses. Consistent troubleshooting of the instrument was required and the ion trap required cleaning at intervals unacceptable for field operation, an issue which had been encountered previously (Brust, 2009). Automatic instrument failed continuously due to a software bug. If the instrument sat idle for several days, mass resolution became poor. Overall, the

TRIDION-9 prototype proved excellent in concept but unsuitable for deployment. Hydrocarbon analysis, however, was determined to be viable using the TRIDION-9 and further research into this area was suggested (Campbell, 2012).

1.9: Other portable gas chromatograph-mass spectrometers

Several companies produce portable GC-MS instruments that are comparable to the TRIDION-9. These products are designed mainly for the defence, environmental and manufacturing industries rather than the forensic market, yet the technology they employ is readily transferrable. One of these companies is Inficon, Inc. (East Syracuse, New York, USA), who produces the HAPSITE ER Chemical Identification System (HAPSITE). The HAPSITE is designed to detect the presence of CWAs, VOCs, SVOCs and TICs (Inficon Inc., 2009). The HAPSITE is advertised to detect in the parts per trillion range and can deliver sample results in less than ten minutes. The HAPSITE weighs 19 kilograms and is carried as a unit on the operator's back. It utilises an electron multiplier MS detector that can detect in a mass range of 41-300 amu. Sample introduction is via an attached probe that is held over the sample matrix (Inficon Inc., 2009).

The HAPSITE ER is an upgrade of the HAPSITE Smart system, discontinued in 2008. Multiple studies have evaluated the efficacy of various HAPSTIE systems. One study aimed to evaluate the ability of the HAPSITE SMART to quantitate a mixture of VOCs commonly associated with vapour intrusion (Fair, et al., 2010). Sample collection and analysis was completed in three minutes and VOC concentrations at the ppb level were detected by the HAPSITE SMART. Conversely, another study found that the HAPSITE was not suitable for initial on-site activities at poisoning locations due to the system's inability to detect some chemical agents, column contamination and low target ranges (Sekiguchi, et al., 2006). A report by the U.S. Environmental Protection Agency in 2001 found that the HAPSITE was uniquely suited to detecting VOCs (particularly trichloroethene) in ground water samples and that the HAPSITE produced identical results to laboratory-based GC-MS systems (Environmental Protection Agency, 2001). A 2004 report by the California Environmental Protection Agency supported these findings and validated the HAPSITE's ability to accurately quantify VOCs in water and air samples (California Envrionmental Protection Agency, 2004).

Critics of the HAPSITE system have focused on detriments to its field-portability. Contreras et al. (2008) suggest that a run time of fifteen minutes is too slow for field applications. The HAPSITE's NEG pump has a lifetime of 150 hours and can only be replaced at the manufacturer's facility, making the carriage of spare pumps a necessity and reducing the overall portability of the device. The membrane sample inlet that leads into the ionization chamber of the HAPSITE mass spectrometer restricts the range of analytes that can be detected (Bier & Cooks, 1987). This drawback of system design was realised in a study where the HAPSITE produced chromatograms with tailing peaks that were likely created by the membrane inlet (Smith, et al., 2004). Despite these limitations, the HAPSITE is used by the U.S. military for CWA detection (Contreras, et al., 2008).

The TRIDION-9 performs favourably when evaluated side-by-side with comparable instruments. Pacific Northwest National Laboratory (PNNL) performed a market research survey of commercial off-the-shelf (COTS) portable GC-MS systems (Hart, et al., 2013). When compared to six other ion trap instruments, the TRIDION-9 exhibited good sensitivity in compared to other instruments. Only two instruments, the Thermo Scientific LTQ XL and LCQ GC-MS systems, could detect sub-nanogram quantities of analyte. The TRIDION-9's primary benefit, however, is its low weight. This scales well compared to all other COTS instruments surveyed by PNNL, with the second lightest instruments weighing 19 kilograms (the Inficon HAPSITE and OI Analytical IonCam). Whilst the Thermo Scientific systems mentioned previously were reported to have greater sensitivity, they also cost approximately three times as much and weigh almost eight times as much as the TRIDION-9. Only the OI Analytical IonCam and Griffin 824 have a lower initial purchase price than the TRIDION-9. However, these instruments are unsuitable for field use due to low dynamic range and high power requirements, respectively (Hart et al., 2013).

Shimma and Toyoda (2012) examined several commercial and some prototype portable GC-MS instruments, one of which was the GUARDION-7. Compared to other commercial instruments (Inficon HAPSITE, FLIR Griffin 450 and OI Analytical IonCam), the GUARDION-7 boasted a higher resolution as well as a broader mass range. While such devices are suitable for field deployment, their sensitivity and mass resolution is necessarily lower than what can be achieved with laboratory instrumentation, partly because ion traps, by design, cannot attain high mass resolution (Shimma & Toyoda, 2012). However, Shimma and Toyoda (2012) concede that ion trap mass analysers reduce total instrument weight and some compromises in terms of resolution must be made for the sake of portability.

The advantage of hand-portable instrumentation is the ability to take it directly to the sampling site. Mobile laboratory setups or vehicle-borne GC-MS systems do not have this same mobility. Systems such as the CT-1128 (Constellation Technologies, Largo, USA), Agilent 5975 LTM GC/MSD (Agilent Technologies, Santa Clara, USA) or the Griffin 400 (FLIR Systems, Inc., Wilsonville, USA) are examples of semi-portable GC-MS instruments that fit into this category. Such instruments have previously been evaluated for their ability to analyse forensic specimens (Ring, et al., 2007; Ring & Grates, 2007), but excessive weight, size and power requirements make them operationally unappealing for on-site analysis.

1.10: Conclusions

Accurate location of ILR at a fire scene can improve the integrity of samples sent to the laboratory. Several detection techniques can locate ILR, such as ADCs, electrochemical sensors and portable gas chromatographs. None of these techniques are simultaneously sensitive and selective, and most cannot screen fire debris for ILR effectively due to interfering compounds. There is a need for portable instrumentation that can be taken to the scene and used to screen samples for quality control and forensic intelligence purposes. Screening of fire debris samples at the scene ensures that the laboratory receives the best samples possible. The production of raw intelligence at the scene allows evidence to influence the investigation in real time, as is the traditional role of forensic evidence. Australian forensic services currently lack this capacity for accurate, actionable intelligence gathering at the fire scene.

Recent advances in portable GC-MS instrumentation have made this capacity possible. The TRIDION-9 GC-MS, manufactured by Torion Technologies, Inc. (American Fork, Utah, USA), is a person-portable GC-MS which has shown promise in its ability to analyse ILR. A literature base exists which validates both the technology behind the TRIDION-9's design, as well as its detection abilities. The TRIDION-9 is significantly more portable than other commercially available systems and has analytical capabilities comparable to a laboratory instrument. More research into the TRIDION-9's abilities is warranted to fully validate its utility as a presumptive tool for the identification of ILR at the fire scene.

2. Research Methodology

2.1: Setting

The TRIDION-9 was evaluated for its ability to analyse ILR in two main locations. Method development, instrument maintenance and general analyses were performed at the University of Canberra's Bruce campus. The instrument was housed in the main area of the forensic laboratory (room 7D26) and connected to mains power and laboratory helium. Analysis of operational samples gathered from a fire scene was performed on-site in Gilgandra, New South Wales.

2.2: Ignitable liquid, target compound and chemical standard selection

Four ignitable liquids were selected for analysis (Table 1). Neat unleaded petroleum and three weathered petroleum variants were selected for analysis. Weathered petroleum samples were evaporated to levels of 70%, 90% and 97%. These liquids were intended to simulate partially combusted ILR. Petroleum (gasoline) is prevalent in casework; a study in Australia revealed that petroleum was found in approximately 69% of fire debris samples containing an ignitable liquid (Jackowski, 1997). Other ignitable liquids selected for analysis (diesel fuel, kerosene, mineral turpentine) are widely available, making them likely liquid accelerants. Neat petroleum was sourced from a nearby service station. 90% and 97% weathered petroleum samples were sourced from the Australian Federal Police's Chemical Criminalistics laboratory. Existing laboratory supplies of 70% weathered unleaded petroleum, kerosene and diesel fuel were used. Mineral turpentine was purchased from a local supermarket.

Table 1: Ignitable liquids chosen for analysis. Classifications are based on ASTM Standard Test Method E1618-10.

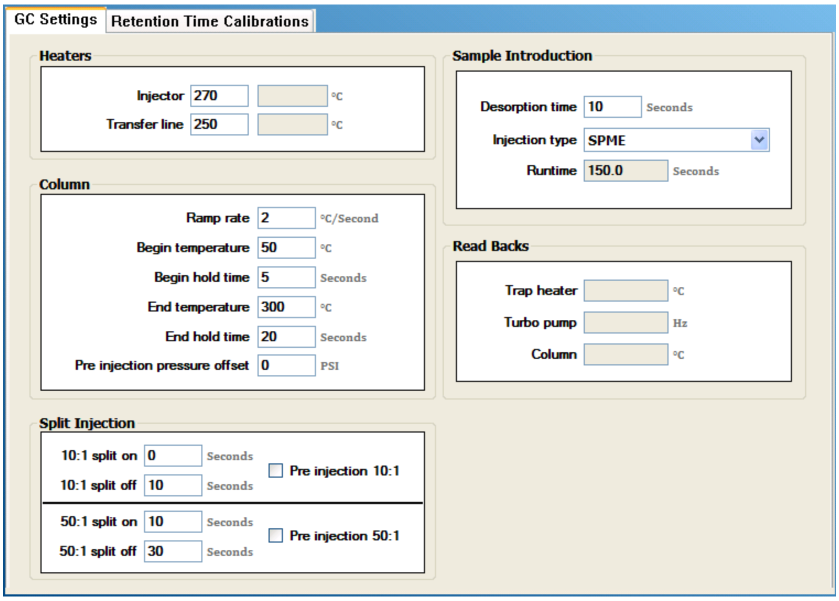
Ignitable Liquid	Classification
Unleaded petroleum	Gasoline
Unleaded petroleum (70% weathered)	Gasoline
Unleaded petroleum (90% weathered)	Gasoline
Unleaded petroleum (97% weathered)	Gasoline
Diesel fuel	Heavy petroleum distillate
Kerosene	Medium petroleum distillate
Mineral turpentine	Medium petroleum distillate

Each of the above ignitable liquids is composed of many chemical compounds. Some of these compounds were selected as target compounds for identification purposes. Target compounds were chosen based on their relative concentration in the liquid and how easily they could be detected by the TRIDION-9. Additionally, compounds which were considered diagnostically relevant due to their unique chromatographic peak patterns were also selected as target compounds. Some target compounds were selected based on their listing in ASTM Standard Test Method E1618-10 as target compounds. The final list of target compounds was the basis for the custom compound library on the TRIDION-9. Selected target compounds appear in Appendix A: Table of Target Compounds.

Most target compounds were also ordered as chemical standards. This allowed the target compounds to be analysed by the TRIDION-9 and entered into the compound library with objective retention time and mass spectrum data. Standards used in this study appear in Appendix B: Table of Chemical Standards. Not all of the target compounds could be ordered separately as standards due to budgetary constraints and availability. Most target compounds could still be identified accurately in ignitable liquid samples based on their mass spectra and retention times.

2.3: Method development

The operating parameters of analytical instrumentation can affect result quality. This stage of research focused on developing a method to optimise the TRIDION-9's gas chromatograph and mass spectrometer for FDA. This method could then be used to analyse all unknown ignitable liquids and produce reasonable results. Default methods supplied by the manufacturer were used as a base for modification. Parameters were adjusted using the CHROMION software package (version 1.1.1.6, Torion Technologies, Inc., American Fork, Utah, USA) (Figure 7) and sent to the instrument using a data cable. Non-instrumental parameters such as sampling time were also examined.



Heaters

Injector 270 °C
Transfer line 250 °C

Column

Ramp rate 2 °C/Second
Begin temperature 50 °C
Begin hold time 5 Seconds
End temperature 300 °C
End hold time 20 Seconds
Pre injection pressure offset 0 PSI

Split Injection

10:1 split on 0 Seconds
10:1 split off 10 Seconds
☐ Pre injection 10:1
50:1 split on 10 Seconds
50:1 split off 30 Seconds
☐ Pre injection 50:1

Sample Introduction

Desorption time 10 Seconds
Injection type SPME
Runtime 150.0 Seconds

Read Backs

Trap heater °C
Turbo pump Hz
Column °C

Figure 7: Gas chromatograph operating parameters as they appear in CHROMION.

Gas chromatograph parameters were tested using 0.1 μL of unleaded petroleum in 1 litre paint tins. Each parameter was adjusted in sequence until all test values were run through (Table 2). The value which produced the best chromatographic results was incorporated into the method.

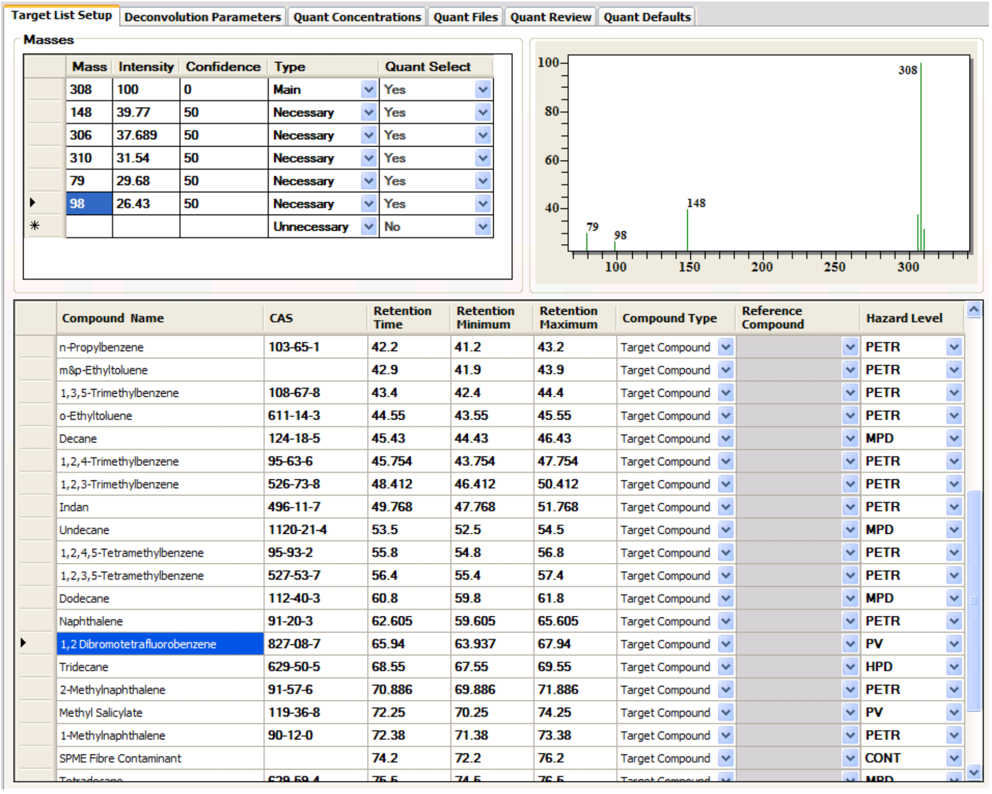
Table 2: Gas chromatograph parameters and test values.

Parameter	Test values
Sampling time	10, 30, 60, 120, 180, 300 seconds
Temperature ramp rate	1, 2, 3°C per second
Starting column temperature	30, 40, 50°C
Starting temperature hold time	0, 10, 20, 30, 60 seconds
Final column temperature	255, 270, 300°C
Final temperature hold time	0, 10, 20, 30, 60 seconds
Injection port temperature	270°C
Transfer line temperature	250°C (specified by manufacturer)
Split ratio	Splitless, 10:1, 50:1, mixed split, delayed split
Desorption time	10 seconds (specified by manufacturer)

Mass spectrometer settings were adjusted on an as-needed basis when the instrument needed recalibration or when advised by the manufacturer. The most commonly adjusted mass spectrometer settings were the detector voltage, filament current and ion target. These values required adjusting when the instrument was disassembled; therefore their values were arbitrary with respect to analysis output. Determining a set of standard mass spectrometer settings was inconsequential due to inter-instrument variability.

2.4: Compound library compilation

Compounds selected as target compounds were added to the TRIDION-9's on-board library using the target library editor function in CHROMION (Figure 8). Library data consisted of compound names, retention time windows, CAS numbers, mass spectrum data and hazard level designations.



Mass	Intensity	Confidence	Type	Quant Select
308	100	0	Main	Yes
148	39.77	50	Necessary	Yes
306	37.689	50	Necessary	Yes
310	31.54	50	Necessary	Yes
79	29.68	50	Necessary	Yes
98	26.43	50	Necessary	Yes
			Unnecessary	No

Compound Name	CAS	Retention Time	Retention Minimum	Retention Maximum	Compound Type	Reference Compound	Hazard Level
n-Propylbenzene	103-65-1	42.2	41.2	43.2	Target Compound		PETR
m&p-Ethyltoluene		42.9	41.9	43.9	Target Compound		PETR
1,3,5-Trimethylbenzene	108-67-8	43.4	42.4	44.4	Target Compound		PETR
o-Ethyltoluene	611-14-3	44.55	43.55	45.55	Target Compound		PETR
Decane	124-18-5	45.43	44.43	46.43	Target Compound		MPD
1,2,4-Trimethylbenzene	95-63-6	45.754	43.754	47.754	Target Compound		PETR
1,2,3-Trimethylbenzene	526-73-8	48.412	46.412	50.412	Target Compound		PETR
Indan	496-11-7	49.768	47.768	51.768	Target Compound		PETR
Undecane	1120-21-4	53.5	52.5	54.5	Target Compound		MPD
1,2,4,5-Tetramethylbenzene	95-93-2	55.8	54.8	56.8	Target Compound		PETR
1,2,3,5-Tetramethylbenzene	527-53-7	56.4	55.4	57.4	Target Compound		PETR
Dodecane	112-40-3	60.8	59.8	61.8	Target Compound		MPD
Naphthalene	91-20-3	62.605	59.605	65.605	Target Compound		PETR
1,2 Dibromotetrafluorobenzene	827-08-7	65.94	63.937	67.94	Target Compound		PV
Tridecane	629-50-5	68.55	67.55	69.55	Target Compound		HPD
2-Methylnaphthalene	91-57-6	70.886	69.886	71.886	Target Compound		PETR
Methyl Salicylate	119-36-8	72.25	70.25	74.25	Target Compound		PV
1-Methylnaphthalene	90-12-0	72.38	71.38	73.38	Target Compound		PETR
SPME Fibre Contaminant		74.2	72.2	76.2	Target Compound		CONT
Tetradecane	629-59-4	75.5	74.5	76.5	Target Compound		MPD

Figure 8: The target library editor as seen in CHROMION.

Retention times were determined by running compound standards. If no separate standards were available, ignitable liquid samples were analysed and the compound of interest was identified based on its mass spectrum. Retention time windows allowed for a margin of error in the specified retention time. These windows were set 1-2 seconds wide and compensated for minute shifts in retention time. Mass spectrum data for each compound consisted of a list of ions and their relative intensities. 'Main' ions (base peaks) were the most intense while 'necessary' ions were required for identification. 'Unnecessary' ions were not required for identification, but increased match factors when they were present. Mass data entered into the library was gathered from the 2008 NIST/EPA/NIH mass spectral library, as well as from the analysis of standards.

Hazard levels, while initially intended to alert the user to harmful chemical warfare agents, were adjusted. Several new 'hazard levels' were created, including petroleum (PETR), medium petroleum distillate (MPD), heavy petroleum distillate (HPD), performance validation compound (PV) and contaminant (CONT). Compounds in the library were assigned a hazard level based on the category of ignitable liquid they typically occurred in. Hexadecane, for example, was assigned the HPD level. The contaminant hazard level was used to notify the operator when known contaminants were detected during analysis, such as a SPME fibre contaminant which leeches from degraded fibres.

2.5: General instrument usage

A specific procedure was followed at the beginning of each analysis period to ensure that the instrument was ready for analysis. If the instrument was not online, it was turned on and allowed to pump down for several minutes. A system blank was performed to determine if any contaminants were present in the column. If contaminants were detected, successive system blanks were performed until they were no longer present. If the chromatogram baseline was too high, the system was allowed to pump down until levels were acceptable.

A SPME fibre blank was then performed. This ensured the SPME fibre was free of contaminants. If the SPME blank was contaminated, the fibre was reconditioned by placing into the heated injection port for one minute. Another SPME blank was then run and if contaminants were detected again, a longer reconditioning time was used. This was repeated until SPME blank chromatograms were peak-free.

Finally, a performance validation using a CALION PV mixture (Torion Technologies, Inc., American Fork, Utah, USA) was performed. An example of a PV run chromatogram and a list of CALION compounds appear in Appendix C: CALION Performance Validation mixture. PV runs allowed the instrument to recalibrate itself and alert the user to system problems. Various instrument functions were tested during PV, including filament emission, signal resolution and electromagnetic detector response (Torion Technologies, Inc., 2011). Symptoms such as peak resolution and mass spectral quality are evaluated to determine which spectrometer components require tuning. If the instrument passed PV, it was deemed ready for analysis. If PV failed, an automated tuning wizard suggested changes to mass spectrometer parameters to fix the issues detected. These suggestions, in combination with operator experience, were used to troubleshoot the instrument until it passed PV. Regular system maintenance was also necessary. This was performed on an as-needed basis in consultation with the operating manual and the manufacturer. A user logbook was maintained with records of when the instrument was used and how many runs were performed.

2.6: Sample preparation

2.6.1: Neat ignitable liquids

Ignitable liquids were sampled from 1 litre unlined paint tins supplied by NCI Packaging (Victoria, Australia). These tins were the same type and size used by New South Wales Police to collect samples of fire debris. Ignitable liquids were deployed at volumes of 0.1 μL onto Kimberly-Clark® (Milsons Point, NSW) Kimwipe segments using a BrandTech® Scientific (Essex, Connecticut, USA) Transferpette® S D-1 1-0.1 μL pipette. These segments were then transferred into sample tins, sealed with lids and allowed to equilibrate.

Sampling was performed via passive headspace SPME. A hole was pierced in the centre of the sample tin lid using a hammer and nail. The SPME needle was inserted into the tin above the sample, ensuring the tin lid was flush with the bottom of the syringe. The fibre was then exposed to the headspace of the sample and left in position for the desired sampling time. After sampling, the SPME fibre was retracted from the sample tin. A length of adhesive tape was applied to the tin lid, covering the sampling hole and preserving the sample.

2.6.2: Blank substrates

Blank substrate materials were sourced from various locations around Canberra. Nylon, polypropylene and wool carpet swatches were collected from a flooring retail outlet in Belconnen (Figure 9, Figure 10, Figure 11). Samples of rubber and foam carpet underlay were obtained from a carpet store (Figure 12, Figure 13). A length of raw pine as well as a children's fold-out sofa (as a source of polyurethane) were obtained from a waste recycling centre (Figure 14, Figure 15).

Figure 9: Nylon carpet

Figure 10: Polypropylene carpet

Figure 11: Wool carpet

Figure 12: Foam carpet underlay

Figure 13: Rubber carpet underlay

Figure 14: Raw pine wood

Figure 15: Children's sofa (polyurethane)

Carpet and carpet underlays (including their backing materials) were cut into segments of approximately 5 cm^2. Pine was cut into small sections measuring approximately 9 × 3 × 3 cm. The fold-out sofa (together with upholstery) was cut into larger sections of 8 × 8 × 8 cm. These samples were then placed into tins and sampled in the same way as neat ignitable liquids.

2.6.3: Burned substrates

After cutting each substrate to size, the substrates were burned using a butane/propane camping burner. Substrates were held above the burner and burned as evenly as possible across their surface area. Observations relating to the physical degradation of samples as they pyrolysed were made. Samples such as pine and wool carpet, which did not combust readily, were burned until significant charring was visible on all sides (Figure 16). All other samples were burned until most of the original sample mass had been burned (Figure 17). Polyurethane, foam carpet underlay and polypropylene carpet burned rapidly and easily, to a point where most of the sample mass was consumed by fire. Some of these samples were extinguished before they burned away completely. This was done by placing the substrate into a 1 litre stainless steel sample tin and covering it with a lid, suffocating the fire. Other substrates were allowed to self-extinguish. After extinguishment, substrates were allowed to vent for several seconds before they were sealed into tins.

Figure 16: A burned section of pine wood.

Figure 17: A burned swatch of carpet.

2.6.4: Simulated (burned and spiked) samples

Simulated samples were created in the laboratory and replicated realistic fire debris by combining ignitable liquids with burned substrate materials. Liquids were added to the substrates after they had been burned according to the above procedure (see Section 2.6.3: Burned substrates). Adding the ignitable liquid after burning the substrate allowed detection of a consistent amount of ignitable liquid, whereas burning the substrates after ignitable liquid deployment would weather the accelerant unevenly, depending on how the substrate was burned.

2.6.5: Operational samples

Operational samples were obtained from a real fire scene to supplement results obtained in the laboratory. The author attended a research burn exercise hosted by Fire and Rescue New South Wales (FRNSW). The exercise took place in Gilgandra, New South Wales and focused on the controlled burn of a single-storey house (the Gilgandra Old Aerodrome Clubhouse, Figure 18) and two adjacent bedsits.

Figure 18: The Old Gilgandra Aerodrome Clubhouse building.

Samples were obtained from several burn exercises. In the first, simulated house floor surfaces were burned. The floors consisted of a shipping pallet supporting the floor materials, flanked by two sections of plasterboard which acted as adjoining walls (Figure 19).

Figure 19: The burning of a simulated timber floor surface.

Six simulated floors were burned in total. The surfaces included treated timber, synthetic carpet, linoleum, wool carpet, ceramic tiles and a wooden floating floor. Each of these burns was accelerated by a petroleum pour in the corner of the floor area. Floor materials burned until self-extinguishment.

Floor samples were collected approximately twenty-four hours after they were lit, on the next day of the research exercise. The floors were exposed to ambient day temperatures of approximately 15.5°C and were wet due to condensation overnight. Weather conditions were otherwise mild and sunny. Debris samples were taken from as close to the centre of the burn pattern as possible via direct excision (Figure 20). Control substrate samples were also collected. Samples of carpet and linoleum were cut away using a knife, while timber and tiles were broken into pieces to allow for collection. Samples were sealed into 1 litre tins before being analysed on-site.

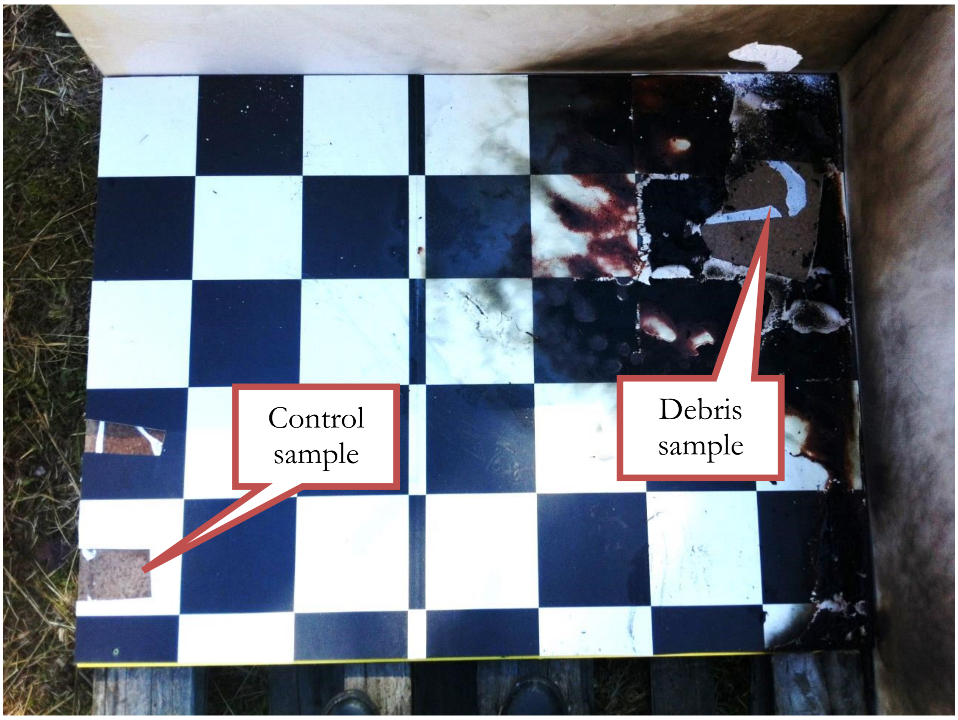


Figure 20: A burned linoleum floor. Control and debris sample collection sites are labelled.

Two samples were retrieved from the controlled burn of a bedsit structure. The point of origin of the bedsit fire was in the structure's roof cavity. The fire broke through the ceiling and dropdown (burning debris from the roof) began a secondary blaze in the main room. A petrol accelerant had been poured in two locations in the bedsit: on top of a cushion on a desk and on the corner of a chest of drawers. Extinguishment of the fire took place after flashover (full room involvement) had occurred. Sample collection took place approximately one hour after extinguishment.

After the fire, the cushion no longer existed and an unidentifiable pile of debris was visible atop the table where the cushion originally was. All of this debris was collected into a 1 litre sample tin and sealed. The chest of drawers was badly burned but still intact. The corner of the chest, where the accelerant had been poured, was excised and sealed in a tin. This sample was mostly composed of pieces of wood. Both samples were analysed on-site.

Three more samples were collected from the controlled burn of the living room area of the main clubhouse building. A kerosene accelerant was sprayed in three places in the room: on the arm of an armchair adjacent to the entry door, the floor area behind a couch and the arm of a two-seater couch by the window. The fire in this room advanced quickly and flashover was achieved. A sample of floor debris was taken from the floor area behind the couch. Wood frame and fabric material was taken from the arm of both accelerated chairs.

2.7: In-field instrument evaluation

The aim of in-field instrument was to determine how robust the instrument was for portable use. Factors such as the longevity of the instrument's battery power supply were examined. The battery pack was evaluated while debris samples from the Gilgandra burn exercise were analysed on-site. A subsequent battery examination took place in the laboratory. Sample blank runs were performed continually on the instrument until battery power was depleted. Two battery packs were evaluated. The time until depletion and the number of runs each component was able to complete were recorded.

An informal evaluation of the instrument's portability was also conducted, assessing how easy it was to move around, set up and perform analyses. The instrument's usability was also appraised by consultation with members of interstate fire and police services, as well as a personal evaluation by the author.

2.8: Data interpretation

Interpretation of TRIDION-9 data was performed initially based on ASTM Standard Test Method E1618-10 (ASTM International, 2010), as well as Australian Standard 5239-2011 (Standards Australia, 2011). Data obtained on the TRIDION-9 was transferred to a connected laptop with CHROMION installed. CHROMION was used as the data system to manipulate and analyse chromatographic and mass spectrometric data. TIC data was interpreted first. This included sample elution range and peak distribution. Second, ion profiles were extracted for all major compound types of interest. The most abundant ion profiles were compared to those extracted from reference chromatograms. If similarities were observed at this level, diagnostic peak patterns were examined and individual peak ratios were confirmed between the sample and the standard. If extraneous peaks were observed, the sample was compared to an unburned substrate to determine whether or not the extraneous peaks originated from the substrate matrix. Alternatively, a burned control sample was consulted to determine if the extra compounds may have been pyrolysis products. In samples where pyrolysis product interference made visualisation of target compounds difficult, analysis was conducted using extracted ion profiles (EIP).

Individual compounds were identified according to their mass spectra and retention times. Sample mass spectra were compared to library data. Peak identification focused on target compounds listed in Appendix A: Table of Target Compounds. Provided that most target compounds were found in the expected ratios, the ignitable liquid was positively identified.

3. Results

3.1: Method development

3.1.1: Sampling time

Sampling times of 10, 30, 60, 120, 180 and 300 seconds were tested. Longer sampling times provided better results. Increasing sampling time increased the abundance of compound peaks as a larger amount of analyte was able to adsorb onto the SPME fibre. Peak height was several orders of magnitude better between the shortest (10 seconds) and longest (300 seconds) sampling time. While the shortest sampling time provided adequate data, resolution was not ideal. Conversely, a sampling time of 300 seconds (five minutes) was deemed unnecessary since sample analysis only took about two minutes. A modest sampling time of 180 seconds (three minutes) was chosen as it provided the best balance between rapidity and reliability. A comparison between all six sampling times appears in Figure 21.

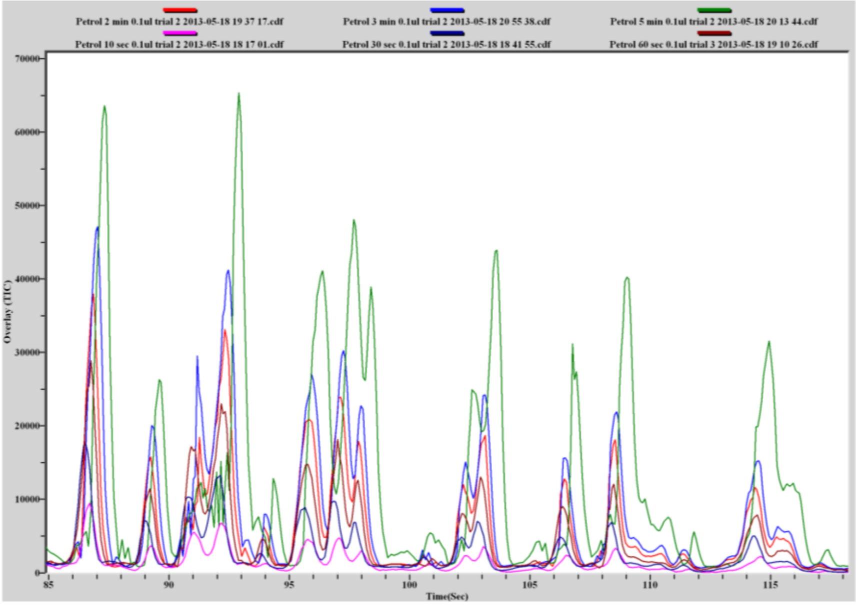
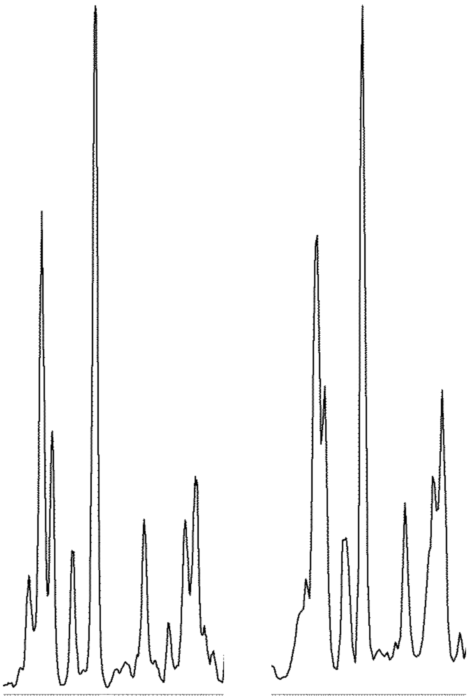


Figure 21: Six chromatograms representing six different sampling times, superimposed on top of each other. Green represents a 300 second sapling time, blue is 180 seconds, red is 120 seconds, maroon is 60 seconds, dark blue is 30 seconds and pink is 10 seconds.

3.1.2: Temperature ramp rate and temperature hold times

Column temperature ramp rates of 1, 2 and 3 degrees Celsius per second (°C/sec) were evaluated. Higher ramp rates decreased the analysis time significantly as the analyte was pushed through the column more quickly. However, this came at a cost of reduced separation power (Figure 22). Poorly resolved chromatograms made compound identification difficult as diagnostic peak patterns were harder to visualise.



1°C/sec ramp rate 3°C/sec ramp rate

Figure 22: A comparison of the separation power of different column temperature ramp rates. Both chromatograms above represent the same group of compound peaks. Peaks are better resolved using the slower ramp rate.

A ramp rate of 1°C/sec provided the best chromatographic separation. However, using this ramp rate setting was impractical because the instrument's PV method used a ramp rate of 2°C/sec. This meant that PV retention time calibrations and spectral quality adjustments were based on compound peaks as they appeared at a 2°C/sec ramp rate. Using a lower ramp rate defeated the purpose of PV as any adjustments it made were void as soon as the ramp rate was changed. For this reason, a ramp rate of 2°C/sec was selected. This ramp rate offered an efficient analysis turnaround time in combination with a three minute sampling time. A representation of the ramp rate's effect on analysis time is shown in Figure 23.

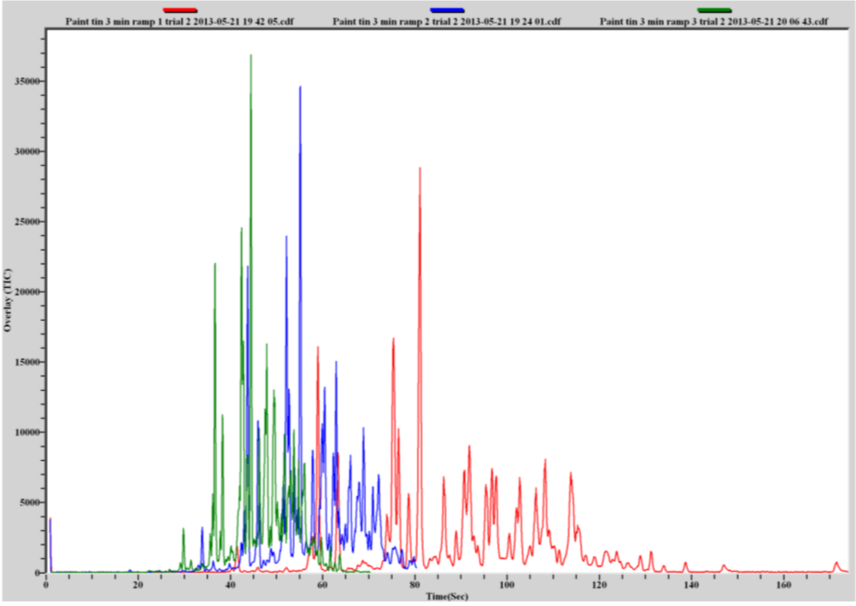


Figure 23: Three chromatograms from the same sample using three different column temperature ramp rates. Green represents a 3°C/sec ramp rate and is the fastest analysis. Blue represents a 2°C/sec ramp rate. Red represents a 1°C/sec ramp rate.

Column temperature hold times were found to have a negligible impact on analysis. High begin hold times increased the resolution of early-eluting peaks. Without a begin temperature hold time of at least several seconds, very light compounds would elute as an unresolvable compound mass. Few peaks of interest ever occurred in this early elution range. Toluene or octane were typically the earliest eluting peaks of interest and were unaffected by changes to begin hold times. Therefore, the begin temperature hold time was reduced to zero.

Final temperature hold times were more useful. Some high molecular weight compounds would not elute from the column after the final column temperature had been reached and would present in the next sample run as ghost peaks. A final temperature hold time extended the analysis period, giving more time for these compounds to escape from the column before it began to cool down. This prevented them from bleeding into subsequent analyses and kept the column clean. A final temperature hold time of five seconds was determined to be adequate for this purpose.

3.1.3: Starting and final column temperatures

Column start temperature had little effect on analysis results. Since early-eluting compounds were not of interest (see Section 3.1.2: Temperature ramp rate and temperature hold times), a particularly low starting temperature was not necessary. A start temperature of 50°C was utilised.

Final column temperature required some tuning. A final column temperature was required which was high enough to allow high molecular weight compounds of interest to elute from the column, but not too high that it would drag analysis time out. Diesel, the heaviest petroleum distillate analysed, was used to determine the highest temperature necessary. Alkanes up to octadecane could be visualised in diesel fuel chromatograms and compounds eluting after this point could not be differentiated from the baseline. At the elution point of octadecane, the column temperature was 244°C. A final column temperature slightly above this, 260°C, was therefore selected, which allowed all target compounds enough time to elute.

3.1.4: Injection port and transfer line temperatures

These parameters were set to values recommended by the manufacturer. Initially, the transfer line was set to 300°C. However, problems experienced by the manufacturer with thermal degradation of the transfer line at these temperatures forced this value down. A temperature of 250°C was adequate for this component as the transfer line was under vacuum and did not require high temperatures to force analytes through it. The injector could operate at any temperature up to 300°C. It was regarded unnecessary to have the injector hotter than the final column temperature, as not everything volatilised in the injector at a higher temperature would elute properly from the column. Keeping the injector temperature slightly above the final column temperature ensured that all analytes of interest were volatilised by the injector and could pass through the column. The injector was set to 270°C.

3.1.5: Injection split

Several injection types were investigated, ranging from splitless injections to basic 10:1 and 50:1 splits and combination splits. Combination splits involved using both split ratios (10:1 and 50:1, one after another) and a delayed split (turning the split on several seconds after the injection).

Splitless injections were not appropriate as a large amount of background noise was generated in the chromatogram, reducing peak resolution. Basic splits were more effective.

10:1 and 50:1 splits run for 10 seconds produced clean chromatograms. However, the 50:1 split reduced the concentration of analytes hitting the detector significantly. The 10:1 split produced larger, better resolved compound peaks. Mixed splits involved the use of both injection splitters. One split was activated (10:1) for several seconds before it was closed and the larger split (50:1) was then opened. There was little difference between mixed split and basic 10:1 split results. A mixed split was employed to ensure that all analytes were cleared from the injector.

Results were significantly improved with the use of a delayed mixed split. This employed the mixed split described above, but delayed it so that the first split would activate two seconds after the sample was injected. This resulted in a large increase in sensitivity. Delays of one, two, five and ten seconds all increased analysis sensitivity, though longer delays also generated background noise. Two second delays provided the best balance between increased sensitivity and background interference.

3.1.6: Desorption time

SPME fibre desorption time was not evaluated as a part of method development. This value was kept at ten seconds, as recommended by the manufacturer. Informal evaluation of faster desorption times revealed that times as short as five seconds were also effective. However, a longer desorption time of ten seconds was useful as this allowed several seconds for sample desorption and time for fibre reconditioning, ensuring that the fibre was clean.

3.1.7: Summary of method development

The following table (Table 3) summarises the optimal instrument parameters selected from this phase of the study.

Table 3: Summary of method development operating parameters

Parameter	Test values
Sampling time	180 seconds (3 minutes)
Temperature ramp rate	2°C per second
Starting column temperature	50°C
Starting temperature hold time	0 seconds
Final column temperature	270°C
Final temperature hold time	5 seconds
Injection port temperature	270°C
Transfer line temperature	250°C
Split ratio	Splitless (2 seconds) 10:1 split (10 seconds) 50:1 split (8 seconds)
Desorption time	10 seconds

3.2: Neat ignitable liquid analysis

Compounds identified in the following section are identified numerically in chromatograms. Compounds and the number allocated to them are consistent throughout this report and are listed in Table 4.

Table 4: Neat ignitable liquid chromatogram compounds and their associated numeric labels.

Label	Compound	Label	Compound
1	Toluene	**18**	2-methylnaphthalene
2	Ethylbenzene	**19**	1-methylnaphthalene
3	m-/p-xylene	**20**	1,3-dimethylnaphthalene
4	o-xylene	**21**	2,3-dimethylnaphthalene
5	Propylbenzene	**22**	Octane
6	m-/p-ethyltoluene	**23**	Nonane
7	1,3,5-trimethylbenzene	**24**	Decane
8	o-ethyltoluene	**25**	Undecane
9	1,2,4-trimethylbenzene	**26**	Dodecane
10	1,2,3-trimethylbenzene	**27**	Tridecane
11	Indane	**28**	Tetradecane
12	1,2,4,5-tetramethylbenzene	**29**	Pentadecane
13	1,2,3,5-tetramethylbenzene	**30**	Hexadecane
14	4-methylindane	**31**	Heptadecane
15	5-methylindane	**32**	Octadecane
16	4,7-dimethylindane	**33**	trans-decalin
17	Naphthalene		

3.2.1: Neat unleaded petroleum

Neat unleaded petroleum (Figure 24 and Figure 25) produced a chromatogram with compounds in the C_7 to C_{13} range. All compounds of interest eluted from the column within 80 seconds. Several distinct clusters of peaks were dispersed in a roughly Gaussian distribution. Small concentrations of alkanes were apparent. There was a negligible presence of cycloalkanes. The aromatic ion profile was the most abundant. Toluene was noticeable as the first distinct peak in the chromatogram. C_2, C_3 and C_4 alkylbenzenes were present in ratios typical of petroleum. Ethylbenzene and m-/p-xylene (extracted with ion 91) exhibited slight co-elution, but o-xylene was distinct.

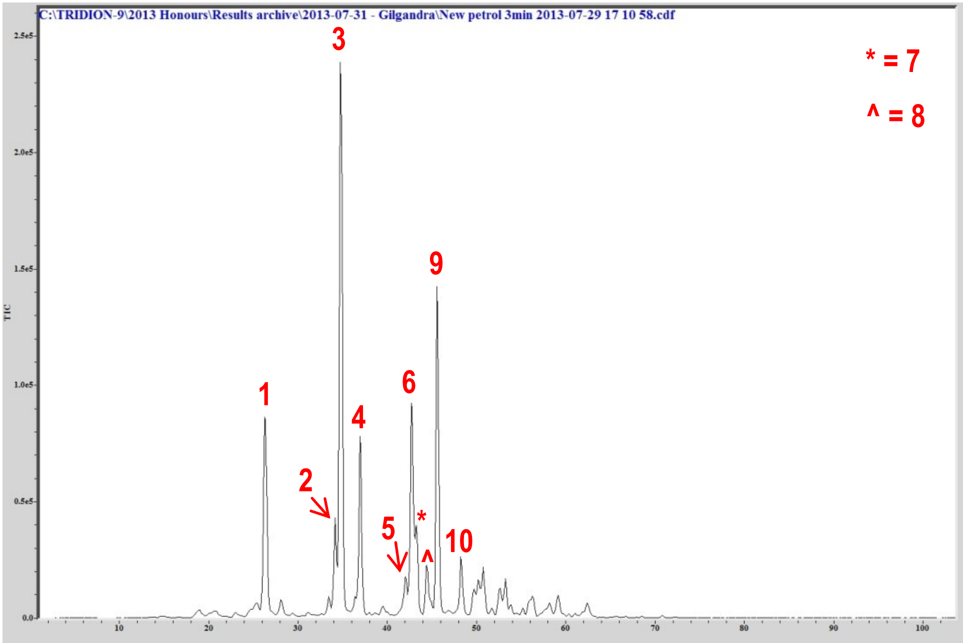


Figure 24: Neat unleaded petroleum sample chromatogram.

Compounds specified as mandatory for an identification of gasoline according to Standard Test Method E1618-10 (m-ethyltoluene, p-ethyltoluene, o-ethyltoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene) were also found. Most of the C_3 alkylbenzenes co-eluted, producing a peak group which was not entirely consistent with the classic 'castle' peak group referred to in the literature (see Appendix H: Diagnostic Peak Patterns in Petroleum). m-Ethyltoluene and p-ethyltoluene co-eluted, with differentiation between the two impossible. Propylbenzene possessed a small peak which merged into the larger peak of m-/p-ethyltoluene. 1,3,5-Trimethylbenzene was a shoulder on the right side of the m-/p-ethyltoluene peak, while o-ethyltoluene was a discrete peak on its own. Ions 105 and 120 were most effective at visualising the C_3 alkylbenzenes.

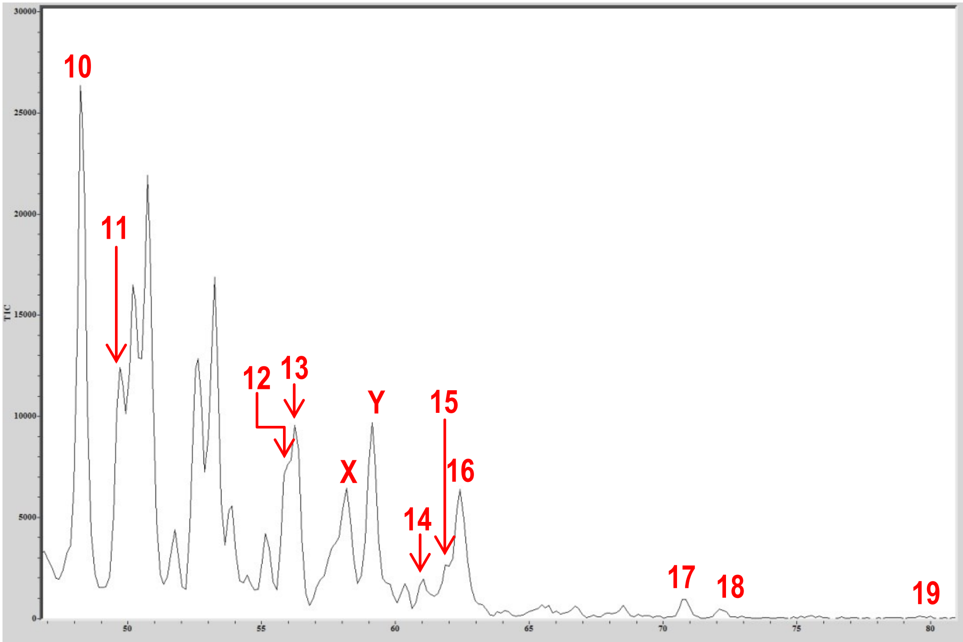


Figure 25: An enlarged view of the later elution range of neat petroleum.

Other target compounds listed in Standard Test Method E1618-10 could also be identified. 1,2,3-Trimethylbenzene eluted soon after 1,2,4-trimethylbenzene and signified the end of the C_3 alkylbenzene range. A triplet of three co-eluting peaks followed, with indane identified as the first peak in this group. Several C_4 alkylbenzenes eluted after this point, the most significant being 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene. These compounds eluted at the same time and resolution of both peaks was poor. Ion 119 was used to extract the tetramethylbenzene compounds.

A number of condensed ring aromatics were present. Two methylindanes (4-methylindane and 5-methylindane) were target compounds according to Standard Test Method E1618. Peaks likely to represent these compounds were located in the chromatogram based on mass spectra. However, in the absence of chemical standards for these compounds, their presence in the chromatogram could not be confirmed. They were not used for identification purposes.

4,7-Dimethylindane eluted just before naphthalene. The compound was deemed significant due to its status as an E1618 target compound. However, it could only be identified based on its mass spectrum and no distinct peak was observed. The low concentration of dimethylindane, as well as the fact that it co-eluted with naphthalene, made it difficult to identify.

Methyl- and ethylnaphthalenes were difficult to identify due to their low concentrations and high molecular weight compared to other petroleum target compounds. 2-methylnaphthalene and 1-methylnaphthalene were best visualised by extracting ion 142. Otherwise, normalisation of the chromatogram based on the most abundant peak meant that the methylnaphthalenes disappeared into the baseline. Ethylnaphthalenes could rarely be found in neat petroleum samples. In some analyses, 1,3- and 2,3-dimethylnaphthalene could be visualised by extracting ion 156, however their appearance was not consistent.

3.2.2: 70% weathered petroleum

Samples of 70% weathered petroleum (Figure 26) produced an almost identical chromatographic pattern to neat petroleum. The most significant difference was the lower concentration of toluene and C_2 alkylbenzenes, which were represented by a smaller peaks in the 70% weathered sample. Otherwise, all other chromatographic features were the same. The same target compounds as were present in neat petroleum could be identified, and with similar peak ratios. A small degree of skewing to the heavier end of the chromatogram was apparent, with compounds such as indanes and C_4 alkylbenzenes possessing larger peaks than in neat petroleum.

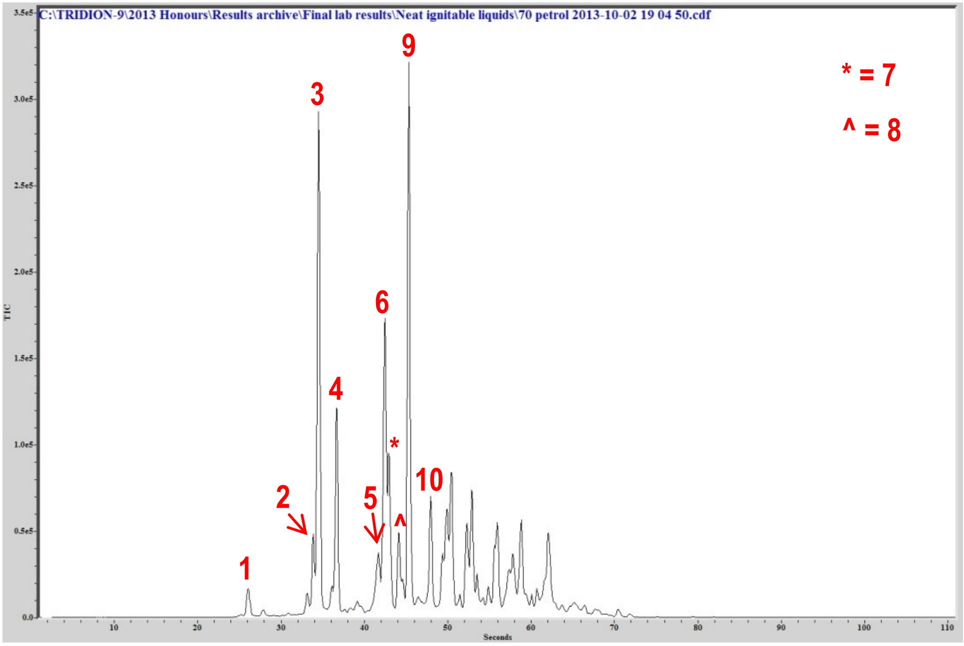


Figure 26: 70% weathered unleaded petroleum sample chromatogram.

3.2.3: 90% weathered petroleum

The 90% weathered petroleum (Figure 27) differed more noticeably from the neat petroleum standard than the 70% weathered sample. Samples of 90% weathered unleaded petroleum produced compounds which eluted in the C_9 to C_{13} carbon range. Compounds of interested eluted within 75 seconds. The chromatogram retained a Gaussian shape, though it was skewed slightly towards higher retention times. An aromatic profile predominated.

The most obvious difference between 90% weathered and neat petroleum was the total loss of toluene and all other compounds which eluted before the C_2 alkylbenzenes. The C_2 alkylbenzenes themselves were still identifiable, though they were less concentrated than the C_3 alkylbenzenes. Heavier compounds were therefore more highly concentrated. Most petroleum target compounds in the C_2 alkylbenzene range and later were detected. For the first time in petroleum samples, ion fragments of dimethylnaphthalene target compounds could be reliably reproduced.

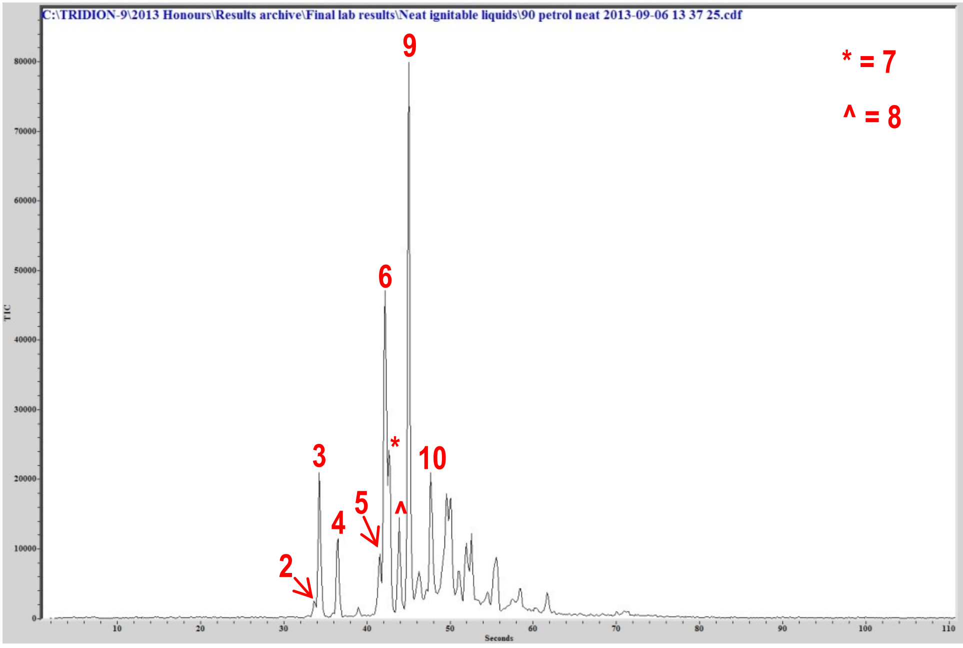


Figure 27: 90% weathered unleaded petroleum sample chromatogram.

3.2.4: 97% weathered petroleum

97% weathered petroleum (Figure 28) followed the trend of 70% and 90% weathered petroleum in terms of chromatogram skewing and compound loss. Lighter components such as toluene and C_2 alkylbenzenes were absent in 97% weathered petroleum.

Propylbenzene was the first readily identifiable compound of interest. Compounds eluting after the C_3 alkylbenzenes were significantly more abundant than in less weathered samples, shifting the centre of the chromatogram towards indane. Heavy compounds such as the dimethylnaphthalenes were visible as discrete peaks, as opposed to in less weathered samples where they could only be identified by their mass spectral footprints.

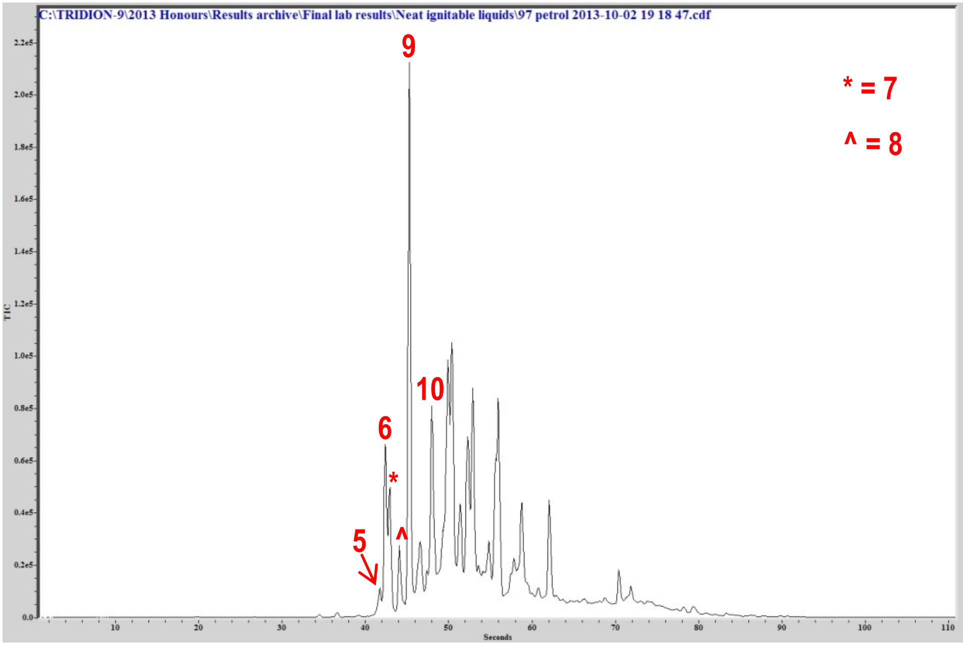


Figure 28: 97% weathered petroleum sample chromatogram.

3.2.5: Diesel fuel

Diesel fuel, an HPD, produced a very broad chromatographic pattern with peaks in a Gaussian arrangement (Figure 29). Normal alkanes in the C_9 to C_{18} range were identifiable (nonane to octadecane). The main bulk of the chromatogram began with decane, at which point alkane concentrations rose until tridecane. There was then a gradual decrease in peak height until the end of the sample run, with octadecane being the last recognisable alkane compound. Nonane could be recognised by its mass spectrum, but was low in concentration. Pentadecane and later eluting alkanes exhibited tailing chromatographic artefacts. Octadecane was particularly poorly resolved, though a compound peak was still visible. A small shoulder was observed on the heptadecane peak which suggested the presence of pristine, but resolution was too poor for this to be confirmed. These alkanes dominated the chromatogram and were mirrored by smaller cycloalkane and alkylcyclohexane ion profiles. Cycloalkanes in the range of butylcyclohexane to undecylcyclohexane eluted at the same time as their respective alkanes. An aromatic profile was present but insignificant. Condensed ring aromatics such as naphthalene, methylnaphthalenes and dimethylnaphthalenes were also apparent, but in low amounts. Trimethylnaphthalenes were undetectable. Indanes may have been, but co-eluted to a point where their presence could not be confirmed.

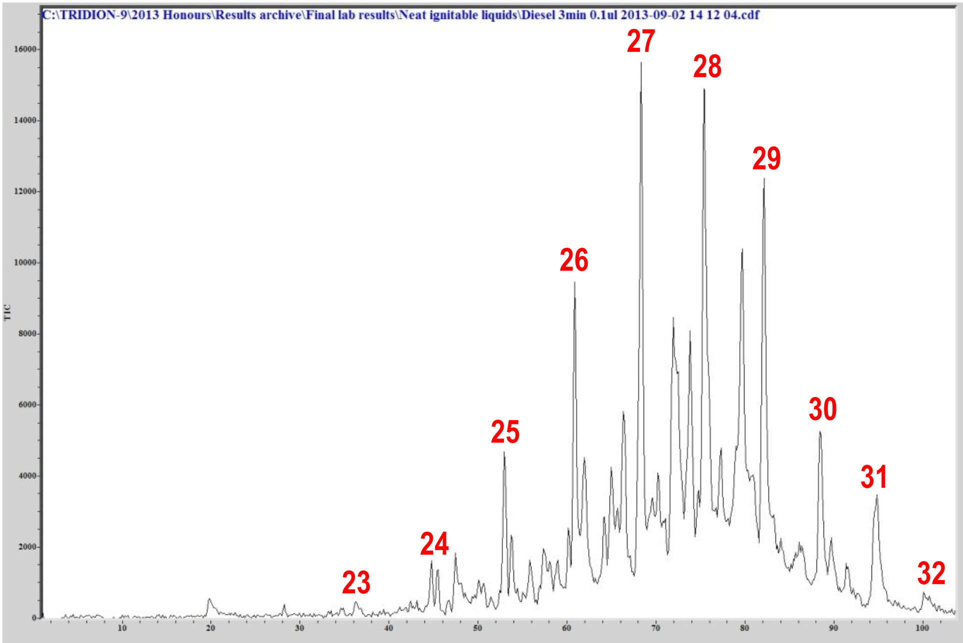


Figure 29: Diesel fuel sample chromatogram.

3.2.6: Kerosene

Kerosene was classified as a medium to heavy petroleum distillate (Figure 30). The chromatographic pattern of kerosene was moderately distributed. Alkanes dominated the chromatogram, ranging from C_9 to C_{15} (nonane to pentadecane). A baseline consisting of various unresolved alkane isomers and cycloalkanes occupied the space between each n-alkane. Cycloalkane and alkylcyclohexane profiles were present in lower abundances.

Various aromatic compounds were present, though most exhibited large degrees of co-elution and could only be visualised using EIP. Toluene and C_2 alkylbenzenes were present and maintained ratios similar to petroleum. C_3 alkylbenzenes were also present. Trans-decalin was identified. C_4 alkylbenzene target compounds could also be identified. Naphthalene, methylnaphthalenes and dimethylnaphthalenes were present.

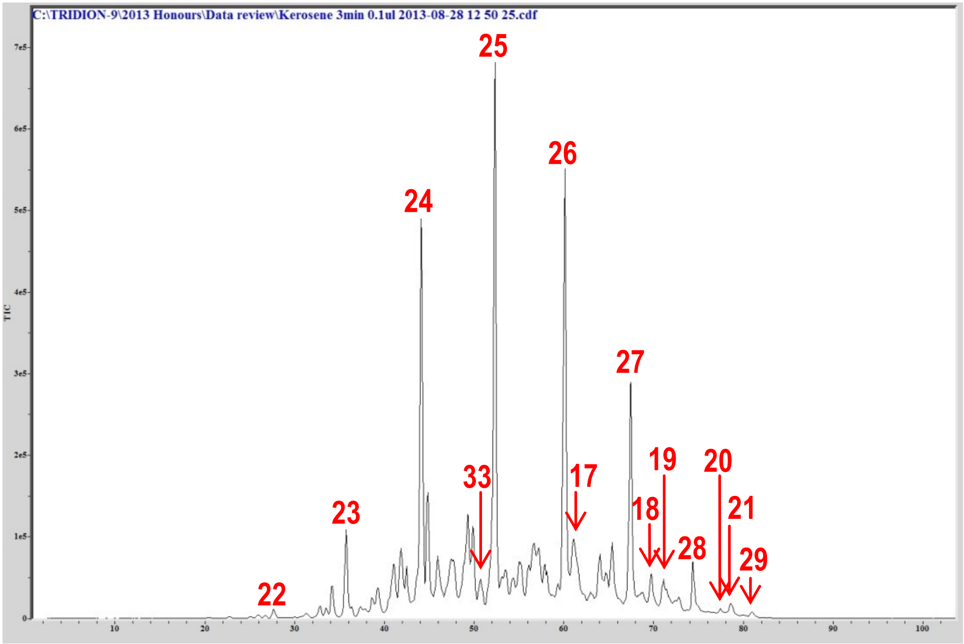


Figure 30: Kerosene sample chromatogram.

3.2.7: Mineral turpentine

Mineral turpentine was classified as an MPD (Figure 31). Peaks of interest in mineral turpentine chromatograms were dispersed throughout a C_8 to C_{13} range in a Gaussian pattern. Ion profile dominance was shared by aromatic and alkane ion profiles. Normal alkanes from octane to dodecane were present. Decane was the most intense of these peaks, located at the very centre of the chromatographic pattern.

Peaks associated with C_2 alkylbenzenes such as ethylbenzene, m-/p-xylene and o-xylene were identified, however o-xylene co-eluted strongly with nonane. The o-xylene peak was just as intense as m-/p-xylene, throwing out the traditional C_2 alkylbenzene peak ratio. C_3 alkylbenzene compounds (propylbenzene, m-/p-ethyltoluene, 1,3,5-trimethylbenzene and o-ethyltoluene) formed the most obvious aromatic peak group in the chromatogram. C_3 alkylbenzene peak ratios were consistent with a petroleum product. 1,2,4-Trimethylbenzene and 1,2,3-trimethylbenzene eluted shortly after the C_3 alkylbenzenes. Indane eluted as the shoulder of another compound peak, while trans-decalin appeared as its own peak. C_4 alkylbenzenes (1,2,3,4- and 1,2,3,5-tetramethylbenzene) were poorly resolved and eluted as a single peak. Naphthalene was the last compound of interest to be detected and no polynuclear aromatics were present. This was consistent with the target compound elution range suggested by Standard Test Method E1618-10 for MPDs.

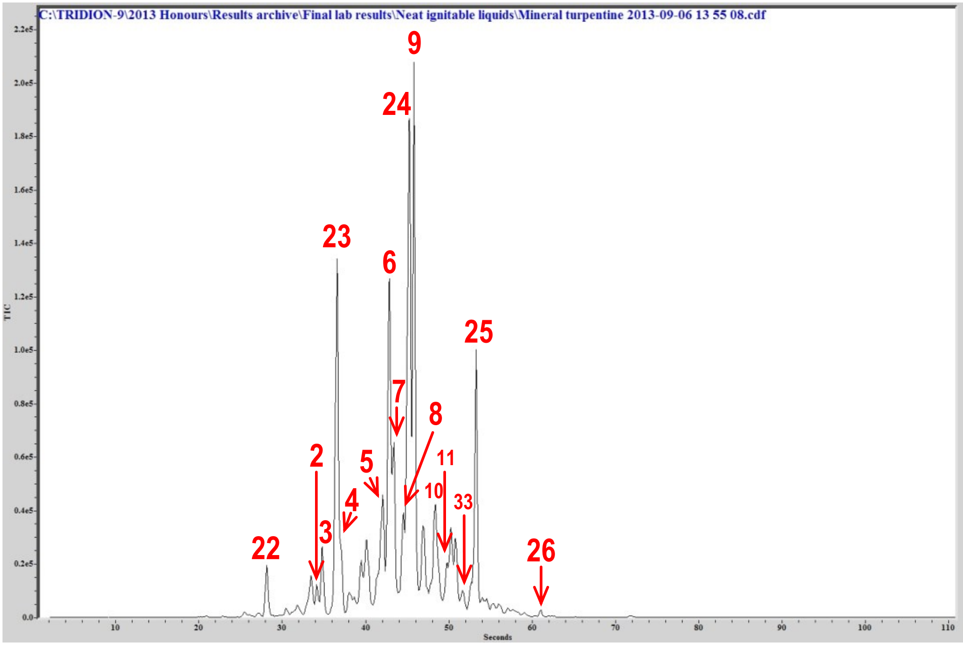


Figure 31: Mineral turpentine sample chromatogram.

3.3: Blank substrate analysis

In all cases, compound peaks in blank substrate chromatograms were much less intense than in their burned counterparts. Most carpet and underlay substrates showed little volatile content, except for pine, which produced intense peaks. Figures referenced in this section are presented in full in Appendix D: Blank Substrate Results.

3.3.1: Nylon carpet

The nylon carpet compounds eluted in the C_9 to C_{12} carbon range (Figure 37). None were identifiable as the chromatographic pattern was dominated by an unresolvable complex mixture with a Gaussian distribution. The mass spectrum across this group of peaks was similar to a cycloalkane ion profile, with a base ion of 69. No compounds of interest were present.

3.3.2: Polypropylene carpet

Polypropylene carpet exhibited a narrowly distributed chromatographic pattern (Figure 38). The majority of compounds in the polypropylene carpet sample eluted in the C_9 to C_{12} boiling point range. The ion profile was similar to that present in the nylon carpet sample (cycloalkane).

3.3.3: Wool carpet

Wool carpet exhibited a chromatographic pattern similar to that of the nylon and polypropylene carpets (Figure 39). The chromatogram was dominated by an unresolvable mass eluting in the C_9 to C_{12} boiling point range. The predominant ion profile was cycloalkane in nature. A small toluene peak was visible which eluted before the main unresolvable compound mass. One compound peak in the mass was characteristic of m-/p-ethyltoluene, but no other individual compounds were resolvable.

3.3.4: Rubber carpet underlay

No significant chromatographic peaks were observed in the samples of rubber carpet underlay.

3.3.5: Foam carpet underlay

Foam carpet underlay chromatograms were dominated by a small number of peaks (Figure 40). The first, largest peak in the chromatogram appeared to be a mixture of several poorly separated compounds. Mass spectra across this peak were composed mainly of ion 45, suggesting that a number of alcohols were present in the underlay. The second largest peak was toluene. Other peaks were not considered to be significant due to their low abundance.

3.3.6: Pine

Raw pine produced two main compound peaks (Figure 41) which were so highly concentrated that other compounds in the sample were difficult to visualise. A short sampling time was necessary to better visualise other compounds. Four compounds were identified in total. The two largest peaks in the sample represented α-pinene and β-pinene. One of the smaller peaks was identified as camphene. The last significant peak was limonene.

3.3.7: Polyurethane

Polyurethane samples produced chromatograms displaying several compounds (Figure 42). None could be identified.

3.4: Burned substrate analysis

Figures referred to in this section appear in Appendix E: Burned Substrate Results.

3.4.1: Nylon carpet

Nylon carpet burned consistently once ignited. Liquefaction and bubbling of the carpet pile was observed as the dye in the carpet evaporated. Burned nylon carpet chromatograms exhibited several pyrolysis products (Figure 43). The most intense peak was identified as styrene. Small traces of target compounds were detected, but these were of very low intensity compared to styrene. The target compounds detected were toluene, ethylbenzene, propylbenzene and naphthalene.

3.4.2: Polypropylene carpet

The polypropylene carpet burned readily. Carpet pile structure disintegrated soon after ignition as each pile loop separated and liquefied. The carpet dripped significantly during burning. Sample data showed several distinguishable peaks (Figure 44), some of which were also present in the burned nylon carpet. The most significant peak was styrene. Small amounts of toluene, ethylbenzene, propylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, indane and naphthalene were also present.

3.4.3: Wool carpet

The wool carpet did not burn for more than several seconds without the assistance of a flame. The wool carpet pile liquefied and formed a viscous aqueous layer on top of the carpet backing, but did not readily drip. Toluene was the first recognisable compound in the sample chromatogram (Figure 45), followed by ethylbenzene and styrene. A small propylbenzene peak was present before a benzaldehyde peak. Naphthalene was present in small amounts.

3.4.4: Rubber carpet underlay

The rubber carpet underlay burned unassisted once it was ignited. The underlay material burned more easily than the paper-based backing. Underlay sloughed off in segments rather than dripping or disintegrating. The burned rubber carpet underlay chromatograms displayed compounds over a large boiling point range (Figure 46). Toluene and m-/p-xylene were evident. The most abundant pyrolysis product was limonene.

3.4.5: Foam carpet underlay

The foam carpet underlay burned readily and at a rapid rate. Almost none of the original sample mass remained after burning. The underlay liquefied shortly after ignition and fell apart as drips. Much of the underlay mass was air which escaped as the foam burned. The foam underlay liquid was thin and runny. Only one pyrolysis product could be easily identified in the burned foam carpet underlay chromatogram – styrene (Figure 47). Three major peaks which eluted before styrene could not be identified, though they possessed mass spectra indicative of ketone compounds. Small concentrations of toluene and ethylbenzene were also present.

3.4.6: Pine

Pine did not combust easily and required a sustained flame in order to burn. All sides of the pine sample were burned until black char covered the sample surface area. The total mass of the sample was only slightly reduced by burning. The burned pine chromatogram differed marginally from the unburned sample (Figure 48). Unburned sample compounds, α-pinene, camphene, β-pinene and limonene were still present.

3.4.7: Polyurethane

The polyurethane sofa cushions with fabric upholstery burned with ferocity. Once ignited, samples burned intensely until completion and almost none of the original sample mass remained. A number of pyrolysis products appeared in the sample chromatogram (Figure 49). Ions 43, 45 and 87 were prevalent in mass spectrometer scans, suggesting various unsaturated hydrocarbons were the main pyrolysis products. Styrene was present in low concentrations, as well as tetradecane.

3.5: Simulated (burned and spiked) sample analysis

Highly-detailed chromatogram and mass spectrum data analysis was possible using the TRIDION-9 and CHROMION. Analysis of each sample allowed it to be placed into one of three categories:

1. Contains ILR;
2. Possibly contains ILR, pending laboratory confirmation;
3. Does not contain ILR.

Samples which were found to contain a large number of target compounds and possessed EIPs which closely represented a reference ignitable liquid were assessed as containing ILR. Sometimes, compound peak ratios were not entirely consistent with reference liquids and some target compounds could not be detected. In these cases, samples were assessed as possibly containing ILR, pending laboratory analysis. Samples in which few target compounds were found and where chromatograms did not represent reference ignitable liquids were determined to contain no ILR.

The results of analyses include chromatogram classification and target compound identifications which appear in Appendix F: Simulated Sample Results and Discussion. A summary of all simulated sample results can be found in Table 5.

3.5.1: Substrates spiked with unleaded petroleum

3.5.1.1: Nylon carpet

Simulated nylon carpet debris samples produced chromatograms which were consistent with petroleum. A large number of compounds of interest were found and compound peak ratios were consistent with an unleaded petroleum standard. Substrate interference was minimal.

3.5.1.2: Polypropylene carpet

A styrene compound peak dominated the polypropylene sample chromatogram. An aromatic profile was present, but less abundant than the alkylstyrene profile. A variety of petroleum target compounds were detected. Alkylbenzene peak ratios were typical of a petroleum product.

3.5.1.3: Wool carpet

Wool carpet spiked with unleaded petroleum yielded a TIC pattern consistent with a petroleum standard. No matrix interferents could be visualised.

3.5.1.4: Rubber carpet underlay

When rubber carpet underlay was burned and spiked, the resulting chromatogram displayed peak patterns diagnostic of petroleum. All petroleum target compounds up to naphthalene were identifiable, except for 4,7-dimethylindane, which was present in only trace amounts.

3.5.1.5: Foam carpet underlay

Simulated foam carpet underlay samples were partially obscured by pyrolysis compounds from the foam. Nevertheless, most petroleum target compounds could be visualised.

3.5.1.6: Pine

The chromatograms from pine spiked with neat unleaded petroleum were difficult to interpret due to interferents released by the substrate. No recognisable EIP was detectable. Target compounds identified were very low in concentration.

3.5.1.7: Polyurethane

Spiked polyurethane sample chromatograms were dominated by compounds originating from unburned polyurethane. The largest compound peak in the chromatogram could not be identified; however, petroleum could still be identified in the sample.

3.5.2: Substrates spiked with 70% weathered petroleum

3.5.2.1: Nylon carpet

Unleaded petroleum residues were clearly visible in the burned nylon carpet sample. Characteristic C_2 and C_3 alkylbenzene peak groups were easily identified. Substrate effects were minimal.

3.5.2.2: Polypropylene carpet

Styrene was the largest compound peak in the chromatogram, slightly obscuring ignitable liquid compounds which were otherwise readily observable in the chromatogram.

3.5.2.3: Wool carpet

A single styrene peak dominated the chromatogram of the spiked wool carpet sample. EIP was necessary to locate compounds of interest.

3.5.2.4: Rubber carpet underlay

Pyrolysis products eluting in the C_3-C_4 alkylbenzene range made target compound identifications problematic. Nevertheless, an aromatic ion profile was dominant which was characteristic of a petroleum product.

3.5.2.5: Foam carpet underlay

A number of discrete peaks which eluted before toluene were present in this sample, most of which were thought to be ketone interferents. An aromatic profile extract revealed a pattern expected of a petroleum product.

3.5.2.6: Pine

Interferent compounds related to the pine substrate dominated this sample chromatogram. Many smaller pyrolysis product peaks were also present. Most were terpenes, though they could not be identified exactly. No peaks of interest could be located.

3.5.2.7: Polyurethane

Combustion products dominated the low end of the polyurethane samples. Various compounds of interest were also detected, but peak ratios were not consistent with the petroleum standard.

3.5.3: Substrates spiked with 90% weathered petroleum

3.5.3.1: Nylon carpet

Nylon carpet samples spiked with 90% weathered petroleum produced chromatograms which were identical to those of the burned substrate. Styrene dominated the chromatogram. Other pyrolysis products could not be identified. Target compounds were present but peak ratios were inaccurate.

3.5.3.2: Polypropylene carpet

Spiked polypropylene carpet sample chromatograms were composed mainly of pyrolysis products. Target compounds were visible in higher concentrations than the nylon carpet sample, allowing for more accurate identification.

3.5.3.3: Wool carpet

ILR was more easily visible in wool carpet samples than other carpet samples. Target compounds were visible on the TIC level. While the most dominant ion profile was contributed by styrene, an aromatic profile was clearly visible.

3.5.3.4: Rubber carpet underlay

Spiked rubber underlay sample chromatograms were very similar to burned rubber underlay substrate data. However, peaks of interest were not completely obscured by pyrolysis product peaks and some could be made out in the TIC.

3.5.3.5: Foam carpet underlay

Peaks of interest were readily visible in the chromatogram of the spiked foam carpet underlay sample. Foam pyrolysis products were also apparent.

3.5.3.6: Pine

Spiked samples of pine revealed peaks related to the pine substrate.

3.5.3.7: Polyurethane

A benzene pyrolysis product peak was the dominant feature of the spiked polyurethane sample data. However, compounds of interest were also easily visible in the chromatogram.

3.5.4: Substrates spiked with 97% weathered petroleum

3.5.4.1: Nylon carpet

Nylon carpet pyrolysis products dominated sample data. Compounds of interest were restricted to the C_3 alkylbenzenes and later eluting compounds. Diagnostic peak patterns which were characteristic of petroleum could be identified using EIP.

3.5.4.2: Polypropylene carpet

Sample data was characteristic of a burned polypropylene chromatogram. C_3 alkylbenzenes were not useful for identification of residues due to interferents.

3.5.4.3: Wool carpet

Petroleum compounds were readily visible in the wool carpet simulated sample. Pyrolysis products produced limited interference. The alkylstyrene profile was only slightly more abundant than the aromatic ion profile.

3.5.4.4: Rubber carpet underlay

The C_3 alkylbenzene peak groups were heavily influence by pyrolysis products. There was an appreciable difference between aromatic and polynuclear EIPs of the sample and the burned substrate, allowing for residue identification.

3.5.4.5: Foam carpet underlay

The aromatic ion profile of the simulated foam sample was slightly more abundant than the natural ketone profile of the substrate. The chromatogram appeared as two separate Gaussian peak distributions, one belonging to the foam pyrolysis products on the left and the other belonging to petroleum compounds on the right.

3.5.4.6: Pine

For the first time in simulated pine samples spiked with any ignitable liquid, target compounds of a significant abundance could be identified on a pine substrate. Pine products still dominated the chromatogram, but ion profiles revealed target compounds across the elution range. Some C_3 alkylbenzenes were unidentifiable due to pine product interference.

3.5.4.7: Polyurethane

Petroleum products were visible in the simulated polyurethane sample chromatogram. Skewing of the chromatogram towards the C_4 alkylbenzenes and heavier compounds was evident.

3.5.5: Substrates spiked with diesel fuel

3.5.5.1: Nylon carpet

Pyrolysis products were prevalent in the nylon carpet sample. Benzaldehyde dominated the chromatogram and styrene was also visible. The chromatogram was Gaussian in shape but few compounds of interest were detected.

3.5.5.2: Polypropylene carpet

The polypropylene carpet sample was typical of burned polypropylene with a large styrene peak in the centre of the chromatographic pattern. A short series of n-alkanes was detected.

3.5.5.3: Wool carpet

Burned wool spiked with diesel fuel produced a chromatogram which contained a consecutive series of alkanes as well as various aromatic products. The data was skewed towards lighter compounds.

3.5.5.4: Rubber carpet underlay

The rubber carpet underlay chromatogram was dominated by the presence of limonene. Trace amounts of pentadecane were visible. Alkanes were present in a roughly Gaussian distribution, though missing alkanes eluting before undecane made this pattern more difficult to visualise.

3.5.5.5: Foam carpet underlay

The foam carpet underlay sample chromatogram was easily comparable to the diesel fuel standard. The pattern was broadly distributed and Gaussian in shape. A consecutive alkane series was identified.

3.5.5.6: Pine

Pine products were abundant in the pine sample chromatogram. A small number of alkanes and other target compounds were detected.

3.5.5.7: Polyurethane

The polyurethane sample produced a broad, Gaussian pattern with alkane species spread throughout the chromatographic range. Normal alkanes in a consecutive sequence were detected. Some ion fragments of octadecane were visible.

3.5.6: Substrates spiked with kerosene

3.5.6.1: Nylon carpet

Nylon carpet samples spiked with a kerosene accelerant formed a simple chromatogram dominated by a large styrene peak. Most other visible peaks in the chromatogram belonged to pyrolysis products. An alkane and aromatic ion profile were also present in the sample. Alkane species in the sample maintained a Gaussian distribution.

3.5.6.2: Polypropylene carpet

A styrene peak represented the most abundant compound in the sample. An alkylstyrene profile was therefore dominant; though a Gaussian alkane ion profile was also present. Some ion fragments of dimethylnaphthalenes could be seen.

3.5.6.3: Wool carpet

When kerosene was spiked onto samples of wool carpet, the resulting chromatogram was dominated by styrene. Co-elution with pyrolysis products made identification of some target compounds difficult, such as isomers of trimethylbenzene, tetramethylbenzene, methylnaphthalene and dimethylnaphthalene. A normal alkane series was present in a Gaussian distribution.

3.5.6.4: Rubber carpet underlay

Burned rubber underlay spiked with kerosene produced a dominant terpene profile due to the presence of limonene. Aromatic and alkane profiles also existed. A series of alkanes were present, ranging from decane to tetradecane.

3.5.6.5: Foam carpet underlay

Burned foam carpet underlay produced chromatograms with a clear Gaussian distribution as a result of pyrolysis products on the lighter end and petroleum distillate products on the heavy end merging together. Styrene was the most abundant compound in the sample. A continuous alkane series was readily visible.

3.5.6.6: Pine

Burned pine spiked with kerosene samples resulted in chromatogram data which was representative of unburned pine. A terpene ion profile was therefore abundant. Only a small number of peaks of interest could be located.

3.5.6.7: Polyurethane

The most concentrated compound in spiked polyurethane samples could not be identified. A number of target compounds were found. A Gaussian alkane profile and an alkylstyrene ion profile were equally abundant.

3.5.7: Substrates spiked with mineral turpentine

3.5.7.1: Nylon carpet

Mineral turpentine spiked onto nylon carpet produced Gaussian chromatograms. The sample was heavily influenced by pyrolysis products which defeated the identification of some target compounds. As a result, peak ratios could not be established with certainty. Detected target compounds could not be confirmed as originating from the ignitable liquid or the substrate.

3.5.7.2: Polypropylene carpet

Spiked polypropylene carpet chromatograms retained similar characteristics to those of nylon carpet. Styrene dominated the chromatogram. Several aromatic peaks of interest were found, as well as a Gaussian distribution of alkanes in the medium distillate range.

3.5.7.3: Wool carpet

Wool carpet samples resembled the mineral turpentine standard closely. Many target compounds were detected in expected peak ratios. Pyrolysis product interference was low. An alkane ion profile was slightly more dominant than the aromatic profile in this sample.

3.5.7.4: Rubber carpet underlay

Spiked rubber carpet underlay samples were dominated by a limonene interferent. Limonene and other interferents co-eluted significantly with some target compounds. Alkane and aromatic profiles were similarly abundant.

3.5.7.5: Foam carpet underlay

An alkane profile was more abundant than the alkylstyrene profile in simulated foam carpet underlay samples. A Gaussian normal alkane series from octane to dodecane was present. Aromatic target compounds were also present.

3.5.7.6: Pine

Burned pine spiked with mineral turpentine sample chromatograms were dominated by pine products. Small amounts of other compounds were detectable, though no consistent ion profile was apparent.

3.5.7.7: Polyurethane

Burned polyurethane spiked with mineral turpentine yielded a simple chromatogram with only a limited number of compounds visible. Only one could be identified (benzene), the largest compound peak. No peaks of interest could be detected.

3.6: Operational sample analysis

Similarly to simulated (burned and spiked) samples, operational samples were placed into one of three categories: contains ILR, possibly contains ILR and does not contain ILR.

The results of operational sample analyses include chromatogram classification and target compound identifications. These appear in Appendix G: Operational Sample Results and Discussion. A tabulated summary of all operational sample results can be found in Table 6.

3.6.1: Simulated floor surface samples

3.6.1.1a: Treated timber (control sample)

The treated timber control sample chromatogram distribution was broad and non-Gaussian. Many interferent peaks were present, few of which could be positively identified. Most were terpene derivatives ranging from monoterpenes to sesquiterpenes. Some ignitable liquid target compounds were detected in the control sample and occurred in ratios expected of a petroleum product.

3.6.1.1b: Treated timber (debris sample)

The treated timber debris sample displayed petroleum target compounds in the TIC. An aromatic profile was slightly less abundant than the terpene profile. Higher boiling point range target compounds could not be detected. The aromatic content of the control was mirrored closely by the debris sample and peak ratios were consistent with a petroleum product.

3.6.1.2a: Synthetic carpet (control sample)

Synthetic carpet control samples produced few interferents. The majority of the chromatogram was taken up by an unresolvable mixture of cycloalkane compounds which eluted in the C_9 to C_{12} range. Two distinct terpene compounds were visible which eluted before the main unresolvable mass of carpet compounds. An aromatic profile was present, and some target compounds including m-/p-xylene, m-/p-ethyltoluene, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene were present. However, aromatic abundances were low and the presence of these compounds could not be established with certainty.

3.6.1.2b: Synthetic carpet (debris sample)

Synthetic carpet debris samples contained several peaks of interest but peak ratios expected of petroleum were not present. Some target compounds were absent due to pyrolysis product interference. C_4 alkylbenzenes and later eluting compounds were also not present. The most concentrated peak in the chromatogram represented styrene. Ultimately, the synthetic carpet control sample contained similar target compounds and EIPs from the sample chromatogram. The sample could not be related to a reference ignitable liquid.

3.6.1.3a: Linoleum (control sample)

The linoleum control samples contained several interferent peaks, the most concentrated of which were α- and β-pinene. Camphene and limonene were also present. Only one ignitable liquid-relevant compound could be identified: ethylbenzene.

3.6.1.3b: Linoleum (debris sample)

The linoleum debris sample produced an aromatic ion profile with C_3 alkylbenzenes dominating the mass chromatogram. The TIC was comparable to the reference unleaded petroleum standard. Interfering compounds from the linoleum substrate and pyrolysis products were not readily apparent, while most target compounds were easily identified.

3.6.1.4a: Wool carpet (control sample)

Two terpene compound peaks dominated the wool carpet control chromatogram. Some compounds in the control sample were identified as ignitable liquid compounds of interest.

3.6.1.4b: Wool carpet (debris sample)

The wool carpet debris sample chromatogram was consistent with the unleaded petroleum standard. Interfering compounds from the wool carpet substrate and pyrolysis products were unnoticeable due to the high abundance of ignitable liquid compounds.

3.6.1.5a: Ceramic tiles (control sample)

Interferent products in the ceramic tiles occupied a compound mass in the medium product range. Peaks were distributed in a Gaussian pattern. The majority of background compounds were alkanes or alkylbenzenes. Alkylbenzene peak ratios were similar to the petroleum standard.

3.6.1.5b: Ceramic tiles (debris sample)

A reduced sampling and a high split injection were required to resolve compound peaks which otherwise overloaded the column. Interferents from the ceramic tile control were not apparent in the debris sample chromatogram. The chromatogram was skewed slightly towards the lighter boiling point range and most petroleum target compounds up to naphthalene were detected. Peak group ratios were consistent with a petroleum reference standard.

3.6.1.6a: Wooden floating floor (control sample)

The two largest interferent peaks in the floating floor control chromatogram were terpenes. Several ignitable liquid target compounds could also be detected with peak patterns consistent with a petroleum sample.

3.6.1.6b: Wooden floating floor (debris sample)

Default sampling methods did not produce satisfactory chromatograms from the wooden floating floor debris sample. Like the ceramic tile debris, a reduced sampling and a high split injection were required to improve resolution. The chromatographic profile of the floating floor sample was very similar to that of the unleaded petrol standard. Most target compounds were detected and peak group ratios were characteristic of petroleum.

3.6.2: Bedsit structure debris samples

3.6.2.1: Cushion

An aromatic ion profile dominated the cushion debris sample chromatogram and was similar to the petroleum standard. Several target compounds could be identified. Petroleum target compounds were readily visible in the chromatogram. Only a small number of pyrolysis peaks were evident.

3.6.2.2: Chest of drawers

Debris from the chest of drawers produced a sample chromatogram which was characteristic of petroleum. All ignitable liquid target compounds could be detected in the debris sample, including C_2 naphthalenes. Peak pattern ratios were consistent with petroleum.

3.6.3: Main clubhouse structure living room debris samples

3.6.3.1: Armchair adjacent to entry door

The armchair debris sample consisted mainly of wooden fragments of the chair frame and strips of upholstery. The sample produced a Gaussian chromatogram with similarly abundant alkylbenzene and alkane ion profiles in the medium product range.

3.6.3.2: Floor materials behind couch

This sample consisted of floor materials and carpet debris. Small sections of carpet and clumps of ashen debris made up the sample. The sample produced a dominant alkane ion profile. Normal alkanes from octane to dodecane, distributed in a Gaussian arrangement, were identifiable. Some aromatic compounds were also detected, though were mostly obscured by the alkane and cycloalkane profile.

3.6.3.3: Couch in front of window

A high split ratio and a thirty second sampling time were employed to increase chromatographic resolution for this sample. This debris sample was similar to the entry door armchair sample in terms of composition, including wood chunks, upholstery and some polyurethane. Several n-alkane peaks in a Gaussian distribution dominated the chromatographic pattern. The alkane profile of the sample was equally abundant as the aromatic profile. Target compounds relating to petroleum and an MPD were detected.

3.7: Summary of instrumental detections

A summary of all instrumental detections performed during this study is tabulated in Table 5 and Table 6. Positive identifications indicate that the identification made based on instrument data was correct (green), whereas negative identifications (red) indicate no ignitable liquid could be satisfactorily identified. Only ILR classes were identified (as is realistic in casework). Where positive identifications could not be made with certainty, presumptive identifications were made (orange). While these samples did not produce results on-site as obvious as positively identified samples, they were not regarded as negative identifications and were still likely to yield positive result in the laboratory.

Some diesel fuel samples produced results which suggested an MPD was present, rather than an HPD (which is the correct classification for diesel). These results were still deemed positive, for reasons discussed in Appendix F: Simulated Sample Results and Discussion, Section G10: Substrates spiked with diesel fuel (discussion).

3.7.1: Simulated (burned and spiked) sample results summary

Table 5: Summary of simulated (burned and spiked) sample analysis results.

		Ignitable liquids detected						
		Unleaded petroleum	**70% weathered petroleum**	**90% weathered petroleum**	**97% weathered petroleum**	**Diesel fuel**	**Kerosene**	**Mineral turpentine**
Substrate	**Nylon carpet**	Petroleum	Petroleum	Petroleum	Petroleum	None	MPD	MPD
	Polypropylene carpet	Petroleum	Petroleum	Petroleum	Petroleum	MPD	MPD	MPD
	Wool carpet	Petroleum	Petroleum	Petroleum	Petroleum	HPD	MPD	MPD
	Rubber underlay	Petroleum	Petroleum	Petroleum	Petroleum	MPD	MPD	MPD
	Foam underlay	Petroleum	Petroleum	Petroleum	Petroleum	HPD	MPD	MPD
	Pine	None	None	None	Petroleum	HPD	None	None
	Polyurethane	Petroleum	Petroleum	Petroleum	Petroleum	HPD	MPD	None

3.7.2: Operational sample results summary

Table 6: Summary of operational sample analysis results.

	Substrate									
	Simulated floor surfaces						***Bedsit debris samples***		***Living room debris samples***		
	Treated timber	**Synthetic carpet**	**Linoleum**	**Wool carpet**	**Ceramic tiles**	**Wooden floating floor**	**Cushion**	**Chest of Drawers**	**Armchair by entry door**	**Flooring behind couch**	**Couch in front of window**
Residue detected	Petroleum	None	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	MPD	MPD	MPD
Accelerant deployed	None	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	Petroleum	Kerosene	Kerosene	Kerosene

3.8: Portable instrument performance

3.8.1: Battery lifespan

The first battery (evaluated during the Gilgandra burn exercise) was depleted after approximately two and a half hours of operation (approximately twenty-five runs). This included system start-up, PV, system blanks and a sample runs. Subsequent laboratory analysis of battery power yielded similar results. Running blank samples continuously depleted the power supply of one battery pack in approximately two hours and forty-five minutes (twenty-five runs). Evaluation of a second battery pack revealed that it could last two and a half hours and performed thirty-eight runs in this time.

3.8.2: Usability

When operating in portable mode, several issues were encountered which made operation of the TRIDION-9 cumbersome. The hardware/software interface which reported the battery charge level to the instrument's software was dysfunctional. Low battery power alerts would appear on the user interface even when the battery was not low on charge. As a result, the TRIDION-9 would often begin shutting down. This was problematic when the system was in the middle of a sample run, as the run would not complete and analytes would be trapped in the column until cleared out by the next system blank. Cancelling the shutdown procedure via a button on the user interface was useful in these instances. This did not occur when running off battery power in a laboratory setting.

The TRIDION-9 also lost time and date data randomly when operating off battery power, particularly after restarting. This may have been due to the removal and reinsertion of the battery pack in between restarts, which temporarily cut off power to the instrument. However, in several cases the battery pack was not removed at all, yet time and date data was still lost. This may have been a result of the battery pins moving and losing their connection to the battery pack momentarily as the instrument was moved. Nevertheless, the issue could be resolved by correcting the time and date settings manually. This issue also occurred several times when the instrument was running off mains power in the laboratory, without a battery pack installed.

4. Discussion

4.1: Method development

The SPME sampling procedure used in this study was based on ASTM Standard Practice E2154-01 (ASTM International, 2008). Several modifications were made in order to make the procedure compatible with the TRIDION-9. For example, E2154-01 recommends the use of rubber sleeve septa for sampling from metal tins, but these were not available during this study. Inserting the CUSTODION directly into the sample tin through a hole was found to be just as effective for sampling. Desorption times and temperatures specified by E2154-01 were not compatible with the TRIDION-9 as the standard was designed for use with laboratory-based instrumentation.

Heating samples is standard practice when using activated charcoal for passive headspace sampling (ASTM International, 2000; ASTM International, 2008). However, heating of samples was impractical for on-site sampling using the TRIDION-9. A heating apparatus would make sampling more complicated and increase analysis turnaround. All neat ignitable liquids used in this study could be identified when sampled at room temperature, thus heating the sample before analysis was deemed unnecessary. Samples adversely affected by competitive adsorption are exceptions to this rule, since heating reverses these effects. Ultimately, introducing a heating apparatus to obtain ideal results at the scene is excessive. Instead, laboratory analyses can be relied upon to heat samples to obtain ideal results when scene results are subpar.

A five to fifteen minute sampling time is standard practice for headspace SPME extractions (ASTM International, 2008). In reality, an ideal extraction period is difficult to calculate for unknown samples. The amount of analyte adsorbed onto the SPME fibre depends on the thickness of the stationary phase coating and the distribution constant for the analyte (Supelco, 1998). The distribution constant generally increases with higher molecular weight and boiling point compounds, therefore longer extraction times become necessary. The results of this study confirmed that long SPME sampling times (three minutes or longer) generally provided better results, but were excessive for on-site applications, particularly when speed of analysis is an important criterion.

Only a small range of fibre types have been used in the literature for the analysis of ignitable liquids. The most common is the 100 µm PDMS fibre. This type of fibre has been used for the recovery of gasoline from skin (Almirall, et al., 2000), accelerants from fire debris (Furton, et al., 1995; Kaneko & Nakada, 1995; Furton, et al., 1996; Steffen, et al., 1996; Ren & Bertsch, 1999), and accelerants in liquid residue (Almirall, et al., 1996). However, PDMS fibres are less appropriate for the detection of highly volatile ignitable liquid compounds compared to sorbents such as Carboxen (Keneko, 1999). The 65 µm general-purpose PDMS/DVB fibre used in this study proved appropriate for FDA applications. It was able to capture many compounds of interest over a broad chromatographic range; compounds as light as heptane (C_7) and as heavy as octadecane (C_{18}) could be detected. Nevertheless, examination of other fibre types, particularly multiple sorbent fibres, is warranted. Addition of sorbent layers such as Carboxen would aid in the analysis of light compounds, increasing the utility of the TRIDION-9 for light ILR analysis.

4.2: Neat ignitable liquid analysis

4.2.1: Unleaded petroleum

Petroleum identification relies significantly on the presence of diagnostic peak patterns. These diagnostic peak patterns are well-known among fire debris analysts and a specific nomenclature describing the shape of these peak patterns has evolved (i.e., the three musketeers, the castle, etc.). These patterns appear differently on the TRIDION-9 compared to laboratory instrumentation. The TRIDION-9's shorter column means that mixtures are necessarily separated less effectively, resulting in co-elution of similar molecular weight compounds. Traditional diagnostic peak patterns were re-examined and a new set of patterns unique to the ILR method on the TRIDION-9 was identified (Appendix H: Diagnostic Peak Patterns in Petroleum).

Some target compounds based on compounds listed in ASTM Standard Method E1618-10 were less useful than anticipated. 4,7-Dimethylindane, in particular, was difficult to detect in simulated samples. The compound co-eluted with naphthalene and was poorly resolved even in the standard. As it was not detectable in all samples, it could not be relied upon as a target compound. Other target compounds peaks were resolvable but not ideal for identification purposes. Indane, for example, co-eluted significantly with C_4 alkylbenzenes. Other target compounds were difficult to detect due to low concentrations. 2- and 1-

methylnaphthalene were the last compounds which could reliably be identified in the petroleum standard, but were not always present. Dimethylnaphthalenes often occurred in such low concentrations that ion fragments were visible in only one or two mass analyser scans. Ultimately, C_2, C_3 and C_4 alkylbenzenes proved to be the most reliable compounds by which to identify the presence of petroleum. Peak group ratios across these compounds were consistent between the standards and samples.

4.2.2: Diesel fuel

Diesel fuel was the heaviest ignitable liquid analysed and was classified as an HPD as it contained a series of at least five n-alkanes and occupied the C_9 to C_{20} carbon range (ASTM E1618-10 criteria). Target cycloalkanes could also be detected. 1,2,3,5-Tetramethylbenzene was visible as a small compound peak, but would quickly be drowned out by pyrolysis products in real samples. Trans-decalin could not be detected. Methylnaphthalene and dimethylnaphthalene target compounds could be found, but were poorly resolved against a high alkane/cycloalkane background. 2,3,5-Trimethylnaphthalene was not visible. Pristane and phytane, while traditionally very useful in the identification of heavy distillate residues, could not be detected. Pristane may have been present as a shoulder on the more obvious heptadecane peak, but this could not be confirmed as compounds of this weight were generally beyond the adsorption range of the SPME fibre. The identification of diesel fuel (and other distillates) relied on the presence of an unbroken alkane chain in a Gaussian distribution.

4.2.3: Kerosene

Kerosene is typically regarded as an HPD (ASTM International, 2010). However, results obtained using the TRIDION-9 placed it in between an MPD and HPD. Tetradecane is typically used as the demarcation point between an MPD and HPD (ASTM International, 2010). In the kerosene sample analysed, no alkanes eluted after pentadecane. A mixture of MPD and HPD target compounds as listed in E1618-10 was used for classification purposes.

A Gaussian distribution of alkanes was the most reliable feature for kerosene detection. Cycloalkanes were not abundant enough to warrant identification. As in diesel fuel, trimethylnaphthalene could not be visualised, though trans-decalin was readily apparent. The aromatic profile of kerosene was similar to that of petroleum but was not significant.

4.2.4: Mineral turpentine

Pure turpentine cannot easily be purchased in Australia, thus it is not a common accelerant. Mineral turpentine, a turpentine substitute (UN 1300), is more readily available. Turpentine substitutes are not made to a standard and contain a wider variety of ingredients than pure turpentine. A large variety of turpentine substitutes (such as mineral turpentine, white spirit, etc.) should be included in any FDA library.

Mineral turpentine contained comparable levels of aromatic and alkane compounds. Therefore, its detection involved the identification of both petroleum and MPD compounds. Mineral turpentine could still be classified as an MPD; however, real turpentine would more appropriately be classed as a miscellaneous-class ignitable liquid. ASTM E1618-10 aromatic and alkane target compounds were relevant to mineral turpentine and all could be identified. Cycloalkane compounds were less useful for identification as they were disguised by the alkane profile. Trans-decalin was useful as it allowed differentiation between pure petroleum products, which do not normally contain trans-decalin, and distillates, which do.

4.3: Blank substrate analysis

Substrates examined in this study represented realistic exhibits. Carpet and carpet padding, for example, make up approximately 52% of exhibits submitted to laboratories for FDA (Bertsch & Zhang, 1990). This is because liquid accelerants are often poured onto the floor of a structure in an attempt to spread the fire over a larger area (Stauffer, et al., 2008). The nylon, polypropylene and wool carpets used in this study were monofibrous (composed of a single fibre type). They were made up of carpet pile glued to a backing material. Blank carpet chromatograms were relatively bare apart from an unresolvable cycloalkane mass. This mass most likely represented the ion profile of the glue used in the carpet as it appeared in all carpet blanks.

The pine substrate used in this study was untreated. Wood such as pine is a cellulosic natural polymer (Stauffer, et al., 2008) containing a high concentration of volatile hydrocarbons. Terpenes are common in wooden substrates, both as a natural product of the wood and as pyrolysis products (Stone & Lamonte, 1984). α-Pinene was the most abundant compound in the pine samples examined and has previously been identified as the most concentrated compound in softwood pine (Trimpe, 1991). The high concentration of these compounds saturated the SPME fibre and allowed few other compounds to adsorb (preferential adsorption). This made all identifications involving pine substrates difficult. Rubber underlay, foam underlay and polyurethane produced minimalist chromatograms with few or no peaks of interest.

4.4: Burned substrate analysis

The release of matrix compounds, triggered by fire, produced many volatile compounds in burned substrate chromatograms. Styrene dominated burned carpet chromatograms and is known to be a common carpet pyrolysis product (Smith, 1982; Bertsch, 1994). Other aromatic hydrocarbons were present in small amounts in burned carpet, such as ethylbenzene and propylbenzene in burned wool. Varied concentrations of aromatic hydrocarbons ranging from benzene to naphthalene have previously been detected in burned carpet or carpet underlay samples (DeHaan & Bonarius, 1988; Bertsch, 1994; Howard & McKague, 1984).

Rubber carpet underlay contained high concentrations of toluene, m-/p-xylene and limonene. The underlay was attached to a paper-based backing which was the most likely origin of the terpene content in the sample. The m-/p-xylene peak interfered with C_2 alkylbenzene identification in simulated samples. Foam underlay produced a Gaussian pattern. Apart from styrene, pyrolysis products in foam appeared to be ketones. Pine produced the same four terpene compounds, in the same relative intensities, as in the unburned sample. The high concentration of these compounds overwhelmed the headspace of the sample, making detection of other pyrolysis products difficult.

Evaluation of burned substrates was problematic due to the fact that no substrate could be burned the same way twice. Amount of burning was a difficult parameter to quantify and control. While each substrate sample was burned in a similar way, chromatographic similarity was not always guaranteed. For example, burned nylon typically produced a dominant styrene peak (Figure 43). Some nylon carpet samples produced different results. While the compounds detected were the same, their relative intensities were not. Several swatches of burned nylon carpet produced a dominant benzaldehyde peak instead of the expected styrene (Figure 32). Similar effects were observed when polyurethane was burned. Some polyurethane chromatograms produced few significant peaks, while others produced multiple pyrolysis products including styrene.

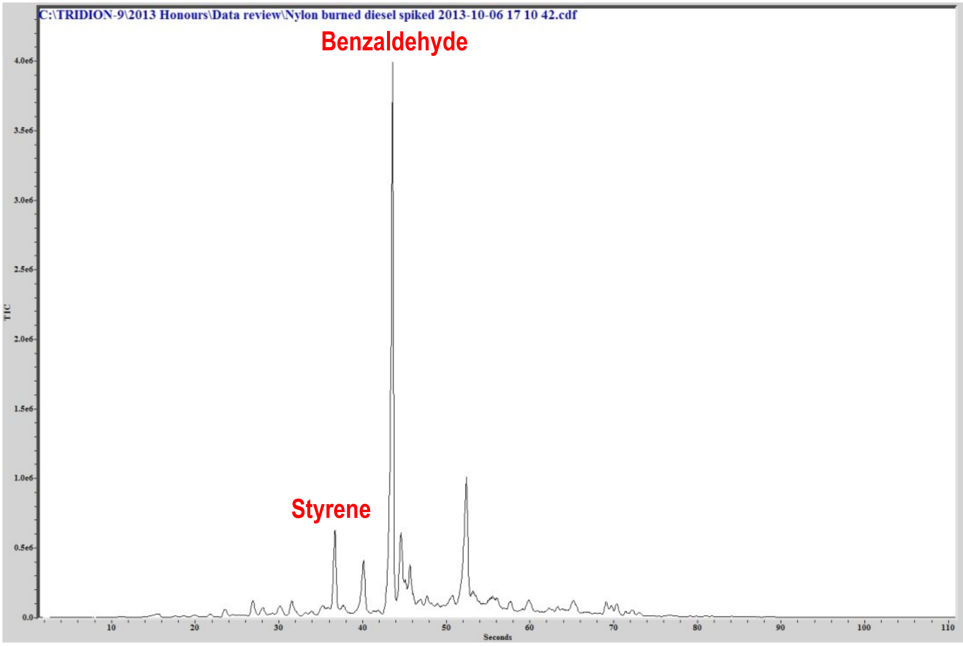


Figure 32: Burned nylon carpet substrate chromatogram with a dominant benzaldehyde peak.

4.5: Simulated (burned and spiked) and operational sample analysis

On-site data analysis as detailed as the results obtained in this study has not previously been possible for FDA applications. CHROMION allowed for all the basic functions of popular data analysis software to be brought to the scene and used on real-time data. While other accelerant detection techniques lack specificity (Thatcher & Kelleher, 2000), the TRIDION-9 is well-suited to on-site FDA applications. Simulated samples yielded a high number of positive identifications. Ignitable liquids could be identified on most substrates except for pine samples, which were overloaded with pine substrate compounds. Inconclusive results accurately predicted ignitable liquid content. A full discussion relating to simulated samples is presented in Appendix F: Simulated Sample Results and Discussion. Operational results reflected favourably upon the TRIDION-9's on-site performance and operational utility. Two samples could not be positively identified, though this was due to sampling issues. Most other samples yielded high concentrations of ILR. Samples retrieved from the burned structure were good analogues for casework fire debris samples and produced positive results. A full discussion of operational results appears in Appendix G: Operational Sample Results and Discussion.

4.6: Issues with simulated and operational sample analysis

4.6.1.1: Small ignitable liquid volumes

The small ignitable liquid volume chosen for spiking simulated samples (0.1 μL) was based on the minimum requirement for detection as specified by ASTM Standard Practices E2154-01 (ASTM International, 2008) and E1412-00 (ASTM International, 2000). Standard Practice E2154-01 states that "[SPME is] capable of isolating small quantities of ignitable liquid residues from a sample, that is, a 0.1 μL spike of gasoline on a cellulose wipe inside of a 1-gal can is detectable" (ASTM International, 2008).

This gave birth to the methodology used in this study, whereby a 0.1 μL volume of ignitable liquid was to test both the sensitivity of the TRIDION-9 and the sampling power of the SPME fibre. According to Standard Practice E2154-01, this 0.1 μL value was the minimum limit of detection when sampling from clean, known samples. Detection of ignitable liquids at this volume proved that SPME was capable of sampling trace volumes and the TRIDION-9 was able to detect them. However, operational fire debris samples are rarely clean and this makes residue identification more difficult. Using only 0.1 μL of liquid for simulated samples deliberately challenged the analytical capabilities of the TRIDION-9 as well as the data analysis capabilities of CHROMION. Positive identification of residues in such small volumes in burned debris was an impressive outcome given the speed of analysis and the portability of the TRIDION-9.

4.6.1.2: Ignitable liquid residue overloading

At first, substrates were burned and placed into sample tins to cool before an ignitable liquid was added. This process sometimes took up to twenty minutes, particularly with substrates that burned readily and reached high temperatures. During this time, the substrates were left in a fume hood to cool. Substrates which cooled this way released a large amount of pyrolysis products to the atmosphere. When an ignitable liquid was added and the tin was sealed, pyrolysis products released by the substrate were already gone. As a result, even the small amounts of accelerant used in samples overwhelmed the headspace. Simulated samples prepared in this way yielded high concentrations of ILR and little interference from the substrate matrix. This effect was noticed in some simulated samples spiked with petroleum. Pine was the only exception to this rule, as the background compounds in pine were normally dominant over ILR.

4.6.1.3: Pyrolysis product overloading

Burned substrates were sealed into sample tins immediately after extinguishment. Sealing substrates into sample tins while they were warm kept them hot even after they were extinguished and they continued to smoulder. Pyrolysis therefore continued and loaded the headspace with pyrolysis products. It has been suggested that this procedure may produce more pyrolysis products than are realistic for a typical fire debris sample (Stauffer, et al., 2008).

Substrates which burned very rapidly were extinguished by starvation of oxygen to prevent all of the substrate matter from being consumed. Extinguishment of substrates by suffocation has been shown to release up to ten times the amount of volatile organic compounds as is released when water is used to extinguish the substrate instead (Stauffer, 2001). This may have contributed to high pyrolysis product concentrations in substrates which burned readily and required manual extinguishment.

4.6.1.4: Competitive adsorption

It was noted that if sampling took place very soon after a sample was prepared (within one or two hours), ILR yield was much higher than if the sample was taken later. After the ignitable liquid was deployed into the sample tin, most of its vapours occupied the headspace of the sample. If sampling was conducted at this time, ILR adsorbed more quickly onto the SPME fibre as the headspace had not yet reached equilibrium. This was the case in some simulated samples spiked with petroleum. As a result, ILR compounds dominated chromatograms and matrix compounds were insignificant. On the other hand, when samples were left for a period of several days, the liquid residues had time to adsorb to the surface of the burned substrate, particularly if it was significantly charred. Identifying residues in 90% weathered petroleum samples, which were sampled several days after creation, proved difficult for this reason.

This mechanism, competitive adsorption, is recognised as a problem when analysing fire debris (Kuk & Spagnola, 2008). When sampling a neat liquid, only two phases exist in the equilibrium process: the SPME fibre and the liquid. However, when sampling debris, a new phase is introduced – the substrate. Substrate materials can adsorb ILR before headspace sampling has occurred. The residues and the substrate matrix then form a combined headspace, containing both substrate and ignitable liquid compounds in equilibrium. However, once adsorbed into the sample, heavier target compounds are likely to remain locked there unless forcefully desorbed by heating. Once this has occurred, the relatively high strength of this interaction will result in a very small headspace pressure above the substrate for a regular SPME fibre to equilibrate with. This results in an incomplete collection of heavier target compounds and a skewing of sample chromatograms towards the lighter end.

This effect was noticed when simulated samples which had been left for several days were analysed and became more pronounced over time. The chromatogram in Figure 33 focuses on the C_4 alkylbenzene range of a burned nylon carpet sample spiked with 97% weathered petroleum. This range of analytes is usually quite pronounced, as was the case when the sample was taken immediately after the petroleum was added (red chromatogram). After three days, however, many of the expected compound peaks were absent or significantly diminished (green chromatogram), likely due to competitive adsorption. Competitive adsorption contributed to difficulties detecting 70% and 90% weathered petroleum in simulated samples. Heating samples prior to sampling may have reversed the effects of competitive adsorption, but is unnecessary if an indication of ILR is still obtainable.

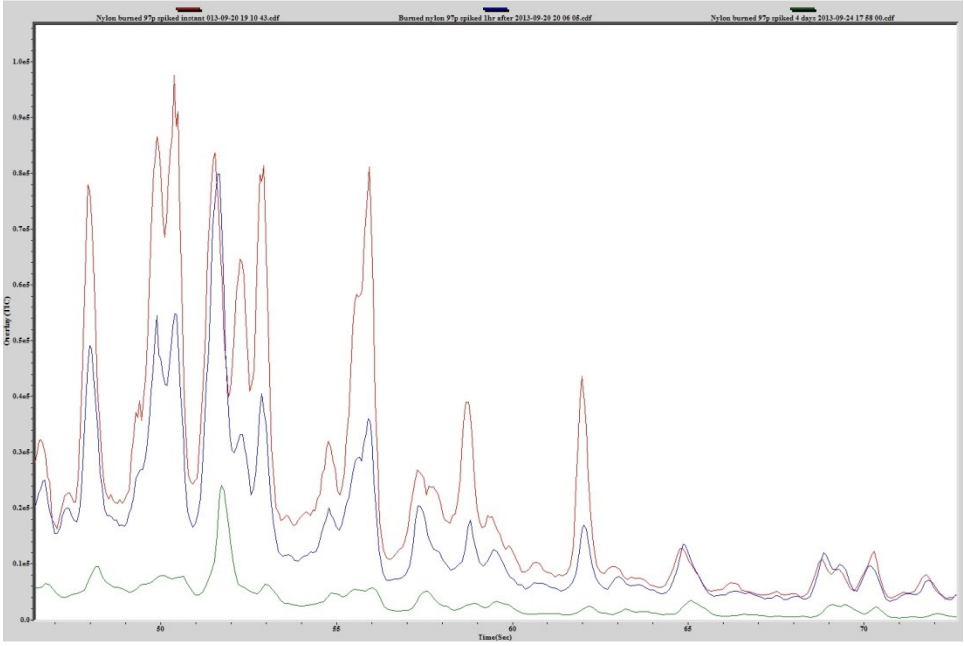


Figure 33: An overlay of three chromatograms representing three samples of the same debris, taken at different times. The red chromatogram represents a sample taken instantly after the ignitable liquid was added (high concentration of ILR compounds). Blue represents sampling after one hour. Green is a sample taken 3 days later (low concentration of ILR compounds).

4.6.1.5: Preferential adsorption

It was consistently difficult to recover the heaviest ILR target compounds from simulated samples. For example, tetradecane and pentadecane were rarely evident in simulated kerosene samples, yet they were obvious in the kerosene standard. In unleaded petroleum samples, methylnaphthalene detection was inconsistent. Preferential SPME fibre adsorption may have been responsible. The SPME fibre has a very limited number of active adsorbent sites (Stauffer & Lentini, 2003). Many simulated samples contained high levels of pyrolysis products. Styrene, for example, was the most prominent pyrolysis product peak in burned carpet. The high concentration of this compound correlated to a high concentration in the sample headspace (pyrolysis product overloading). As a result, styrene and other pyrolysis products were adsorbed preferentially by the SPME fibre as there was an abundance of them in the sampling space. This left little capacity for the heavier target compounds such as pentadecane or methylnaphthalene to attach to the fibre. While these target compounds may have been present in the sample's headspace, they may not have been accurately represented by the analytes desorbed in the injector as the SPME fibre collected proportionally more low-weight compounds. Variable sampling efficiency is a known disadvantage of SPME (Yoshida, et al., 2008), though it had little effect on residue classification during this study. Use of additional fibre adsorbents may circumvent preferential adsorption.

4.7: Instrument usage

4.7.1: General use

When in a laboratory setting, the TRIDION-9 was left on and only switched off when maintenance was required. This meant that the instrument was ready for sampling at all times. When the instrument was turned off and then subsequently back on at a later stage, it required a short time to pump down. This allowed the baseline to stabilise. In some cases, restarting the instrument also necessitated recalibration of mass spectrometer settings (see Section 4.7.5: Maintenance and troubleshooting), which was time consuming. Due to the ruggedness of the instrument and the ease with which it could be moved around, keeping it online as long as possible was the best way to ensure consistency and result reproducibility. Moreover, this maximised the time spent analysing samples on-site rather than running system blanks and PVs as is required when the instrument is booted.

The instrument's user interface was easy to use and navigate. Menu items on the LCD interface were all that were required to run analyses. The instrument was generally controlled using the touch screen stylus, as using the front control panel buttons proved tedious. Entering data using the on-screen keyboard with the stylus or using scroll bar interface items was frustrating at times when the stylus needed recalibration. However, the recalibration process was simple to do following on-screen instructions. Stylus input was otherwise reliable and was generally superior to using fingers to navigate the user interface. Controlling the instrument from a computer over a network using TightVNC software (GlavSoft, Tomsk, Russian Federation) also worked well, though this ability seemed unnecessary since it was easier to interact with the instrument directly.

Instrument controls such as the power and reboot buttons were used on rare occasions when the instrument stopped responding to user input. Data export methods including Universal Serial Bus (USB) and wireless Bluetooth transfer were not used during this study, though both were functional. A feature of the TRIDION-9 which was not mentioned in the operating manual was the circular side ports. These ports, when opened, allowed for faster instrument cooling and a lower internal operating temperature, potentially allowing for lower column start temperatures.

4.7.2: Sampling

When co-operating with other members of a fire investigation team and assisting with their enquiries, sampling procedures which do not require prolonged periods of concentration are beneficial and reduce the risk of operator error. Unlike in the laboratory, the TRIDION-9 operator in the field must focus on exhibit collection, sampling and analysis with multiple samples. This is a lot to consider at any one time, especially when moving in and out of a hazardous fire scene.

SPME has long been established as an effective sampling method for FDA (Snow & Slack, 2002; Almirall & Furton, 2002). SPME proved to be even more useful as a sampling technique in the field. Its portability, ease of use and the absence of solvents make it an ideal sampling technique, specifically designed for fast GC applications such as with the TRIDION-9 (Muller, 1999; Hook, et al., 2002). SPME fibres, though recommended by the manufacturer for replacement after approximately fifty analyses (Supelco, 2004), proved usable after approximately two thousand injections, with negligible loss in adsorption effectiveness. Analysis of volatile molecules which are adsorbed and desorbed easily from the fibre matrix (as is typical in FDA) does not damage the fibre adsorbent easily. Immersion of the fibre into solutions, on the other hand, will significantly decrease the life of the fibre (Doong, et al., 2000). Fibre blanks run after each sample typically showed no signs of ghost peaks or other contamination artefacts. Highly concentrated samples (especially single-compound samples) did overload the SPME fibre occasionally, leaving analytes on the fibre after the first injection. One or two additional injections were sufficient to clean the fibre in these cases.

Steel paint tins proved to be effective for in-field sampling. Piercing the lid of the containers and balancing the SPME fibre in the hole for the duration of the sampling period allowed for the tin to be placed down and other tasks to be attended to. The size of the tins (1 litre) was also appropriate for the debris being collected, though some samples of wood had to be broken into several pieces. Care was required when inserting the SPME fibre into the sample tin to ensure that the fibre was not damaged by contact with the debris. The only extra equipment necessary for this type of sampling was a hammer and nail to pierce the sample tin lids. This was more efficient than having to manipulate tape and scissors to seal nylon bags. The hard, physical barrier of the tin prevents contamination and sample loss, which is important in a fire scene environment (Carlson, et al., 1995). Concerns over the potential leakage of paint tins over longer periods of time (Mann, 2000) are not as relevant when analyses can be performed immediately.

4.7.3: Portability and field deployment

The TRIDION-9 performed similarly in the field to how it performed in the laboratory. Difficulties encountered in previous studies such as poor performance on battery power (Brust, 2009), damage to the instrument during transportation and long temperature stabilisation times (Campbell et al., 2012) were absent during this study. However, some minor software issues were apparent (see Section 3.8.2: Usability). The TRIDION-9 was picked up and moved around while performing sample runs. No adverse effects on the analysis were observed.

The TRIDION-9 was easy to pack, unpack and move around. The instrument's Pelican carry case allowed for the instrument, laptop and accessories to be moved with ease as a single unit. The Pelican case fits easily into the boot of most cars, though it can be heavy for a single person to carry, especially if it is loaded with additional accessories. The wheels on the case make it easy to move the instrument around on flat surfaces. The instrument survived several small impacts while housed in its Pelican case.

During the research burn exercise, the TRIDION-9 was deployed in the boot of a car (Figure 34). This proved to be an efficient mobile laboratory setup, allowing for samples to be brought to the instrument from the fire scene, while keeping the instrument and samples out of contaminated areas. All accessories and sampling equipment could be kept in this same space. The boot could easily be closed to protect the instrument or move the vehicle. Connection to a laptop was also possible in this configuration, and allowed for detailed data analysis to be performed when the LCD screen and limited data analysis capabilities of the TRIDION-9 were not appropriate. Packing up the instrument was also a simple process, though it took several minutes for the instrument to cool down enough for it to be safely packed into its Pelican case.

Figure 34: The mobile laboratory setup employed during the Gilgandra research burn.

Field battery tests revealed that the TRIDION-9 was able to analyse samples for thirty minutes longer than the manufacturer's two hour runtime estimate. This difference may have simply been the result of a lower frequency of injections. The length of time the battery can sustain the instrument is an inaccurate metric for the evaluation of battery lifespan. A more useful metric is the total number of runs the battery can perform before depletion. Laboratory testing revealed that the TRIDION-9 was able to perform an average of thirty-one runs across two battery packs. The first battery pack performed twenty-five runs (2 hours, 45 minutes), while the second battery pack allowed for thirty eight runs to be performed (2 hours, 30 minutes hours). Differences in injection frequency account for the thirteen-run difference between battery packs. Previous evaluations of the instrument had revealed that a similar number of runs were possible on a single battery charge (Campbell, 2012).

Battery power lasted slightly longer during laboratory analysis than during field evaluation. This was because battery power in the laboratory was used to perform system blank runs only, whereas in the field it was used to perform data analysis as well, which consumed more power. Field battery life is a more realistic representation of the instrument's operational ability. Battery life of two to three hours is adequate for a number of sample analyses on-site, but insufficient if the instrument is expected to analyse samples for several hours at a time, such as at a very large fire scene. The number of runs the instrument will be able to perform in the field is dependent on the dirtiness of samples and the number of compounds detected in each. It is advisable that several fully-charged backup batteries be kept with the instrument, allowing for many hours of use. Alternatively, the TRIDION-9 can utilise an inverter to run off a car battery. This has the added benefit of allowing battery packs to be changed without shutting down the instrument. The TRIDION-9 can be configured to operate using third-party batteries, or generators, which can supply power for longer periods of time. It is up to the instrument operator to decide how to power the instrument, depending on the facilities available at the scene.

The manufacturer recommended that up to 150 runs were possible on the TRIDION-9 using a single helium canister (Torion Technologies, Inc., 2012). Previous studies indicated only 20-30 analyses could be run on each helium canister (Campbell, 2012). Such a low sample throughput is normally indicative of a gas leak, though no gas leaks were found during the aforementioned study. Although a full helium canister was not evaluated in this study, a single canister outlasted two fully-charged battery packs with approximately 50% of the canister remaining. This is congruent with the manufacturer's 150-run canister lifespan guideline. A single canister can provide sufficient carrier gas supply for all but the longest field deployments.

4.7.4: Ease of use

While at the research exercise in Gilgandra, several members of Fire and Rescue New South Wales were consulted about the instrument's possible future uses. No FRNSW member consulted had a background in chemical FDA. Use and manipulation of instrument controls was easily picked up. However, instrument output in the form of chromatograms and mass spectra were confusing to FRNSW staff and could not be utilised by them to reach a conclusion as to the presence ILR in a sample. On the other hand, several chemists from the University of Western Sydney, who were also attending the exercise, were familiar with GC-MS instrumentation. Their ability to interpret sample data from the TRIDION-9 was better as they understood the mechanisms of chromatography and mass spectrometry. However, they still could not make recommendations as to the presence or absence of ILR in samples as they were not sure of what to look for in the sample data. Software which is specifically written to aid in the detection of ILR may be useful in this context. However, the responsibility of residue identification will ultimately fall upon the expertise of the instrument operator.

While technical officers and laboratory technicians may be able to use the instrument and understand data output, their ability to interpret the data to determine whether or not ILR is present will be limited by their experience in forensic chemistry. It has been realised previously that such novel instrumentation requires a good knowledge of chemistry as well as chromatography to be used optimally (Stauffer et al., 2007). Similar conclusions have been reached in the evaluation of other portable instruments for FDA purposes (Casamento, 2005). In order to use the TRIDION-9 for this application, experience with the use of GC-MS for fire debris sample analysis is essential. It is recommended that the TRIDION-9 be deployed with a forensic chemist who has been specially trained in the operation of the instrument. Alternatively, the instrument can be used by an experienced TRIDION-9 operator who has been supplementarily trained in FDA.

4.7.5: Maintenance and troubleshooting

General maintenance operations are simple to perform and described clearly enough in the instrument operating manual for most operators to follow. Performance validation using the CALION PV mixture is simple and effective and provides confidence in the instrument. Disassembly of the instrument, while unlikely to be required in the field, can be accomplished by anyone with a basic understanding of how the instrument works.

However, disassembly of internal componentry such as the mass analyser or the electron multiplier detector should only be performed in a clean laboratory environment as the entrance of dirt into the system will render analyses inaccurate. Such cleaning procedures should only be performed by personnel familiar with the instrument and specifically trained to undertake the maintenance. Reassembly and proper alignment of the ion trap, for instance, is a precise process and can have varying degrees of success. The manufacturer discourages complete disassembly of the trap by untrained operators for this reason. Instrument output must be examined at the end of each maintenance action to ensure that the instrument is performing optimally. In this study, for example, the ion trap sometimes required reassembly and realignment several times after a clean in order to attain acceptable mass resolution. The ion trap required cleaning approximately every 500-600 analyses.

Opening the vacuum chamber in which the ion trap resides introduced contaminants into the system which had to be cleared out before routine analysis could continue. These contaminants appeared as chromatographic background noise, raising the baseline of chromatograms significantly. Turning the instrument back on and allowing it to pump for at least one or two hours appeared to be the most effective way to clear the column and vacuum chamber. At any point where the internal components of the system were changed or replaced, mass spectrometer settings usually required adjustment. Some general rules applied to this process. For example, cleaning the ion trap generally allowed a lowering of detector voltage, and cleaning the Einzel lens in the filament assembly allowed the filament current to be lowered. These settings should only be adjusted by a trained technician as incorrect values can damage internal components.

General troubleshooting of the instrument requires some experience. Advice is given by the automated tune wizard on the instrument to correct PV failures and a SOP can be followed to accomplish the same task. However, the tune wizard was found to sometimes give ambiguous or unhelpful advice. It was noted that, in the previous study of this instrument (Campbell et al., 2012), the electron multiplier detector was damaged by following tune wizard advice and raising the detector's voltage past recommended levels.

Unfortunately, the tune wizard makes recommendations in a limited binary fashion, whereby a failed PV test will trigger a certain type of advice. For example, a failed space charge test will result in advice to raise the detector's voltage. In reality, a low detector voltage may not necessarily be the cause of the problem. Space charge can be caused by too many ions in the trap or trap contamination, both of which will be unaffected by a change in detector voltage. The instrument manufacturer is currently working on improvements to the tune wizard that makes its advice less ambiguous (Sadowski, *pers. comm.*, 30 October 2013). Nevertheless, only an operator with experience using the instrument should be allowed to tune it when it begins to fail PV consistently. Basic sampling and system adjustments can be made by less experienced operators, such as increasing detector voltage to increase sensitivity, though these still require a basic knowledge of chromatographic processes and system hardware.

The instrument's firmware was updated once during the research period. The manufacturer provided a firmware update on an SD card, a new version of CHROMION, and an updated PV method. The firmware update process was simple; it involved the insertion of the new SD card into the instrument and turning the instrument on, at which point the instrument updated its firmware automatically. Updating CHROMION followed a similar process to the installation of any other software program in Windows. Experience in Windows file management systems is recommended as transferring results, methods and procedures to and from the instrument requires interaction with such systems. Experience with Windows operating systems (particularly Windows CE) is recommended in case software bugs or failures require changes to the operating system on the TRIDION-9.

4.7.6: Standard compliance

Instruments used for laboratory analysis of fire debris must comply with ASTM Standard Practice E1618-10 and AS 5239-2011 (though the latter mirrors the ASTM standard closely). These specifications include hardware requirements of the GC column and MS detector, as well as data handling and sampling requirements. The TRIDION-9 meets almost all apparatus requirements set out in Standard Practice E1618-10. Unfortunately, the TRIDION-9 falls short of full E1618-10 compliance in two main areas. The standard specifies that the mass spectrometer used for FDA must be able to detect in a mass range of 40 – 500 amu. The advertised detection range for the TRIDION-9 is 45 – 500 amu, though 43 amu appeared to be the actual lower limit during this study. Better than unit mass resolution is possible up to mass 300. Operationally, a difference in capability of two or three atomic mass units is irrelevant.

E1618-10 also specifies that the instrument must be capable of separating and detecting each compound in a hydrocarbon-based test mixture. The TRIDION-9 uses a proprietary test mixture in the form of the CALION PV mixture. As this mixture is used to perform instrument calibrations, a secondary mixture made up of ignitable liquid components should not be necessary. Over the course of this study, reference liquids were often used as pseudo test mixtures. Depending on the temperature program employed, some petroleum test mixture compounds may not separate completely. A definition for adequate separation is not provided by the E1618-10 standard, but it is assumed that the less powerful separation offered by the TRIDION-9 may not be standard compliant.

Improvements to TRIDION-9 hardware may allow it to become a validated technique for FDA in the future. TRIDION-9 results may potentially be deemed of sufficient quality to be used for court purposes as the differences between the TRIDION-9's capabilities and standard requirements are minor. Results shown in this study reflect an analytical ability of the TRIDION-9 which is very comparable to that of laboratory instrumentation. This type of utility in such a small instrument is rare. Compliance with laboratory-focused standards, while advantageous, is not necessary for on-site presumptive testing applications.

4.7.7: Operational utility

No amount of analytical power can substitute a properly collected sample. Thus, a detection method should be used to locate samples containing ILR which can then be analysed using the TRIDION-9. The evaluation of the instrument in Gilgandra showed that it can be deployed alongside ADCs in the field. The canine can locate a sampling site and the handler can pass this information on to the TRIDION-9 operator, who can then take the debris sample and analyse it. This workflow disrupts other fire investigation staff minimally and is easy to implement. Moreover, the TRIDION-9 operator can provide timely feedback to the canine handler regarding his canine's performance.

The TRIDION-9 cannot be used to conclusively identify ILR. Confirmatory testing in the form of laboratory analysis is still a legal requirement for court evidence purposes. Nevertheless, each sample analysed by the TRIDION-9 can be operationally significant. The TRIDION-9 can provide accurate information to the officer-in-charge of the fire scene regarding the presence of an ignitable liquid (and possible accelerant) at the scene. Investigating officers can then use this intelligence in the planning of their investigation. However, it must be made clear to personnel unfamiliar with the instrument that TRIDION-9 results are presumptive. Negative samples are also useful as they can be used to better target sampling areas.

Current on-site analysis methods cannot provide the same depth of sample data offered by the TRIDION-9. As a result, samples deemed to contain ILR by the TRIDION-9 are more likely to produce positive results in the laboratory. To emulate a realistic operational scenario, a small selection of simulated samples, which produced positive results on the TRIDION-9, was submitted to the Australian Federal Police for confirmatory testing. Laboratory results confirmed the presence of ILR in all samples. While only three samples were submitted for confirmation, this pilot exercise suggested that laboratory analyses corroborate TRIDION-9 detections reliably.

TRIDION-9 false negative result rates are low. ADCs are known to alert positively to materials which do not contain traces of ignitable liquids, or negatively to those that do (Kurz, et al., 1994). On the other hand, mechanical detection methods such as electronic sniffers can be unselective (Byron, 1982) or insensitive (Hilliard & Thomas, 1976). In comparison, the TRIDION-9 is capable of detecting volumes of ILR which are at current sampling limits (ASTM International, 2008), making false negative detections unlikely. False positive detections were not examined during this study but, given the nature of GC-MS analysis, are unlikely to occur unless as a result of operator error. This can be combated by ensuring the operator is adequately trained in FDA. If the TRIDION-9 is to be operated by several people or multiple instruments are deployed, a SOP should be drafted to ensure consistency in the use of the TRIDION-9.

While the TRIDION-9 may be seen by laboratories as a potential threat, the relationship between the two is symbiotic. Laboratory backlogs are a significant issue, especially for laboratories which receive exhibits requiring DNA extraction (Pinchin, 2007). Many forensic laboratories are overworked and understaffed due to the large number of samples they receive (Lovrich, et al., 2003). A reduction in this number allows laboratory staff and instrument resources to be used more efficiently. Depending on the effectiveness of the detection method used, fire scene investigations can produce a large number of debris samples which require confirmatory testing. The early elimination of negative samples and the selection of good quality positive samples at the scene allow this number to be reduced. As a result, the positive result rate achieved by the laboratory may increase.

4.8: Instrument limitations

4.8.1: Mass spectral library searches

The establishment of custom compound libraries is particularly important when using the TRIDION-9 and has been recommended previously (Brust, 2009). CHROMION allows for compounds to be added to the instrument's library easily. However, adding compounds to the library can be tedious. Utilising third party mass spectral libraries is therefore tempting. CHROMION allows sample mass spectra to be compared against third party mass spectral libraries such as the NIST/EPA/NIH mass spectral library, provided the operator of the instrument has access to these databases. Unfortunately, the usefulness of third party databases is limited.

Compound library data were initially based off mass spectra in the 2008 NIST/EPA/NIH mass spectral library (version 2.0f). However, these spectra often differed from those which were obtained using the TRIDION-9. The main difference was in the relative abundance of ions. This is a recognised phenomenon (Later, et al., 2009). Differences are a result of the ionisation techniques used by ion trap mass spectrometers compared to NIST instrumentation (which was used to compile data for the NIST/EPA/NIH library). Mass spectra contributed to NIST were obtained from linear quadrupole mass analysers utilising 70eV hard ionisation techniques. While electrons are also ionised at 70eV in the TRIDION-9, they change to the potential of the radio frequency field when they enter the ion trap. The dominant species in the trapping field is helium, thus further ionisation occurs as a result of helium charge exchange with the analyte. This produces a different mass spectrum to what is recorded in popular (hard ionisation only) mass spectral libraries. This makes the identification of unknown compounds via mass spectra complicated, though differences are reproducible and can be recognised by a trained analyst. A mass spectral database containing ion trap mass spectra would have been more useful, but was not accessible during the research. Torion Technologies have developed an improved search algorithm which takes into account differences between ion trap and quadrupole mass spectra (Sadowski, *pers. comm.*, 30 October 2013), though only a subset of 15,000 NIST compounds are included. The compound library established on the TRIDION-9 during this research is restricted to a small number of ignitable liquids. Further expansion of this library is warranted. Operationally, searches of external libraries will not be necessary once a library specific to FDA has been fully established on the TRIDION-9.

4.8.2: Chromatography

Overall, the reproducibility of run-to-run retention times on the MXT-5 column was excellent. Some small shifts in retention time were noted over the course of the research period. This required minor adjustment of retention windows in the compound library. Variability in carrier gas pressure or chemical modification of the stationary phase in the column may have contributed to these minor shifts. Larger retention time windows can alleviate the issue, but regular calibration of the target compound library using ILR standards is recommended.

4.8.3: Mass analysis

Space charge effects were an issue during sample analysis. In the TRIDION-9, space charge is symptomatic of a dirty ion trap or an excessively high filament voltage. Both result in more ions being pushed into the ion trap and overloading it, resulting in higher ion values being recorded by the detector. Space charge is a common pitfall of ion trap technology, as was realised in the NFSTC's evaluation of the GUARDION-7 (Grates, 2009). In most cases, cleaning the ion trap resolved space charge issues. However, some space charge occurred intermittently even when the ion trap was clean, and seemed to be more pronounced in some sample types more than others. This was observed particularly in samples of diesel, where heavier n-alkanes such as tridecane and above would record ion values of 58, 72 and 86 rather than 57, 71 and 85. This resulted in false negative compound identifications by the instrument software. The cause of space charge in these cases was ambiguous, and since it was not always reproducible, was also difficult to troubleshoot.

Two possible causes for this type of space charge were suggested by the manufacturer. First, small leaks in the chromatographic system may have allowed oxygen to enter the ion trap. Oxygen may enter and be ionised in the TRIDION-9 and will boost the number of ions in the analyser. Due to the mass range of the analyser, oxygen cannot be detected, and the mass analyser cannot compensate for its presence. Secondly, as the issue seemed to affect only alkane compounds, it was possible that a detector surface phenomenon was causing alkane ions to be charged differently to other ions ejected from the trap. Overall, space charge of this type posed no real obstacle to sample analysis. If an HPD containing long-chain alkanes was expected in a sample, space charge could be compensated for by extracting ion values one higher than the expected ions.

Loss of high mass resolution occurred sporadically throughout the research period. In the first instance, it occurred due to a bug in the instrument software which discounted all ions with a mass above 250. This was resolved with a software upgrade. Other losses of resolution were encountered generally resolved themselves after several days or after an instrument reset. Towards the end of this study, a persistent loss of high mass resolution was noted. Ions above mass 300 did not resolve optimally, though resolution was still acceptable for routine analysis. Realignment of the ion trap had no beneficial effect, though it was expected that this was a contributing factor. Other possible reasons for this loss in resolution may have been damage to the surface of the trap electrodes or their thermal expansion and contraction. Damage to trap electrodes was recommended by the manufacturer as the most likely cause. In order to counteract this, the ion trap electrodes of the TRIDION-9 are now manufactured using a different surface. The instrument evaluated in this study used a trap made of a gold-cobalt alloy, which hardened the trap and protected it from damage. The solid gold trap used previously was found to be too soft and contributed to resolution problems in a previous study (Brust, 2009). However, over time, the cobalt migrates to the surface of the trap electrodes and contributes to a loss in resolution, particularly above mass 300. Despite these issues, mass resolution was otherwise excellent, with unit mass resolution or better for masses up to 300 amu. Operationally, sporadic losses in high mass resolution are not a concern for FDA applications. Should the instrument be adapted to the analysis of illicit drugs or explosives, resolution of high-mass compounds may become a significant issue.

The TRIDION-9 was not as sensitive as laboratory-based instrumentation. Mass sensitivity could be improved by significantly increasing the voltage of the detector, but this dramatically reduces the lifespan of the detector and introduces mass spectral artefacts. The high speed of the TRIDION-9 column limits the amount of sample that it can mobilise, thus only a small amount of sample will reach the detector. Laboratory columns, in comparison, will typically accept five to ten times more sample volume than the TRIDION-9. For this reason, TRIDION-9 results typically do not include very low intensity ions which are otherwise visible in traditional GC-MS results. For example, mass spectra for 1,2,4-trimethylbenzene on the TRIDION-9 consist primarily of ions 105 and 120 (Figure 35). Other ion fragments such as 91, 79 and 63 are visible, but are very low in intensity. These ion peaks are more visible in library mass spectra (Figure 36). Such differences in ion abundance between the TRIDION-9 and traditional GC-MS have been acknowledged (Later, et al., 2009). Nevertheless, compound identifications do not generally rely on ions so low in intensity. The TRIDION-9's sensitivity is otherwise excellent for presumptive testing purposes

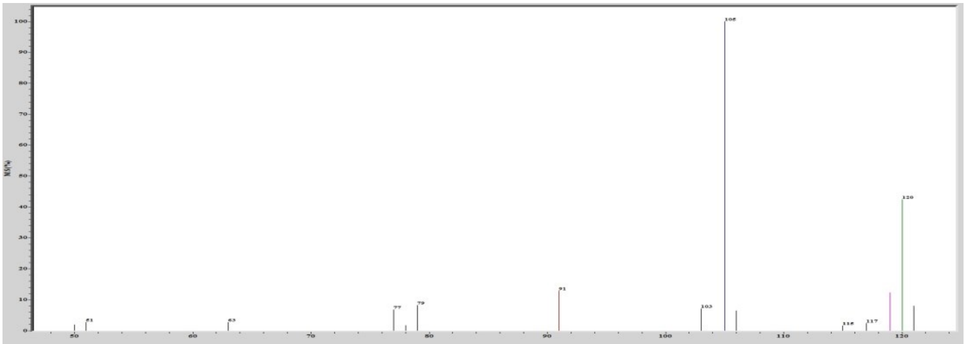


Figure 35: The mass spectrum of 1,2,4-trimethylbenzene as it appears on the TRIDION-9.

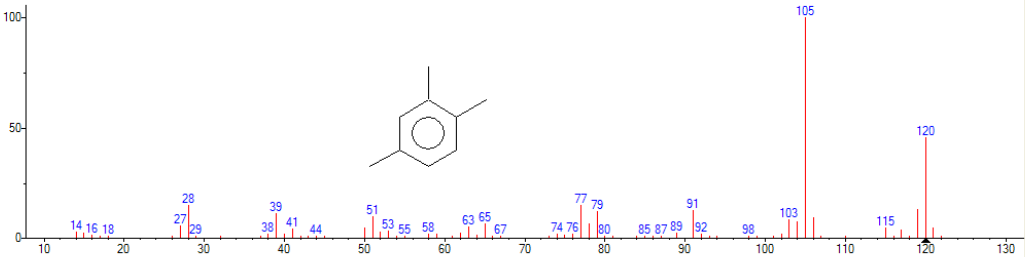


Figure 36: The mass spectrum of 1,2,4-trimethylbenzene, as it appears in a mass spectral library.

5. Conclusions

Over the past four years, the University of Canberra has established a research base evaluating prototypes of the TRIDION-9 for various forensic applications. Previous evaluations of the instrument's analytical abilities have focused on the analysis of illicit drugs and explosives, but have been hindered by technical difficulties. There are currently no reliable techniques for the presumptive identification of ILR at the fire scene other than chemical sensors which either lack sensitivity or selectivity.

The detection abilities of the TRIDION-9 for four ignitable liquids on different substrate matrices were investigated exhaustively during this study. ILR was positively identified in 42 of 49 simulated samples (86%). Of these samples, four were tentative (inconclusive) identifications which required laboratory confirmation, but still accurately predicted the ignitable liquid present in each sample. Only seven samples could not be classified as containing ILR. The ability of the TRIDION-9 to detect volumes as low of 0.1 μL of ignitable liquid in challenging simulated samples is impressive and rivals the sensitivity of laboratory instrumentation.

Identification of ILR in operational samples obtained from a real fire scene reflects the efficacy of using the TRIDION-9 in real fire investigation operations. Of 11 operational samples, 9 were positively identified as containing an ignitable liquid (82%). One sample was negatively identified and another produced inconclusive results. The instrument performed reliably in a field setting. Portable battery packs offered power for approximately two and a half hours.

Maintenance and troubleshooting of the instrument can be a complicated task. A trained and experienced operator is required to perform maintenance on the system if it begins to perform inadequately. Otherwise, the instrument is easy to use and any forensic chemist can be trained in its operation. The instrument cannot be utilised effectively by operators unfamiliar with GC-MS or FDA. Regular maintenance is required to ensure the instrument is performing ideally. The manufacturer, though located overseas, can be contacted easily to resolve serious instrument faults. An active partnership between organisations using the instrument and the manufacturer is recommended.

Portable GC-MS instrumentation is a novel field. The TRIDION-9 has undergone a large number of upgrades and has improved significantly as an analytical instrument since its previous evaluation. The results of this study support the abilities of the TRIDION-9, both as a powerful analytical instrument and an effective, portable technique for the on-site detection of ILR. Some issues with the instrument are persistent, such as sporadic loss of high resolution and space charge, though to a much lesser degree than documented in previous research. Nevertheless, to a skilled operator, these effects make little difference to the data analysis process.

It is the opinion of this author that the TRIDION-9 is a field-ready instrument which can be deployed by Australian forensic service providers. The TRIDION-9 has a dual role at the fire scene. First, it can be used as a presumptive testing tool to screen potential fire debris exhibits on-site. It acts as a level of quality control between the scene and the laboratory, potentially lowering the number of samples sent to the lab. Sending fewer samples to the laboratory reduces backlogs and increases analysis turnaround time. Second, the TRIDION-9 is able to provide rapid forensic intelligence to investigating officers at the scene. This is congruent with the current push in the forensic science community towards intelligence-led policing. Using the TRIDION-9, actionable forensic intelligence can be produced at the crime scene and incorporated into police investigations instead of waiting weeks for laboratory results.

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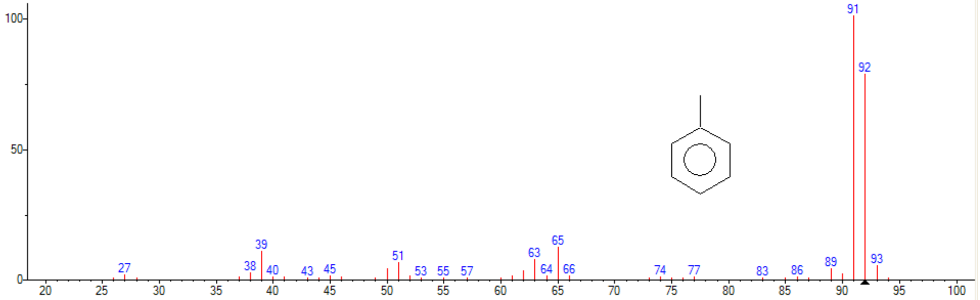
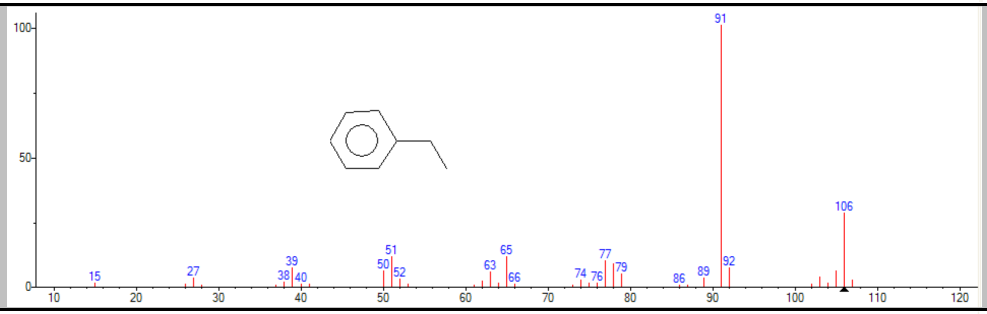
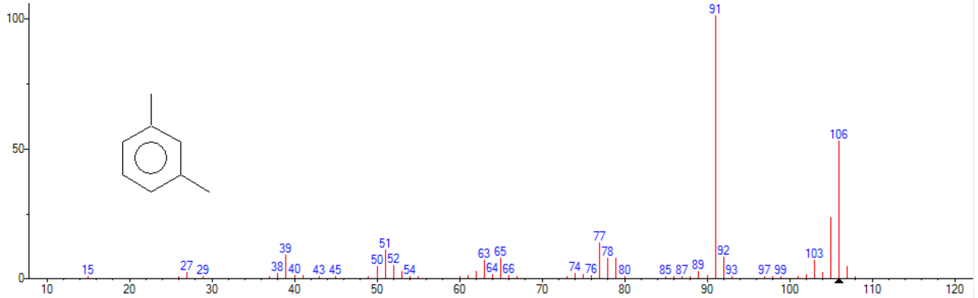
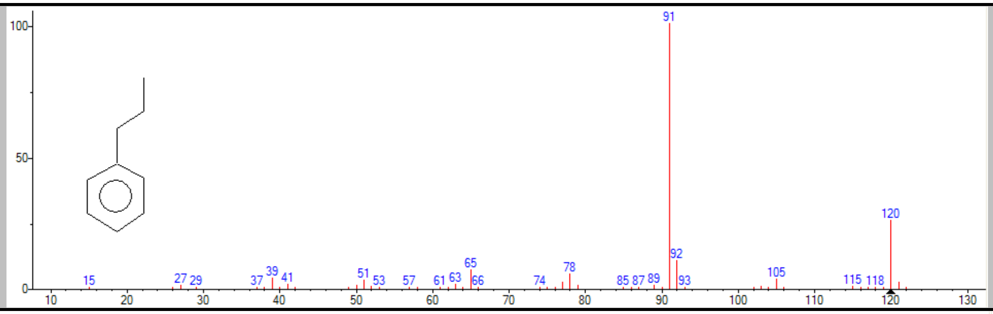
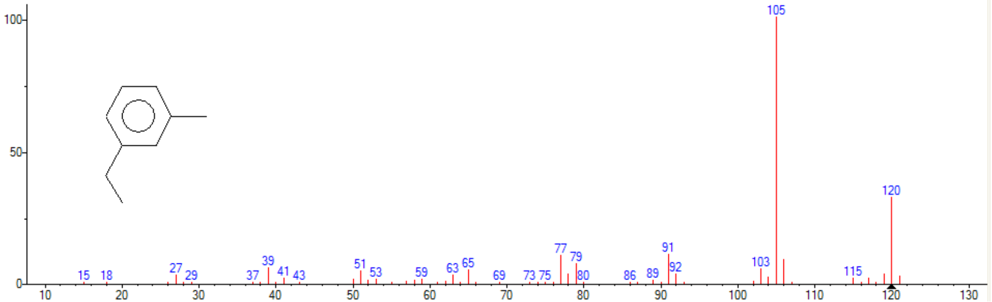
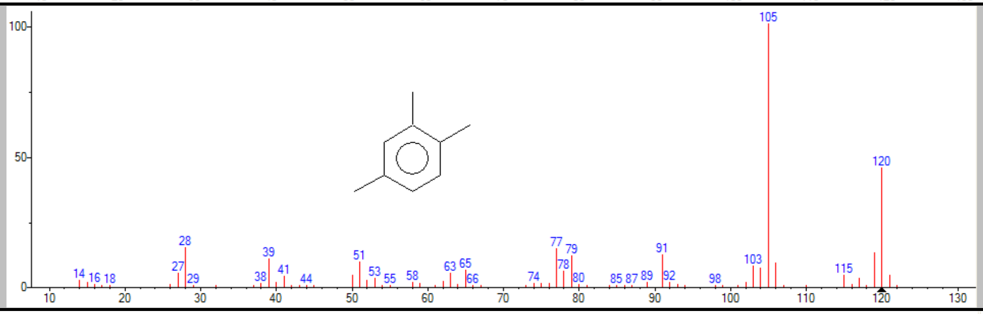
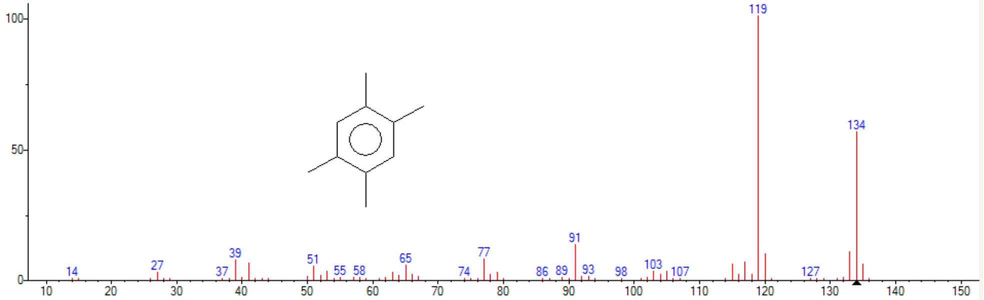
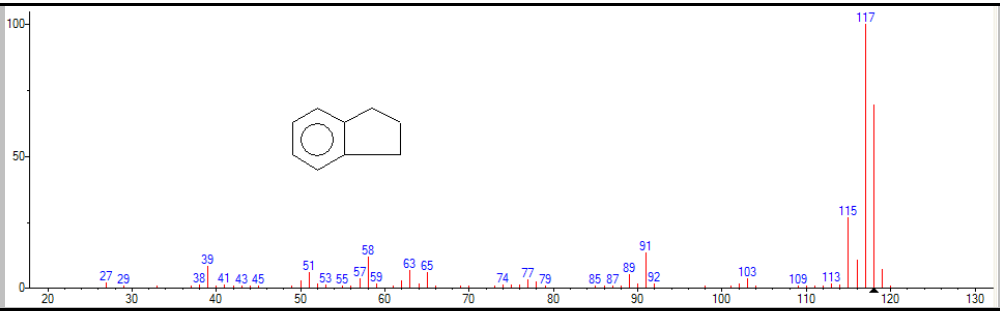
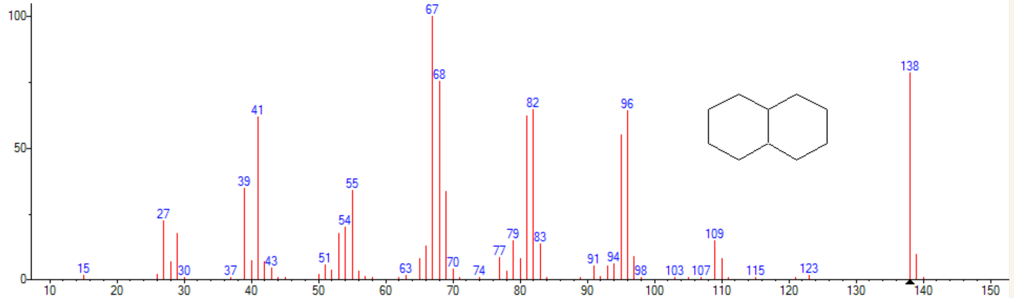
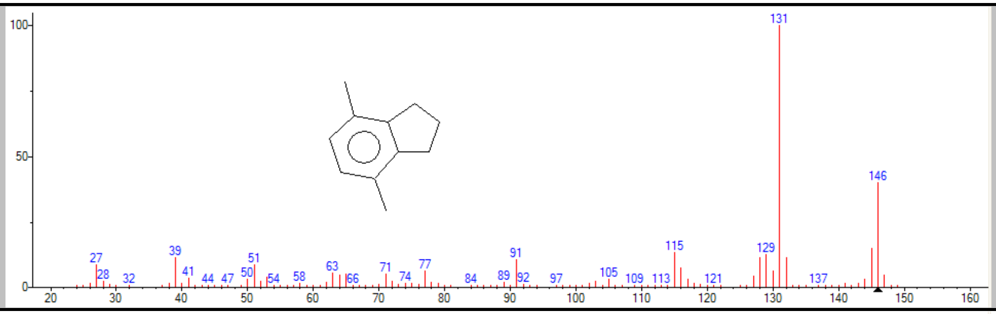
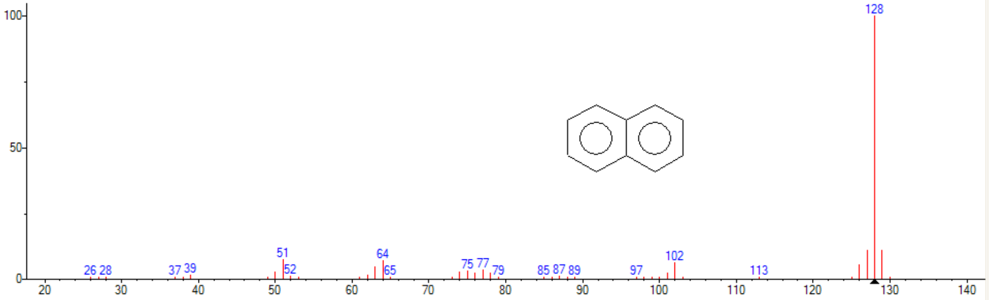
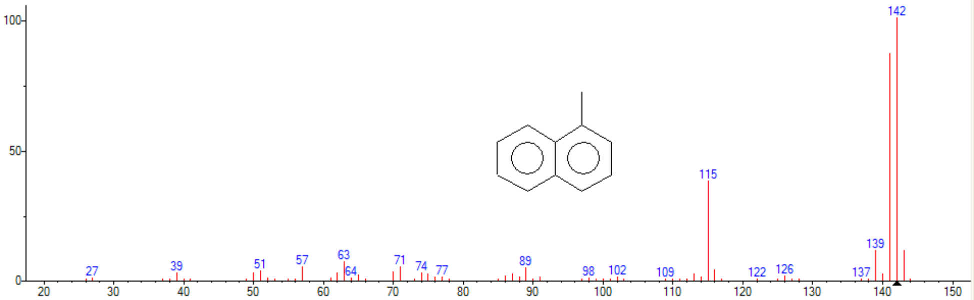
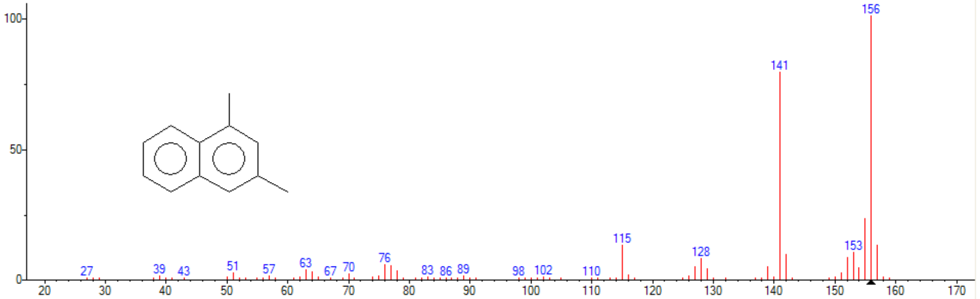
Appendix A: Table of Target Compounds

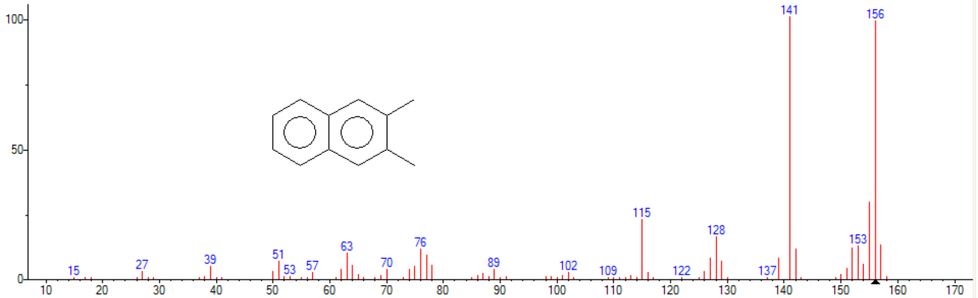
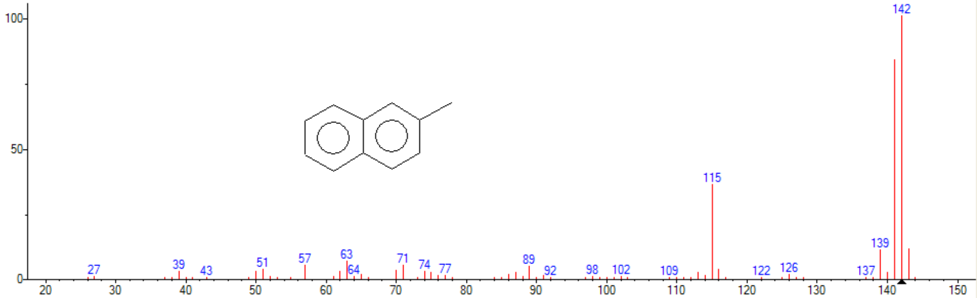
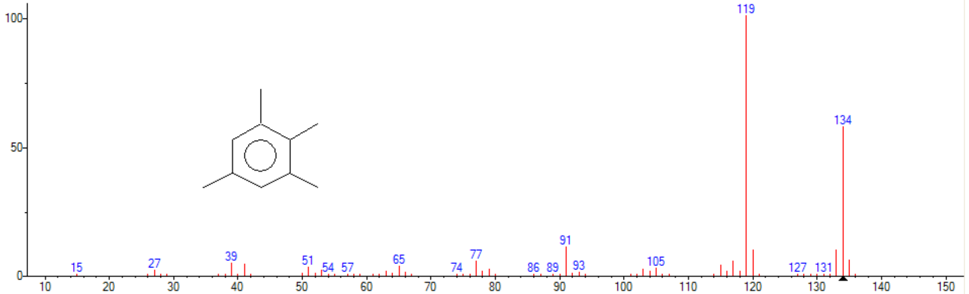
Compound	Type	Formula	Chemical Structure and Mass Spectrum	Target for
Select n-alkanes	Saturated hydrocarbon	C_nH_{2n+2}	Various	Petroleum, petroleum distillates
Toluene	Monocyclic aromatic hydrocarbon	C_7H_8		Petroleum
Ethylbenzene	Monocyclic aromatic hydrocarbon	C_8H_{10}		Petroleum
m-xylene o-xylene p-xylene	Monocyclic aromatic hydrocarbon	C_8H_{10}		Petroleum

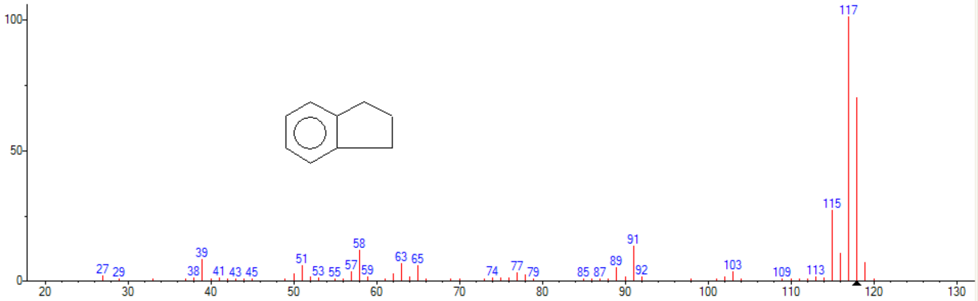
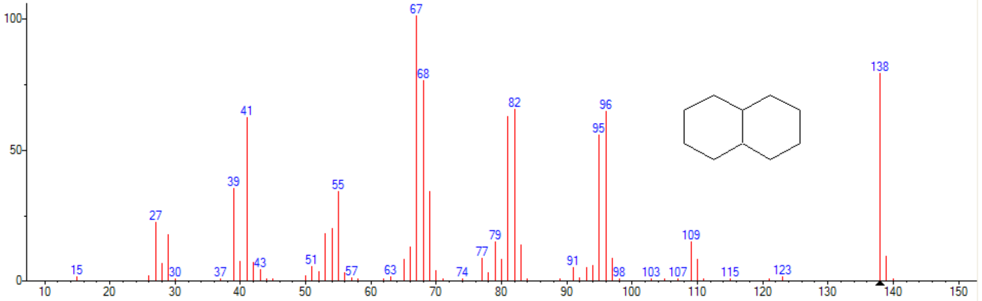
Propylbenzene	Monocyclic aromatic hydrocarbon	C_9H_{12}		Petroleum
m-ethyltoluene o-ethyltoluene p-ethyltoluene	Monocyclic aromatic hydrocarbon	C_9H_{12}		Petroleum
1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene	Monocyclic aromatic hydrocarbon	C_9H_{12}		Petroleum, medium petroleum distillates
1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene	Monocyclic aromatic hydrocarbon	$C_{10}H_{14}$		Petroleum, medium petroleum distillates, heavy petroleum distillates

Indane	Polycyclic aromatic hydrocarbon	C_9H_{10}		Petroleum
trans-Decalin	Bicyclic saturated hydrocarbon	$C_{10}H_{18}$		Medium petroleum distillates, heavy petroleum distillates
4,7-dimethylindane	Polycyclic aromatic hydrocarbon	$C_{11}H_{14}$		Petroleum
Naphthalene	Polycyclic aromatic hydrocarbon	$C_{10}H_8$		Petroleum

1-methylnaphthalene 2-methylnaphthalene	Polycyclic aromatic hydrocarbon	$C_{11}H_{10}$		Petroleum, heavy petroleum distillates
1,3-dimethylnaphthalene 2,3-dimethylnaphthalene	Polycyclic aromatic hydrocarbon	$C_{12}H_{12}$		Petroleum, heavy petroleum distillates

Appendix B: Table of Chemical Standards

Standard	Type	Formula	Chemical Structure and Mass Spectrum	Supplier
C_8-C_{20} Alkanes	Mixture	Multiple	Multiple alkane compounds.	Sigma-Aldrich
2,3-Dimethylnaphthalene	Single compound	$C_{12}H_{12}$		Sigma-Aldrich
2-Methylnaphthalene	Single compound	$C_{11}H_{10}$		Sigma-Aldrich
1,2,3,5-Tetramethylbenzene	Single compound	$C_{10}H_{14}$		Sigma-Aldrich

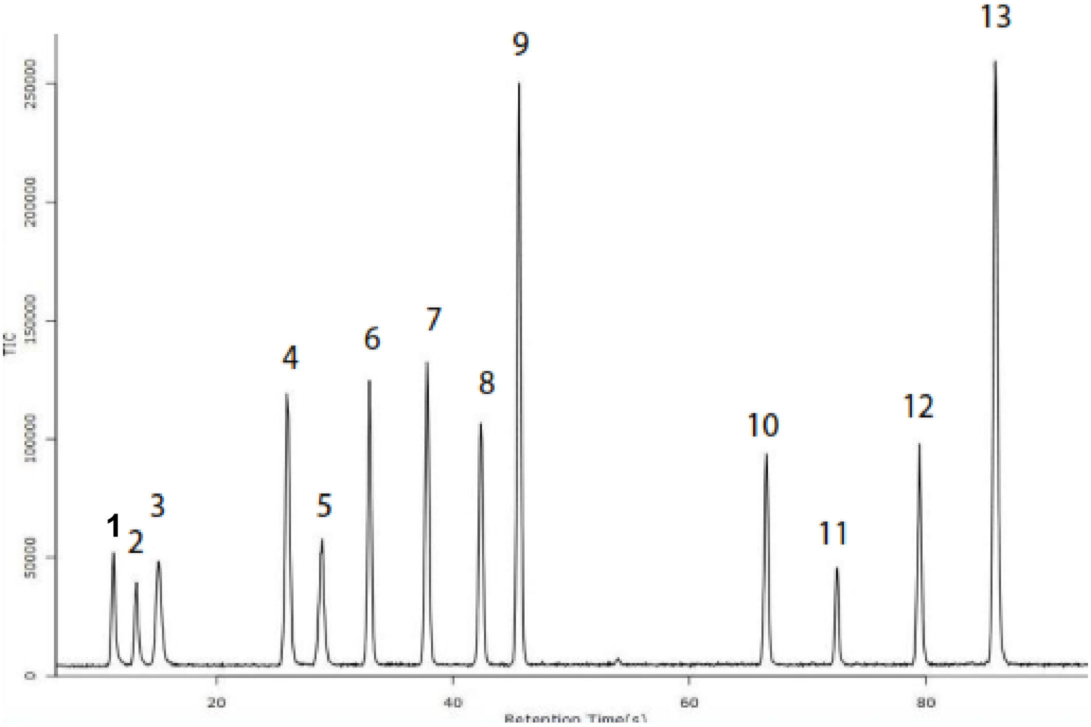
Indane	Single compound	C_9H_{10}		Sigma-Aldrich
trans-Decahydronaphthalene	Single compound	$C_{10}H_{18}$		Sigma-Aldrich
Certified aromatics in gasoline	Mixture	N/A	Multiple compounds found in gasoline including benzene, ethylbenzene, m-ethyltoluene, o-ethyltoluene, p-ethyltolunene, isopropylbenzene, methyl tert-butyl ether, naphthalene, propylbenzene, toluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m-xylene, o-xylene.	Restek

Appendix C: CALION Performance Validation mixture

The CALION PV Mix #1

1. Acetone
2. Methylene chloride
3. Methyl-tert-butyl ether
4. Heptane
5. Methylcyclohexane
6. Toluene-d8
7. Perchloroethylene
8. Bromopentafluorobenzene
9. Bromoform
10.1,2-Dibromotetrafluorobenzene
11. Methylsalicylate
12. Tetrabromoethane
13. Tetradecane

Performance Validation chromatogram



Appendix D: Blank Substrate Results

Blank substrates introduced some volatile compounds which were not detected in neat ignitable liquid reference samples. Volatiles detected in blank samples are shown in Table 7.

Table 7: Blank substrate chromatogram compounds and their associated numeric labels.

Label	Compound
1	Toluene
6	m-/p-ethyltoluene
34	α-pinene
35	Camphene
36	β-pinene
37	Limonene

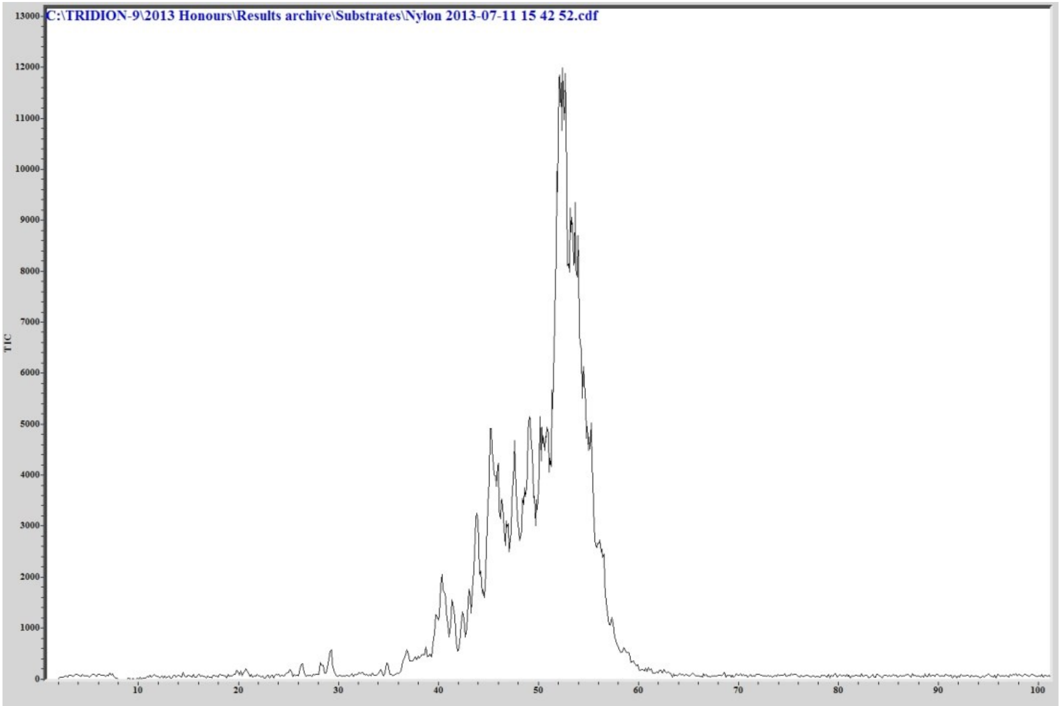


Figure 37: Nylon carpet substrate chromatogram.

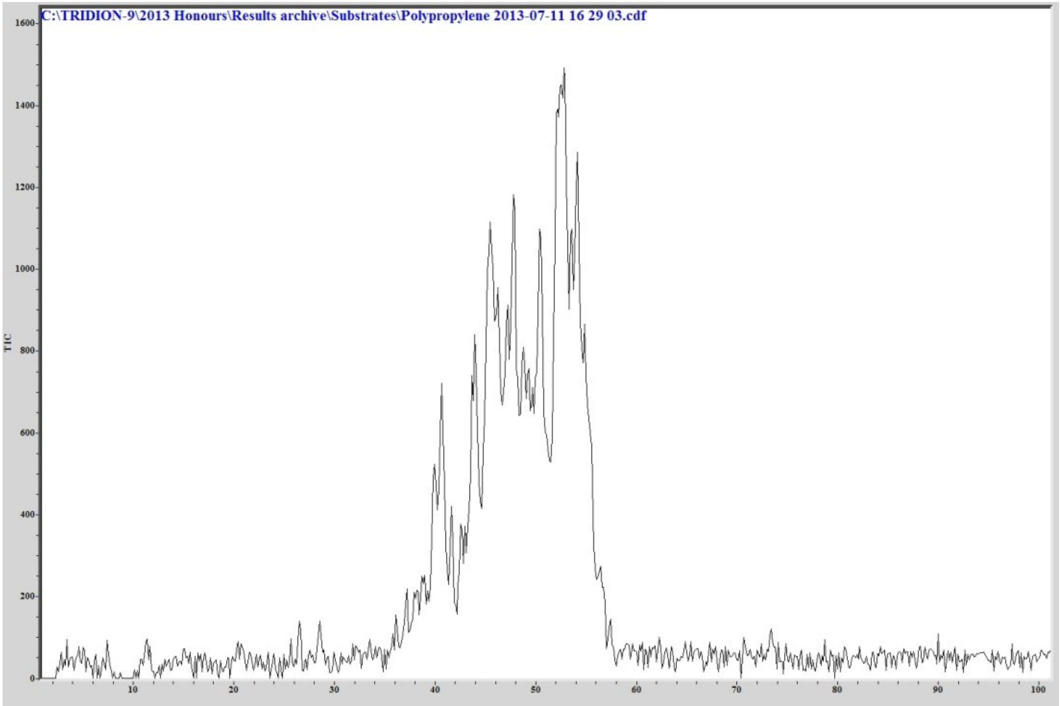


Figure 38: Polypropylene carpet substrate chromatogram.

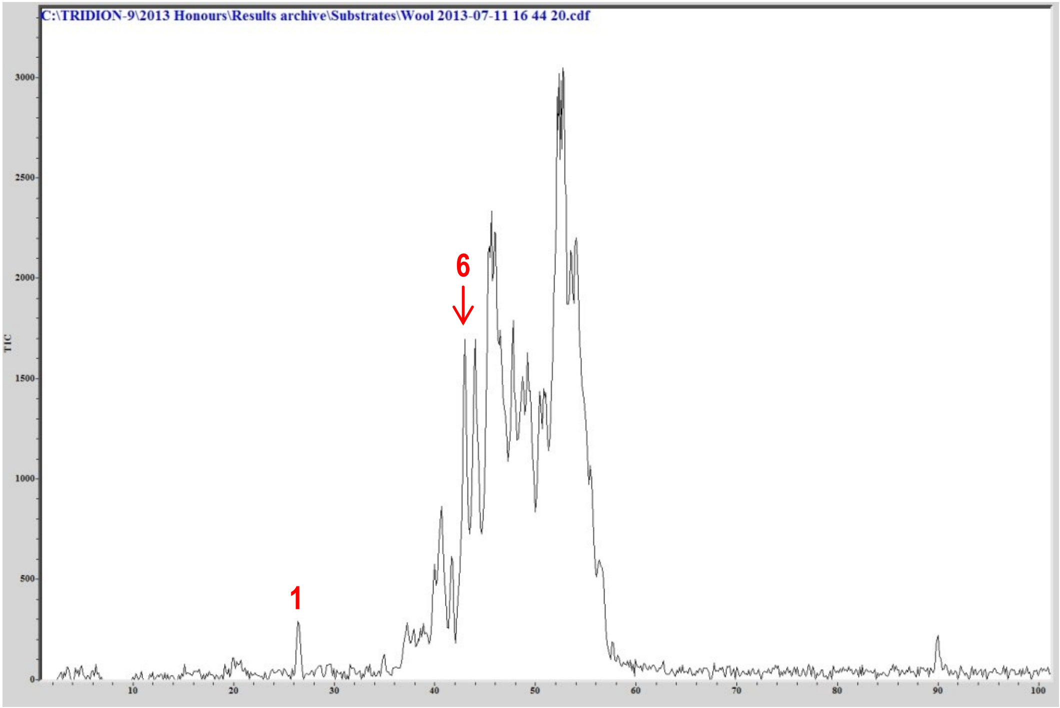


Figure 39: Wool carpet substrate chromatogram.

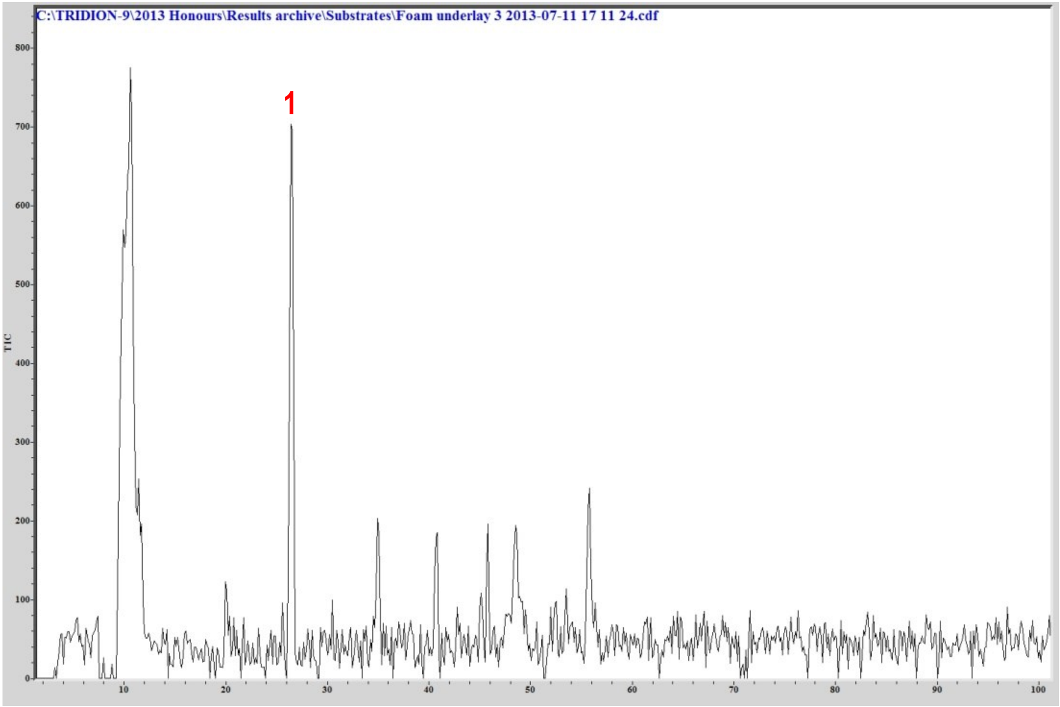


Figure 40: Foam carpet underlay substrate chromatogram.

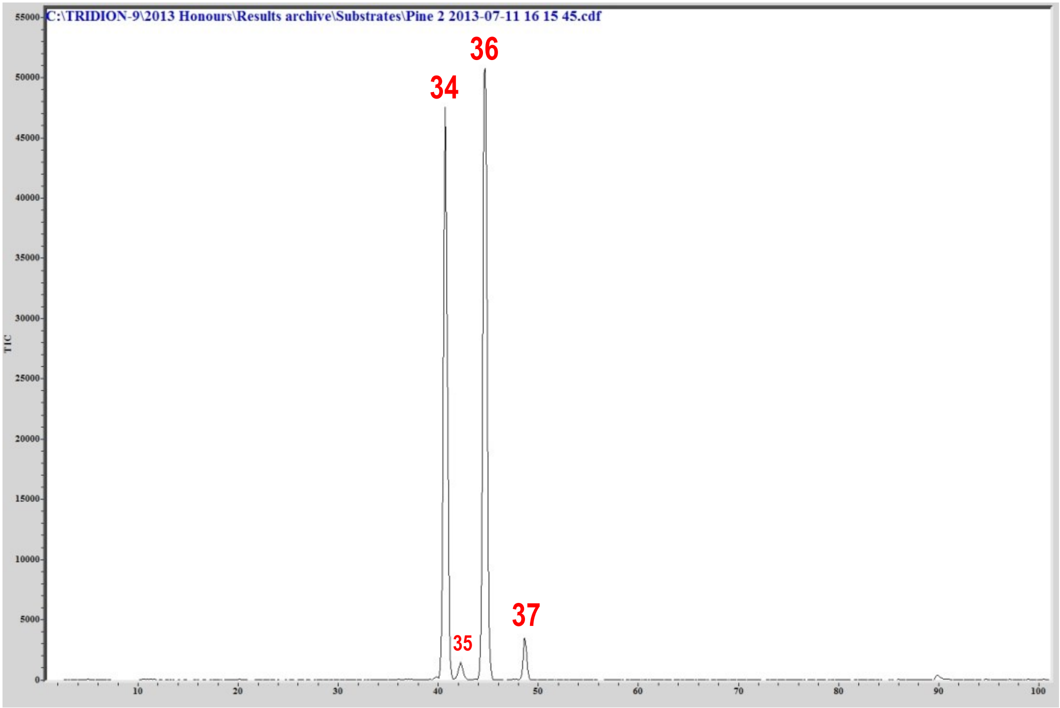


Figure 41: Pine substrate chromatogram.

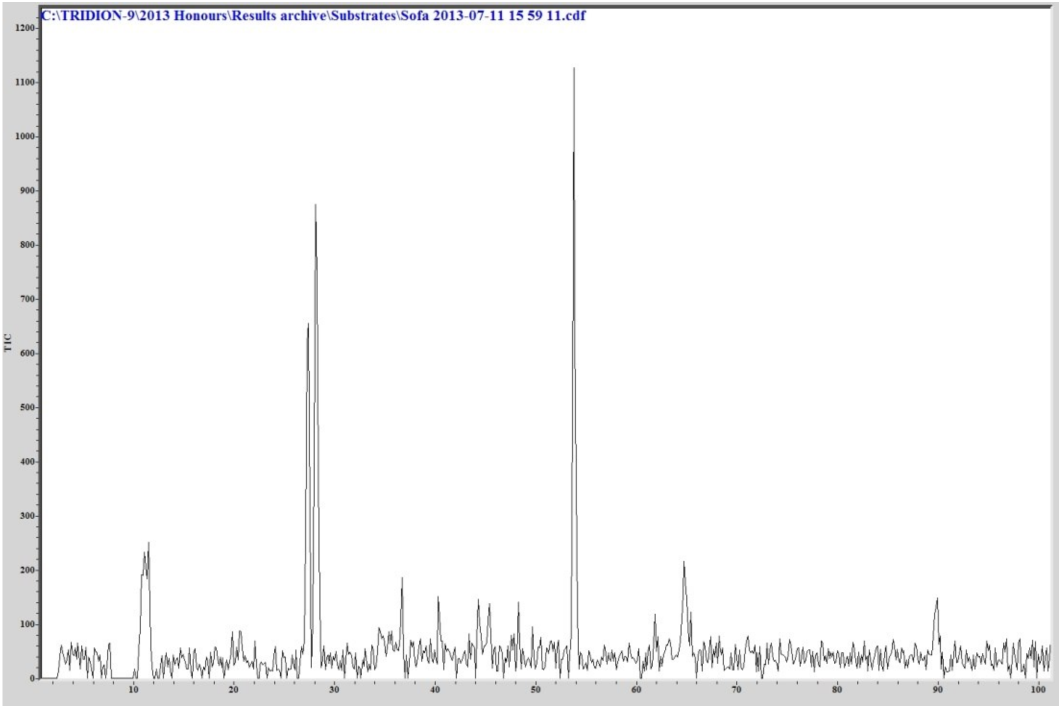


Figure 42: Polyurethane substrate chromatogram.

Appendix E: Burned Substrate Results

Pyrolysis products which occurred in burned substrate samples are listed in Table 8.

Table 8: Burned substrate chromatogram compounds and their associated numeric labels.

Label	Compound
1	Toluene
2	Ethylbenzene
3	m&p-xylene
5	Propylbenzene
28	Tetradecane
34	α-pinene
35	Camphene
36	β-pinene
37	Limonene
38	Styrene
39	Benzaldehyde

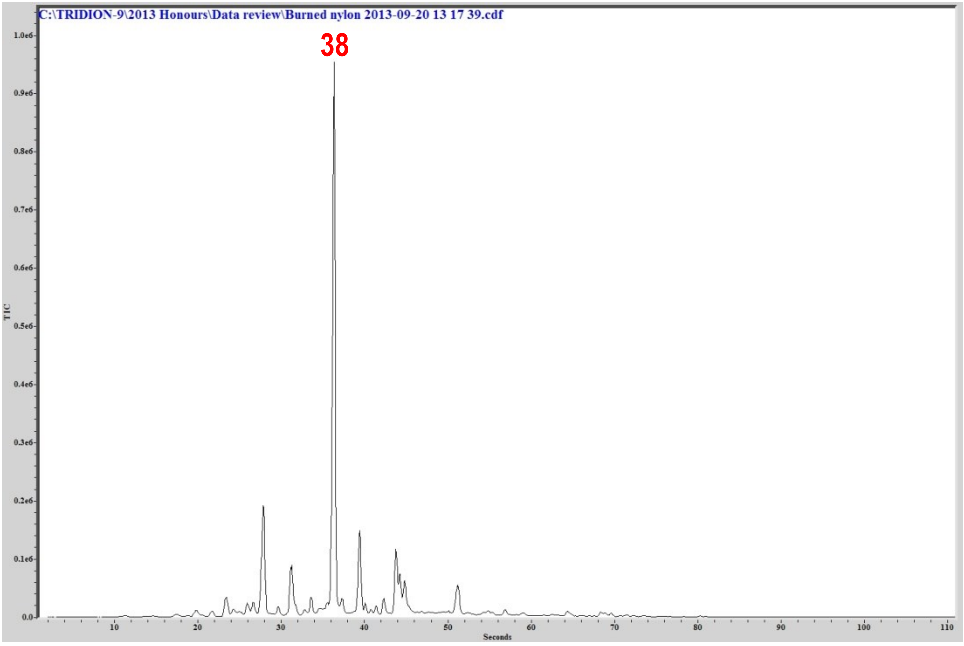


Figure 43: Burned nylon carpet substrate chromatogram.

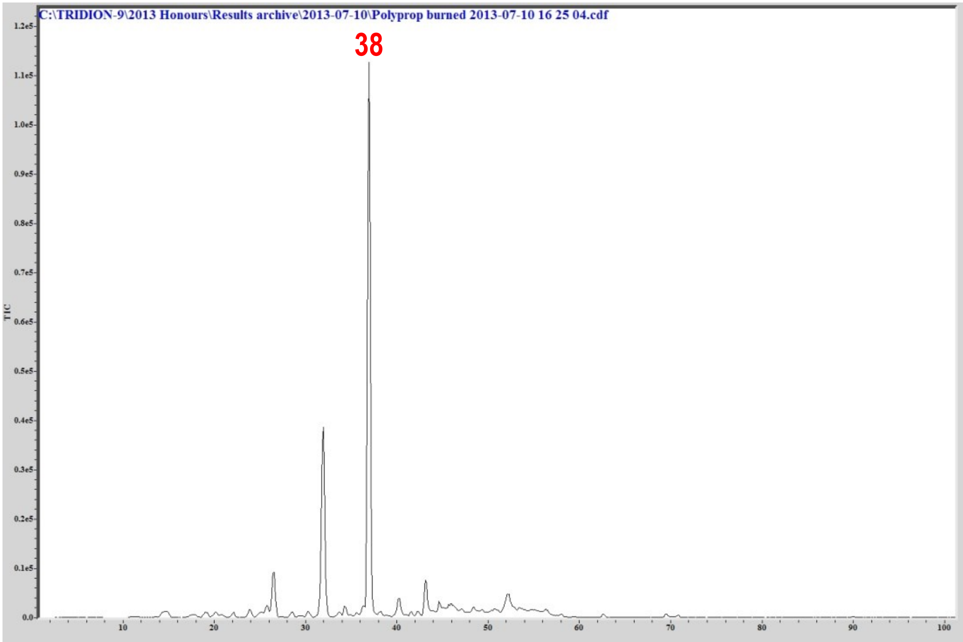


Figure 44: Burned polypropylene carpet substrate chromatogram.

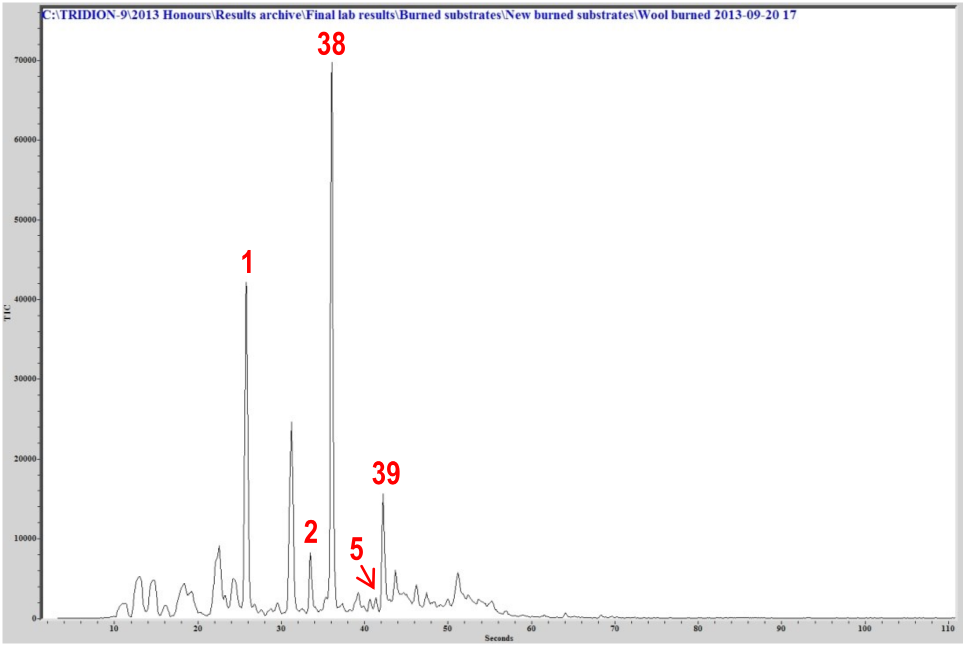


Figure 45: Burned wool carpet substrate chromatogram.

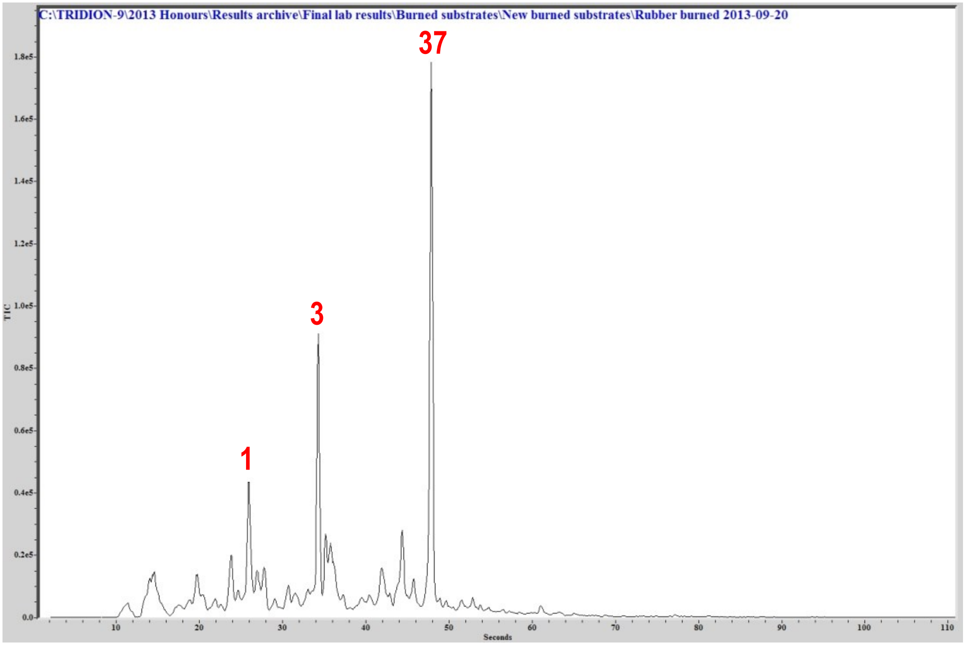


Figure 46: Burned rubber carpet underlay substrate chromatogram.

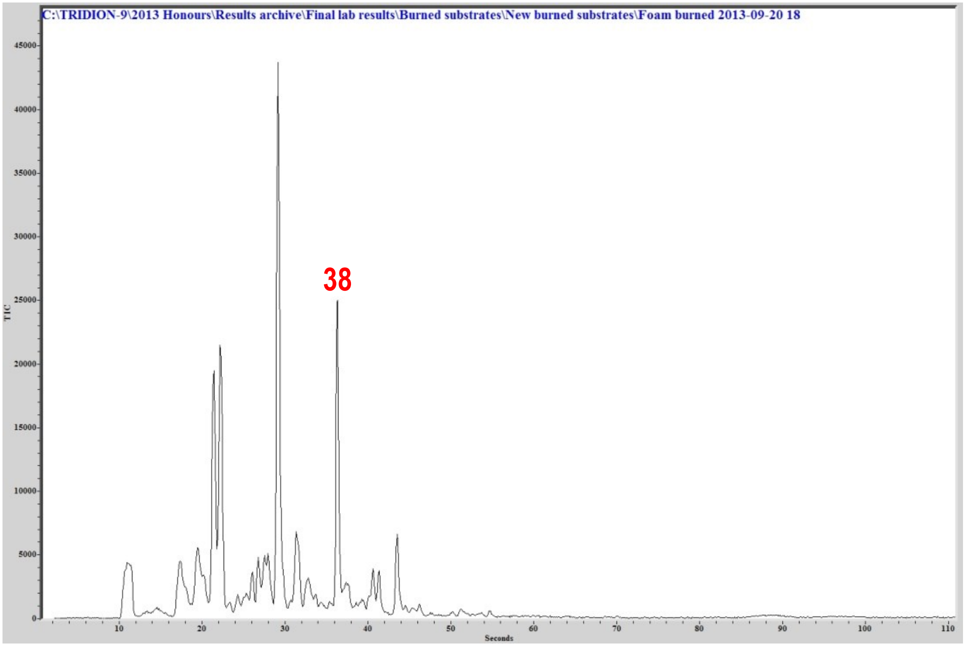


Figure 47: Burned foam underlay substrate chromatogram.

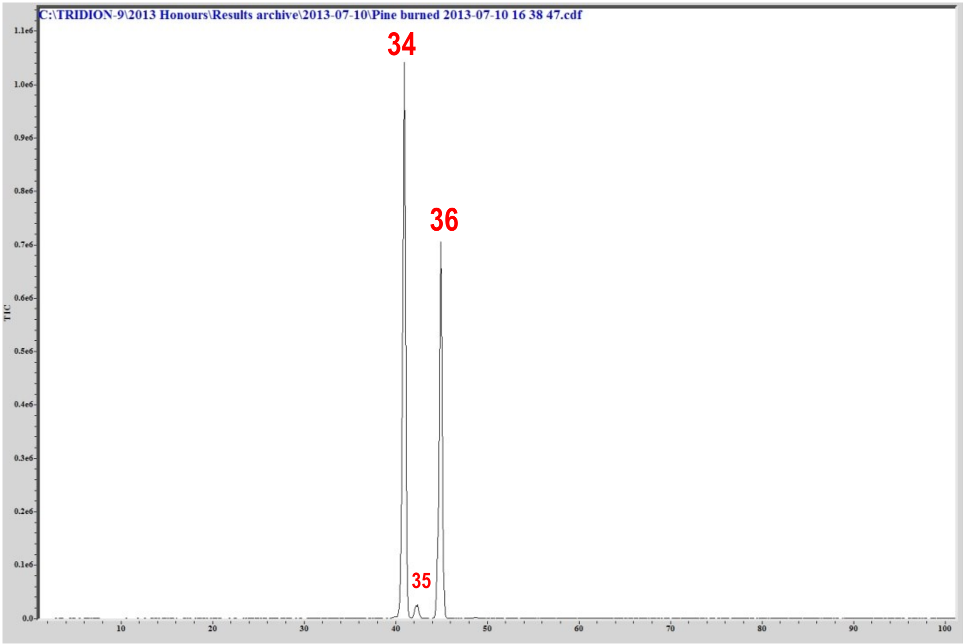


Figure 48: Burned pine substrate chromatogram.

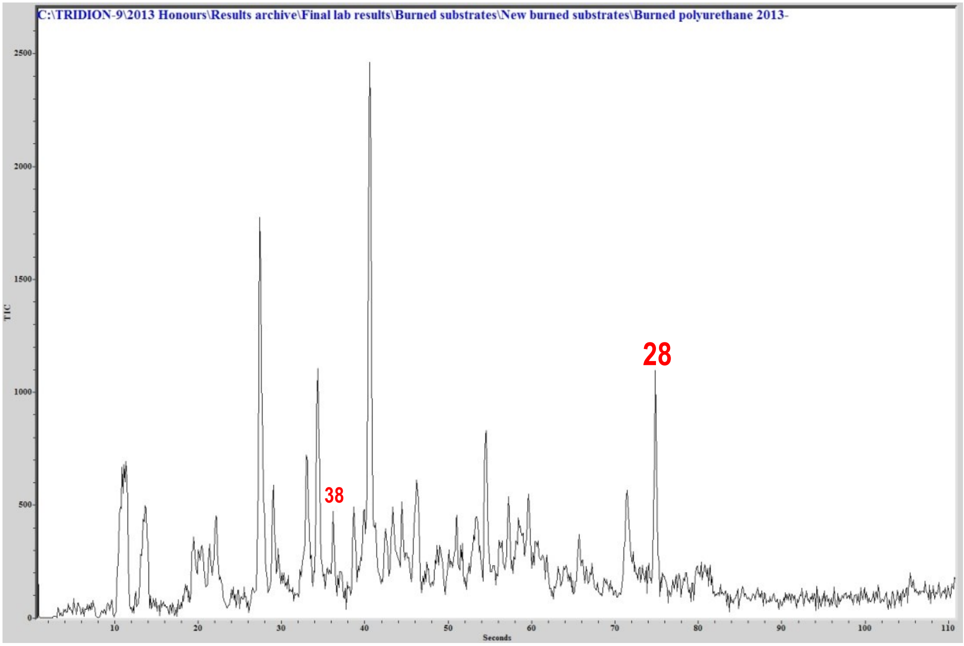


Figure 49: Burned polyurethane substrate chromatogram.

Appendix F: Simulated Sample Results and Discussion

G1: Substrates spiked with unleaded petroleum (results)

Table 9: Burned nylon carpet spiked with unleaded petroleum – analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 50.

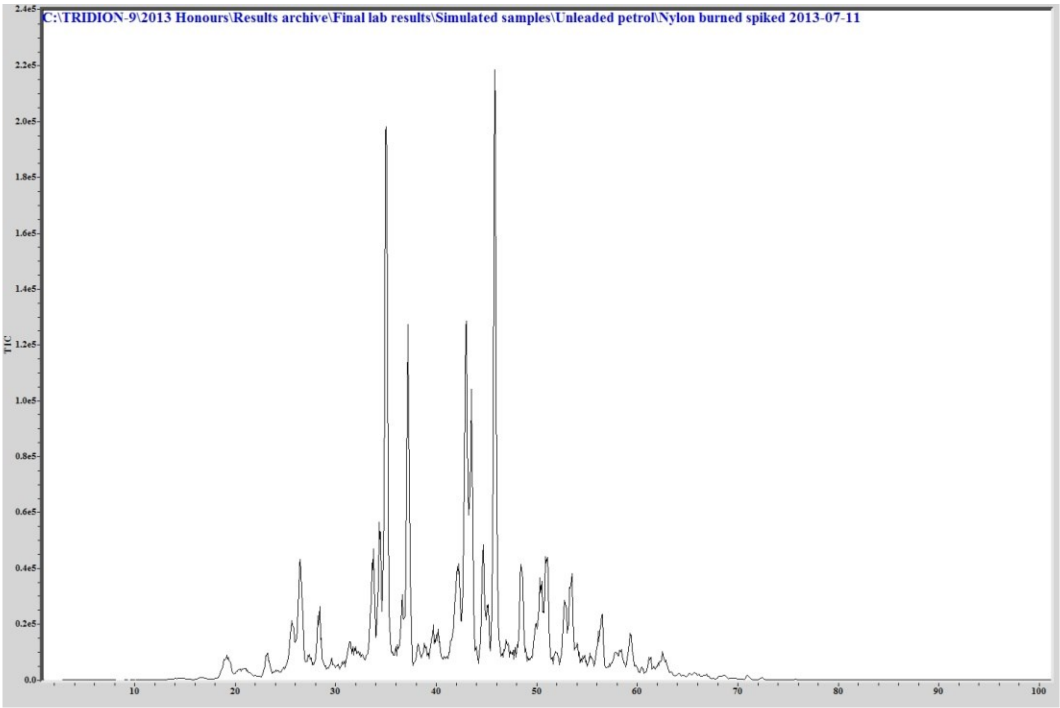


Figure 50: Burned nylon spiked with neat unleaded petroleum sample chromatogram.

Table 10: Burned polypropylene carpet spiked with unleaded petroleum – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 51.

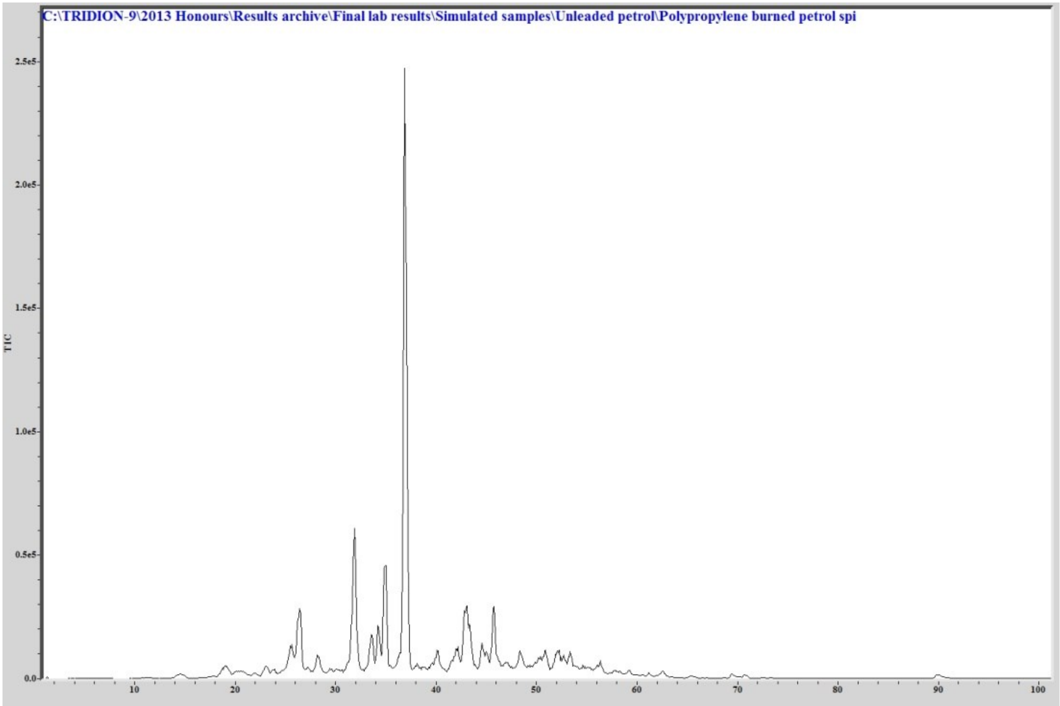


Figure 51: Burned polypropylene carpet spiked with neat unleaded petroleum sample chromatogram.

Table 11: Burned wool carpet spiked with unleaded petroleum – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene 1-merhylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 52.

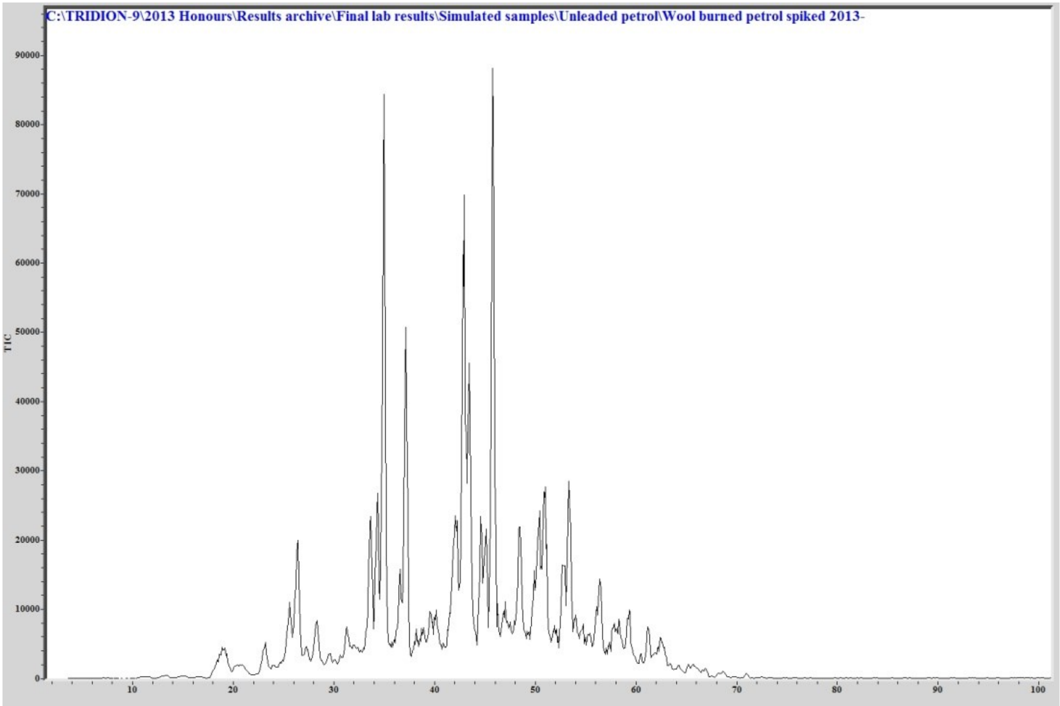


Figure 52: Burned wool carpet spiked with neat unleaded petroleum sample chromatogram.

Table 12: Burned rubber carpet underlay spiked with unleaded petroleum – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	None
Conclusion	Sample contains petroleum residues.
Chromatogram	See Figure 53.

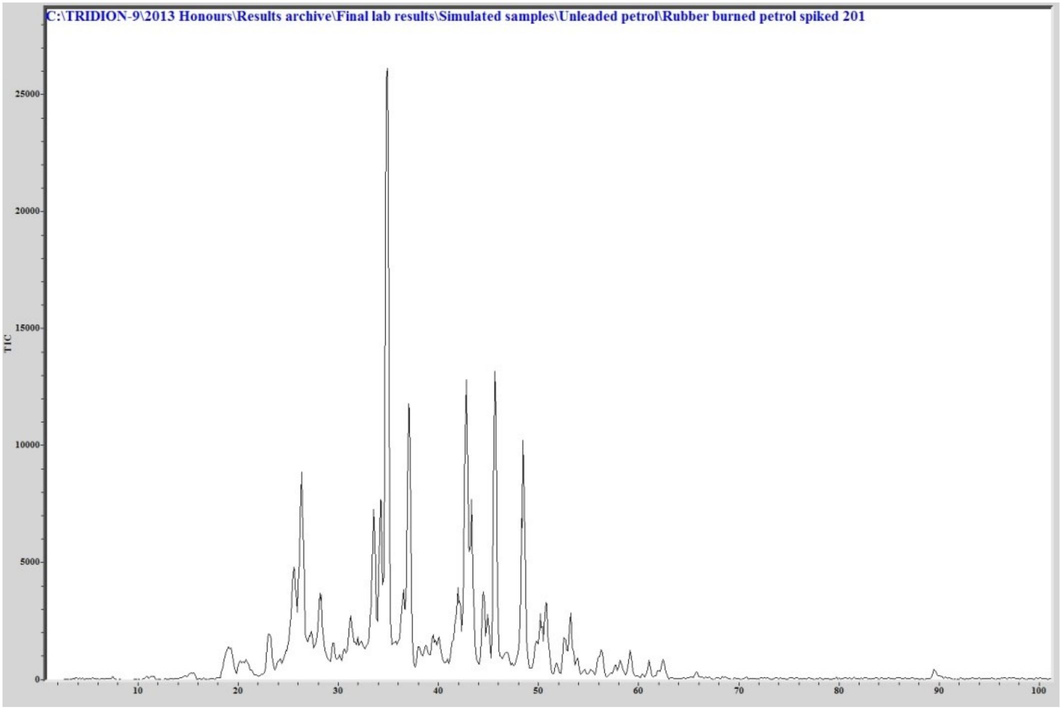


Figure 53: Burned rubber carpet underlay spiked with neat unleaded petroleum sample chromatogram.

Table 13: Burned foam carpet underlay spiked with unleaded petroleum – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Elution range of chromatograph	C_6 to C_{11}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains petroleum residues.
Chromatogram	See Figure 54.

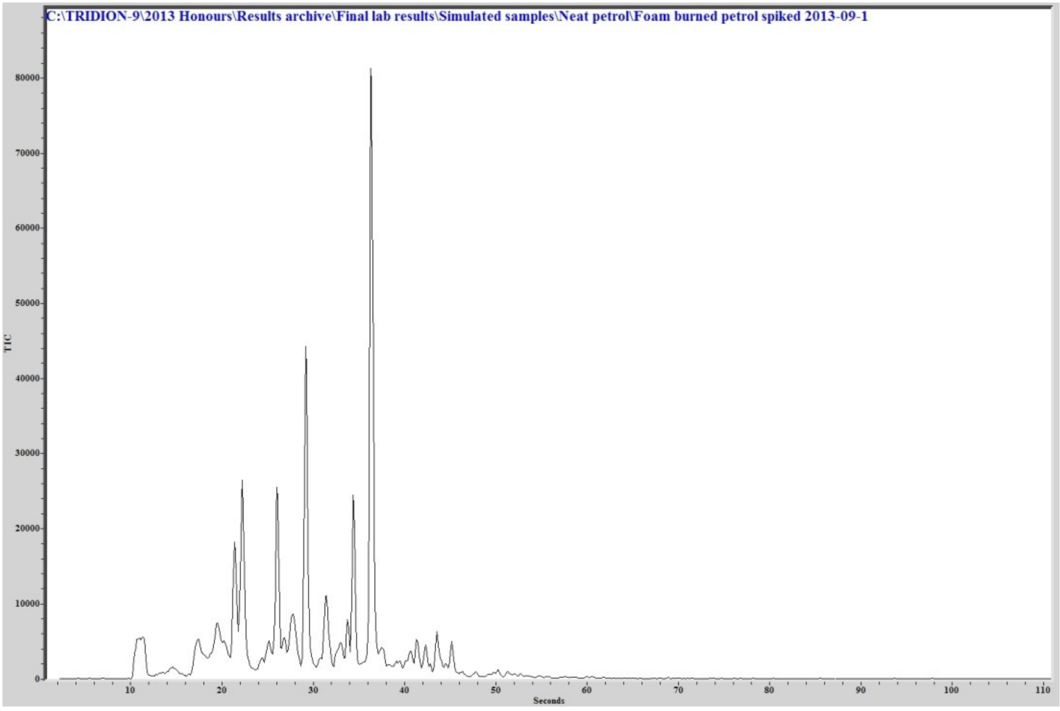


Figure 54: Burned foam carpet underlay spiked with unleaded petroleum sample chromatogram.

Table 14: Burned pine spiked with unleaded petroleum – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 μL)
Elution range of chromatograph	C_7 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	m-/p-xylene o-xylene m-/p-ethyltoluene o-ethyltoluene
Pyrolysis products identified	α-pinene Camphene β-pinene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 55.

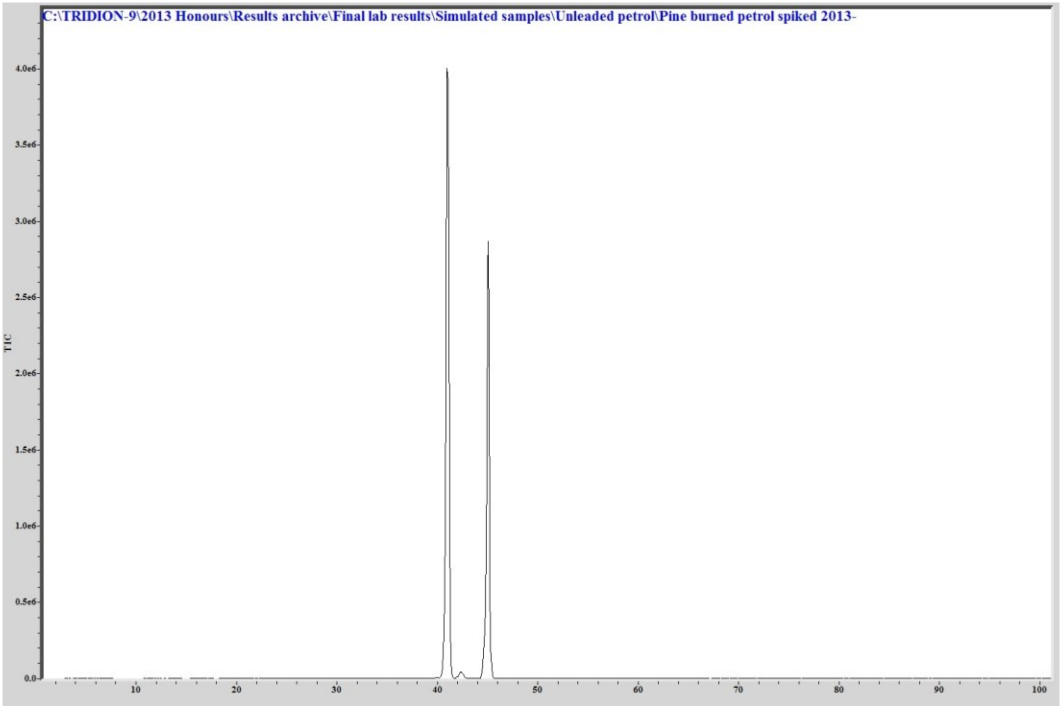


Figure 55: Burned pine spiked with neat unleaded petroleum sample chromatogram.

Table 15: Burned polyurethane spiked with unleaded petroleum – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (0.1 µL)
Elution range of chromatograph	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Unknown
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene
Pyrolysis products identified	None
Conclusion	Sample contains petroleum residues.
Chromatogram	See Figure 56.

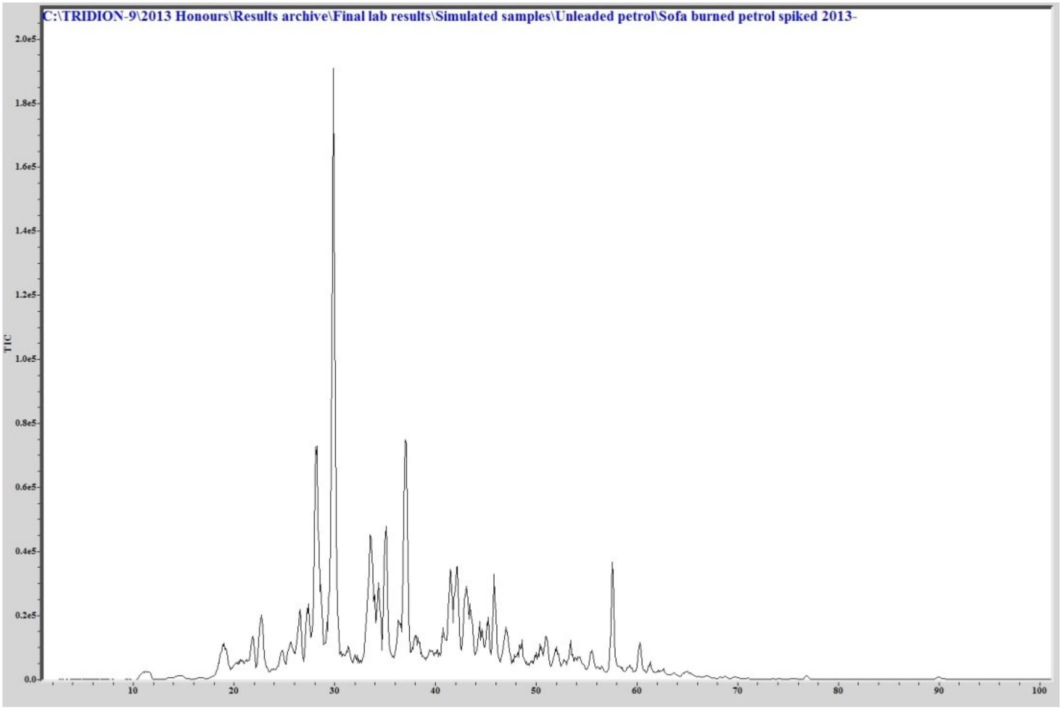


Figure 56: Burned polyurethane spiked with neat unleaded petroleum sample chromatogram.

G2: Substrates spiked with unleaded petroleum (discussion)

Neat unleaded petroleum was the simplest ILR to identify. Neat unleaded petroleum data contained compounds across the entire petroleum elution range. Weathered samples, on the other hand, contained fewer early eluting compounds. Toluene, C_2 and C_3 alkylbenzenes and their respective peak group patterns (see Appendix H: Diagnostic Peak Patterns in Petroleum) were the most obvious components of neat petroleum residues and the most useful for identification.

Several simulated samples showed petroleum residue target compounds plainly in the TIC, such as in nylon carpet, wool carpet and rubber underlay. These samples could be positively identified with ease. Co-elution caused problems for ILR identification in other samples. The polypropylene sample, for example, was dominated by a styrene peak which co-eluted with o-xylene. O-xylene could still be identified as the mass spectrum across the styrene peak was not consistent; ions 91 and 106 became more abundant at the precise elution point of o-xylene. This technique was also used to identify o-xylene in the polyurethane and foam underlay samples. No other pyrolysis products affected neat petroleum identification. Petroleum could not be identified in the pine sample due to the high concentration of terpenes which saturated the SPME fibre.

Target compounds in the upper elution range such as methyl- and dimethylnaphthalene compounds could not always be detected. This was most likely a combination of preferential SPME adsorption and pyrolysis product overloading. However, peaks of interest up to naphthalene could be detected in all samples, thus the loss of a small number of heavier compounds was not significant.

Almost all simulated samples spiked with neat unleaded petroleum appeared to be slightly more weathered than the standard, with diminished toluene peaks. This gave the samples the appearance of 70% weathered petroleum. The cause of this is unknown, though it had little impact on identifications. In total, six of seven samples spiked with neat unleaded petroleum were positively identified. The seventh gave indications of the presence of petroleum, but required laboratory confirmation.

G3: Substrates spiked with 70% weathered petroleum (results)

Table 16: Burned nylon carpet spiked with 70% weathered petroleum - analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 57.

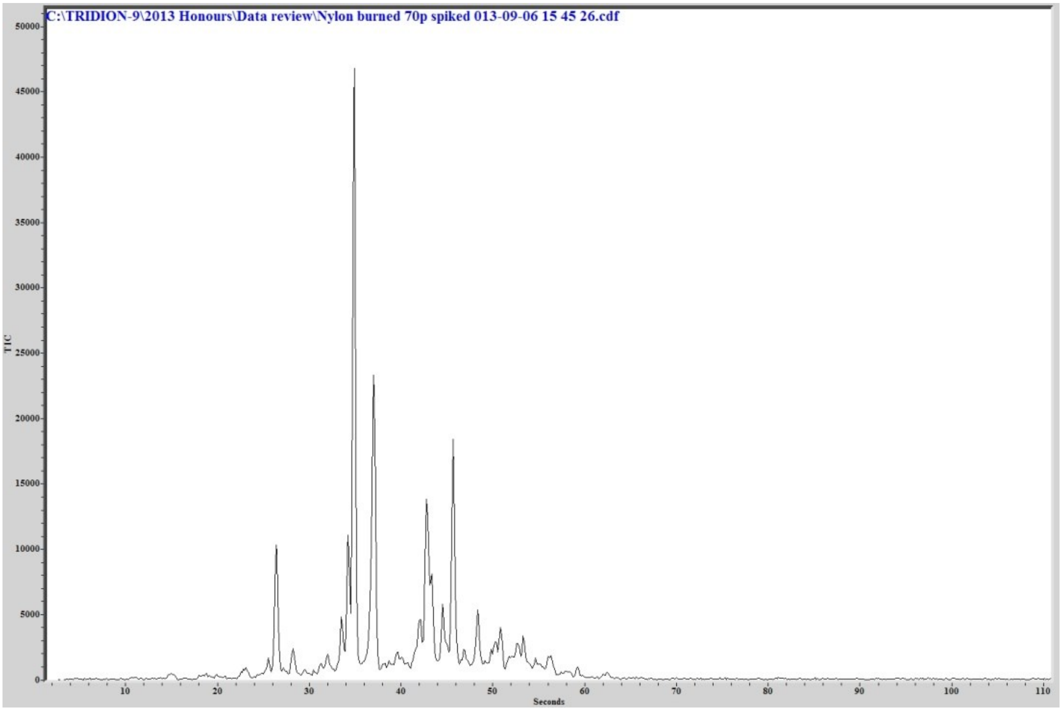


Figure 57: Burned nylon carpet spiked with 70% weathered petroleum sample chromatogram.

Table 17: Burned polypropylene carpet spiked with 70% weathered petroleum – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 58.

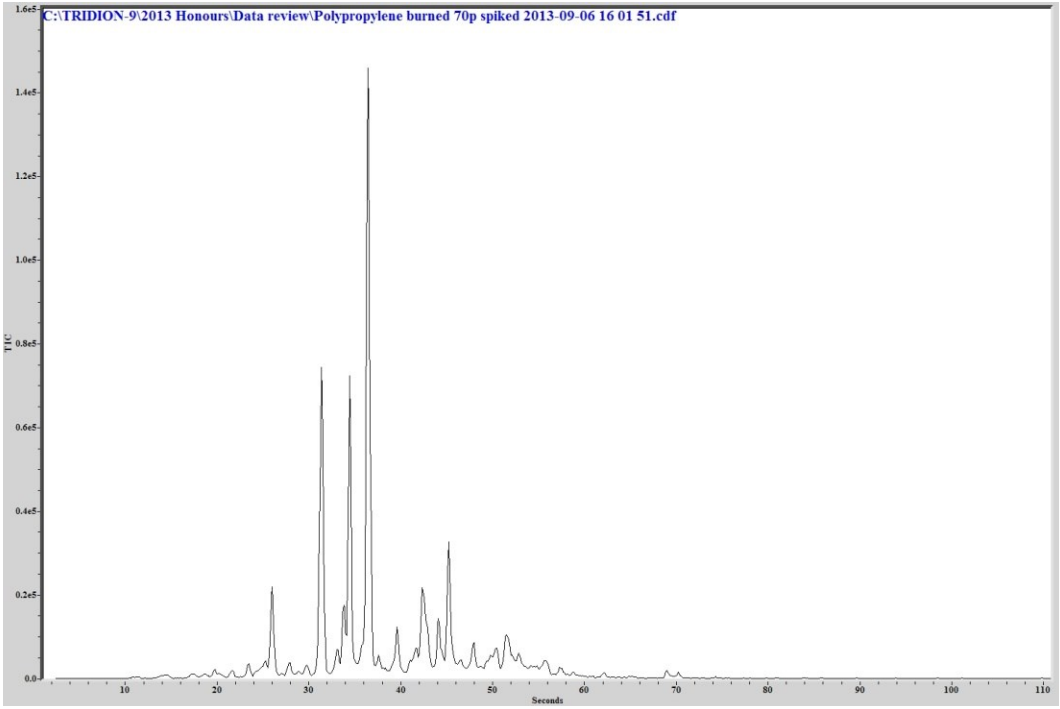


Figure 58: Burned polypropylene carpet spiked with 70% weathered petroleum sample chromatogram.

Table 18: Burned wool carpet spiked with 70% weathered petroleum - analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 59.

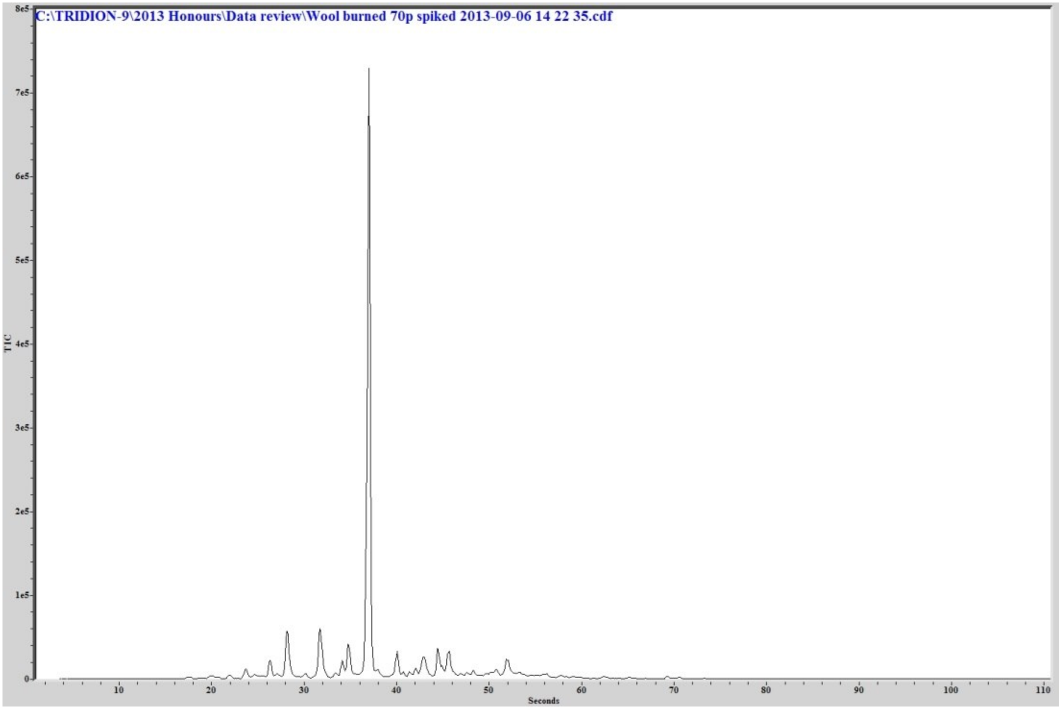


Figure 59: Burned wool carpet spiked with 70% weathered petroleum sample chromatogram.

Table 19: Burned rubber carpet underlay spiked with 70% weathered petroleum - analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,4,5-tetramethylbenzne Naphthalene
Pyrolysis products identified	Styrene Limonene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 60.

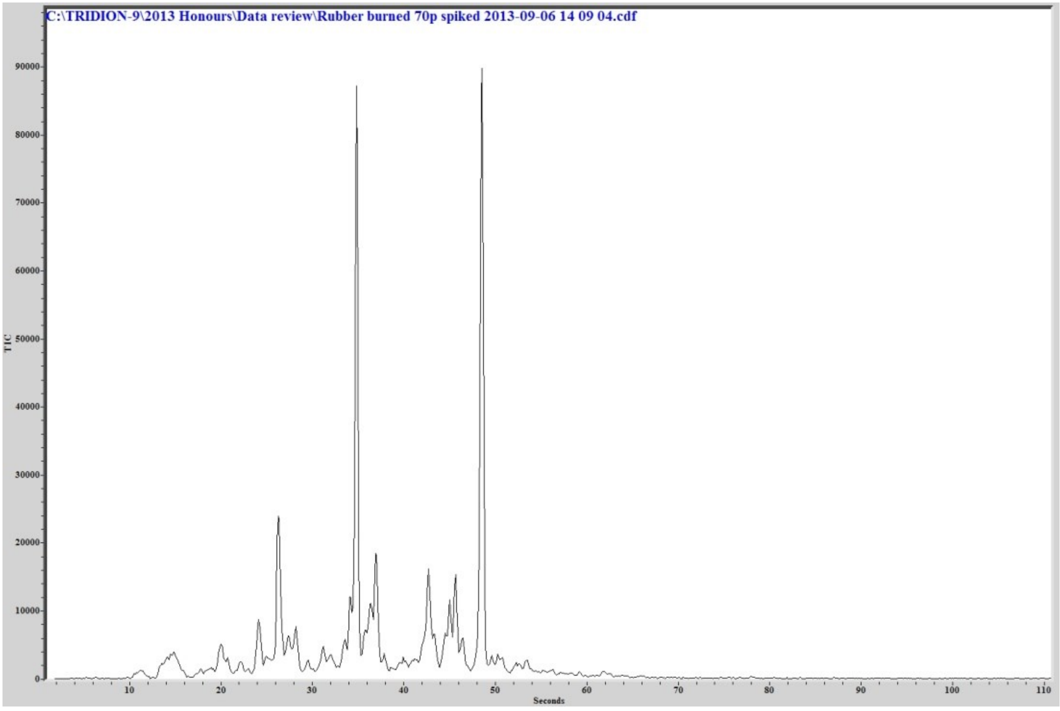


Figure 60: Burned rubber underlay spiked with 70% weathered petroleum sample chromatogram.

Table 20: Foam carpet underlay spiked with 70% weathered petroleum – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene Limonene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 61.

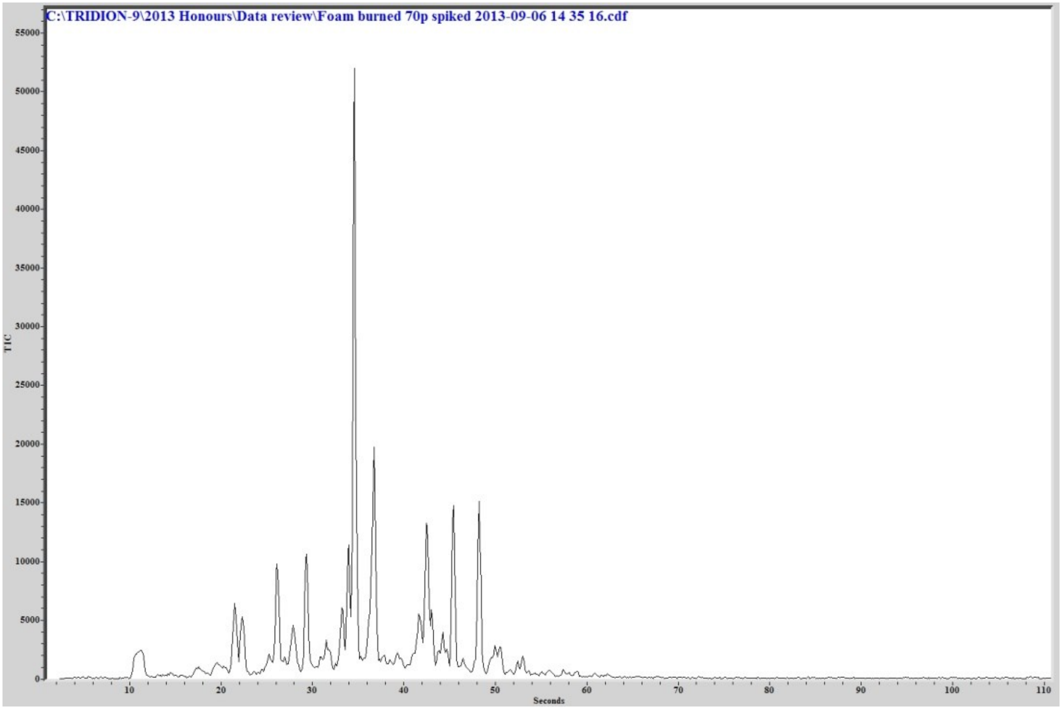


Figure 61: Burned foam carpet underlay spiked with 70% weathered petroleum sample chromatogram.

Table 21: Burned pine spiked with 70% weathered petroleum – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_9 to C_{13}
Peak distribution	Narrow
Dominant ion profile	Monoterpene
Target compounds identified	None
Pyrolysis products identified	α-pinene Camphene β-pinene Limonene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 62.

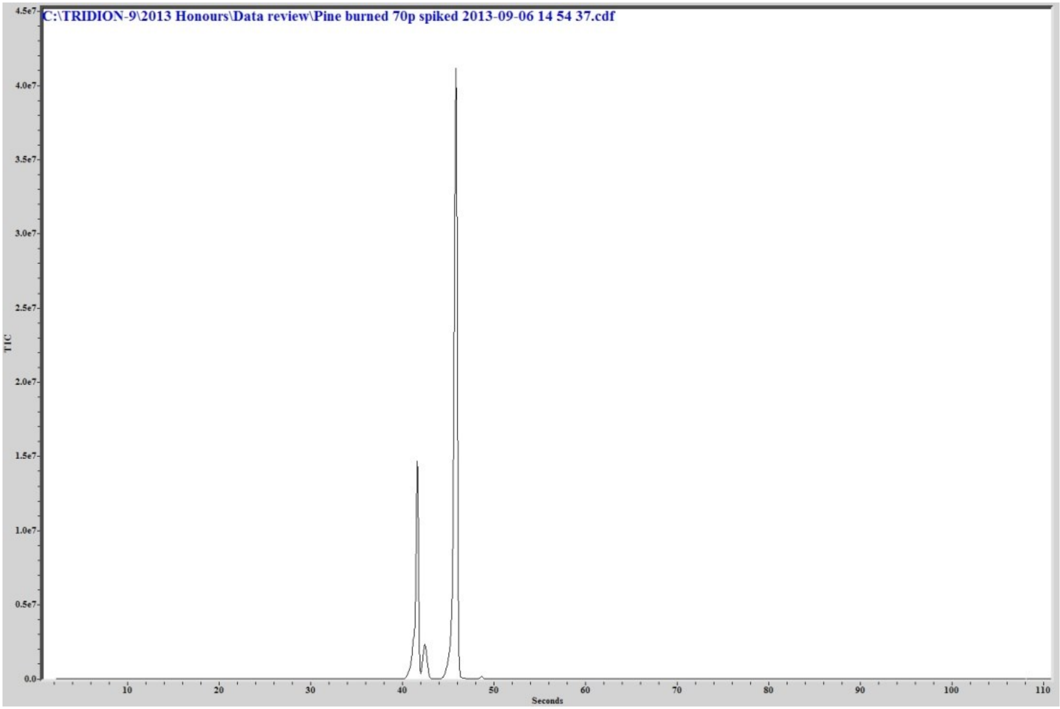


Figure 62: Burned pine spiked with 70% weathered petroleum sample chromatogram.

Table 22: Burned polyurethane spiked with 70% weathered petroleum – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	70% weathered unleaded petroleum (0.1 μL)
Chromatogram elution range	C_6 to C_{11}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene
Pyrolysis products identified	None
Conclusion	Petroleum possibly present. Laboratory confirmation required.
Chromatogram	See Figure 63.

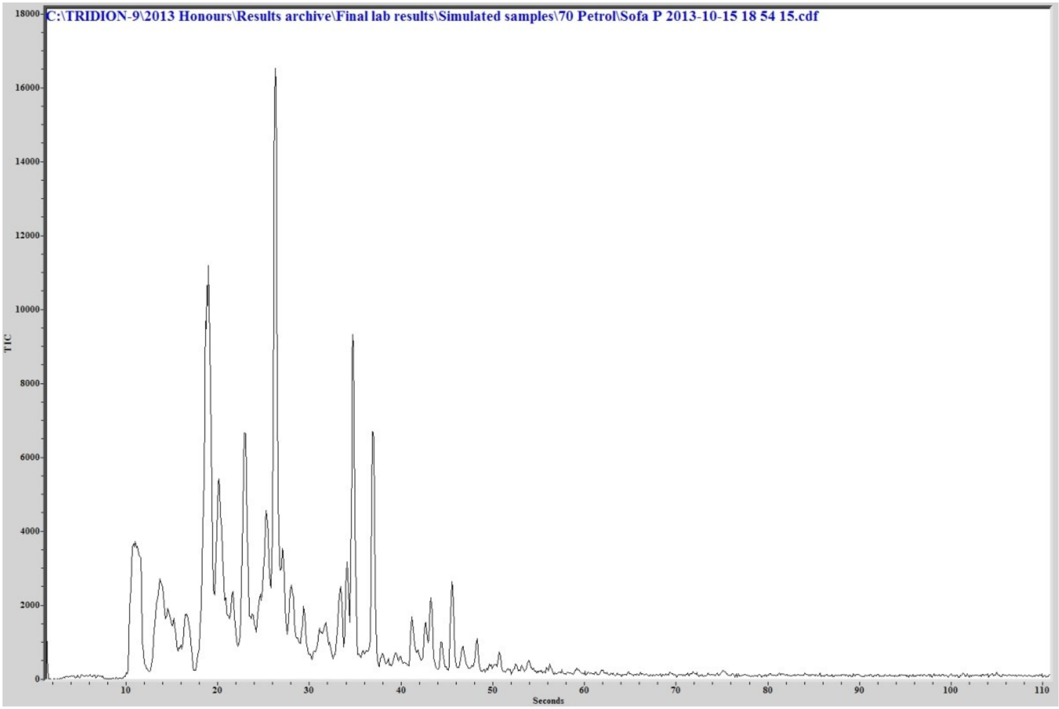


Figure 63: Burned polyurethane spiked with 70% weathered petroleum sample chromatogram.

G4: Substrates spiked with 70% weathered petroleum (discussion)

Some 70% weathered samples could immediately be identified as containing petroleum due to highly abundant C_2 and C_3 alkylbenzene peak patterns. Residues isolated from nylon carpet, polypropylene carpet, rubber underlay and foam underlay were all identified in this manner. The residue identification from the wool carpet was hindered by the presence of styrene as a pyrolysis product, which masked o-xylene. O-xylene could be located within the styrene peak by mass spectral analysis.

Peak patterns were similarly disrupted in samples from the rubber underlay. Limonene obscured 1,2,3-trimethylbenzene and, unlike o-xylene, the mass spectrum of trimethylbenzene was too similar to that of limonene. 1,2,3-Trimethylbenzene could not be identified as a result. M-/p-xylene was also a pyrolysis product in the rubber underlay, as well as a target compound. This resulted in a much larger m-/p-xylene compound peak than was expected.

Target compounds in other samples were relatively unaffected by interferents. Despite this, a residue could not be positively identified in the polyurethane due to the expected peak ratio between m-/p-ethyltoluene and 1,3,5-trimethylbenzene being reversed. A benzaldehyde pyrolysis product contributed to this. Nevertheless, due to the number of target compounds identified, a petroleum product was still suspected of being present. This sample required laboratory confirmation.

As was the case with neat petroleum samples, higher molecular weight target compounds were not detected in most 70% weathered samples. Chromatograms returned to baseline after the elution of naphthalene. However, diagnostic peak patterns before this point provided enough information to detect ILR. Five of seven samples spiked with 70% weathered petroleum were positively identified. One sample was thought to contain petroleum residues, but required confirmation. The pine sample produced a negative result due to saturation by terpene compounds.

G5: Substrates spiked with 90% weathered petroleum (results)

Table 23: Burned nylon carpet spiked with 90% weathered petroleum – analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 μL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene 1,2,4,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Petroleum possibly present. Laboratory confirmation required.
Chromatogram	See Figure 64.

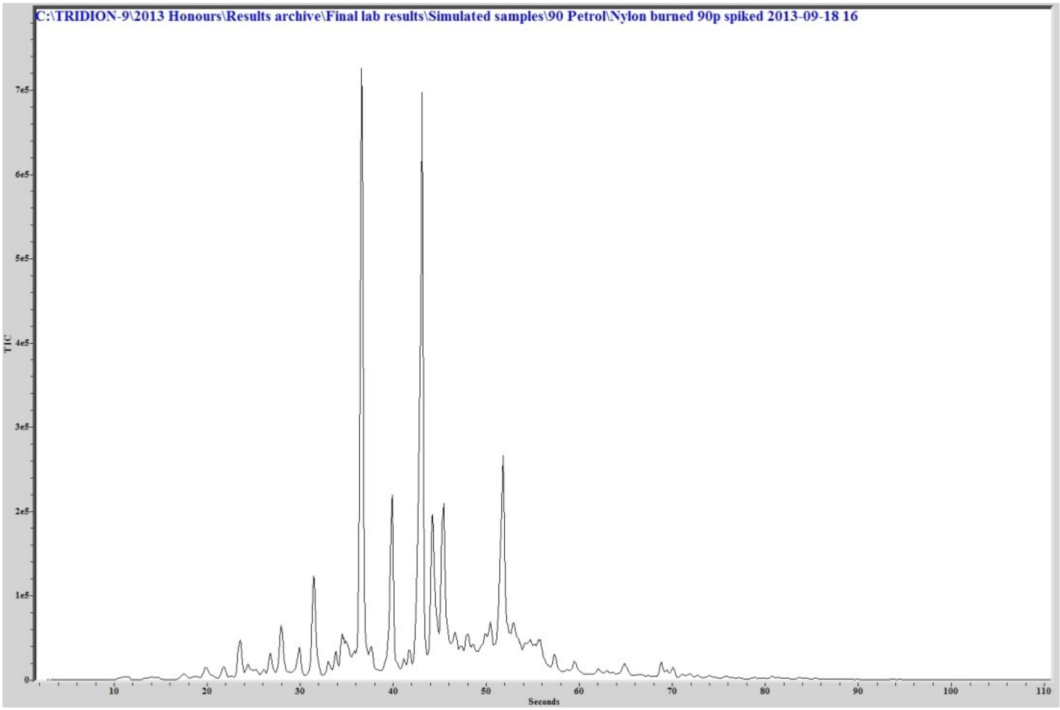


Figure 64: Burned nylon carpet spiked with 90% weathered petroleum sample chromatogram.

Table 24: Burned polypropylene carpet spiked with 90% weathered petroleum – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene Propylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 65.

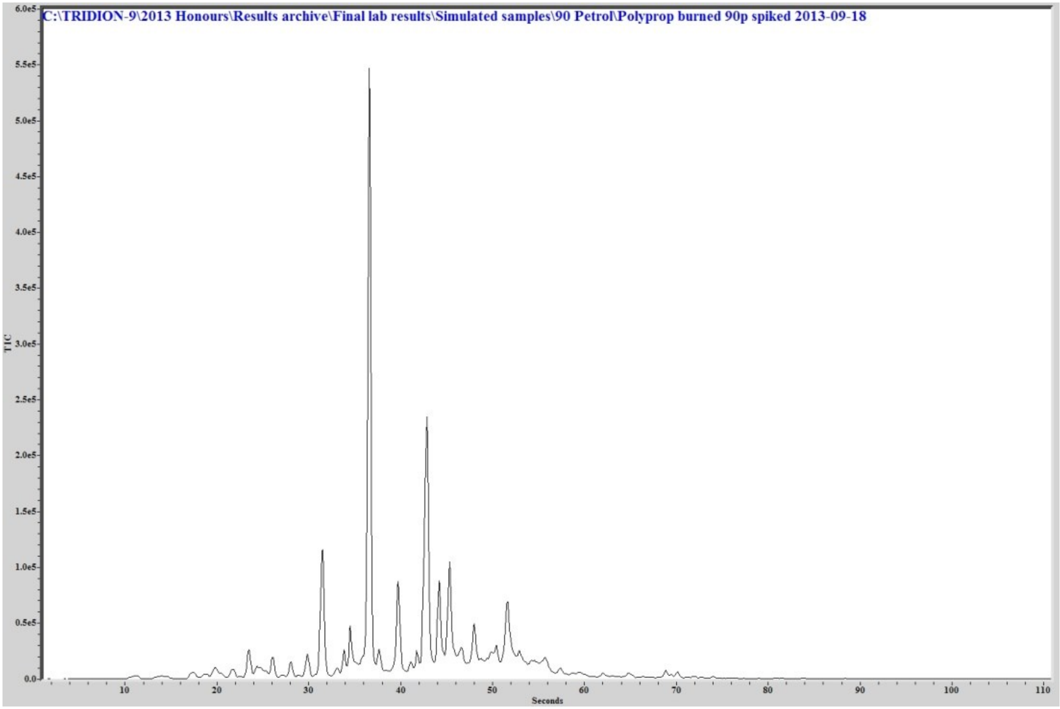


Figure 65: Burned polypropylene carpet spiked with 90% weathered petroleum sample chromatogram.

Table 25: Burned wool carpet spiked with 90% weathered petroleum – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 66.

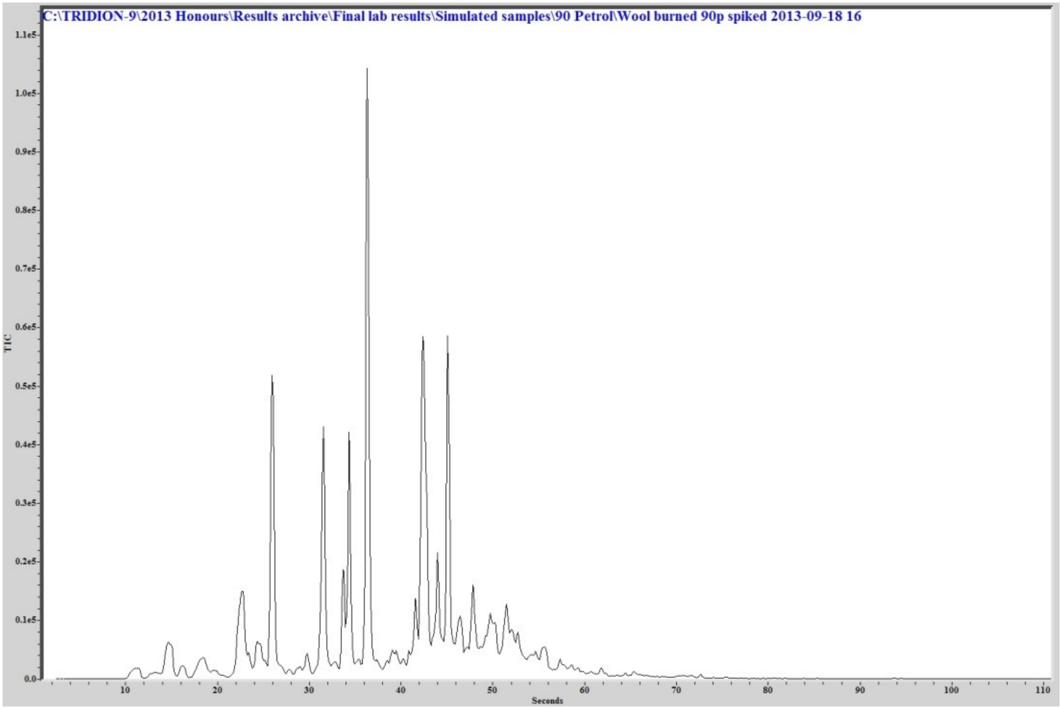


Figure 66: Burned wool carpet spiked with 90% weathered petroleum sample chromatogram.

Table 26: Rubber carpet underlay spiked with 90% weathered petroleum – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,4,5-tetramethylbenzene Naphthalene 2-methylnaphthalene
Pyrolysis products identified	Styrene Limonene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 67.

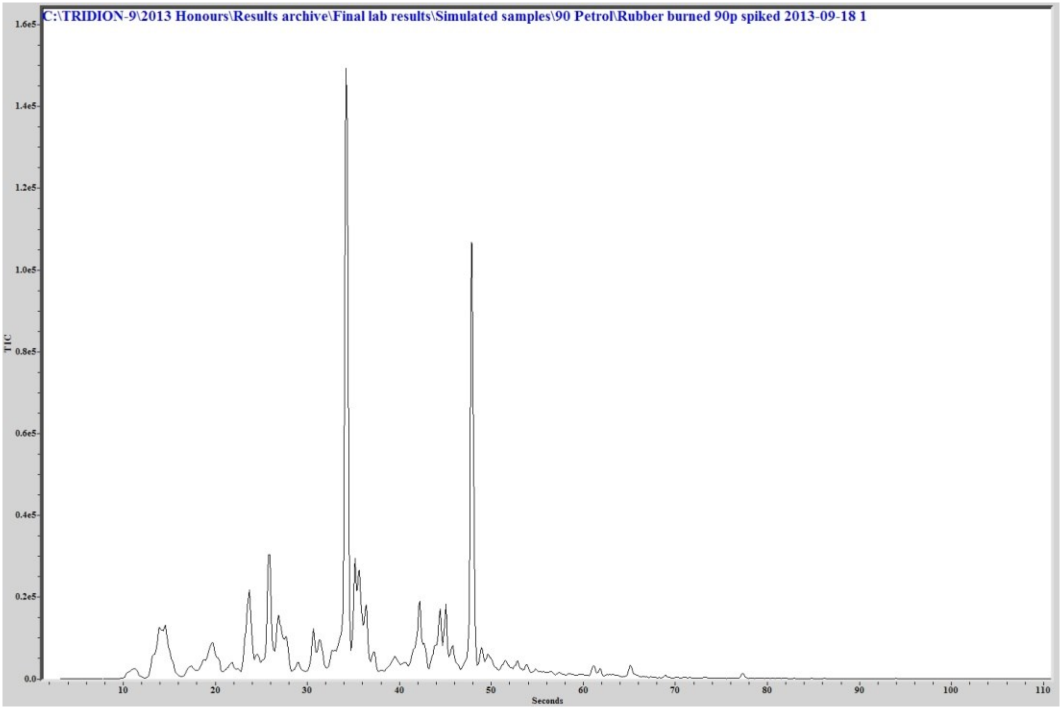


Figure 67: Burned rubber underlay spiked with 90% weathered petroleum sample chromatogram.

Table 27: Burned foam carpet underlay spiked with 90% weathered petroleum – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 68.

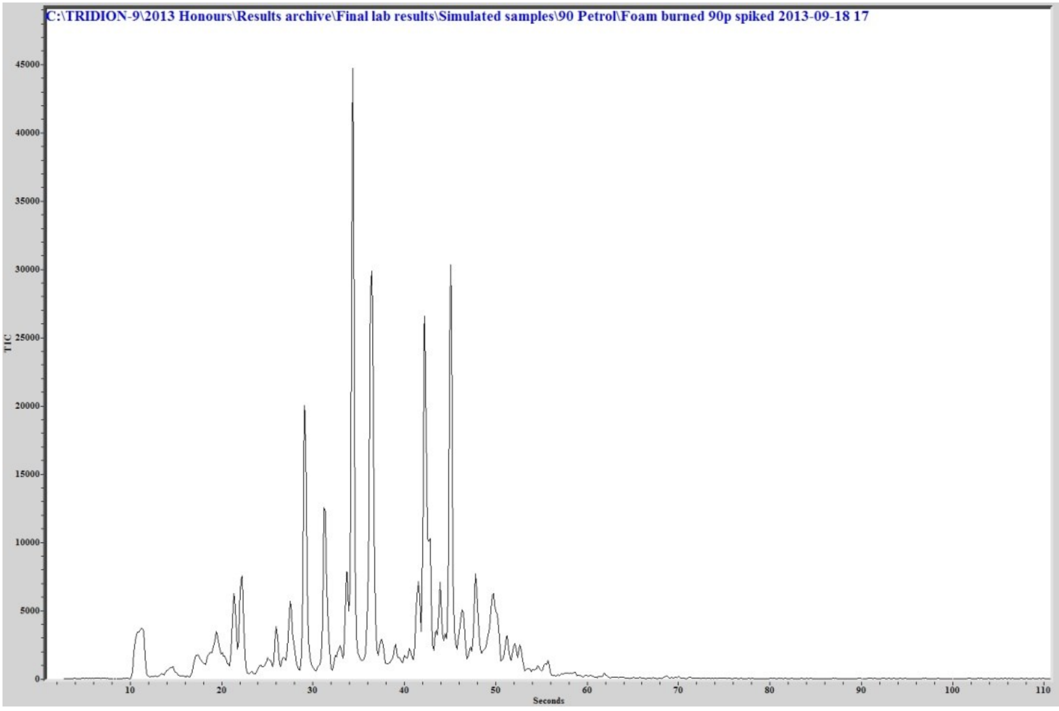


Figure 68: Burned foam carpet underlay spiked with 90% weathered petroleum sample chromatogram.

Table 28: Burned pine spiked with 90% weathered petroleum – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_9 to C_{13}
Peak distribution	Narrow
Dominant ion profile	Monoterpene
Target compounds identified	None
Pyrolysis products identified	a-pinene Camphene b-pinene Limonene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 69.

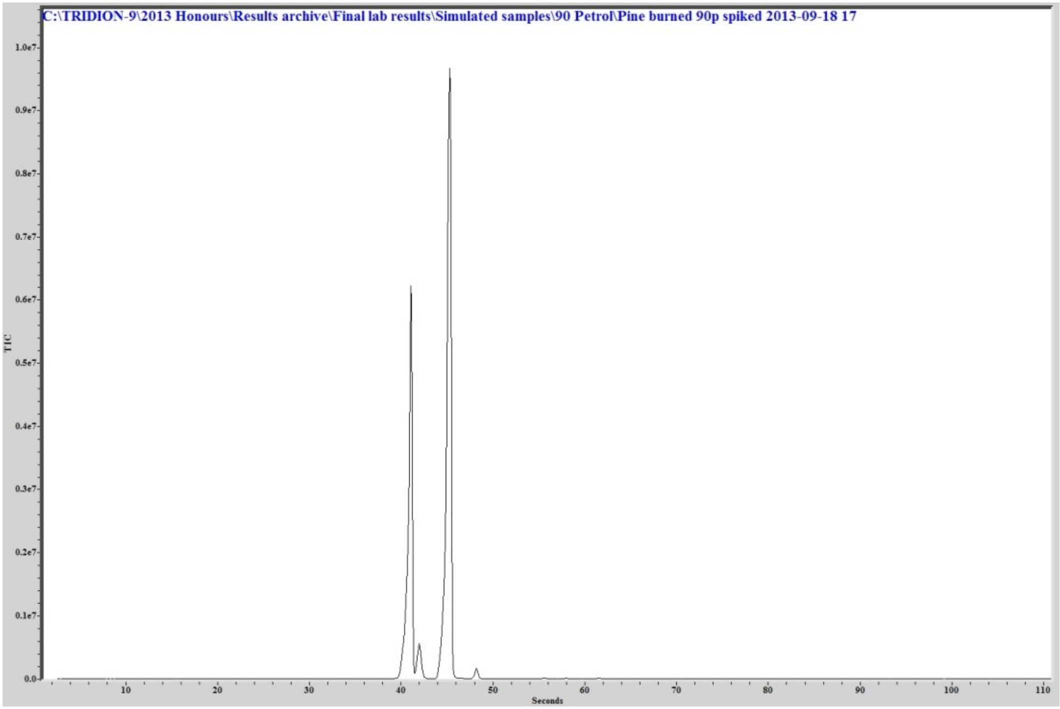


Figure 69: Burned pine spiked with 90% weathered petroleum.

Table 29: Burned polyurethane spiked with 90% weathered petroleum – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	90% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 70.

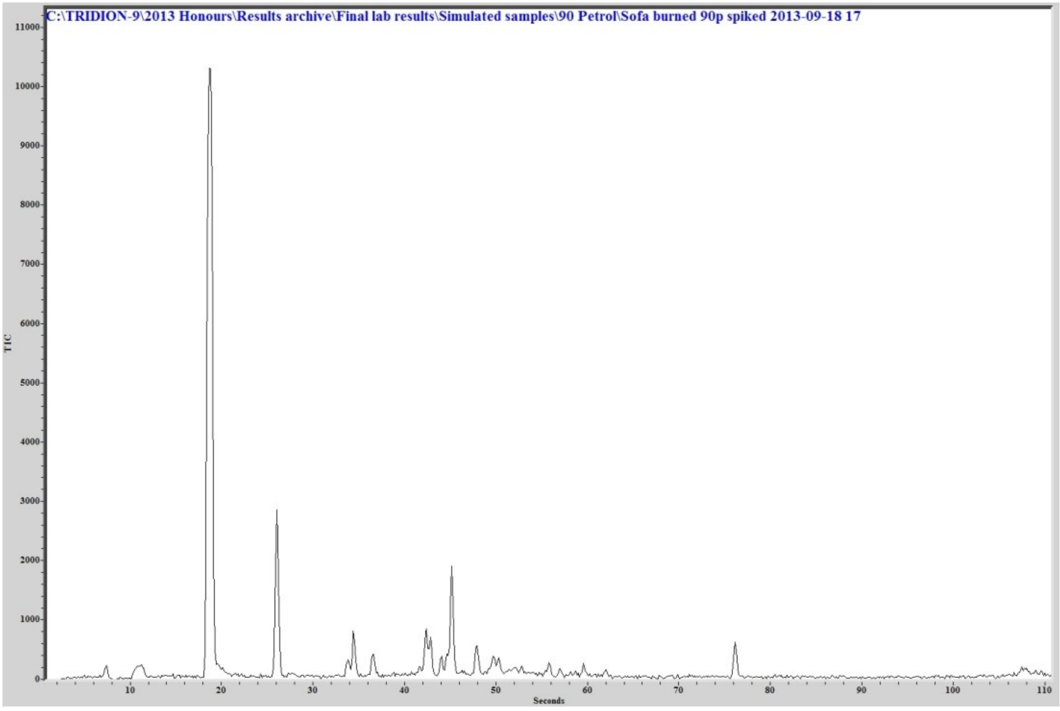


Figure 70: Burned polyurethane spiked with 90% weathered petroleum sample chromatogram.

G6: Substrates spiked with 90% weathered petroleum (discussion)

Pyrolysis product interference was more noticeable in 90% weathered petroleum samples because peak patterns which were typically highly abundant in less weathered petroleum (toluene, C_2 and C_3 alkylbenzenes) were now diminished. Simulated nylon and polypropylene carpet sample chromatograms, for example, looked identical to those from the burned substrates. Wool carpet samples, on the other hand, showed pyrolysis products from the wool in addition to clearly resolved peaks of interest. EIP was necessary in most cases to obtain sufficient detail for analysis.

Even using EIP, pyrolysis products (particularly benzaldehyde in carpet samples) disrupted the identification of some target compounds. Benzaldehyde co-eluted with m-/p-ethyltoluene and 1,3,5-trimethylbenzene. The high abundance of ion 105 in benzaldehyde skewed the mass spectra of m-/p-ethyltoluene and 1,3,5-triemthylbenzene. Neither compound could be identified in any carpet sample spiked with 90% weathered petroleum. Styrene was also abundant and co-eluted with o-xylene. These pyrolysis products prevented the positive identification of petroleum in nylon carpet samples. Other target compounds were still present, warranting laboratory analysis of the sample.

Toluene and C_2 alkylbenzenes were detectable in all samples, except for pine. This was not expected based on the 90% weathered standard, which had little toluene content and significantly diminished C_2 alkylbenzene peaks. Instead, samples displayed relatively equal levels of toluene and C_2 alkylbenzenes which were often more abundant than the C_3 alkylbenzenes. Peak group intensity of this kind was more typical of 70% weathered petroleum. It was assumed that toluene and C_2 alkylbenzene pyrolysis products artificially boosted these compound peaks.

In total, five samples spiked with 90% weathered petroleum were found to contain a petroleum residue. One sample was inconclusively identified and no ILR was detected in the pine sample. As pyrolysis products rendered some target compounds obsolete, residue identification was based mainly on individual peak ratios within diagnostic peak groups.

G7: Substrates spiked with 97% weathered petroleum (results)

Table 30: Nylon carpet spiked with 97% weathered petroleum – analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{15}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene Propylbenzene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthlane 1,3-dimethylnaphthalene 2,3-dimethylnapthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 71.

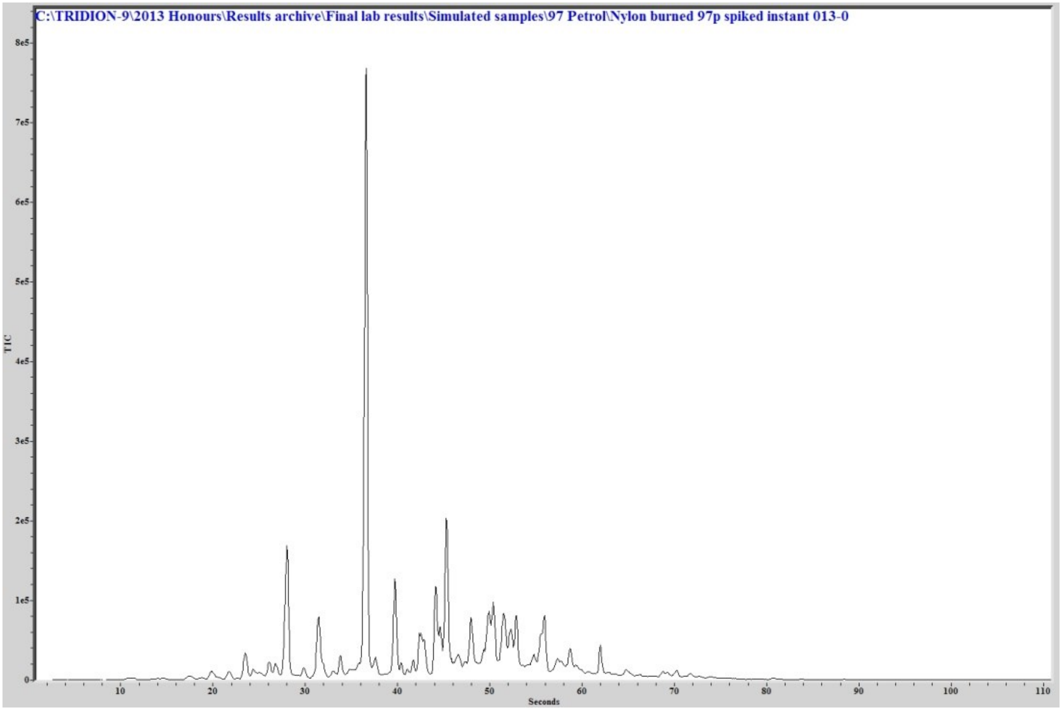


Figure 71: Burned nylon carpet spiked with 97% weathered petroleum sample chromatogram.

Table 31: Burned polypropylene carpet spiked with 97% weathered petroleum – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane Naphthalene 2-methylnapthalene 1-methylnapthalene 1,3-dimethylnapthalene 2,3-dimethylnapthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 72.

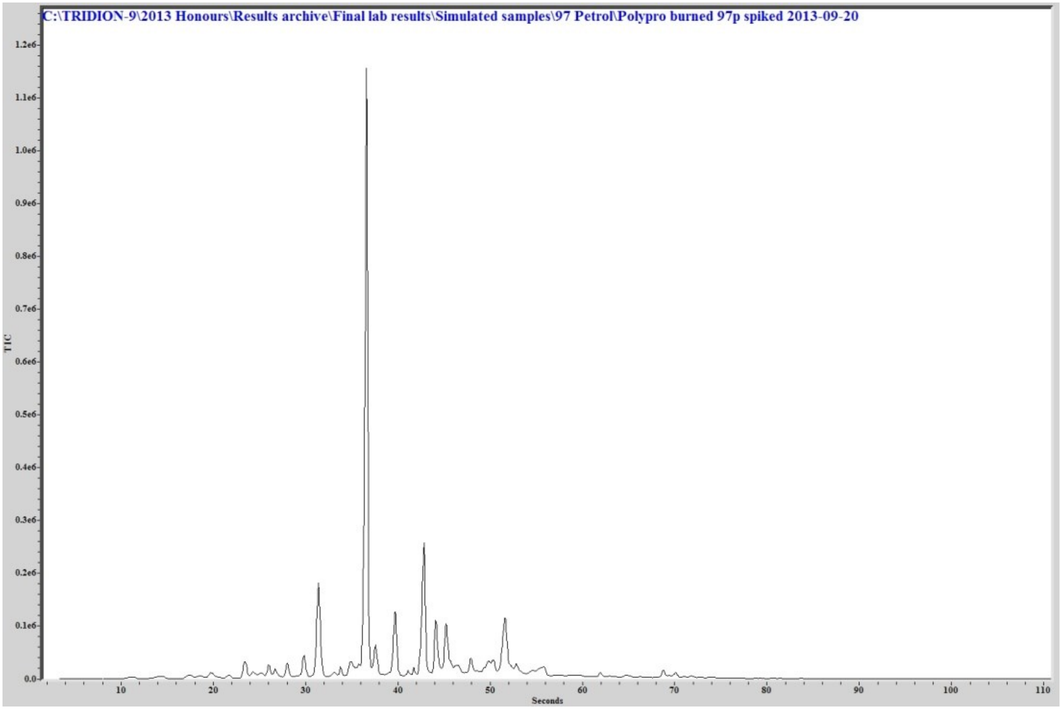


Figure 72: Burned polypropylene carpet spiked with 97% weathered petroleum sample chromatogram.

Table 32: Burned wool carpet spiked with 97% weathered petroleum – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 μL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene Propylbenzene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane Naphthalene 2-methylnapthalene 1-methylnapthalene 1,3-dimethylnapthalene 2,3-dimethylnapthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 73.

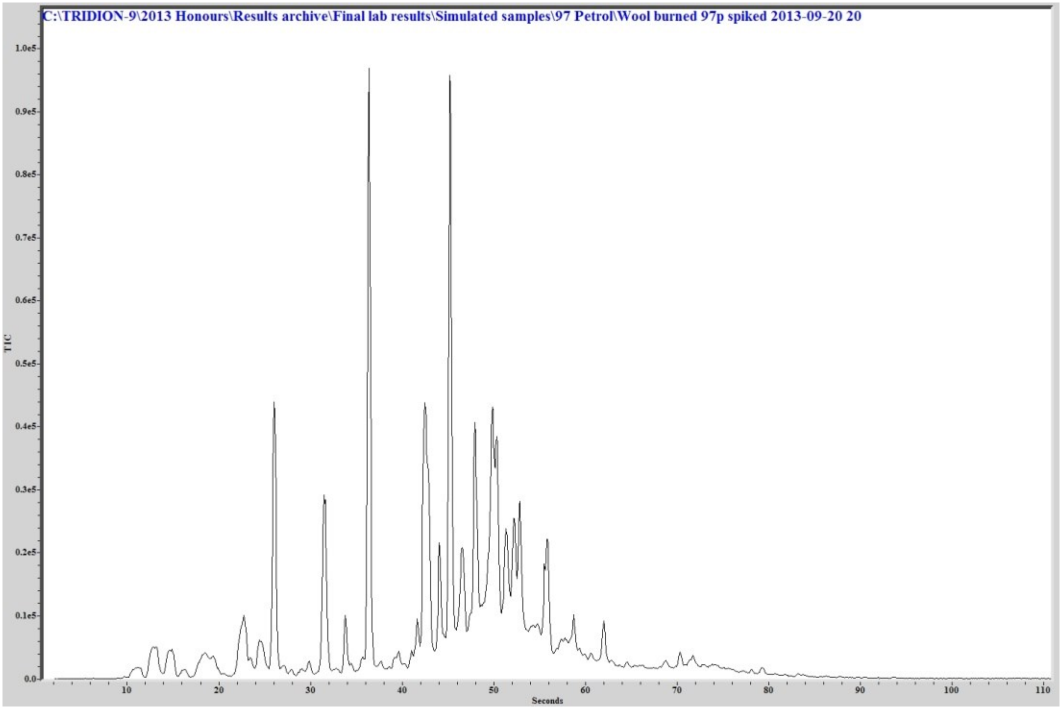


Figure 73: Burned wool spiked with 97% weathered petroleum sample chromatogram.

Table 33: Burned rubber carpet underlay spiked with 97% weathered petroleum – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene m-/p-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Indane Naphthalene 2-methylnaphthalene 1-methylnaphthalene 2,3-dimethylnaphthalene
Pyrolysis products identified	Limonene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 74.

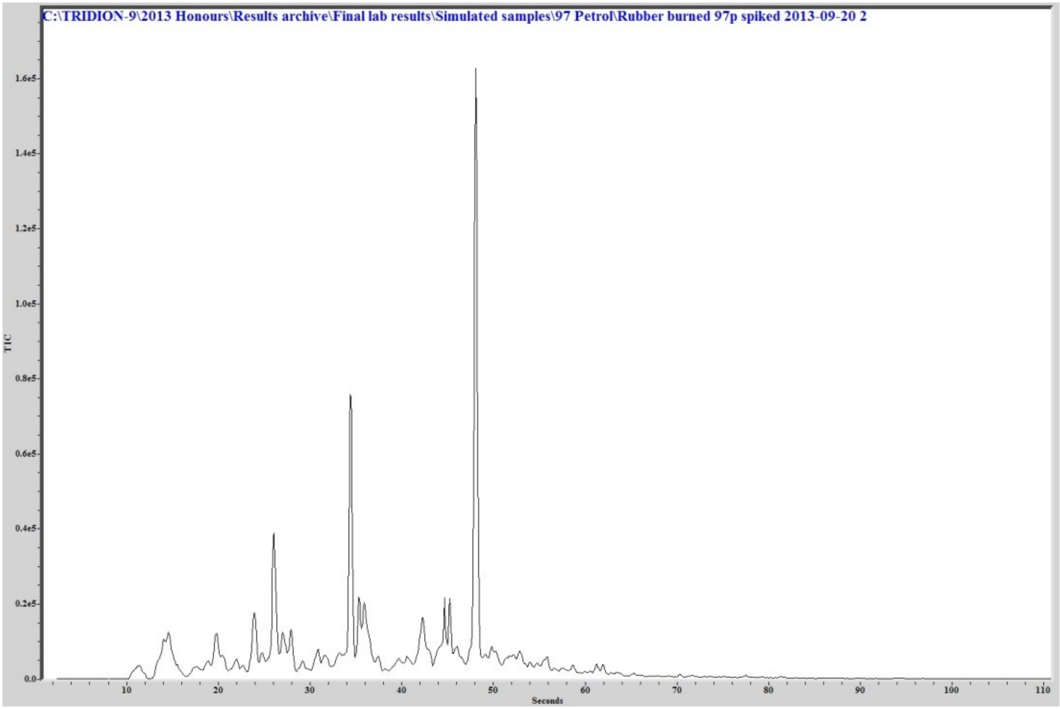


Figure 74: Burned rubber carpet underlay spiked with 97% weathered petroleum sample chromatogram.

Table 34: Burned foam carpet underlay spiked with 97% weathered petroleum – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains petroleum residues.
Chromatogram	See Figure 75.

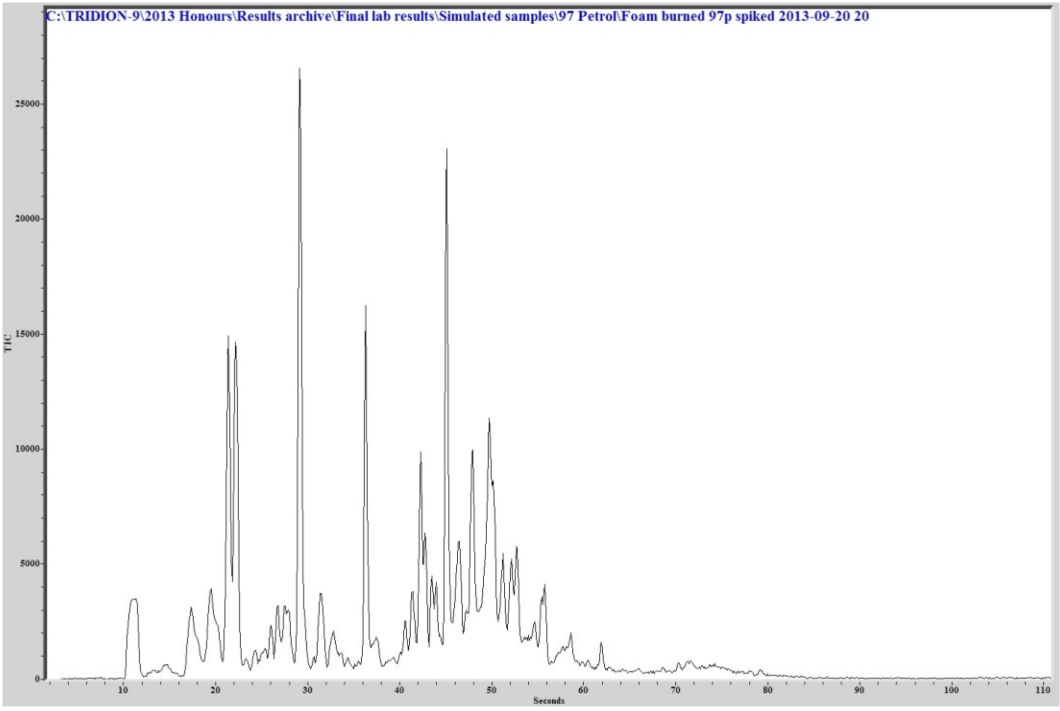


Figure 75: Burned foam carpet underlay spiked with 97% weathered petroleum sample chromatogram.

Table 35: Burned pine spiked with 97% weathered petroleum – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_9 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	Toluene m-/p-xylene o-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene 2-methylnapthalene 1-methylnapthalene 2,3-dimethylnapthalene
Pyrolysis products identified	α-pinene Camphene β-pinene Limonene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 76.

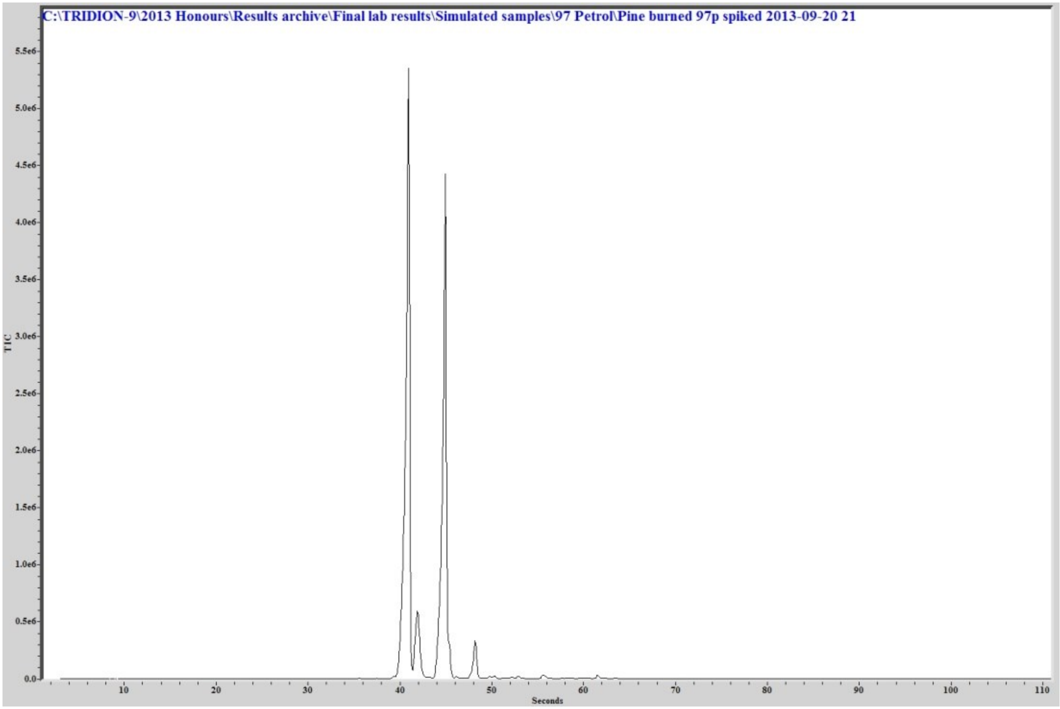


Figure 76: Burned pine spiked with 97% weathered petroleum sample chromatogram.

Table 36: Burned polyurethane spiked with 97% weathered petroleum – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	97% weathered unleaded petroleum (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene 2-methylnapthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 77.

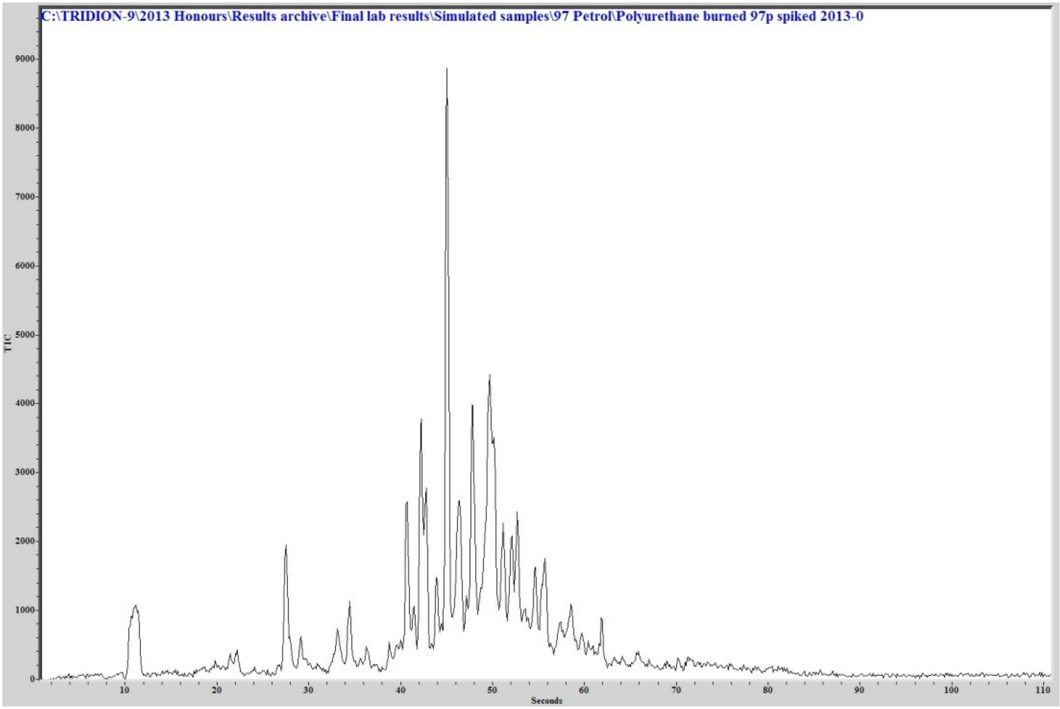


Figure 77: Burned polyurethane spiked with 97% weathered petroleum sample chromatogram.

G8: Substrates spiked with 97% weathered petroleum (discussion)

Unlike previous weathered petroleum samples, 97% weathered petroleum did not contain toluene or any C_2 alkylbenzenes. This eliminated an important diagnostic feature. More emphasis was placed on the identification of C_3 alkylbenzenes and later eluting compounds. The peak groups which were most useful for residue identification were dependant on the sample. Nylon carpet, for example, contained high concentrations of C_3 alkylbenzenes which could be differentiated from the substrate matrix. This was not possible with polypropylene samples due to high levels of benzaldehyde. In this case, the presence of C_4 alkylbenzenes and polynuclear aromatics was more diagnostically useful.

Rubber carpet underlay residue identification followed a similar process. The presence of toluene, m-/p-xylene and m-/p-ethyltoluene was meaningless in the rubber sample as these were substrate pyrolysis products. However, the shoulder on the m-/p-ethyltoluene peak representing 1,3,5-trimethylbenzene and the presence of 1,2,4-trimethylbenzene were useful petroleum residue indicators. The presence of naphthenic species was also useful. Foam underlay was simple to analyse as few pyrolysis products were present in the C_3 alkylbenzene range. Polyurethane pyrolysis products also provided little interference.

It is unclear why the spiked pine samples allowed for a positive identification of 97% weathered petroleum; this was the only pine sample in the research to yield a positive identification. In other simulated pine samples, it was not possible to resolve more than a single ion fragment of a target compound due to low concentrations and interference from pine background products. The 97% weathered sample, on the other hand, showed C_4 alkylbenzene target compounds as discrete peaks in the chromatogram (Figure 78). These samples were sampled several hours after the petroleum was deployed onto the burned pine. It is possible that a short equilibration time allowed more of the petroleum residues to be captured by the SPME fibre, avoiding competitive adsorption. In total, all seven simulated samples spiked with 97% weathered petroleum were found to contain petroleum.

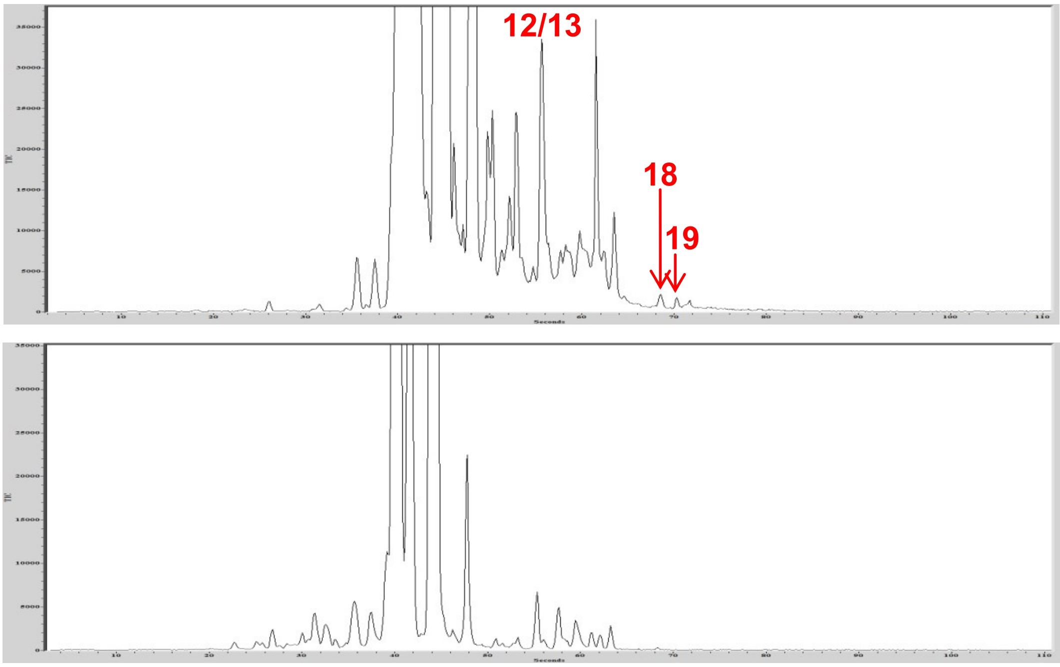


Figure 78: Target compounds visible in a sample of burned pine spiked with 97% weathered petroleum (top), compared with burned pine spiked with mineral turpentine (below). Target compounds are much more apparent in the weathered petroleum sample.

G9: Substrates spiked with diesel fuel (results)

Table 37: Burned nylon carpet spiked with diesel fuel – analysis summary.

Substrate	Nylon carpet
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 μL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Aromatic
Target compounds identified	Toluene Dodecane Naphthalene
Pyrolysis products identified	Styrene Benzaldehyde
Conclusion	Sample contains no ignitable liquid residue.
Chromatogram	See Figure 79.

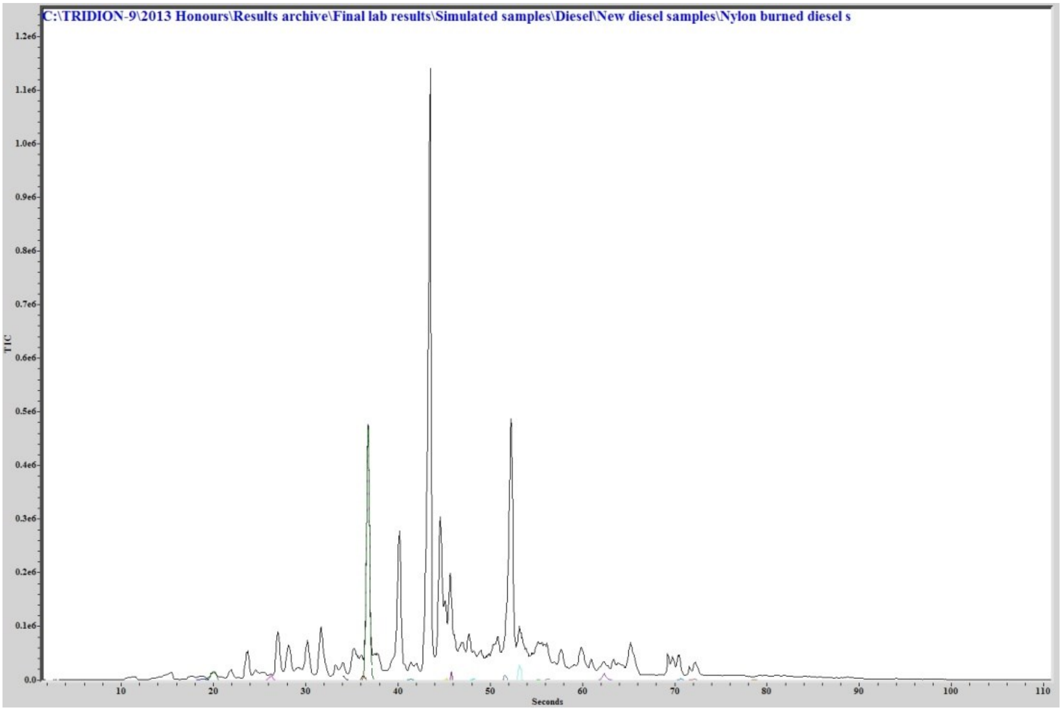


Figure 79: Burned nylon carpet spiked with diesel fuel sample chromatogram.

Table 38: Burned polypropylene carpet spiked with diesel fuel – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Decane Undecane Dodecane Tridecane Tetradecane Toluene Ethylbenzene m-/p-xylene Propylbenzene m-/p-ethyltoluene 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 80.

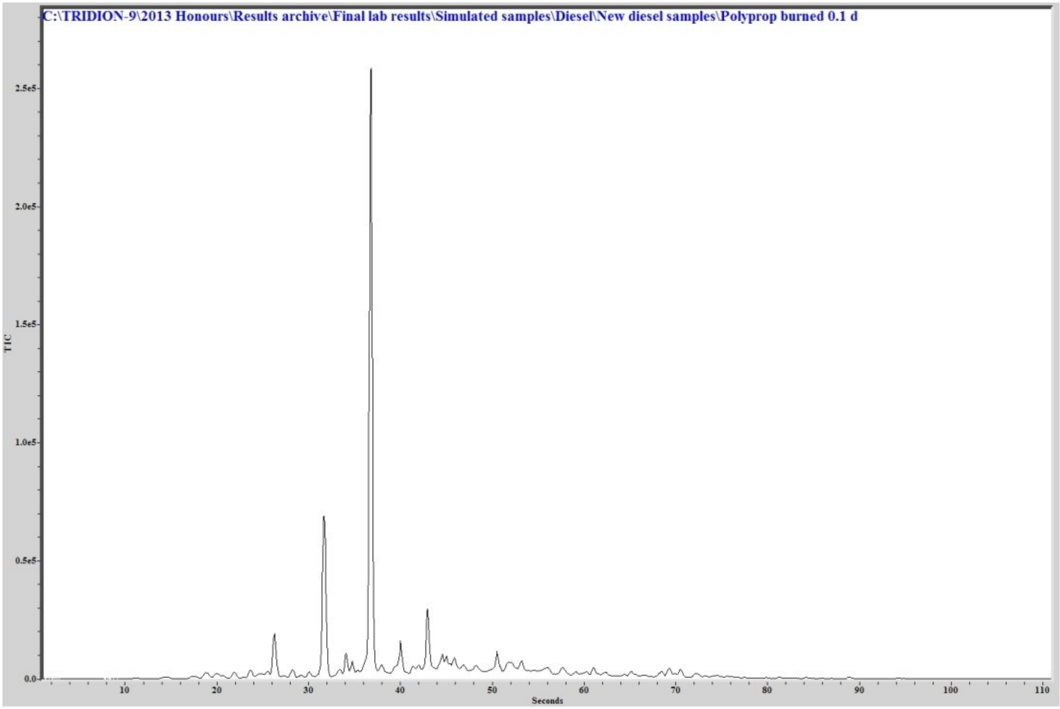


Figure 80: Burned polypropylene carpet spiked with diesel fuel sample chromatogram.

Table 39: Burned wool carpet spiked with diesel fuel – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 µL)
Chromatogram elution range	C_6 to C_{17}
Peak distribution	Broad
Dominant ion profile	Aromatic
Target compounds identified	Octane Nonane Decane Undecane Dodecane Tridecane Tetradecane Pentadecane Hexadecane Heptadecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene trans-decalin Naphthalene
Pyrolysis products identified	Styrene Benzaldehyde
Conclusion	Sample contains residues of a heavy petroleum distillate.
Chromatogram	See Figure 81.

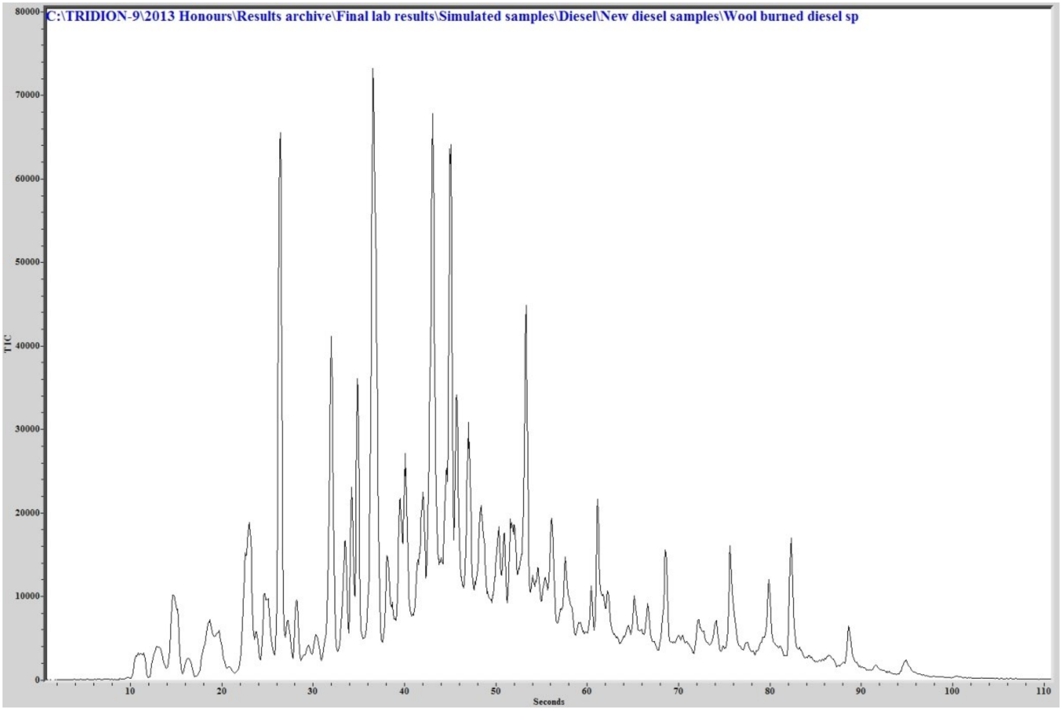


Figure 81: Burned wool spiked with diesel fuel sample chromatogram.

Table 40: Burned rubber carpet underlay spiked with diesel fuel – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 μL)
Chromatogram elution range	C_6 to C_{15}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	Undecane Dodecane Tridecane Tetradecane Toluene m-/p-xylene o-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3,5-tetramethylbenzene 2-methylnaphthalene 2,3-dimethylnaphthalene
Pyrolysis products identified	Limonene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 82.

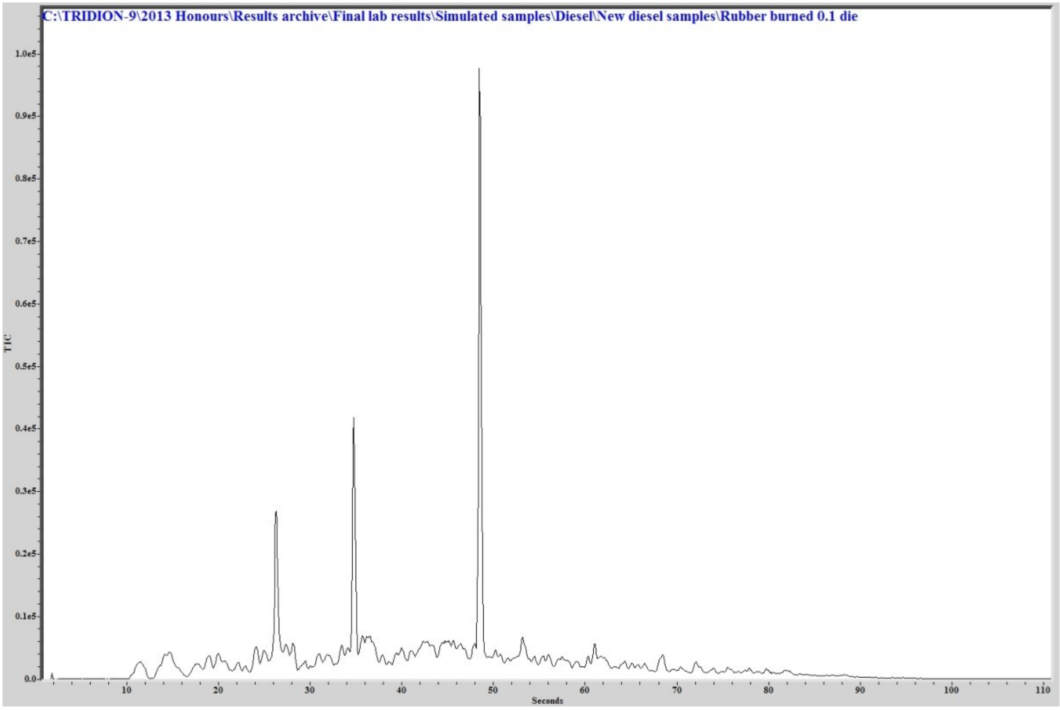


Figure 82: Burned rubber carpet underlay spiked with diesel fuel sample chromatogram.

Table 41: Burned foam underlay spiked with diesel fuel – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 μL)
Chromatogram elution range	C_6 to C_{17}
Peak distribution	Broad
Dominant ion profile	Alkane
Target compounds identified	Octane Nonane Decane Undecane Dodecane Tridecane Tetradecane Pentadecane Hexadecane Heptadecane Toluene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Trans-decalin Naphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of a heavy petroleum distillate.
Chromatogram	See Figure 83.

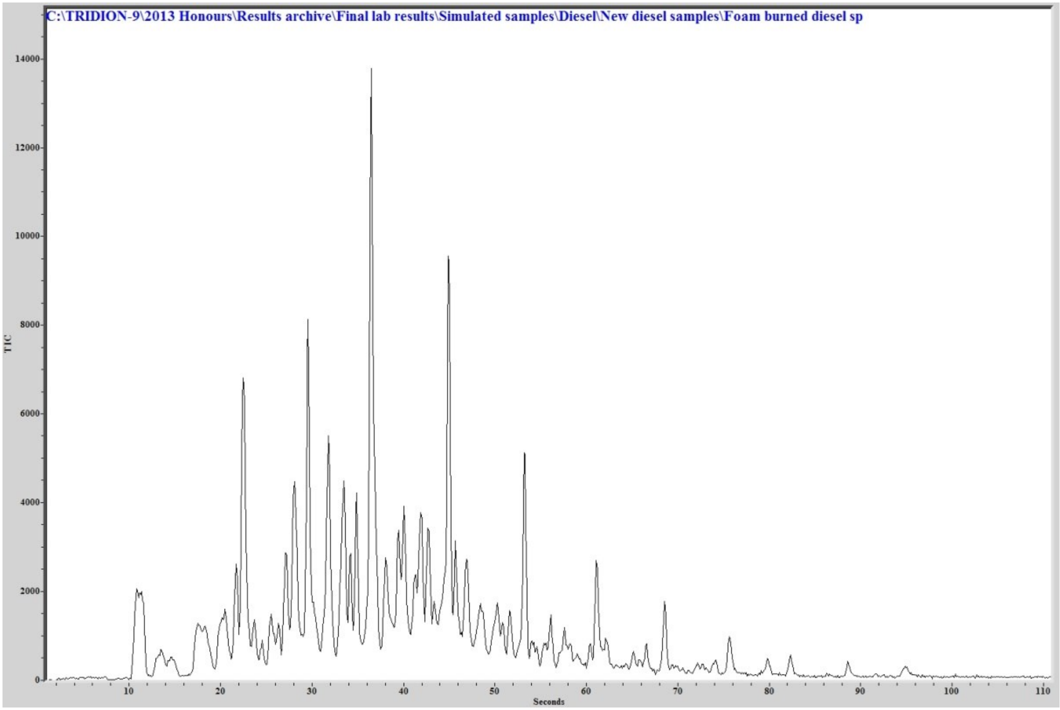


Figure 83: Burned foam carpet underlay spiked with diesel fuel sample chromatogram.

Table 42: Burned pine spiked with diesel fuel – sample chromatogram.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 μL)
Chromatogram elution range	C_9 to C_{13}
Peak distribution	Narrow
Dominant ion profile	Monoterpene
Target compounds identified	Toluene m-/p-xylene Trans-decalin Tetradecane Pentadecane Hexadecane
Pyrolysis products identified	α-pinene Camphene β-pinene Limonene
Conclusion	Heavy petroleum distillate possibly present. Laboratory confirmation required.
Chromatogram	See Figure 84.

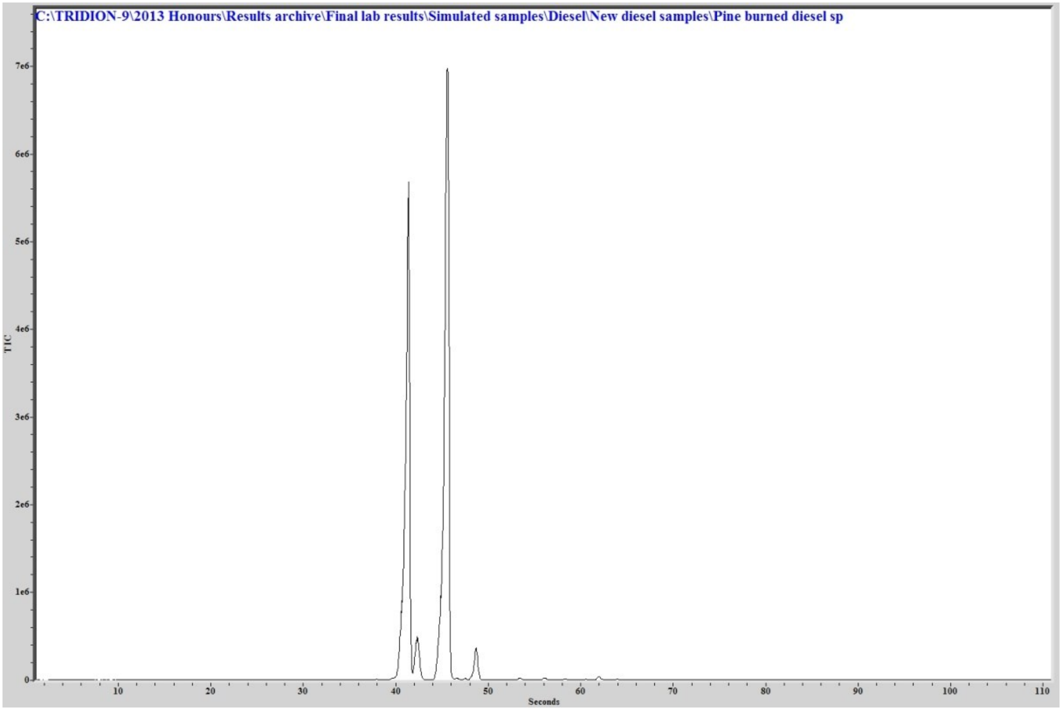


Figure 84: Burned pine spiked with diesel fuel sample chromatogram.

Table 43: Burned polyurethane spiked with diesel fuel – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	Diesel fuel (0.1 μL)
Chromatogram elution range	C_6 to C_{16}
Peak distribution	Broad
Dominant ion profile	Alkane
Target compounds identified	Nonane Decane Undecane Dodecane Tridecane Tetradecane Pentadecane Hexadecane Heptadecane Toluene m-/p-xylene o-xylene 1,2,4-trimethylbenzene Trans-decalin
Pyrolysis products identified	None
Conclusion	Sample contains residues of a heavy petroleum distillate.
Chromatogram	See Figure 85.

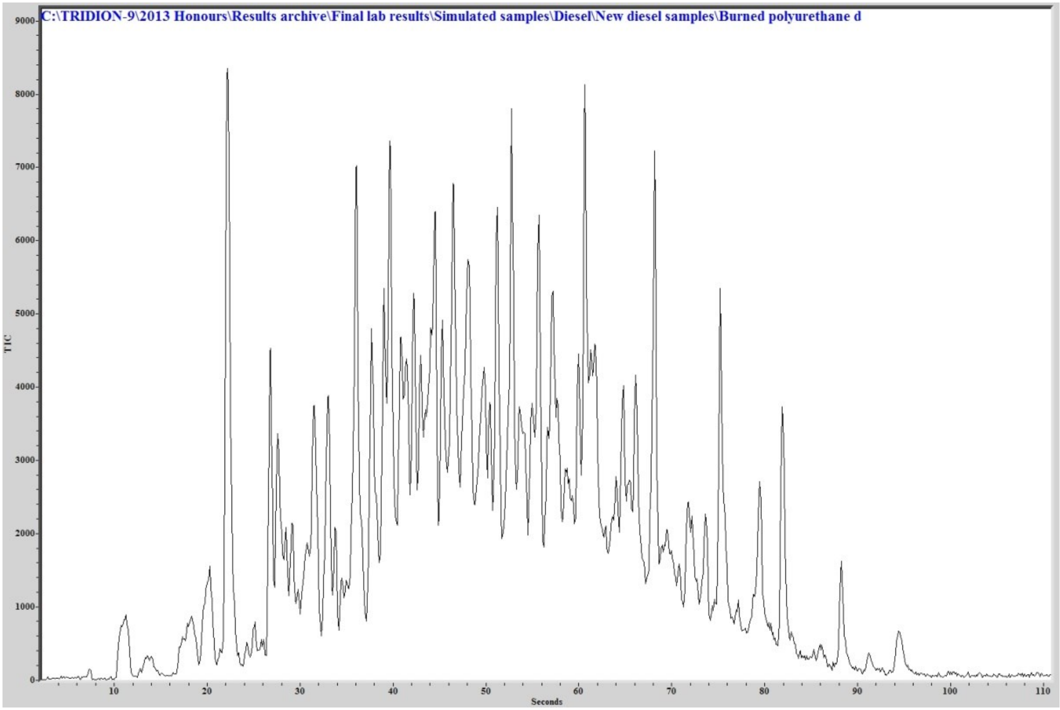


Figure 85: Burned polyurethane spiked with diesel fuel sample chromatogram.

G10: Substrates spiked with diesel fuel (discussion)

Only three of seven samples spiked with diesel fuel were correctly classified as containing an HPD. However, two of seven samples were determined to contain an MPD. In total, ILR of some kind was detected in five of seven samples. Identifications of an MPD are not incorrect. As these samples were still identified as containing a liquid residue, they would have definitely been forwarded to the laboratory for confirmatory analysis. Confirmatory analysis would have revealed that an HPD was actually present; therefore an incorrect presumptive identification at the scene achieves the same operational outcome as a more 'correct' result. It is important to realise that the TRIDION-9 is not intended to provide court-quality results at the scene. Rather, any strong indication of the presence of an ignitable liquid is desirable. The distinction between distillate residues at the scene is relatively arbitrary. Whether or not this classification is correct at the scene is ultimately irrelevant as it is the role of the laboratory to make that decision.

The pine samples provided indications that an HPD may be present as tetradecane, pentadecane and hexadecane were present in low concentrations. Laboratory analysis would have likely revealed a larger range of alkanes in the sample. One sample (nylon carpet) was negative for the presence of ILR, most likely due to competitive adsorption. Heating of this sample may have assisted in drawing more diesel fuel compounds out of the sample matrix.

Diesel fuel residue identification relied heavily on the presence of a Gaussian distribution of alkanes in the heavy distillate range. HPDs were detected in wool carpet, foam underlay and polyurethane. A consecutive range of at least five n-alkanes was detected in each of these samples, meeting E1618-10 criteria for HPD identification. EIPs of characteristic alkane ions (57, 71, 85) allowed alkanes to be counted effectively, as shown in Figure 86.

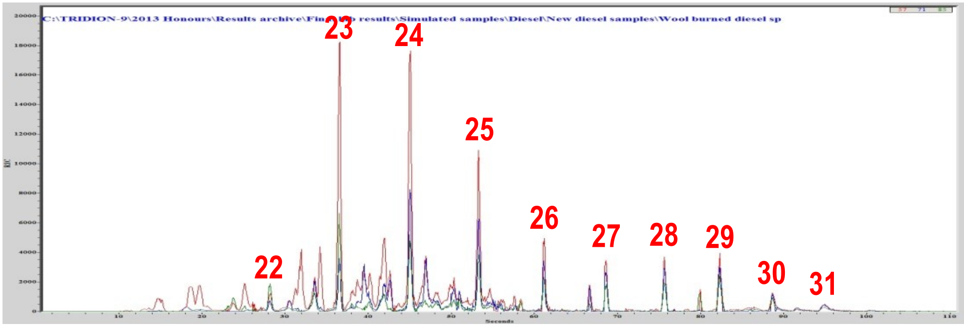


Figure 86: An EIP of alkane ions in a wool carpet sample spiked with diesel fuel.

Samples of polypropylene carpet and rubber underlay were classified as containing MPDs. This was because the heaviest alkane molecule detected was tetradecane, which lay at the upper edge of the MPD range. Moreover, in the rubber underlay sample, only four consecutive alkanes were identified, which was more typical of an MPD. In comparison, neat diesel fuel contained nine consecutive alkanes. Samples classed as MPDs generally contained lighter alkanes (those heavier than C_{15} were absent). Preferential SPME fibre adsorption may have caused this. Diesel fuel identification relies on heavy compounds for identification. However, these were also the most difficult compounds for the SPME fibre to capture, particularly given that the samples were kept at ambient temperature. Heating of samples during sampling may have been advantageous for heavy distillate detection but was considered impractical for field analysis purposes.

Three consecutive alkanes were present in pine. These alkanes were in the HPD range. Laboratory analysis of this sample was necessary to determine if other alkanes were present. Detection of such heavy alkane molecules in a pine sample with significant background interference is impressive. The nylon carpet samples yielded negative results. A negative result for pine was expected given similarly poor results obtained on this substrate. Only one alkane (dodecane) was reliably detected in the nylon sample. Styrene and benzaldehyde were the two most intense peaks in the nylon carpet chromatogram. Pyrolysis product overloading may have prevented the capture of heavier alkane compounds by the SPME fibre, resulting in the detection of only one alkane.

G11: Substrates spiked with kerosene (results)

Table 44: Burned nylon carpet spiked with kerosene - analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 µL)
Chromatogram elution range	C_7 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Nonane Decane Undecane Dodecane Tridecane Toluene m-/p-xylene Propylbenzene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene Naphthalene 1-methylnaphthalene 2-methylnaphthalene 1,3-dimethylnaphthalene 2,3-dimethylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 87.

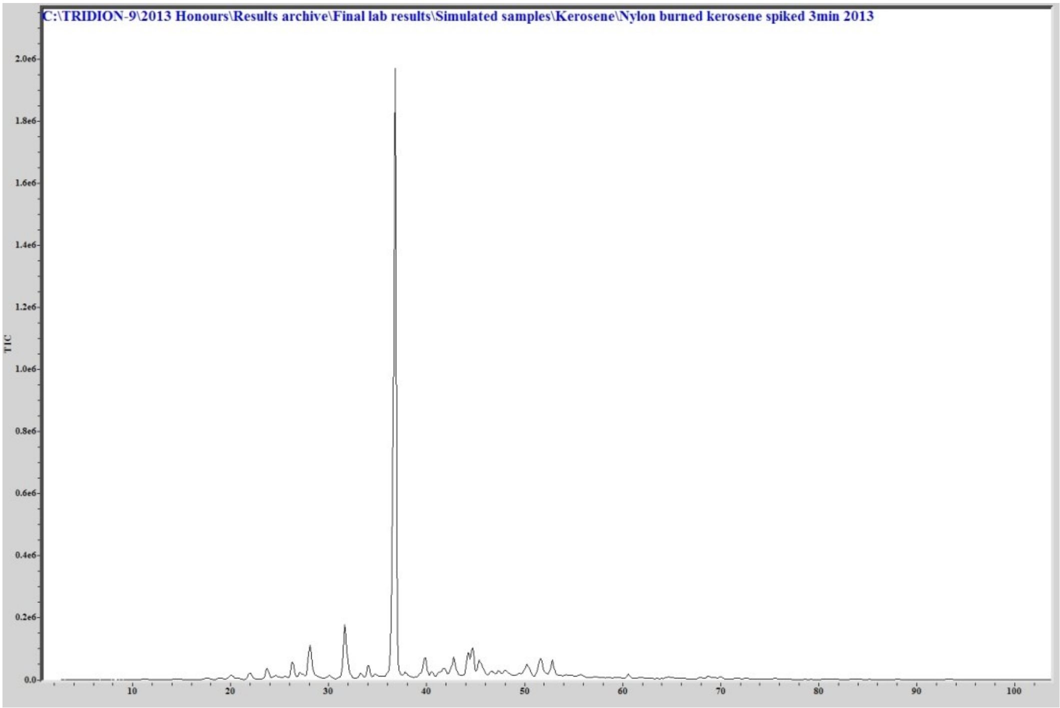


Figure 87: Burned nylon carpet spiked with kerosene sample chromatogram.

Table 45: Burned polypropylene carpet spiked with kerosene – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 µL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Octane Nonane Decane Undecane Dodecane Tridecane Toluene Ethylbenzene m-/p-xylene m-/p-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 88.

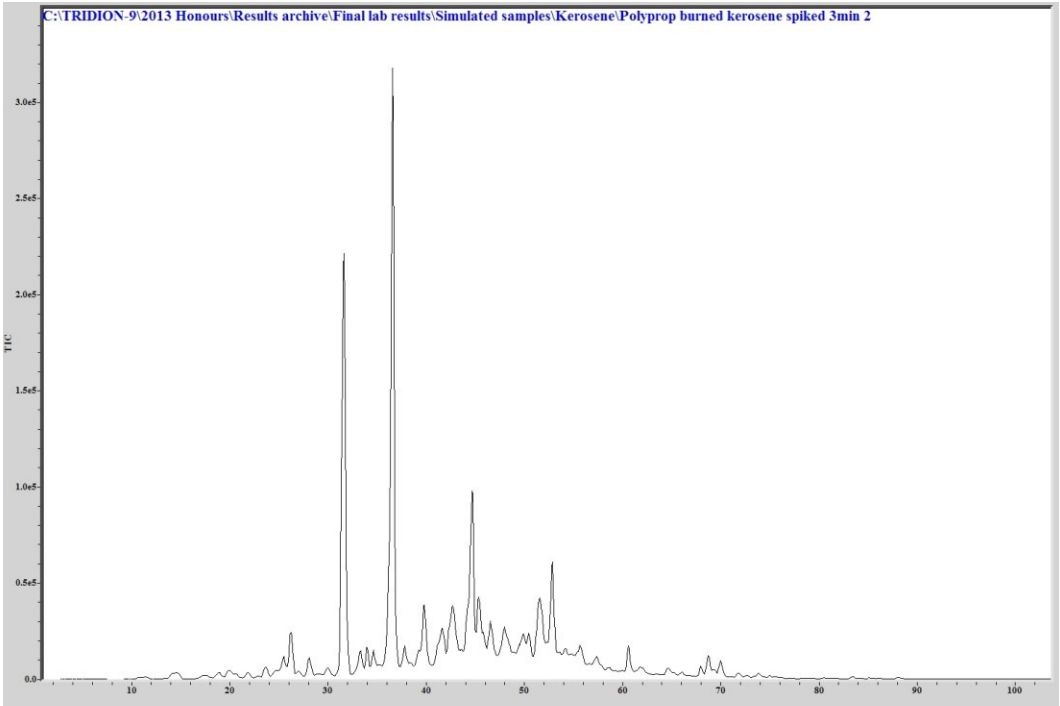


Figure 88: Burned polypropylene carpet spiked with kerosene sample chromatogram.

Table 46: Burned wool carpet spiked with kerosene – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Nonane Decane Undecane Dodecane Toluene Ethylbenzene m-/p-xylene Propylbenzene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene 2-methylnaphthalene 1-methylnaphthalene 1,3-dimethylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 89.

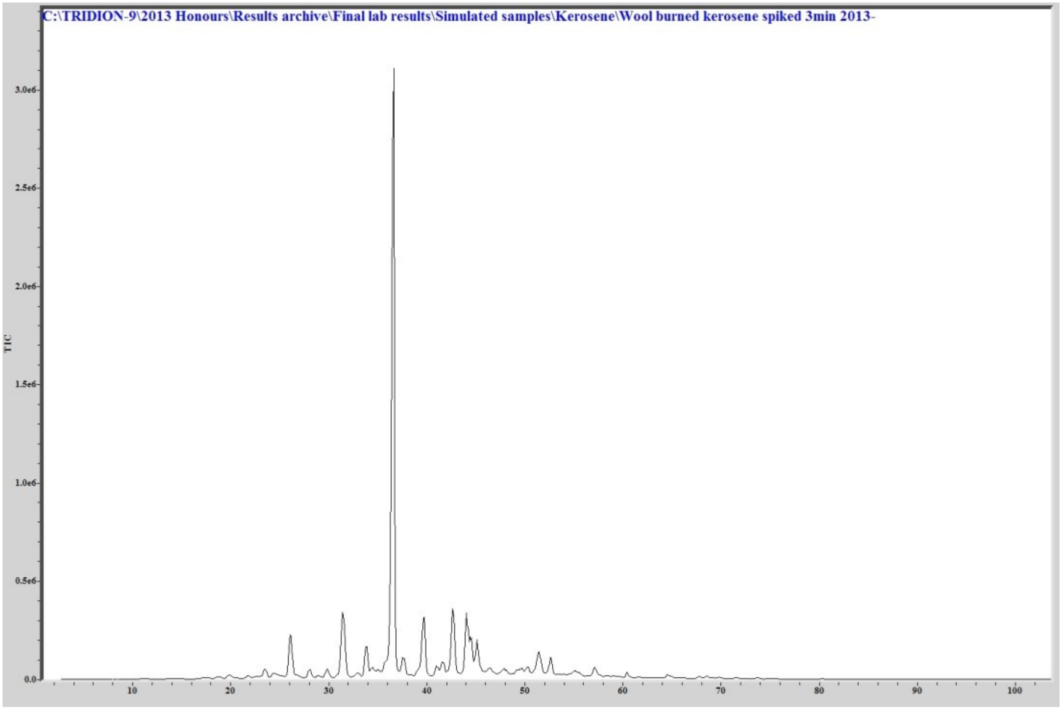


Figure 89: Burned wool carpet spiked with kerosene sample chromatogram.

Table 47: Burned rubber carpet underlay spiked with kerosene – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 μL)
Chromatogram elution range	C_5 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	Decane Undecane Dodecane Tridecane Tetradecane Toluene o-xylene m-/p-ethyltoluene o-ethyltoluene Naphthalene 1-methylnaphthalene 2-methylnaphthalene
Pyrolysis products identified	Limonene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 90.

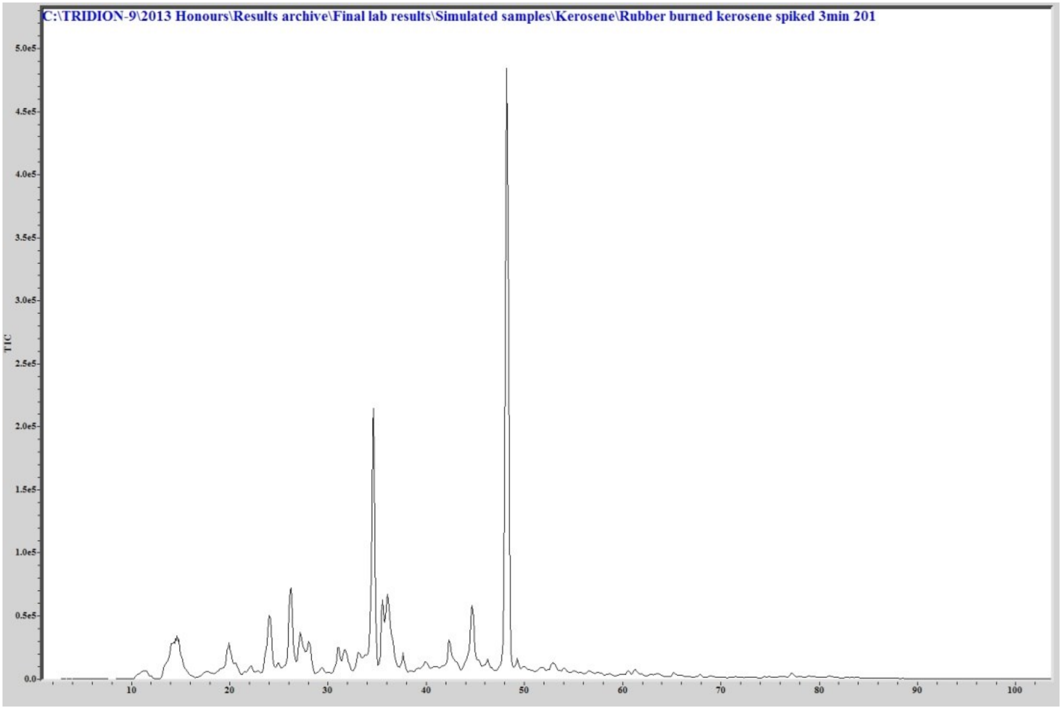


Figure 90: Burned rubber carpet underlay spiked with kerosene sample chromatogram.

Table 48: Burned foam carpet underlay spiked with kerosene – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate, Gaussian
Dominant ion profile	Alkylstyrene
Target compounds identified	Octane Nonane Decane Undecane Dodecane Tridecane Tetradecane Toluene Ethylbenzene m-/p-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-timethylbenzene trans-Decalin Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 91.

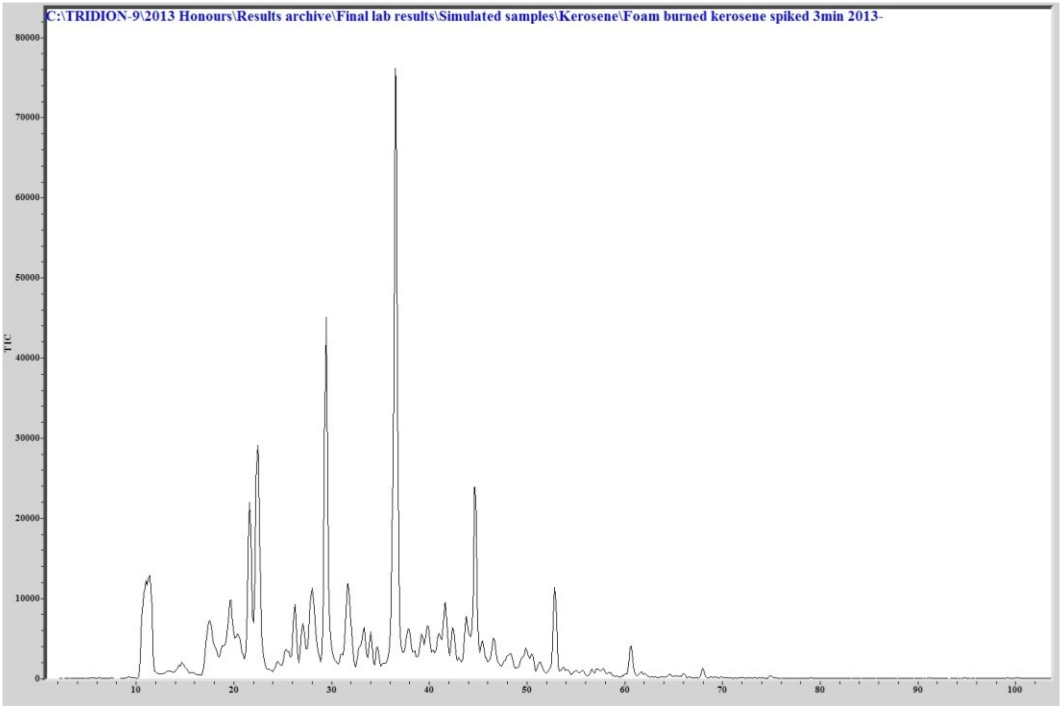


Figure 91: Burned foam underlay spiked with kerosene sample chromatogram.

Table 49: Burned pine spiked with kerosene – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	m-/p-ethyltoluene trans-Decalin
Pyrolysis products identified	α-pinene Camphene β-pinene Limonene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 92.

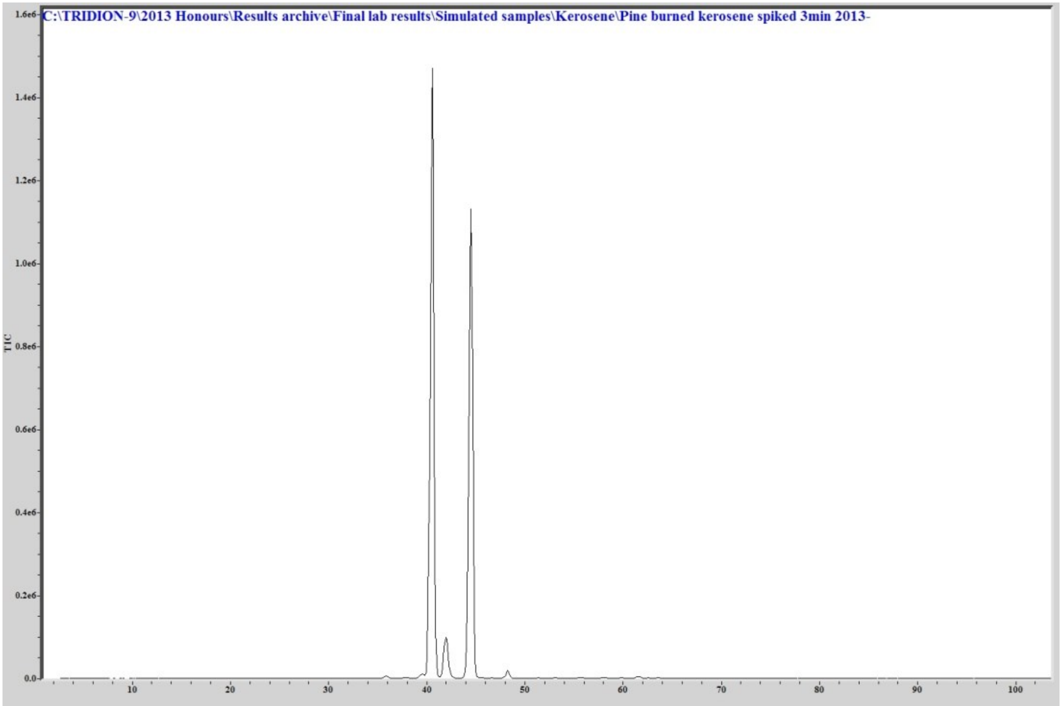


Figure 92: Burned pine spiked with kerosene sample chromatogram.

Table 50: Burned polyurethane spiked with kerosene – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (0.1 μL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene/alkane
Target compounds identified	Nonane Decane Undecane Dodecane Tridecane Tetradecane Toluene Ethylbenzene m-/p-xylene m-/p-ethyltoluene o-ethyltoluene 1,2,4-trimethylbenzene Naphthalene 2-methylnaphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 93.

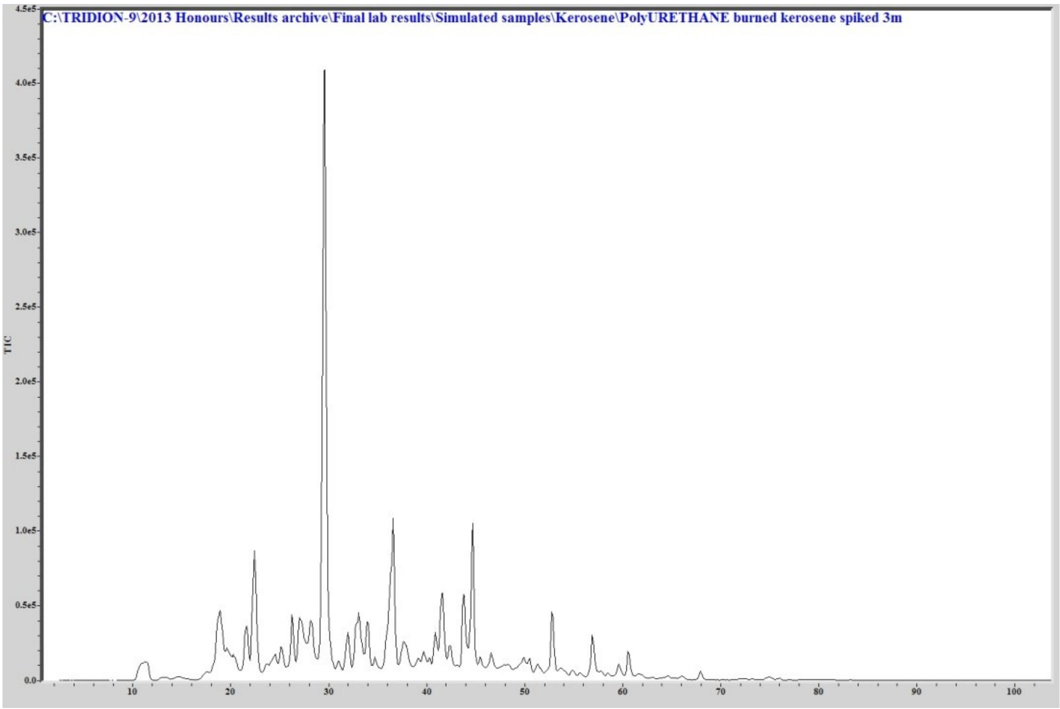


Figure 93: Burned polyurethane spiked with kerosene sample chromatogram.

G12: Substrates spiked with kerosene (discussion)

All simulated samples spiked with kerosene produced a positive result except for pine. The primary identification criterion was the presence of a Gaussian, unbroken chain of n-alkanes in the range of the kerosene standard. Problematically, the same range was rarely seen in the simulated samples. In most samples, the last identifiable alkane in sample data was dodecane or tridecane – two alkanes short of what was expected (Figure 94). The most likely explanations for this are selective fibre adsorption and/or competitive adsorption. Similar phenomena were observed in the analysis of diesel samples and operational samples spiked with kerosene.

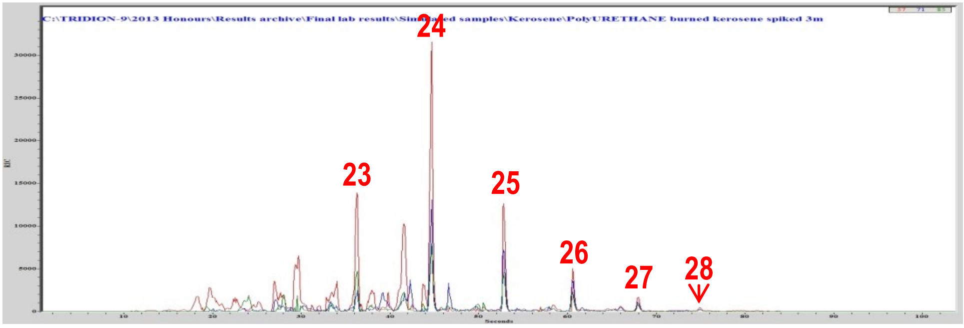


Figure 94: A Gaussian distribution of n-alkanes as present in a burned polyurethane sample spiked with kerosene.

Co-elution presented an obstacle to the identification of nonane in kerosene. Nonane eluted very shortly before styrene and produced a much less intense peak which was covered by the peak of styrene. Peak identification via mass spectral analysis was possible. Tri- and tetramethylbenzenes were listed as target compounds for MPDs (ASTM International, 2010). In reality, these did not contribute much to kerosene identification due to co-elution and low concentrations. Other compounds such as the naphthalenes were also less useful because naphthalene was a common pyrolysis product and other naphthalenes were too low in concentration to be detected consistently. Detection of trans-decalin, however, proved to be a useful mechanism for distinguishing medium distillates such as kerosene from pure petroleum.

G13: Substrates spiked with mineral turpentine (results)

Table 51: Burned nylon carpet spiked with mineral turpentine – analysis summary.

Substrate	**Nylon carpet**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_6 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Octane Nonane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Naphthalene
Pyrolysis products identified	Styrene Benzaldehyde
Conclusion	MPD possibly present. Laboratory confirmation required.
Chromatogram	See Figure 95.

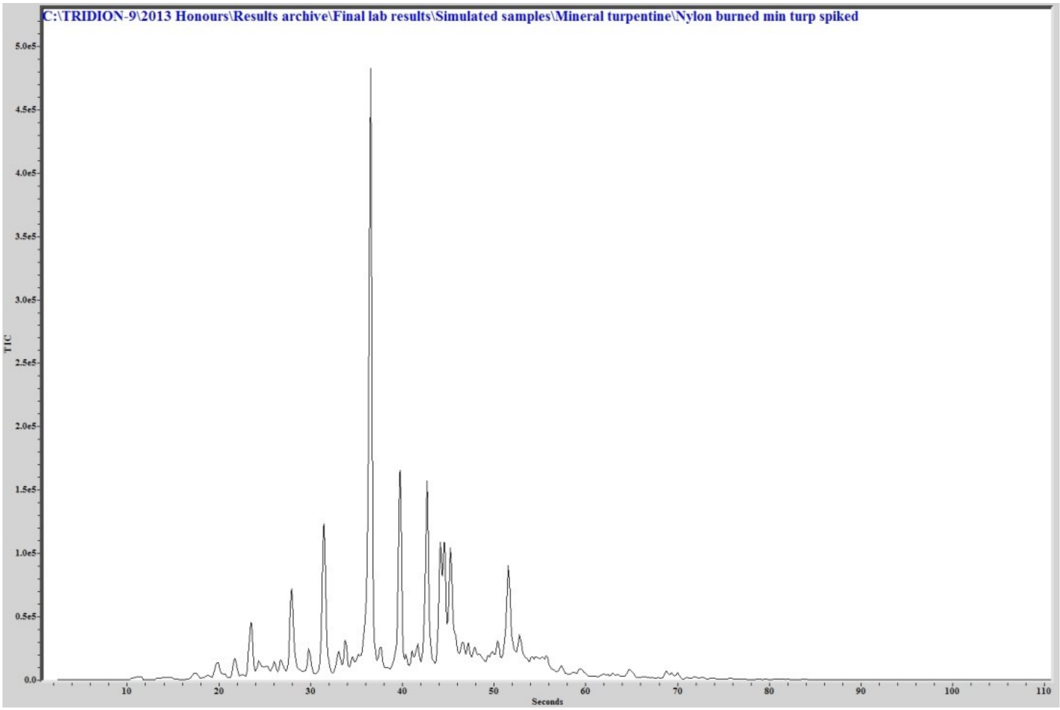


Figure 95: Burned nylon carpet spiked with mineral turpentine sample chromatogram.

Table 52: Burned polypropylene carpet spiked with mineral turpentine – analysis summary.

Substrate	**Polypropylene carpet**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 μL)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Octane Nonane Decane Undecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane Naphthalene
Pyrolysis products identified	Styrene Benzaldehyde
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 96.

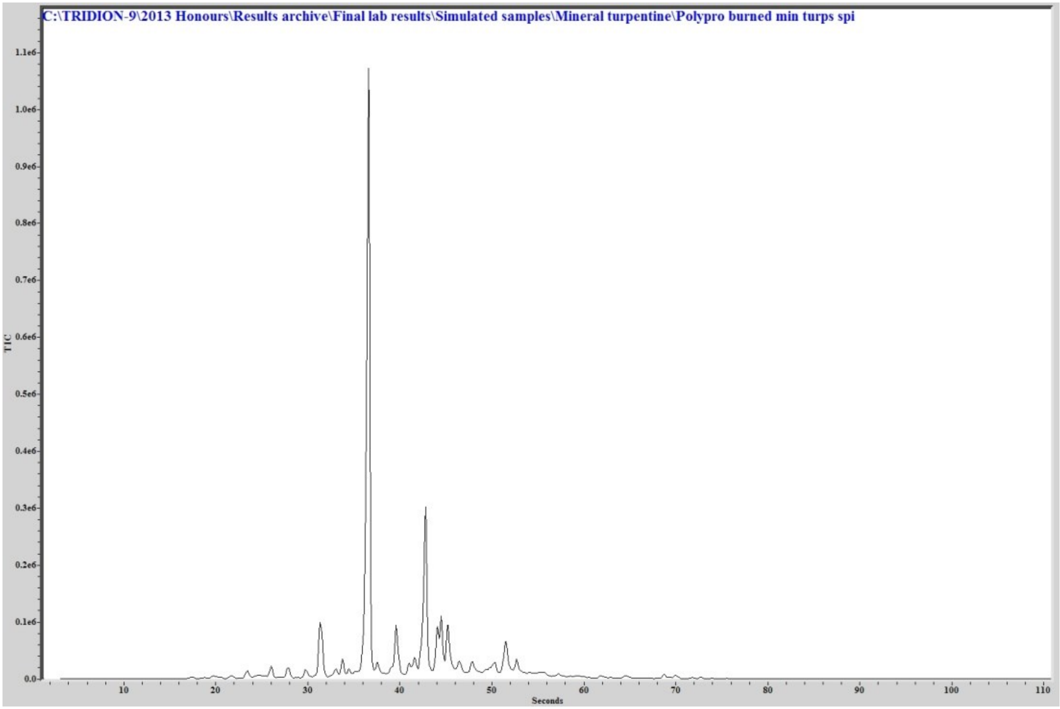


Figure 96: Burned polypropylene carpet spiked with mineral turpentine sample chromatogram.

Table 53: Burned wool carpet spiked with mineral turpentine – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkane
Target compounds identified	Octane Nonane Decane Undecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane trans-Decalin
Pyrolysis products identified	None
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 97.

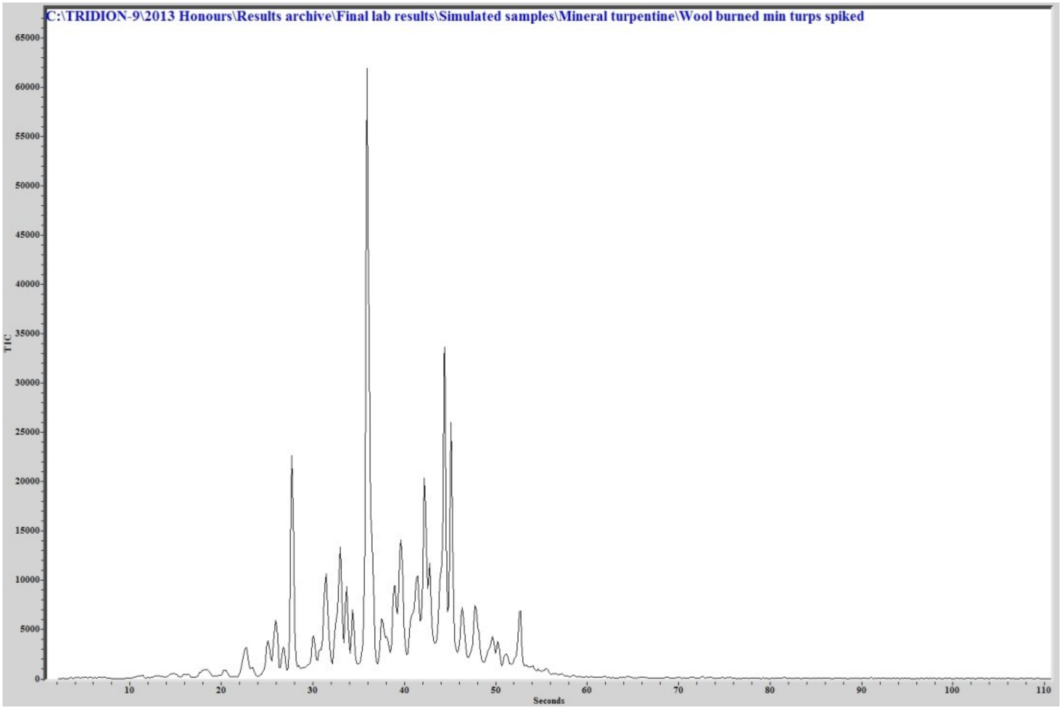


Figure 97: Burned wool carpet spiked with mineral turpentine sample chromatogram.

Table 54: Burned rubber carpet underlay spiked with mineral turpentine – analysis summary.

Substrate	**Rubber carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_6 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	Heptane Octane Nonane Decane Undecane Toluene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Indane Naphthalene
Pyrolysis products identified	Styrene Limonene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 98.

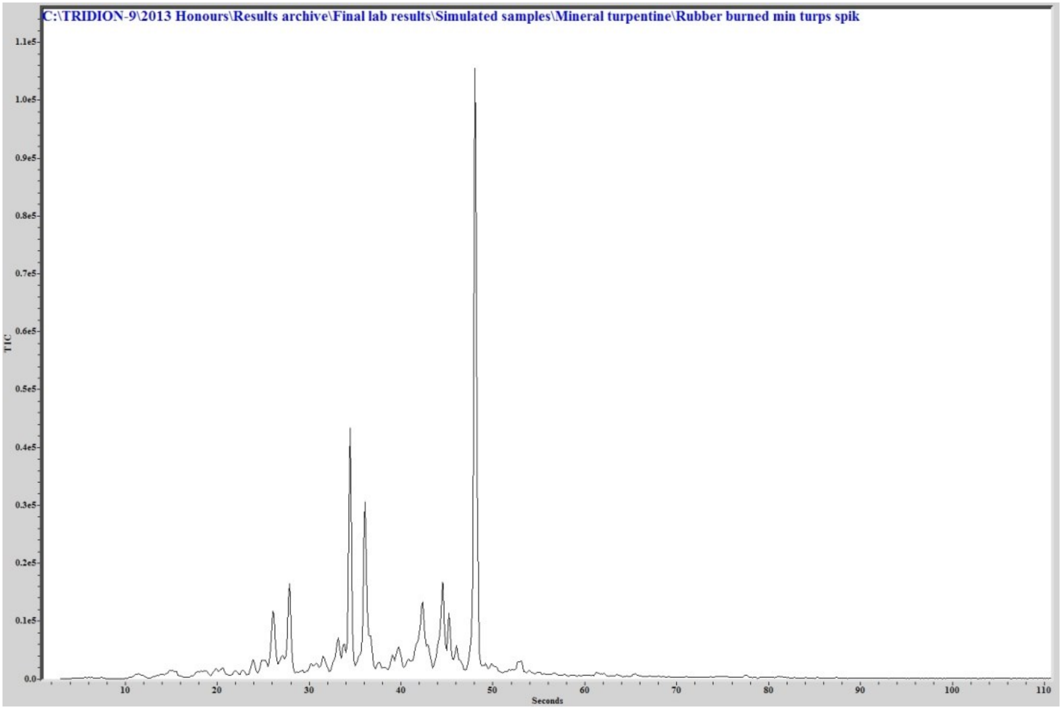


Figure 98: Burned rubber carpet underlay spiked with mineral turpentine sample chromatogram.

Table 55: Burned foam carpet underlay spiked with mineral turpentine – analysis summary.

Substrate	**Foam carpet underlay**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate, Gaussian
Dominant ion profile	Alkane
Target compounds identified	Octane Nonane Decane Undecane Dodecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane trans-Decalin Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 99.

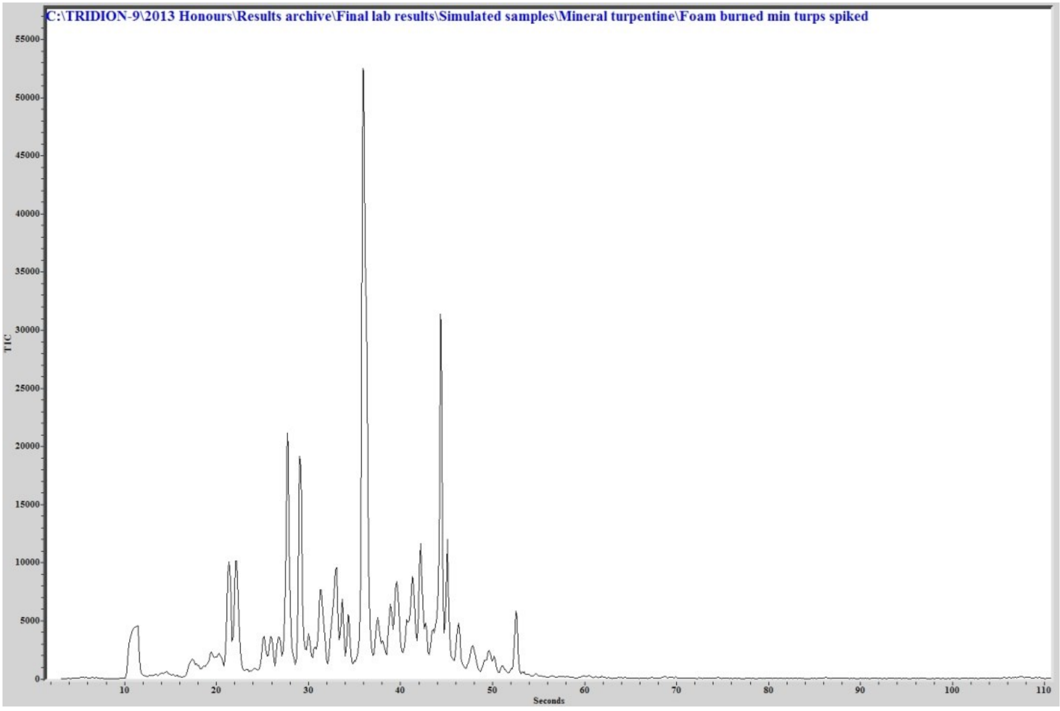


Figure 99: Burned foam carpet underlay spiked with mineral turpentine sample chromatogram.

Table 56: Burned pine spiked with mineral turpentine – analysis summary.

Substrate	**Pine**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	1,3,5-trimethylbenzene trans-Decalin
Pyrolysis products identified	α-pinene Camphene β-pinene Limonene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 100.

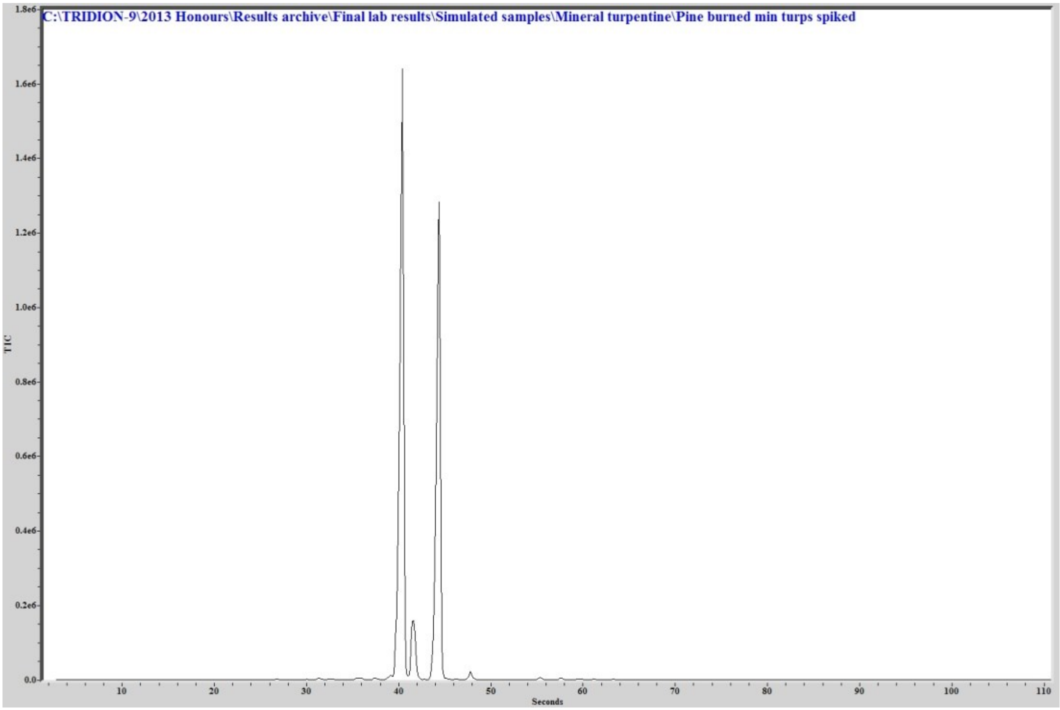


Figure 100: Burned pine spiked with mineral turpentine sample chromatogram.

Table 57: Burned polyurethane spiked with mineral turpentine – analysis summary.

Substrate	**Polyurethane**
Substrate state	Burned
Ignitable liquid deployed	Mineral turpentine (0.1 µL)
Chromatogram elution range	C_6 to C_8
Peak distribution	Narrow
Dominant ion profile	None
Target compounds identified	None
Pyrolysis products identified	Benzene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 101.

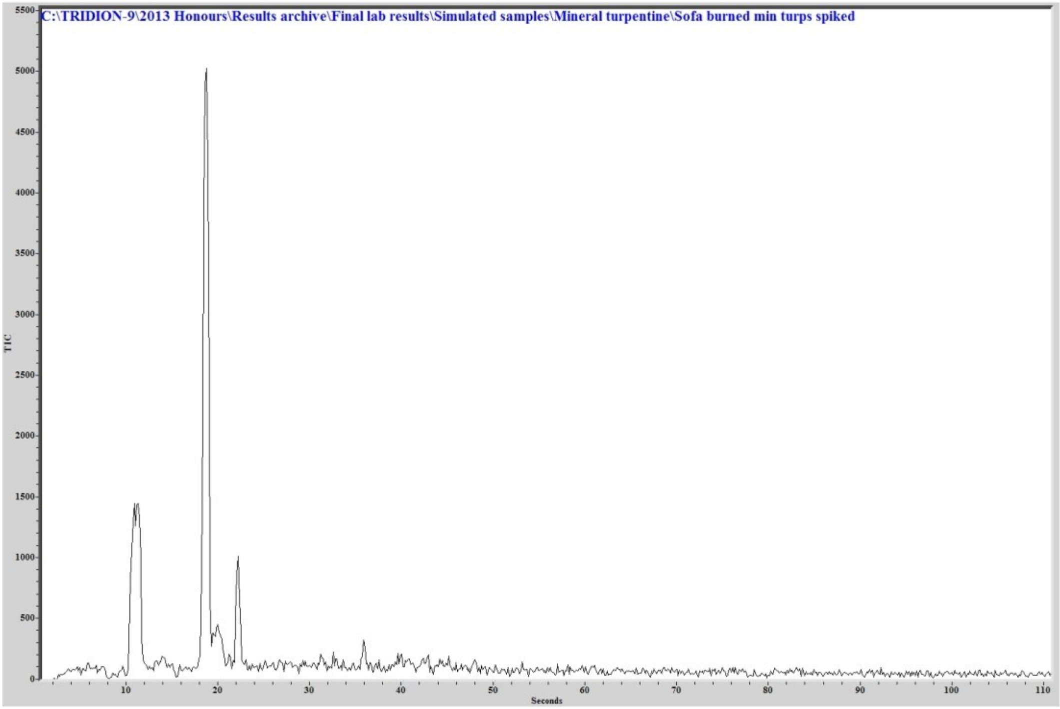


Figure 101: Burned polyurethane spiked with mineral turpentine sample chromatogram.

G14: Substrates spiked with mineral turpentine (discussion)

Mineral turpentine identifications were based both on the aromatic and alkane content of samples, as the mineral turpentine standard possessed equal concentrations of both. The wool carpet, foam underlay and rubber underlay samples were identified as containing MPDs. These samples possessed mineral turpentine-like chromatograms which contained an equal abundance of aromatic and alkane ions. The polypropylene sample, on the other hand, possessed a Gaussian pattern of alkane compounds and little aromatic content. The chromatogram did not suggest the presence of mineral turpentine as specifically as wool carpet or foam underlay, but nevertheless satisfied E1618-10 identification criteria. As was shown by diesel fuel samples, the presumptive identification of the precise ignitable liquid in a sample is not as important as the reliable identification of ignitable liquid class.

Two of seven simulated mineral turpentine samples could not be positively identified (pine and polyurethane). Pine background products, as with other ignitable liquids, overwhelmed the headspace of the sample tin. It could not be determined why the polyurethane sample produced no compound peaks apart from benzene, a pyrolysis product. It is possible that sample degradation due to incorrect packaging or collection was the cause. Interference from styrene and benzaldehyde in the nylon carpet sample disrupted alkylbenzene peak patterns and made evaluation of aromatic content difficult. However, the presence of various aromatic target compounds as well as two alkanes suggested an MPD was still present. The nylon carpet sample was presumptively identified as a medium distillate, pending laboratory confirmation.

Appendix G: Operational Sample Results and Discussion

H1: Simulated floor surface samples

A. Treated timber control sample

Table 58: Treated timber control sample – analysis summary.

Substrate	**Treated timber**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_6 to C_{17}
Peak distribution	Broad
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene m-/p-xylene o-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Naphthalene
Chromatogram	See Figure 102.

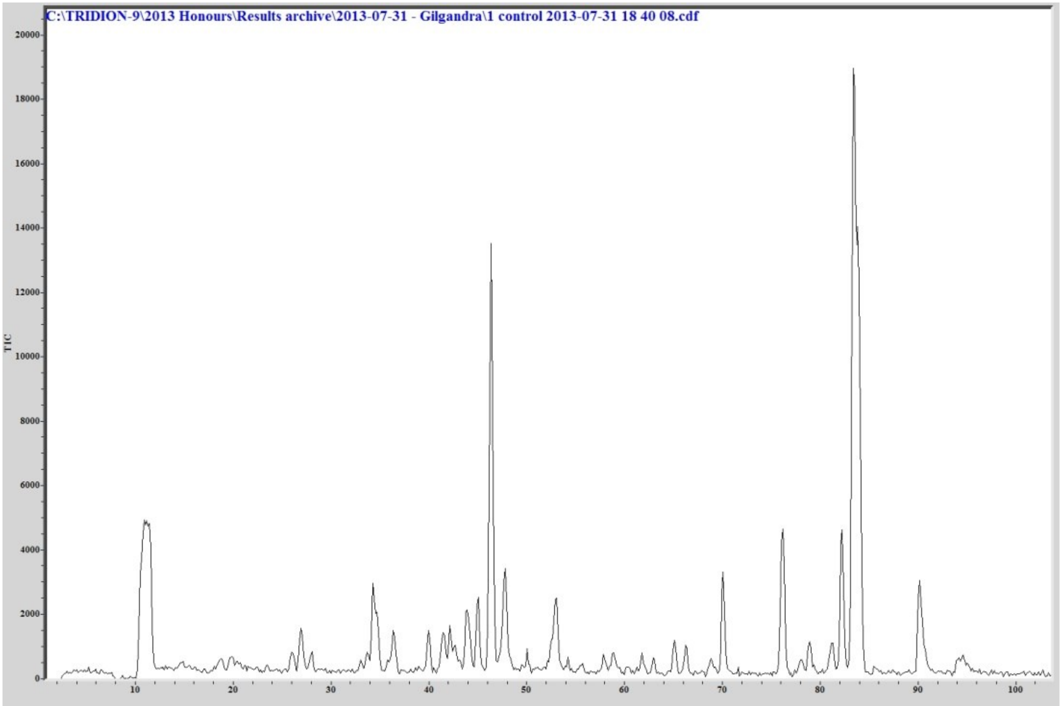


Figure 102: Treated timber control sample chromatogram.

B. Treated timber debris sample

Table 59: Treated timber debris sample – analysis summary.

Substrate	**Treated timber**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{17}
Peak distribution	Broad
Dominant ion profile	Monoterpene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane
Pyrolysis products identified	None
Conclusion	Petroleum possibly present. Laboratory confirmation required.
Chromatogram	See Figure 103.

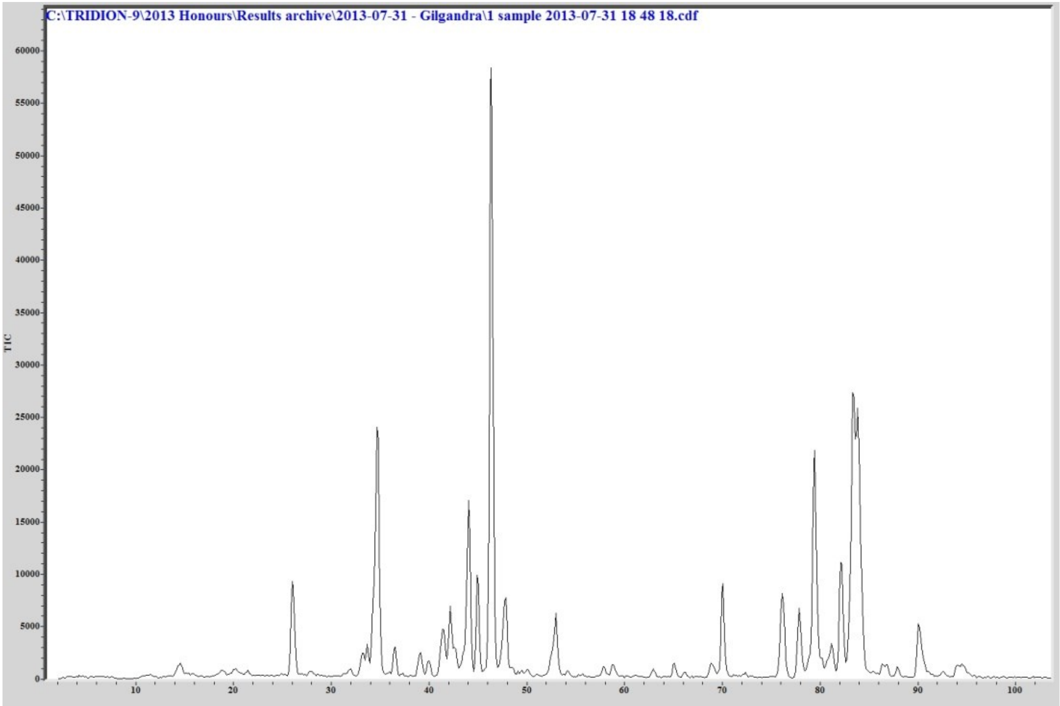


Figure 103: Treated timber debris sample chromatogram.

C. Treated timber debris sample (discussion)

Treated timber floor debris samples produced aromatic profiles similar to a petroleum product. The C_3 alkylbenzenes were the only exception as propylbenzene and o-ethyltoluene were masked by pyrolysis products.

Problems arose when the debris sample was compared to the unburned control. Chromatographically, the two samples were almost identical. Little differentiation could be made between the aromatic content of either, apart from a larger concentration of it in the debris sample. Such a close mirroring of chromatograms was unlikely unless the two samples had the same origin. Two conclusions were therefore possible. First, target compounds in both samples may have been from the timber floor itself. The positive identification of petroleum in this sample would therefore be a false positive. A second explanation may be that a petroleum product was actually present in both the control and the debris samples. When the liquid accelerant was poured onto the substrate, it is possible that a volume of it was splashed onto the area where the control sample was taken from. If this were the case, the control sample was inappropriate. The higher concentration of aromatic compounds in the debris sample compared to the control supports this hypothesis, as the debris sample was taken from the centre of the burn area (high concentration of ILR compounds) whereas the control sample was taken from a corner further away (lower concentration).

An inconclusive identification was made in this case, pending laboratory analysis. This sample was submitted to the Australian Federal Police Chemical Criminalistics laboratory for confirmatory testing. Laboratory analysis revealed that no ignitable liquid was present in the debris sample. An accelerant detection canine was also run over this debris sample at the scene and did not indicate at the sample. These negative results suggest that the first hypothesis was correct: target compounds in the sample were from the substrate itself. This would explain the similarity in control and debris sample chromatograms. It is possible that this area of floor burned to completion and no ILR was actually present when it was collected. The non-porous nature of the substrate suggests that an unburned ILR simply evaporated before collection took place.

Cases such as this were debris and control chromatograms are so similar highlight the importance of proper sampling procedures at the scene. The collection of objective control samples was difficult in this case due to the small size of the simulated floor surfaces. In casework, control samples should be taken as far away from the most damaged area to ensure that they are completely uncontaminated by fire activity. Unfortunately, this could not be guaranteed in the case of the treated timber samples.

D. Synthetic carpet control sample

Table 60: Synthetic carpet control sample – analysis summary.

Substrate	**Synthetic carpet**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_6 to C_{17}
Peak distribution	Broad
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene m-/p-xylene o-xylene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene Naphthalene
Chromatogram	See Figure 104.

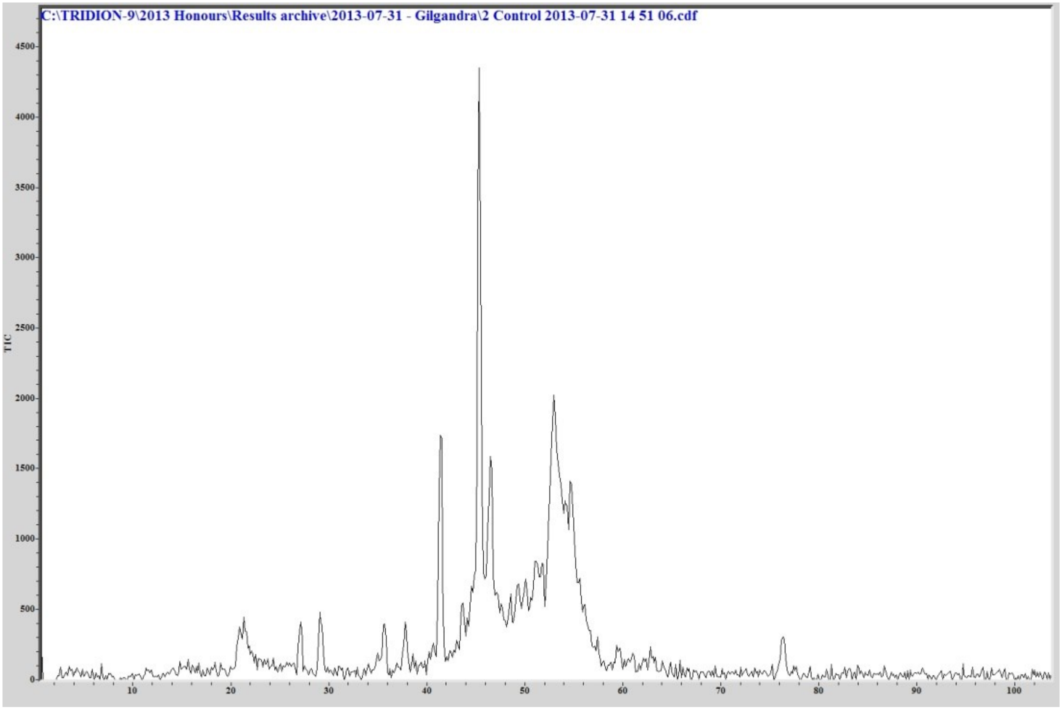


Figure 104: Synthetic carpet control sample chromatogram.

E. Synthetic carpet debris sample

Table 61: Synthetic carpet debris sample - analysis summary.

Substrate	**Synthetic carpet**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{14}
Peak distribution	Moderate
Dominant ion profile	Alkylstyrene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene Propylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Naphthalene
Pyrolysis products identified	Styrene α-pinene Benzaldehyde β-pinene
Conclusion	Sample contains no ignitable liquid residues.
Chromatogram	See Figure 105.

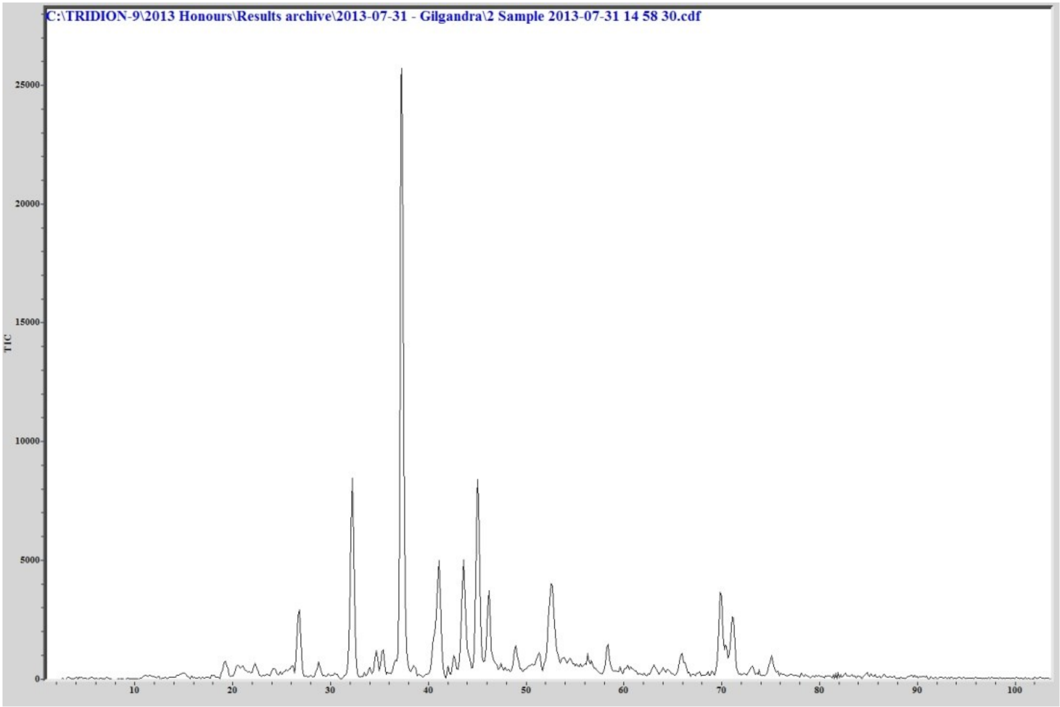


Figure 105: Synthetic carpet debris sample chromatogram.

F. Synthetic carpet debris sample (discussion)

Some target compounds were detected in the synthetic carpet sample. Many were hidden by pyrolysis products such as styrene and benzaldehyde. Diagnostic peak patterns were not representative of petroleum. Most target compounds detected were also common pyrolysis products. Higher molecular weight target compounds were completely absent. As a result, a negative finding was made. Pinene interferents may have been from to the wooden pallet backing which the substrate had been attached to. An accelerant detection canine was run over this sample and did not indicate, corroborating the negative finding.

A lack of petroleum target compounds could be explained by poor sampling technique. This sample was retrieved from the edge of the burned carpet area (Figure 106). Approximately half of the sample consisted of burned carpet and ash, while the other half was made up of unburned carpet. This sample could not have contained much ILR as the carpet and ash had burned completely and any ILR would have been consumed in the fire. The unburned carpet part of the sample was beyond the initial pour area. Literature has suggested that the most appropriate part of a burn pattern to sample is the edge, as this space is more likely to contain ILR (O'Donnell, 1985). This may be effective if the edge of the burn pattern is synonymous with the edge of the accelerant pour, but edge sampling did not appear to be effective in this case. It is also possible that the accelerant burned to completion, which would also account for the difficulty in detection.

Figure 106: Synthetic carpet debris sampling location.

G. Linoleum control sample

Table 62: Linoleum control sample – analysis summary.

Substrate	**Linoleum**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_7 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Monoterpene
Target compounds identified	Ethylbenzene
Chromatogram	See Figure 107.

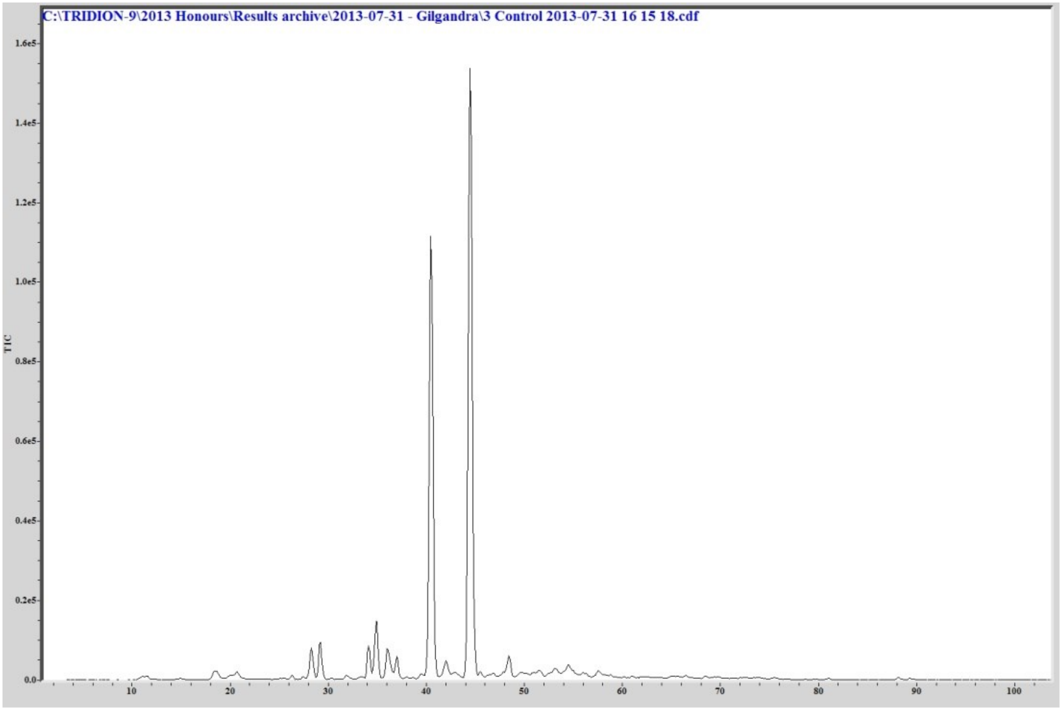


Figure 107: Linoleum floor control sample chromatogram.

H. Linoleum debris sample

Table 63: Linoleum debris sample – analysis summary.

Substrate	**Linoleum**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 108.

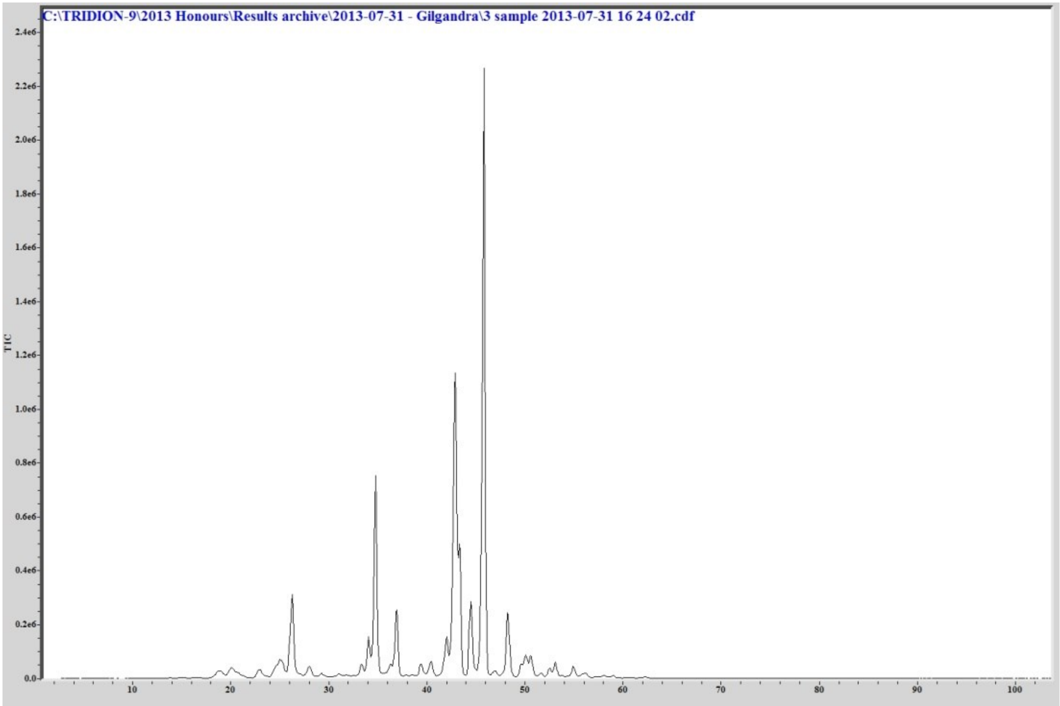


Figure 108: Linoleum floor debris sample chromatogram.

I. Wool carpet control sample

Table 64: Wool carpet control sample – analysis summary.

Substrate	**Wool carpet**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_7 to C_{11}
Peak distribution	Narrow
Dominant ion profile	Monoterpene
Target compounds identified	Toluene m-/p-xylene o-xylene m-/p-ethyltoluene 1,2,4-trimethylbenzene
Chromatogram	See Figure 109.

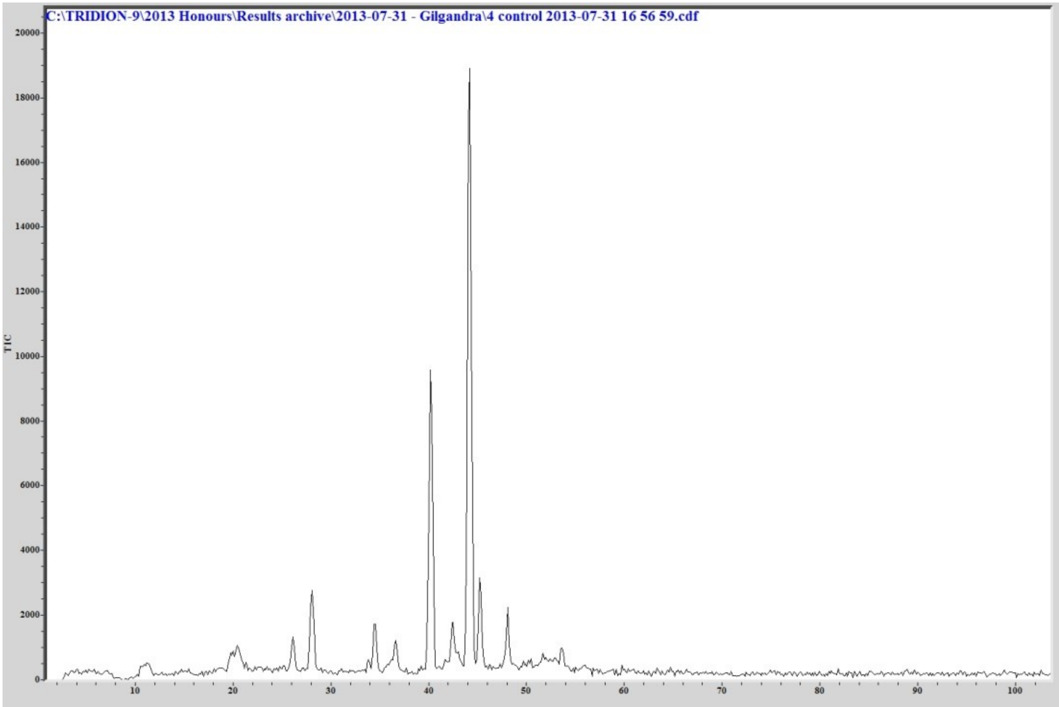


Figure 109: Wool carpet control sample chromatogram.

J. Wool carpet debris sample

Table 65: Wool carpet debris sample – analysis summary.

Substrate	**Wool carpet**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene 1-methylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 110.

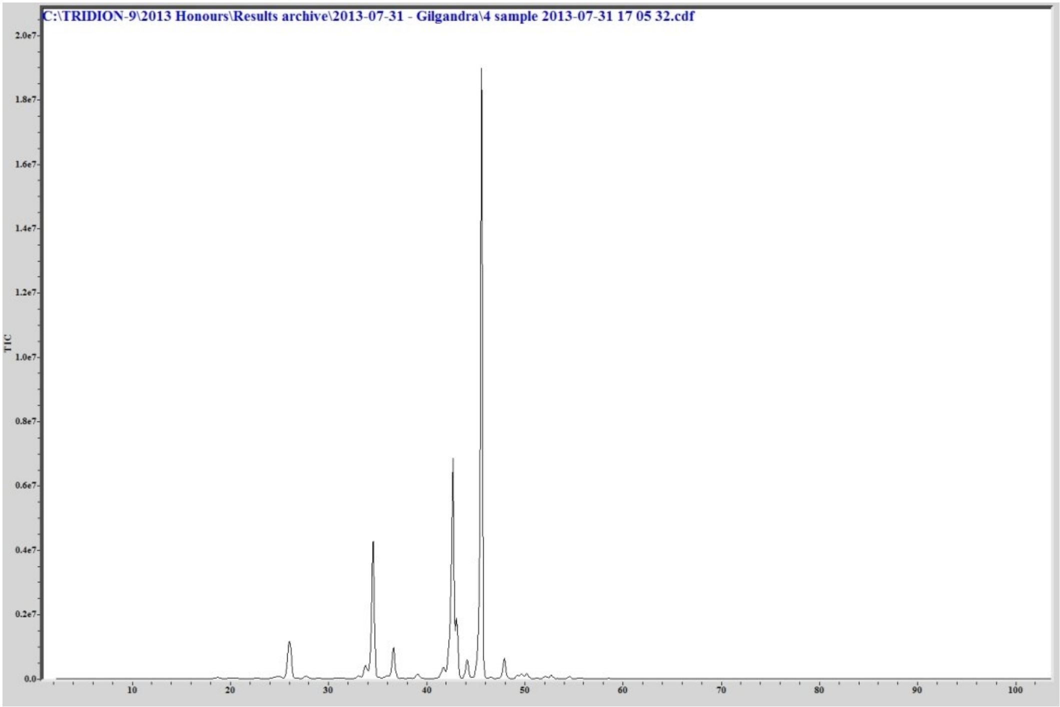


Figure 110: Wool carpet debris sample chromatogram.

K. Ceramic tiles control sample

Table 66: Ceramic tiles control sample – analysis summary.

Substrate	**Ceramic tiles**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_8 to C_{12}
Peak distribution	Narrow
Dominant ion profile	Alkane
Target compounds identified	Octane Nonane Decane Undecane Dodecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene trans-Decalin Naphthalene
Chromatogram	See Figure 111.

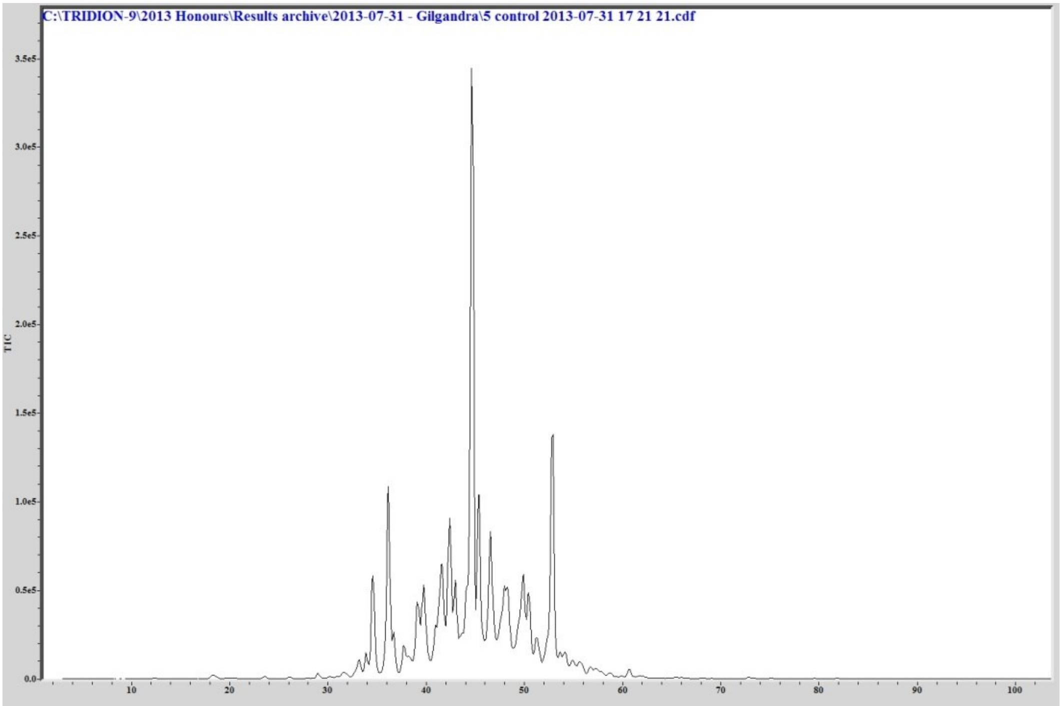


Figure 111: Bathroom tile control sample chromatogram.

L. Ceramic tiles debris sample

Table 67: Ceramic tiles debris sample – analysis summary.

Substrate	**Ceramic tiles**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 112.

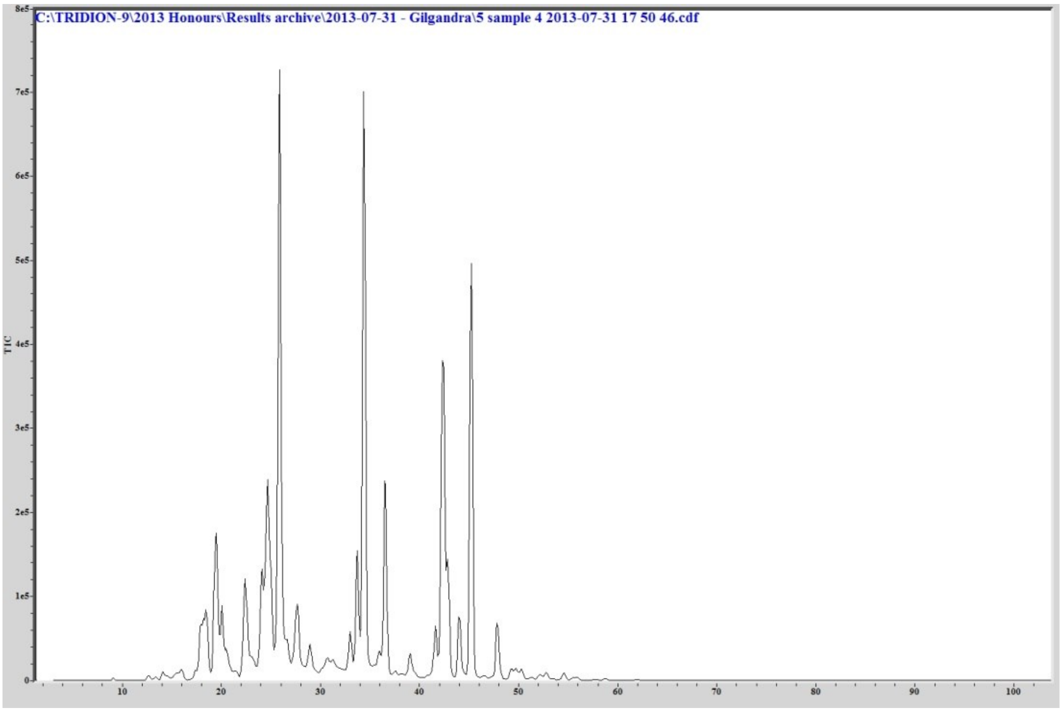


Figure 112: Bathroom tile debris sample chromatogram.

M. Wooden floating floor control sample

Table 68: Wooden floating floor control sample – analysis summary.

Substrate	**Wooden floating floor**
Substrate state	Unburned (control)
Ignitable liquid deployed	None
Chromatogram elution range	C_6 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkane
Target compounds identified	Nonane Decane Undecane Dodecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene trans-Decalin 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Chromatogram	See Figure 113.

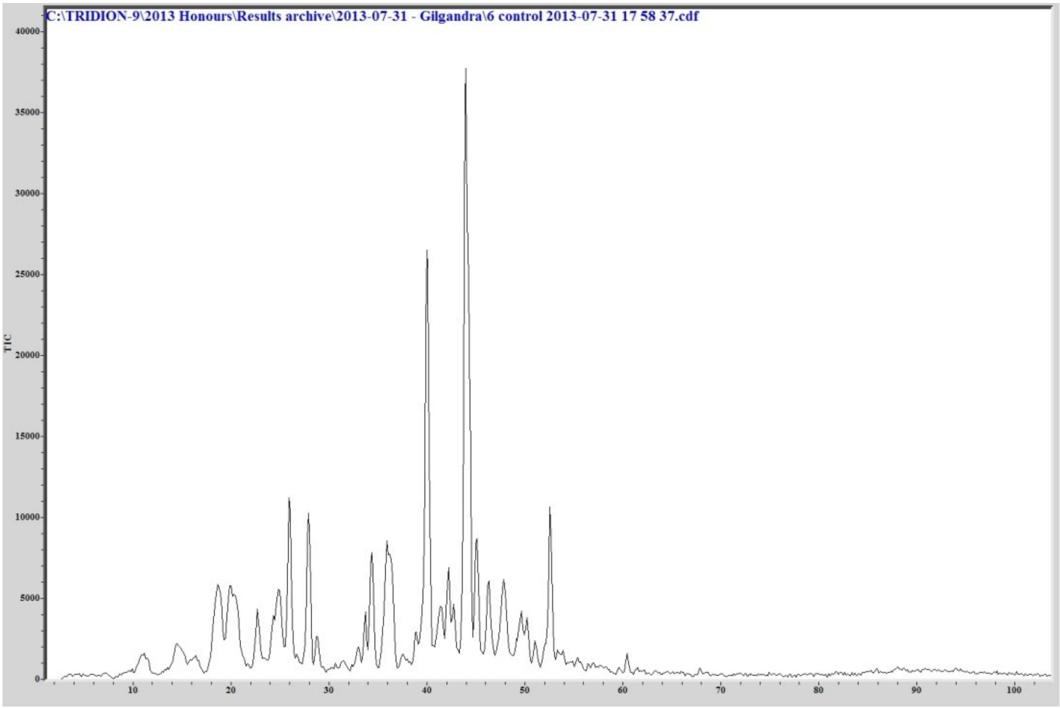


Figure 113: Wooden floating floor control sample chromatogram.

N. Wooden floating floor debris sample

Table 69: Wooden floating floor debris sample – analysis summary.

Substrate	**Wooden floating floor**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 114.

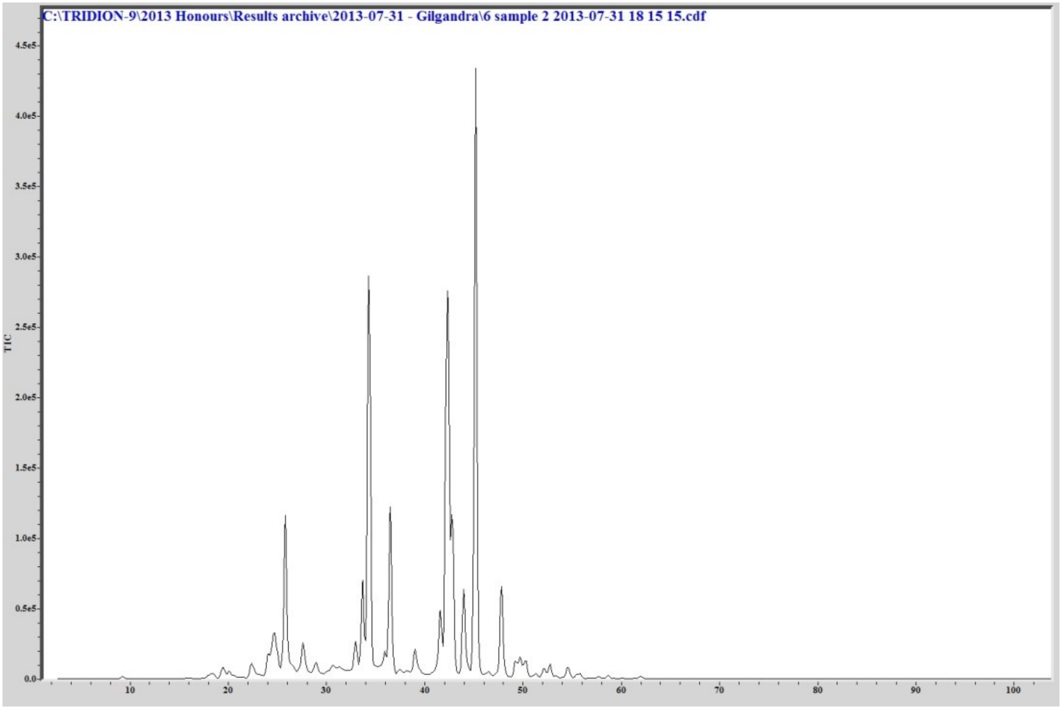


Figure 114: Wooden floating floor debris sample chromatogram.

O. Linoleum, wool carpet, ceramic tile and wooden floating floor debris samples (discussion)

The final four substrate samples were all easily identified as containing petroleum; they possessed obvious target compounds at the TIC level. Characteristic peak patterns were easily visible, and pyrolysis products were not present in significant concentrations. All target compounds into the naphthalene range were detectable. Alkylbenzene target compound concentrations were so high in the ceramic tile and wooden floating floor samples that a high split ratio had to be used in order to improve chromatographic resolution. This may have been due to the flat surfaces of these substrates, which allowed the liquid accelerant to pool, leaving a large amount of residue behind.

H2: Bedsit structure debris samples

A. Cushion

Table 70: Cushion debris sample – analysis summary.

Substrate	**Cushion debris (ash)**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene Naphthalene
Pyrolysis products identified	Styrene
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 115.

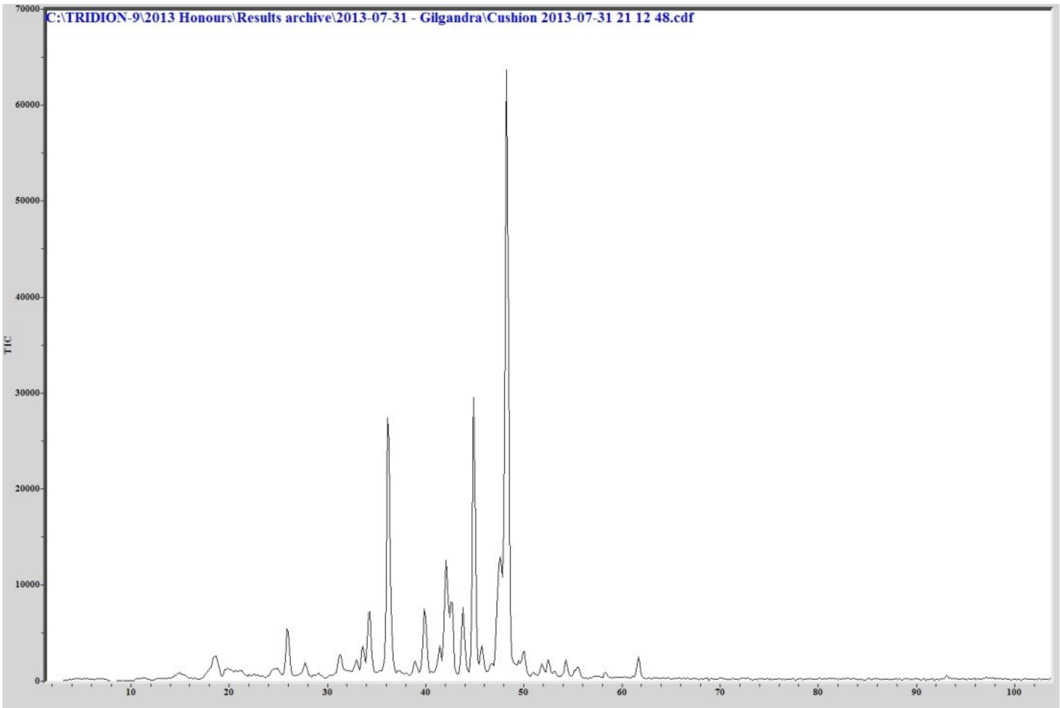


Figure 115: Cushion debris sample chromatogram.

B. Cushion (discussion)

Target compounds were obvious in the cushion sample chromatogram and only two pyrolysis products were visible. One of these pyrolysis products was styrene, while the second possessed mass spectra similar to that of eucalyptol. It could not be determined why eucalyptol may have been present, though a previous study determined the presence of eucalyptol in samples of car carpets (Cavanagh, et al., 2002). Small amounts of pinene products were present, likely due to the fact that fragments of wood debris were also collected in the sample tin.

An accelerant detection canine was run through the bedsit structure after sample collection. The canine indicated at the chair which had been positioned below the desk that the cushion was on top of. The indication of the canine at this site was likely a result of cushion debris falling onto the chair during the fire. The positive alert of the canine corroborates the positive finding of ILR.

C. Chest of drawers

Table 71: Chest of drawers debris sample – analysis summary.

Substrate	**Chest of drawers debris (wood)**
Substrate state	Burned
Ignitable liquid deployed	Neat unleaded petroleum (poured)
Chromatogram elution range	C_7 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene
Target compounds identified	Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene 4,7-dimethylindane Naphthalene 2-methylnaphthalene 1-methylnaphthalene 1,3-dimethylnaphthalene 2,3-dimethylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of petroleum.
Chromatogram	See Figure 116.

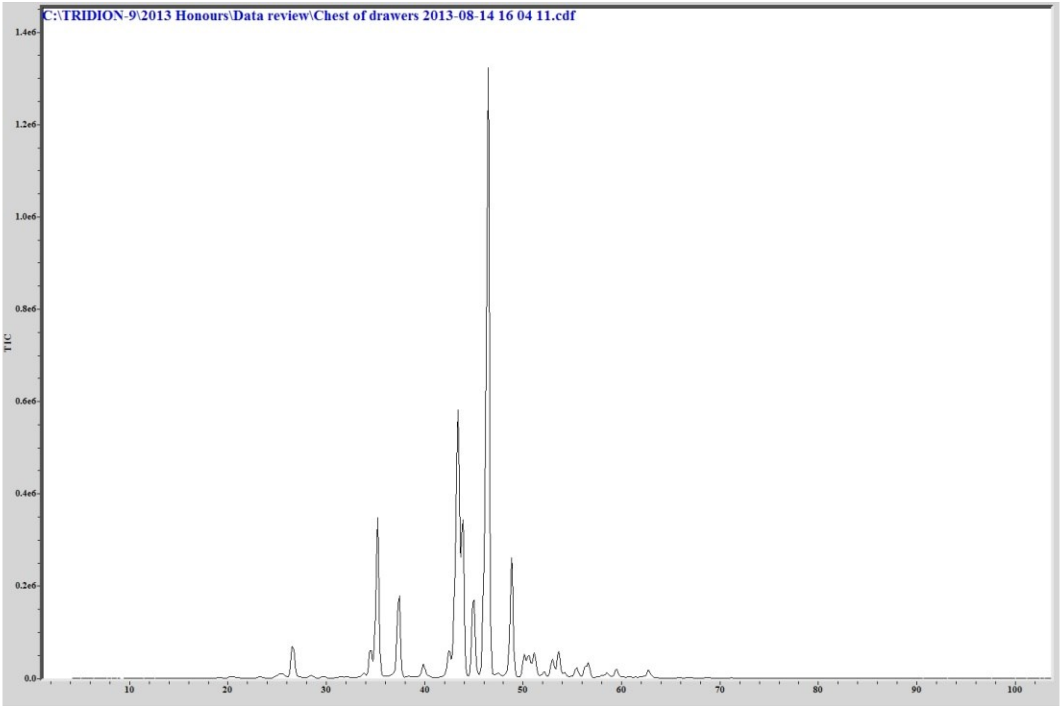


Figure 116: Chest of drawers debris sample chromatogram.

D. Chest of drawers (discussion)

All ignitable liquid target compounds could be detected in the chest of drawers debris sample, including C_2 naphthalenes. Peak pattern ratios were consistent with an unleaded petroleum reference standard; however, the intensity of the 1,2,4-trimethylbenzene peak was many times higher than expected. This may have been the result of the compound's presence as both a pyrolysis product and a liquid residue component.

H3: Main clubhouse structure living room debris samples

A. Armchair adjacent to entry door

Table 72: Armchair adjacent to entry door debris sample – analysis summary.

Substrate	**Armchair (wood and upholstery)**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (sprayed)
Chromatogram elution range	C_8 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene and alkane
Target compounds identified	Octane Nonane Decane Undecane Dodecane Toluene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane trans-Decalin
Pyrolysis products identified	None
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 117.

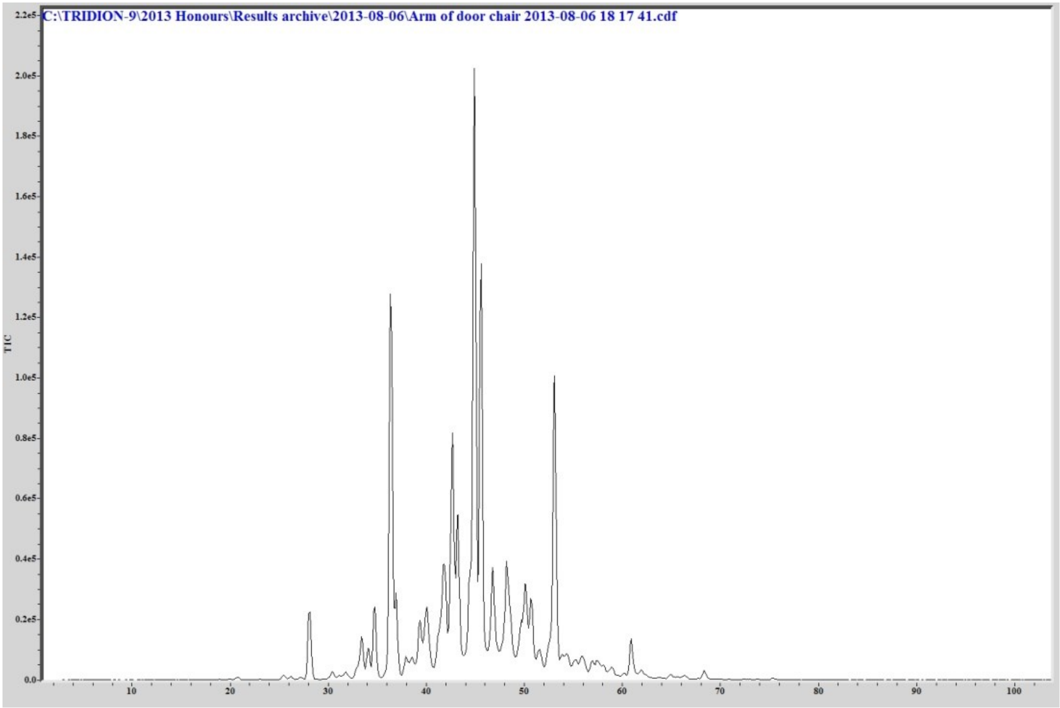


Figure 117: Entry door armchair debris sample chromatogram.

B. Armchair adjacent to entry door (discussion)

A distribution of n-alkanes ranging from octane to tridecane was visible in this sample, as well as trans-decalin. Petroleum target compounds were also present, including C_2, C_3 and C_4 alkylbenzenes, indane and naphthalene. Dominance of the alkane species, coupled with the presence of trans-decalin, suggested that MPD residues were present. The sample chromatogram was similar to the mineral turpentine standard.

As the accelerant used was kerosene, it is uncertain why the yield in aromatic content was relatively high compared to the alkane content. The kerosene standard used in this study contained a much higher concentration of alkanes compared to alkylbenzenes, so much so that aromatic compounds were generally invisible. Pyrolysis products do not generally produce such intense, specific peak patterns. It is possible that the brand of kerosene deployed at the scene was naturally high in aromatic content. Similar results for the sample obtained from the couch in front of the window suggest that this was the case. Differences between different brands of the same ignitable liquid reiterate the importance of a comprehensive collection of ignitable liquid standards.

An accelerant detection canine indicated strongly on the armchair at the site where this sample was taken. The canine's identification was determined to be precisely where the accelerant was deployed. The canine alert corroborated the positive TRIDION-9 result.

C. Floor materials behind couch

Table 73: Floor materials behind couch debris sample – analysis summary.

Substrate	**Floor materials (carpet, underlay, ash)**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (sprayed)
Chromatogram elution range	C_8 to C_{13}
Peak distribution	Moderate
Dominant ion profile	Alkane
Target compounds identified	Octane Nonane Decane Undecane Dodecane m-/p-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene trans-Decalin
Pyrolysis products identified	None
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 118.

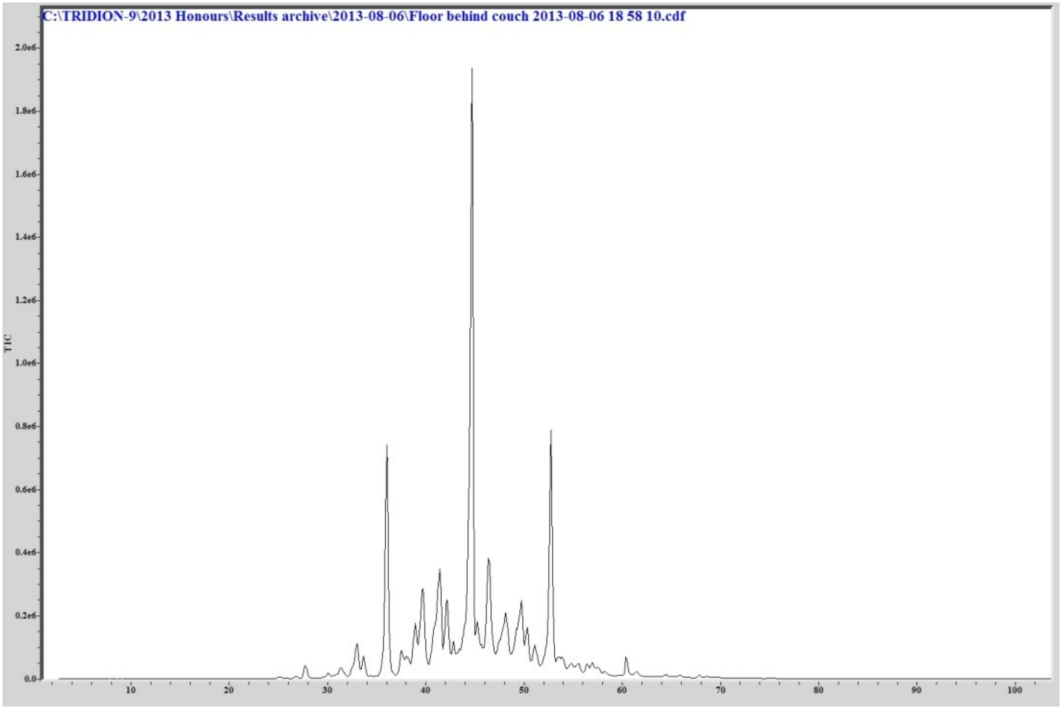


Figure 118: Floor materials from behind couch debris sample chromatogram.

D. Floor materials behind couch (discussion)

A large concentration of mid-range alkane compounds was apparent in the floor material sample. Unlike in the armchair and couch samples, aromatic content in the sample was insignificant. Trans-decalin was positively identified, indicating an MPD was likely to be present. The floor materials behind the couch produced chromatograms more representative of a true MPD (high alkane content, less aromatic content) than other living room samples. One explanation for this may be the fact that the carpet and padding acted as a sorbent, soaking up the kerosene and protecting it from the effects of the fire. The armchair and couch samples, on the other hand, had no such protection and were fully exposed. The preserving effect of porous substrates is a recognised phenomenon in fire debris samples (Turner & Goodpaster, 2013).

E. Couch in front of window

Table 74: Couch in front of window debris sample – analysis summary.

Substrate	**Couch (wood, upholstery, polyurethane)**
Substrate state	Burned
Ignitable liquid deployed	Kerosene (sprayed)
Chromatogram elution range	C_7 to C_{12}
Peak distribution	Moderate
Dominant ion profile	Alkylbenzene and alkane
Target compounds identified	Heptane Octane Nonane Decane Undecane Dodecane Tridecane Toluene Ethylbenzene m-/p-xylene o-xylene Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene Indane trans-Decalin 1,2,4,5-tetramethylbenzene Naphthalene 2-methylnaphthalene
Pyrolysis products identified	None
Conclusion	Sample contains residues of a medium petroleum distillate.
Chromatogram	See Figure 119.

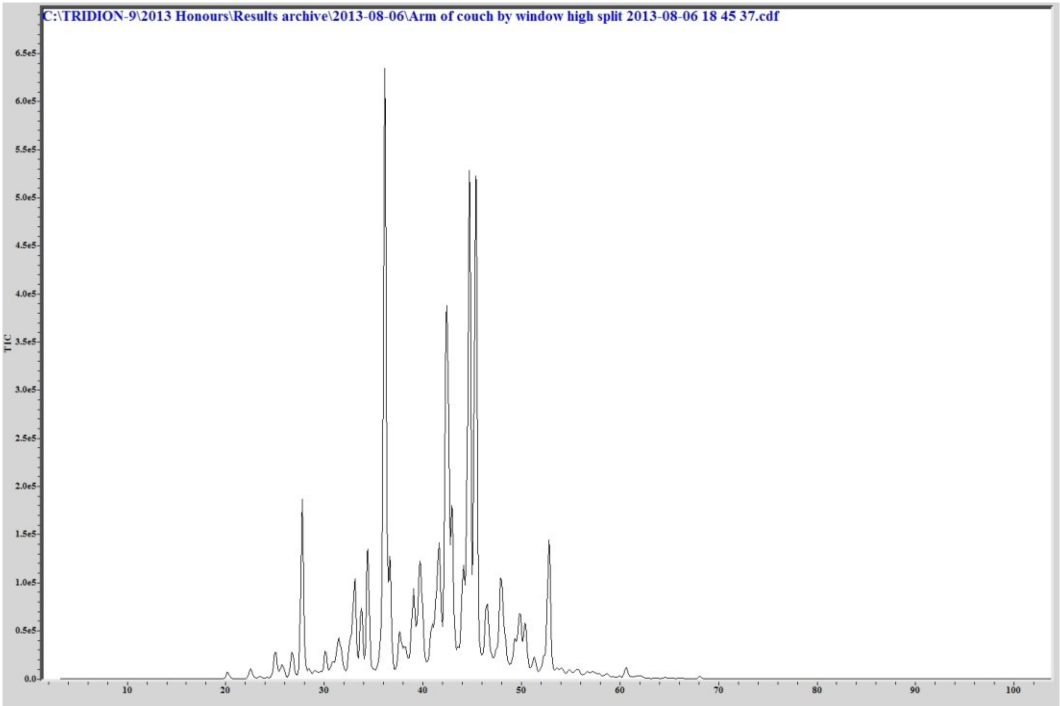


Figure 119: Couch in front of window debris sample chromatogram.

F. Couch in front of window (discussion)

The debris sample obtained from the arm of the two-seater sofa by the living room window produced similar chromatograms to the entry door armchair sample. This was expected as both samples consisted of similar substrate material. Several alkane peaks in a Gaussian distribution dominated the chromatogram. The alkane profile of the sample was equally abundant as the aromatic profile. Target compounds relating to petroleum and MPDs were both detected, including toluene, C_2, C_3 and C_4 alkylbenzenes, indane, naphthalene, trans-decalin and 2-methylnaphthalene.

Like the entry door armchair sample, while an MPD was deployed at this location, chromatograms showed a higher aromatic content than was expected. A high split ratio was used in order to properly resolve all compounds in the chromatogram. It is possible that this high split artificially reduced the intensity of alkane compound peaks, making them appear smaller in comparison to alkylbenzene compounds. The original (non-split) chromatogram clearly shows dominant alkane compounds, of which decane was the most intense peak (Figure 120).

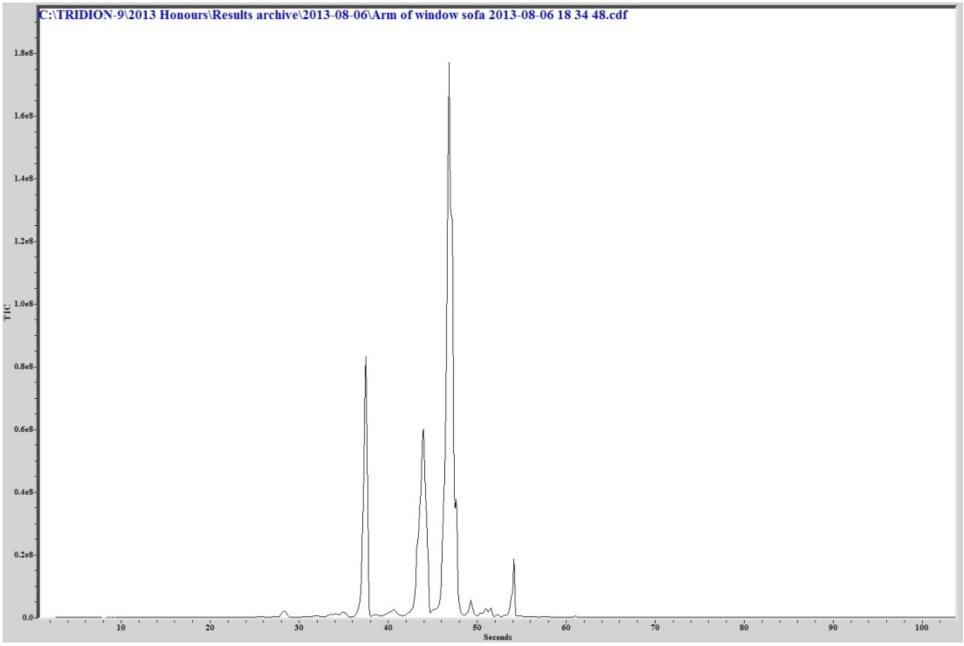


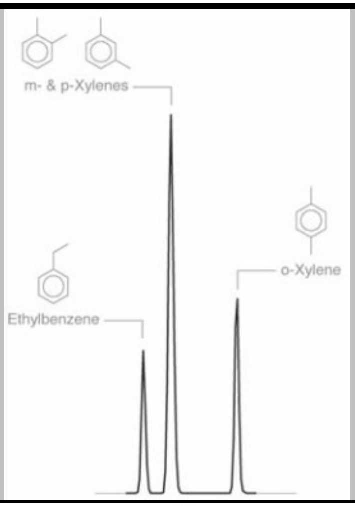
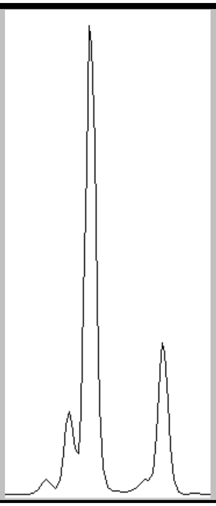
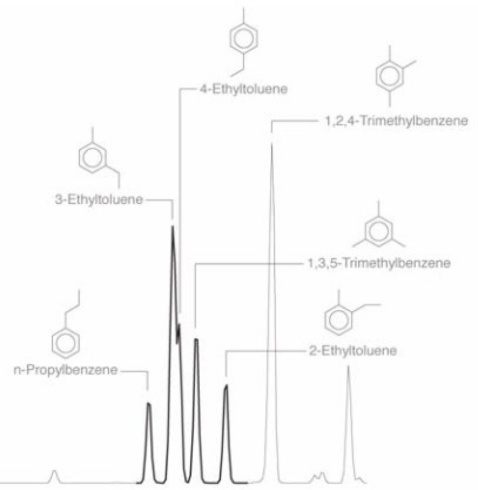
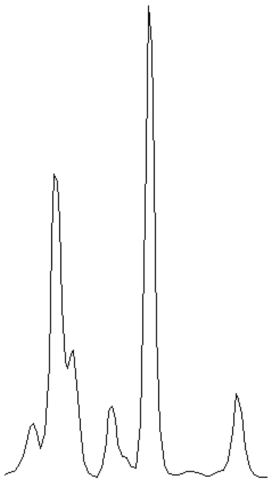
Figure 120: The original sample taken from the couch in front of the window with a lower split ratio. The most intense peak is poorly resolved decane.

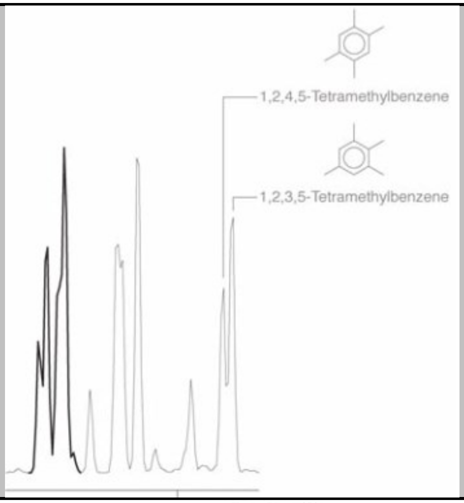
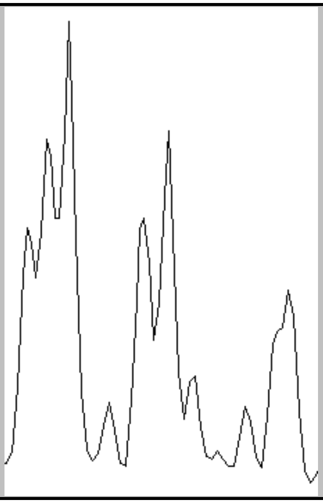
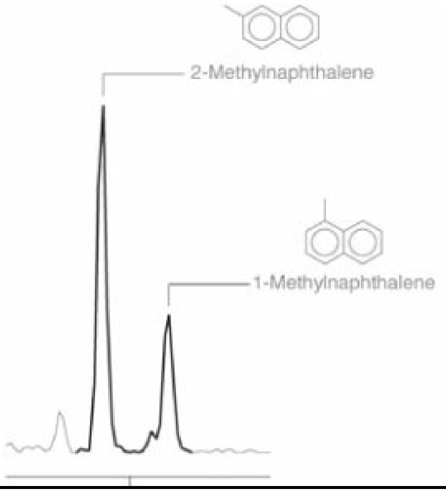
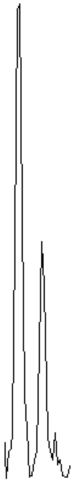
G: General living room debris sample discussion

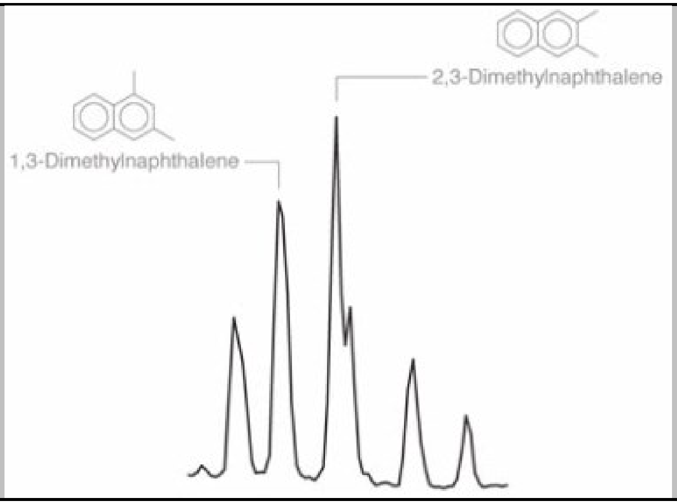
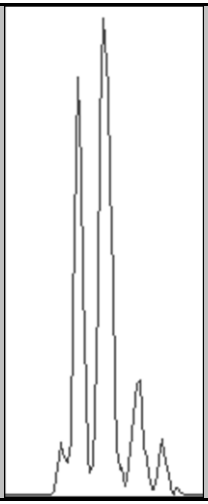
Several factors complicated the collection and interpretation of living room samples. First, the two chair samples were difficult to obtain. These samples consisted of wood which was pried from chair frames and segments of upholstery/fabric. The wood splintered easily and most of the fabric had charred. It is unlikely that these samples represented the ignitable liquid used as well as the floor sample, since the liquid most likely ran down the sides of the chairs and onto the floor. Ignitable liquid runoff is an important consideration when choosing sample collection sites. It is probable that more ignitable liquid was present in the floor debris sample as the liquid would have pooled on that area of the floor. This is supported by the proportionally high alkane content in the floor sample compared to the chair samples.

Unfortunately, reference samples from unburned areas of the room were not collected. The problem faced by fire scene examination personnel was readily apparent when collection of reference samples was attempted. The chairs and sofas, which made up two of the living room samples, were almost completely disintegrated. Little material was left for control sample collection. While there was still a large amount of carpet to collect as a control, debris was scattered all around the floor and it could not be guaranteed that the carpet control samples would contain only carpet. Recommendations regarding the number of samples to take at a fire scene vary, though five has previously been suggested as a standard (Byron, 1990). Control samples proved to be necessary when the questioned samples were examined. High aromatic content in the two chair samples as opposed to the floor material, even though all samples were accelerated with the same liquid, may have been explained by comparisons to control samples. In the absence of a control sample, the ability to assess the aromatic content’s significance was limited. Fortunately, ILR in all samples was still correctly classified.

Appendix H: Diagnostic Peak Patterns in Petroleum

Name	Traditional Pattern	TRIDION-9 Pattern	Compounds	Elution Point (approx.)
The Three Musketeers			Ethylbenzene m-/p-xylene o-xylene	33-38 seconds
The Castle			Propylbenzene m-/p-ethyltoluene 1,3,5-trimethylbenzene o-ethyltoluene 1,2,4-trimethylbenzene 1,2,3-trimethylbenzene	41-49 seconds

The Gang of Four			Indane 1,2,4,5-tetramethylbenzene 1,2,3,5-tetramethylbenzene	49-57 seconds
The Twin Towers			2-methylnaphthalene 1-methylnaphthalene	70-72 seconds

The Five Fingers			1,3-dimethylnaphthalene 2,3-dimethylnaphthalene	76-84 seconds