ANGLIA RUSKIN UNIVERSITY

A New Adsorbent Mixture for the Collection of Common Ignitable Liquid Residue Vapour

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A THESIS IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF ANGLIA RUSKIN UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSPHY

Submitted: August 2014

Acknowledgements

I would like to start by thanking my Director of Studies, Dr. Sarah Hall and the rest of my supervision team, Dr. Lata Gautam and Dr. Trevor Emmett for their continued support and guidance during my studentship. Thanks also go to Dr. Philip Pugh for his assistance and encouragement in statistics training. I am also indebted to all other lecturers and colleagues from Forensic Science and Life Sciences who have assisted me in completing my studentship.

A big thank you goes to Life Sciences (Forensic Science) for funding my studentship and with special thanks to Dr. Sheila Pankhurst for her support. Also, I would like to thank the research, training and ethics manager, Julie Scott for arranging and giving support training which has been of much use to me in my PhD journey. I would like to thank David Hadjicostas (now retired) and Ryan Ainger from Essex Fire & Rescue Services who helped and supported my project at Wethersfield and also the staff at Cambridge Fire & Rescue Services who allowed me to utilise their training facilities at Parkside, Cambridge.

I want to thank the technical staff at the Life Sciences dept. for not only for their continued support and help, but also for keeping my spirits high during the long hours in the laboratory. I would like to also thank my friends at Anglia Ruskin University: Alex; Alix; Ben; Ellen; Chipo; Mark and Olly who provided friendly advice and moral support. A special thank you goes to Agatha Grela from Jagiellonian University, Krakow for her assistance in the laboratory at a key time in my project.

Finally, I would like to dedicate this thesis to my wife Jan, and children Tammy and Stewart, who have provided me not only with financial support, but also their care, loving and encouragement without which I could not have reached this far. I cannot thank them enough!

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ABSTRACT

FACULTY OF SCIENCE AND TECHNOLOGY

DOCTOR OF PHILOSOPHY

A New Adsorbent Mixture for the Collection of Common Ignitable Liquid Residue Vapour

GARRY WHITE

August 2014

United Kingdom fire investigators use ad hoc adsorbents to investigate the suspected use of ignitable liquids and their residues (ILR) at fire scenes. It was unknown whether these materials adsorb all ignitable liquid target compounds specified by ASTM methods, or if they interfered with such analysis and therefore prevented the positive identification of ignitable liquids.

This research has ascertained that adsorbents such as clay based cat litter, montmorillonite, limestone, Tampax®, Tenalady®, talc; sand and the use of a squeegee tool cannot adsorb the full range of ASTM target compounds in common ignitable liquid residues by themselves. However, some can adsorb a limited range of target compounds. For example, cat litter can adsorb C_3 and C_4 alkylbenzenes and other molecules for the identification of petrol, but cannot adsorb heavy alkanes such as those found in diesel fuel. In contrast, limestone can adsorb heavy alkanes but not all aromatic target compounds present in petrol. This study has found that when limestone was mixed with Fuller's Earth (10:1 w/w) that a range of common ignitable liquids and their associated target compounds could be adsorbed and identified. Furthermore, the instrumentation and separation methods used with an automated thermal desorption-gas chromatography-mass spectrometer (ATD-GC-MS) and Tenax TA® were improved and it is hoped that these would form a basis for a new standard method. Limestone and Fuller's Earth as well as the limestone/Fuller's Earth mixture were characterised with Fourier-Transform Infra-Red spectroscopy and X-ray Diffraction. The results showed that mixing the components together did not alter the chemical composition of the adsorbent mixture and that the major phases in the mixture were identified as calcite, quartz and palygorskite.

The performance of the adsorbents was assessed using a combination of a standard ASTM method for analysis using GC-MS and an improved oven separation time of six to nine hours. The ATD method was improved for real fire debris samples by setting the split flow valves to 40 mL/min to minimise instrument overloading. The adsorbents were subjected to evaluation in the laboratory using blind tests and also a field blind test at a real fire scene. The laboratory analysis and fire scene evaluation revealed that the limestone/Fuller's Earth mixture adsorbed all ignitable liquid target compounds from different ignitable liquids and as a result were identified from extracted ion chromatograms. This is the first reported use of this novel mixture as a universal adsorbent for common ignitable liquids.

Key words: ATD-GC-MS, fire debris ; adsorbent; Tenax TA, limestone; Fuller's Earth

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List of Abbreviations

λ	Wavelength
Å	Angstrom
θ	Theta
π	Pi
^{0}C	Degrees Centigrade
μ	Micro
μL	micro litre
ACS	Activated Carbon Strip
Al	Aluminium
ASTM	American Society for Testing and Materials
ATF	Alcohol, Tobacco, Firearms
ATD	Automated Thermal Desorber
BBQ	Barbecue
BET	Brunauer, Emmett, Teller
BP	British Petroleum or boiling point
C	Carbon
C_1	Methyl group
C_2	Ethyl or dimethyl groups
C_3	Trimethyl or combination of methyl and dimethyl groups
Ca	Calcium
CAF	Compressed Air Foam

$CaCO_3$	Calcium carbonate
CEC	Cation Exchange Capacity
cm^{-1}	reciprocal centimetres
CO_2	Carbon dioxide
CSI	Crime Scene Investigator
D	Debye (unit of measurement electric dipole)
d_{hkl}	Miller indices cell dimensions
d-space	dimensional space
DFLEX	Diffuse Flammable Liquid Extraction
DIM	Detection, Investigation, Monitoring
DIY	Do-It-Yourself
ECFRS	Essex County Fire and Rescue Services
EIC	Extracted Ion Chromatogram
ENFSI	European Network of Forensic Science
EPA	Environmental Protection Agency
eV	electron volts
EWCA CRIM	England and Wales Court of Appeal (Criminal Division)
FIR	Far Infrared Range
FE	Fuller's Earth
Fe	Iron
FID	Flame Ioniser Detector
FRS	Fire and Rescue Services
FR-DTGS	Fast Recovery Deuterated Triglycine Sulphate
FTIR	Fourier Transform Infra-red

GC	Gas Chromatography
GmbH	Gesellschaft mit beschränkter Haftung
H	Hydrogen
HDD	Hydrocarbon Detector Dog
HPD	Heavy Petroleum Distillate
ID	Internal Diameter and also Identity
IL	Ignitable liquid
ILA	Ignitable Liquid Absorbent
ILR	Ignitable Liquid Residue
KBr	Potassium Bromide
LPD	Light Petroleum Distillate
M	Molecule
m	metre
MDF	Medium Density Fibreboard
MDPGA	Ministry of Defence Police and Guard Agency
MIR	Middle Infrared Range
MPD	Medium Petroleum Distillate
Mg	Magnesium
m/z	mass to charge ratio
mL	milli litre
ML	Multi-Layer (adsorption)
MS	Mass Spectrometry
MVSP	Multi Variate Statistical Package
N	Number of plates (column)

n	Number
Na	Sodium
NIR	Near Infrared Range
NIST	National Institute of Standards and Technology
NFPA	National Fire Protection Association
O	Oxygen
OH	hydroxyl ion
RF	Radio Frequency
RRF	Relative Response Factor
RPM	Revolutions per Minute
RT	Retention time
R. v	The Crown verses
PPE	Personal Protection Equipment
ppm	parts per million
PTFE	polytetrafluoroethylene
Si	Silicon
Std dev	Standard deviation
STx-1b	Montmorillonite clay Texas 1b (clay standard)
SWy-2	Montmorillonite clay Wyoming 2 (clay standard)
TD	Thermal Desorber
TIC	Total Ion Chromatogram
TOT	tetrahedral-octahedral-tetrahedral
Torr	Unit of pressure
v_1, v_2 v_3, v_4	molecule vibrations

VOC	Volatile Organic Compound
vdW	van der Waals force
v/v	volume/volume
UATR	Universal Attenuated Total Reflectance
U.K	United Kingdom
U.S.A	United States of America
w/w	weight/weight
XRD	X-Ray Diffraction
ZrO_2	Zirconium Oxide

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Chapter One

1 Introduction

Deliberate fire setting including arson, is a criminal act that is malicious in nature and only results in the loss of lives and property. Life changing injuries can result from heat and smoke inhalation, as well as property losses that may be difficult to replace even if insured. It is significant that in the U.K., that over half of all fires attended are started deliberately (Fire Statistics Monitor, 2012). Despite this statistic, Sugg (2003) found that only eight per cent of people in arson cases were cautioned or identified for this offence, suggesting that a low conviction rate exists for this criminal act.

The term 'arson' in England and Wales is a criminal offence that results in the criminal damage or wilful destruction caused to one's own property or to that of another by using fire (Criminal Damage Act, 1971). Further, intending to damage or destroy with the intent of endangering the life of another or being reckless in the act of fire setting is also construed as arson.

The modern U.K. Fire and Rescue Services (FRS) are tasked with fire investigation duties as part of their remit, as well as the normal fire suppression duties. The National Framework Document (Department of Communities and Local Government, 2012), outlines the need to identify and assess fire related risks to communities, and in doing so tasks each FRS authority with risk management plans, with an emphasis on prevention and protection against fires. Each FRS authority is accountable to its own community and gives that community a chance to influence and shape the local policy so that it meets the needs of that community. The (Fire and Rescue Services Act, 2004) gives each FRS authority the power to investigate fires where the supposed cause is not accidental (Pretious, 2006). The empowerment of a FRS officer allows for the investigation of the cause and spread of a fire, although permission is normally sought from the property owner before this is undertaken. Entry is not a right, so a Justice of the Peace warrant may have to be obtained in some circumstances, particularly where entry by force is required. Each authority is responsible for the training of its own FRS personnel. Some authorities in the U.K. such as Essex FRS, train their fire crew lead officers in Level 1 Fire Investigator and Scene Preservation Techniques (Hadjicostas, 2013), which is a basic fire invesigator course.

When the crew attends a fire, the nominated trained person can make initial assessments, collect witness details, and importantly preserve evidence through the careful use of fire suppression techniques and scene preservation *(ibid)*. It is also worth noting that firefighters in the United States of America (U.S.A.) also train public safety personnel in these methods (Samuels, et al., 2000) and so also consider the importance of preserving evidence to assist in the invesigation of a fire. This new mantra of trying to preserve evidence rather than the old attitude of "extinguish the fire and job done", has meant less water is used to suppress fires and less disturbance of potential evidence in situ. The practice of throwing debris out of the window into the garden is not standard practice any longer in the UK FRS (Hadjicostas, 2013).

1.1 The Use of an Ignitable Liquid to Promote Fire Growth

The use of an ignitable liquid to promote a fire for criminal intentions can lead to fire acceleration, which may cause a rapid spread of heat to other nearby fuels such as furnishings (De Haan & Icove, 2011, p.716). The fire growth may be so rapid that it could entrap dwelling occupants before they have a chance to escape. Unaided by an ignitable liquid, fuels take longer to reach their maximum temperature but can achieve the same temperature (Stauffer, et al., 2008, pp. 1-5). Published data on ignitable liquid use in arson cases is not normally disclosed to the public as many cases remain unsolved (Hadjicostas, 2013). However, a physical feature of ignitable liquid used in the promotion of a fire is often seen as irregular shaped burn patterns or radial burn patterns where the liquid has been poured from a container onto the floor (De Haan & Icove, 2011, pp. 282-286). These patterns are also caused by post flash-over floor burning from radiant heat in the ceiling gas layer and debris that has fallen from the ceiling (NFPA 921, 2011). While the pattern may seem suspicious, the analysis of physical evidence for ignitable liquid use can prove or disprove this hypothesis. However, it is also possible that ignitable liquids may have been completely consumed in the fire. Where a compartment has not reached post-flashover stage, the irregular burn patterns may indeed indicate suspicious activity and should be investigated (Putorti, 2001). These areas are a good starting place to sample the fire scene and if the flooring is hard a sorbent material can be used (Section 1.2). Investigators should also seek to investigate unexplained patterns seen such as the result of spreading an ignitable liquid in haste leaving tell-tale signs of use. Figure 1.1 shows the greasy residue left on a wall above the skirting board by the pouring of an ignitable liquid.

A good place to take sample for evidence purposes is the floor directly below this wall area.

Figure 1.1 Greasy marks above a skirting board indicating the possible use of an ignitable liquid

1.2 Preliminary and Detailed Investigation at the Scene

The National Fire Protection Agency manual (NFPA 921, 2011) is used by a fire scene investigator as the recognised method of fire investigation and is taught by U.K. FRS and other training agencies (Hadjicostas, 2013). An investigation into a suspicious fire is broken down into external and internal phases. This is further divided into preliminary and

detailed examinations. So, for example in a preliminary external examination, entry and exit points are defined, as well as safe paths and cordons. Preliminary internal examinations will determine stencilling, smoke staining, char patterns, ventilation and protected areas *(ibid)*. The investigator will try to build a sequence of events from ignition and use evidence to create the 'story' or flow of the fire. A search strategy will be defined and use the correct tools for obtaining evidence and undertaking excavations. Videos, photographs and sketches are made as well as contemporaneous notes. A decision taken at this stage could escalate the case to further investigation using the Police or a Level 2 Fire Investigator. Each FRS should have at least one of these level 2 trained officers on call to attend scenes *(ibid)*. In the U.K., if there is a suspicion of ignitable liquid use, the scene investigator may collect fire debris and place in evidence containers, and may even call for a hydrocarbon detector dog (HDD) or the Detection, Investigation and Monitoring (DIM) team who possess hand-held hydrocarbon detectors and mobile gas chromatography with mass spectrometry (*ibid*). These instruments can assist the scene fire investigator to identify areas for sampling of fire debris. Items of a suspicious nature such as likely sources of ignition or fire acceleration are placed into evidence bags or containers for submission to a laboratory for further testing. These items are removed by hand or with the assistance of a tool *(ibid)*. Scene examiners follow the methods set out by NFPA 921 (2011). Normally, evidence is 'bagged' in gas leak proof bags such as Rilsan® 11 and double-tied (swan-necked) and sealed with plasticuffs, or placed into sealable metal containers. Either method is designed to prevent ignitable liquid vapours escaping.

However, there is a problem in that the use of a tool could create significant disturbance to an evidence scene and potentially destroy or contaminate other evidence, especially if the tool is used to dig up whole chunks of concrete (Tontarski, 1985). Strategies on the collection of fire debris and control samples should be agreed by the investigator(s) prior to collection (Lentini, 2006, pp. 103-105). Non-contaminated comparison samples should be collected first followed by suspect samples. For example, digging an area that contains ignitable liquid residues could send splinters and shards in any direction. If the area containing contaminated material is now sampled for ignitable liquid it may indicate positive leading to a 'false positive', as that area may not have contained any ignitable liquid residue until it was contaminated. This strategy ensures that 'clean' samples are not prone to cross-contamination. Another problem is the decision over what evidence container to use and how to transport it without causing contamination to other evidence containers *(ibid)*. Investigators should therefore plan on what type of evidence containers are used (e.g. glass or metal) and minimise contamination that point onwards.

Areas of a fire scene in a building are difficult to sample due to interference from structural features such as fallen masonry or timbers pose another problem. The investigator has to consider whether there is a health and safety issue and whether the removal of the obstruction to obtain a sample will contaminate the scene. Investigators are taught to identify the 'lowest point of burning' (O'Connor & Redsicker, 1996, p. 111) which can involve the removal of debris and if necessary dig through the debris to determine the lowest point that that combustion has taken place. Often, ignitable liquid residues can be found at this point if any were used to promote the fire *(ibid)*. Care should be taken that whilst digging, contamination to the fire scene should minimise contamination to other areas. It is advantageous to the integrity of evidence that there is a minimum of disturbance as possible to the scene to achieve the aim.

1.3 The Use of Ad- Hoc Adsorbents in Fire Scene Evidence Recovery

To mitigate problems that structural fire scenes poses to an investigator (section 1.2), and for convenience purposes, some fire scene examiners have turned to the use of ad hoc adsorbents to sample fire scenes (Hall, 2009). It was determined through personal conversation *(ibid)* with fire investigators and scene examiners that materials such as Tampax® are used to sample suspicious areas of a fire scene. In addition, a survey by Baccus (2010) revealed that other materials such as the hand-held squeegee combined with water were used to collect suspected ignitable liquid residues (ILR). These materials are placed directly onto the suspected ignitable liquid area and left for a period of time to allow the adsorbent to either adsorb vapours from the ILR, or by direct contact where the ILR binds directly to the surface though van der Waals' forces (section 1.5.2.2), induced dipole – induced dipole (section 1.5.4) and hydrogen bonding (section 2.1.2). The results of the survey show that the range of materials and methods used by fire scene examiners to absorb/adsorb ignitable liquid residues is varied and there does not seem to be any consistency in their use. A survey question asked what sampling techniques were used and why that those methods were chosen. The respondents said they were in use when they first entered the job, and assumed that they worked. The adsorbents used included Tampax®; hand-held squeegee combined with water; sand and cat litter. The response shows that investigators use adsorbents as part of a tradition handed-down from their predecessors but are otherwise uninformed about their usefulness.

Despite the use of these items, there has been no research undertaken to test their ability to adsorb (section 1.5.2.2) common ignitable liquids (section 1.4). In addition, it is unclear if these materials actually allow for the identification of common ignitable liquids through target molecules laid down in the main protocol used for fire investigation published by the American Society for Testing and Materials (ASTM E1618-11, 2011) (Table 1.2). If they do not, it could be argued that these adsorbents do not give a fire investigator the best representation of evidence for use in a court of law to base their expert opinion. If on the other hand if they do work as intended, then it could be argued that adsorbents offer an alternative method of collecting ILR at fire scenes, especially where there is difficulty in extracting a sample for use as evidence such as hard flooring.

The use of adsorbents to sample fire scenes is not new, but little published research exists. Tontarski (1985) explained that the Alcohol, Tobacco and Firearms (ATF) teams in the U.S.A. and the Houston Arson Bureau had used calcium carbonate ($CaCO_3$) to collect ILR but did not publish any results, and so it is not known if the identification of an ignitable liquid using calcium carbonate was a success. Mann & Putaansuu (2006) experimented with five absorbent/adsorbent types to determine if they could identify a 1:1 petrol/diesel test mixture sprayed onto concrete pads. The sorbents chosen for the study were: A commercial adsorbent known as Ignitable Liquid Absorbent (ILA) (section 4.1); clay cat litter; calcium sulphate; baking soda and an activated charcoal strip known as Diffuse Flammable Liquid Extraction (DFLEX). They also used physical force to remove part of the concrete pad creating a ‘bulk’ sample. This was done to simulate the action of an investigator using a tool. Headspace sampling was used for analysis of this sample and this is discussed further in section 1.5.1.2. The results showed that the bulk sample gave the best instrument response in peak height for all of the compounds in a petrol/diesel test mixture. The other sorbents used only partially adsorbed or desorbed the petrol/diesel mixture. Of these, Mann & Putaansuu (2006) described cat litter as the next best with regard to being chromatographically representative of the applied test mixture. However, this statement is flawed as the chromatogram revealed that there was an absence of heavy ignitable liquid compounds, from heptadecane to heneicosane from the diesel fuel used and therefore is not representative of the test mixture. This absence of peaks of these heavier compounds may indicate that the type of cat litter does not adsorb or desorb heavy alkane compounds. However, in their research cat litter did adsorb light to medium petroleum compounds. This shows that it can adsorb at least some petrol compounds. The use of these tested ‘adsorbents’ gives cause for concern as the materials chosen seems to favour either light petroleum compounds with no heavy compound adsorption, or can adsorb

medium/heavy petroleum compounds but cannot adsorb light petroleum compounds. If a perpetrator of a fire used a mixture of ignitable liquids including light and heavy compound types (section 1.4), this could be a problem as the use of one of these adsorbents may mean that a range of target compounds is not adsorbed even though they are present in the ignitable liquid and would give only give a partial evidence picture to an investigator.

1.4 Ignitable Liquids and Chemistry of Combustion Products

Throughout this thesis, the term 'common ignitable liquids' is used to describe any ignitable liquid that is readily available. Although there are many different types of ignitable liquids, deliberate fire setters tend to use those that are easy to purchase and do not come with a high profile audit trail and therefore prevent raising an alert (De Haan & Icove, 2011, p. 714). Ignitable liquids are easy to obtain from refuelling stations and Do-It-Yourself (DIY) stores.

Common ignitable liquids are classified by the ASTM standard test method (ASTM E1618-11, 2011) according to their chemical composition and range of boiling points. The ASTM method includes nine classes of ignitable liquids: Petrol (gasoline); petroleum distillates; isoparaffinic products; aromatic products; naphthenic paraffinic products; *n*-alkanes products; de-aromatised distillates; oxygenated solvents and miscellaneous products. From this list, it can be deduced that ignitable liquids fall into two main classifications. Those that are hydrocarbon based classifications and those that classified as oxygenated products.

The hydrocarbon types are based on refined petroleum products and contain short chain, medium chain and long chain hydrocarbons. These hydrocarbon chains provide high calorific values when combusted when compared to other common materials (Jones, 2003). Typical heat of combustion values for petroleum fractions range from 43 to 46 MJ kg^{-1} *(ibid)*. Hydrocarbons such as pentane and hexane have higher values for heat of combustion due to the ratio of hydrogen to carbon bonds as opposed to lower calorific values found in larger hydrocarbon molecules containing more carbon-carbon bonds *(ibid)*. This classification is further divided into aliphatic and aromatic compounds (Figure 1.2).

Examples of oxygenated ignitable liquids are aldehydes, alcohols, ketones and ethers, as these molecules all contain at least one atom of oxygen. These molecules contain oxygen atoms and generally do not originate from a refinery (Stauffer, et al., 2008, p. 341).

1.4.1 *Precursory, Pyrolysis and Combustion Products*

The combustion of materials at a fire can interfere with analysis as some materials often decompose into hydrocarbon products (Houck & Siegel, 2010, pp 432-440). The same products can also be found in un-combusted ignitable liquids. This can be a major or minor hindrance depending on what instrumentation is available to analyse samples. The problems encountered during analysis using instrumentation are examined in section 1.7. The products can be classified into four types: Precursory; pyrolysis; combustion and fire suppression *(ibid).*

Precursory products include materials that are either natural such as wood or man-made such as textiles, polymers and lubricants and when combusted will distil products. For example when ignited some softwood types would distil terpenes and other phenolic substances (Aseeva, et al., 2005, pp 45-53).

Pyrolysis products, also known as artefacts, are the result of heat being applied to a substrate which subsequently decomposes. Decomposing molecules can lose functional groups or lose mass by random or functional group scission (Stauffer, et al., 2008, p. 461). In effect, the molecule becomes disassembled and re-assembles into separate products. In the example of a polymer such as polypropylene, the re-assembled (breakdown) products may include *n*-alkanes, *n*-alkenes (section 1.4.2) and *n*-alkadienes *(ibid).* In fire debris analysis, breakdown products are often complicated because of the randomness of the scission, but are generally distinctive from ignitable liquid target molecules (ASTM E1387-01, 2001; ASTM E1618-11, 2011) when analysed with the correct instrumentation *(ibid).* For example, the chemical compounds toluene, naphthalene and indene are present in ignitable liquids but also are pyrolysis products. The use of extracted ion chromatograms with Gas Chromatography – Mass Spectrometer (GC-MS) can alleviate most interference sources encountered with fire debris analysis (section 1.8.1.1). These compounds do not appear on the target molecule list for ASTM standards.

Combustion products are a result of reduction and oxidation (redox) processes occurring as substrates are burnt in air. Simple redox products from short chain hydrocarbons yield water and carbon dioxide products. More complicated redox products caused by long chain carbon based molecules include acetophenone and benzaldehyde (section 6.6). The analysis of combustion products with regard to interference is discussed in Section 1.8.1.1.

Fire suppression products vary according to which fire suppression agent has been used. It varies from country to country and also the type of fire will dictate what type of agent is used to suppress the fire. For example, a carbon dioxide extinguisher can be used to suppress an electrical fire, whereas foam such as Compressed Air Foam (CAF) may be used to suppress an oil spill fire or structure fire (Grant, 2012). The chemical agents added to water allow several advantages to fire crews. The main advantage is the preservation of scene evidence due to less water used to suppress the fire than by just water alone (Hadjicostas, 2013). However, the extra chemicals added to fire suppression agents may add to the interferences at a fire scene. A study of CAF interferences at a fire scene by Dawkins, et al. (2010) found that CAF did not interfere with the analysis of ignitable liquids. Chemical agents added to water is not a feature of this Thesis. Only mains powered water was used in this study (section 6.2).

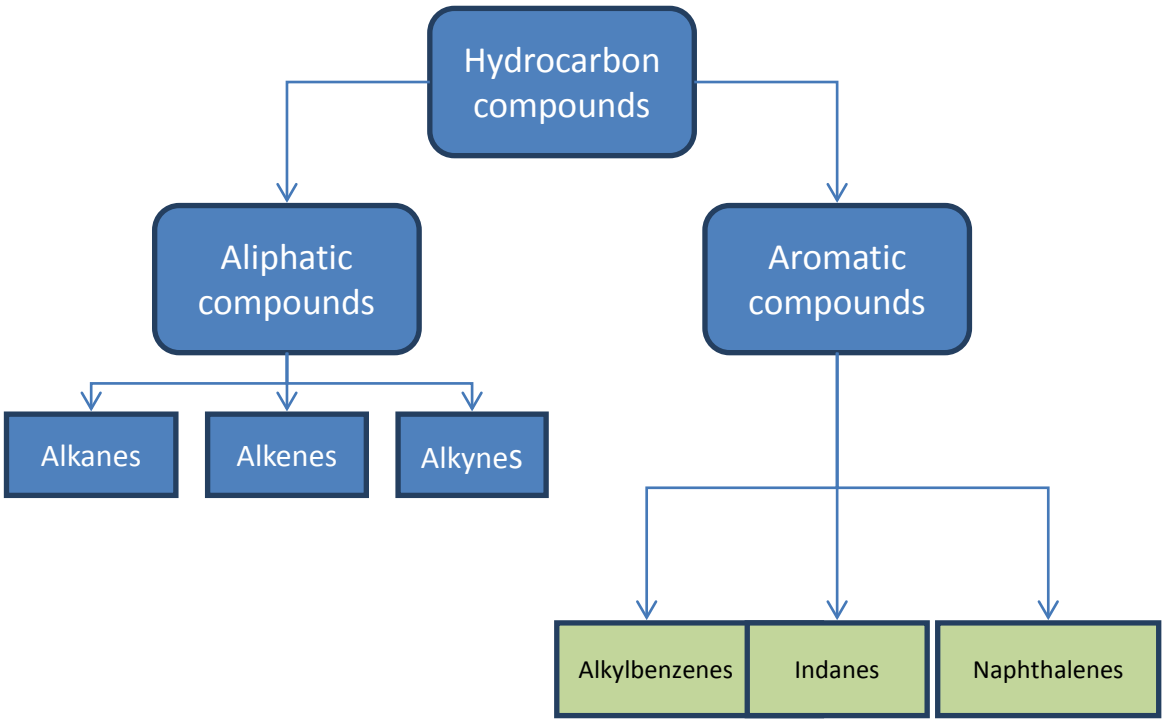

Figure 1.2 The classification of compound types that feature in many common ignitable liquids

1.4.2 *Aliphatic Compounds - Alkanes, Alkenes and Alkynes*

Alkanes are found in crude oil (Freund, et al., 1982, p. 11) and are characterised by their C-C and C-H bonds and have a general formula C_nH_{2n+2}. The bonds can be straight chained or branched. The branched alkanes may have the same chemical formula as a straight chain alkane but have different properties because of differences in inter-molecular bonding (Allinger, 2010, pp. 51-89). Straight chain, branched and cycloalkanes are found in many medium and heavy petroleum distillates, but do not feature in most light petroleum distillates (Stauffer, et al., 2008, p. 296). The alkanes are important markers or target compounds for common ignitable liquids such as diesel and other heavy/medium petroleum distillates as they are abundant in many ignitable liquid types *(ibid)*. In ASTM E1618-11 (2011) diesel is regarded as a heavy petroleum distillate and target compounds range from nonane to heneicosane. The C-H bond angle symmetry contributes to zero dipole moments ($\mu = 0$ D) (Bruice, 1998) and therefore alkanes are regarded as non-polar molecules. This feature is important to bear in mind when considering potential adsorbents of diesel and other similar ignitable liquids as non-polar molecules can be adsorbed by adsorbents that prefer to adsorb non-polar compounds. This discussed in more depth in section 4.2.

Alkenes are essentially C-C bond chains that have a single double bond (C=C) in the chain and have a molecular formula of C_nH_{2n}. Isomers are common but due to the restriction of atom rotation around the double carbon bond (Bruice, 1998, p. 109) are restricted to configurational isomers. Alkenes are found in combustion and pyrolysis products (section 1.4) but are not searched for when trying to identify ignitable liquids as they are too common (Stauffer, et al., 2008, pp 457-463) and are not included as target compounds. They are regarded as interference products and during analysis can largely be ignored by filtering results within the analytical software when using GC-MS (section 1.8.1.1).

Alkynes are denoted by triple bonded carbon atoms and are very reactive. They have the general formula C_nH_{2n-2}. The simplest form of an alkyne is ethyne which is used as a welding gas. These compounds are not found in ignitable liquids.

1.4.3 *Alkylbenzenes, Indanes and Naphthalenes*

Alkylbenzenes are aromatic compounds (Figure 1.2) that are found in some petroleum distillates (Newman, 2004). These compounds consist of a benzene ring and there is one or more substitution of hydrogen atoms for an alkyl group on the ring (Figure 1.3). One methyl functional group attached to a benzene ring gives rise to the name methylbenzene, commonly called toluene. The position of the alkyl group on the benzene ring determines the isomer name. The presence of pi bonds from the benzene ring (arene) and the position of substituted alkyl groups give the molecule a slight polarity. This polarity is important to consider when choosing a suitable adsorbent (section 4.2). Alkylbenzenes are found in petroleum distillates as they are formed from the cracking process at a refinery. Some of these compounds are isomers (Figure 1.3) that are used as target compounds for identifying ignitable liquids such as petrol or diesel (ASTM E1618-11, 2011). In this thesis, these compounds are referred to as C_2, C_3 and C_4-alkylbenzenes.

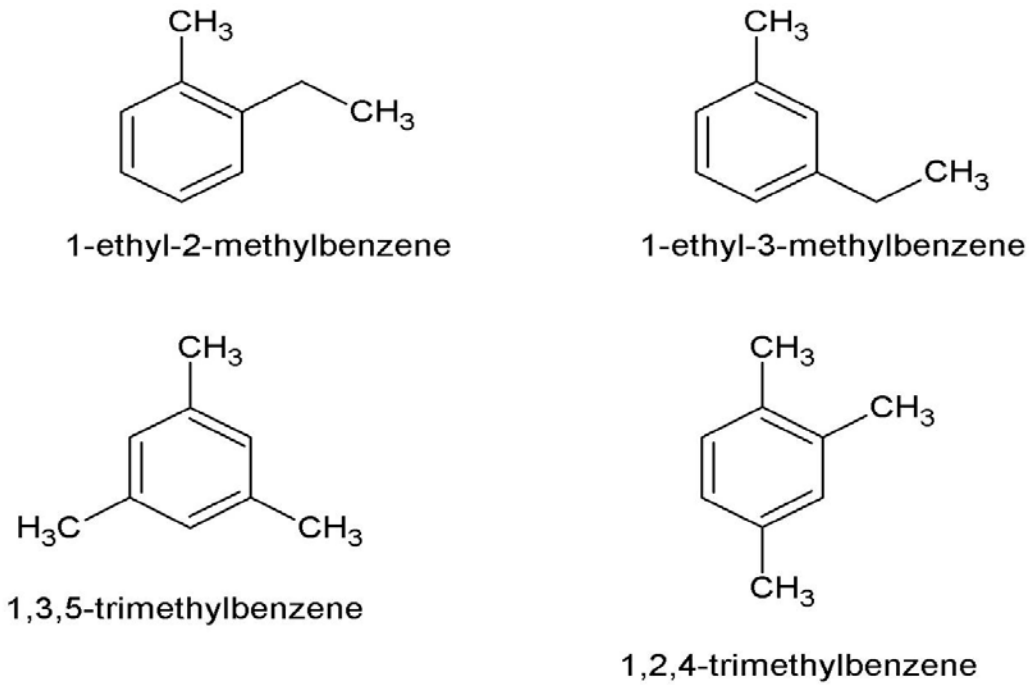

Figure 1.3 C_3-akylbenzene isomer structures found in petrol and diesel fuels

Indane (C_9H_{10}) and certain alkylindane isomers are found in ignitable liquids as they account for some of the compounds found in medium and heavy petroleum distillates (Newman & Lothridge, 1998; Figure 1.4). The conjugated *pi* bonds of indane contribute to a dipole moment of μ = 0.55 D (Committee on Digest of Literature, 1968) making this molecule slightly nucleophilic and therefore slightly polar, which also is significant when considering a suitable adsorbent that will adsorb these compounds (section 4.2). The molecule indane is a common compound in fire debris analysis as it is often found as a pyrolysis product (section 1.4; Stauffer, et al., 2008, p. 464). However, C_1 and C_2 indane isomers (Figure 1.4) are not found in pyrolysis products and are used as target compounds (ASTM E1618-11, 2011) to identify petrol and diesel fuels.

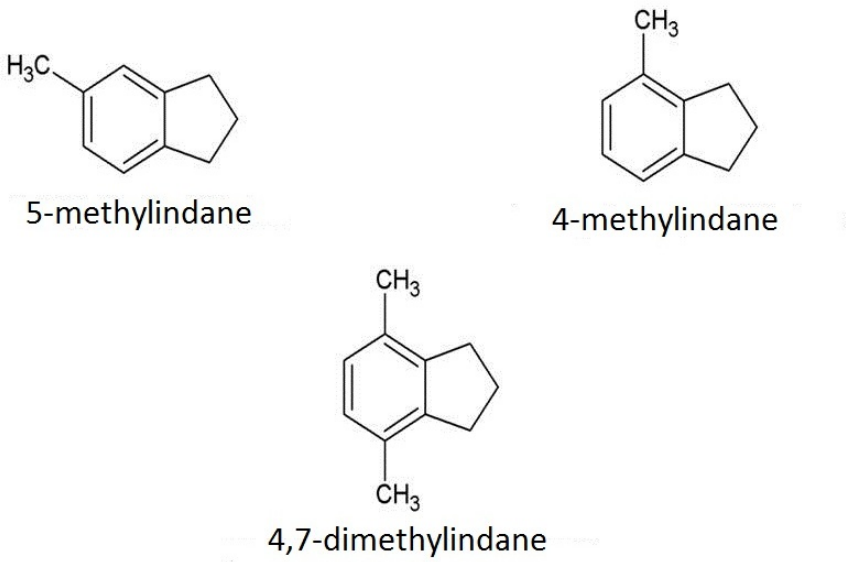

Figure 1.4 C_1 and C_2-indane isomer structures used as target molecules for some ignitable liquids

Naphthalene ($C_{10}H_8$) and some alkylnaphthalene isomers (Figure 1.5) are also classed as polycyclic aromatic compounds and are found in both medium/heavy petroleum distillates and in combustion products (Newman & Lothridge, 1998). Naphthalene has a no dipole moment (Committee on Digest of Literature, 1968) so is considered non-polar. However substituted alkyl groups will slightly affect polarity because of nucleophilic attraction of the H atoms on the alkyl group to the *pi* bonds on the naphthalene structure *(ibid)*. Naphthalene is a common combustion or pyrolysis product (Stauffer, et al., 2008, p. 464)

so is not used as a target molecule in fire debris analysis but the isomers of C_1, C_2 and C_3-methylnaphthalene at Figure 1.5 are used as ignitable liquid target compounds, although 1-methylnaphthalene and 2-methylnaphthalene are also found as common pyrolysis products *(ibid)*. The peak ratio of each of these two compounds is taken into account when analysing chromatograms and this is discussed in section 1.8.1. The compound 2-methylnaphthalene is always more abundant when found in an ignitable liquid *(ibid)*. However, the identification of these compounds as target molecules (ASTM E1618-11, 2011) should be carried-out with caution. It is possible that an analyst may confuse the discovery of these compounds as ignitable liquid compounds when they are in fact pyrolysis products. Studying the ratio of 2-methylnaphalene to 1-methylnaphthalene (discussed in section 1.8.1) and comparing control samples taken from the fire scene will assist in making a correct identification. Note that 1,6,7-trimethylnaphthalene in Figure 1.5 is a synonym of 2,3,5-trimethylnaphthalene (Table 1.2).

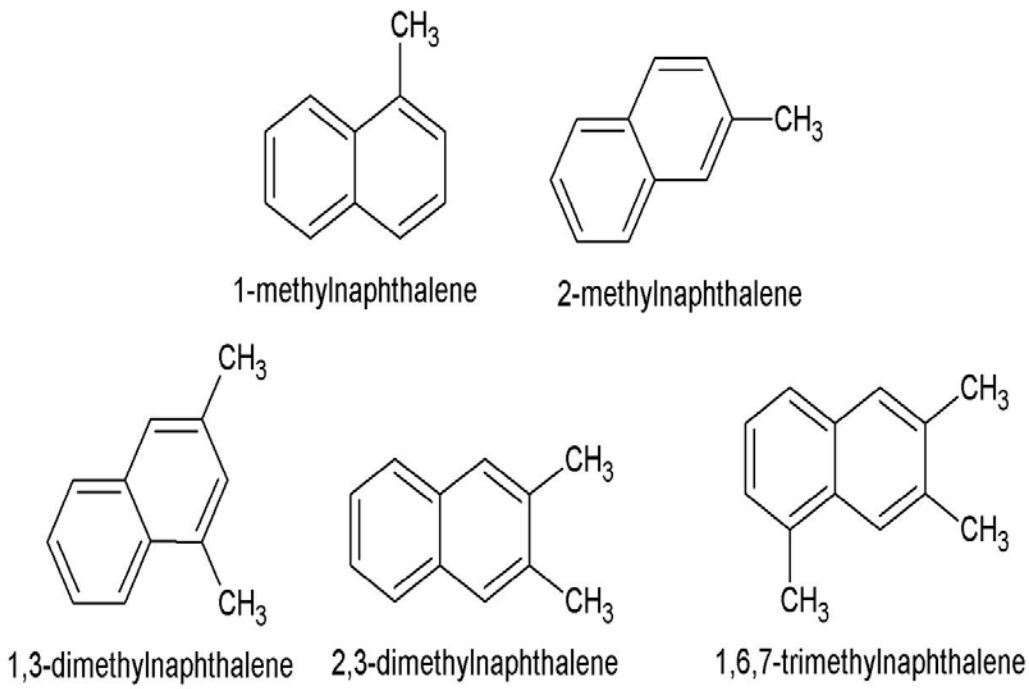

Figure 1.5 Alkylnaphthalene isomers structures found in heavy petroleum distillates

1.5 Laboratory Techniques for Fire Debris Analysis

After fire debris is collected from a fire scene it is sent to a laboratory for testing. Methods of separating ignitable liquids from residues exist for the purpose of providing standard methods (ASTM E1386-10, 2010; ASTM E1388-12, 2012; ASTM E1413-07, 2007; ASTM E1412-07, 2007) depending on the type of separation chosen. These protocols allow analysts to prepare a sample for instrument analysis. Methods focus on different stages of evidence collection and analysis: The first stage is the detection and collection of evidence from the fire scene and includes handling and packaging (section 1.2). The second stage is the extraction of ignitable liquid compounds from fire debris (section 1.5.1). The analysis stage (Section 1.7) entails the analysis of samples by a GC-MS using the protocol ASTM E1618-11 (2011). Until recently a gas chromatograph with a flame ionisation detector (GC-FID) was supported by ASTM as a viable method (ASTM E1387-01, 2001), but this method is no longer supported. The last stage is the interpretation of the results that leads to a conclusion.

1.5.1 *Separation techniques for ignitable liquids from fire debris*

There are several techniques to separate ignitable liquids from fire debris in order to prepare the sample for analysis by a scientific instrument for the purpose of confirmation and identification of ignitable liquids.

1.5.1.1 Solvent Extraction and Steam Distillation

Solvent extraction is a technique that uses a solvent to break bonding forces between compounds present in ignitable liquids and a substrate and in so doing eluting those compounds from the fire debris into the solvent. The fire debris samples are ‘extracted’ with the solvent and the solvent is subsequently filtered to remove solid matter to prevent damage to the GC instrument. Typical solvents used are pentane or carbon disulfide (Newman, 2004; Keto & Wineman, 1991) but diethyl ether has also been used (Lentini & Armstrong, 1997). The technique has been superseded by more modern techniques (section 1.5.2) but it is still supported by ASTM E1386-10 (2010). The biggest disadvantage is that

in ‘washing’ the fire debris, other compounds that are not from ignitable liquids enter the solvent. Subsequent analysis is made more difficult as chromatograms tend to be complex with multiple peaks (Bertsch & Ren, 2000, p. 617-78). This used to be a major problem when analysis was achieved with older detectors such as the flame ioniser detector (GC-FID) but now EIC analysis used with GC-MS can distinguish between compounds of interest and those that are not like pyrolysis and combustion products (section 1.4).

Steam distillation relies on the separation of water insoluble hydrocarbons from fire debris using water. This technique lowers the boiling point of hydrocarbon compounds and so vaporise the compounds at a much lower temperature than normal (Stauffer, et al., 2008, p 380-383). This occurs because water and hydrocarbons are immiscible to one another and their total vapour pressure combined lowers their respective boiling point temperatures. Also, the steam is itself a solvent for polar compounds and may dilute any ignitable liquids that are polar in nature such as ethanol.

This technique has been superseded by modern techniques and ASTM withdrew (ASTM E1385-00, 2000) in 2009. Compared to other methods it is complex, work-intensive, and insensitive (Newman, 2004).

The main drawback to both solvent extraction and steam distillation is that they were used where analysis was completed with GC-FID and so the resulting complicated matrix of compounds which was difficult to interpret. The advent of new adsorption media and mass spectroscopy has sealed the fate of these work-intensive techniques.

1.5.1.2 Headspace Sampling Techniques

There are two main ways of sampling the headspace above fire debris in a closed container. These are known as: *dynamic headspace adsorption* and *passive headspace adsorption* (Pert, et al., 2006). Dynamic adsorption is discussed further in section 1.5.3. This is a standard method for fire debris analysis using (ASTM E1388-12, 2012) but other headspace techniques exist (see sections 1.5.3 & 1.5.4). A volume of the headspace is withdrawn into the heated syringe and injected directly into a GC. The principle of this technique is for the container with the fire debris inside to reach an optimum temperature, so that all compounds of interest are in the vapour phase. According to Stauffer, et al. (2008), pp 421-423, a volume from 0.5 cm^3 to 1.0 cm^3 is normally sufficient amount to withdraw.

The main problem with this technique is obtaining the correct temperature for the container to release all of the target compounds as vapours *(ibid)*. High vapour pressure, low boiling point compounds release into the vapour phase earlier than later boiling point compounds in a heated environment, diffuse faster to the GC column and so they are often over-abundant (Klee, 2013). On the examination of a subsequent TIC the peak ratios may be skewed in favour of low boiling point compounds compared to a standard ignitable liquid control. Consequently, chromatograms may feature a false representative picture of what ignitable liquid is mixed with the fire debris. Another problem is the temperature of the syringe and needle. If the syringe needle is exposed to ambient temperatures during the withdrawal of headspace air, condensation of higher boiling point compounds can occur and may not reach the GC when injected. A subsequent chromatogram may also then give false information about whether an ignitable liquid is present or not.

Despite the drawbacks, this technique is still a viable method for screening prior to using a separation method to separate ignitable liquids from fire debris (Karkkainen, et al., 1994) and can be used in lieu of olfactory analysis to determine if there is an ignitable liquid present (section 3.4). The main advantages of this technique is that it is rapid compared to solvent extraction and is also non-destructive to the evidence sample. Because the sample remains in the heated container it remains undamaged and uncontaminated. Any positive indications of ignitable liquids at this stage are to be viewed as tentative and should follow onto the next stage which involves extraction of ignitable liquids by adsorption.

1.5.2 *Modern Adsorption and Desorption Headspace Sampling Techniques*

Most modern laboratories that investigate fire debris now use different adsorption and desorption techniques. Adsorbents are used in the sampling of fire scenes (Section 1.3), but certain special types of adsorbent are used to separate ignitable liquids from fire debris (section 1.5.1) and these are introduced in this section.

Sorbent materials are classified by their mechanism of sorption. For adsorption, the mechanisms are chemisorption and physisorption. These types are further divided into how adsorption is achieved. Modern techniques utilise dynamic (section 1.5.3) or passive adsorption (section 1.5.4). All of these mechanisms rely on the adsorbent and adsorbate being in a different phases from each other.

$$A + B \Leftrightarrow AB \qquad \textit{Equation 1.1}$$

Where A is the adsorbate, B is the adsorbent and AB is the adsorbed species. Gas phase adsorbates go through a process of accommodation and binding or 'sticking' (Ranke, 2008) to achieve adsorption to a solid surface (Kisliuk, 1957). Adsorption is achieved by either physical sorption (physisorption) or chemical sorption (chemisorption) (Ebbing & Gammon, 1999, p. 591).

1.5.2.1 Chemisorption

Chemisorption is a chemical reaction that occurs between the solid surface and gaseous or liquid molecules. An adsorbate is said to chemisorbed if it undergoes changes in its electronic structure when bound to a surface than from its electronic structure in the gas phase, and that the electrons are shared by the adsorbate and adsorbent (Masel, 1996, p. 112). Typical sorption energies for chemisorbed molecules range from 62 to 418 kJ mol^{-1} *(ibid)*. This type of sorption is not usually encountered in fire debris analysis and so is not discussed further.

1.5.2.2 Physisorption

Physisorption is the attraction of gaseous or liquid species attracted to a solid surface by weak inter-molecular forces such as van der Waals' (vdW) forces and go through a cycle of adsorption and desorption from the adsorbent (Sun, et al., 2013). In this study only gaseous species are considered. The bonding forces used in this type of adsorption are comparatively weak when compared to chemisorption (typically 8 to 42 kJ mol^{-1}; Masel, 1996, pp. 126-127). Weak inter-molecular forces are a feature of petroleum distillates and therefore this type of sorption is utilised in fire debris analysis. Straight chained *n*-alkanes including the *n*-cycloalkane compounds have low dipole moments (section 1.4.2). This means that the distribution of the charge is spread around a few atoms and is termed non-polar. Non-polar gaseous species adsorb onto solid non-polar surfaces. Non-polar compounds such as alkanes (section 1.4.2) weakly bond to adsorbents such as activated

carbon strips (ACS) or Tenax TA®, which are both used in the extraction of ignitable liquids from fire debris (section 1.6.3).

1.5.2.3 Isotherms

At a constant temperature, molecules can indefinitely bind to a solid surface (Langmuir, 1918). Molecules may return into the gas phase due to vapour pressure and kinetic energy of surface molecules (Ebbing & Gammon, 1999, p. 460). This is achieved through heat energy applied to the surface of the adsorbent. The more molecules that are in the vapour phase, the more likely that molecules will adhere to the surface as condensed molecules. When the rates of condensation and vaporisation are equal, the liquid and vapour are said to be in a state of equilibrium.

Some adsorbents such as Tenax TA® and ACS contain pores that vary in size but have been measured to a mean value of 200 nm (Puype, et al., 2012) and the pore sizes are selective for certain molecules (Schneider & Goss, 2009). Vapour phase molecules that can fit into the pores will adsorb while those that do not fit will not adsorb efficiently but may adhere after the pores are filled (Brunauer, et al., 1938). The order of pore filling of an adsorbent in the presence of an adsorbate starts with an increase of vapour pressure through heat that increases the likelihood that molecules fill and condense into the pores first Barrett, et al. (1951). As the vapour pressure is increased the adsorbent uptake will continue until a monolayer is formed (Figure 1.6). As the vapour is increased further, more adsorbate condenses using van der Waals' forces on top of the monolayer until a multilayer is formed and all pores are filled with liquid (Masel, 1996, p.111).

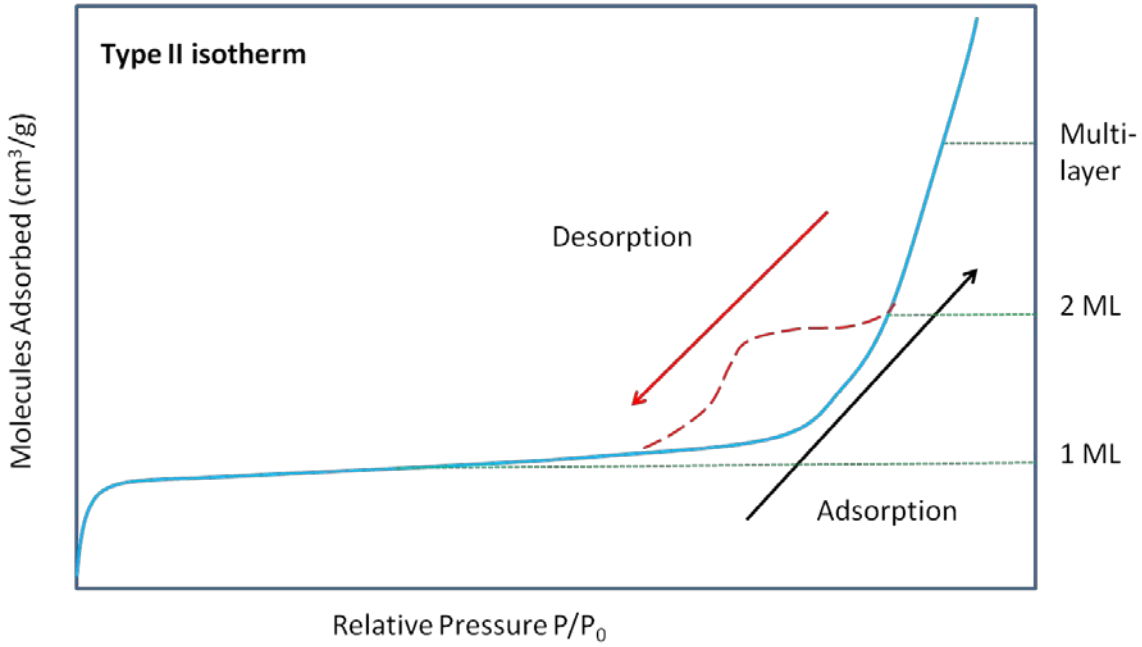

Figure 1.6 Type II isotherm showing adsorption and desorption of molecules in multi-layers (ML)

If an adsorbent contains pores as part of its morphology, the pores will also become filled with adsorbate. The filling of pores is known as capillary condensation and is characterised by a rate limiting uptake of adsorbate with increasing relative pressure (Figure 1.7) and is known as Type IV isotherm (Brunauer, et al., 1938). The Type IV model is applicable to the adsorbents chosen for this study. Synthetic adsorbents such as Tenax TA® have pores as do some natural materials such as clay and limestone. This is discussed more in depth in section 3.7.3.

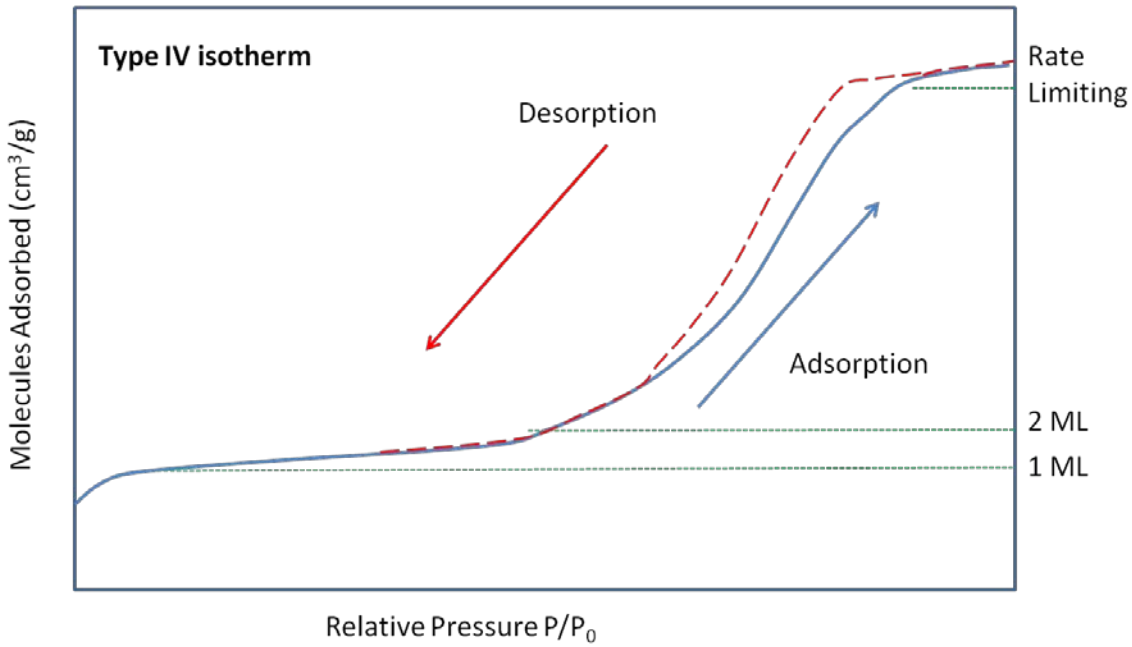

Figure 1.7 Type IV adsorption isotherm showing adsorption and desorption

1.5.2.4 Desorption

When the vapour pressure is reduced, the rate of molecules transiting to the vapour phase increases and molecules in a condensed phase decreases This process is known as desorption. This process is equally important as adsorption and is also known as inverse-adsorption (Ranke, 2008). The isotherms shown at Figure 1.6 & Figure 1.7 show desorption curves for Type II and Type IV sorption models.

The desorption curve starts to fall steeply as the outer molecules in the multi-layer are further away from the surface and so less energy is needed to remove them from the layers. The curve reaches a plateau as the second multilayer (2 ML) is reached, but as pressure is reduced, these molecules are desorbed. The last layer of molecules (1 ML) is removed after relative pressure falls. The surface forces have a significant effect on the first multi-layer, so more energy is required to desorb this layer. A combination of heat and pressure with a constant flow releases the molecules from the adsorbent into the vapour phase. This technique is known as thermal desorption and is discussed in (section 1.6.4).

1.5.2.5 Competitive Adsorption

Where there are more than one adsorbate in an environment with a single adsorbent, competitive adsorption may occur (Snoeyink, 1990, pp. 781-867). This idea was developed by Radke & Prausnitz (1972) as an extension of the Freundlich equilibrium (Freundlich, 1906) and modified by Crittenden, et al. (1985) in which the proposed theory described equilibrium in a two-solute environment. The important factor is the strength of adsorption of the competing molecules. So, this depends on the affinity of molecule one vs the affinity of molecule two. If an adsorbent that prefered to adsorb non-polar compounds was used, it would adsorb non-polar molecules instead of slightly polar or fully polar compounds (discussed further in sections 3.7.3 & 4.7.2.4). In ignitable liquid analysis this becomes important as many petroleum distillates have a mixture of paraffinic, naphthenic and aromatic compounds and therefore have different adsorbent properties as discussed previously in sections 1.4.2 & 1.4.3. Williams, et al. (2005) found that hydrocarbons with a low molecular mass, were displaced from the surface of activated carbon strips (ACS) by those with a higher molecular mass when the surface of the ACS (further discussed in

section 1.6.1) had reached saturation (section 1.5.2.2). This shows that there is a relationship between adsorbent capacity and the competition for adsorbent sites. This phenomenum could become a problem for fire debris analysts as there may be less adsorption sites available for low molecular mass trace compounds due to competition. It is likely that competitive adsorption becomes more problematic with increasing oven time, as the longer the adsorption time, the more probability of a compound could be displaced by a compound that has more affinity for the adsorbent. This was experienced in this study and is discussed in section 3.7.3.

1.5.3 *Dynamic Adsorption*

Dynamic adsorption is a standard ASTM method (ASTM E1413-13, 2013). In this technique, an adsorbent material is placed for a period of time in the headspace of a container above the heated fire debris, to adsorb gas phase molecules (section 1.5.1.2). A pressure is applied in either positive (forced air) or negative (withdrawal of air) mode. Stauffer, et al. (2008), pp 415-421, suggested that activated carbon strips (ACS) have the greatest affinity for volatile ignitable liquid compounds but noted that Tenax TA® is an adsorbent that would be of most use in a negative pressure dynamic headspace adsorption but did not explain why. ACS has a few drawbacks that make it suitable in some situations and not others. The main reason for not using ACS in a dynamic headspace setup is that activated carbon is known to adsorb water (Ahnert, et al., 2003), although it is not known how significant this problem is. This is discussed in section 1.6.1. However, Tenax TA® is non-polar (polypropylene) in nature, has low water retention and has been used to adsorb gases in a wet stream of gas (Moldoveanu & David, 2002, p. 124).

A typical setup for dynamic headspace sampling technique involves a heated headspace such as a Rilsan® polyamide fire debris bag (Arkema, 2013); a gas syringe; Tenax TA® tube, two short sections of polytetrafluoroethylene (PTFE) tubing and a 100 cm^3 heat resistant gas syringe (Figure 1.8).

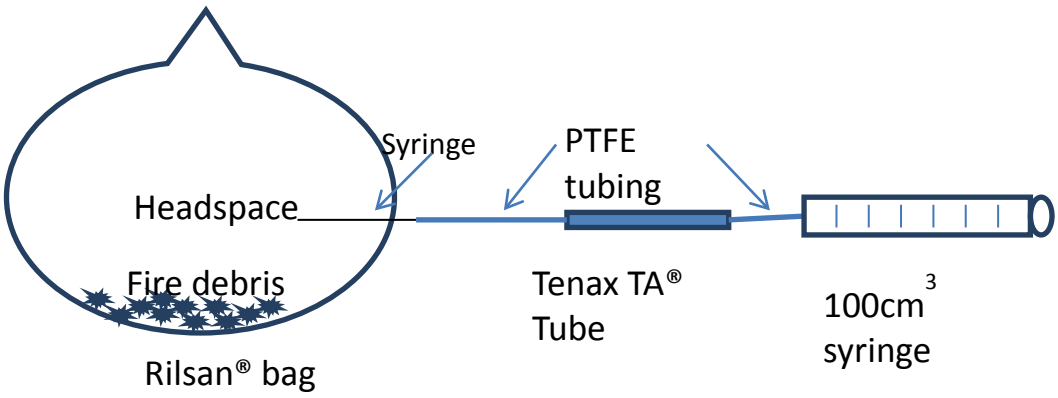

Figure 1.8 A simple setup of dynamic headspace adsorption within a Rilsan® bag containing fire debris

A volume of heated air 60 - 100 cm^3 is withdrawn using a heated syringe and molecules in the vapour phase are adsorbed by the adsorbent inside the tube. The tube is then desorbed by a thermal desorber (TD) (section 1.6.4) for GC analysis. Karkkainen, et al. (1994) used this technique with Tenax TA® and concluded that thermal desorption is also superior to headspace sampling (section 1.5.1.2).

Dynamic headspace adsorption might work well if sampling the headspace is over a period of a few minutes and there is no reduction in temperature during the procedure. As far as available literature is concerned, there is no automated way to achieve a constant temperature throughout the procedure. A consequence of not achieving this will be that vapour phase compounds may well condense and so these compounds are not transferred to the adsorbent. For this reason, dynamic headspace adsorption was not chosen for this study.

1.5.4 *Passive Adsorption*

Passive headspace adsorption is a process that takes place through the diffusion of adsorbates in the vapour phase, adsorbing to the surface of an adsorbent in a closed container. When ACS is the adsorbent of choice for passive headspace adsorption, a standard method (ASTM E1412-12, 2012) is available for use. However, currently there is no standard method for passive headspace adsorption utilising Tenax TA®. Despite this, both ACS and Tenax TA® provide scope for use when using passive headspace sampling. Both can be placed in the head space of a sealable container such as a paint can, which is heated in an oven to ensure the release of volatile compounds from the fire debris evidence

present. This is normally achieved through the application of isothermic heat for a determined length of time. The constant temperature ensures that a state of equilibrium is reached inside the container as compounds become volatile and also condense (section 1.5.2.3). Diffusive sampling is normally limited to compounds that have an affinity for the adsorbent such as non-polar volatile species with non-polar sorbents (Tolnai, et al. 1999). For example, natural zeolites have an affinity for water and alcohols; activated carbon is slightly polar (EPA, 1999) so has an affinity with alkylbenzenes, indanes and naphthalenes; non-polar polymer adsorbents such as Tenax TA® are hydrophobic so have an affinity for non-polar molecules such as alkanes (Scientific Instrument Services, 2009).

Tenax TA® is ideally suited to the adsorption of hydrocarbon based Ignitable liquids such as petrol and diesel as these fuels consist mainly of volatile non-polar hydrocarbons and are adsorbed due mainly to van der Waals' forces and induced dipole – induced dipole interactions (section 1.5.2). Jackowski (1997) used Tenax TA® with passive headspace sampling and found that a wide range of ignitable liquids were adsorbed and identified. These ranged from water-soluble components such as ketones and alcohols through to heavier alkanes present in diesel. The wide range of molecules and compounds adsorbed shows that Tenax TA® is suitable for use in ignitable liquid analysis.

1.6 Adsorbent Materials used in Analysis Methods

In section 1.3, ad hoc adsorbents were introduced as a method of adsorbing ignitable liquids and their residues from fire scenes. However adsorbent materials are also used in the laboratory for analysis methods to investigate fire debris. The three main analysis methods are Activated Carbon Strips (ACS) (section 1.6.1); Graphitised Carbon Resins (section 1.6.2) and Tenax TA® (section 1.6.3).

1.6.1 *Activated Carbon*

Activated carbon has long been used to adsorb contaminants in water and soil. For example water treatment plants use activated carbon to filter contaminants from the water supply. A critical review of the adsorption of phenols using activated carbon, centred on the best material to manufacture activated carbon (Dąbrowski, et al., 2005). Raw materials considered for activated carbon depend on several factors:

- High organic matter and low inorganic composition
- How easy it is to activate the carbon
- Cost and availability
- Susceptibility to degradation

Activation of the carbon is achieved by physical or chemical means. Physical activation uses carbonisation in an inert atmosphere and a partial gasification with steam and carbon dioxide *(ibid)*. Chemical activation is achieved by coating the raw material in phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$). The material is pyrolysed and washed to remove the coating agent *(ibid)*.

Activated carbon contains carbon basal planes (90%), heterogeneous surface oxygen groups and Ash (Arafat, et al., 1999) The surface oxygen groups can contribute to H-bonding with molecules that can achieve this type of bonding and therefore chemisorption (section 1.5.2.1) (Ahnert, et al., 2003). Activated carbon has a preference for the adsorption of molecules containing oxygen and readily adsorbs water *(ibid)*. The presence of water can affect surface chemistry (surface charge, acidity and hydrophobicity) and therefore can inhibit the adsorption of aromatic molecules due to the repulsion of electronegative groups *(ibid)*. ACS strips are packaged with silica gel to remove water vapour and once a strip is removed from its pack it starts to adsorb atmospheric water vapour. This is also an issue with the adsorption of ignitable liquid vapours or residue, as there may still be residual fire suppression liquids or vapours present and ACS may prefer to adsorb these compounds over ignitable liquid compounds. Despite this drawback, ACS are still used with passive headspace diffusion in fire debris analysis (section 1.5.4).

Dietz (1991) used ACS and shaped paper impregnated with activated charcoal called ‘The C-bag’. The ACS and C-bag were suspended within the headspace of the fire debris for one hour to seventy two hours at various temperatures. He reasoned that ambient temperature was sufficient to create enough volatile diffusion within the evidence

container with just 1 hour heated to either 50 ^{0}C or 90 ^{0}C. This time and heat setting would have contributed to some adsorption by the activated carbon, but it may be insufficient if there is only a trace amount of ignitable liquid present. He further suggested that C-bags or the ACS should be used in pairs, so that evidence could be retained for future use. This suggestion has its merits in that the second sample can be run again on an instrument, but there may be evidence storage and contamination issues which are valid from a judicial perspective.

1.6.1.1 ACS Method for Fire Investigation in a Laboratory

Newman, et al. (1996) used a range of temperatures to determine the optimal temperature for adsorption of ACS in a passive headspace environment. The temperatures ranged from 60^0 C to 120^0 C. As the temperature increased, the more the higher boiling point compounds were adsorbed, but in preference to lighter boiling point compounds, effectively displacing these compounds. The author referred to this phenomena as 'competitive adsorption' (section 1.5.2.5). At the lower oven temperatures there was a problem with the adsorption of the heaviest target compounds and this may be significant if diesel is analysed, as the heaviest target compound heneicosane (section 1.4.2 and 2.4.1) may not be adsorbed at these temperatures. This may lead to an incorrect conclusion of identity between a medium petroleum distillate and a heavy petroleum distillate *(ibid)*. There was a further suggestion in that study that an oven time period of 16 hours @ 70 ^{0}C should be used but it was also remarked that this was a convenient time that fitted into staff schedules. Sixteen hours is a long time to wait for optimised adsorption which results in the maximum number of layers of condensed molecules on an adsorbent and competitive adsorption could become a problem (section 1.5.2.5). The suggested time of 16 hours is discussed further in section 3.7.3.

Desorption of ignitable liquid compounds from ACS can be achieved through solvent extraction (section 1.5.1.1). A popular choice of solvent carbon disulphide (CS_2) has been used in research (Waters & Palmer, 1993; Dietz, 1991; Newman, et al., 1996). The ACS is inserted into a volume of CS_2 and agitated or vortexed to assure elution of compounds from the ACS surface. A typical volume of CS_2 to achieve elution is from 100 µL to 1000 µL. Other popular solvents used are diethyl ether and pentane. A study by (Lentini & Armstrong, 1997) of the solvents CS_2 and diethyl ether revealed that the latter solvent was

just as effective at eluting bonded compounds but with a much reduced health and safety risk, as CS_2 is a known human carcinogen and has an auto-ignition temperature of 90 ^{0}C. In contrast, diethyl ether has an auto-ignition temperature of 180 ^{0}C and is not considered a human carcinogen. Pentane has an auto-ignition temperature of 260 ^{0}C (Sigma-Aldrich, 2012) and also is not considered as a human carcinogen, it has been known to contain trace alkanes other than pentane (Lentini & Armstrong, 1997), so should be checked before use to ensure it is contamination free. All of these solvents are highly flammable and care needs to be taken to reduce the risk of fire and to the health by reducing exposure to inhalation and skin.

1.6.2 *Graphitised Carbon Resins*

Graphitised carbon is used to adsorb volatile compounds from air and are generally used in conjunction with packed tubes and a TD for desorption (Sigma-Aldrich, 2013). Table 1.1 shows the various forms of graphitised carbon resins contained in a Carbotrap 300® thermal desorption tube. Carbotrap C® has the smallest surface area and is the weakest of the adsorbents in that prefers to adsorb non-polar molecules *(ibid)*. Carbotrap B® has a larger surface area than Carbopack C® and prefers aromatic molecules such as alkylbenzenes *(ibid)*. Carbosieve S-III is a molecular sieve with micro and mesopores, has the largest surface area of the three adsorbents and prefers to adsorb small molecules *(ibid)*.

The effectiveness of Carbotrap 300® as an adsorbent for ignitable liquid compounds was researched by (Borusiewicz & Zięba-Palus, 2007) using passive headspace diffusion and an ATD with gas chromatography – mass spectroscopy (ATD-GC-MS) and concluded that Carbotrap 300® is suitable for polar and volatile compounds. The efficiency was calculated by the thermodesorption effectiveness for an ignitable liquid compound using 18 compounds. The smallest compound was ethanol and the largest compound was n-C_{16}. The effectiveness was very high for light compounds and started to become less effective after n-C_{12}. The adsorption range of graphitised carbon resins is too narrow to be used as a general adsorbent for ignitable liquids as singularly they do not allow the adsorption of both light and heavy ignitable liquids. Carbotrap C may be able to adsorb medium and heavy ignitable target compounds (Table 1.1).

Table 1.1 Adsorbents contained in Carbotrap 300®, adapted from (Sigma-Aldrich, 2013)

Type	Surface area (m^2/g)	Suitable for adsorption of analyte size	Strength of adsorbent
Carbotrap graphitised carbon black (20/40 mesh)			
Carbotrap C®	10	C_{12} - C_{20}	Weak
Carbotrap B®	100	C_5 - C_{12}	Moderate
Carbon Molecular Sieve			
Carbosieve S-III®	975	C_2 - C_5	Strong

1.6.3 *Tenax TA®*

Tenax TA® is a synthetic polymer molecule (2,6-diphenylene-oxide) (Alfeeli, et al., 2011). It was conceived and patented by the General Electric Company (Hay, 1969) as an insulation polymer. This particular molecule is non-polar in nature (Moldoveanu & David, 2002, p. 124) and has an affinity for other non-polar molecules or compounds. Vapour phase compounds are attracted to the surface atoms which are incompletely bound and so give rise to reactivity at that site and adsorption (section 1.5.2.2) is achieved by van der Waals' forces, induced dipole – induced dipole and hydrogen bonding forces (Sun, et al., 2013).

The non-polar feature of Tenax TA® has an obvious advantage over ACS strips as Tenax TA®, prefers to adsorb ignitable liquids in preference to water (Goodman, 2008). When investigating water soaked fire debris, Tenax TA® is the adsorbent of choice.

The desorption of condensed compounds from the Tenax TA® surface is completed through the application of heat and there is no use of a solvent as these dissolve the polymer (Stauffer, et al. (2008), p. 423-439 & section 1.6.4).

Tenax TA® is an adsorbent with a mean pore sizes of 200 nm and a pore volume of 2.4 cm^3/g (Alfeeli, et al., 2011). The pores are filled first (section 1.5.2.3) until a monolayer is achieved and then a multilayer forms until the pores are filled and the adsorbent surface is saturated in liquid molecules. Capillary condensation ensures that pores are filled first before a monolayer and multi-layer adsorption takes place *(ibid)*.

Breakthrough data volume for a compound is a volume of carrier gas per gram of adsorbent resin that causes the compound to migrate from the front of the adsorbent bed to the rear of the adsorbent bed (Manura, 1999). The calculation is:

$$V_B = \frac{(t_R \; x \; F)}{m_A} \qquad \textit{Equation 1.2}$$

Where V_B = breakthrough volume (L/g); t_R = retention time (minutes); F = flow rate (L/min) and m_A = mass of adsorbent (g)

The breakthrough data for Tenax TA® (Scientific Instrument Services, 2009) suggests that at 90 ^{0}C, the adsorbent can adsorb C_4 to > C_{25} alkanes; alcohols/glycols; aromatics; terpenes and ketones. The data also shows desorption temperature at 300 ^{0}C to desorb compounds < C_{21}. This data set is important when considering the optimum adsorption parameters for using Tenax TA® in association with fire debris in an oven used for separating an ignitable liquid from fire debris (section 3.1). Common ignitable liquids contain hydrocarbons and aromatics in the range C_4 to C_{21} and in relation to Equation 1.2 for dynamic adsorption (section 1.5.3), the oven temperature of 90 ^{0}C was used as an initial start point to allow this research to further investigate a suitable temperature when using passive headspace adsorption.

Jackowski (1997) placed Tenax TA® tubes inside sample containers and placed them in an oven overnight. The samples contained many different types of ignitable liquids and the oven temperatures used were: 60 ^{0}C for petrol and mineral spirits samples and 90 ^{0}C for all other samples. Desorption was carried out with an ATD. The author concluded that alcohols, ketones and heavier distillate fuels such as diesel were identified. The research extended to 437 submitted cases, of which there were 1040 items. Of these ignitable liquid was found in 47.4% of items. Petrol was the most common ignitable liquid found. This clearly shows that temperatures between 60 ^{0}C to 90 ^{0}C is a prudent choice for oven adsorption temperature and that Tenax TA® is able to adsorb a wide range of ignitable liquids.

In section 1.6.2 graphitised carbons were introduced including the adsorbent Carbotrap®. Borusiewicz & Zięba-Palus, (2007), evaluated Tenax TA® and Carbotrap 300® desorption of a range of compounds a fan oven for adsorption followed by desorption with an ATD. It was concluded that Tenax TA® is suitable for the adsorption of non-polar high boiling

point compounds. The adsorbent started to become effective at *n*-C_7 and was very effective at *n*-C_{16}. If the study was extended to incorporate compounds >*n*-C_{16} this would have added to the overall study as the identification of heavy petroleum distillates (ASTM E1618-11, 2011) up to *n*-C_{21} is a requirement of the protocol.

In another study by Borusiewicz & Zięba-Palus (2004), they used passive headspace adsorption to determine oven temperature range for Tenax TA®, for the effective adsorption of ignitable liquids using gasoline; kerosene and diesel. They concluded that the adsorbent optimal temperature was 60 ^{0}C. For practical reasons they kept the oven time to sixteen hours. The adsorption time of sixteen hours was originally determined to be optimal for activated carbon (Newman, et al., 1996) but it may not be optimal for Tenax TA®. This is discussed further in section 3.1.

1.6.4 *Automated Thermal Desorber (ATD)*

After the adsorption of compounds has been completed from fire debris, those compounds are desorbed into an analytical instrument for investigation. This can be achieved with a thermal desorber instrument such as an Automated Thermal Desorber (ATD). Activated Carbon Strips (ACS) (section 1.6.1) are used by many members of The European Network of Forensic Science (ENFSI) laboratories (Hendrikse, 2007) and ACS is a recognised adsorbent capable of extracting ignitable liquids from fire debris (Newman, et al., 1996). However, the strips are not compatible with the ATD. Various derivations of activated carbon in granular form are compatible such as Carbotrap 300® (Borusiewicz & Zięba-Palus, 2007) and these are loaded in either glass or steel tubes. Tenax TA® and Carbotrap 300® are used exclusively with thermal desorption methods. The ATD incorporates a computer controlled carousel for automated loading and synchronisation with the attached gas chromatograph. According to Hendrikse (2007), the ATD is not as prevalent as the use of ACS with solvent desorption (section 1.6.1). However, some fire debris analysis laboratories do use thermal desorption instrumentation for the investigation of fire debris (Haworth, 2011).

Desorption of a tube containing an adsorbent complete with adsorbate requires an automated stage in order to work effectively (section 1.6.4). A stainless steel or thermal glass tube pre-packed with a suitable adsorbent such as Tenax TA® or Carbotrap 300® is placed on a computer controlled carousel. The tube is grabbed with a mechanical arm, both

end-caps are removed and the tube is placed into the instrument. It is held in place by hydraulic seals. A carrier gas such as helium is pumped through the tube to purge to waste. This ensures any water in the adsorbent tube is removed and does not reach the cold trap. After the purge, the instrument opens a seal to the trap where the contents of the now heated tube are carried along with the flow. An inlet split control valve at this point determines how much flow reaches the cold trap. This valve is set by the user according to how much sample is required to reach the trap. In fire investigation there are likely to be many desorbed compounds that could contaminate the instrument or overload the detector which will increase the difficulty of identifying target molecules. Therefore the inlet split is set to guard the trap from overloading. The flow that does reach the trap carries volatile compounds where the temperature is low enough to condense and concentrate compounds into a small surface area. The trap is flash-heated and the sample is carried by the carrier gas to the GC column where it can re-condense again due to the start temperature of the programme. However, after the flow leaves the trap it must enter another checkpoint. This is the outlet split control valve and operates in the same way as the inlet split valve. This valve determines how much sample actually reaches the column. One of the drawbacks to the ATD is there is a risk of overloading the instrument and subsequently the detector if the split valves are not set to their optimum setting. The setting requires a balance of allowing enough compounds through the ATD onto the column without reducing the sensitivity of the detection capability. This is discussed in depth at section 3.4. Typical parameters for the ATD for the analysis of fire debris vary, but once the parameters are chosen they are difficult to alter as the parameters are often recorded as part of laboratory quality management (Haworth, 2011). The carrier flow can be as low as 30 mL/min (Borusiewicz & Zięba-Palus, 2004) and as high as 100 mL/min (Haworth, 2011). The differences of these values are based on laboratory testing for the lower flow value and water soaked samples from a working laboratory. Typical split valve values are 7.8 mL/min for inlet and 30 mL/min for outlet. The cold trap is set to operate between -25 ^{0}C to -30 ^{0}C and flash temperature values range from 250 ^{0}C (Goodman, 2008; Borusiewicz & Zięba-Palus, 2004). The flash temperature is designed to flash-heat the compounds so that they quickly enter the gas phase and exit the trap with the carrier gas en-mass. Some ignitable liquid compounds have high boiling points in excess of 250 ^{0}C from pentadecane (bp 271 ^{0}C) upwards (ScienceLab.com, 2013); therefore a temperature range of 300 ^{0}C to 350 ^{0}C is preferable.

1.7 The analysis of ignitable liquids from fire debris

Once the separation of volatile compounds has been achieved, they can be analysed by a gas chromatograph (GC) through injection as a liquid or as a gas from an ATD (section 1.6.4) and detected with either a flame ionisation detector (FID) or mass spectrometry (MS).

1.7.1 *Gas Chromatography*

The GC is an excellent tool for separating chemical compounds especially from each other so that an analysis of compounds can be undertaken. Each compound has a specific boiling point and it is this property that is exploited to achieve separation. To help it achieve this, the liquid sample is vaporised through an injection port. With the assistance of an inert carrier gas flow, the gaseous sample is passed to a capillary column inside an oven and is swept along by the carrier gas. The carrier gas acts as a mobile phase to carry the sample along to the detector.

The most important step in selecting a column is choice of stationary phase (Kitson, et al., 1996). The stationary phase is a film that coats the inside of the column and contains either polar compounds (polar phase) or non-polar compounds (non-polar phase). The choice of column phase is ultimately determined by the protocol being used. If mass spectrometry (MS) (section 1.7.2) is used as the detector, the standard method (ASTM E1618-11, 2011) requires that the column must be non-polar phase or relatively non-polar phase such as a 1% phenyl coating.

Thin column films should be used for high boiling point compounds (McNair & Miller, 2009, p. 44). This is important an important factor when analysing ignitable liquids, as heavy alkane compounds in diesel and bio-fuels have high boiling points. In searching literature for GC methods on the analysis of ignitable liquids, the 25 m and 30 m column lengths are the most common (Newman & Lothridge, 1998; Borusiewicz & Zięba-Palus, 2007; Nowlan, et al., 2007). From the factors discussed in this section, the ideal column for the analysis of ignitable liquids is a 1-5% phenyl polysiloxane; 25 mm ID; 25 µL film and 25-30 m column.

The phase selection is important but just as important is the temperature selection or temperature programme for the GC oven where the column is located. As column temperatures increase (15 – 20 ^{0}C), retention times decrease by a factor of two (Hinshaw, 2001) and the vapour pressure of the solute increases logarithmically (McNair & Miller, 2009, pp. 29-41) and therefore oven temperature variance leads to variable elution times. The increase in vapour pressure also increases the volume of solute in the mobile phase (carrier gas) so decreases the adsorption or the retention factor of analyte species. This leads to a decrease in selectivity. The decreased selectivity can be explained by the decreased adsorption and therefore the relative spatial differences in the retention of different compounds are lessened.

In ignitable liquid analysis the vapour pressures of compounds are wide ranged such as kerosene or diesel and as a consequence, the oven has a range of programmed temperatures to separate all of the compounds (Newman, 2004). A low starting temperature with a hold time and a gradual temperature increase (ramp) ensures that low boiling point compounds are separated. When the sample exits the GC inlet onto a cool column and remains in a condensed state. As the temperature is increased low boiling point compounds start to volatilise and flow along the column (Kitson, et al., 1996, p. 6). The partition co-efficient of an analyte decreases as the temperature increases and this aids flow. The rate of flow of an analyte is increased until the temperature is held or the analyte is eluted from the column by the mobile phase *(ibid).*

One of the considerations for choosing a temperature controlled programme is that the end temperature is normally higher than the highest boiling point of the analytes. This ensures that the column is cleaned of the sample and is verified by running blanks between samples and ensures sample-sample contamination is minimised. Another advantage is better peak shapes and precision for later eluting analytes (McNair & Miller, 2009, pp. 156-157). Newman & Lothridge (1998) designed a GC-MS programme suitable for the analysis of ignitable liquids. It was adapted by ASTM E1618-11 (2011) and this was used a starting point for projects undertaken in this thesis (section 2.2.3).

1.7.2 *Gas Chromatography-Mass Spectrometry (GC-MS)*

By itself, the GC cannot identify compounds from chromatograph peak signals. Retention times of compounds can be identified by observing peak retention times, but these are not

unique (McNair & Miller, 2009, p. 156). A mass spectrometer is a detector that can qualitatively identify peak signals and give quantitative information. The MS is easily coupled to a GC and is comprised of three main components: an ion source; a mass analyzer and a detector (Westman-Brinkmalm & Brinkmalm, 2009, pp. 15-115). In this thesis only electron ionization (EI) is considered as this method is the most relevant means of achieving ionisation in ignitable liquid analysis (Stauffer, et al., 2008, pp. 265-271).

Ignitable liquid compounds libraries of spectrograms have been extensively integrated into the National Institute of Standards and Technology (NIST) database used on the computer attached to the GC-MS instrument. The separation of positive charged ions is achieved by the ion source and then a coupled mass analyser separates ions according to their mass-to-charge ratio (*m/z*). In ignitable liquid analysis ASTM E1618-11 (2011) requires a mass spectrometer capable of aquiring mass spectra from *m/z* 40 to *m/z* 400 with continuous data output.

According to Newman (2004), pp. 189-195, the most important feature of GC-MS is the ability to produce EICs as it is this feature that allows users to identify compounds according to the spectral profile (section 1.8). Extracting target ions can exclude most of the clutter associated with a TIC. This simplifies data making it more efficient to recognise specific molecules in ignitable flammable liquid residue.

1.8 Interpretation of GC-MS Data

Many ignitable liquids contain hundreds of individual compounds (Dolan, 2004, pp. 133-158). Analysing all of these compounds through gas chromatography would be time-consuming and not necessary to achieve the aim of identifying an ignitable liquid. Research carried out by Keto & Wineman (1991) established a list of useful target compounds. The list consisted of persistent compounds that were found in ignitable liquids. Compounds that were found in other substrates such as toluene and naphthalene as well as ignitable liquids were not on the list as the identification of these compounds could be argued as ambiguous. The list of suggested target compounds (Table 1.2) was incorporated by ASTM as a standard method for identifying ignitable liquid target compounds from fire debris with GC-MS (ASTM E1618-11, 2011).

Table 1.2 Target compounds listed for petrol and diesel in ASTM E1618-11 (2011)

Chemical Name	Chemical Group	Boiling Point (BP) ^{0}C STP[1]	Ions monitored (m/z)
ethylbenzene	C_2-alkylbenzenes	136	91
m,p-xylene		144	
o-xylene		144	
propylbenzene		159	
1-methyl-3-ethylbenzene	C_3-alkylbenzenes	161	105
1-methyl-4-ethylbenzene		162	
1,3,5-trimethylbenzene		164	
1-methyl-2-ethylbenzene		165	
1,2,4-trimethylbenzene		169	
1,2,4,5-tetramethylbenzene	C_4-alkylbenzenes	195	119
1,2,3,5-tetramethylbenzene		197	
indane;	indanes	176	117, 131
5-methylindane		203	
4-methylindane		206	
4,7dimethylindane		227	
2- methylnaphthalene	polynuclear	241	142, 156, 170
1-methylnaphthalene		243	
1,3-dimethylnaphthalene		264	
2,3-dimethylnaphthalene		269	
2,3,5-trimethylnaphthalene		287	
Nonane	*n*-alkanes	151	43, 57
Decane		174	
Undecane		196	
Dodecane		216	
Tridecane		235	
Tetradecane		254	
Pentadecane		271	
Hexadecane		287	
Heptadecane		302	
Octadecane		316	
Nonadecane		330	
Eicosane		343	
Heneicosane		356	
Pristine	branched alkanes	296	57
Phytane		322	
n-butylcyclohexane	*n*-cycloalkanes	171	83
n-pentylcyclohexane		203	
n-hexylcyclohexane		225	
n-heptylcyclohexane		245	
n-octylcyclohexane		264	
n-nonylcyclohexane		283	
trans-decalin	decalin	191	138

[1] Values obtained from Guidechem, 2012

1.8.1 *Pattern Recognition of Ignitable Liquid Residues*

The interpretation of a sample run from GC-MS begins with a brief look of a total ion chromatogram (TIC). Preliminary identification of common ignitable liquids can be made by the analysis of peak patterns and peak ratios compared to laboratory purchased standards *(ibid)*. The diagnostic patterns are useful for preliminary identification of target compounds but they cannot be positively identified without references to EIC spectra, retention/elution time, laboratory controls and standards. Despite this, it remains a useful tool in screening samples for further analysis. Table 1.2 shows the boiling points of ignitable liquid target compounds and the elution order of these compounds is dependent on the boiling point. The lower boiling points are able to progress through the column quicker as they reach their boiling points earlier during the temperature controlled programme (McNair & Miller, 2009, p. 159). Subsequently, the compounds with higher boiling points elute and reach the detector later, hence resulting in longer retention times.

Each diagnostic group can be viewed on GC-MS software using an extracted ion chromatogram (EIC). For example, an EIC ion 91 will reveal compounds that have an m/z of 91 in their structure (ASTM E1618-11, 2011). A typical TIC (Figure 1.9; 4.30 – 4.85 minutes) shows a C_2-alkylbenzene diagnostic group of three peaks referred to as 'The Three Musketeers' (Stauffer, et al., 2008, p. 310). In the example shown, ethylbenzene is the first peak at 4.31 minutes, followed by *meta* and *para* xylene (*m,p*-xylene) at 4.43 minutes. These two compounds are seen as a single peak because their molecular mass is identical and their polarities are very similar *(ibid)*, which means that there is co-elution using the GC-MS method described in ASTM E1618-11 (2011). This does not represent too much of a problem as C_2-alkylbenzenes are not used for target molecules with that method. Last in the group to elute is *ortho* xylene (*o*-xylene) at 4.76 minutes. Although propylbenzene (Figure 1.9; 5.72 minutes) is identified in this group through EIC ion 91, it is considered a C_3-alkylbenzene.

In the C_3-alkylbenzene group (Figure 1.9; 5.75 – 6.20 minutes) five major peaks can be identified. In retention time order they are: *n*-propylbenzene; 3-ethyltoluene and 4-ethyltoluene (partial co-elution); 1,3,5-trimethylbenzene; 2-ethyltoluene. This has been referred as the 'Castle Group' (Stauffer, et al., 2008, p. 311) as the peak pattern resembles the Disney Orlando (U.S.A) castle. However, the group does not include the compound

1,2,4-trimethylbenzene (Figure 1.9; 6.12 minutes) which elutes after 2-ethyltoluene. Although 1,2,4-trimethylbenzene does not fit into the 'Castle Group' pattern it should not be excluded from the group of C_3-alkylbenzenes and is just as significant in relation to peak heights and ratios as the compounds of the group and as Stauffer, et. al (2008), p. 311 admits, is still an important marker for many petroleum ignitable liquid products.

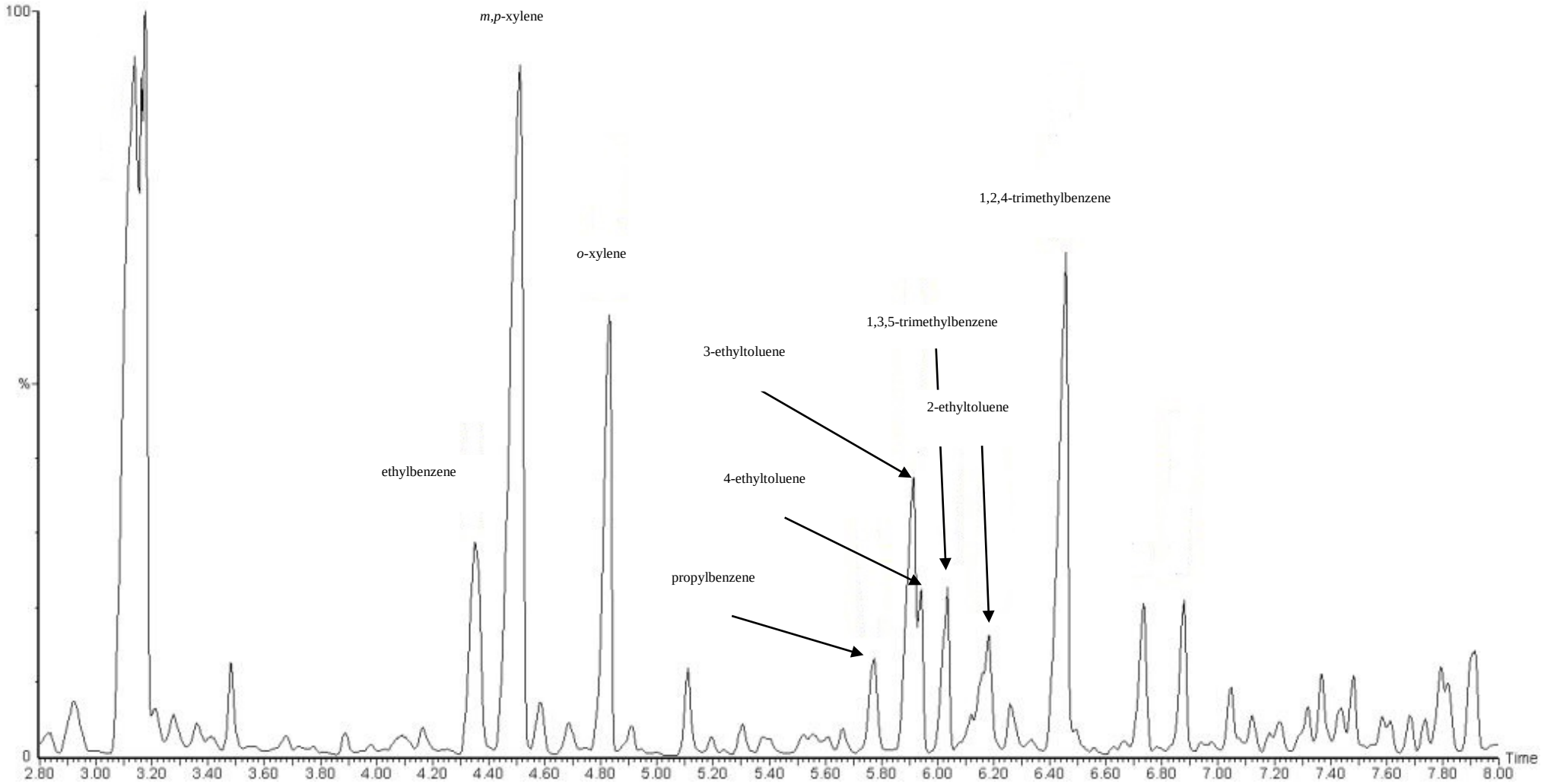

Figure 1.9 TIC of Petrol standard with C_2-alkylbenzene 'Three Musketeers' group and C_3-alkylbenzene 'Castle' group

Other aromatic and polynuclear target compounds in ignitable liquids such as methylindanes and methylnaphthalenes are difficult to visualise in a TIC because of their low abundance in comparison to other compound types. Extracted ion chromatograms (EIC) (section 1.8.1.1) are used to identify these compounds (Table 1.2).

The C_4-alkylbenzene compounds can be viewed on EIC ion 119 (Figure 1.10) and some of these appear as doublets (Stauffer, et al., 2008, pp. 312-313). There are two important target compounds (ASTM E1618-11, 2011) in this group that elute towards the end of the *n*-C_4 range, and these compounds are present in petrol, aromatic solvents (Stauffer, et al., 2008, pp. 312-313) and diesel (Song, 2000). These compounds are 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene respectively.

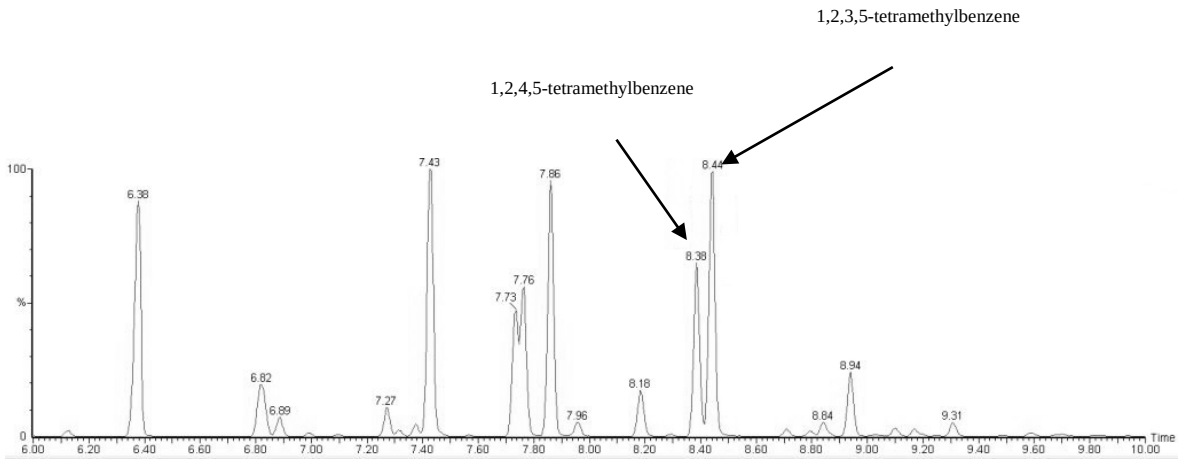

Figure 1.10 EIC (ion 119) showing important C_4-alkylbenzene target compounds in petrol and diesel

The C_1 and C_2 indane target molecules (5-methylindane; 4-methylindane and 4,7-dimethylindane) can be seen on EICs 117 and 131 respectively (Figure 1.11). These compounds are found in medium petroleum distillates and heavy petroleum fuels such as diesel or kerosene as well as petrol (Song, 2000, pp. 1-10).

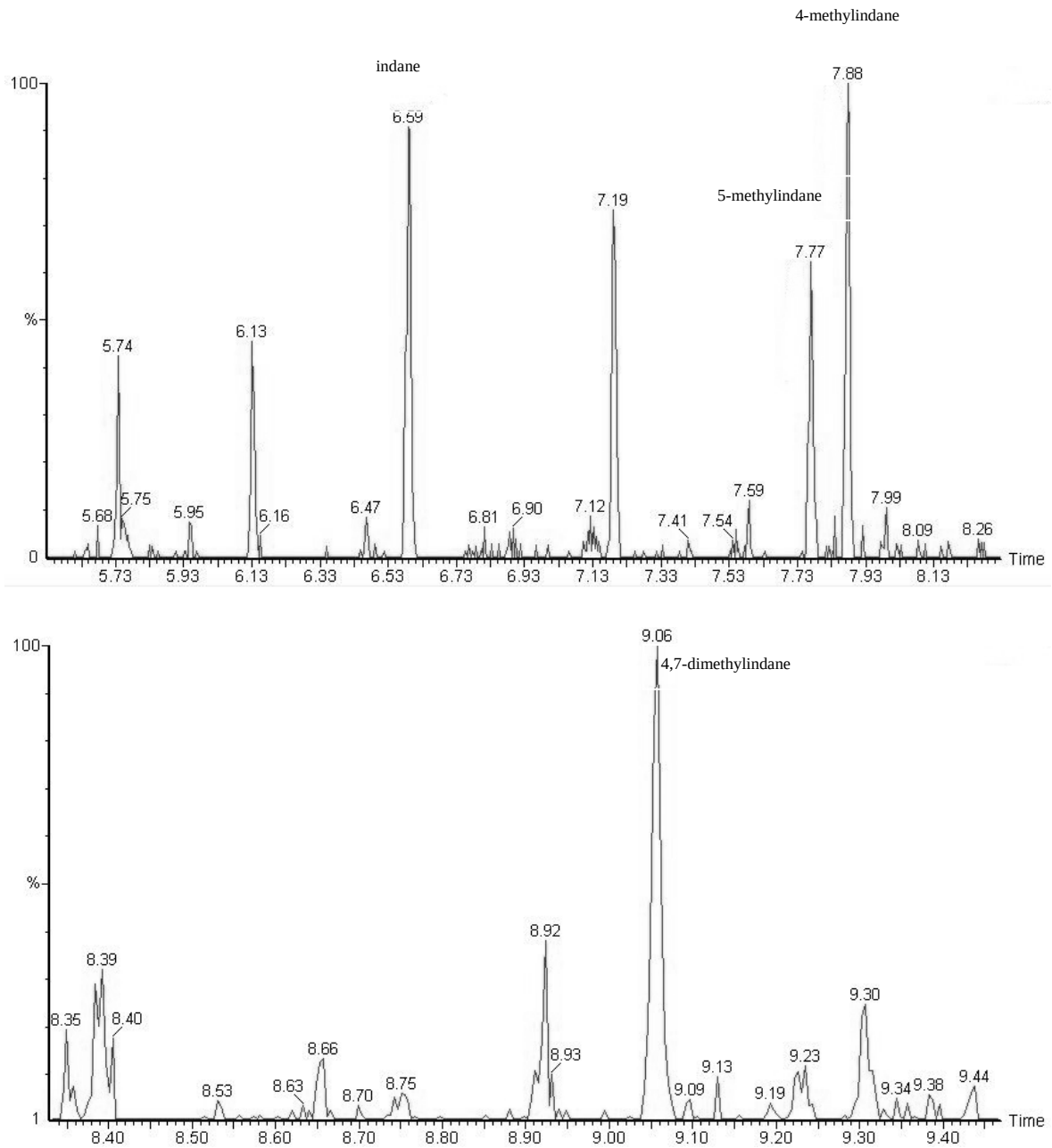

Figure 1.11 EICs (top) Ion 117, C_1-indane target molecules; (bottom) Ion 131 C_2-indane target molecule

The polycyclic aromatic target compounds C_1, C_2 and C_3-naphthalenes are found using ion 142, ion 156 and ion 170 respectively (Figure 1.12). Although 2-methylnaphthalene and 1-methylnaphthalene are listed as pyrolysis products, ASTM E1618-11 (2011) still has these compounds as indicators of an ignitable liquid (section 1.4.3) as they are also found in the range of heavy petroleum distillates (Stauffer, et al., 2008, pp. 312-313).

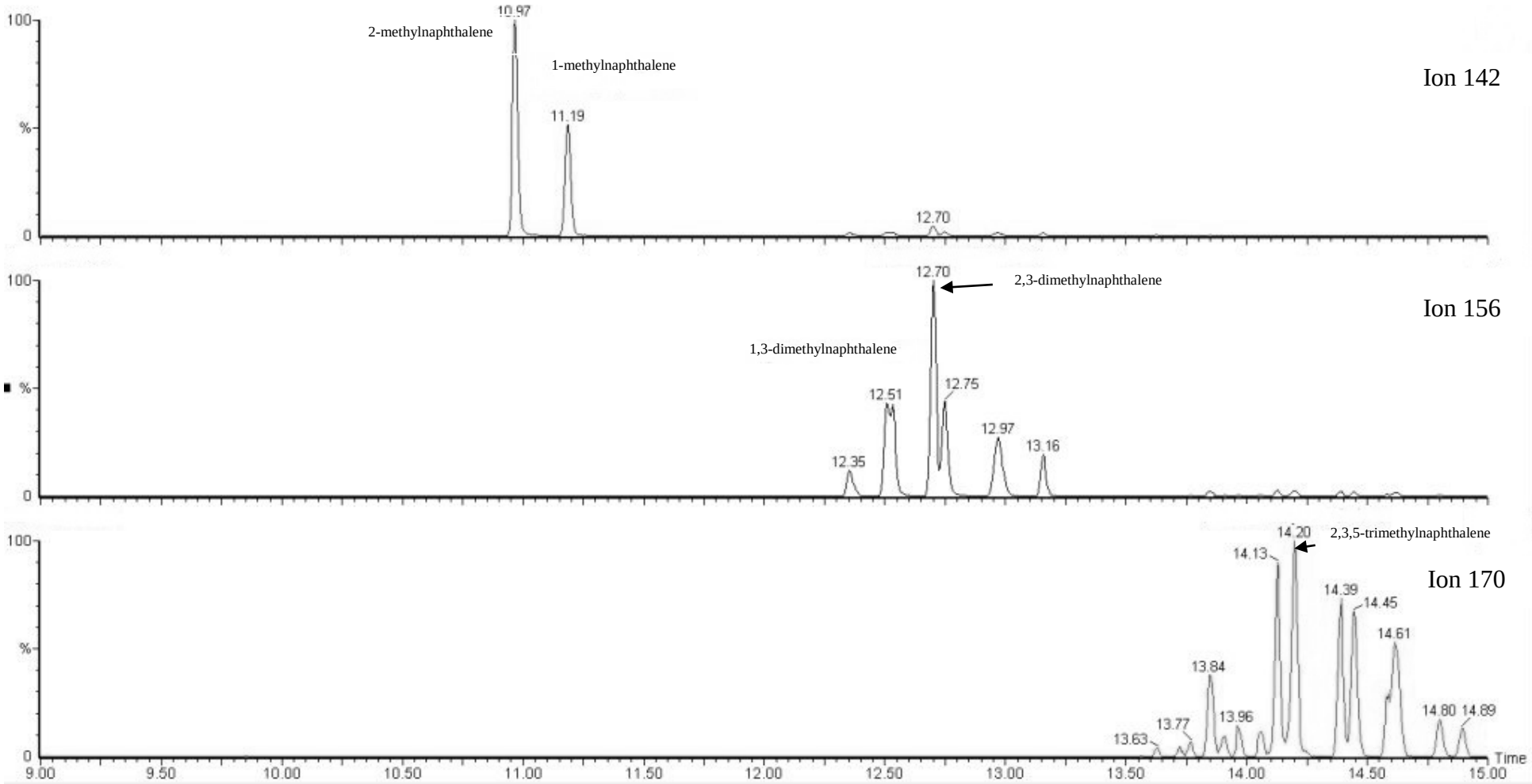

Figure 1.12 EICs showing ASTM E1618-11(2011) target compounds C_1-naphthalenes; C_2-naphthalenes and C_3-naphthalene target compounds

The *n*-alkanes and *n*-cycloalkane target compounds for ignitable liquids can dominate a TIC if the ignitable liquid is a heavy or medium petroleum fuel such as diesel or kerosene. The abundance of the peaks is referred to as 'Hash and Trash' *(ibid)* and this nomenclature also includes branched alkanes (Newman & Lothridge, 1998). To make sense of a chromatogram an EIC is produced for *n*-alkanes (ion 57), *n*-cycloalkanes (ion 83) and trans-decalin (ion 138). An example of an ion 57 EIC is at Figure 1.13. The ASTM E1618-11 (2011) target compound range list of *n*-alkanes starts at nonane (5.05 min) and finishes at heneicosane (20.82 min), even though the alkane series on the chromatogram may continue past this point. The visual recognition of a heavy petroleum distillate is a Gaussian shaped pattern culminating in high abundance between tridecance to hexadecane *(ibid)*.

Pristane and phytane can be observed on EIC ion 57 and these compounds are considered essential in the identification of petroleum distillates (Stauffer, et al., 2008, pp. 314-315). These compounds can be seen on Figure 1.13 (16.64 mins and 17.82 mins). They are found between the heptadecane and nonadecane compounds. Normally pristane is more abundant than phytane but are dwarfed by the *n*-alkanes they are next to, namely heptadecane and octadecane respectively. However, a recent study by Sherry, et al. (2014) shows that pristane and phytane are compounds that do not biodegrade very well and is one of the reasons they are added to the fuel at the refinery. If diesel is left to weather, all of the compounds that make-up diesel will biodegrade except pristane and phytane *(ibid)*, which makes them even more important as a marker for diesel fuel when investigating ignitable liquids. In section 4.7.3.3 partially weathered diesel fuel was responsible for these two compounds dwarfing heptadecane and octadecane.

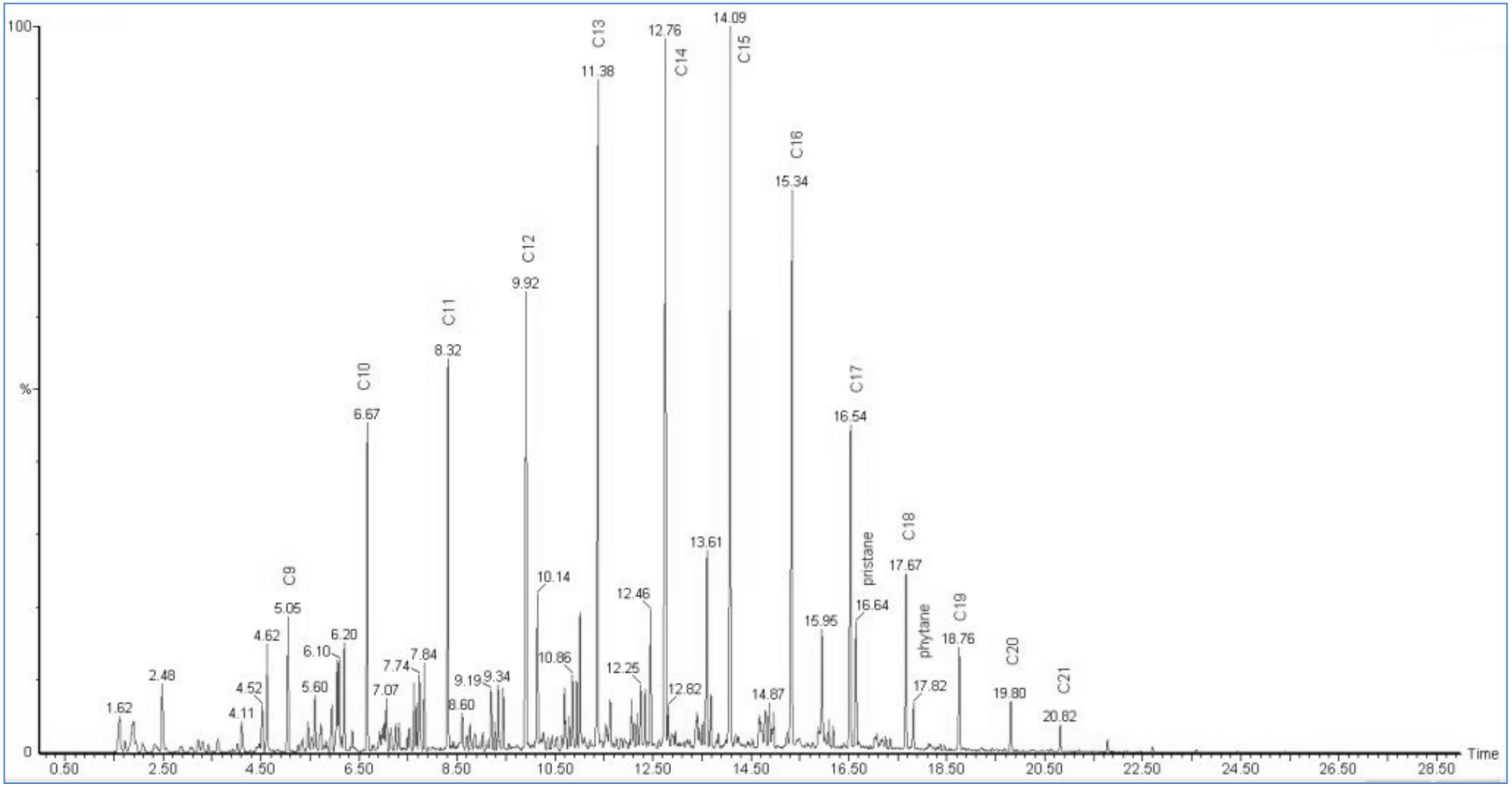

Figure 1.13 EIC (ion 57) of a diesel sample showing the evenly spaced n-alkanes from n-C_9 to n-C_{25}

1.8.1.1 Extracted Ion Chromatograms (EIC)

Identification of target molecules from ignitable liquid residues is achieved by studying extracted ion chromatograms (EIC) and associated spectra to identify compounds from their known *m/z* ratio. Identified compounds in unknown samples are compared to reference spectra, a positive control spectra and compound retention times (ASTM E1618-11, 2011).

The EIC shows structural information about a particular compound elution time and enables a selection of *m/z* ions. The structural information can reveal the *m/z* of an ion in relation to its relative abundance. This includes: a molecular ion; isotopic ion; a base ion and other qualifying ions (section 1.7.2).

Figure 1.14 shows a digitised mass spectrum of *m/z* 83 (Table 1.2). The fragmentation of ions differ by 14 Daltons and can be observed at *m/z* 41, 55, 67 and 97 and these are indicative of the *n*-alkane side chain (Kitson, et al., 1996, pp. 9-14). Cleavage of a cycloalkane occurs where it connected to the aliphatic chain and the ring is depleted of one or two hydrogens (H) giving $[M-H]^+$ or $[M-2H]^+$ giving a base *m/z* ion of 83 or 82. The molecular ion is at *m/z* 140 ($[M]^{+\cdot}$) *(ibid)*. This combination of fragmentation ions is the ionic fingerprint of butylcyclohexane and can be identified as such after comparison with a positive control.

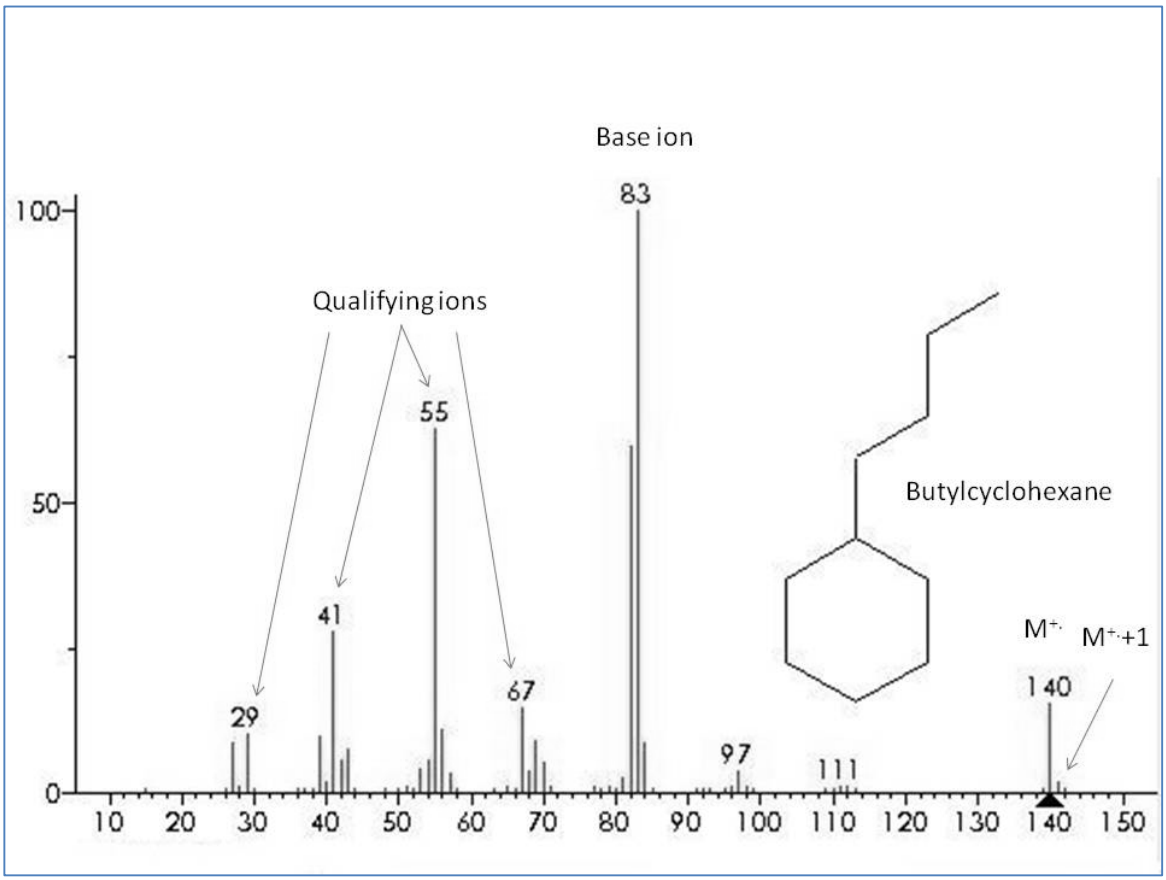

Figure 1.14 Mass Spectrum of m/z 83 from NIST 2.0 MS Search software library

1.9 Testing and Method Validation

In general testing is designed to assure users that new scientific methods or new products are safe to use, they are fit for purpose and that the results of experiments are consistent and repeatable. The products should be able to survive the toughest tests that are likely to face in the laboratory and the field. Only after the tests and evaluation have been completed should the method or product be adopted. In this study laboratory testing included repeat testing to ensure result repeatability. This was normally $n = 5$, but in Chapter 5 where spectroscopy was undertaken this was reduced. A gaseous internal standard (toluene-*d*8) was used to calculate peak areas in Chapter 3 and 4 and this lead to the generation of statistics. Peak signals were investigated by retention time and then by spectrum comparison with controls (section 1.8) to prove or refute errors and to further understanding. Blind tests were also adopted to evaluate without bias (Jackson, 2012, p. 240). Method validation was conducted with blind tests and this is explained in more detail at sections 3.6.5 & 4.7.4 and Chapter 6.

1.10 Aims and objectives

The aims and objectives of thesis are as follows: (also see Table 1.3 for more detail).

i) To determine by experimentation if selected past and present adsorbents used by fire scene examiners can singularly adsorb/desorb common ignitable liquids.

ii) Use a suitable fire debris separation method and analytical method that allows for reproducible and robust results.

iii) Generate an alternative adsorbent to those currently in use that can adsorb/desorb common ignitable liquids that can replace current adsorbents and become a universal adsorbent.

iv) Characterise and evaluate the new adsorbent to establish if the adsorbent allows for repeatable results in the laboratory and investigate what properties of the adsorbent shape the results. Determine if the adsorbent can perform at the fire scene whilst remaining reliable and also survive the harsh rigours that a fire scene presents.

Table 1.3 A table of objectives for this thesis

Objectives	Why?	How?	Found in...
Preliminary evaluation of current and past sorbents – Do they adsorb common ignitable liquids?	To determine if these materials can adsorb/desorb common ignitable liquids and thus be a universal adsorbent for these liquids and their residues.	Use current fire investigation protocols (NFPA 921, 2011) (ASTM E1412-12, 2012) (ASTM E1618-11, 2011). Passive headspace adsorption on ACS and GC-MS analysis. In order to mimic the conditions of a fire scene and to generate possible contamination that an analyst would encounter, a suitable location was found, courtesy of Cambridgeshire Fire and Rescue Services. A 'smoke house' used for the setting of small fires was used in this study.	Chapter 2
Use an analytical and separation method that allows for reproducible and robust results	No ATD-GC-MS standard method exists for the analysis of fire debris. Therefore the creation of a standard method is desirable. If results are not reproducible or sorbents have a complex matrix, the quality of results may be questionable.	Start with Newman & Lothridge (1998) method; if possible adapt it to ATD-GC-MS. If method is modified, test the validity of the results. Further evaluation through the use of 'blind testing'	Chapters 3, 4 and 6
Consider the use of alternate adsorbents as candidates, or design a new adsorbent	If the current or past adsorbents do not work or partially work (allow identity of common ignitable liquids), there is no point in using that sorbent. Find one that does work or create one that can adsorb a large range of ignitable liquids and their residues and be therefore considered a universal adsorbent	Research literature in other scientific fields including acid bleaching of clays, surfactants or simple mixing of sorbents. Evaluation of selection through qualitative laboratory tests.	Chapters 4 and 6
Characterise selected adsorbent	Investigate what properties are characteristic of the adsorbent? And do the properties contribute to ignitable liquid adsorption?	Use scientific instruments to determine vibrational bond behaviour; determine crystalline properties and unit cell dimensions.	Chapter 5
Evaluate selected adsorbent	New or modified adsorbents need to be tested to confirm common ignitable liquid are adsorbed/desorbed, results are repeatable, robust and without a complicated background matrix.	Test with an internal standard (IS) for semi-quantitative results; blind laboratory evaluation and blind field testing.	Chapters 4 and 6

Chapter Two

A Preliminary Evaluation of Adsorbent Materials to Collect Ignitable Liquid Residues

2 Introduction

Modern fire investigation techniques such as scene preservation and the collection of evidence for forensic analysis start at the preliminary and detailed examination phases (section 1.2). The collection of evidence and particularly the use of a sorbent material to sample suspicious areas of a fire scene is a technique now used by some investigators (section 1.3). Hall (2009); Baccus (2010), determined that the adsorbent materials currently used were: Sand; talc; Tampax®; TENA Lady®; flour; cat litter; Garden Lime (limestone) and a hand-held squeegee with water (Table 2.1). These materials appear to be random and no survey respondent could say why that particular material was used *(ibid).* Also, the types of adsorbents listed could have been from any variant from that type. For example, sand is a heterogeneous mixture of quartz and other minerals such as opal, feldspar, garnet, mica and calcium carbonate. Some of the adsorbents listed have also been tested by Tontarski (1985) and Mann and Putaansuu (2006) such as plain flour, cat litter and calcium carbonate (section 2.1 & section 4.2).

There is no documentary evidence that the adsorbents used by UK fire investigators actually work. This is important as the results of analysed adsorbents are used to help an investigator reach a conclusion on whether an ignitable liquid is present or not. Therefore, it was important to establish whether the adsorbent materials were able to adsorb common ignitable liquid residues and their vapours (section 1.8.1), desorb the condensed vapours into a solvent and further lead to the correct identification of ignitable liquids with the aid of gas chromatography-mass spectrometry (GC-MS). If the adsorbent could adsorb a large range of ignitable liquids it could then be considered as a universal adsorbent.

2.1 Adsorbents chosen for study

A number of adsorbents were chosen for this part of the study and these adsorbents are introduced in this section and listed in Table 2.1. The adsorbents are: sharp sand; talc; Tampax®; TENA Lady®; ultra-clumping clay cat litter; garden lime and a hand-held squeegee.

Plain flour was not chosen for this study as it is generally well-known to absorb water. Tontarski (1985) used flour and specified that only plain flour should be used because of a release of CO_2 from self-rising flour could explode inside the evidence container when heated. Mann & Putaansuu (2006) tested plain flour but concluded that it was the least compatible sorbent in a water environment.

2.1.1 *Sand*

Sharp sand was chosen for this study as it contains many types of aggregates (grain size < 3 mm) such as found in gravel, clay and chalk deposits compared to the finer soft building sand and so was considered the most abundant and cheapest of the sand options available (£4.99 for 25 KG, Thetford Garden Centre U.K). The J. Arthur Bower's Sharp Sand was described as limestone free. This was important as limestone was another adsorbent on the list to be tested. The fact that sand may have an abundance of SiO_2 quartz which prefers to interact with slightly polar vapour phase molecules, suggested that sand may be a good adsorbent of aromatic compounds (Hawkins, et al., 1986).

2.1.2 *Talc*

Talc is a common clay from the smectite group of clays with the chemical formula $Mg_3Si_4O_{10}(OH)_2$. It is composed of layered sheets of magnesium between two layers of silicon oxide (SiO) (Rotenburg, et al., 2011). The magnesium charge is off-set against hydroxyl (OH) groups and therefore has a negligible overall charge. There are weak van der Waals' forces that hold the layers together (Virta, 2000) and this accounts for the talc texture as soft and silky to touch. However, the hydroxyl groups are oriented perpendicular

to the surface and these groups can participate in hydrogen bonding (Rotenburg, et al., 2011). Once a monolayer of water is adsorbed the perpendicular hydroxyl groups are saturated with water molecules and there is no further adsorption as Talc cannot overcome cohesive interactions at a relative high water vapour stage (*ibid*). This factor may suggest that Talc should not be used on wet (fire suppressed) fire scenes (section 2.4.5), but the non-polar nature of the adsorbent suggests that it may adsorb non-polar components of ignitable liquids such as alkanes.

2.1.3 *Tampax® and TENA Lady®*

These commercial products have been grouped together as they have been designed as feminine sanitary products. Although both products contain cotton, the physical similarity ends there. TENA Lady® contains two or more layers of fluff pulp and a super-absorbent polymer that can absorb up to twenty times their own weight (Wahlström, et al., 2006) and is designed to absorb body fluids. Because this product is designed to be worn outside the body, it contains a plastic outer area that is designed to keep any moisture inside the product. In contrast, Tampax® is made from rayon and alloyed co-polymeric fibres (Allen & Denning, 1975) and is worn inside a body cavity to absorb body fluids. The array of materials used in TENA Lady® may interfere with gas chromatography-flame ioniser analysis of fire scene samples as it contains laminate materials (Wahlström, et al., 2006). Tampax® contains co-polymer fibres which may indicate it has a background matrix that could is visible on a TIC (Allen & Denning, 1975). The fact that these materials contain compounds that could interfere with analysis may be a problem, especially as some laboratories still use GC-FID as the standard analysis tool (Hendrikse, 2007). However, interference is a common problem and should be overcome by using GC fitted with a mass spectrometer (GC-MS) and extraction ion chromatograms (EIC) (section 1.7.2 & 1.8.1.1).

2.1.4 *Clay Cat Litter*

Cat litter is normally a mixture of materials but all versions have the task of absorbing feline body fluids. Cellulosic material is often used, especially in non-clumping cat litter which can be found on the shelves of supermarkets and grocery stores. However, two other

adsorbents chosen for this study already contained these materials (TENA Lady® and Tampax®); therefore the cat litter chosen for the study was made from clay. Both Tontarski (1985) and Mann & Putaansuu (2006) used granulated clay cat litter and they both concluded that the material was able to absorb petrol (section 1.3). Mann & Putaansuu (2006) also found that clay cat litter did not readily adsorb heavy petroleum distillate compounds and attributed this to the size of the granules.

A number of different clays are available as mixtures in cat litter including kaolin; smectites and palygorskite (Murray, 2000). A clumping cat litter was chosen for this study as the contents contained the smectite, sodium montmorillonite, (section 4.4). It was hypothesised that this brand of cat litter (Sainsbury's Ultra-Clumping Cat Litter) would preferentially adsorb aromatic compounds over non-polar compounds (alkanes) because of the variable charge (Brindley & Brown, 1980, p. 5) would attract slightly polar compounds. The variable charge results from magnesium substitution in the dioctahedral layer (Martin, 2008) and this is discussed in depth in section 4.3.

2.1.5 *Garden Lime (Limestone)*

Limestone exists both in rocks and in the shells of some animals (Ni & Ratner, 2008). It is a common mineral and has important uses in industry. For example it is used in building material as an aggregate (Grabiec, et al., 2012) and in the steel making blast furnaces as part of a slag to help reduce carbon dioxide emissions (Eloneva, et al., 2008). It is popular as a filler material in plastics (Zuiderduin, et al., 2003) and is used as a conditioner for acidic soil, where it is known as Garden Lime (Cooke, 2007, p. 22). Limestone contains calcium carbonate polymorphs such as calcite, aragonite and the less common vaterite. These polymorphs are distinguishable from their crystal structure (section 5.2.2). Calcite is made from a lattice structure of calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) (Farmer, 1974, p. 227). Limestone (calcite) has been used to adsorb phosphates in wastewater (Karageorgiou, et al., 2007) and metal ions from water (Kerisit & Parker, 2004) making it a popular decontamination adsorbent. The cations or anions in the lattice may be substituted yielding impure calcite lattices (Eriksson, et al., 2007). For example, iron or manganese oxyhydroxides and arsenites are known to compete with carbonate ions and may be substituted in the lattice (Bardelli, et al., 2011). The substitution may cause fluctuations in electric surface potential (Zeta potential) and is different for every calcite

lattice *(ibid)*. Consequently, this may have an effect on the preferred adsorbed species. Common ignitable liquids generally do not contain metal ions and therefore the lattice cation substitution is not considered for calcite as a lone adsorbent. However, substitution could occur if limestone is mixed with other minerals that have an iron, manganese or arsenite content *(ibid)*.

2.1.6 ***Squeegee***

The squeegee (Table 2.1) in normal use is used as a remover of water from car windows to aid better vision through the windshield and other windows. There are various designs, but nearly all feature a flexible rubber blade held in place by rigid plastic and the squeegee is able to be turned through a range of angles in the hand because of the shape of the handle. Respondents to the Bacchus (2010) survey claimed that they squirted water onto the suspected area to lift hydrophobic compounds to the surface of the water and then scooped the water into a bag which then was sealed. This technique could be useful if the ignitable liquid was in liquid form as the compounds would float to the surface of the water pool.

Petroleum ignitable liquids are generally non-polar or slightly polar (section 1.4) and water is an example of a polar compound. These liquids are repelled by the surface of the water and the molecules clump together on the surface. It is hypothesised that the application of water onto an ILR area may not release all ILR compounds from the surface they are adsorbed to. And therefore some ignitable liquid compounds may be left behind. Mann & Putaansuu (2006) also suggested that squeeging water will leave hydrocarbon residues behind. Another point to consider is that the water may actually contaminate the crime scene as it will unlikely to have been certified as contaminate free. If alcohol or other water soluble liquids were used to promote the fire, water could dissolve and dilute potential evidence and may this not be detected depending on what volume of water was used.

2.2 Materials and Methods

2.2.1 *Materials*

A list of adsorbents used in this study is shown in Table 2.1. These were representative of the type of adsorbents used by UK based Fire Investigators.

Chemical reagents were purchased from Fisher Scientific and Sigma Aldrich, UK. These included: *n*-octane (C_8); *n*-decane (C_{10}); *n*-dodecane (C_{12}); tetradecane (C_{14}); hexadecane (C_{16}); octadecane (C_{18}); eicosane; (C_{20}) 3-ethylmethylbenzene; 4-ethylmethylbenzene and 1,2,4-trimethylbenzene. These reagents were used as individual standards and as a test mixture (0.05 µL/mL in *n*-pentane).

Other equipment used in the study included: Heraeus UT6 oven (Thermo Electron Corporation); Pipetman pipettes (Gilsen); paint cans (2.5 L) with sealable lids (Birmingham Tin Box Company, England); Activated Carbon Strips (ACS), 10 mm x 10 mm (Pro-Tek Systems); Rilsan® polyamide 11 bags and bag ties (WA Products, England) a conventional fan-assisted oven.

Petrol and Diesel fuel were purchased from BP (Thetford, England). The fuels were mixed 1:1 v/v for use as an ignitable liquid and as a reference standard.

2.2.2 *Methods for Use of Adsorbents at Scene and Subsequent Laboratory Analysis*

This part of initial research was undertaken within certain conditions, which were beneficial to all parties, owing to time constraints of using a working smoke house normally utilised for Fire and Rescue training by Cambridge Fire & Rescue Services. Therefore, the visits to the test area were minimised due to this constraint, and so it was decided to conduct the tests on three separate days. This also meant that each adsorbent was only repeated three times (n = 3) and therefore optimisation of variables was not applicable or have been discussed in relation to these results. The floor surfaces of the smoke house were considered dry. An ignitable liquid mixture of petrol/diesel (1:1 v/v) (5.0 mL) was applied onto the concrete floor surface. The mixture was left for two hours to

simulate a realistic time delay for a fire investigator to gain access to a scene. Then the selected adsorbent (Table 2.1) was sprinkled or placed onto the ILR and left for 20 minutes. Adsorbents were also placed close to, but not in an area containing the ignitable liquid for background control samples, so that a determination of any contamination from the absorbent itself and environment could be made. All air temperatures were considered ambient. Paint cans were conditioned prior to use (200 ^{0}C for 2 hours). Negative controls of all adsorbents was undertaken to ensure that adsorbents were not contributing any matrix of their own.

2.2.3 *Gas Chromatography Parameters*

A Perkin Elmer Clarus 500 GC-MS in positive electon ionisation mode; injection port temperature was 280 ^{0}C, with a split ratio of 20:1; a Phenomenex ZB-1 column (30 m x 0.25 mm x 0.25 µm); helium carrier gas (0.68 mL/min); injection volume 1.0 µL. The oven was set initially at 50 ^{0}C, held for 2 minutes and ramped at 15 ^{0}C /min to 300 ^{0}C and held for 5 minutes.

The injection port temperature was high enough to ensure all ignitable liquid compounds were in the gas phase assisted by the helium gas flow allowed the compounds to reach the column. Only 1/20th of the gas in the injection port was channelled onto the column as the remainder was pushed to waste. This ensured that the column was not overloaded with ignitable liquid compounds which could have resulted in a loss of compound sensitivity and risked causing interference to samples.

As the compounds entered the column the initial temperature was cool enough for medium and heavy compounds to condense and they were held in this state whilst lighter boiling point compounds remained in the gas phase and were assisted by the mobile phase towards the detector. The temperature of the column was incrementally raised to ensure that medium and then heavy compounds entered the gas phase and were carried-along by the mobile phase. The instrument was held at a high temperature to ensure that all ignitable liquid compounds exit the column, leaving the column ready for the next injection.

2.2.4 *Mass Spectrometer Parameters*

The following mass spectrometer settings were used: Transfer line temperature 280 ^{0}C; electron energy 70 eV; trap emission 100; source temperature 250 ^{0}C; electron multiplier voltage 350 V; Scan mode (40 - 400 *m/z*).

The transfer line from the GC remained at a high temperature to allow all ignitable liquid compounds to remain in the gas phase. The quadrupole ion filter voltage ensured that excessive fragmentation of ions did not occur.

Table 2.1 A list of adsorbents used by fire scene investigators tested in this study

Adsorbent	Type
Arthur Bower's Sharp Sand	Fine quartzite sand granules
Arthur Bower's Garden Lime	Fine limestone granules
Sainsbury's Non-Clumping Cat Litter	Sodium bentonite coarse granules
Simple Baby Pure Talc	Hydrous magnesium silicate powder
Hand held Squeegee with de-ionised water and lifted with a Rilsan® bag	Rubber blade and polypropylene handle
Tampax® Regular	Cellulosic (cotton, rayon)
TENA Lady® Normal	Fluff pulp, polyacrylate

Each adsorbent was recovered using disposable paint-brushes and were double-bagged (Rilsan), swan necked and sealed with plasticuff bag ties. When using the squeegee, de-ionised water was squirted onto the ILR pool and the squeegee was used to scrape the sample into the Rilsan bag.

The separation of the ignitable liquid from the adsorbent was carried out in accordance with ASTM E1412-07 (2007). The adsorbents were transferred to watch glasses which were placed into pre-conditioned paint cans. The activated charcoal strip was then suspended using a paper clip with cotton thread in the headspace and the tins were placed in an oven at 70 ^{0}C for 18 hours. The charcoal strips were then eluted in 1.0 mL *n*-pentane (Newman, et al., 1996).

All of the adsorbents were analysed with a Perkin Elmer, Clarus 500 GC-MS in electron ionisation mode (ASTM E1618-11 (2011); Newman, et al. (1996); sections 1.7.1. & 1.7.2).

Peaks signals were denoted by the height of a signal in relation to the blank signal. This was set at least five times the height of the blank signal and also had to be identifiable and reproducible (Food and Drug Administration, 2001).

2.3 Results

The positive identification of the ignitable liquid reference test standard (section 2.2.1), was carried out using ASTM E1618-11 (2011) standard method for GC-MS. The target compounds from this protocol are specified in Table 1.2, which lists the diagnostic groups, target molecules and their ion fragments. Then data was analysed using extracted ion chromatograms (EIC) to identify target compounds.

Seven adsorbents (Table 2.1) were evaluated in this study as described in the previous section. Over the course of the three days, the difference of initial ambient temperature during the experiments was only 1 ^{0}C, with the highest reading at 20 ^{0}C and the lowest at 19 ^{0}C.

Preliminary analysis of target compounds was made using TICs. Compound mean elution times (n = 3) and main ion used to identify is at Table 2.2. Identification of target compounds of a petrol/diesel 1:1 v/v mixture was made using the retention time of each target compound concordant with each compound ion profile in spectra using EICs (section 1.8.1.1).

Table 2.2 Target compounds identified from seven different adsorbent materials (n = 3)

Petrol/Diesel Target Compounds	Compound ID number	Mean Retention time (Mins)	Main ion used to identify compound (m/z)	Arthur Bower's Garden Lime	Arthur Bower's Sharp Sand	Sainsbury's Ultra Clumping Cat Litter	Simple Baby Pure Talc	Squeegee with de-ionised water	Tampax Regular	TENA Lady Normal
ethylbenzene	1	4.46 ± 0.00	91	x	x	√	x	x	x	x
m,*p*-xylene	2	4.57 ± 0.00	91	x	√	√	x	x	x	√
o-xylene	3	4.86 ± 0.00	91	x	√	√	x	x	x	√
nonane (n-C_9)	4	5.13 ± 0.00	57	**Contamination peak at this retention time**						
propylbenzene	5	5.58 ± 0.03	91	x	√	√	x	x	x	√
3-ethyltoluene	6	5.74 ± 0.01	105	√	√	√	√	√	√	√
1,3,5-TMB	7	5.84 ± 0.00	105	√	√	√	x	√	√	√
2-ethyltoluene	8	5.95 ± 0.00	105	√	√	√	x	√	√	√
1,2,4-TMB	9	6.14 ± 0.00	105	√	√	√	√	√	√	√
decane (n-C_{10})	10	6.36 ± 0.01	57	x	√	√	x	x	x	√
indane	11	6.59 ± 0.00	117	x	√	√	x	√	√	√
n-butylcyclohexane	12	6.72 ± 0.01	83	x	√	√	x	x	x	√
undecane (n-C_{11})	14	7.50 ± 0.00	57	√	√	√	√	√	√	√
1,2,4,5-TMB	15	7.56 ± 0.00	119	√	√	√	√	√	√	√
1,2,3,5-TMB	16	7.59 ± 0.00	119	√	√	√	√	√	√	√
5-methylindane	17	7.77 ± 0.01	117	√	√	√	√	√	√	√
4-methylindane	18	7.88 ± 0.00	117	√	√	√	√	√	√	√
n-pentylcyclohexane	19	7.87 ± 0.00	83	√	√	√	√	√	√	√
Dodecane (n-C_{12})	20	8.54 ± 0.01	57	√	√	√	√	√	√	√
n-hexylcyclohexane	21	8.94 ± 0.01	83	√	√	√	√	√	√	√
4,7-methylindane	22	9.06 ± 0.00	131	x	√	√	√	x	√	√
2-methylnaphthalene	23	9.31 ± 0.01	142	x	√	√	√	√	√	√
1-methylnaphthalene	24	9.46 ± 0.01	142	x	√	√	√	√	√	√
tridecane (n-C_{13})	25	9.51 ± 0.00	57	√	√	√	√	√	√	√
n-heptylcyclohexane	26	9.92 ± 0.00	83	√	√	√	√	√	√	√
1,3-dimethylnaphthalene	27	10.34 ± 0.01	156	x	√	√	√	√	√	√
tetradecane (n-C_{14})	28	10.41 ± 0.00	57	√	√	√	√	√	√	√
2,3-dimethylnaphthalene	29	10.46 ± 0.01	156	x	√	√	√	√	√	√
n-Octylcyclohexane	30	10.83 ± 0.01	83	√	√	√	√	√	√	√
pentadecane (n-C_{15})	31	11.27 ± 0.01	57	√	√	√	√	√	√	√
n-nonylcyclohexane	33	11.70 ± 0.00	83	√	√	√	√	√	√	√
hexadecane (n-C_{16})	34	12.05 ± 0.00	57	√	√	√	√	√	√	√
heptadecane (n-C_{17})	35	12.83 ± 0.00	57	√	√	x	√	√	√	√
Pristane	36	12.91 ± 0.00	57	√	x	x	√	√	√	√
octadecane (n-C_{18})	37	13.56 ± 0.00	57	√	x	x	√	√	√	√
Phytane	38	13.65 ± 0.01	57	√	x	x	√	√	√	√
nonadecane (n-C_{19})	39	14.25 ± 0.00	57	√	x	x	√	√	√	√
eicosane (n-C_{20})[1]	40	14.91 ± 0.00	57	√	x	x	x	√	x	x
heneicosane (n-C_{21})	41	x	57	x	x	x	x	x	x	x

√ = Compound identified (n = 3)
x = Compound not identified

[1] Compound identified (n = 2)

2.4 Discussion

Besides recovering samples of adsorbents laid on ILR, each adsorbent was used to sample close to the area but not on the ILR and these were used as background controls. These area samples show the background compounds present in the environment and can be seen at Appendix 1 through Appendix 7. Additionally, EICs of adsorbents are at Appendix 19 through Appendix 25. There was no indication of control interference on chromatograms. Each adsorbent had a negative control to determine if there was likely to be any matrix interference. These are discussed in the sub sections for each adsorbent (sections 2.4.1 to 2.4.7). Only a 1 ^{0}C difference was recorded over the period of three days and therefore was not considered to adversely affect results.

Each adsorbent sample was repeated (n = 3) and a preliminary assessment of TICs indicated that peak shapes were sharp and narrow with no fronting or tailing indicating that the conditions were acceptable for peak identification. A pentane blank control sample was run between each sample and it was apparent that an extra peak was present at 5.13 minutes (Figure 2.2). The peak was identified as nonane (n-C_9) and was present on all blanks controls and samples. As this compound was present in the solvent (pentane), and also was a target compound. The peak was significant enough owing to the size of the peak in comparison to the positive control, to interfere with making an incorrect identity of this target compound. Therefore it was decided to deduct this peak from all results (Table 2.2). A TIC of example blank controls is at Appendix 8.

An overview of compound adsorption is shown at Figure 2.1 and illustrates that each adsorbent adsorbs different compounds. For example cat litter and TENA Lady® adsorb light and some medium compounds, yet they do not adsorb heavy compounds. Conversely, talc, garden lime and squeegee do not adsorb light compounds but adsorb medium and heavy compounds. Each adsorbent is now discussed in depth.

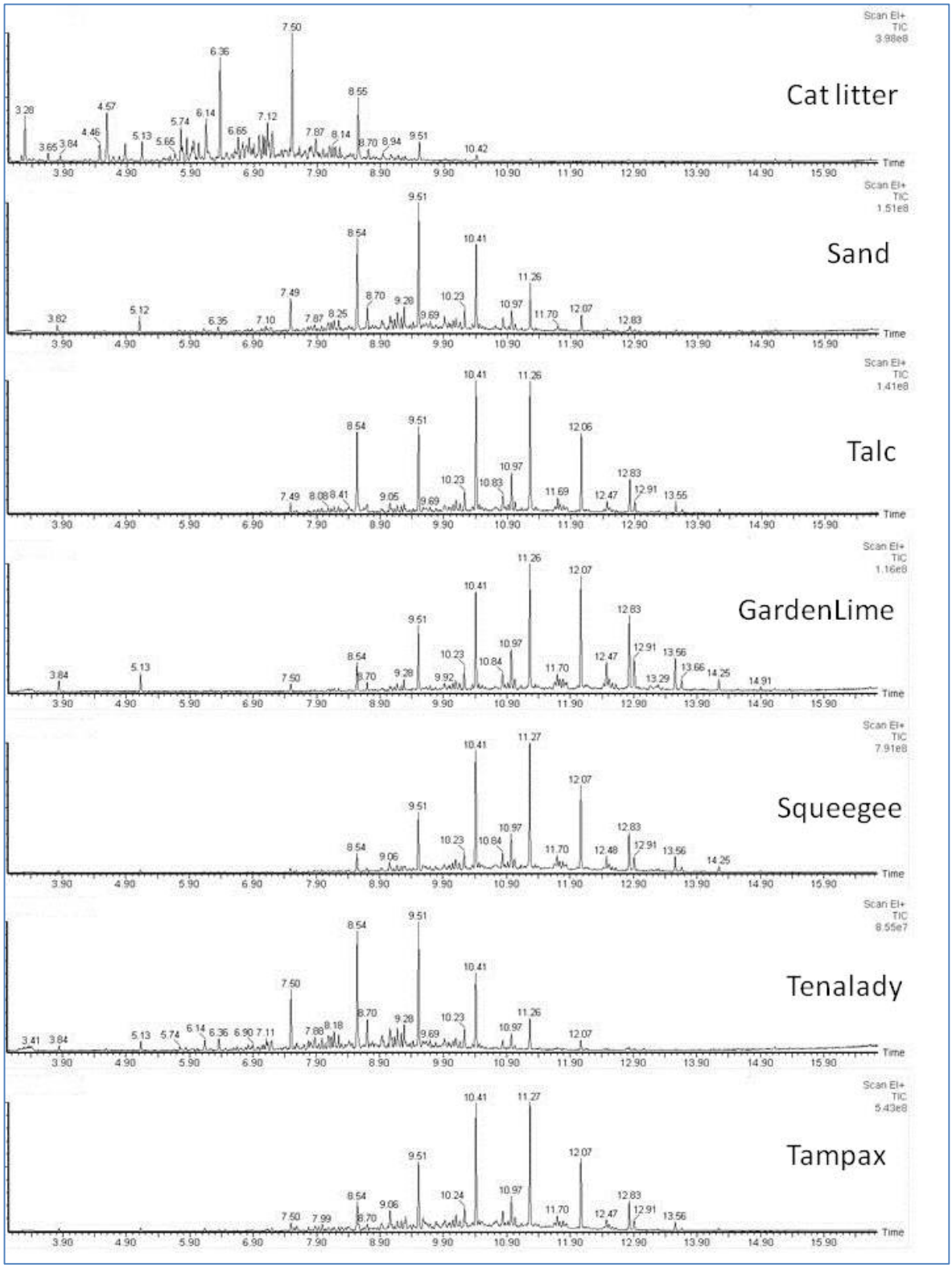

Figure 2.1 Comparison of TICs when using various adsorbents (Table 2.1) to adsorb a petrol/diesel mixture (1:1 v/v)

2.4.1 *Garden Lime (Limestone)*

Garden Lime was a coarse grain adsorbent (grain size 0.5 mm to 1.0 mm). This adsorbent adsorbed the ignitable liquid mixture compounds from 3-ethyltoluene to eicosane (5.74 to 14.91 minutes, Table 2.2). However the C_2 alkylbenzene target compounds were less abundant which indicated that these compounds are at the early end of the adsorption range, No further target compounds were able to be identified until the elution of undecane (7.47 minutes). The background control TIC for Garden Lime is at Appendix 2. The *n*-alkane compounds from undecane to pentadecane were identified in the background control but not in the negative control and so are specific to the scene. The peaks were regarded as non-significant as there were much larger peaks on the actual samples (Figure 2.2). These peaks were also detected on the talc background control (section 2.4.5). Garden Lime and Talc were situated near each other, and it therefore likely that both adsorbents adsorbed whatever was on the ground at the time.

Using EICs (Appendix 19), there was no identification of alkylnaphthalenes (ions 142, 156) or the identification of alkylindanes (ions 117 and 131) as these compounds only showed as small peaks and not enough spectrum data was available for positive identification. The adsorption of *n*-alkanes showed a Gaussian distribution from undecane to eicosane (n-C_{11} to n-C_{20}) (ion 57) (Figure 2.2 and Appendix 19) and *n*-cycloalkanes (*n*-pentylcyclohexane to *n*-nonylcyclohexane) (ion 83). All target compounds were identified in these ranges. However, there was no adsorption of the heaviest listed ASTM E1618-11 target compound (heneicosane), but this could be due to the oven temperature. At 70 ^{0}C the heaviest compounds may still be condensed on the substrate and not enough of them are in the gas phase, which means that at that temperature those compounds are not adsorbed by ACS (section 1.6.1) and this is supported by Newman, et al. (1996) results and many other research authors use this method. Another possibility as to why heneicosane was not adsorbed at all by Garden Lime is that the adsorbent is not capable of adsorbing that compound. However this was found not to be the case as later experiments showed that this adsorbent does adsorb heneicosane and docosane and this is discussed in section 4.7.2.1. It may also be a limitation of ACS's not to adsorb heneicosane and heavier compounds. This was not examined in this thesis as the focus shifted to Tenax TA®.

Garden Lime (limestone) preferentially adsorbs non-polar compounds such as alkanes and cycloalkanes as seen in Table 2.2 and adsorbent bonding is achieved through van der Waals' forces (section 1.5.2.2). It is also possible that grinding the grain size to a powder would increase the adsorbent surface area and increase the number of surface sites for adsorbing vapour phase compounds. These changes were incorporated into later experiments as improvements in Chapters 4 and 6.

The results of its capacity to adsorb petrol/diesel mixture is summarised and compared to the other adsorbents investigated in Table 2.3. However, as a short summary Garden Lime (limestone) can adsorb many diesel compounds, it did not adsorb the lightest (decane) or the heaviest (heneicosane) and did not adsorb many petrol compounds.

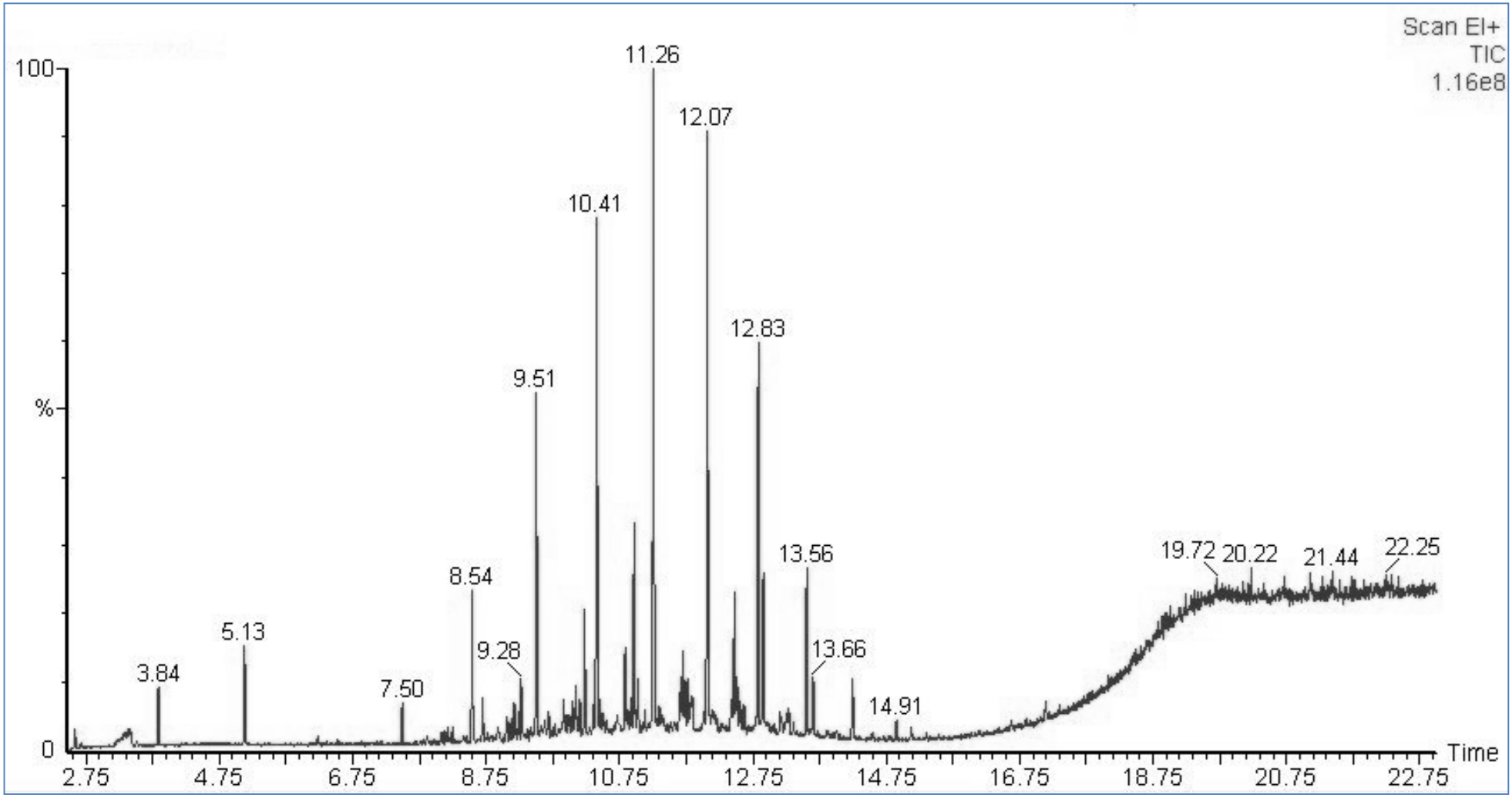

Figure 2.2 TIC of Garden Lime after the adsorption of a petrol/diesel 1:1 v/v mixture

2.4.2 *Sharp Sand*

The sand was composed of grain sizes from <1.0 mm to 3.0 mm in size obtained from the bag packaging. This adsorbent was able to adsorb compounds from 4.56 minutes (*m,p*-xylene) to 12.83 minutes (heptadecane; Table 2.2), with the most relative abundant signal at 9.51 minutes which is tridecane (Figure 2.3). The negative control had no peaks but the control TIC for sharp sand is at Appendix 3 and shows minor peaks that are much shorter than the contamination peak (nonane). The C_2 and C_3 alkylbenzene group of target molecules were tentatively identified by peak pattern/ratio section 1.4.3 and it is believed that there was either a residue of where the control was placed or the sand adsorbed the volatile compounds in the room due to circulating air currents within the room. The peaks were so small in comparison to the actual sample (Figure 2.3) that it was decided that these peaks did not pose a threat to compound identification. An examination of the sample EICs (Appendix 20) showed that apart from ethylbenzene, adsorption of compounds from C_2-alkylbenzenes to heptadecane was achieved. All alkylindane and alkylnaphthalenes were adsorbed as were all *n*-cycloalkane target compounds. Straight chain alkanes were adsorbed from decane to heptadecane (Figure 2.3). This shows that sharp sand falls short of adsorbing all petrol or diesel compounds.

Sand has particles that are charged that prefer to interact with polar gases and also others that are more neutral tending to be non-polar in nature (Zheng, 2009, pp. 106-110). Each sand mixture is composed of different minerals and therefore has different charges. The charging mechanism is not completely understood but is believed to be influenced by water as this enables the carriage of electrons *(ibid)*. It is postulated that the overall net charge (section 2.1.4) on the mixture tested was marginal polar leading to adsorption of medium boiling point compounds of both non-polar (alkanes and cycloalkanes) and slightly polar compounds (C_2, C_3 and C_4-alkybenzenes and polyaromatics) as shown by the results (Table 2.2).

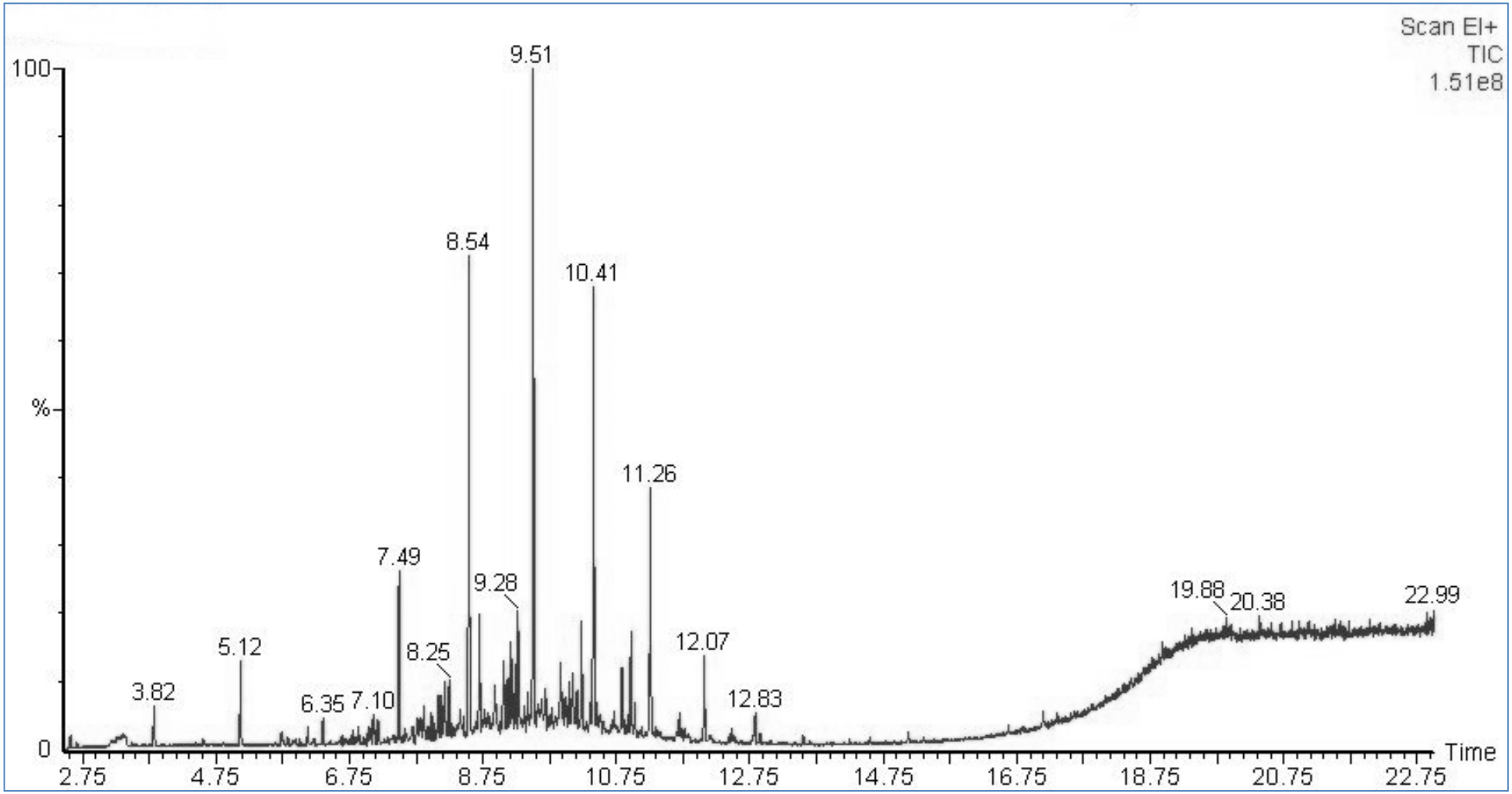

Figure 2.3 TIC of Sharp Sand after the adsorption of a petrol/diesel 1:1 v/v mixture

2.4.3 *Cat Litter*

The results at Table 2.2 show that light and medium target compounds were adsorbed but no heavy target compounds were adsorbed. The TIC (Figure 2.4) and EICs at Appendix 21 showed that early eluting compounds such as the alkylbenzenes had been adsorbed. This was apparent due to the three distinctive C_2-alkylbenzene peaks eluting between (4.46 to 4.86 minutes). Also, the five peak pattern of C_3-alkylbenzenes was prominent (section 1.8.1). The non-polar alkane and cycloalkane range of adsorption was decane to hexadecane and *n*-butlycyclohexane to *n*-octylcyclohexane. The control TIC for cat litter at Appendix 1 shows minor unidentified peaks that did not interfere with analysis. The negative control of cat litter showed no peaks and confirms that there is almost no background interference from this material.

The packaging of this cat litter described the contents as bentonite; a smectite clay that is rich in sodium. Smectite clays are generally described as 2:1 clays as they have a configuration of tetrahedral/octahedral/tetrahedral layers (Newman, 1987, pp. 48-55). The area in between the layers is known as the 'interlayer space'. In bentonite, sodium ions are situated in the interlayer and are readily exchangeable with other ions (Lee, et al., 2004). However, their presence is enough to cause the interlayer to widen enough so that water can be adsorbed into these spaces and this is what causes the smectite to swell *(ibid)*. This is ideal for cat urine, but in the absence of polar liquid sorbates, gases are adsorbed onto the surface and the interlayer spaces. The adsorption of gases onto surfaces was introduced in section 1.5.2 and smectite adsorption is discussed further in section 4.3.

Examination of EICs (Appendix 21) confirmed the identity of all alkylbenzene, alkylindane and C_1, C_2-alkylnaphthalene target compounds (Figure 2.4). All of the target compounds for petrol were positively identified. However, there was no adsorption of compounds from *n*-C_{17} onwards. These heavier compounds are required to positively identify a heavy petroleum distillate such as diesel.

This brand of cat litter prefers to adsorb low and medium molecular weight compounds and is particularly efficient at adsorbing C_2, C_3 and C_4 alkylbenzenes. This could be because of the slight polar nature of the smectite content of this product (section 2.1.4 and further discussed in section 4.4). On one hand this adsorbent is ideal for the identification of petrol, and confirms the observations of Mann & Putaansuu (2006) as it can adsorb all petrol target compounds.

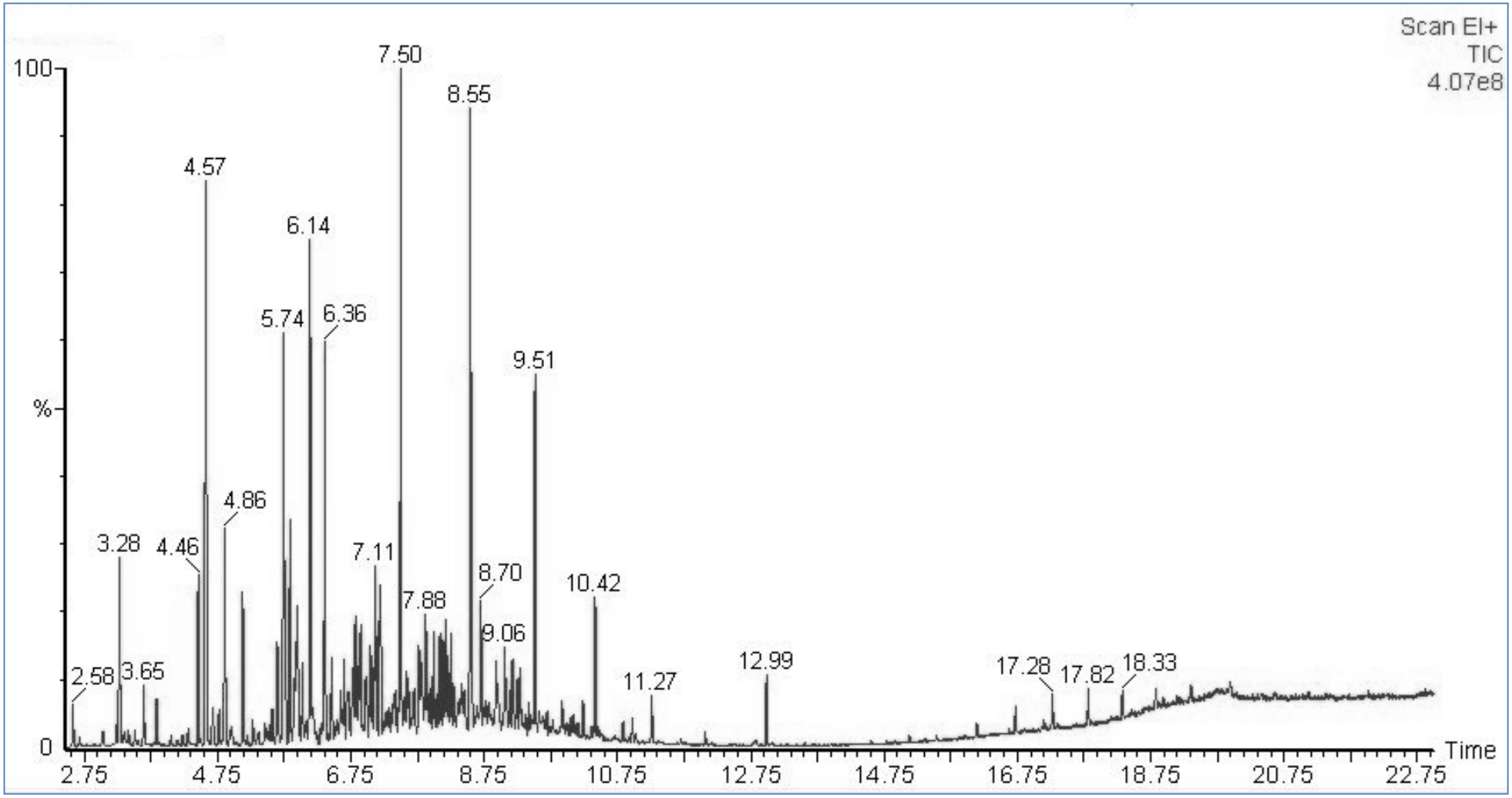

Figure 2.4 TIC of Cat Litter after the adsorption of a petrol/diesel 1:1 v/v mixture

2.4.4 *Squeegee*

The squeegee is not an adsorbent, but is a tool to assist in the collection of ignitable liquid residues with the aid of de-ionised water (section 2.1.6). Table 2.2 shows that the earliest compound adsorbed was 3-ethyltoluene (5.74 minutes) and the last target compound adsorbed was eicosane (14.91 minutes). The TIC (Figure 2.5) showed a classic Gaussian peak distribution from 8.54 to 14.92 minutes indicative of *n*-alkane adsorption (Stauffer, et al., 2008, p. 310). The most relative abundant peak signal was at 11.27 minutes (pentadecane). The background control TIC of Squeegee is at Appendix 5 and has only a couple of unidentified peaks. These peaks also appear on the negative control. The squeegee has a rubber blade and plastic main structure and it may be that these compounds were oxidation products as a result of heating the squeegee in the oven. However they were minor peaks and did not interfere with analysis.

EIC analysis (Appendix 23) confirmed the absence of early eluting C_2-alkylbenzenes, decane (*n*-C_{10}), butylcyclohexane and 4,7-dimethylindane (Table 2.2). All *n*-alkanes from *n*-C_{11} to *n*-C_{20} were identified as was the cyclohexane compounds *n*-pentylcyclohexane to *n*-nonylcyclohexane.

This technique has shown that most medium and heavy petroleum distillates can be leached from a substrate using water as a repelling agent and the liquid is captured as a collection method for ILR, but the aromatic fraction including alkylbenzenes, alkylindanes and alkylnaphthalenes are not recovered to the same extent as alkanes as these aromatic compounds are slightly polar and therefore have a slight affinity to water. The technique is cumbersome in that a squeegee is used to push the water into a Rilsan® bag means that some of the ILR may be left behind and may further spread any liquid to other areas. This technique does allow for the adsorption of either petrol or diesel shown in the results at Table 2.2. The absence of C_2-alkylbenzene target compounds means that this method of collection is not suitable for lighter ignitable liquids such as petrol. The use of water may even dilute oxygenated and polar compounds of certain ignitable liquids such as ethanol which makes this technique non-recommendable.

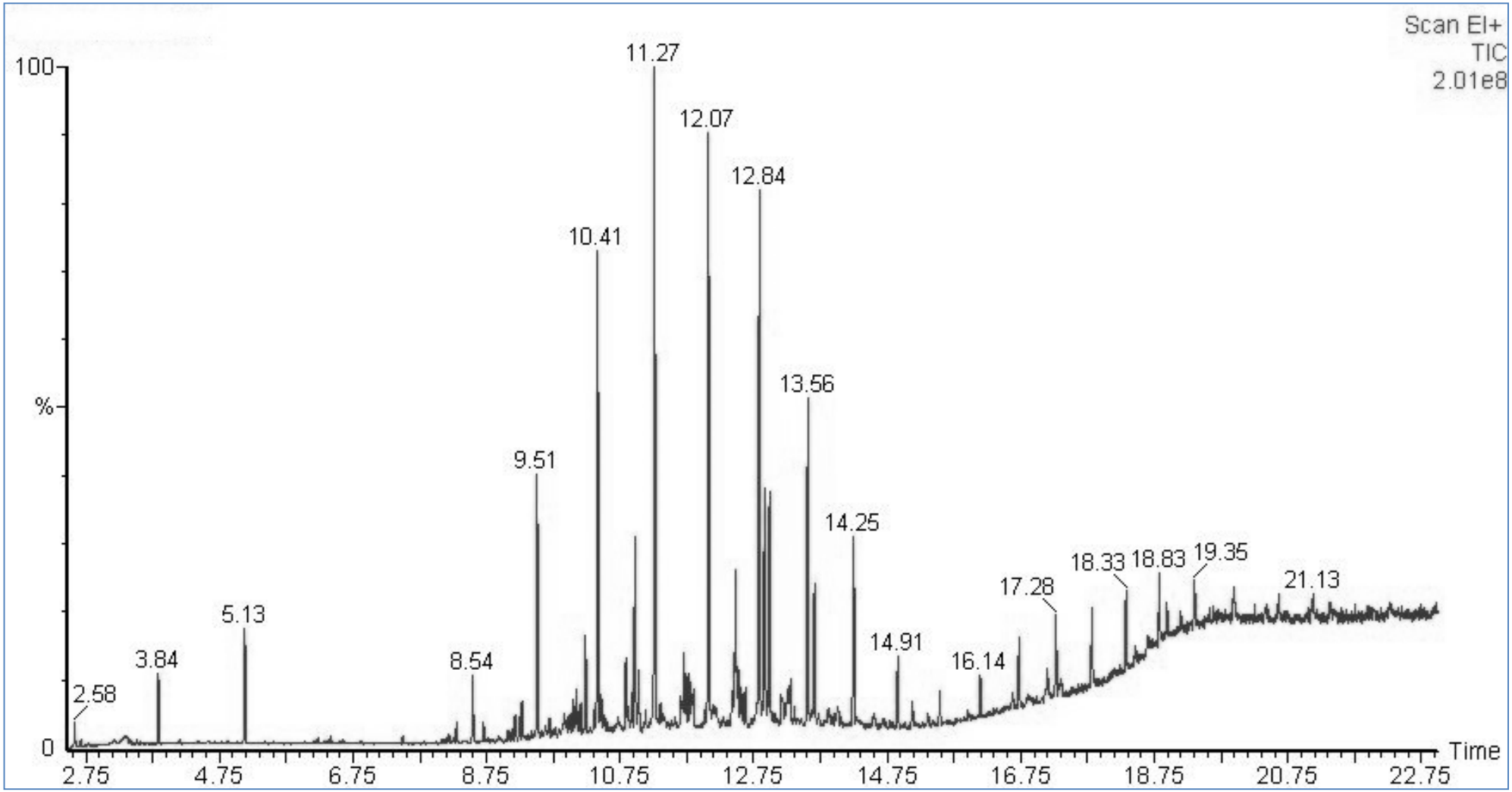

Figure 2.5 TIC of Squeegee technique with de-ionised water after collecting a sample of a petrol/diesel 1:1 v/v mixture

2.4.5 *Talc*

Table 2.2 shows that the earliest adsorbed target compound was *m,p*-xylene (4.57 minutes) and the last target compound adsorbed was (nonadecane) 4.25 minutes. The Talc TIC (Figure 2.6) showed a similar Gaussian curve to that seen on the Squeegee TIC except the peaks for undecane and dodecane (7.49 and 8.54 minutes) appeared more abundant when compared to Squeegee peaks, suggesting that Talc adsorbs these compounds better than Squeegee. The highest relative abundant peak was at 10.41 minutes (tetradecane). Alkane and cycloalkane compounds dominate the TIC. This is because Talc preferentially adsorbs non-polar compounds such as alkanes and cycloalkanes (Rotenburg, et al., 2011). The background control TIC for Talc is at Appendix 4. Minor peaks can be seen on that TIC which were identified as undecane, dodecane, tridecane and tetradecane. These peaks are the same as found in the background control for garden lime (section 2.4.1) but are small in comparison to the sample chromatogram peaks and so were ignored. The negative control showed no peaks on the TIC.

EIC analysis (Appendix 22) confirmed that alkane target compounds adsorbed by Talc ranged from undecane to nonadecane and also adsorbed all *n*-cycloalkanes (Table 2.2). However nonane and decane were not adsorbed, which suggests that Talc does not adsorb lighter alkane compounds or C_2 and C_3 alkylbenzenes with the exception of 1,2,4-trimethylbenzene (6.14 minutes). However, later aromatic compounds such as alkylindanes and alkylnaphthalene target compounds were identified and target compounds up to nonadecane suggesting that Talc preferentially adsorbs the heavier compounds. The failure to adsorb decane and lighter compounds means that this adsorbent can neither adsorb all petrol or all diesel target compounds.

In section 2.1.2 it was proposed that Talc adsorbs hydroxyl ions from water *(ibid).* It should be noted that the preference for the adsorption of water does not make this adsorbent a good candidate for use at fire scenes, although no water was used at any time in experiments with this adsorbent.

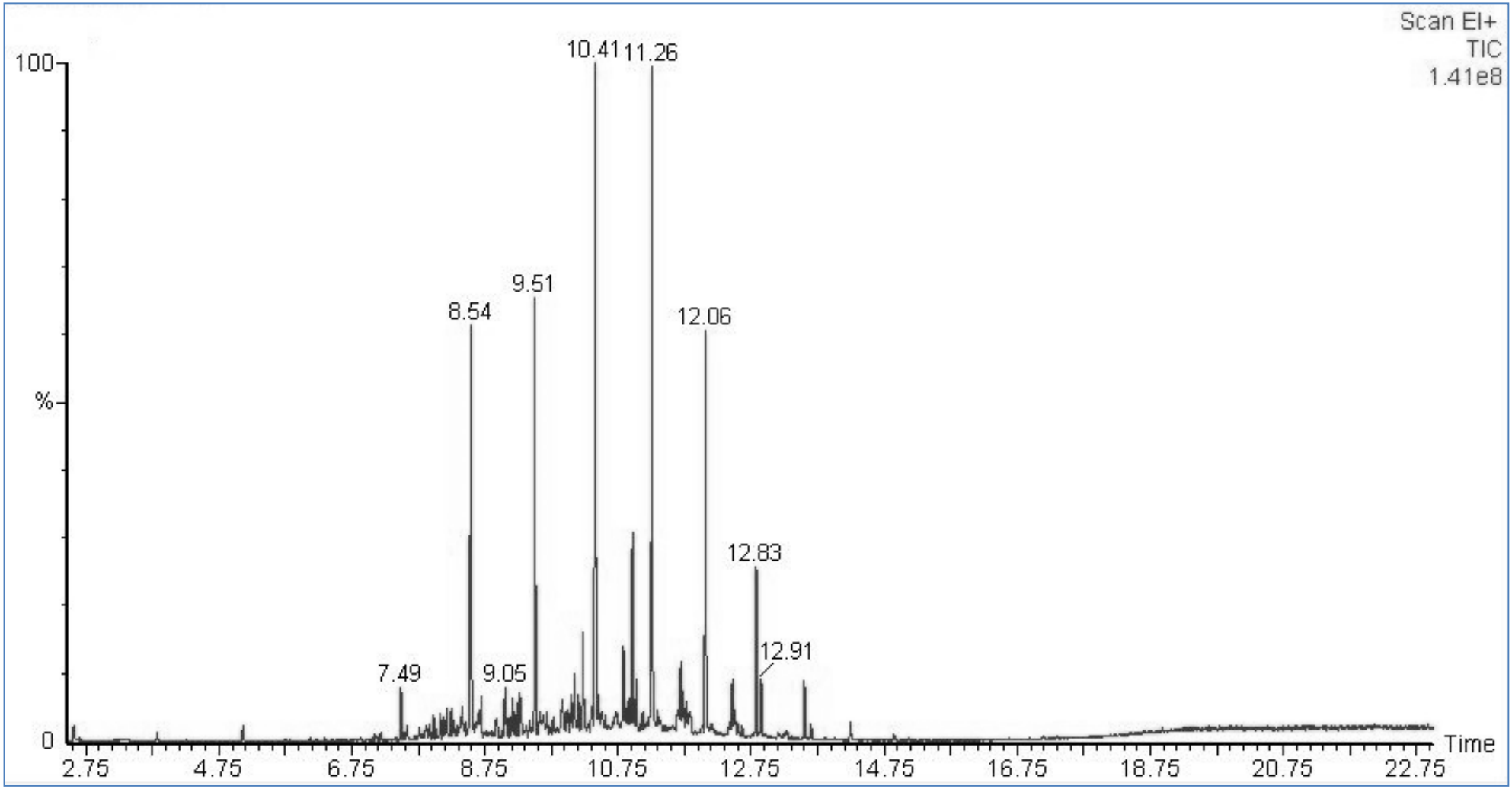

Figure 2.6 TIC of Talc after the adsorption of a petrol/diesel 1:1 v/v mixture

2.4.6 ***Tampax®***

The Tampax® sample showed peak signals from 5.74 minutes (3-ethyltoluene) to 14.25 minutes (nonadecane) (Table 2.2). Overall the TIC peaks conformed to a Gaussian shape and appeared similar to the TIC of Squeegee (Figure 2.7) as it was dominated by *n*-alkane peaks with the most abundant compound at 10.41 minutes (tetradecane).

Tampax® is made from rayon and polymeric fibres (Allen & Denning, 1975). Despite these materials being present, the control TIC showed only a minimum of background interference and did not interfere with analysis. This was confirmed by an examination with EICs that interference was not a problem. The background control is at Appendix 6 and only very small peaks were visible and it was very similar in respect to the Tampax® negative control which has small peaks that were not identified as target compounds.

The EICs at Appendix 24 revealed that *n*-alkanes; branched alkanes and *n*-cycloalkanes target compounds were readily adsorbed apart from *n*-decane and *n*-butylcycloheaxane. C_2-alkylbenzene compounds (ion 91) were not adsorbed but C_3-alkylbenzenes and all other heavy alkylbenzenes, indane and naphthalene target compounds were adsorbed. The fact that lighter compounds are not adsorbed indicates a preference to adsorb heavier compounds, and shows that Tampax® does not adsorb all petrol compounds and not all of the diesel compounds.

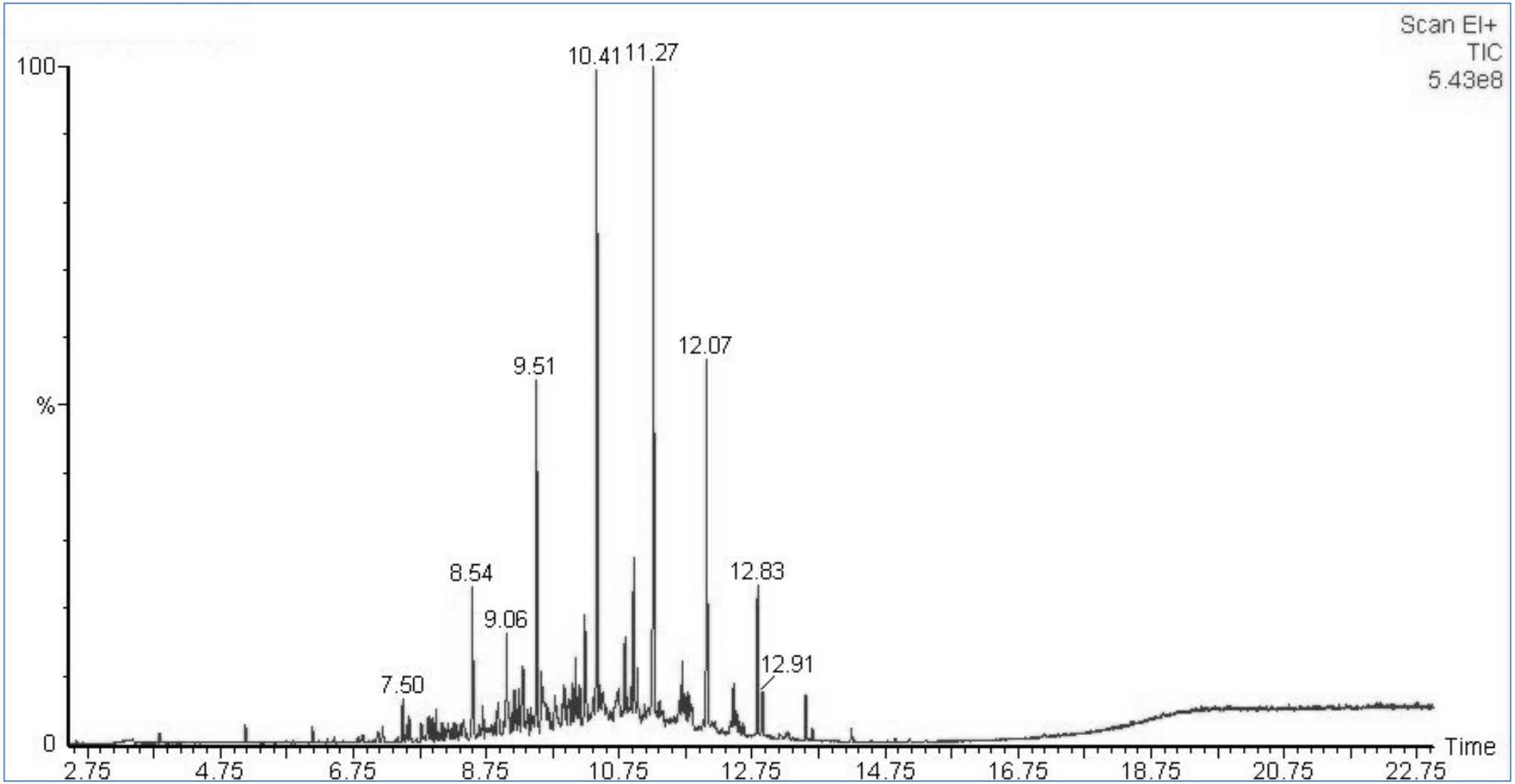

Figure 2.7 TIC of Tampax® after the adsorption of a petrol/diesel 1:1 v/v mixture

2.4.7 *TENA Lady®*

Table 2.2 shows that TENA Lady® adsorbed target compounds from 4.57 minutes (*m,p*-xylene) to 14.25 minutes (nonadecane) with the highest relative abundance peak at 9.51 minutes (tridecane) (Figure 2.8). The Gaussian peak shape (6.12 to 12.89 minutes) and diminished aromatic peaks (4.57 to 6.59 minutes) suggest that alkanes are favoured for adsorption by this adsorbent. The negative and background control of TENA Lady® showed a noisy baseline from 9.49 to 15.11 minutes (Appendix 7) which is indicative of the plastic and cellulosic material that the product is made from. Crucially, using EICs at Appendix 25 these peaks were identified as tridecane; tetradecane; pentadecane; hexadecane; heptadecane; octadecane and nonadecane which are also target compounds. The tallest peak was at 12.06 minutes (hexadecane) with the peak height at 9.79×10^6. However, the TIC peak heights were much larger 8.55×10^7 at 9.51 minutes (tridecane). Although there appears to be a height difference it is not that much and although the adsorption for this sample was distinguishable from the control, trace samples of ILR might not show the same height advantage as this study. TENA Lady® does contain *n*-alkanes and so there is a risk of mis-identification.

Although TENA Lady® adsorbed most target compounds from petrol and diesel it did not adsorb the lightest (ethylbenzene) or the heaviest (eicosane and heneicosane) so it cannot adsorb all target compounds in either petrol or diesel.

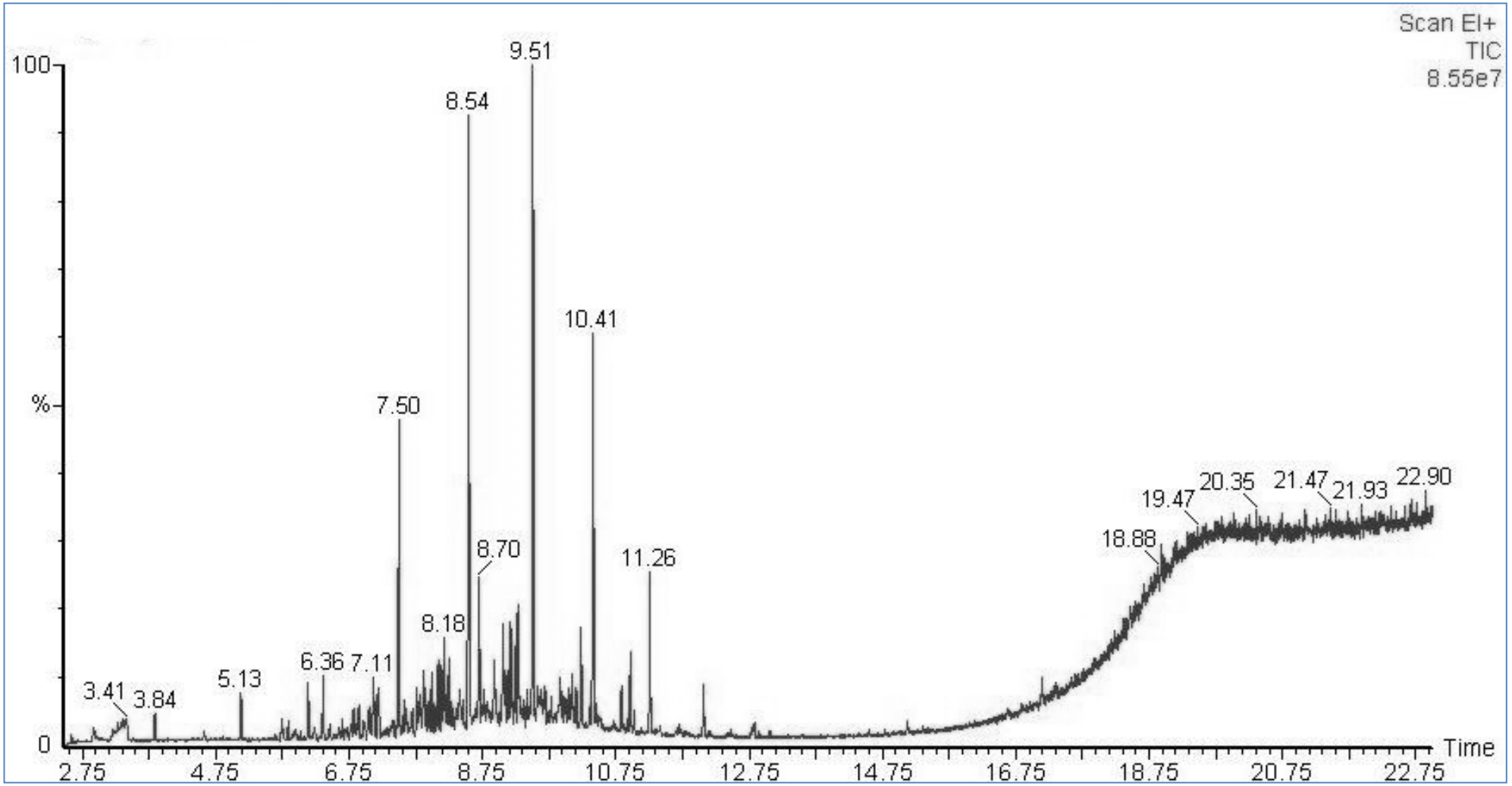

Figure 2.8 TIC of TENA lady® after the adsorption a petrol/diesel 1:1 v/v mixture

2.5 Conclusion

Seven adsorbents were evaluated for their ability to adsorb ignitable liquid residues from a 'smoke house' operated by Cambridge Fire and Rescue Services (FRS) (Table 2.3). Adsorbents were deployed and recovered using industry standard methods (NFPA 921, 2011). Separation of target compounds from adsorbents was achieved using industry standard passive headspace adsorption, ACS and pentane (ASTM E1412-12, 2012). Analysis was achieved with a GC-MS (ASTM E1618-11, 2011). All of the adsorbents were easy to use as they were sprinkled from a container, and a clean paintbrush was used to recover the granules/powder into a Rilsan bag. However, the Squeegee was used by hand to scrape the residue into a Rilsan® bag and found to be difficult to use even after some practice beforehand.

Table 2.3 The advantages and disadvantages of evaluated adsorbents

Adsorbent	Easy to use	Easy to recover	Adsorbs all petrol target compounds	Adsorbs all diesel target compounds	Recommended as a universal adsorbent for ignitable liquid residues?
Ultra clumping cat litter	yes	yes	yes	no	no
Sharp Sand	yes	yes	no	no	no
Tampax® Regular	yes	yes	no	no	no
TENA Lady® Normal	yes	yes	no	no	no
Garden Lime	yes	yes	no	no[1]	no
Talc	yes	yes	no	no[1]	no
Squeegee	no	no	no	no[1]	no

[1] *Heneicosane and decane was not adsorbed/desorbed by any of these adsorbents*

The only evaluated adsorbent to adsorb all petrol target compounds was cat litter and if petrol was the only ignitable liquid used by the arsonist, then cat litter would be able to adsorb the petrol compounds and subsequently be identified. However, adsorption stopped at *n*-hexadecane (Table 2.2) and thus cat litter did not adsorb all diesel compounds. This shortfall makes cat litter unsuited to being used as a universal adsorbent. The other adsorbents did not adsorb all of the petrol compounds and likewise with diesel containing a range of medium to heavy target compounds they did not adsorb all of the diesel target

compounds either and therefore unsuitable as universal adsorbents. Only garden lime, talc and the Squeegee adsorbed the heavier target compounds in diesel, but they did not adsorb the target compound heneicosane. However, Garden Lime was the only adsorbent that was able to adsorb from a range of n-C_{11} – $n$$C_{20}$ and therefore has the potential to adsorb the majority of diesel compounds. It is possible that the ACS did not adsorb the compound heneicosane, or more likely that the oven temperature was not high enough to force heneicosane into the gas phase. This was encountered in findings by Newman, et al. (1996). It is recommended that none of these adsorbents should be used as a universal adsorbent for common ignitable liquids as they lack the adsorption ability for all petrol compounds with the exception of clay cat litter or all diesel compounds.

Common ignitable liquids have a wide range of compounds that are generally slightly polar or non-polar, with the exception of oxidants. It is suggested that ion exchange and adsorbent surface modifications can be made to clays such as bentonite to engineer the compound types that can be adsorbed (Bergaya, et al., 2006, pp. 263-265). Also, it is possible that a mixture of clays and minerals could be enhanced by mixing these materials in the correct amounts to achieve the same result as the surface modification. Given the range of adsorption of cat litter and the range of garden lime, it is possible that a mixture of these two materials may yield adsorption of both petrol and diesel compounds. This latter recommendation was the route taken for the next stage and is investigated further in section 4.7.3. Although limestone did not adsorb all petrol compounds in this study, the mineral is versatile enough in terms of availability, hydrophobicity (which would make a good fire scene adsorbent) and able to mix with minerals of similar grain size. Initially limestone, which has been shown to adsorb heavy non-polar compounds, was mixed with different ratios of other adsorbents such as bentonite or montmorillonite to increase the net charge of the mixture so to adsorb the lighter and aromatic target compounds and this step is included and is discussed further in section 4.7.3.

It was a concern that heneicosane was not adsorbed due to extraction limitations, so it was decided to improve the method by changing the separation adsorbent to Tenax TA®. That adsorbent is desorbed by heat and not a solvent (section1.6.3) so an ATD was used for that stage. This gave an opportunity to improve both separation and instrumental methods and is introduced and discussed in the next chapter.

Chapter Three

Improvements to the Use of Tenax TA® in the Separation of Ignitable Liquids from Fire Debris and Instrumental Improvements to ATD-GC-MS

3 Introduction

In Chapter 2 it was discovered that ad hoc adsorbents did not adsorb all target compounds of a petrol/diesel mixture 1:1 (v/v), and this could have been due to the methods or materials used. It was necessary to ensure that the analytical method was not contributing to the adsorbent poor performance, so it was decided to improve both the separation method (section 1.5.4) and the instrument method. Therefore, Tenax TA® (section 1.6.3) was chosen as the laboratory adsorbent instead of ACS. Tenax TA® does not use a solvent to desorb compounds (Borusiewicz & Zięba-Palus, 2007). Instead, thermal desorption is used with the aid of a manual or automated thermal desorber (ATD) (section 1.6.4). The preliminary work in Chapter 2 was completed in laboratory conditions with set volumes of a petrol/diesel mixture. It was planned to use the same ignitable liquid (IL) mixture but in a series of experiments that focussed on separation stage oven time changes to determine an optimal adsorption (oven) time for the ignitable liquid mixture. It was also planned to optimise the instrument parameters and finally it was planned to evaluate both methods with a blind test (Jackson, 2012, p. 240). Blind tests were introduced in section 1.9 and are discussed in sections 3.6.5 and 3.8. In sections 1.6.1 & 1.6.3 it was discussed that the separation of ignitable liquid vapours in an oven (currently 16 hours) contributes significantly to overall laboratory time for samples. Newman, et al. (1996) used 16 hours for activated carbon strips (ACS) and Borusiewicz & Zięba-Palus (2004) used Tenax TA® for also for 16 hours. It was noted by those authors that the suggested time span was selected to fit in with analyst schedules and convenience. It was the opinion of the author of this thesis that sixteen hours was not the optimum time for adsorption, as this could lead to competitive adsorption (section 1.6.1) and thus incomplete adsorption, which may create difficulty in the identification of early eluting target compounds such as C_2-alkylbenzenes. This is discussed further in section 3.7.3.

3.1 Passive Headspace adsorption with Tenax TA®

Tenax TA® (section 1.6.3) is used in glass or stainless steel tubes as micro sized spheres to adsorb volatile organic compounds (VOCs) in water or soil (EPA Method TO-1, 1984) and in VOC analysis of chemical weapons (EPA Method 8170, 2007). As far as ignitable liquid separation is concerned, the use of Tenax TA® adsorption in fire debris has been researched but not to the same extent as the ACS and solvent method. Borusiewicz & Zięba-Palus (2004) used Tenax TA® and GC-FID to detect and identify ignitable liquids from a fire scene. The adsorption temperature for Tenax TA® was suggested to be 60 ^{0}C for 16 hours. This was undertaken in a conventional oven with hermitically sealed jars. The adsorption temperature (60 ^{0}C) is suitable for fast retention time compounds such as C_2-alkylbenzenes. However, target compound analysis starts after these compounds have eluted from a GC column. The fastest retention time named target compound is nonane (ASTM E1618-11, 2011), but more importantly the last target compound with the slowest retention time is heneicosane. It is believed that 60 ^{0}C is too low a temperature to adsorb heneicosane because this compound may not desorb from fire debris efficiently due to its high boiling point of 356 ^{0}C @ 760 mm Hg (Chemical Book, 2007). Therefore an oven temperature of 90 ^{0}C was judged as a suitable compromise to allow sufficient desorption of target compounds from fire debris and also adsorb them with Tenax TA®.

Another study by Borusiewicz & Zięba-Palus (2007) compared two adsorbents (Tenax TA® and Carbotrap 300®) in relation to their ability to adsorb/desorb a range of ignitable liquids with passive headspace adsorption and ATD-GC-MS. The adsorption temperatures at 60 ^{0}C and 90 ^{0}C were investigated. A number of different ignitable liquids were used in a test mixture which included petrol; methanol; ethanol; acetone; *n*-propanol; butanol; Benzyna Ekstrakcyjna and diesel. Analysis was conducted with GC-MS but only TICs were shown in the results. When analysing ignitable liquid compounds there may be multiple compounds that appear to be present in the same chromatogram peak. This is true if compounds elute very close to one another. Without the use of extracted ion analysis, the separation of those compounds may not be achieved. This was discussed previously in section 1.8.1.1. Their focus for their research was the adsorption of Tenax TA® and Carbotrap® to those ignitable liquids and the subsequent desorption efficiency (Equation 3.1) when the tube was placed into the ATD. The efficiency refers to the volume of sample carry-over after the tube was desorbed. This was achieved by comparing two analyses of the same sample tube. The first analysis used target compound peak area data (*a*) and

compared this to a second desorption of the same tube with the same compound peak area (b). This was calculated as:

Thermodesorption efficiency = *(a / a + b) x 100%)* *Equation 3.1*

It is of note that the desorption temperature the authors used for Tenax TA® was 330 ^{0}C which is higher than the manufacturer recommended temperature of 300 ^{0}C (PerkinElmer Inc, 2014) and does not allow much leeway for conditioning the tubes, which is recommended by PerkinElmer (2014) to be at least 10 ^{0}C above the desorption temperature. The maximum temperature for Tenax TA® is 350 ^{0}C. As the temperature approaches the maximum, artefacts can appear and reduce adsorbent life (Markes International Ltd, 2000). The authors concluded that Tenax TA® showed characteristics of the displacement of low molecular weight polar compounds in favour of high weight non-polar compounds which was more pronounced at the higher oven temperature (90 ^{0}C) during headspace adsorption. When the lower temperature was used (60 ^{0}C) Tenax TA® was superior for the adsorption of both polar and non-polar molecules compared to Carbotrap 300® (section 1.6.2). However, Carbotrap 300® was suggested to be a superior adsorbent for lower weight and increasingly polar compounds. Also, the adsorption temperature for this adsobent was found to be optimal at 90 ^{0}C *(ibid)*.

The Borusiewicz & Zięba-Palus (2007) study also considers desorption factors (section 1.5.2.4) where the data is derived from desorption data using chromatogram peak areas. The two adsorbents (Carbotrap 300® and Tenax TA®) have different desorption properties. For example with Carbotrap®, at a desorption temperature of 360 ^{0}C, volatile polar compounds such as ethanol, acetone and butanol were not totally desorbed and some volatile non-polar compounds such as hexane, methylhexane and heptane were not desorbed fully. Whereas with Tenax TA®, at a desorption temperature of 330 ^{0}C, only hexane was not desorbed fully but all other compounds were desorbed. The same authors noted that after the first desorption, Tenax TA® was ready for reuse and that Carbotrap 300® needed additional conditioning as compounds were not completely desorbed. This was achieved by desorbing the tubes again, but the conditioning temperatures were not published by the authors. These results show that there is potential for carry-over when using Carbotrap® tubes for the analysis of fire debris and that Tenax TA® does not have this problem. This leads to the conclusion that Tenax TA® is the preferred adsorbent when using similar desorption temperatures.

Rothweiler, et al. (1991) used Tenax TA® and Carbotrap® to adsorb and desorb VOCs in air and determined that Tenax TA® could desorb heavy alkane compounds but Carbotrap could not quantitatively desorb compounds with boiling points that exceed 270 ^{0}C. This means that ignitable liquid compounds from pentadecane (n-C_{15}) with a boiling point of 270 ^{0}C (ScienceLab.com, 2013) and upwards cannot be completely removed during desorption. However, subsequent tube conditioning for Carbotrap 300® at 400 ^{0}C should remove all compounds lower than tetracosane (n-C_{24}) (boiling point 391 ^{0}C; Griesbaum, et al., (2000). In section 2.4.1 it was shown that the heaviest compound adsorbed or desorbed was eicosane (n-C_{20}). The ASTM E1618-11 (2011) method requires the identification of heneicosane (n-C_{21}). However, it is recognised by the author of this thesis that ignitable liquid compounds contain compounds heavier than heneicosane, such as biodiesel as this was found by Stauffer & Byron (2007). Therefore, even heavier compounds should be targeted by ASTM methods. In view of this, it was important that this point was considered when trying to find a universal adsorbent as future deliberate fire cases may use new fuels such as biodiesel or an as yet undiscovered ignitable liquid. In consideration of these factors, the oven adsorption temperature and time chosen for Tenax TA® in this study was 90 ^{0}C and time was the variable (90 minutes to 960 minutes).

3.2 Method Improvements to Oven Adsorption with Tenax TA®

The use of GC-MS to analyse ignitable liquids was introduced in Section 1.7.2. Both Hendrikse (2007) and Pert, et al. (2006) suggested that GC-MS has become the defacto standard for fire debris analysis and has its own ASTM method (ASTM E1618-11, 2011). However, there is currently no standard method for the use of Tenax TA® and an automated thermal desorber for fire debris investigation. Yet there are fire debris analysis laboratories actively using this technique (Hendrikse, 2007; Haworth, 2011) which indicates that the method is a viable alternative to ACS and solvents as described in section 1.6.1.1. Therefore it was decided that if Tenax TA® and an ATD were used to investigate a new adsorbent that the method used by Borusiewicz & Zięba-Palus (2004) would need some improvements, such as oven adsorption time as described in the previous section. The method would have to be capable of the adsorption and desorption of compounds found in common ignitable liquids which was introduced in section 1.4 and ultimately be identified with the aid of extracted ion chromatograms (section 1.8.1.1). One of the considerations for this research was: What ignitable liquid(s) should be used as a

representation of common ignitable liquids? This was not only considered for method improvements but also for analysis of any new adsorbent created later in the research. The ASTM E1618-11 (2011) method suggested that many ignitable liquids are characterised by their aromatic or aliphatic composition (section 1.4). Both petrol and diesel contain these types of compounds and the range of compounds is wide. Therefore, it was decided to use both petrol and diesel, as these ignitable liquids have a widest range of target compounds listed in the ASTM E1618-11 (2011) method. Other ignitable liquids with the exception of some oxygenated products consist of compounds that are extracted from aliphatic or aromatic fractions but essentially fall within the compound span of petrol and diesel. For example, white spirit (paint thinner) has well defined chromatogram peaks for the compounds *n*-nonane through *n*-dodecane and some brands have 1,2,4-trimethylbenzene (National Centre for Forensic Science, 2006). All of these compounds fall within the compound span of a petrol/diesel mixture. Therefore, a petrol/diesel mixture was determined to represent a common ignitable liquid. However it is recognised that compounds outside those of a petrol/diesel mixture exists such as terpenes and oxygenated solvents. It was decided for the purpose of analysis in this part of the research, to only include a select few compounds that are considered representative of early eluting, medium eluting and late eluting compounds in the petrol/diesel mixture.

The early eluting light compounds chosen were: octane; ethylbenzene; *m,p*-xylene and *o*-xylene. The medium eluting compound was hexadecane and the late eluting heavy compounds were; octadecane, eicosane and docosane.

Octane is present in petrol fuel and kerosene *(ibid)* but is not a target compound designated in ASTM E1618-11 (2011). This compound elutes from a non-polar GC column before the C_2-alkylbenzene compounds. This compound has a smaller retention time than early target compounds, therefore it was reasoned that if the method used can identify this compound, compounds that elute after octane would also be able to be identified. Likewise, docosane (n-C_{22}) (also not a target compound) elutes after the heaviest target compound heneicosane (n-C_{21}) on the same column as previously mentioned. If this compound could be identified during analysis, lower boiling point compounds should also be able to be identified and also enabled the assessment of the effectiveness of the oven time on adsorbents. The target compound hexadecane (n-C_{16}) was also chosen as it was one of the most relative abundant compounds on a petrol/diesel mixture TIC (Figure 2.1).

3.3 Relative Response Factor (RRF)

It was important to calculate ratios of peak areas or heights of different compounds as in gas chromatography as small changes in carrier gas velocity and GC oven temperature fluctuations and the unrepeatable nature of volatilising a liquid to gas can change an analyte signal (peaks area or height) by broadening their width (Grob & Barry, 2004, pp. 43-57). An internal standard injected into a Tenax TA® tube is automated by the ATD and injects the same volume to every tube. Because it is the same volume, the signal response is recorded as a peak area or peak height and can be used as a reference to calculate a sample response factor with a sample peak area/height. Where there are differences in a response between an internal standard (IS) and a sample signal, a factor can be used to correct for this difference. This is known as the relative response factor (RRF) *(ibid)*. The RRF is equal to the analyte signal divided by the internal standard signal. At this time there are no publications on the use of an internal standard with passive adsorption of Tenax TA® and GC-MS analysis of fire debris. The ATD-GC-MS is designed to use a vapour phase internal standard and toluene-*d*8 was chosen for this purpose. Toluene and toluene-d_8 have similar retention times on a TIC. However, the use of EIC ion 98 only shows a signal for toluene-d_8 and not toluene (ion 91) and therefore identification and interpretation of data can be completed using this ion.

3.4 Practical Considerations with Real Fire Debris

When working with known volumes and concentrations of ignitable liquids in the laboratory there is little need to stray from the designated method as the volumes and concentrations are controlled by the analyst and not likely to overload the GC-MS. However, in real world fire debris, the volumes and concentrations of unknown ignitable liquids may saturate the instrument or contaminate it so much that component parts may have to be replaced and this could lead to ruin real case samples. To prevent overloading the ATD-GC-MS (section 1.6.4) with excess ignitable liquid vapours, a preliminary screening scheme was devised to minimise saturation by conducting a small test directly after the evidence container is opened. Preliminary screening can also be achieved with instruments designed to analyse headspace including the use of a mobile hydrocarbon

monitor. The use of a fume cupboard is always advised if the olfactory analysis option is taken.

The presence of a strong smell of hydrocarbons or high concentration reading on the headspace monitor could mean that subsequent thermal adsorption with Tenax TA® in a fan oven would take place relatively quickly. This is because of the higher concentration of volatile compounds in the headspace would quickly fill adsorption sites on the adsorbent. The reverse is true for a weak smelling or low hydrocarbon concentration as there are fewer molecules in the vapour phase and a longer oven time is necessary to fill adsorption sites on Tenax TA®. However, competitive adsorption discussed in section 1.5.2.5 associated with long oven times may become evident as oven times increase. Therefore, a range of oven times starting at ninety minutes and ending at sixteen hours were chosen to determine if this phenomenon affected results.

3.5 Aim and Objectives for Separation Method and Instrumental Method Improvements

It was introduced in section 3.2 that there is no standard method for ATD-GC-MS when analysing fire debris. It was the aim of this research to create such a method that could be used by fire debris analysts when employing such an instrument, and in the future has the potential to become a standard method in its own right.

The first objective was to determine an optimum oven heating time period with a fixed temperature of 90 ^{0}C (section 3.1), for the adsorption/desorption of petrol/diesel compounds onto the surface of Tenax TA® using passive headspace adsorption.

Another objective was to adjust the ATD split flow valves to ensure that column overloading did not occur, as the saturation of the ATD, column and detector will degrade the instrument (section 1.6.4) and introduce possible contamination through carry over.

The last objective was to evaluate the improved methods by using a series of blind tests (section 1.9) with real fire debris samples that contain unknown substrates, contamination and ignitable liquids.

3.6 Materials and Methods

3.6.1 *Materials*

Factory pre-packed stainless steel Tenax TA® tubes were supplied by Markes International Inc; the Heraeus UT6 oven was supplied by the Thermo Electron Corporation for passive headspace adsorption; 2.5 L paint cans and lids supplied by the Birmingham Tin Box Company; Pipeteman pipettes were supplied by Gilsen; diesel fuel and petrol fuel (UL95) was obtained from BP Express, Thetford; a test mixture (ASTM E1618-11, 2011) of alkanes: *n*-octane; *n*-decane; *n*-dodecane; *n*-tetradecane; *n*-hexadecane; octadecane; eicosane; docosane; 3-methyl-ethylbenzene (3-ethyltoluene); 1,2,4-trimethylbenzene; 1,2,3-trimethylbenzene; butylcyclohexane; *trans*-decalin; 1-ethylnaphthalene and 1,3-dimethylnaphthalene were purchased from Fisher Scientific UK, each component was prepared as 0.005 % v/v in *n*-pentane (supplied by Fisher Scientific UK).

3.6.2 *Method for the Optimisation of Time for Passive Headspace Adsorption with Tenax TA®*

Aliquots (10.0 µL) of a fresh 1:1 petrol/diesel v/v mixture were pipetted onto a watch glass and the watch glass was placed into an empty paint can that had been previously conditioned at 200 ^{0}C for 2 hours. Tenax TA® adsorbent tubes were pre-conditioned using the ATD (335 ^{0}C; desorb flow 20 minutes @ 50 mL /min helium. The Tenax TA® tube was balanced between two 50 mL beakers so that the tube was horizontal and above the fire debris.

The can was sealed with its lid and placed in a preset temperature oven (90 ^{0}C). Each tube number was recorded and each can was assigned a letter (Figure 3.1). Fan oven times varied (90; 180; 360; 540 and 960 minutes). Each can contained the same volume of petrol/diesel mixture and an adsorbent tube with Tenax TA®. The can was then placed into the oven for the specified time.

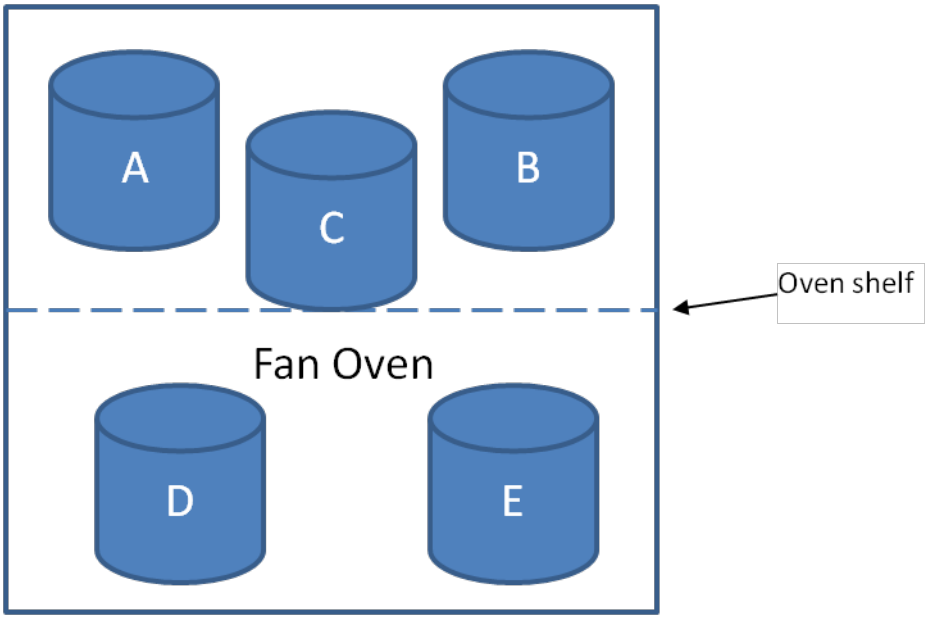

Figure 3.1 Fire debris can positions inside a fan oven

3.6.3 *Desorption of Compounds from Tenax TA®and Internal Standard Injection*

After removal from the oven, each adsorbent tube was placed onto TurboMatrix ATD carousel. The tube is loaded onto to the ATD and is heated to 280 ^{0}C. It is then purged with N_2 gas for one minute to remove excess water at 50 mL/min. After the purge is complete, the gaseous internal standard (500 ppm, toluene-d_8 in N_2), supplied by BOC, UK was injected into the tube from the internal standard module (duration = 1 minute). The tube was heated for a further ten minutes before entering the next stage. After this time, desorption from the tube onto the cold trap occurs: Two-stage desorption (helium, 50 mL/min); inlet split flow 10 mL /min; cold trap low: -30 ^{0}C; cold trap high: 300 ^{0}C (40 ^{0}C /sec); trap hold 10 min; outlet split flow 10 mL /min; transfer line: 280 ^{0}C. Tubes were re-conditioned overnight according to manufacturer instructions: temperature: 335 ^{0}C (Markes International Ltd, 2000).

3.6.4 *Method for the Analysis of Desorbed Compounds Using GC-MS*

Analysis was carried out on a Perkin Elmer, Clarus 500 GC-MS in electron ionisation mode with: Phenomenex ZB-1 column (30 m x 0.25 mm, 0.25 µm); helium carrier gas (15

psi). The GC oven was set initially at 50 ^{0}C, held for 2 min and ramped at 10 ^{0}C /min to 300 ^{0}C and held for 2 min. The mass spectrometer settings are the same as those used in section 2.2.4.

A further quality control check was necessary as the adsorbent tubes are loaded onto the ATD by a robot arm and the caps are removed, so that the tube is exposed to the atmosphere in the laboratory. Therefore a laboratory air sample of 60.0 mL (Dietz, 1991) was taken with each batch run using a hand drawn pump. Blank tubes only containing Tenax TA® were run between each sample and these were checked for carry over from the previous sample. Statistical analysis was completed with Microsoft Excel 2007 and Minitab 15.1.30.

3.6.5 *Method for Laboratory Blind Experiment*

In section 1.9 it was discussed that the evaluation of any improvements made to laboratory methods would include the testing of the methods on real fire debris samples. This would add to the robustness and ruggedness of the methods and eliminate pre-bias from the analyst. The evaluation was planned as a laboratory experiment where a third party would submit fire debris containing not only fire debris, but also a possibility of extra contaminants and ignitable liquids. To remove bias from the analyst, the experiments would be conducted as blind experiments (Jackson, 2012, p. 212). Specifically, the third party who created the fire debris knew what was inside the evidence bag, but the analyst would not. Once analysis had been conducted on the evaluation samples, the third party then revealed the actual contents of the evidence bags. The methods employed for blind trials were the the same separation and analysis methods that were previously used in sections 2.2.2, 2.2.4, 3.6.2, 3.6.3 and 3.6.4.

3.7 Results and Discussion

Peak retention times, mean elution times, mean RRF values (section 3.3) and corresponding passive headspace oven times are given in Table 3.1. Selected compounds were identified from EICs. Each compound was tested at each chosen oven time (90 to 960 minutes). Therefore for each compound there were n = 5 responses at each temperature.

Each sample was initially assessed by observing peak patterns and ratios (section 1.8.1) with the aid of a TIC for each time period that was tested. Target compound retention times (Table 3.1) were noted and were compared to standards, laboratory controls and a test mixture (section 3.6.1) under the same method conditions. Further analysis and interpretation using EICs was then used to confirm the identity of these compounds (Table 3.1).

Table 3.1 Table of results of selected compounds for statistical analysis

Selected compounds	**Mean RT[1] (mins, *n* =5)**	**Selected ion (m/z)**	**Oven time/min**	**Mean RRF[2] (*n* = 5)**	**t_{STAT}[3]**	**H_1 supported?**
Octane	3.66 ± 0.00	43	90	0.008 ± 0.004	2.05	x
			180	0.009 ± 0.004	1.98	x
			360	0.012 ± 0.005	2.68	x
			540	0.020 ± 0.006	1.75	x
			960	0.021 ± 0.011	6.83	√
ethylbenzene	4.32 ± 0.01	91	90	0.076 ± 0.036	1.63	x
			180	0.108 ± 0.028	2.19	x
			360	0.135 ± 0.053	2.71	x
			540	0.301 ± 0.132	4.61	√
			960	0.304 ± 0.150	5.91	√
m,*p*-xylene	4.45 ± 0.01	91	90	0.268 ± 0.118	1.52	x
			180	0.408 ± 0.091	2.75	x
			360	0.546 ± 0.156	2.62	x
			540	0.893 ± 0.148	5.25	√
			960	0.986 ± 0.206	7.85	√
o-xylene	4.78 ± 0.01	91	90	0.114 ± 0.046	1.29	x
			180	0.176 ± 0.036	2.46	x
			360	0.267 ± 0.078	2.55	x
			540	0.446 ± 0.048	2.52	x
			960	0.488 ± 0.105	4.17	√
Hexadecane	15.28 ± 0.01	57	90	0.053 ± 0.010	2.00	x
			180	0.116 ± 0.011	0.02	x
			360	0.325 ± 0.028	0.72	x
			540	0.523 ± 0.024	2.49	x
			960	0.784 ± 0.027	2.28	x
Octadecane	17.63 ± 0.01	57	90	0.031 ± 0.010	1.51	x
			180	0.072 ± 0.012	0.39	x
			360	0.240 ± 0.024	0.28	x
			540	0.403 ± 0.027	0.08	x
			960	0.647 ± 0.031	1.70	x
Eicosane	19.76 ± 0.01	57	90	0.009 ± 0.005	1.43	x
			180	0.025 ± 0.007	0.66	x
			360	0.119 ± 0.020	0.18	x
			540	0.228 ± 0.038	0.93	x
			960	0.367 ± 0.035	0.64	x
Docosane	21.77 ± 0.01	57	90	0.000 ± 0.000	2.19	x
			180	0.003 ± 0.002	1.27	x
			360	0.026 ± 0.005	0.28	x
			540	0.049 ± 0.017	1.39	x
			960	0.086 ± 0.015	2.04	x
Tricosane	22.62 ± 0.01	57	360	0.009 ± 0.002[4]	0.26	x
			540	0.018 ± 0.008	1.60	x
			960	0.031 ± 0.007	1.57	x
Tetracosane	23.54 ± 0.01	57	540	0.005 ± 0.03[5]	1.26	x
			960	0.009 ± 0.01	1.58	x

[1] RT = Retention time of compound
[2] RRF = Relative Response Factor (Grob & Barry, 2004)
[3] t-CRIT value = 3.18
[4] Tricosane was identified at 360 minutes and later
[5] Tetracosane was only identified at 540 minutes and later

3.7.1 *Compound identification*

Table 3.1 shows that all selected compounds were identified at studied oven times. After an initial appraisal of the results it appeared that the peak area values for cans A, B and C were different from cans D and E (Figure 3.1), and this generated higher standard deviation for many compounds (Table 3.1). The difference appeared more pronounced for heavy compounds at a short oven time where cans A and B and C had much larger peaks those from cans D and E. For lighter compounds at longer oven times cans D and E had much larger peaks than those of cans A, B and C. These differences indicated that the cans that had smaller peak sizes did not adsorb or desorb target molecules so well at those oven times. It was considered that there was a difference in adsorption of gas phase compounds that was dependant on the position of the Tenax TA® tubes within the fan oven. To illustrate the differences in adsorption, Table 3.2 shows the standard deviation for four compounds (octane; ethylbenzene; hexadecane and eicosane) at 960 minutes. The lighter compounds octane and ethylbenzene have large peak differences for all oven times leading to larger standard deviation. Heavier compounds exhibit adsorption differences but are not as pronounced as those of octane or ethylbenzene. It was also determined that eicosane and docosane had increased standard deviation values at shorter oven times (Table 3.1).

It was hypothesised that not only was the oven temperature having an effect on adsorption of the lightest and heaviest compounds, but also that the compounds were affected by where they were placed within the oven (Figure 3.1) and this lead to greater variation in adsorption. It is possible that at lower oven times (Table 3.1), heavy compounds are still entering the gas phase and a small difference in temperature caused by position in the oven is sufficient for a large difference in adsorption. Conversely, the lightest compounds at the longest oven times (Table 3.1) undergo competitive adsorption for surface adsorption sites (section 1.5.2.5). Again, the position in the oven may affect the temperature slightly but this may be all that is needed to show large variations in adsorption.

The focus for the differences in adsorption was to test the mean values to determine if the distribution of means were normal or not. It was decided to analyse the adsorption differences with statistics. A two sample, two-tailed *t*-Test with *t*-CRIT value was carried out in section 3.5.2 and was used to determine if there was any relational significance between the adsorption results.

Table 3.2 Target compound adsorption in a fan oven for five Tenax TA® tubes in cans at 960 minutes

Target Compound	RRF Can 'A'	RRF Can 'B'	RRF Can 'C'	RRF Can 'D'	RRF Can 'E'	Mean RRF	Std Dev
octane	0.01	0.01	0.02	0.03	0.04	**0.02**	±0.013
ethylbenzene	0.16	0.17	0.26	0.43	0.49	**0.30**	±0.15
hexadecane	0.82	0.77	0.80	0.77	0.74	**0.78**	±0.03
Eicosane	0.37	0.31	0.41	0.38	0.38	**0.37**	±0.04

3.7.2 *t-Test for fan oven adsorption*

A statistical test was used to examine what appeared to be a difference in sample results that lead to large difference of means and therefore abnormal standard deviation. For the purpose of the test, the results for cans A-C (top of the oven; labelled Array *x*) were separated from the results of cans D and E (bottom of the oven; Array *y*), thereby creating two arrays. A statistical "choosing chart" (Hawkins, 2009, p. 285-289) was used to determine a suitable statistics test: the test being to compare the mean RRF data of the adsorption of Tenax TA® tubes in relation to where they were situated in the fan oven. From the chart a two sample, two-tailed test was chosen, as the samples consisted of two arrays. Array *y* had three samples (n = 3), whilst Array *z* had two samples (n = 2), which meant that the unequal sample count for each array was different and therefore the two-tailed version of the t-Test was chosen. The Array means were calculated from RRF data and standard deviation was generated. A null hypothesis H_0 was defined as: The values for both $\bar{x}_y$ and array $\bar{x}_z$ are the same and that the observed mean values originated as two random values from a single distribution of values. Whereas, the proposed hypothesis stated that the values for $\bar{x}_y$ and array $\bar{x}_z$ are different and therefore adsorption is determined by tube location within the oven. The statistical calculation was completed first by the calculation of pooled standard deviation (Currell & Dowman, 2009, p. 269; Equation 3.2)

$$\acute{s} = \sqrt{\frac{(n_y-1)s_y^2+(n_z-1)s_z^2}{(n_y+n_z-2)}}$$ *Equation 3.2*

Where s is standard deviation; *n* is the count for each array; *y* and *z* refer to the two separate arrays.

A working example is given as follows:

Mean *y* = 401071 ± 319468, *n* = 3, mean *z* = 811447 ± 83514, *n* = 2

Pooled standard deviation = $\acute{s} = 196646.6$

Then the t $_{STAT}$ value was calculated using Equation 3.3:

$$t_{STAT} = \frac{(\bar{x}_y - \bar{x}_z)}{\acute{s}\sqrt{{}^{1}/_{n_y} + {}^{1}/_{n_y}}}$$ *Equation 3.3*

$t_{STAT} =$ **2.29**, degrees of freedom (*df*) = 3 + 2 – 2 = 3

two tailed t_{CRIT} 95% confidence ($\alpha = 0.05$) = 3.18 *(ibid)*

Since $t_{STAT} < t_{CRIT}$ the proposed hypothesis H_1 is not accepted, and therefore there is no significant difference ($\alpha = 0.05$) in the two sets of data.

In general Table 3.1 shows that the H_1 is not accepted at most oven times for most compounds suggesting that there is no significant difference of where the Tenax TA® tube is placed at different oven times. However there are some exceptions and these are explained in the next sub-sections.

The t_{CRIT} value was determined to be 3.18 *(ibid)*. Compounds that followed the proposed hypothesis H_1, were octane at 960 minutes; ethylbenzene at 540 and 960 minutes; *m,p*-xylene at 540 and 960 minutes and *o*-xylene at 960 minutes. Therefore all the lighter compounds (octane and C_2-alkylbenzenes) were affected by oven position at 960 minutes and the C_2-alkylbenzene compounds minus *o*-xylene were affected at 540 minutes. At 540 minutes and beyond, there appeared to be a small difference in adsorption of aromatic compounds which is dependent on oven position. It is proposed that a small increase in temperature over a longer time period is enough for heavier compounds to out-compete for

adsorption sites to force these compounds off the adsorbent surface and back into the gas phase. In other words competitive adsorption (section 1.5.2.5) is taking place. Octane was only affected by competitive adsorption at longer oven times, as it is non-polar in nature having more of an affinity for Tenax TA® than aromatic compounds (section 1.6.3) and therefore, requires more energy to move it from the adsorbent surface to the gas phase (Ranke, 2008). *Ortho*-xylene did not exhibit a significant difference in adsorption at 540 minutes and it is possible that this compound and heavier compounds are not affected so much by the oven position at that time period. However, further statistical examination of other aromatic and aliphatic compounds heavier than *o*-xylene is recommended to confirm this.

It is projected that even longer oven times than those tested will mean more light compounds will suffer from competitive adsorption even more. This has been reported in research by (Borusiewicz & Zięba-Palus (2004); Newman, et al. (1996). The null hypothesis H_0 is supported at all oven times for alkane compounds: hexadecane; octadecane; eicosane and docosane. This shows that the heavier compounds are not affected by oven position.

3.7.3 *Adsorption of ignitable liquid target compounds*

Figure 3.2 shows the comparison of oven time and the adsorption of octane, hexadecane, octadecane, eicosane and docosane. At 180 minutes, it shows there is a change in the rate of adsorption for the heavier compounds (hexadecane, eicosane and docosane). This could be that the first layer of molecules has filled the surface adsorption sites. In other words, the monolayer adsorption phase is now complete and molecules are starting to form layers on top of already adsorbed molecules (multilayer adsorption) (section 1.5.2.3) and there is a similarity between Figure 3.2 and the Type IV adsorption curve shown on Figure 1.7. At 540 minutes the curves appear to decrease in rate and this is indicative of pore filling or capillary condensation that was introduced in section 1.5.2.3. Medium and heavy petroleum compounds did not show signs of competitive adsorption. Therefore, at the times tested, hexadecane and heavier alkanes are not affected by competitive adsorption. Octane was steadily adsorbed by Tenax TA® but at a lesser rate than the heavier alkanes. This alkane enters the gas phase quickly at the oven temperature used. There is a change in increased adsorption between 360 and 540 minutes (Table 3.1) which suggests that octane

is also participating in multi-layer adsorption and the rate limit appears to be reached between 540 and 960 minutes. There is also the possibility of competitive adsorption at this time in that octane molecules are displaced from the adsorbent by the heavier compounds. Less energy is required to remove lighter compounds the further they are from the adsorbent surface (Ranke, 2008).

Figure 3.2 also shows that medium alkanes hexadecane and octadecane adsorb at a faster rate than the heavier eicosane and docosane. As an example, at 360 minutes the adsorption rate (slope) of hexadecane (n-C_{16}) = 0.33 / 360 = 9.17 x 10^{-4} and at 540 minutes is 0.52 / 540 = 9.63 x 10^{-4}. Therefore the slope for this compound from 360 minutes to 540 minutes is 9.17 x 10^{-4} - 9.63 x 10^{-4} = $\underline{9.0 \times 10^{-6}}$. For docosane ($n$-$C_{22}$) at the time intervals the calculation is: 0.02 / 360 = 5.55 x 10^{-5} and 0.05 / 540 = 9.26 x 10^{-5}. This gives a slope value of: 9.26 x 10^{-5} - 5.55 x 10^{-5} = $\underline{3.71 \times 10^{-5}}$ min^{-1}.

This variation can be explained by the difference in boiling points (bp) and therefore vapour pressure of the compounds even though the temperature was constant. For example, hexadecane bp is 287 ^{0}C and eicosane bp is 343 ^{0}C (Table 1.2). The difference is enough to ensure that there are increased numbers of hexadecane molecules available for adsorption in the vapour phase than those of eicosane. Table 3.1 shows that the next largest n-alkane compound (docosane) is adsorbed (RRF 0.26 ± 0.005) and can be identified from EIC (ASTM E1618-11, 2011) and therefore heneicosane should also be identified at this oven time also. This is significant as 180 minutes oven time is sufficient to identify common ignitable liquids using this method and 960 minutes (9 hours) oven times described in section 1.6.3 is excessive. It is also significant that Tenax TA® is a superior adsorbent for heavy petroleum distillates compared to ACS as it was discussed in section 2.4.1 that heneicosane could not be identified using ACS with passive headspace adsorption but Tenax TA® was able to adsorb and desorb heneicosane, docosane, tricosane and tetracosane, although tricosane could only be identified at 360 minutes (6 hours) onwards and tetracosane from 540 minutes onwards (9 hours) (Table 3.1). These compounds were identified with the GC-MS software database Although the ASTM E1618-11 (2011) method only requires identification of target compounds up to heneicosane for heavy petroleum distillates, it is desirable to detect heavier compounds such as those encountered in rapeseed oil-based biodiesel (Stauffer & Byron, 2007) as rapeseed compounds can extend to tetracosane and therefore these are also important to identify. This further reinforces the idea that oven times below 360 minutes should not be used for fire debris analysis using this method because the heavy ignitable liquid compounds will not have

sufficient numbers of molecules in the vapour phase. Because compounds up to tetracosane was identified at an oven time of 540 minutes it is recommended that future analysis should be conducted at either that time or 360 minutes if there is reason to believe that ignitable liquids may saturate the instrument and this is discussed in section 3.8.

At 960 minutes, the heavy alkanes are still being adsorbed faster than the lighter compounds. It is hypothesised that any greater oven time than 960 minutes would result in an increase of abundant peaks that do not normally interfere with analysis, but the increased oven time allows their adsorption to partly obscure target compound peaks. This is commonly referred to as 'hash and trash' and was introduced in section 1.8.1. The obscurification on a chromatogram results in loss of peak resolution due to the overlap of peaks and makes identification more difficult for the analyst. TICs of all adsorption times 90 minutes through 960 minutes are included in Appendix 9 to Appendix 13.

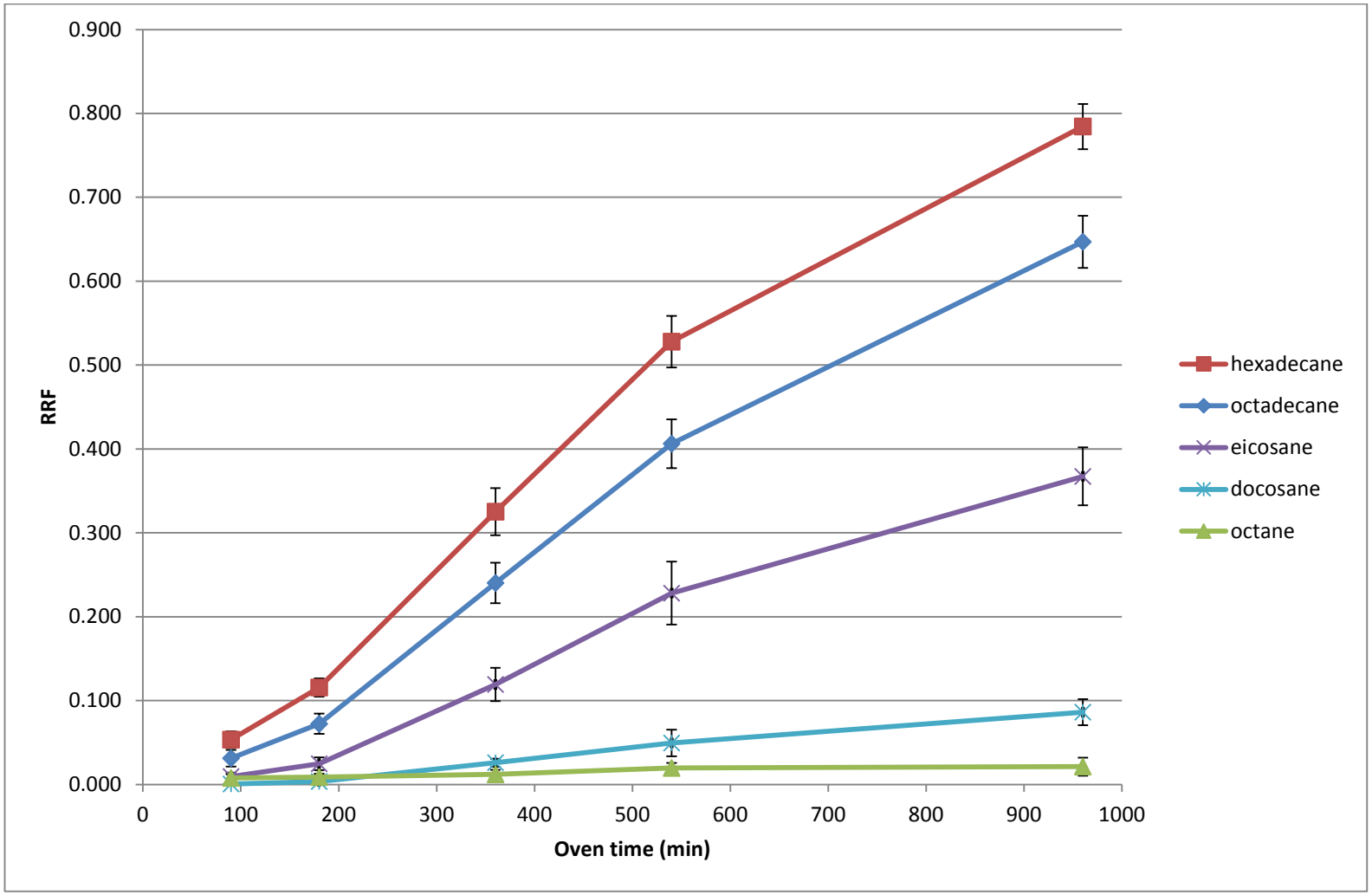

Figure 3.2 Adsorption of octane, hexadecane, octadecane, eicosane and docosane over a period of 960 minutes (n = 5)

Figure 3.3 shows the adsorption C_2-alkylbenzene target compounds include time periods as described for alkanes. Ethylbenzene and *o*-xylene appear similar with respect to the initial adsorption rate and participate in multi-level adsorption from 360 minutes but starts to plateau at 540 minutes. The initial increase could be due to multilayer adsorption and starts to reach the rate limit after 540 minutes and is likely to be involved in competitive adsorption with heavier molecules from this time onwards. It was described earlier in sections 1.6.3 & 3.1 that Tenax TA® has a preference for non-polar compounds such as alkanes and these molecules preferentially bond with Tenax TA® and this preference forces more polar compounds such as alkylbenzenes away from the multi-layer. The process of adsorption and desorption is a dynamic process (Freundlich, 1906, pp. 385-470) in that compounds may adsorb and desorb normally until the adsorption sites are filled but this alters slightly when multi-layer adsorption is taking place. It is hypothesised that in the multi-layer phase, molecules are still adsorbing while others desorb and it is then that preferential adsorption will decide which molecules adsorb and which do not. The standard deviation error bars at 540 minutes and 960 minutes for this compound show variation in results, and this reflects upon the wide variation of results discussed in section 3.7.2 for this compound and other C_2-alkylbenzene target compounds and this is believed to be due to position of Tenax TA® in the oven and competitive adsorption.

The compounds *m*-xylene and *p*-xylene also followed a similar adsorption rate to the other alkylbenzenes but at 360 minutes multi-layer adsorption is increased. This is likely to be due to the high volume of this compound in petrol compared to the other compounds. It is one of the most abundant compounds seen on a chromatogram (Newman & Lothridge, 1998) and therefore as this compound is desorbed by competitive adsorption, the compound volume compensates for the loss and so a greater abundance is still adsorbed.

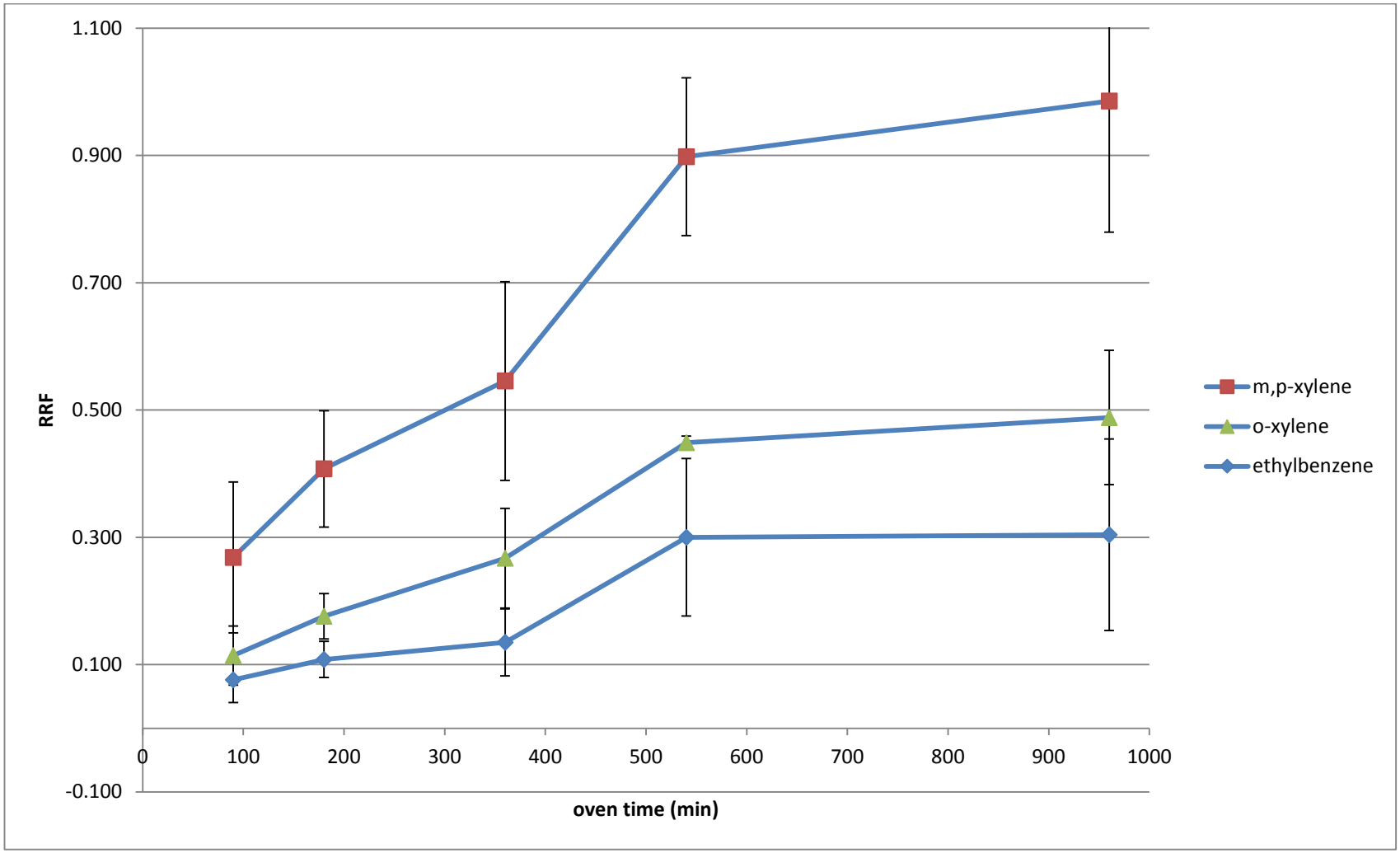

Figure 3.3Adsorption of C_2-alylbenzene compounds over a period of 960 minutes (n = 5)

3.8 Laboratory Blind Experiment Results and Discussion

A series of blind tests were conducted to ensure that the analytical method could be used to identify common ignitable liquids in a repeatable and robust fashion. The results were qualitative because all fire debris samples were created by a third party and so were all different to one another and therefore $n = 1$ for all tests. Five samples were carried out and three ignitable liquids were identified from the five tests, one test correctly identified as not containing an ignitable liquid. The identification of the ignitable liquid in the remaining test was not possible owing to the detector overloading (Table 3.3).

Olfactory analysis of blind test samples was used to determine the strength of smell of a possible ignitable liquid in fire debris (section 3.4). However, some pyrolysis products also smell of an ignitable liquid (DeHaan, 2007, p. 311). Therefore, the important thing at this stage was to set the oven time according to how strong the smell was. The strongest smelling fire debris (samples 1, 4 and 5; Table 3.3) was only allowed to be heated for six hours (section 3.7.3). All the other debris samples were placed in the oven for an adsorption time of nine hours.

Table 3.3 Results of blind samples analysed and ASTM E1618-11 target compound groups identified on ATD-GC-MS

ID number	**Result (*n* = 1)**	**Identity of ignitable liquid (if any) on fire debris[1]**	**Screening Stage - Smell of ignitable liquid?**	**Oven time chosen (hours)**	**alkane and cycloalkane range identified (ion 57, 83)**	**alkylbenzene range identified (ions 91, 105, 119)**	**indane range identified (ions 117, 131)**	**naphthalene range identified (ions 142, 156, 170)**
1	No ignitable liquid identified due to alkylbenzene compound overloading. Partial identification only	Petrol/Diesel Mixture (1:1)	Yes (strong)	6 hours	$C_8 – C_{21}$	Column overload so none identified	C_1 and C_2	C_1 to C_3
2	Target compounds ID show Heavy Petroleum Distillate (HPD)	Diesel	Yes (slight)	9 hours	C_9 - C_{22}	C_2 & C_3	Ion 117 overloaded so no ID for C_1 but ID on C_2 indane	C_1 to C_3
3	No ignitable liquid present	No ignitable liquid	no	9 hours	none	none	C_1 only	none
4	Target compounds ID show Heavy Petroleum Distillate (HPD)	Diesel	Yes (strong)	6 hours	$C_8 – C_{22}$	$C_1 – C_3$	C_1 and C_2	$C_1 – C_3$
5	Target compounds ID show Heavy Petroleum Distillate (HPD)	Petrol/Diesel Mixture (1:1)	Strong unknown smell	6 hours	$C_8 –C_{24}$	$C_1 – C_3$	C_1 and C_2	$C_1 – C_3$

[1] Identity of samples was revealed post examination

3.8.1 ***Blind Sample Results***

Total ion chromatograms (TIC) of blind samples are at Figure 3.4. TICs 1, 2 and, 4 appear similar in their overall peak shape pattern and have many even spaced peaks that resemble *n*-alkanes, signifying a heavy petroleum distillate as described by Stauffer, et al. (2008), p.311, and introduced in section 1.8.1. The diesel biomarkers 'pristane' and 'phytane' along with their accompanying alkanes (heptadecane and octadecane) can clearly be seen on TICs 1, 2, 4 (16.50 minutes to 17.83 minutes; Figure 3.4) indicating the possibility of a diesel type ignitable liquid.

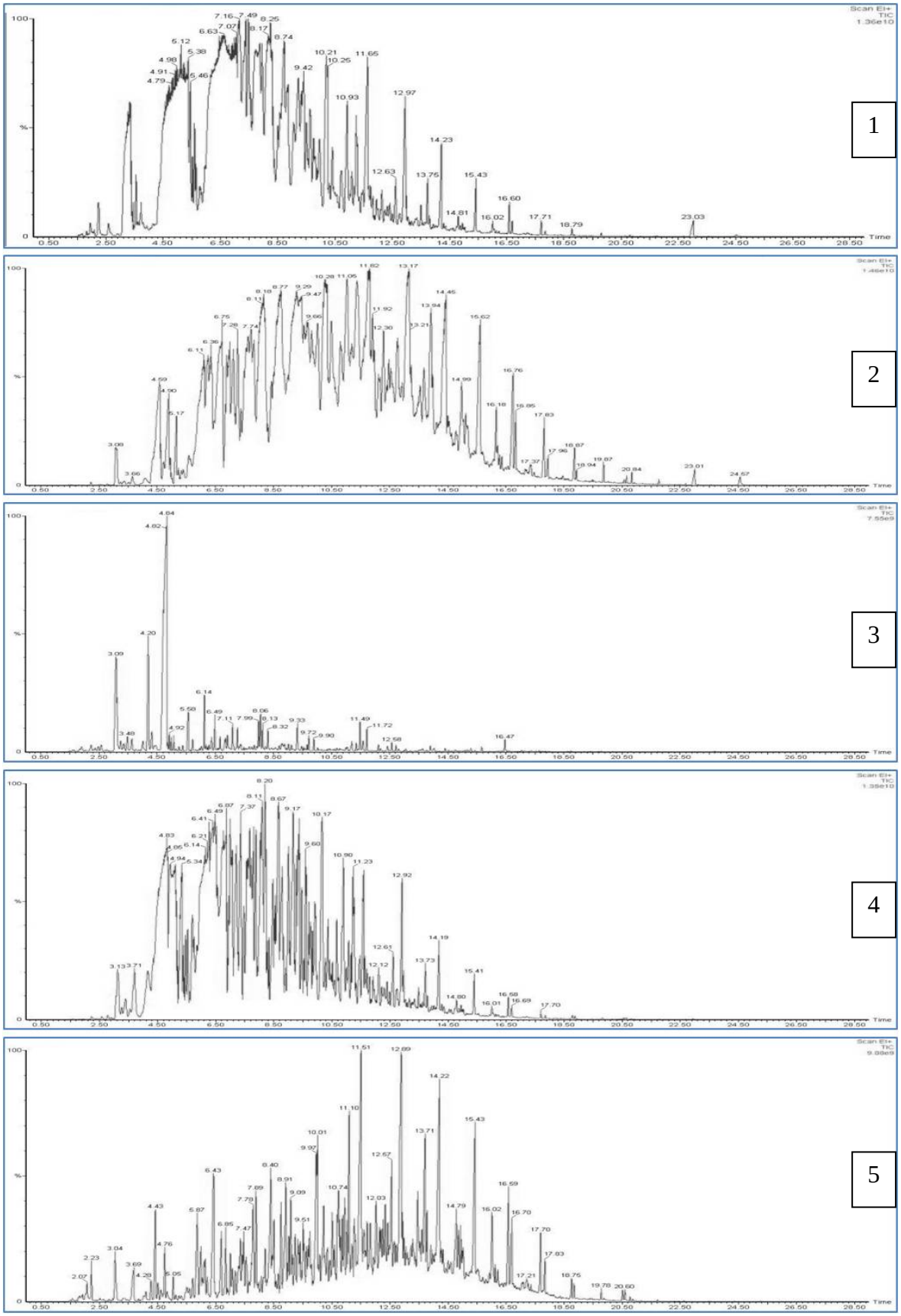

Figure 3.4 TICs of blind test samples numbered 1 through 5 (see Table 3.3)

3.8.2 *Discussion of Laboratory Blind Samples*

Samples 1, 2 and 4 also appear to have overloaded the ATD-GC-MS with ignitable liquid compounds as the peak heights had reached a very high value for the displayed chromatogram (1.46×10^{10}) and resolution appeared much reduced due to peak mergence. The length of time an adsorbent tube spends in the oven is dependent on the olfactory screening stage result. Because there was a lack of a strong smell from either sample 2 (diesel) or sample 3 (no ignitable liquid; Table 3.3) these samples had an adsorption time of nine hours. Despite having no smell, sample 2 overloaded the ATD-GC-MS. The EICs were used to identify for ignitable liquids (Appendix 26 to Appendix 30). Sample 2 overloaded the instrument and affected the identification of indane and methylindanes (ion 117, Appendix 27). However, there was no problem with sample 3 as there was no ignitable liquid identified in this sample. Many peaks were present on the chromatogram (Figure 3.4) but these were not identified as target compounds for ignitable liquids (Appendix 28). The fire debris for this sample consisted of pieces of charred wood and it is likely that these compounds are precursory and combustion products (see section 1.4 for an explanation of these terms).

The decreased time of six hours was set for sample 1 (petrol/diesel mixture), sample 4 (diesel) and sample 5 (petrol/diesel mixture) (Table 3.3; Appendix 29; Appendix 30) because there was either a strong smell of an ignitable liquid or a strong unknown smell. Despite the reduced adsorption time, sample 1 could not be identified because of instrument overloading due to a high volume of alkylbenzenes in the fire debris (Figure 3.5; Appendix 26). However, apart from those compounds, all other target compounds were identified and so overall it was partially identified due to the use of EICs, but not totally identified as an ignitable liquid due to the masking of alkylbenzene target compounds. The same type of problem occurred for sample 2 but to a lesser extent. In this case the C_1-indanes (5-methylindane and 4-methylindane) were not identified but the C_2-indane (4,7-dimethylindane) was able to be identified. This sample was identified as HPD because enough target compounds were present for positive identification (Appendix 27).

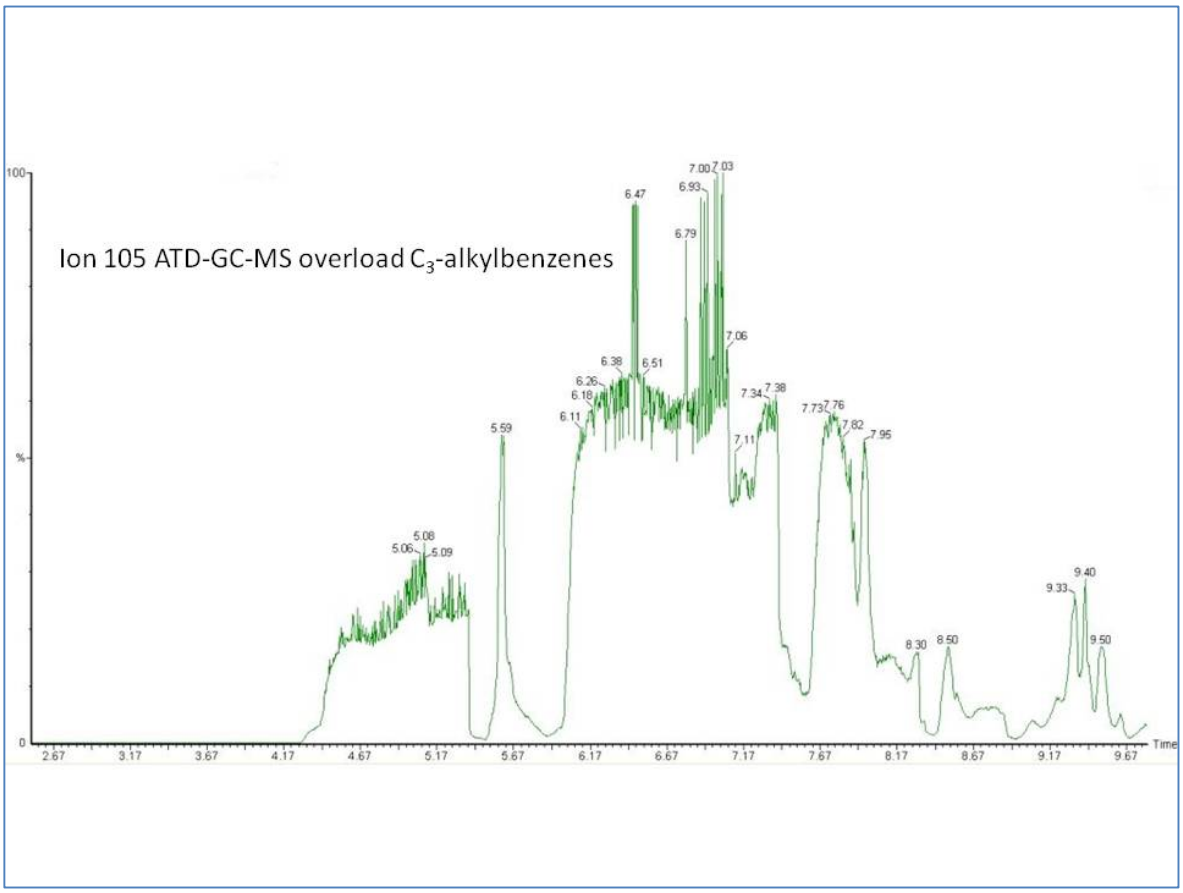

Figure 3.5 GC-MS detector saturation during blind testing at 6 hours oven time (Blind Sample 1)

The original idea of setting up the adsorbent tube inside the paint can was to expose both ends of the Tenax TA® tube so that passive diffusion could occur at both ends. However, it is possible that exposing the end closest to the trap could have overloaded the trap and then the instrument. Therefore, it is recommended that if the preliminary screening identifies a strong smell or is indicated by headspace sampling that only one end of the adsorbent tube be exposed in the headspace (the end furthest from the trap when loaded). This can be achieved by placing the tube in a vertical position inside a 50 mL beaker.

Although samples 4 and 5 were able to be identified as HPD, some of the compounds were more difficult to identify as jagged peak tops were evident for alkylbenzenes and alkanes nonane to tetradecane. It is possible that six hours is sufficient time for oven adsorption at 90 ^{o}C and this was adopted for the field test in Chapter 6. It is also recommended to use two blanks between each sample to eliminate carry-over from the instrument cold trap and column as one condition may leave unwanted compounds in the adsorbent tube and this was also implemented in Chapter 6.

Real fire debris is likely to contain a range of compounds from ethanol to tetracosane and only have only trace amounts of ignitable liquids and also fuel soaked items could have large volume of ignitable liquids. The ATD-GC-MS method must be able to cope with both of these types of samples. The instrument must be setup so that sensitivity is not affected and ignitable liquid is detected if present. Conversely, the setup should not allow the saturation of the column, trap and detector with high volumes of ignitable liquid as this can reduce efficiency and instrument life. Therefore a balanced approach is needed when considering the instrument parameters such as the split flow valve. After the blind evaluation it was decided to change the original split valve settings from 10 mL/min (section 3.6.3) to 20 mL/min for both inlet and outlet flows while the carrier gas flow through the ATD remained the same at 50 mL/min. The reduction in the amount of flow reaching the trap also reduced the load that reached the cold trap, so that contamination was kept to a minimum.

3.9 Conclusion

The purpose of the study was to find an optimal fan oven time period for Tenax TA® adsorption (separation) and to cope with real fire debris samples. In laboratory sample tests, all ASTM E1618-11 target compounds of a petrol/diesel (1:1 v/v) were identified at 90 ^{0}C, and optimal oven times were identified as six hours for fire debris that smelled of ignitable liquids and nine hours for weak or no smells on the fire debris.

A two sample, two-tailed t-Test (section 3.7.2) using t-CRIT values, showed that heavy alkane compounds were not affected so much by the 'hot-spots' and 'cold-spots' in a fan oven, but lighter compounds and especially aromatic compounds such as *m,p*-xylene and ethylbenzene were affected by the position within the oven. The hotter parts of the oven are likely to cause competitive adsorption at 540 minutes (nine hours) onwards.

The blind tests consisted of real fire debris and only three out of four ignitable liquids were identified while one sample had no ignitable liquid at all. The fire debris sample that was not positively identified as containing ignitable liquid contained a number of unidentified compounds but mainly obscured the identification of alkylbenzenes and therefore target compounds and so only a partial identification was made.

There is risk of losing evidence due to de-sensitising the instrument in the case of an excess ignitable liquid present in fire debris. If olfactory analysis indicates that a reduced oven time should be used, then that oven time should be able to allow the adsorption of all target compounds of common ignitable liquids while the analytical instrument has sufficient sensitivity to detect those target compounds. In this part of the research oven times of six hours and maximum time of nine hours were established as adsorption within these times yielded the best results for identification of ignitable liquid target compounds and also as a result of instrument overloading, ATD inlet and outlet split flow valve parameters were changed (from 10 mL to 20mL) to reduce the volume of compounds entering GC-MS from the ATD but without compromising sensitivity. Further samples were tested at these settings and this is discussed in section 4.7.4.5.

3.10 Recommendations for the methods

The oven time should be dependent on how strong the smell of a possible ignitable liquid is in the fire debris. The separation of ignitable liquids and their residues from fire debris can be achieved by setting the oven temperature to 90 ^{0}C at 3 hours for moderate for strong smelling samples and 90 ^{0}C at 6 hours for weaker smelling samples and should definitely be shorter than the current adopted time of 16 hours.

The efficiency of Tenax TA® to adsorb volatile compounds during passive headspace extraction did highlight a sensitivity of the instrument in that adsorption/desorption efficiency can lead to the GC-MS detector to become saturated with ignitable liquid compounds and then identification of target compounds becomes a challenge for the analyst. The instrument parameters in individual fire debris laboratories are normally set in quality management policy and so are rarely changed as changing settings costs money (Haworth, 2011). Changing the parameters will mean further evaluation and validation is then necessary. It is of paramount importance that the instrument settings are chosen to remove excess sample through the use of the inlet and outlet split valves. Once, these are set, the analyst can prevent instrument overload by adjusting the adsorption oven time and exposing one end of the adsorbent tube by placing the tube in a Pyrex beaker one end up.

These methods have not been published before. The improvements made in this part of the study will contribute to standard method for the casework investigation of possible ignitable liquid residues in fire debris or adsorbent samples from fire scenes.

Although at this stage the laboratory tests yielded promising results in terms of identifying ignitable liquid target compounds, the methods were not considered robust enough and further validation of this method was conducted with more laboratory tests samples (Chapter 4) and there was also a field test from adsorbed samples obtained at a real fire scene (Chapter 6).

Chapter Four

The Creation of a Limestone and Fuller's Earth Mixture Capable of the Adsorption of Common Ignitable Liquids

4 Introduction

In section 2.5, it was shown by results and discussion that single adsorbents used by U.K. fire investigators did not allow for the identification of common ignitable liquids. In section 1.3 it was discussed that adsorbents including limestone; plain flour; a sweeping compound; Ignitable Liquid Adsorbent (ILA) (section 4.1) and cat litter have been used worldwide in trying to ascertain whether ignitable liquids have been used to promote deliberate fires. Some of these adsorbents were also tested in section 2.4. These adsorbents could not provide sufficient chromatographic information to form an informed judgement that ignitable liquid was positively identified, or was not present in a sample because the adsorbent was only capable of adsorbing either light to medium petroleum distillates, or it was capable of adsorbing medium to heavy petroleum distillates. No adsorbent tested could adsorb all light, medium and heavy petroleum distillates. In this chapter, it is proposed that a mixture of mineral adsorbents composed of Fuller's Earth and limestone could provide a scene investigator with a universal adsorbent that could help identify common ignitable liquids, and so give the analyst the best information possible to form a valid opinion on whether an ignitable liquid is present in the adsorbent sample or not.

4.1 Ignitable Liquid Absorbent (ILA)

Although this product is discontinued and no longer available, it is worth introducing a commercial product named ignitable liquid adsorbent (ILA). According to ILA's inventor (Woodland, 2003), the ILA mixture consisted of three compounds that deal with different aspects of ignitable liquid identification. The primary material is composed of polypropylene and other cross-linked carbon chain polymers. This absorbent forms 70-80 % of the mass of the mixture. The second compound in the mixture is stearic acid, which acts as a binder for hydrophobic compounds and makes up 10-25 % of the mixture mass.

The final part to the ILA mixture is a solvent indicator dye (Solvent Blue #36) (1,4-bis(isopropylamino)anthraquinone mixed with a titanium dioxide powder. The titanium oxide accounts for 9-14 % of the mass of the ILA mixture and the dye accounts for 0.03–1.00 % of the mixture mass (Woodland, 2003).

The key feature of this mixture was the ability to reject water as the primary component (polypropylene) is hydrophobic by nature. This is an obvious advantage when using an absorbent at a fire scene, as fire suppression may have taken place before the arrival of an investigator on the scene. It was suggested by Byron, 2004 that ILA could be placed on any surface and would absorb any ignitable liquid. Yet the publication only showed results for gasoline. Therefore in order to substantiate the claim about 'any ignitable liquid' more research is needed.

Another feature of this mixture was the solvent indicator dye. According to Byron (2004), when the dye comes into contact with an ignitable liquid it turns from a white colour to a blue colour and can help a jury understand how a fire was started. However, it was stated that the dye can also turn to blue if in contact with pyrolysis products. This admission completely nullifies the previous claim that the action of turning blue indicates to a jury that an ignitable liquid was used. As an example, pyrolysis products can originate from plastics, furniture and other synthetic materials, which are abundant in homes and other buildings. Contact with pyrolysis products, such as benzene, methylbenzene and phenylethene could form 'Solvent Blue' (Kirk & Othmer, 2008, pp. 111-183) and so induce a false positive that could lead to an incorrect assumption being made by the investigator.

The polymer based ILA product was reviewed by Mann & Putaansuu (2006). In their article they compared ILA to a number of other sorbents (section 1.3). The measurement of this comparison was in terms of what constituted the best representation of the original sample. They concluded that ILA did not adsorb the ignitable liquid and the chromatogram background was complicated although no explanation was given for this. The structure of polymers in this commercial ILA can be altered by heat causing random chain degradation and scission (Chapiro, 1964).

Nowlan, et al., 2007 also reviewed the ILA product and directly compared the results to the ability of a Hydrocarbon Detection Dog (HDD). The authors set three room fires and each room contained a different ignitable liquid. The ignitable liquids used on panels situated in the rooms were: an odourless paint thinner, a camp fuel and gasoline. The HDD alerted the

handler on sixteen out of eighteen panels. In comparison, the ILA dye only changed colour on three out of the eighteen panels. ILA did absorb five out of six panels containing paint thinner; four out of six panels containing camp fuel. However all six panels containing gasoline were not indicated by the ILA dye. These results do not conclude that ILA can or cannot absorb all types of ILR and the random scission of the polymer shows that the product is unreliable for use in ignitable liquid analysis.

4.2 The Potential of Minerals as Common Ignitable Liquid Adsorbents

Minerals are regarded as inorganic surfaces if they are largely devoid of carbon atoms, whereas the most popular ignitable liquids have carbon based molecules in abundance. This is a good starting point for an adsorption medium that has a clean chromatographic background. According to Schwarzenbach, et al. (2003), p. 391, only a few studies have taken place involving the exchange of volatile organic compounds (VOC) to inorganic surfaces in air. The majority of research is based on VOC to inorganic surfaces in water. However major studies have been carried out with organic compounds and liquids. Understanding the sorption process between volatile compounds in the gas phase and the surface of a sorbent in solid phase is important when trying to find a suitable adsorbent for identifying ignitable liquids.

Schwarzenbach, et al. (2003), pp. 393-399, provided some experimental data on the processes and characterisation of mineral surfaces. They used five inorganic mineral surfaces that were tested under variable relative humidity conditions and values were given for surface conditions of the minerals. They found that increasing humidity inhibited the available adsorption sites and that the greater the presence of water on the surface of the mineral, the greater the decrease in the number of available sites. Water has a greater affinity for clay mineral surfaces when competing with most organic molecules (Brindley & Brown, 1980, pp. 199-202); therefore organic volatile compounds can only bind to the surface of the mineral if is not saturated with water. This is important for any adsorbent used in fire investigation, as the scene is often filled with water or foam from fire suppression. So, any adsorbent used must be robust enough to largely preferentially reject water molecules in favour of ignitable common liquid compounds. Potentially, there is a problem when a polar ignitable liquid such as ethanol or other water miscible ignitable liquid are used, as these have more affinity for water and are less likely to be adsorbed by

Tenax TA® as this adsorbent preferentially adsorbs non-polar compounds (section 1.6.3). Therefore this type of ignitable liquid may be difficult to detect as it could be diluted by the water used in fire suppression. To combat this, all of the adsorbents selected undergo partial dehydration in an oven overnight to reduce the volume of adsorbed atmospheric water to maximise surface adsorption sites.

It has long been known that clay and associated clay minerals have the ability to adsorb VOCs onto mineral surfaces and absorb water into the clay volume to aid clay swelling (Inglethorpe, et al., 1993). A study carried out by Rhue, et al. (1988) used water, toluene, *p*-xylene and ethylbenzene with bentonite and kaolin. Both of the clays are from different phyllosilicate family groups and have differing charges per formula unit (Table 4.1). In the study, bentonite (smectite) adsorbed more water than alkylbenzene compounds, whilst kaolin adsorbed equal volumes of water and alkylbenzenes. This shows that bentonite (a type 2:1 layer smectite) has a higher affinity for water than kaolin (type 1:1 layer serpentine-kaolin phyllosilicate) because of the increased charge on bentonite, which is caused by interlayer ion exchange (see section 2.1.4 for an in-depth explanation). However, kaolin layer sheets are held together by van der Waals' forces (Martin, 2008) and no exchangeable ions dwell in this layer and so the overall charge is neutral and does not prefer to adsorb water. Palygorskite is also included in Table 4.1 as this phyllosilicate was found in Fuller's Earth during characterisation and this is discussed in section 5.5.2. Palygorskite has a 2:1 inverted ribbon structure with variable charge due to exchangeable cations Ca^{2+} or Mg^{2+} between opposing ribbon layers (Brindley & Brown, 1980, pp. 104-106) and this means that for adsorption purposes palygorskite may behave in a similar way to smectites. The fact that bentonite prefers to adsorb water is not ideal to use at fire scenes. It is preferable to use phyllosilicates that do not adsorb water so well and this is introduced in Section 4.3.

Table 4.1 Classification of a few examples of clay materials adapted from Brindley & Brown (1980), p.5

Clay Layer Type	charge per formula unit (x)[1]	Sub-group	Species
1:1	Serpentine-kaolin (x = ~0)	Kaolin	Kaolinite, dickite and nacrite
2:1	Talc-pyrophyllite (x = ~0)	Talc	Talc, willemsite
	Smectite (x = ~0.2 - 0.6)	Saponite	Saponite, hectorite
		Montmorillonite	Na-Montmorillonite (bentonite) Ca-Montmorillonite[2]
2:1 inverted ribbons	Sepiolite-palygorskite (x = variable)	Sepiolites	Sepiolite
		Palygorskites	Palygorskite

[1] x is a reference to a layer charge for each formula unit $O_{10}(OH)_2$ for the clay types specified
[2] Includes Fuller's Earth sub-species

4.3 Smectite Clays

Smectites are phyllosilicate minerals that have been used in several market areas such as foundry work, oil well drilling and pet litter (Moorlock & Highley, 2006; section 2.1.4). One type of smectite named calcium montmorillonite (Fuller's Earth) was a popular mineral that was in demand by various industries but has recently declined due to a lack of demand for it. Production in the United Kingdom peaked in the late 1980's at around two hundred thousand tonnes per annum *(ibid)*. Production ceased in 2005 due to the exhaustion of allocated reserves *(ibid)*. This means that although Fuller's Earth is inexpensive (£7.66 /Kg, Sigma-Aldrich, August 2013), demand for the product and foreign currency exchange rate fluctuation may drive these prices up or down.

Smectites have exchangeable cations (Table 4.1) and it is these cations that determine the different properties and industrial use. In the UK, a smectite dominated by a calcium ion (Ca-smectite) is generally referred to as montmorillonite and a smectite dominated by sodium ions (Na-smectite) is generally referred to as bentonite, although these terms differ outside of the U.K. Ca-montmorillonite is non-swelling, whereas Na-montmorillonite is prone to swelling from hydroxyl (OH) groups (Inglethorpe, et al., 1993). This is particularly true when the clay is introduced to hydroxyl or diol chemicals such as water or ethylene glycol *(ibid)*. Also, Na-montmorillonites are relatively rare compared to discovered deposits of Ca-montmorillonites, but Ca-montmorillonite can be chemically modified to become Na-montmorillonite through ion-exchange *(ibid)*. The blending of Na and Ca-montmorillonite has achieved optimum properties for the moulding sand needed in metal foundries Murray (2000). This is important for this research, as mixtures of clays can be adapted to target particular chemicals such as ignitable liquids by varying the quantities of the mixture components.

The general chemical formula of the smectite group is:

$$(X)_{0.7}\,(Y)_{4\text{-}6}\,(Z)_{8}\,O_{20}\,(OH)_{4}\,nH_2O \qquad \textit{Equation 4.1}$$

Where X are cation exchange capacity (CEC) ions such as sodium and calcium; Y are structural octahedral cations such as iron, magnesium and aluminium and Z are structural tetrahedral cations such as silicon and aluminium. The substitution of Al^{3+} ions for Si^{4+} ions in the tetrahedral layer and Mg^{2+} ions substitution for Al^{3+} ions in the octahedral layer gives rise to the variable charge (x = 0.2 - 0.6; Table 4.1), (Martin, 2008). As an example of charge difference, aluminium has an Allred-Rochow scale value of 1.47 as opposed to magnesium which has a same scale charge of 1.23. This difference is enough to cause a charge difference in the sheet layers. In a 2:1 layer smectite such as montmorillonite, the sheets are composed of tetrahedral-octahedral-tetrahedral (TOT) layers with exchangeable ions (X) and water inhabiting these layers each TOT and is known as the interlayer. It is the CEC of sodium and calcium that maintain charge balance and the overall net charge *(ibid)*. The interlayer space is variable in dimensions and is governed by CEC bonding which determines how the clay swells in water. This concept is introduced in section 4.4. Besides sheet ions and CEC ions, smectites can contain admixtures made-up from minerals such as quartz, feldspar, opal, calcite and other clay types such as kaolinite (Moll, 2001). Each of these minerals could exert an influence on the variable charge (x) and the quantities of the different minerals may vary widely. Therefore batches purchased from different sources may have variable charge differences, but the charge variability should fall within the stated range on Table 4.1.

4.4 Montmorillonite

Montmorillonite is a clay mineral of the smectite family formed from volcanic rock alteration or found in sedimentary rock and is a 2:1 layer phyllosilicate (Bergaya, et al., 2006, p. 4). If the layers are not electrostatically neutral, the cations and anions in the interlayer will neutralise this charge (Brindley & Brown, 1980, pp. 166-175), but overall the layers have a slightly negative layer charge (Newman, 1987). The charge gives rise to attracting molecules or ions that that are slightly or strongly polar such as found in aromatic compounds found in ignitable liquids. The charge can be altered by chemically modifying montmorillonite by ion exchange using strong acids to remove divalent and trivalent cations and applying monovalent cation surfactants (Komadel & Madejova, 2006, pp. 263-274). It is also hypothesised for this research that combining the montmorillonite with limestone (section 2.4.1) will alter the overall mixture charge towards neutral so that

non-polar molecules are adsorbed and this will assist in adsorbing petroleum distillates such as *n*-alkanes that are found in ignitable liquids.

Three montmorillonite clays were used in this research, two of which are from different regions of the U.S.A and have different chemical and physical properties. According to a study by Moll (2001), SWy-2 montmorillonite (also known as Wyoming bentonite) is grey in colour, and rich in sodium. The clay also possesses a high CEC which enables the clay to swell. The swelling ability of na-montmorillonite as it adsorbs water makes this clay useful as a sanitary adsorbent found in cat litter boxes but the affinity for water is not useful for fire scenes.

The second montmorillonite used in this study is STx-1b from Gonzalez County, Texas, U.S.A. It is white in colour and has been used as an oil bleaching agent and ceramic binder owing to its white colour (Moll, 2001). It has only a small percentage of sodium (0.23%) compared to its calcium percentage mass (1.24%) (Mermut & Cano, 2001). This clay does not have the same affinity for water as Na-montmorillonite and it is hypothesised that the clay will adsorb aromatic compounds found in petroleum distillates.

The third montmorillonite used in this study is British Fuller's Earth. The British Geological Survey (2006) describes Fuller's Earth as montmorillonite clay that contains calcium, sodium and magnesium ions in the inter-layer. The smectite clays offer a unique combination of physical and chemical properties that is characterised by the clay found in a particular region and this gives rise to industrial applications such as refining impurities from edible oils and fats *(ibid)* and a decontamination agent in chemical and biological warfare (Seto, 2009). The slight polar nature of Fuller's Earth used to its potential in industry makes it a good candidate adsorbent for this study. The reduced layer charge the calcium ions provide is likely to reject water in favour of slightly polar compounds like petroleum aromatic compounds found in ignitable liquids. The origin of this montmorillonite was unknown but later work in this research was carried out to investigate the composition through spectroscopic characterisation (section 5.5.2).

4.5 Limestone

Limestone is not a clay but is a commonly found mineral (Ni & Ratner, 2008). This adsorbent was tested and discussed in section 2.4.1 as Garden Lime (limestone). As a

summary, in those tests limestone preferentially adsorbed non-polar medium to heavy petroleum target compounds from undecane to eicosane. It is believed that this sorbate can adsorb compounds beyond eicosane when used with Tenax TA® adsorbent tubes on ATD-GC-MS, as Tenax TA® is a superior adsorbent of heavy alkane compounds compared to activated carbon strips ACS (sections 1.6.3, 2.5 and 3.7.3). The adsorption range of limestone is significant in fire investigation as it enables the ability to identify the heaviest ignitable liquid target compounds and this can lead to differentiation between a heavy petroleum distillate and a medium petroleum distillate (section 1.4.2).

4.5.1 *What Qualities Should an Adsorbent Possess?*

There are likely to be more candidates for an adsorbent material to assist in the analysis and identity of an ignitable liquid. However, this study focuses on those materials that this research had investigated and that had shown an ability to adsorb ILR. But what constitutes a potential adsorbent material for this task? The end product should be:

4.5.1.1 Selective and Specific

Be able to adsorb chemical compounds of a range of ignitable liquids at the scene and desorb those compounds under normal laboratory sampling conditions. This includes polar compounds such as alcohols; aldehydes and ketones, slightly polar compounds such as aromatic and polyaromatic compounds; alkanes and olefins. The guidance and instructions with regard to the identification of ignitable liquids is in ASTM E1618-11 (2011). The selective range on a gas chromatograph is from ethanol (light mass alcohol) to the heavy *n*-alkane heneicosane (n-C_{21}) using the same chromatographic column.

4.5.1.2 Reliable

The adsorbent material itself should be free from contamination and not present a complicated background matrix that interferes with the detection of target compounds used for identification. Polymers such as ILA (section 4.1) are not considered reliable due to the scission of polymer chains during the separation stage caused by the increased radiation of the oven. However the negative control of cat litter (Na-montmorillonite) used in the study (section 2.4.3; Appendix 1) showed no evidence of matrix interference during analysis

resulting in clean chromatography. An adsorbent must survive and/or not react with fire suppression agents found at fire scenes or dissolve in water.

4.5.1.3 Practical and Easy to Use

The adsorbent material should not complicate the collection of actual evidence at the scene and certainly not interfere with potential evidence. If there is a risk of contamination from the adsorbent material, it would not be viable to use as evidence in a court of law, as contamination can result in the disregard of evidence. This can be mitigated to some extent by using EIC but there is always a possibility that the material has the *m/z* ion or fragmentation ions as ignitable liquids. Also, some laboratories still use GC-FID but this technique cannot distinguish target molecules as well as GC-MS which uses extracted ion chromatograms to cut through the clutter of compounds to view only selected target compounds, but the use of GC-FID for fire debris analysis is being phased out now as ASTM E1387-01 (2001) which is the correct standard method for that technique has now been discontinued.

The use of any such material as an alternative collection method should not require significant training for end users. The product should be easy to deploy and collect and not impact on any protocols used by the analysis laboratory. A material that can be used on multiple surface types and not just concrete surfaces will have better commercial potential. In section 2.5 it was recommended that minerals be ground to provide a larger surface area for adsorption by providing more adsorption sites. This was implemented in this part of the study.

4.5.1.4 Affordable

New methods employed by laboratories cost money to implement. So ideally, the laboratory analysis of the new material should be treated as fire debris and use existing protocols such as ASTM E1386-10 (2010) or ASTM E1388-12 (2012). The substitution of a powder for fire debris does not alter the approach to analysis. If possible, the price should not add significantly to the decision about submitting samples for analysis. Therefore, any new adsorbent material used should ideally be of low cost and the training costs required for the use of a new material by scene investigators should be kept to a minimum.

4.5.2 *What Adsorbents should be Included in This Study?*

From the criteria discussed in section 4.5.1, any new material to be considered as an adsorbent to identify ignitable liquid from residues would have to conform to this list as close as possible. In Chapter 2, the investigation into current adsorbents used by fire investigators showed that low cost materials are being used for this purpose. It was found that some adsorbents such as TENA Lady® could complicate analysis due to matrix interference as it has carbon based compounds due to cellulosic and plastic components in the material (section 2.4.7 and Appendix 7). The use of EICs could be used to mitigate this problem but if the matrix contains compounds that are also found in ignitable liquids or if the method of analysis did not use EIC to reduce this problem it is clearly not viable to use that product/material. Adsorbents such as clay cat litter (section 2.4.3) and limestone (section 2.4.1) had less matrix interference (Appendix 1, Appendix 2), and if used correctly, they present minimal contamination to other evidence types as they are easy to use and recover.

The conclusion from section 2.5 suggested the use of cat litter and garden lime as adsorbents. However, it was not known whether the cat litter was pure bentonite (section 2.1.4) or if unknown substrates were in the composition. A further concern was that bentonite (sodium montmorillonite) can adsorb more water when compared to calcium montmorillonite (section 4.4) due to its high CEC (Moll, 2001), which is not preferable at fire scenes due to water being present after fire suppression is complete. Therefore, the use of cat litter was discarded and the focus shifted to calcium montmorillonite, and this decision is reinforced later by calculations involving loss of adsorbent mass by dehydration (section 4.7.1).

Two standard montmorillonites were purchased that had been the subject of baseline studies. One being calcium montmorillonite and the other being sodium montmorillonite. These standard clays were viewed as too expensive (£2.54/g each) to be used in the field but they had been the subject of baseline studies (section 5.1.1) and therefore it was advantageous to see if the Fourier Transform Infrared (FT-IR) and X-Ray diffraction results in this study (section 5.5) bore any resemblance to those studies by Chipera & Bish (2001); Mermut & Lagaly (2001) and Madeova & Komadel (2001). Another calcium montmorillonite (Fuller's Earth) (section 4.4) was also purchased as less expensive option

(£0.01/g) but still representative of what was needed for the study. It was hoped that like the cat litter, Fuller's Earth had a preference for adsorbing compounds of a slightly polar nature from ethylbenzene to hexadecane. Limestone was purchased (£0.001/g) to replicate the results from garden lime in section 2.4.1. Limestone had the task of adsorbing target compounds that were non-polar in nature up to and beyond heneicosane. It was hypothesised that the net charge of the two types of materials could be altered to accommodate common ignitable liquid adsorption by adjusting the ratio of each ingredient in the mixture. Although limestone mainly consists of calcium carbonate, a commercial bag of Garden Lime may not just contain calcium carbonate but possibly other minerals and clays also. With this in mind it was decided to investigate the composition of Garden Lime with spectroscopy methods and this is discussed in Chapter 5.

Consideration was given to using bleaching clays (Bergaya, et al., 2006, pp. 263-281), a technique that forces cation exchange through the use of a strong acid to replace interlayer multi-valent cations with hydrogen ions. The result of this is to reduce the electronic charge of smectite clays (*ibid*, p.263) and broaden the interlayer space allowing longer chain molecules to be adsorbed (Williams-Daryn & Thomas, 2002). This technique was rejected in favour of a simpler method of mixing materials together the materials which could achieve the same goal.

In this part of the study it was planned to test adsorbents in three phases. Phase one was the analysis of individual adsorbents. Phase two was the analysis of mixtures of adsorbents and the final phase was the evaluation by the use of a blind trial (sections 3.6.5 & 4.5.4). The final choices made for testing were: British Fuller's Earth; Wyoming Na-montmorillonite (SWy-2) (standard reference clay); Texas Ca-montmorillonite (STx-1b) (standard reference clay) and limestone. The results from these individual performances of these adsorbents would determine which ones were selected for mixtures. The selection of the final mixture was determined by which mixture matched the criteria (section 4.5.1) most closely.

4.5.3 *Determination of a Representative Common Ignitable Liquid*

The adsorption of a range of alkylbenzene, paraffinic and naphthenic compounds (section 1.4.3) by the selected mixture of montmorillonite and $CaCO_3$ was essential as a potential adsorbent of ignitable liquids. A petrol/diesel mixture (1:1 v/v) was chosen as a good

representative ignitable liquid as the compound identification criteria (ASTM E1618-11, 2011) demands that compounds from early eluting C_2-alkylbenzenes to late eluting heneicosane be identified. Of course there are other ignitable liquids that fall outside this range. Alcohols such as ethanol and propan-1-ol are light early eluting compounds and in Chapter 6 this ignitable liquid type was used in a field evaluation with the selected adsorbent.

4.5.4 *Adsorbent Blind Experiment*

A successful adsorbent mixture would be a mixture that fulfilled the criteria from section 4.5.1. An additional factor in this phase of the study was to validate any mixture selected for meeting those criteria. The validation procedure was designed so that the analyst did not know the identity of the ignitable liquid used in the validation test and the identity of the ignitable liquid was only revealed after analysis had been complete. Two separate blind experiments were arranged for this task. The first experiment was set in a laboratory environment (Section 4.7.4) with a third party choice of whether an ignitable liquid or no ignitable liquid was used and the type of ignitable liquid used. The second experiment was conducted in a field environment and is discussed in Chapter 6.

4.6 Materials and methods

4.6.1 *Materials*

Mixture materials were: Fuller's Earth (Fisher UK Ltd); J. Arthur Bowers Garden Lime (limestone) (Thetford Garden Centre, U.K); two montmorillonite clays (SWy-2 and STx-1b, Clays.org, U.S.A). The following ignitable liquids were purchased: Easy Start BBQ lighter fluid (Homebase) and Woolworth's White Spirit (Woolworth); diesel fuel, petrol fuel (UL95) (BP Express, U.K). Other materials included: Concrete paving slabs 50 cm x 50 cm (Homebase, U.K); 2.5 L paint cans with lids (Birmingham Tin Box Company, U.K); standard copier paper (Staples, U.K); disposable paint brushes (Homebase); Pipetman pipettes (various sizes) (Gilsen) with tips; Heraeus UT6 oven; grinding apparatus (Retsch

GmbH) PM100 with 80 mL ZrO_2 jar, and 5 x 20 mm ZrO_2 balls. Pyrex 50.0 mL beakers; factory pre-packed stainless steel Tenax® TA tubes (Markes International Inc). A home-made air sampler was constructed in the laboratory, consisting of a 100.0 mL glass syringe (Samco Scientific), and 5cm of PTFE tubing (Samco Scientific). A test mixture of compounds: *n*-octane; *n*-decane; *n*-dodecane; *n*-tetradecane; *n*-hexadecane; octadecane were purchased from Fisher Scientific UK. Test standards of eicosane, 3-methyl-ethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, butylcyclohexane, *trans*-decalin, 1-ethylnaphthalene and 1,3-dimethylnaphthalene were also purchased from Fisher Scientific UK, each component was prepared as 0.005 % v/v in *n*-pentane.

4.6.2 *Methods*

4.6.2.1 Preparation of adsorbents

All adsorbents were subjected to grinding with a Retsch PM100: six minutes at 500 rpm in an 80 mL jar with five zirconium oxide balls (each at 20 mm) to reduce the number of larger grain sizes. Each adsorbent was then subjected to overnight conditioning as described in section 3.6.3 to reduce as much water as possible on the adsorbent. Table 4.2 shows the mean loss of mass after dehydration has occurred for all adsorbents. The oven temperature was set to 90 ^{0}C to remove water and yet not make the adsorbent brittle (Emmett, 2012). The adsorbent mixtures were created by weighing individual components and then adding them together in a clean plastic bottle before shaking the bottle for five minutes.

4.6.2.2 Deployment and Collection of adsorbent

A mixture of petrol/diesel (1:1 v/v; 5.0 mL) was poured onto paving slab and left to stand for two hours. After this time period the pre-conditioned adsorbent material was sprinkled onto the ILR (Table 4.2). After leaving the adsorbent to stand for twenty minutes, a sheet of standard copier paper and fresh paint brush was used to recover the adsorbent into a paint can.

4.6.2.3 Passive Headspace Separation Method

This method is the same as the method used in section 3.6.2. The Tenax TA® stainless steel tube was numbered and placed inside the paint can balanced between two Pyrex beakers as previously described in section 3.4.2. The can lid was sealed with its lid before placing into the oven. The adsorption time used was 540 minutes and the temperature was 90 ^{0}C following improvements carried out in this research (section 3.9).

4.6.2.4 ATD-GC-MS Methods

The methods used for this part of the study for ATD-GC-MS are identical to the methods employed in sections 3.6.3 and 2.2.4, with the exception that the split flow valve parameters for both inlet and outlet were set to 20 mL/min following improvements made to the ATD as discussed in section 3.8.

4.6.2.5 Instructions for the Third Party in the Blind Experiment

This method was the same as described in section 3.6.5. In addition, five paving slabs were setup in five different fume cupboards and were numbered according. A third party was instructed to either pour 5.0 mL of ignitable liquid of their choice onto each slab or to not use an ignitable liquid. The discovery of an actual ignitable liquid used or not was revealed after the analysis had been completed.

4.7 Results and Discussion

This is discussed in two parts. The first section deals with individual adsorbent and subsequent mixtures (Table 4.2; Table 4.4) and what constitutes the best adsorbent for the identification of petrol and diesel compounds. The second section discusses the results obtained from the blind experiment for the best adsorbent found in the first section.

4.7.1 *Loss of Adsorbent Mass from Dehydration*

Each adsorbent was subjected to grinding in the Retsch grinder. Before grinding there was a slight grain size difference of limestone (100 - 150 µm) to the montmorillonites (10 – 100 µm). The grinding program ensured that the grain size and texture of each mineral was similar so that the minerals mixed well together.

Table 4.2 shows the mass of each adsorbent and mixture of adsorbents after dehydration in an oven overnight at 90 ^{0}C. The montmorillonite SWy-2 had the greatest loss of mass at 1.60 % with STx-1b losing 1.51 % of its total mass. This confirms the fact that sodium montmorillonite has a greater capacity for water retention than calcium montmorillonite (Hawkins, et al., 1986) and is the basis for rejecting the use of cat litter for use at fire scenes.

The least loss of mass was limestone at 0.02 %, showing that limestone does not have an affinity for water (section 2.4.1). Although Fuller's Earth is classed as a Ca-montmorillonite is only lost 0.55 % of its total mass after dehydration. This is attributed to the fact that it is not a pure montmorillonite but a collection of clays and minerals including limestone and palygorskite (section 5.5.2). This is significant as the tested batch of Fuller's Earth is not susceptible to the condensation of water on its surfaces as the other montmorillonites and therefore there will be more adsorption sites available for adsorption of target molecules at fire scenes.

Table 4.2 Individual and mixture adsorbents, composition, mean mass and ratio used

Adsorbent Component Composition (*n* = 5)	**Mean mass[3] (g)**	**Net mass loss[4] (%)**	**Ratio (w/w)**
Fuller's Earth	49.96 ± 0.83	0.55 ± 0.09	Not applicable
SWy-2 Montmorillonite	53.06 ± 1.21	1.60 ± 0.68	Not applicable
STx-1b Montmorillonite	52.65 ± 1.13	1.51 ± 0.04	Not applicable
Limestone	55.96 ± 1.70	0.02 ± 0.01	Not applicable
Limestone, Fuller's Earth, SWy-2 Montmorillonite	53.29 ± 1.12	0.53 ± 0.02	2: 1: 1
Limestone, STx-1b Montmorillonite	56.93 ± 1.17	0.34 ± 0.16	10: 3
Limestone, Fullers' Earth	54.05 ± 1.10	0.08 ± 0.03	9: 1

[3] Mean mass after dehydration step with standard deviation
[4] Percentage net mass loss after dehydration with standard deviation

4.7.2 *Individual adsorbent analysis*

Three clay based adsorbents (Fuller's Earth, Montmorillonite SWy-2 and Montmorillonite STx-1b) and the mineral limestone were tested with a petrol/diesel mixture (1:1 v/v), in the procedure described in Section 4.6. An internal standard (IS) was used to calculate a relative response factor (RRF) (section 3.3) as shown in Table 4.3. This was used to normalise the peak height data for better accuracy and precision of results using five data sets for each sorbate.

The adsorbents were assessed by using the table of results and identification of target molecules from ASTM E1618-11 (2011) and the ability to adsorb compounds beyond these parameters due to other types of ignitable liquids that have not been considered by ASTM. Adsorbents were considered against the selection criteria in section 4.5.1.

Table 4.3 Single adsorbent with Relative Response Factor and standard deviation (n = 5)

Target Compound	**RT[5] (mins)**	***m/z*[6]**	**RRF Fuller's Earth[7]**	**RRF SWy-2**	**RRF STx-1b**	**RRF Limestone**
ethylbenzene	4.27	91	16.20 ± 3.55	22.22 ± 13.24	66.29 ± 21.76	0.11 ± 0.17
m,p-xylene	4.42	91	88.29 ± 23.36	98.33 ± 54.97	280.21 ± 70.98	0.40 ± 0.69
o-xylene	4.75	91	40.89 ± 12.43	38.64 ± 20.05	161.66 ± 44.22	0.17 ± 0.26
n-nonane	5.04	57	4.21 ± 1.69	2.04 ± 1.32	8.60 ± 1.53	Not Identified
propylbenzene	5.70	91	18.29 ± 7.85	20.78 ± 8.22	34.40 ± 9.09	0.04 ± 0.05
3-ethyltoluene	5.85	105	106.08 ± 46.36	126.27 ± 38.53	219.12 ± 42.36	0.17 ± 0.15
1,3,5-trimethylbenzene	5.98	105	42.70 ± 19.18	37.70 ± 14.24	110.99 ± 21.58	0.09 ± 0.09
2-ethyltoluene	6.12	105	26.12 ± 11.16	26.70 ± 6.23	68.88 ± 15.49	0.06 ± 0.06
1,2,4-trimethylbenzene	6.40	105	140.96 ± 72.05	156.70 ± 36.07	309.70 ± 61.70	0.45 ± 0.39
n-decane	6.67	57	28.54 ± 12.66	10.32 ± 1.57	25.17 ± 12.54	0.08 ± 0.08
indane	6.98	119	9.71 ± 4.32	10.95 ± 1.23	15.85 ± 4.65	0.04 ± 0.03
n-butylcyclohexane	7.16	83	4.27 ± 2.02	1.62 ± 0.39	2.94 ± 0.58	Not Identified
trans-decalin	7.52	138	1.50 ± 0.65	0.57 ± 0.24	1.45 ± 0.44	Not Identified
n-undecane	8.34	57	76.91 ± 60.88	16.81 ± 7.60	54.71 ± 37.33	0.82 ± 0.72
1,2,3,5-tetramethylbenzene	8.39	119	14.33 ± 12.08	11.48 ± 4.93	28.31 ± 16.35	0.30 ± 0.20
1,2,4,5-tetramethylbenzene	8.45	119	22.80 ± 18.79	20.20 ± 7.42	35.08 ± 22.89	0.50 ± 0.35
5-methylindane	8.70	117	12.94 ± 10.26	9.11 ± 3.93	15.01 ± 6.65	0.23 ± 0.17
4-methylindane	8.86	117	19.54 ± 15.88	11.63 ± 4.51	25.88 ± 10.83	0.39 ± 0.28
n-pentylcyclohexane	8.85	83	10.02 ± 6.82	2.06 ± 0.97	5.83 ± 3.79	Not Identified
n-dodecane	9.93	57	118.68 ± 119.05	14.76 ± 8.16	65.25 ± 56.15	5.41 ± 4.11
n-hexylcyclohexane	10.49	83	14.68 ± 12.21	1.75 ± 0.94	5.73 ± 4.23	0.52 ± 0.43
4,7-dimethylindane	10.66	131	13.09 ± 14.93	8.23 ± 4.01	17.82 ± 11.48	2.26 ± 1.50
2-methylnaphthalene	11.02	142	9.83 ± 10.54	4.91 ± 2.49	10.08 ± 7.05	3.22 ± 1.86
1-methylnaphthalene	11.23	142	5.22 ± 5.41	2.47 ± 1.24	6.42 ± 3.98	1.94 ± 1.16
n-tridecane	11.40	57	120.12 ± 135.58	9.03 ± 6.03	51.01 ± 47.02	23.17 ± 18.28
n-heptylcyclohexane	11.95	83	17.58 ± 18.27	1.17 ± 0.74	5.37 ± 4.83	2.56 ± 2.11
1,3-dimethylnaphthalene	12.58	156	2.04 ± 2.39	0.77 ± 0.52	2.40 ± 2.05	3.33 ± 2.38
n-tetradecane	12.73	57	91.94 ± 112.52	4.20 ± 2.95	32.24 ± 32.01	56.79 ± 51.27
2,3-dimethylnaphthalene	12.80	156	2.74 ± 3.62	0.51 ± 0.30	1.96 ± 1.77	3.86 ± 3.36
n-octylcyclohexane	13.36	83	10.79 ± 11.92	0.47 ± 0.30	3.13 ± 3.34	6.19 ± 5.71
n-pentadecane	14.07	57	48.81 ± 61.93	1.62 ± 1.06	17.31 ± 19.06	87.78 ± 80.86
2,3,5-trimethylnaphthalene	14.23	170	0.41 ± 0.44	0.16 ± 0.10	0.66 ± 0.61	2.25 ± 1.85
n-nonylcyclohexane	14.71	83	5.11 ± 5.84	0.20 ± 0.12	1.63 ± 1.82	7.45 ± 5.96
n-hexadecane	15.32	57	15.54 ± 18.59	Not Identified	6.91 ± 7.99	94.83 ± 94.83
n-heptadecane	16.52	57	7.11 ± 9.10	Not Identified	Not Identified	62.89 ± 63.82
pristane	16.63	57	Not Identified	Not Identified	Not Identified	20.01 ± 18.92
n-octadecane	17.65	57	Not Identified	Not Identified	Not Identified	28.76 ± 29.73
phytane	17.80	57	Not Identified	Not Identified	Not Identified	7.44 ± 7.37
n-nonadecane	18.73	57	Not Identified	Not Identified	Not Identified	12.47 ± 13.57
n-eicosane	19.77	57	Not Identified	Not Identified	Not Identified	4.39 ± 4.93
n-heneicosane	20.77	57	Not Identified	Not Identified	Not Identified	1.51 ± 1.78
n-docosane	21.72	57	Not Identified	Not Identified	Not Identified	0.044 ± 0.52
n-tricosane	22.64	57	Not Identified	Not Identified	Not identified	0.015 ± 0.13

[5] Mean retention time. Standard deviation error was from 1.0% to 4.0%
[6] Ion used to identify compound
[7] RRF and standard deviation multiplied by 10^2

4.7.2.1 Limestone

Limestone was able to adsorb the ignitable liquid residue from dodecane to heneicosane (Table 4.3 & Figure 4.1). Compounds that were not adsorbed are as follows: nonane (*n*-C_9); butylcyclohexane; trans-decalin and pentylcyclohexane. All alkylbenzene, alkylindane and alkylnaphthalene target compounds were adsorbed. The last alkane in the series to be identified was tricosane (*n*-C_{23}). From previous testing (section 2.4.1) it was known that limestone could adsorb heavy petroleum distillates but not adsorb light-medium petroleum distillate target compounds very well (section 2.1.5). It is possible that medium and heavy alkanes are preferred for adsorption by limestone and therefore the lighter compounds are not readily adsorbed or they may be out-competed for adsorption sites by the larger molecules (section 1.5.2.5). Table 4.3 also shows high standard deviation values for the RRF of most compounds. For example the RRF of dodecane = 0.058 ± 0.041. The most abundant compound adsorbed was hexadecane (RRF = 1.067 ± 0.948) and docosane (*n*-C_{22}) was RRF = 0.005 ± 0.005. This topic is discussed in section 4.7.2.4.

Limestone showed that it can repeatedly adsorb medium to heavy ignitable liquid compounds and was therefore used in the next stage of testing (section 4.7.3).

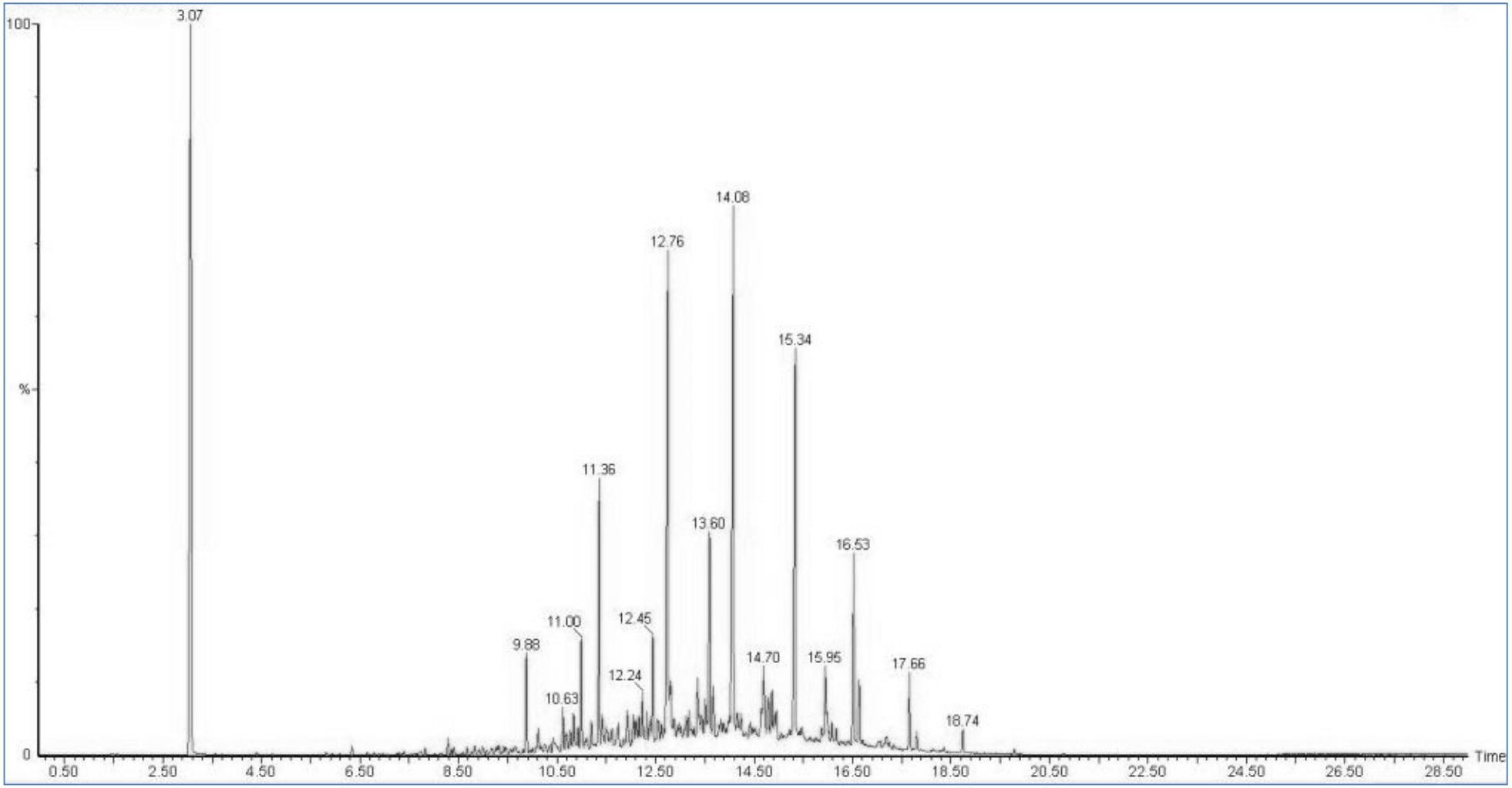

Figure 4.1 TIC of limestone adsorption of a 1:1 v/v petrol/diesel mixture

4.7.2.2 SWy-2 Montmorillonite

This sodium rich smectite (van Olphen & Fripat, 1979, p. 346) was able to adsorb all alkylbenzene target compounds and all indane and naphthalene target compounds and *n*-cyclohexanes (Table 4.3; Figure 4.2). The montmorillonite was only able to adsorb *n*-alkanes from nonane (n-C_9) to pentadecane (n-C_{15}) and trans-decalin. All compounds eluting after this (14.23 minutes) (Table 4.3) were not identified. This is believed to be the limit of adsorption of for this sorbate. This montmorillonite is considered a good adsorbent of light to medium ignitable liquid compounds and could make a good adsorbent to mix with limestone owing to the preferential adsorption of aromatic compounds. This montmorillonite is a standard reference clay and so is expensive in comparison to Fuller's Earth, so it does not quite meet the criteria requirements in section 4.5.1. Despite this drawback, it is believed that lower cost Na-montmorillonites are available on the market. Another drawback is the Na-montmorillonite preference for the adsorption of water as previously indicated in section 4.4. Despite these flaws and the ability to adsorb ignitable liquid compounds, it was decided to mix this clay with limestone for further testing (section 4.7.3.1).

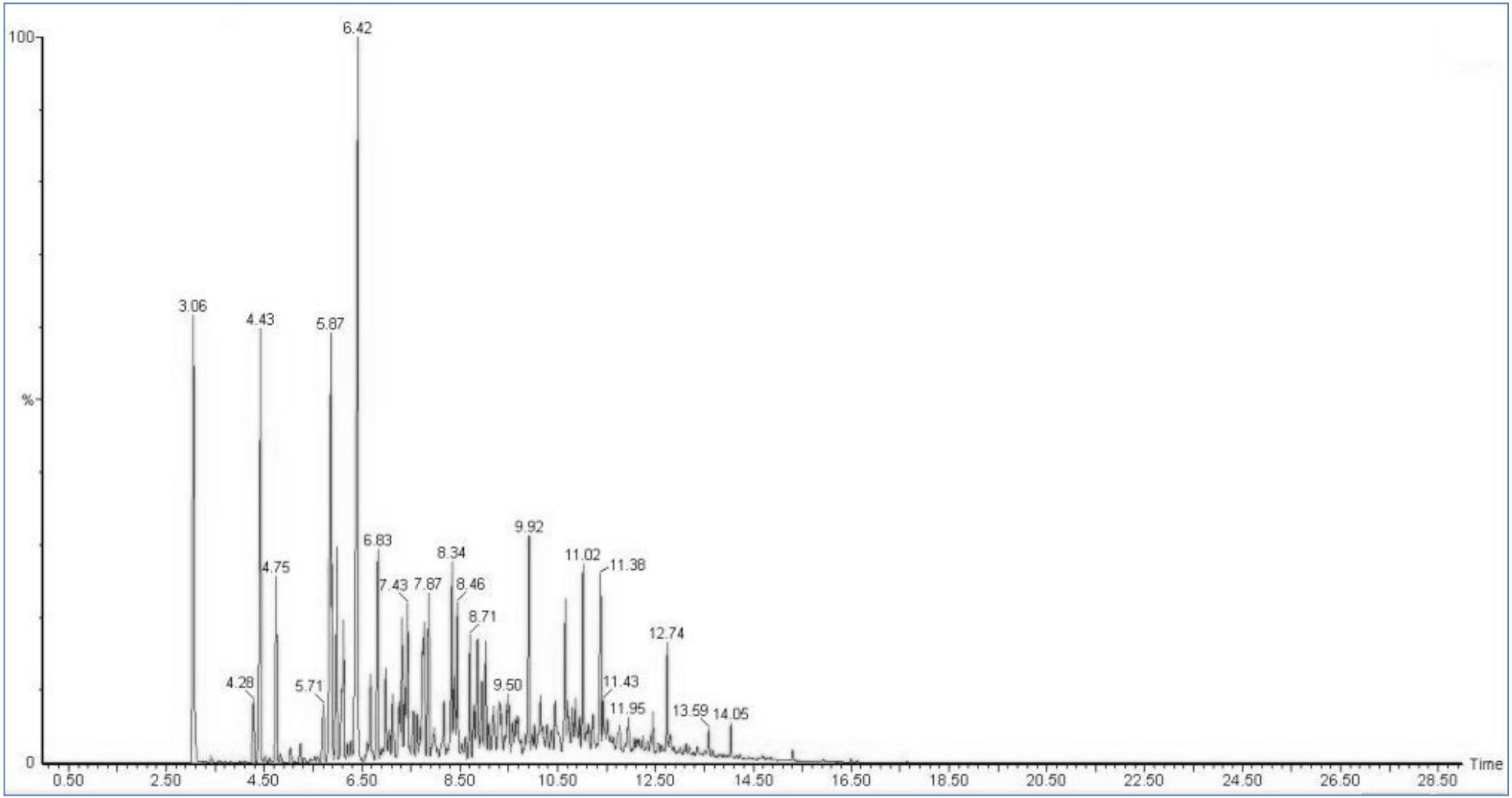

Figure 4.2 TIC of sodium montmorillonite (SWy-2) adsorption of a 1:1 v/v petrol/diesel mixture

4.7.2.3 STx-1b Montmorillonite

The calcium montmorillonite STx-1b, adsorbed the same compounds as the sodium montmorillonite SWy-2, but the adsorption RRF for STx-1b was greater in every case (Table 4.3). Target compounds heavier than hexadecane (*n*-C_{16}) (Figure 4.3) were not identified and it was believed to be the limit of adsorption for this sorbate. At 6.67 minutes and greater (Table 4.3) it was no longer the most efficient adsorbent for decane, but was superseded by Fuller's Earth (section 4.7.2.4). The *n*-alkanes from heptadecane (*n*-C_{17}) to tricosane (*n*-C_{23}) were absent from the chromatogram and was due to these compounds not being adsorbed. The calcium ions in the interlayer exert a greater electronic charge that keeps the 2:1 layer sheets close together and does not allow the adsorption of larger molecules as they cannot fit into the smaller interlayer space (Brindley & Brown, 1980, pp. 169-170). This would explain the non-adsorption of heavy compounds in ignitable liquids. Nevertheless, this montmorillonite showed that it could adsorb ignitable liquid compounds and so it was decided to mix this montmorillonite with limestone for the next stage of testing (section 4.7.2.3).

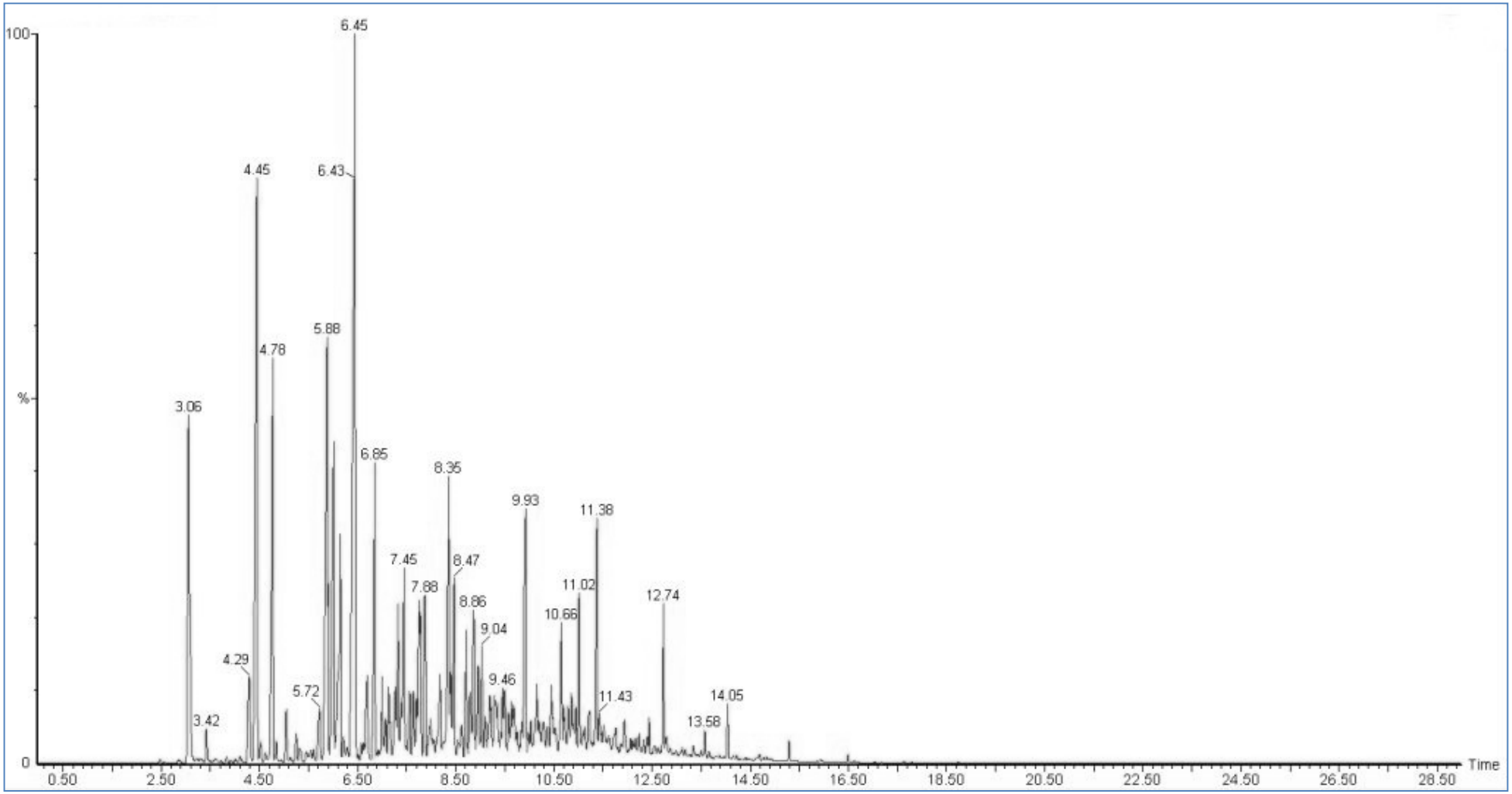

Figure 4.3 TIC of calcium montmorillonite (STx-1b) adsorption of a 1:1 v/v petrol/diesel mixture

4.7.2.4 Fuller's Earth

All target compounds identified from the other two montmorillonites (section 4.7.2.2 & 4.7.2.3) were also identified when Fuller's Earth was used. In addition, hexadecane (*n*-C_{17}) was also identified (Table 4.3; Figure 4.4). Standard deviation of RRF values for other minerals tested showed a high variance (section 4.7.2.1). For Fuller's Earth, RRF standard deviation values from dodecane to hexadecane and C_2-naphthalene compounds were numerically greater than the mean values of these target compounds. This variance showed that for later eluting compounds there is a wide variability of adsorption. Figure 4.5 shows five stacked EICs (ion 57) of Fuller's Earth adsorption of pentadecane (14.0 – 14.1 minutes); hexadecane (15.3 minutes) and heptadecane (16.5 minutes). Each Fuller's Earth sample was in the same oven order as discussed in section 3.7.2 (labelled Cans A to E).

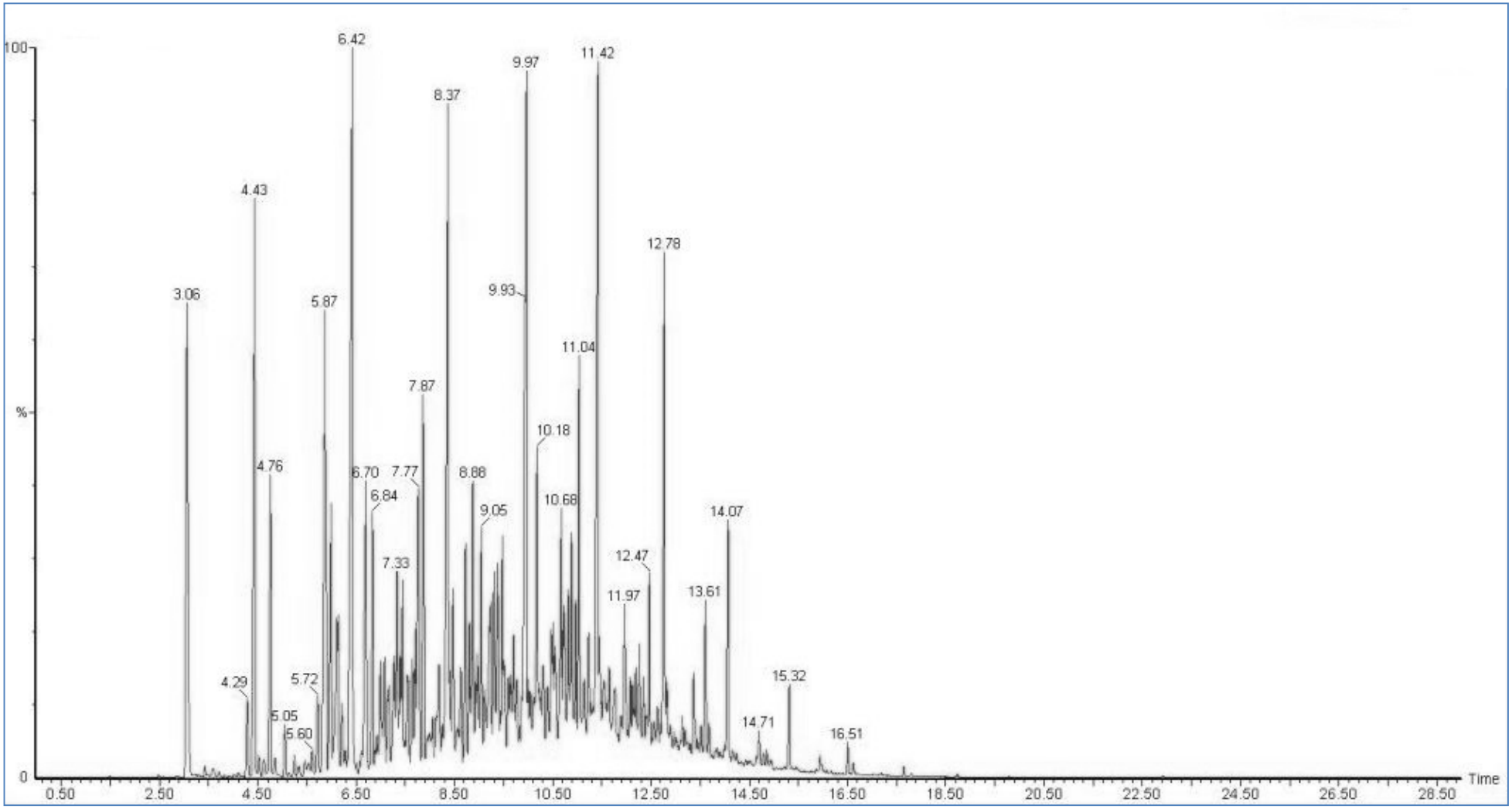

Figure 4.4 TIC of Fuller's Earth adsorption of a 1:1 v/v petrol/diesel mixture (n = 5)

Fuller's Earth does adsorb C_2-alkylbenzenes but not as well as the other two montmorillonites. From the retention time of decane onwards (6.67 minutes) until heptadecane (16.52 minutes; Table 4.3), this clay is a superior adsorbent compared to the other montmorillonites because of the increase in peak signal for all compounds in that time range. The lower adsorption of light compounds and increased adsorption of heavier compounds up until heptadecane shows that Fuller's Earth does not carry such a high negative charge as the other montmorillonites and there is slightly less polar in nature and preferentially adsorbs medium petroleum distillate compounds. This was a key factor in deciding to use this as a mixture adsorbent in the next stage (sections 4.7.3.1; 4.7.3.2 & 4.7.3.3). At this stage there was concern over the decreased adsorption of lighter petroleum fraction compounds, so it was decided to mix Fuller's Earth with Swy-2 to increase aromatic and other light petroleum distillate compound adsorption.

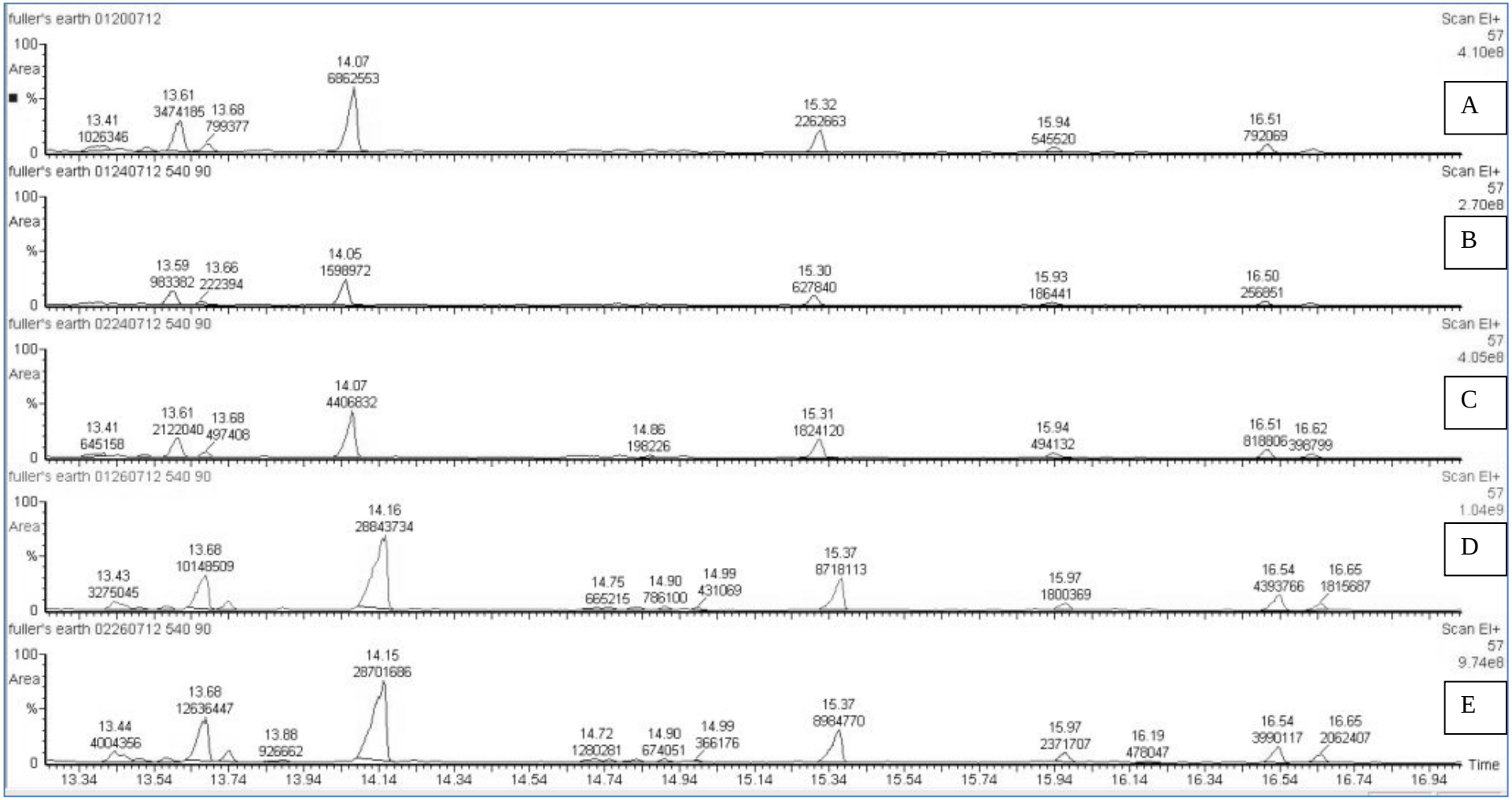

Figure 4.5 EIC (ion 57) adsorption of pentadecane, hexadecane and heptadecane from a petrol/diesel 1:1 v/v mixture by Fuller's Earth in five different cans A-E

4.7.3 *Mixtures of Montmorillonite with Limestone*

The results from Table 4.3 led to further investigation into using mixtures of the different montmorillonites with limestone. Initially a combination of limestone was mixed with Fuller's Earth and Na-montmorillonite SWy-2, because both of those montmorillonites showed improved adsorption in light to medium petrol/diesel target compounds. A mixture of limestone (50 %) to Fuller's Earth (25 %) to SWy-2 montmorillonite (25 %) (2:1:1 (w/w)) was used for the first mixture tested (Table 4.4) as this equated to limestone/smectite ratio of 1:1. It was thought that adjustments could be made to the ratio after an assessment of results and this proved to be the case. Changes were made to mixture ratios to increase the range of target compound adsorption and this is further discussed in sections 4.7.3.1 to 4.7.3.3.

Table 4.4 Mixed adsorbents Relative Response Factor with standard deviation (n = 5)

Target Compound	RT[1] (mins)	*m/z*[2] used	RRF Limestone: SWy-2:FE[3]	RRF Limestone: STx-1b	RRF Limestone: FE
ethylbenzene	4.27	91	7.36 ± 5.27[4]	17.47 ± 7.24	1.37 ± 0.45
m,p-xylene	4.42	91	38.80 ± 28.58	78.81 ± 31.17	6.97 ± 2.16
o-xylene	4.75	91	20.46 ± 15.02	47.03 ± 18.49	4.92 ± 1.52
n-C_9	5.04	57	1.28 ± 0.66	2.30 ± 0.88	0.34 ± 0.11
propylbenzene	5.70	91	13.16 ± 7.58	26.13 ± 9.24	4.72 ± 1.35
3-ethyltoluene	5.85	105	83.08 ± 49.20	154.06 ± 50.19	28.87 ± 8.81
1,3,5-trimethylbenzene	5.98	105	37.91 ± 16.49	73.26 ± 24.53	15.64 ± 4.37
2-ethyltoluene	6.12	105	25.13 ± 13.54	45.41 ± 15.25	8.85 ± 2.50
1,2,4-trimethylbenzene	6.40	105	131.73 ± 69.61	215.48 ± 68.32	56.25 ± 15.27
n-C_{10}	6.67	57	12.19 ± 8.31	14.47 ± 5.12	4.71 ± 1.44
indane	6.98	119	7.84 ± 5.70	14.94 ± 5.37	2.92 ± 0.82
n-butylcyclohexane	7.16	83	1.84 ± 1.46	2.70 ± 0.98	0.78 ± 0.21
trans-decalin	7.52	138	0.66 ± 0.52	0.98 ± 0.40	0.28 ± 0.09
n-C_{11}	8.34	57	42.65 ± 29.28	33.26 ± 14.23	24.36 ± 7.80
1,2,3,5-tetramethylbenzene	8.39	119	18.97 ± 13.29	30.01 ± 14.44	16.82 ± 5.32
1,2,4,5-tetramethylbenzene	8.45	119	28.28 ± 16.98	49.47 ± 21.57	26.58 ± 8.25
5-methylindane	8.70	117	11.76 ± 8.18	16.54 ± 10.38	8.19 ± 2.67
4-methylindane	8.86	117	16.16 ± 10.66	27.04 ± 10.52	12.96 ± 3.98
n-pentylcyclohexane	8.85	83	5.27 ± 3.84	4.91 ± 2.15	3.56 ± 1.10
n-C_{12}	9.93	57	67.07 ± 48.63	34.15 ± 13.34	57.19 ± 22.33
n-hexylcyclohexane	10.49	83	8.18 ± 5.53	5.52 ± 2.20	9.84 ± 3.25
4,7-dimethylindane	10.66	131	16.74 ± 11.11	22.61 ± 8.54	20.01 ± 7.34
2-methylnaphthalene	11.02	142	9.98 ± 6.71	12.31 ± 4.67	11.84 ± 4.52
1-methylnaphthalene	11.23	142	4.73 ± 3.00	7.15 ± 2.56	7.67 ± 2.81
n-C_{13}	11.40	57	59.36 ± 41.44	25.50 ± 8.89	73.41 ± 32.47
n-heptylcyclohexane	11.95	83	8.39 ± 5.73	4.27 ± 1.58	17.81 ± 5.35
1,3-dimethylnaphthalene	12.58	156	2.06 ± 1.37	2.89 ± 1.09	3.43 ± 1.43
n-C_{14}	12.73	57	34.58 ± 24.83	14.51 ± 5.04	53.39 ± 24.84
2,3-dimethylnaphthalene	12.80	156	1.92 ± 1.18	1.88 ± 0.68	3.20 ± 1.57
n-octylcyclohexane	13.36	83	4.71 ± 3.35	2.03 ± 0.71	15.89 ± 5.42
n-C_{15}	14.07	57	16.81 ± 12.69	6.79 ± 2.34	25.92 ± 11.61
2,3,5-trimethylnaphthalene	14.23	170	0.52 ± 0.29	0.75 ± 0.28	0.86 ± 0.38
n-nonylcyclohexane	14.71	83	2.19 ± 1.61	1.08 ± 0.34	9.74 ± 3.43
n-C_{16}	15.32	57	5.36 ± 4.12	2.03 ± 0.60	8.68 ± 3.83
n-C_{17}	16.52	57	1.77 ± 1.34	0.55 ± 0.15	3.07 ± 1.30
pristane	16.63	57	1.24 ± 0.85	0.46 ± 0.13	5.41 ± 1.78
n-C_{18}	17.65	57	0.55 ± 0.44	0.12 ± 0.03	0.89 ± 0.34
phytane	17.80	57	0.37 ± 0.27	0.11 ± 0.03	1.48 ± 0.43
n-C_{19}	18.73	57	0.24 ± 0.16	0.04 ± 0.01	0.37 ± 0.10
n-C_{20}	19.77	57	Not Identified	0.01 ± <0.01	0.09 ± 0.05
n-C_{21}	20.77	57	Not Identified	Not Identified	0.03 ± 0.02
n-C_{22}	21.72	57	Not Identified	Not Identified	0.01 ± 0.01

[1] Retention Time
[2] Ion used to identify compounds
[3] FE = Fuller's Earth
[4] RRF and standard deviation multiplied by 10^2

4.7.3.1 Limestone, Montmorillonite SWy-2 and Fuller's Earth Mixture

Adsorption for early eluting compounds such as the C_2 and C_3-alkylbenzenes for this mixture showed no improvement over any of the three montmorillonite clays when they were tested individually. However, all target compounds in this range were easily identified from EICs. Later eluting peaks from tridecane (*n*-C_{13}) onwards showed greater RRF values than individual tests of SWy-2 and STx-1b but not surpass the RRF values of Fuller's Earth. In all, this mixture adsorbed all target compounds up to nonadecane (*n*-C_{19}) (Table 4.4; Figure 4.6).

The mixture had improved the range of compounds adsorbed when compared to single use (Table 4.4) up to nonadecane but this still was not adequate to fulfil the selectivity criteria (section 4.5.1). The results also showed that the mixture adsorbed aromatic and medium petroleum distillates of petrol/diesel but did not adsorb the heaviest *n*-alkanes such as eicosane and heneicosane. It was thought that the ratio of montmorillonite to limestone was too high and prevented the adsorption of the heavier alkanes. Therefore in later experiments (sections 4.7.3.2 and 4.7.3.3) the mass of montmorillonite was reduced to allow adsorption of heavier compounds.

Literature regarding the mixing of minerals to achieve a specific goal is scarce, as most research in this field focuses on interspace layer mixing of different minerals and clays occurs during natural formation or can be carried out experimentally. Mixing minerals together in solution may force ion exchange from the interlayer by ion substitution (Bergaya, et al., 2006, pp. 263-267). However, all mixtures used in this research were not in solution and therefore chemical mixing was not considered. Surface hydroxyl and oxygen groups from the clay components may play a role in inter-molecular bonding, as observed by (Mortland, 1970). However, this was suggested as weak bonding when compared to inter-layer bonding and therefore may not have much influence on the components of a mixture.

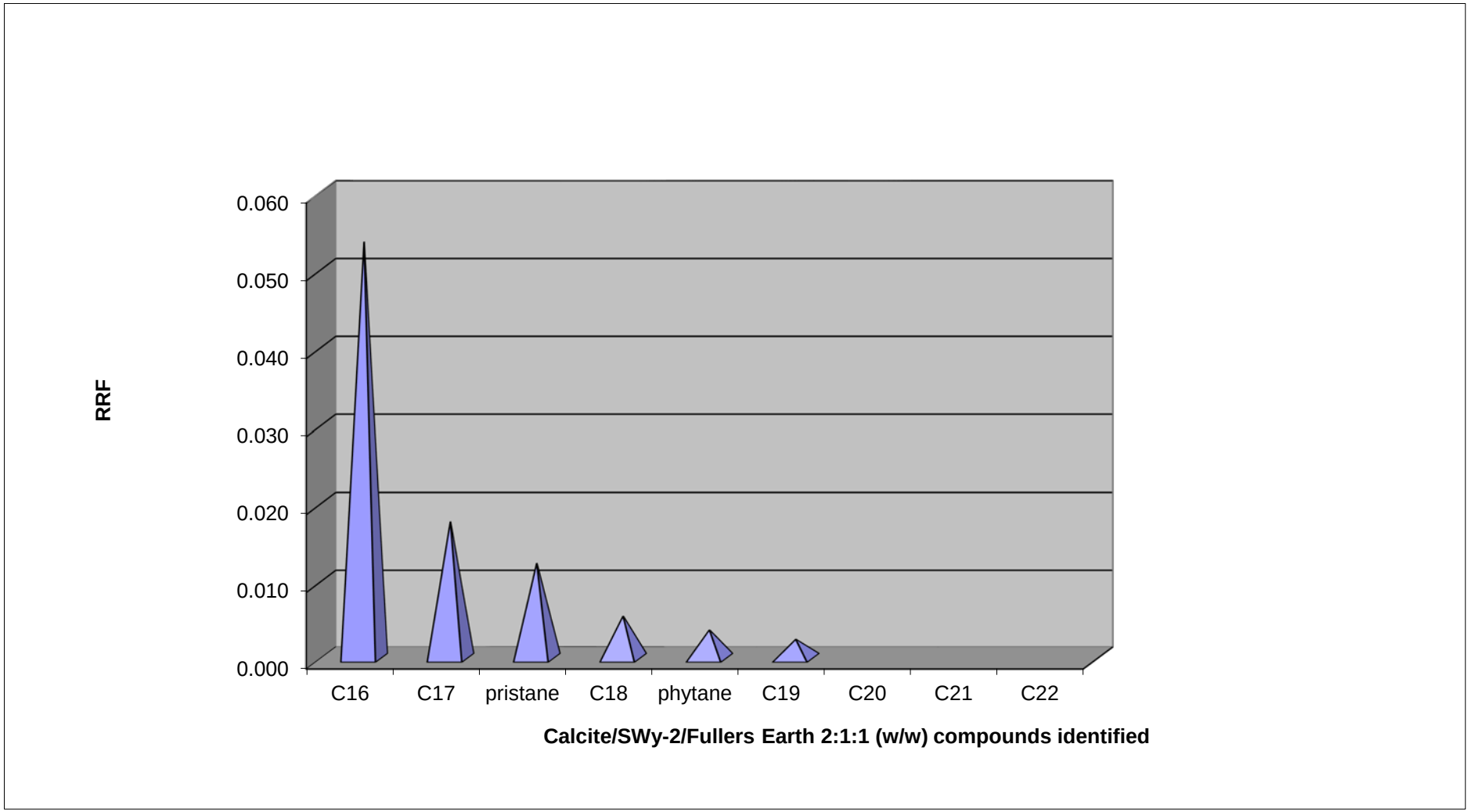

Figure 4.6 Heavy target compounds identified for the mixture that contained limestone, Swy-2 montmorillonite and Fuller's Earth (2:1:1)

4.7.3.2 Limestone and Montmorillonite STx-1b mixture

This mixture comprised of limestone and STx-1b in a ratio of 10:3 (w/w). The reason for reducing the montmorillonite mass was discussed in section 4.7.3.1, because the mass charge of the mixture needed to become more non-polar to adsorb heavy alkanes. This mixture was able to adsorb most petrol/diesel target compounds of alkylbenzenes, indanes, naphthalenes and alkanes from nonane to eicosane. However, heneicosane was not identified (Table 4.4; Figure 4.7 and Figure 4.8) and so did not meet the selectivity criteria (section 4.5.1) but is an improvement over the first mixture (section 4.7.3.1). It was postulated that the electronegative influence of the montmorillonite inhibits the adsorption of heavy alkanes.

It was decided that the next mixture should have an increased ratio of limestone to montmorillonite of 9:1 (w/w) and thus decrease the montmorillonite influence on the mixture. It was hypothesised that the reduction of the net electronegative charge on the mixture by increasing the ratio of limestone to montmorillonite and this would lower the electronegative influence component in the mixture (montmorillonite) would result in the adsorption of heneicosane (section 4.7.3.3).

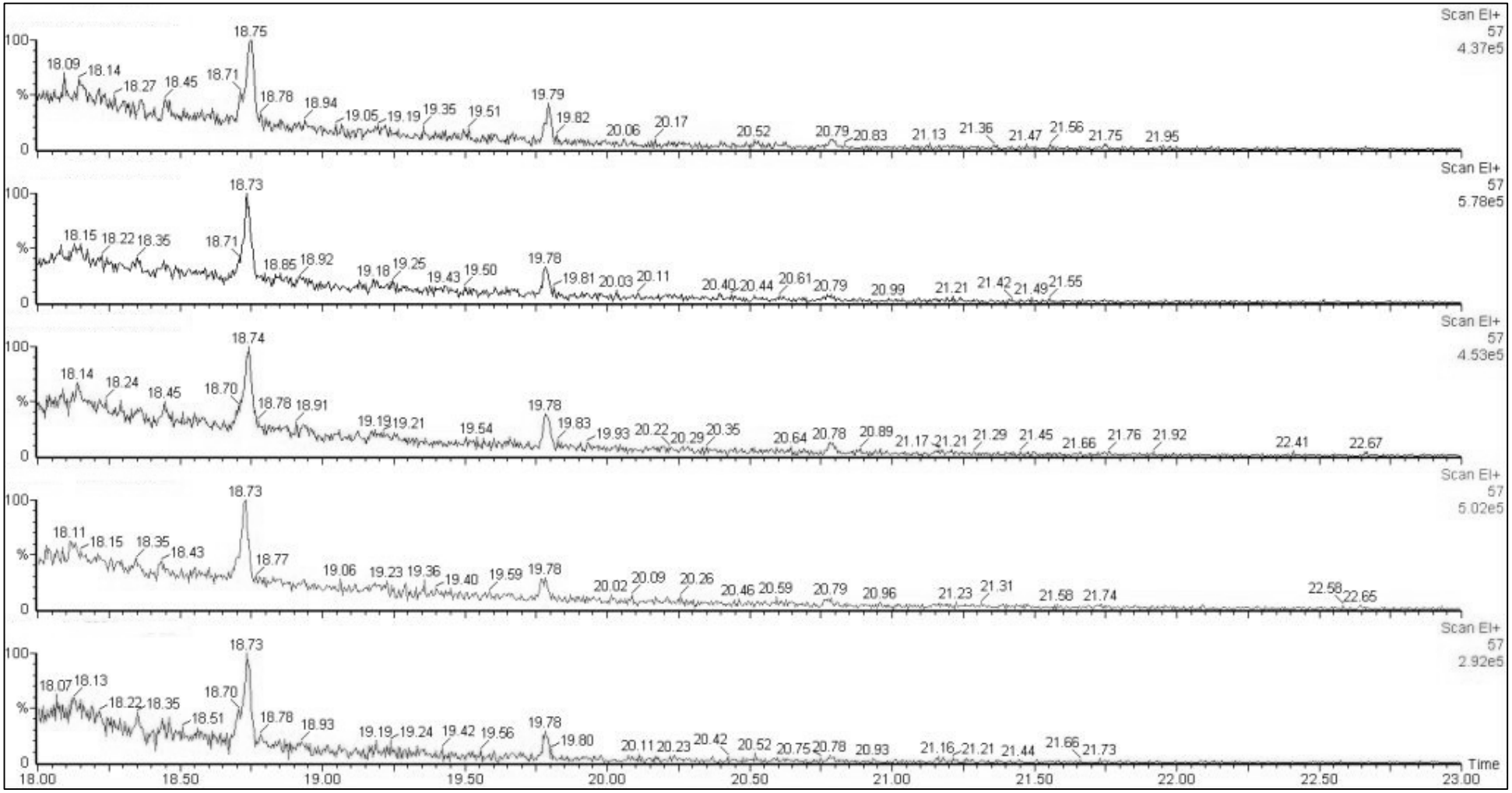

Figure 4.7 Five stacked EICs (ion 57) of limestone/montmorillonite STx-1bs (10:3 w/w) mixture showing the adsorption of nonadecane (18.74 minutes) and eicosane (19.78 minutes)

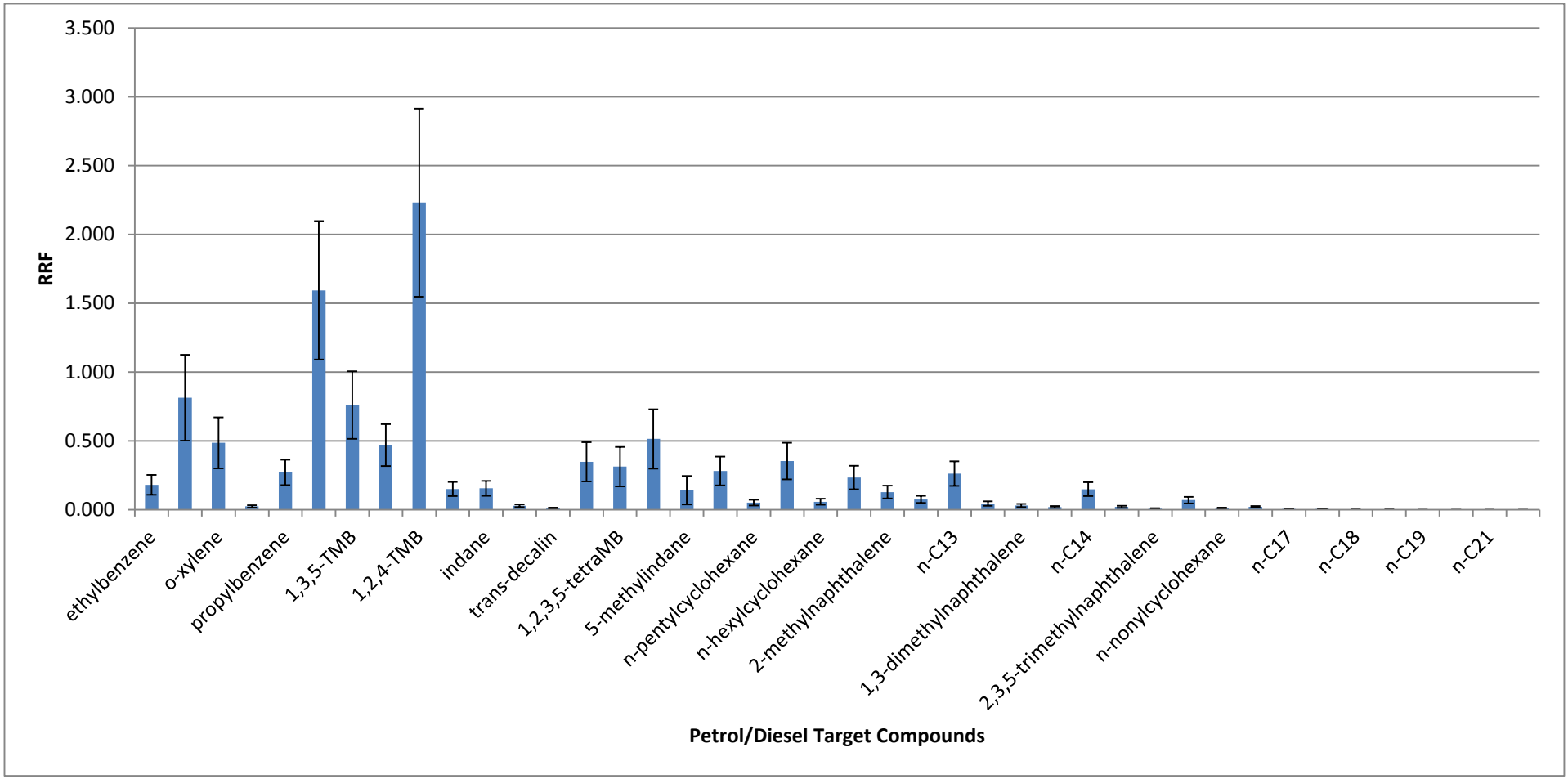

Figure 4.8 Limestone: STx-1b (10:3) mixture adsorption of a 1:1 v/v petrol/diesel mixture (n = 5)

4.7.3.3 Limestone and Fuller's Earth Mixture

The results for limestone/Fuller's Earth mixture are at Table 4.4. A quick appraisal of the TIC, using retention time and peak patterns (section 1.8.1) of alkylbenzenes showed that the mixture had adsorbed the Three Musketeers group and the Castle group (section 1.8.1). Many medium and heavy alkanes were visible in the classic Gaussian pattern. However, when viewing the heavy alkanes Figure 4.11, it was noticeable that the peak height ratio pattern for (heptadecane and pristine) and (octadecane and phytane) did not conform to the biomarker pattern found in Stauffer, et al. (2008), p. 311-312; and discussed in section 1.4.2. A check was made of the positive control petrol/diesel EIC made at the start of this part of the project but this showed heptadecane/pristine and octadecane/phytane in the normal ratios (section 1.8.1). Knowing that pristane and phytane are important biomarkers in diesel fuel and also knowing that they are not prone to degradation (Sherry, et al., 2014), lead to the conclusion that the diesel fuel used for this part of the project was weathered (section 1.8.1). However, this did not have a major impact on the study as when viewing the EICs for compound identity the limestone/Fuller's earth mixture was able to adsorb every target compound required by ASTM E1618-11 (2011).

Analysis of peak areas and subsequent conversion to RRF values (Table 4.4 and Figure 4.10) show that there was an improvement in the adsorption of heavy alkane compounds (n-C_{18} to n-C_{22}) compared to the other mixtures, while the adsorption of C_2-alkylbenzenes and C_3-alkylbenzenes is not as proficient as the other mixtures. In early eluting compounds (Figure 4.9) it can be seen that limestone/Fuller's Earth (FE) is the least proficient at the adsorption of these compounds. This can be explained by the increased non-polar nature of this mixture due to the decreased mass of Fuller's Earth in the mixture.

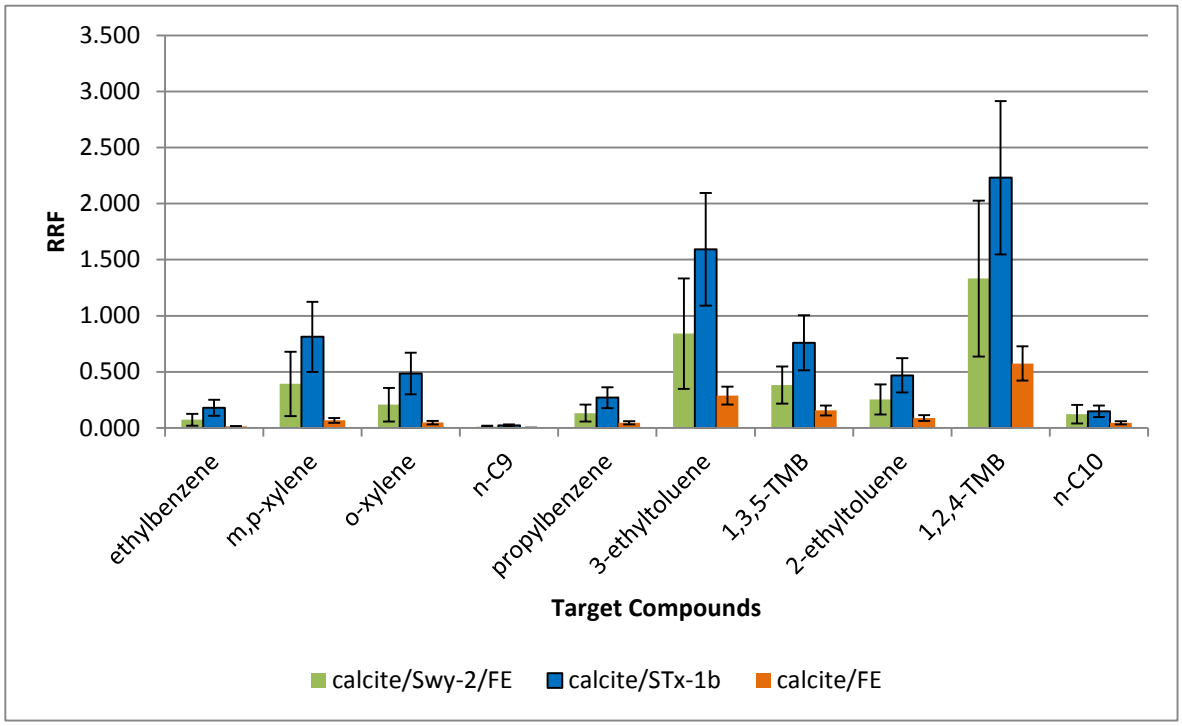

Figure 4.9 Adsorption of early eluting compounds from a petrol/diesel mixture by three different adsorbent mixtures (n = 5)

With regard to compounds at longer retention times, limestone/FE is still adsorbing all compounds but does not become the most proficient sorbate until the elution of tridecane (*n*-C_{13}) (Figure 4.10). From that point onwards limestone /FE is regarded as a superior adsorbent of medium petroleum compounds when compared to the other two mixtures.

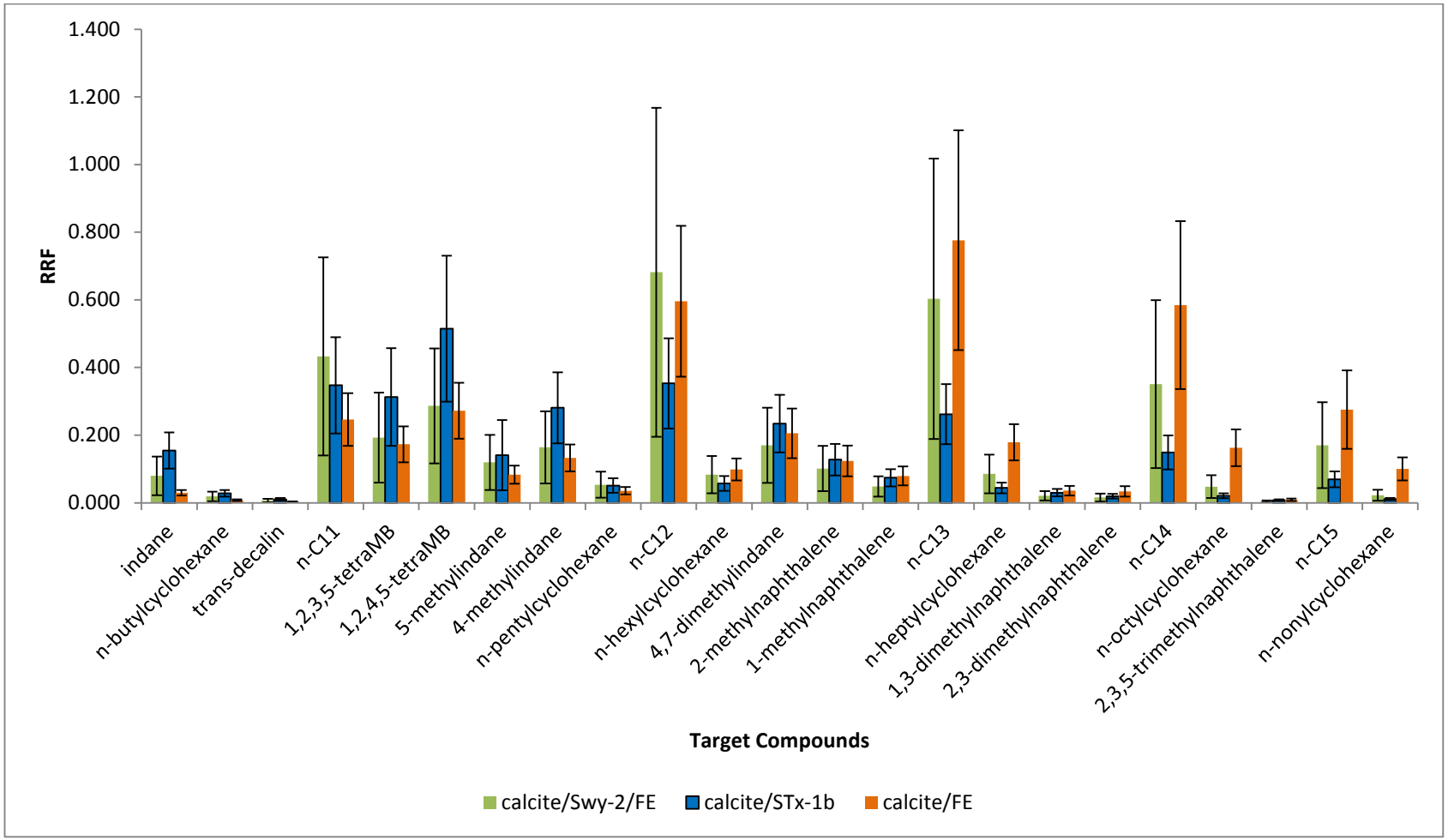

Figure 4.10 Adsorption of medium petroleum compounds from a petrol diesel mixture by three different adsorbent mixtures (n = 5)

Limestone/FE was able to adsorb all heavy target compounds and these were identified up to docosane (*n*-C_{22}) (Figure 4.11). The RRF values indicated that adsorption of the target mixture was more effective due to the increase in peak area value, subsequent RRF values and therefore target compound adsorption was improved. This adsorption goes beyond the requirements for fire debris investigation target compounds (*ibid*).

This mixture was the best match of any of the mixtures tested in terms of fulfilling the criteria for selection (section 4.5.1). The increased ratio of limestone in the mixture (9:1 w/w) contributed to the adsorption of the heavier alkanes, while the Fuller's Earth sufficiently allowed the adsorption of aromatic compounds. It was recommended that this mixture was evaluated further as it was the only adsorbent (singular or mixture) that could adsorb all ignitable target molecules from petrol and diesel.

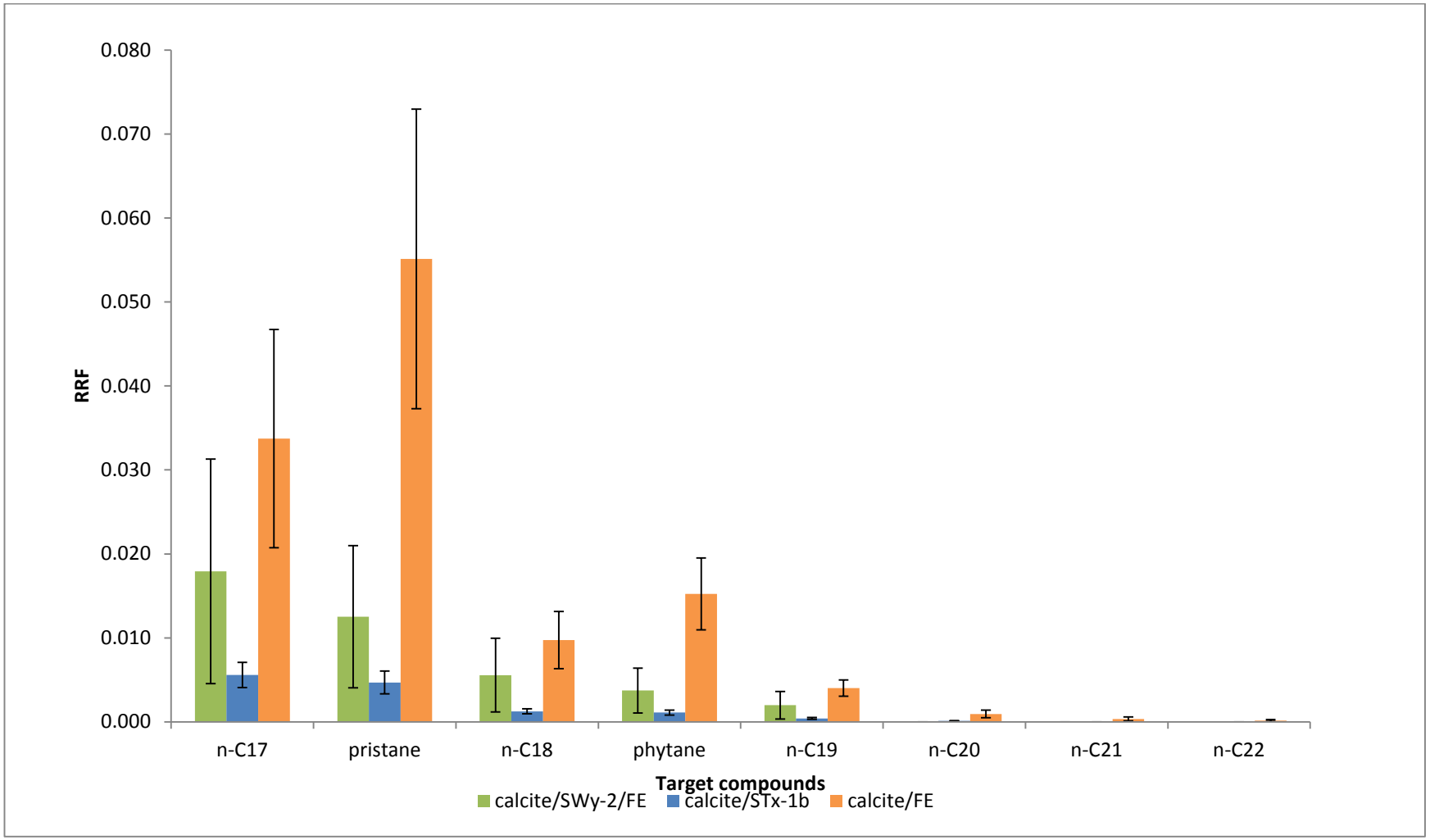

Figure 4.11 Adsorption of heavy target compounds from a petrol/diesel mixture by three different adsorbent mixtures (n = 5)

4.7.4 *Adsorbent Laboratory Blind Experiment*

The blind experiment was created by employing the same methods as already described in section 4.6.2. In short, an unknown ignitable liquid was poured onto a paving slab and left for two hours. The limestone/Fuller's Earth was then used to cover the paving slab for twenty minutes. It was then recovered for adsorption in an oven with subsequent desorption into the ATD-GC-MS. In addition, improvements to split flow settings were adopted (section 3.9) to combat MS detector overload of ignitable liquid compounds. The analyst did not know the identity of any ignitable liquid that was used for any of the tests (n = 5). The results were not declared by the third party until after analysis had been completed.

As these tests used unknown volumes of ignitable liquid the consideration of overloading the analytical instrument was a risk (section 3.4). To mitigate this risk, samples were recovered from the paving slab and a quick olfactory test (section 3.8.1) was conducted to ascertain if there were any strong smells. Those samples that did have a strong smell were allocated six hours oven time. Those samples that did not have a strong smell were allocated nine hours (section 3.10).

Target compounds were identified by comparing retention times to standards, and by the analysis of EICs and spectrums for each ion used (Table 4.5).

Table 4.5 Compounds identified from blind tests using mixture limestone/Fuller's Earth (9:1 w/w)

Target Compound			Identified or Not?				
	Compound ID number	***m/z* used to ID**	**Test 1 - Diesel**	**Test 2 - No Ignitable Liquid**	**Test 3 - White Spirit**	**Test 4 - Petrol**	**Test 5 - BBQ Lighter Fluid**
Analyst identified as?	n/a	n/a	HPD[1]	No ignitable liquid	MPD[2]	Petrol	Not identified
Screen Test – Strong smell?	n/a	n/a	√	No	√	√	√
Oven Adsorption Time	n/a	n/a	6 hours	9 hours	6 hours	6 hours	6 hours
ethyl benzene	1	91	√	√	√	√	x
m,p-xylene	2	91	√	√	√	√	x
o-xylene	3	91	√	√	√	√	x
n-nonane	4	57	√	x	√	√	x
propylbenzene	5	91	√	x	√	√	x
3-ethyltoluene	6	105	√	x	√	√	x
1,3,5-trimethylbenzene	7	105	√	x	√	√	x
2-ethyltoluene	8	105	√	x	√	√	x
1,2,4-trimethylbenzene	9	105	√	x	√	√	x
n-decane	10	57	√	x	√	x	x
indane	11	117	√	x	x	√	x
n-butylcyclohexane	12	83	√	x	√	x	√
trans-decalin	13	138	√	x	x	x	x
undecane	14	57	√	x	√	x	x
1,2,3,5-tetramethylbenzene	15	119	√	x	x	√	x
1,2,4,5-tetramethylbenzene	16	119	√	x	x	√	x
5-methylindane	17	117	√	x	x	√	x
4-methylindane	18	117	√	x	x	√	x
n-pentylcyclohexane	19	83	√	x	√	x	x
n-dodecane	20	57	√	x	√	x	x
n-hexylcyclohexane	21	83	√	x	√	x	x
4,7-dimethylindane	22	131	√	x	x	√	x
2-methylnaphthalene	23	142	√	√	√	√	x
1-methylnaphthalene	24	142	√	x	√	√	x
n-tridecane	25	57	√	x	x	x	x
n-heptylcyclohexane	26	83	√	x	x	x	x
1,3-dimethylnaphthalene	27	156	√	x	x	√	x
n-tetradecane	28	57	√	x	x	x	x
2,3-dimethylnaphthalene	29	156	√	x	x	√	x
n-octylcyclohexane	30	83	√	x	x	x	x
n-pentadecane	31	57	√	x	x	x	x
2,3,5-trimethylnaphthalene	32	170	√	x	x	x	x
n-nonylcyclohexane	33	83	√	x	x	x	x
n-hexadecane	34	57	√	x	x	x	x
n-heptadecane	35	57	√	x	x	x	x
pristane	36	57	√	x	x	x	x
n-octadecane	37	57	√	x	x	x	x
phytane	38	57	√	x	x	x	x
n-nonadecane	39	57	√	x	x	x	x
n-eicosane	40	57	√	x	x	x	x
n-heneicosane	41	57	x	x	x	x	x
n-docosane	42	57	x	x	x	x	x

[1] Heavy Petroleum Distillate
[2] Medium Petroleum Distillate

4.7.4.1 Test 1 – Diesel

All petrol and diesel target compounds were identified with the exception of heneicosane (Table 4.5). The preliminary screening smell test (section 3.4) indicated that an ignitable liquid could be present in the sample so a three hour oven time was allocated. The TIC at Figure 4.12 shows a Gaussian shape to the peaks and the retention range time indicate that this liquid could be a heavy petroleum distillate (Stauffer, et al., 2008, pp. 312-313). All target compounds (Table 4.5) except heneicosane (n-C_{21}) and docosane (n-C_{22}) were identified (Appendix 31) indicating that a heavy petroleum distillate (ASTM E1618-11, 2011) had been adsorbed. The actual identity of the ignitable liquid type by the analyst was correct and was later confirmed after analysis was completed (5.0 mL of diesel fuel).

The absence of heneicosane on the EIC suggested that the montmorillonite content was still too high and it was reasoned that an adjustment to the content of the mixture was necessary to increase the adsorption of heneicosane. The change increased the limestone content and reduced the Fuller's Earth content to give a new ratio of 10:1 w/w. This change was adopted for the blind field evaluation in Chapter 6.

4.7.4.2 Test 2 - No Ignitable Liquid

The preliminary screen test indicated no noticeable smell of an ignitable liquid. The TIC showed there were no peak patterns that resembled any ignitable liquids and EIC analysis (Appendix 32) confirmed this (Table 4.5). Therefore there was no ignitable liquid in this sample. After the test it was revealed that this sample only contained charred wood and the peaks seen on the chromatogram are a result of precursory, pyrolysis and combustion products.

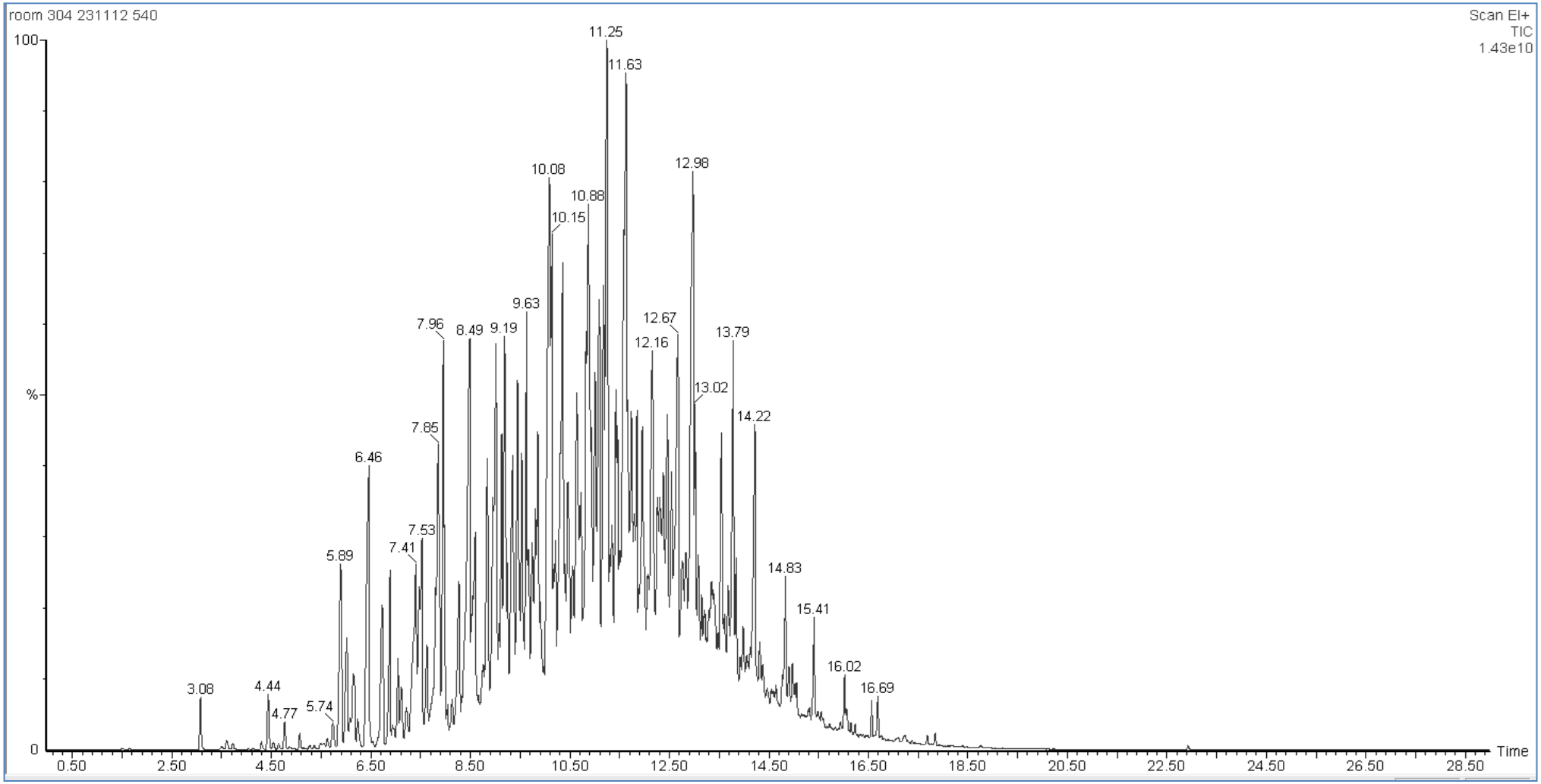

Figure 4.12 TIC of diesel residue adsorbed from a paving slab with limestone/Fuller's Earth mixture 9:1 w/w

4.7.4.3 Test 3 – White Spirit

While recovering this residue from the paving slab, there was a strong smell of an ignitable liquid. The TIC of this sample (Figure 4.13) revealed a narrow Gaussian peak shape of compounds from 5.12 minutes to 11.26 minutes retention time with the tallest peak at 8.62 minutes. The overall peak pattern suggested a medium petroleum distillate had been adsorbed (Stauffer, et al., 2008, pp. 312-313). Extracted ion chromatograms (Appendix 33) were examined and the following target compounds were identified (Table 4.5): *n*-alkanes (nonane to tridecane); *n*-cycloalkanes (*n*-C_4 to *n*-C_8-cyclohexanes; alkylbenzenes (C_2 to C_4); indane, C_1-indanes and C_1-naphthalenes. With the aid of ASTM E1618-11 (2011) this sample was identified correctly as a medium petroleum distillate. Later, the identity of this sample was revealed by the blind tester as white spirit.

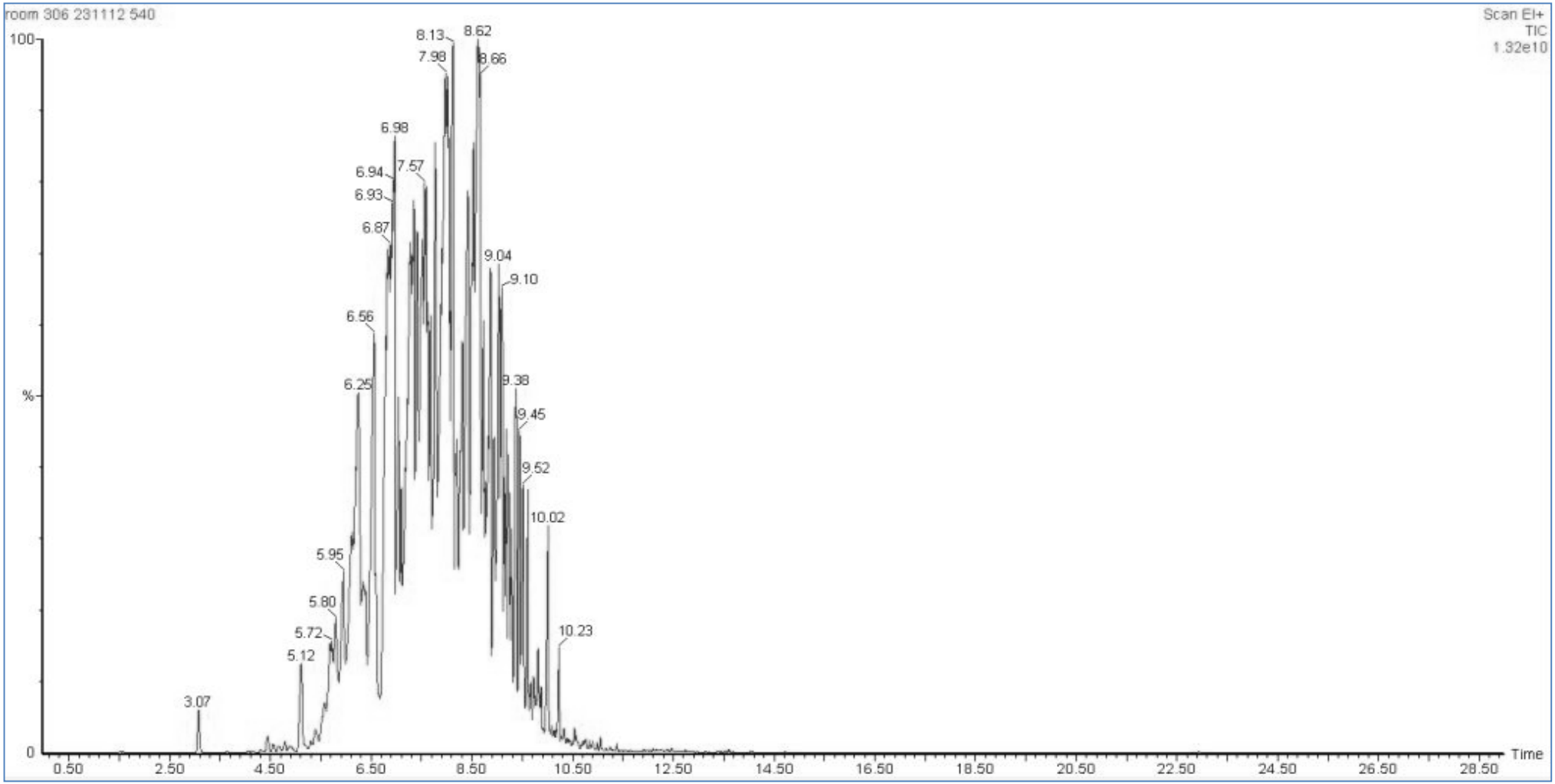

Figure 4.13 TIC of white spirit residue adsorbed from a paving slab with limestone/Fuller's Earth mixture 9:1 w/w

4.7.4.4 Test 4 – Petrol

Preliminary screening indicated a smell of an ignitable liquid but the smell was not as intense compared with those in Test 1 or Test 3. However, the oven time was set to three hours for this sample. The TIC at Figure 4.14 showed the classic patterns of 'The Three Musketeers' group and the castle group which is the signs of C_2 and C_3-alkylbenzenes (section 1.8.1). Target compounds were identified from EICs (Appendix 34). All alkylbenzene, indane and naphthalene target compounds were identified except for 2,3,5-trimethylnaphthalene. Neither *n*-cylcohexane target compounds nor target *n*-alkane target compounds were identified. The lack of paraffinic compounds and increased aromatic content enabled the correct identification of the ignitable liquid as petrol.

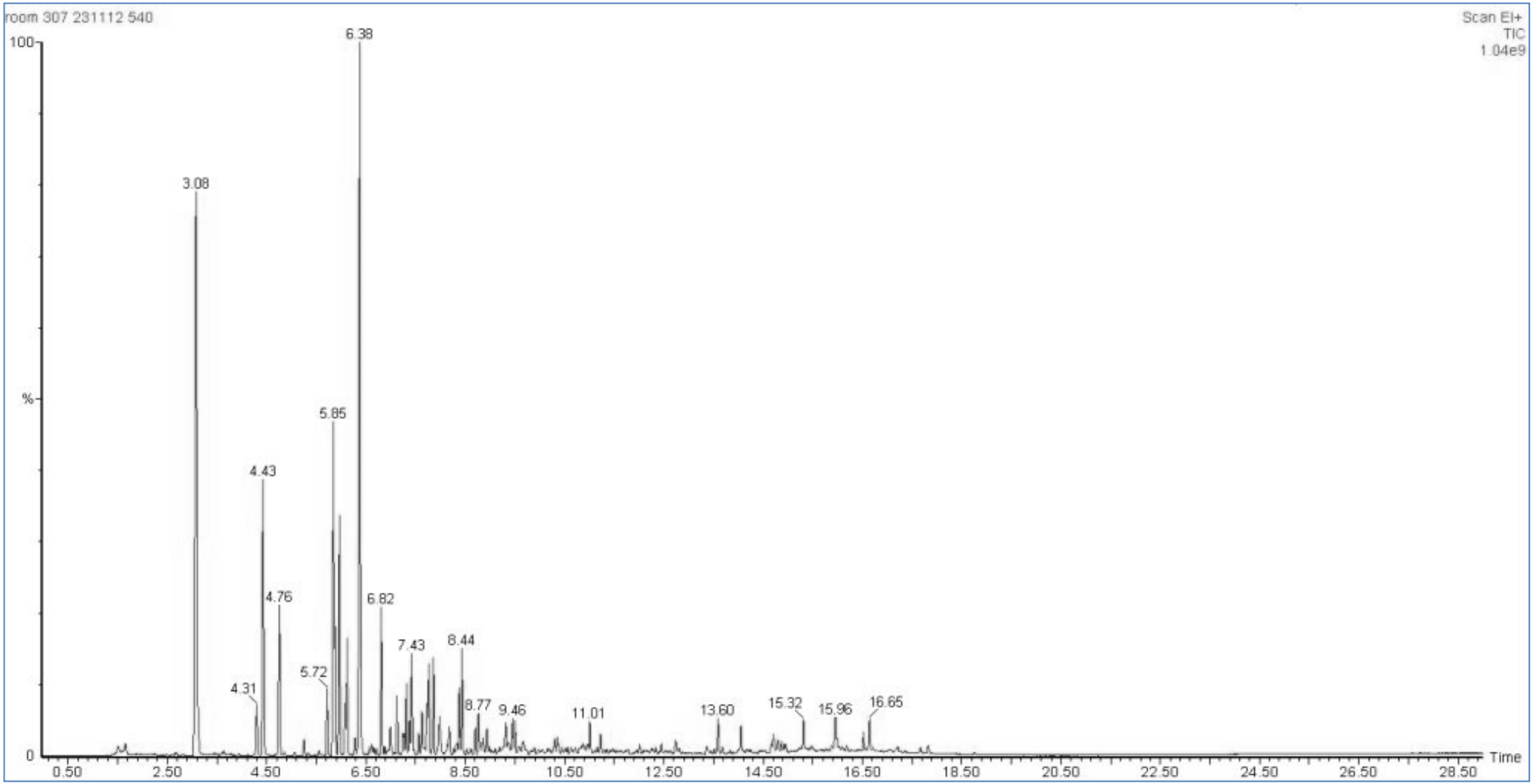

Figure 4.14 TIC of petrol residue adsorbed from a paving slab with limestone/Fuller's Earth mixture 9:1 w/w

4.7.4.5 Test 5 - Barbecue (BBQ) lighter fluid

The results of this test are included in Table 4.5 which shows that the only target compound identified was butylcyclohexane. At the preliminary screening stage a strong smell of an ignitable liquid was indicated. An inspection of the TIC (Figure 4.15) exhibited a wide Gaussian curve shape from 6 minutes to 16 minutes and peaks had overlapped so that individual peaks were indistinguishable from each other on this chromatogram. It appeared that the mass spectrometer had been saturated with unknown compounds. The bell shaped curve of peaks suggested that a medium paraffinic product was present (Stauffer, et al., 2008, pp. 312-313). However, the merging of peaks and therefore loss of resolution problem was also apparent when using EICs (Appendix 35) and this lead to no identification of any compounds apart from *n*-butylcyclohexane.

Although the earlier screening precaution recommended in this research was used to determine ignitable liquid smells and from that the subsequent three hour oven time (section 3.10), it is postulated that the inlet and outlet split flow settings were set too low (both set 20 mL/min in section 3.8.2) and so allowed the cold trap and column to become overloaded, which naturally led to the detector becoming overloaded. In light of this, and from a previous recommendation in this research (section 3.10) it was recommended to increase both the inlet and outlet split flow to 40 mL /min to reduce the chance of overloading at the expense of sensitivity and this was implemented for the field test (section 6.4.5). The identity of the sample was revealed as barbecue (BBQ) lighter fluid after the testing was complete.

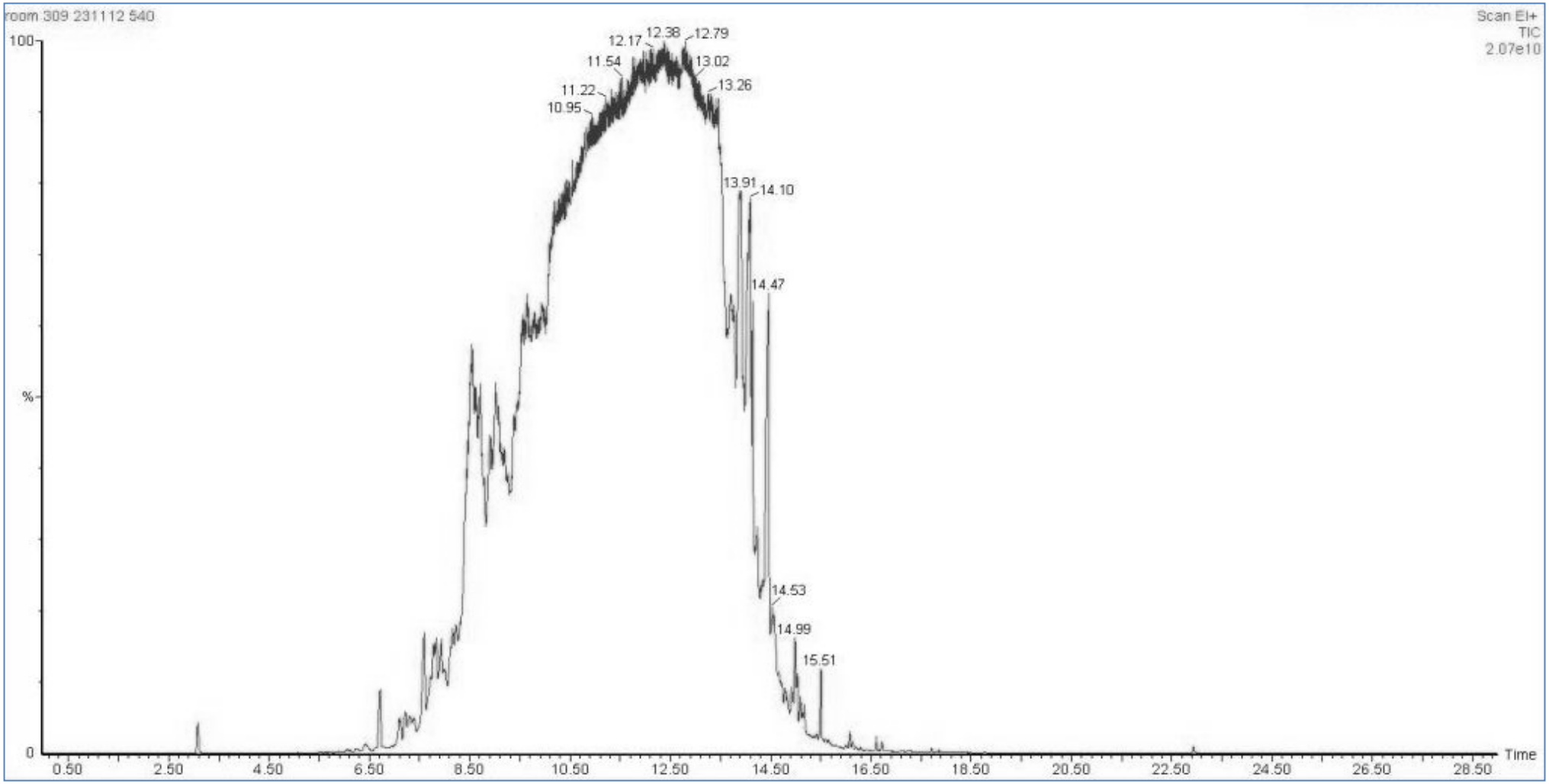

Figure 4.15 TIC of barbecue lighter fluid residue adsorbed from a paving slab with limestone/Fuller's Earth mixture 9:1 w/w

4.8 Conclusion

The aim of this chapter was to create a mixture of adsorbents that could both adsorb and desorb common ignitable liquids. The adsorbents were assessed in conjunction with the criteria set out in Section 4.5.1. If any single or mixture adsorbent had the potential to fulfil the assessment criteria, it would be subjected to blind testing and then field testing (Chapter 6) and only then would it be able to fulfil all the criteria.

It was already known from preliminary testing (section 2.4.1) that limestone adsorbed heavy *n*-alkane and *n*-cycloalkane non-polar compounds allowing the identity of heavy petroleum distillate compounds from diesel, and that cat litter adsorbed aromatic slightly polar compounds allowing the identity of petrol. In this chapter, cat litter (section 2.1.4) was substituted by three different montmorillonites and individually achieved the same result in that the target compounds of petrol were adsorbed and identified. It was determined that none of the single adsorbents could adsorb the entire target compound range of petrol and diesel mixture set-out by ASTM E1618-11 (2011).

The first mixture tested (limestone/Swy-2/Fuller's Earth 2:1:1 w/w) did not adsorb heavy target compounds (eicosane and heneicosane) and so did not meet the criteria. The ratio of montmorillonite to limestone was lowered to 33% and also used a less polar montmorillonite (limestone/STx-1b 10:3 w/w). Although this mixture was able to adsorb eicosane, it still did not fulfil the criteria as heneicosane was not identified. For the final mixture, STx-1b was substituted for Fuller's Earth and the montmorillonite content was further lowered to 11.1%. In laboratory experiments the mixture limestone/Fuller's Earth (9:1 w/w) adsorbed all target compounds and also docosane (*n*-C_{22}) which is beyond the requirement for heavy petroleum distillate identification and is beneficial as it allows future ignitable liquids to be identified.

In the laboratory blind tests the mixture limestone/Fuller's Earth (9:1 w/w) passed four out of the five blind experiments. The fifth test did not succeed due to instrument overloading. In the diesel sample (section 4.7.4.1), heneicosane was not identified, and it was thought that there was still too much Fuller's Earth in the mixture. Therefore the course of action taken was to increase the limestone ratio further to 10:1 w/w (discussed in section 4.7.4.1). This ratio change was implemented in the next phase of evaluation (Chapter 6) where the adsorbent mixture would be subjected to a real fire scene including fire suppression and

pyrolysis products. However, spectral characterisation of the mixture was only completed for the 9:1 w/w ratio (Chapter 5). This was due to spectral analysis being conducted before the laboratory blind tests were carried-out. The recommendation of the instrument inlet and outlet split flow valves on the ATD were also implemented for field testing (40 mL /min) to reduce the risk of concentrated samples overloading the instrument and prolonging the life of the instrument.

Chapter 5

Spectroscopic Characterisation of a New Adsorbent

5 Introduction

In section 2.1.5, it was highlighted in previous research by Eriksson, et al. (2007) that oxyhydrides, iron and arsenates could substitute anions and cations in a calcium carbonate lattice which is the major molecule found in limestone. Therefore, with regards to this study, it was unclear as to what phases were present in limestone (section 2.1.5) and Fuller's Earth (Section 4.7.2.4). However, it was suspected that smectite and other minerals including those that contain iron were present in Fuller's Earth. Although there is no literature on the mixing of these two components together, it was possible that mixing limestone and Fuller's Earth together may cause $CaCO_3$ substitution. The substitution of ions could affect the adsorption properties of the material and therefore it was decided to characterise the individual mixture ingredients (limestone and Fuller's Earth) and the mixture itself (ratio 9:1 w/w).

Techniques such as X-Ray Diffraction (XRD) and Fourier Transform Infra-Red Spectroscopy (FT-IR) (Farmer & Russell, 1964; Presenti, et al., 2008) are well known methods for the characterisation of minerals. Therefore, this research also used these instruments to determine any characteristic changes of limestone and Fuller's Earth when in the form of a single adsorbent, compared to mixing them together to make an adsorbent mixture. Changes would be denoted in the form of band shifts when using infra-red spectroscopy and phase data when using XRD. These instruments have been used by Komadel & Madejova (2006); Chipera & Bish (2001); and Mermut & Lagaly (2001) to show band shift and phase changes on montmorillonites.

It should be noted that there was a recommendation in section 4.8 to increase the ratio of limestone to Fuller's Earth to 10:1 w/w. However, the findings of this chapter were concluded before that recommendation was introduced. Therefore the ratio used in this chapter is 9:1 w/w.

Both limestone and Fuller's Earth are found in many parts of the world and they have characteristics that set them apart as unique to where they are found (Hawkins, et al., 1986). For example the shells of molluscs may have settled and decomposed and even many centuries later may be found as tiny fragments. Mollusc shells contain limestone (Karleskint, et al., 2010, p. 36) and subsequent spectroscopy of the sample identified this. Another example is environmental activity such as volcanic eruptions or meteorite impact that resulted in it melting into sedimentary rocks which then eroded over time due to atmospheric conditions. Therefore in a sample of clay there may be variations due to compositions and defect structures. All of these natural variations add to the characteristics of the soil.

Both SWy-2 montmorillonite and STx-1b montmorillonite had been previously characterised by baseline studies (Chipera & Bish, 2001; Mermut & Lagaly, 2001; Madeova & Komadel, 2001; Mermut & Cano, 2001). These clays are regarded as reference clays and are stored by The Clay Minerals Society (2014). Both clays were used to compare results from this research to those of the baseline studies. Numerous studies have been undertaken to characterise limestone (Andersen & Brečević, 1991; Farmer & Russell, 1964; Farmer, 1974) and British Fuller's Earth (Hawkins, et al., 1986). These minerals were chosen as potential adsorbents for common ignitable liquids (section 4.5.2). Both limestone and Fuller's Earth used in this research are not classed as standard clays or standard minerals as they were purchased with no information about their origin. It was therefore likely that results would be different from previous research as the composition of each of these minerals was unknown. However, certain characteristics of those minerals such as molecular bond types and unit cell dimensions can be determined by vibrational spectroscopy and XRD.

5.1 Vibrational (Infrared) Spectroscopy

Vibrational spectroscopy offers a wealth of data on clay and mineral structures. The data gives information about molecular bond types in the sample and hence structure (Farmer, 1974). Data is obtained by using a concentrated photon source focussed on the sample, and then capturing resultant reaction of the sample to the photon source by a detector. Raman uses a single source frequency laser to obtain information on the energy gain or loss of photons as they pass through the sample (Smith & Dent, 2005, pp. 2-6) and an Infrared

instrument uses a range of frequencies to achieve the same result. The objective of each technique is to vibrate bonds in the molecule and then observe changes in polarisation (Raman) or changes in dipole (Infrared). The resultant spectrum derives information about the molecule structure in the form of bands (infra-red) or stokes lines/anti-stokes lines (Raman). In the case of this research, the study would apply the theory of interaction of the adsorbent mixture with gas phase ignitable liquids using infra-red spectroscopy.

Infrared (IR) spectroscopy is the application of electromagnetic energy in the frequency range 100 to 1.0 μm (10000 cm^{-1} to 100 cm^{-1}) (Geiger, 2004, p. 8) and the changes observed in the vibrational and rotational status of the molecules in the tested sample. Each molecule has absorption frequencies that are dependent upon the vibrational frequencies of that molecule (Åmand & Tullin, 1999). The absorption intensity is dependent on the effectiveness of the energy transferred from an infrared photon to the molecule. Absorption of the photon leads to vibration of bonds in the molecule which in turn leads to a change in dipole moment *(ibid)*. The molecule will only absorb infrared energy if the dipole moment is changed and occurs for all molecules other than diatomic and linear molecules *(ibid)*. A molecule can stretch in either symmetrical or asymmetrical form and can also bend/deform (Smith & Dent, 2005, pp. 8-11) which is dependent on the IR frequency. For example, in a water molecule, the two hydrogen atoms could stretch in unison in that they are stretching away from the oxygen atom together (symmetrical), or one hydrogen may stretch while the other remains static and as the stretched atoms returns in the same way that a spring returns. The other hydrogen then starts to stretch and this is referred to as asymmetric stretching. Molecules can also change angles between two bonds as this is known as bending vibrations *(ibid)*. For example, the angle between the two hydrogen atoms in water may close and make the angle smaller, which is similar to the action of a pair of scissors. Molecules can also twist, rock and wag which leads to a shift in the electron cloud, which causes a change in the dipole moment and the molecule then becomes infra-red active and is detected. All of these vibrations can be determined by using infra-red spectroscopy (Lin-Vien, et al., 1991, pp. 9-14).

The bonds in clays and minerals are generally in a lattice form. For example, silicon dioxide (SiO_2) is in a covalent network (Reger, et al., 2010, p. 447), and calcium carbonate found in limestone is found in a giant lattice made up of opposite charge ions and these two examples are infrared active (Smith & Dent, 2005, pp. 81-84). Hence this approach

was adopted to assess different characteristics of single adsorbents and when mixed together.

Farmer (1974), p. 11, observed that mineral specimens are best tested in the wavelength range 4000 to 400 cm^{-1} and possibly down to 200 cm^{-1} as most of the structures in minerals will absorb in this wavelength range. Also, it is also desirable to eliminate water vapour which absorbs strongly below 300 cm^{-1} *(ibid)*, as the hydroxyl (-OH) bands could overlap characteristic bands of the mineral on a spectrogram.

The FT-IR instrument used in this study (section 5.4) used an incandescent ceramic source (7800 to 240 cm^{-1}), potassium bromide (KBr) beam splitter (7800 to 350 cm^{-1}) and a fast recovery deuterated triglycine sulphate (FR-DTGS) detector (7800 to 240 cm^{-1}). Therefore, the effective wavelength range of the instrument was 7800 to 350 cm^{-1}. The use of the KBr beam splitter was chosen instead of the Universal Attenuated Total Reflectance (UATR) zinc selinide (ZnSe) accessory as UATR has a lower wavelength limitation of 650 cm^{-1} (Perkin Elmer Inc., 2004). The main benefit of using the KBr beam splitter was to view deformation bands of silicon oxide and aluminium at infra-red frequencies below 650 cm^{-1} (Table 5.1). However, it was necessary to prepare KBr discs to hold the sample in a disc holder. KBr ionic bonds are unaffected by IR radiation as there is virtually no change in dipole moment at any IR frequencies (Emmett, 2012) and therefore becomes an ideal mounting medium for samples. The creation of a disc is explained in section 5.4, but to summarise, a dehydrated KBr disc is made by pressing the KBr and small mass of clay or mineral (1-2% w/w) in a hydraulic press and then inserted into disc holder in the IR beam (McKee, 2010). The subsequent spectrum can reveal bands as low as 400 cm^{-1}.

An IR spectrum is the result of the reaction of sample molecules absorbing radiation in the frequency range set by the scan parameters in the IR beam. Generally, the spectrum can be displayed in %Transmission (*%T*) or absorbance (*A*), but other modes are available such as Kubelka Munk units which are used in quantitative analysis. In *%T* mode the sample absorbs IR energy and there is a drop in the amount of transmitted IR that reaches the detector. This is shown in Figure 5.1 as bands that appear to point in a downward direction. The area to the right hand side of the spectrum (below 1500 cm^{-1}) generally yields the most information about the analysed sample and this is known as ‘the fingerprint region’ as it contains deformation or stretch bands that are characteristic of the sample (Compton & Compton, 1993, p. 85).

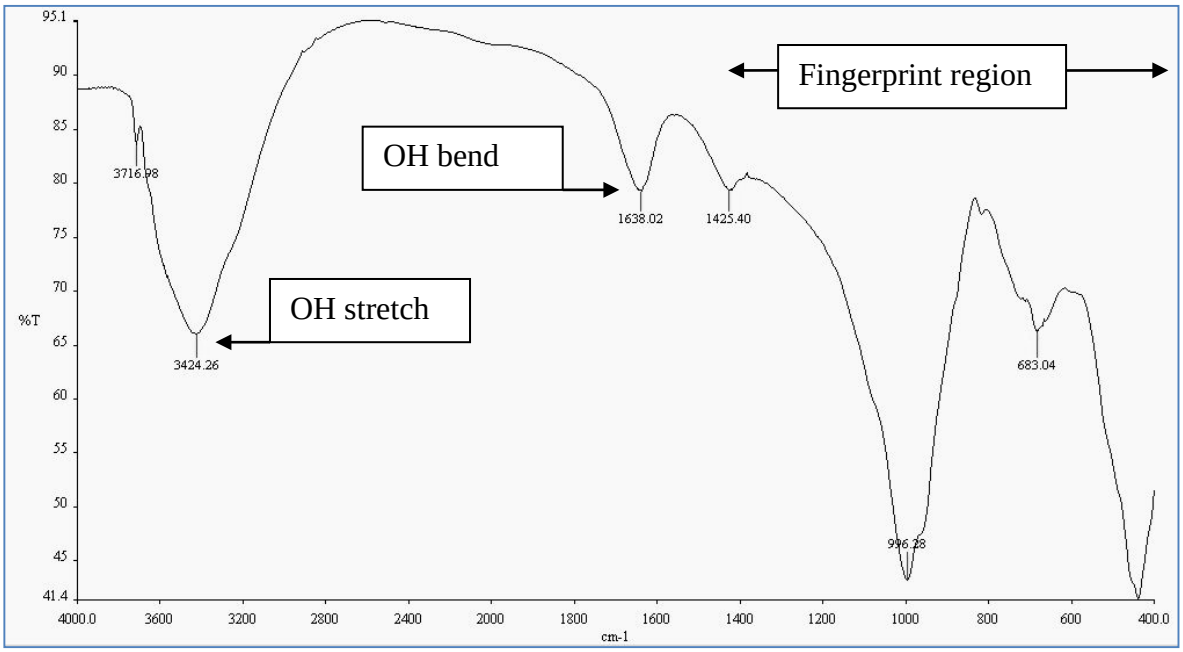

Figure 5.1 Example of a spectrum of dehydrated vermiculite showing IR bands in %T mode

In qualitative analysis of a spectrum, the aim is to identify bands in the fingerprint region and assign those bands to structures in the molecules in the sample (Åmand & Tullin, 1999). In Figure 5.1 the fingerprint region is from 1425 cm^{-1} to 400 cm^{-1} and represents the bond types and intensity absorption found that molecule (Farmer, 1974, pp. 5-6). Common band assignments for montmorillonite, calcium carbonate, quartz, cristobalite and opal using infrared spectroscopy coupled with a beam splitter and KBr discs are shown in Table 5.1. The bands are described as location, intensity and shape. The location refers to the corresponding wavenumber (*v*) or absorption range of the absorption minimum; the intensity refers to %T axis and describes how strong or weak the band is in terms of intensity; the shape refers the transmission band width dimension. For example in Figure 5.1 the band at 996.28 cm^{-1} could be described as: 996 cm^{-1}, strong, sharp.

Table 5.1 Infrared vibrational assignments for commonly used clays and minerals

Wavenumber (cm^{-1}) KBr	**Band Assignment**
Montmorillonite bands[1]	
1036-1016	Si-O stretch in-plane
917-915	Al-Al-OH deformation
885	Al-Fe-OH deformation
846-836	Al-Mg-OH deformation
626-620	Coupled Al-O and Si-O out-of-plane bend
523-521	Al-O-Si deformation
467-463	Si-O-Si deformation
$CaCO_3$ bands[2]	
1420	$CaCO_3$ asymmetric stretch (v_3)
875	$CaCO_3$ in-plane bend (v_4)
712	$CaCO_3$ out-of-plane bend (v_2)
Quartz, Opal, Cristobalite bands	
1089-1084	Si-O stretch cristobalite and quartz[3,]
798-794	Si-O stretch cristobalite, quartz and silica[2,3]
778	Si-O stretch quartz[1,2]
697	Si-O quartz[1]
626-623	Si-O stretch cristobalite[2,3]

[1] Madeova & Komadel (2001)
[2] Farmer (1974) and (Andersen & Brečević, 1991)
[3] Madeova & Komadel (2001) and confirmed by Chipera & Bish (2001)

5.1.1 *X-Ray Diffraction*

X-ray diffraction is an essential tool for the determination of cell dimensions and therefore atomic structure and has been used in mineral analysis for many years to assist in the identification of main phases in soil samples such as clay or clay mineral types and admixtures such as opal and cristalobite. The majority of clay fractions in soil samples are crystalline, as are many minerals and these can identified by using a combination of cell dimensions (XRD), bond types (infrared analysis) and chemical analysis (Harris & White, 2008, pp. 95-96).

If parallel beams of monochromatic X-rays are passed through a crystal, some will be reflected, or diffracted by the sample. Bragg & Bragg (1913), p. 436, proposed that X-rays give constructive interference in certain directions that depend upon the interplanar spacing of the diffracting planes. This is a derivation of Bragg's law which states that two reflected rays will constructively interfere if:

$$ABC = n\lambda \qquad \textit{Equation 5.1}$$

Where n is an integer >1; λ is photon wavelength; A and B are incident beams and A and C are the diffracted beams. Bragg & Bragg, (1913), p. 436, described crystals in terms of layers and planes within a lattice, where an atom resides at each lattice point. The expression of the diffraction of photon beams through a crystal is described as:

$$AB = AC = 2d_{hkl} \sin\theta \qquad \textit{Equation 5.2}$$

Where: θ is the angle of incidence and reflection. This in turn gives rise to Bragg's Law at Equation 5.3.

$$n\lambda = 2d_{hkl}\, sin\, \theta \qquad \textit{Equation 5.3}$$

This can be re-arranged by transposing Equation 5.3 to show a calculation for unit cell size (*d*) in Ångstroms:

$$d_{hkl} = n\lambda/2\, sin\, \theta \qquad \textit{Equation 5.4}$$

For example θ is 25.20 degrees, *n* = 1 and λ = 1.5406 Å gives:

$$d = \frac{1.5406}{2\ x\ 0.4258} = 1.8091\ \text{Å} \qquad \textit{Equation 5.5}$$

Equations 5.1 to 5.5 illustrate how cell dimensions are calculated and the *d*-space value is used to determine the phases and subsequent identity of clays and minerals. All of the clays and minerals used in this research are formed from a lattice (Chipera & Bish, 2001; Farmer & Russell, 1964) but each has lattice construction differences and so each have different interplanar spacing of diffracting planes. The perpendicular distance d_{hkl} between adjacent unit cells is represented by the Miller indices *hkl* and is defined as the relationship of the cell dimension divided by the sum of h^2 , k^2 , and l^2 to the power of ½ and represents the spacing plane (or phase) *d* (Hammond, 2009, pp. 137-138). It is this spacing plane that identifies the lattice type. For example, the spacing plane of calcium montmorillonite (*d* = 13.54 Å) is different to that of sodium montmorillonite (*d* = 11.03 Å) (Chipera & Bish, 2001). Other phases may or may not be present and these are also indicated by the spacing plane result. This makes XRD an obvious instrument to use in order to determine those differences and identify phases within samples.

Powder diffractometry is used in mineral analysis as samples can ground into a powder. The ideal grain size for this technique is 2-10 μm (Jenkins & Snyder, 1996; McCrone, 1976, p. 115). The sample is presented in a random fashion and loaded onto a rotating stage, where X-rays are directed onto the sample while the X-ray beam is fired at the sample stage at different angles and the diffracted X-rays are captured by a detector. This

has the advantage that unit cell dimensions can be accurately calculated by the instrument and can also be used to measure a range of samples such as paint, drugs and paper. In comparison, single crystal diffractometry uses non-random orientation of crystals within samples and this can complicate analysis and lead to inaccuracies in the calculation of cell dimensions (Jenkins & Snyder, 1996).

Significant research by The Clay Minerals Society (2014) has led to baseline studies on a number of clays including kaolinite, chlorite, illite, vermiculite, smectite and palygorskite (Chipera & Bish, 2001). Further studies have been completed by Nayak & Singh (2007) into instrumental characterisation of clays using XRF, XRD and FT-IR. Studies that include limestone and other minerals include Ferrell, (1971) and Presenti, et al., (2008). These studies have contributed to a greater understanding of characterisation techniques and help identify unknown mineral types.

Advantages of using XRD to analyse clays and minerals are speed of analysis, minimum sample preparation times and non-destruction of sample. However, full characterisation of minerals requires that samples be firstly analysed untreated; then glycolated with ethylene glycol to expand a clay by swelling; then heated to 400 ^{0}C which can affect mineral structure due to collapse and lastly heated to 550 ^{0}C (Poppe, et al., 2001). These physical changes can alter crystalline structure and so differences in 2θ may be evident and therefore an identification of components in the sample can be made. A full characterisation of samples in this research was not necessary as only qualitative results were needed.

The Clay Mineral Society baseline studies by Chipera & Bish (2001) prepared samples without modification and used a sieve to fractionate them to remove mineral impurities < 2µm. X-ray diffractograms were produced for standard clays STx-1b montmorillonite and SWy-2 montmorillonite and resulted in the following results (Table 5.2):

Table 5.2 Standard montmorillonite percentage composition, derived from Chipera & Bish (2001)

Montmorillonite	**Smectite %**	**Opal %**	**Quartz %**	**Feldspar %**	**Kaolinite %**	**Talc %**	**Others %**
STx-1b	68	30	2	< 1	< 1	< 1	< 1
SWy-2	95	Nil	4	1	< 1	< 1	< 1

Percent transmission infrared spectra of these source clays are at Appendix 17 and Appendix 18.

5.2 Components of the new absorbent mixture

The composition of each component of the mixture was subjected to characterisation with FT-IR and XRD to obtain structural data and phase data. In doing so, it was hoped to identify minerals that were also resident in the mixture. The characterisation determined the uniqueness of the components that made up the mixture and the mixture itself.

5.2.1 *Fuller's Earth*

The origin of the Fuller's Earth in this study was unknown, and as such is likely to be an un-purified mixture of different minerals and clays (section 4.4), so a full characterisation was necessary to establish what minerals and clays were in this mixture. Previous infrared spectroscopy studies by Russell, et al. (1970) on UK Fuller's Earth focussed on samples from the production mine at Woburn, UK. Vibration bands from that study were: Al-Al-OH (920 cm^{-1}); Al-Fe-OH (875 cm^{-1}); Al-O-Si (520 cm^{-1}) and Si-O-Si (450 cm^{-1}). These bands are common with the montmorillonite bands shown in Table 5.1.

A study by (Hawkins, et al., 1986) on a Fuller's Earth formation near Bath, UK included XRD analysis with treated (glycolated) and untreated samples. The untreated samples showed a mixture of montmorillonite, illite, kaolinite, quartz and limestone. However, the likelihood of the Bath sample may not resemble the Fuller's Earth sample used in this study, so the data from the Hawkins, et al., (1986) was only used as a guide and comparison.

5.2.2 *Limestone*

The label of the J. Arthur Bowers Garden Lime bag stated that the active ingredient was screened limestone. This may indicate that although it mainly consists of calcium carbonate, there could be impurities as well (section 4.5.2). It was therefore important to determine if any other minerals were present as this may affect adsorbent properties of powdered limestone. Carbonate minerals may be present in different soil types as it is a

very common mineral (Ni & Ratner, 2008). Carbonates have the structure CO_3^{2-} and have been studied extensively, including studies by Andersen & Brecevic (1991), Wei & Shou-Ci (2003), Farmer (1974), p. 227-284 and Coblentz Society Collection (2009). The carbonate ion exhibits four modes of vibration (v_1 - v_4) (Farmer, 1974, p. 233). The modes are attributed as follows: v_1 = symmetric stretch; v_2= out-of-plane bend; v_3 = asymmetric stretch and v_4= in-plane bend (Table 5.1). The two main mineral forms of calcium carbonate are calcite and aragonite, and there is one other form named 'vaterite' (Farmer, 1974, pp. 246-249; Andersen & Brečević, 1991) which is mainly synthesised in the laboratory. An interesting aspect here is that the v_1 mode is not visible in calcite using infrared spectra due to a weak shift in dipole, but is visible in aragonite, thus making this a useful way of differentiating between the two minerals. With regard to vaterite, all four modes are visible in IR v_1 (1085cm^{-1}, 1070cm^{-1}); v_2= (870cm^{-1}); v_3 = (1490cm^{-1} and 1420cm^{-1}) and v_4= (750cm^{-1}) (Farmer, 1974, pp. 246-249).

Calcite bands found by Farmer (1974), p. 233, were at 712 cm^{-1} (v_4 out-of-plane bend, strong sharp); 876 cm^{-1} (v_2 in-plane bend weak sharp); 1435 cm^{-1} (strong broad) and 1435 cm^{-1} (v_3 asymmetric stretch, strong broad). Symmetric stretch vibrations (v_1) have very little change in dipole and so are not infrared active. However this is visible using Raman as the polarisability of the molecule with this mode of stretching makes it Raman active (Smith & Dent, 2005).

X-Ray diffraction data for calcite and other minerals was published by Chen (1977). This document provides 2θ and *d*-space information about the minerals including calcite and was used in this research for comparison purposes.

The sample used in this study was powdered limestone (Garden Lime). The label on the bag with which it came stated that the contents included calcium carbonate, but this was used only as a guide. All three polymorphs of $CaCO_3$ (calcite, aragonite and vaterite) were considered before analysing the sample.

5.2.3 *Adsorbent Mixture Limestone/Fuller's Earth/ (9:1 w/w)*

In Section 4.7.3, three different mixtures were tested in the laboratory. Those mixtures were: limestone /SWy-2 Na-montmorillonite/Fuller's Earth (2:1:1 w/w); limestone/STx-1b Ca-montmorillonite (3:1 w/w) and limestone/Fuller's Earth (9:1 w/w). The latter mixture

(limestone/Fuller's Earth 9:1 w/w) was chosen as the mixture of interest and characterisation as this mixture had absorbed all target molecules from common ignitable liquids (section 4.7.3.3) and now with the use of FT-IR and XRD it was important to characterise the components of the mixture and also reveal why the mixture was able to adsorb light compounds such as propylbenzene to heavy target compounds such as heneicosane.

5.3 Aims and Objectives

The aim of this part of the research was to investigate the characteristic properties of limestone and Fuller's Earth and determine any band shift differences or phase shift differences when mixed together in a 9:1 w/w ratio.

The first objective was to compare previous research data on two standard montmorillonites (SWy-2 and STx-1b) by Chipera and Bush (2001), and compare them to the results obtained in this research.

Limestone and Fuller's Earth results was analysed singularly for vibrational bond types and unit cell dimensions and also to determine if any admixtures were present.

The final objective was to analyse the limestone/Fuller's Earth 9:1 w/w mixture and determine if there were any band shift changes or phase shift changes from the singular analysis and whether the changes were significant to explain why this mixture adsorbs common ignitable liquid.

5.4 Materials and Methods

Two instruments were used to characterise clays and minerals: Perkin Elmer Spectrum One FT-IR fitted with a KBr beam splitter and disc holder and a Bruker D2 Phaser XRD.

The materials required for the analysis of clays and minerals include: Fuller's Earth from Fisher UK; J. Arthur Bowers Garden Lime; agate pestle and mortar; Mixture: Limestone/Fuller's Earth (9:1 wt/wt); Specac Atlas Series Laboratory Manual Hydraulic

Press (15 Ton); 13 mm evacuable pellet die (<10 Ton); vacuum pump kit; dehydrated potassium bromide (KBr) granules (Fisher, UK); 10 mm poly(methyl methacrylate) (PMMA) sample mounts and corundum standard for XRD; grinding apparatus (Retsch GmbH) PM100 with 80 mL ZrO_2 jar, and 5 x 20 mm ZrO_2 balls.

FTIR parameters: Middle Infrared (MIR) KBr beam splitter; scan 4000 to 400 cm^{-1} and 1400 to 400 cm^{-1}; count 10 and resolution 4.0.

XRD parameters: An application from the instrument manufacturer was used (Bruker, 2009) as this was recommended for geological material. Bruker D2 Phaser with Lynxeye detector (opening 5^0 2θ); Cu radiation (30 kV, 10 mA) with Ni filter; 2.5^0 soller collimator; 0.6 mm divergence slit and 1.0 mm anti-scatter screen; continuous scan from 3^0 to 55^0 2θ; step width 0.02^0 and count time 3 seconds per scan. A corundum standard was used to calibrate the instrument. Match 2 software (Crystal Impact GbR, 2014) was used to interpret data. Diffractograms were baseline corrected, raw data smoothed the software option was enabled for K-Alpha2 stripping.

5.4.1 *Sample preparation*

All samples that underwent tests were subjected to sample preparations. Both the individual components Fuller's Earth and limestone were ground down to a fine powder using the Retsch grinder to grain sizes 60 – 100 μm. Then the samples were kept in an oven overnight at 90 ^{0}C to reduce absorbed water on the smectite, limestone and adsorbent mixture.

200 mg of KBr was weighed on a balance and then ground to a fine powder using an agate pestle and mortar. The powder was placed into an evacuable die, and then placed into a hydraulic press where a force of 8000 to 9000 kg was applied to the powder. A vacuum pump attached to the die was used to remove any atmospheric water. After 10 minutes the disc was removed from the die and was mounted onto a KBr disc holder and then placed onto the KBr beam splitter module. This disc acted as the blank.

Sample discs were created using the same method but a small mass of sample (2 mg) was added to the KBr when weighing. The ratio of KBr to sample should be 100:1 with a total mass of 200 mg loaded into the die (Watson, 2012, p. 121). The preparation of samples for

XRD analysis involved only the dehydration and grinding steps as above before loading onto a 10 mm PMMA sample holder.

5.5 Results and discussion of adsorbent characterisation with FT-IR and XRD

The FT-IR was initially set to scan the MIR range 4000 cm^{-1} to 400 cm^{-1}. This included the hydrous region 3200 cm^{-1} to 3000 cm^{-1}. However the focus was on the fingerprint region (1420 cm^{-1} to 400 cm^{-1}) as this region contains unique vibrational bands for each clay or mineral (Åmand & Tullin, 1999), so the results are centred on this region because the results showed characteristic bands in this wavelength range. Table 5.3 shows the results from infrared analysis and also comparisons to reference clays SWy-2 and STx-1b (Madeova & Komadel, 2001).

Table 5.3 Results of tested and compared band assignments using infrared spectra with a FT-IR KBr beam splitter

Vibration Assignment	Wavenumber (cm^{-1}) KBr beam splitter (n = 3)						
	SWy-2 this research	**SWy-2 results by** Madeova & Komadel, 2001	**STx-1b this research**	**STx-1b results by** Madeova & Komadel, 2001	**Fuller's Earth**	**Limestone (calcite)**	**Mixture Limestone / Fuller's Earth (9:1 w/w)**
Calcite asymmetric stretch (v_3)	-		-	-	-	1420	1420
Si-O stretch in-plane	-		-	-	1200	-	
Si-O stretch	1060-1040	1041	1000-1250	1089-1036	1060-975	1016	1031
Al-Al-OH deformation	915	917	915	915	915	-	-
Calcite in-plane bend (v_4)	-	-	-	-	875	875	875
Al-Fe-OH deformation	875	885	-	-	-		
Al-Mg-OH deformation	848	842	840	846	840	-	-
Si-O Quartz or opal impurity stretch	798	798	794	794	798	-	799
Si-O Quartz impurity stretch	778	778	-	-	778	-	-
calcite out-of-plane bend (v_2)	-	-	-	-	712	712	712
Quartz	697	-	-	-	-	-	-
Coupled Al-O & Si-O out-of-plane bend	620	620	623	626	-	-	-
Al-O-Si deformation	524	524	522	521	520	-	521
Si-O-Si deformation	466	466	468	467	467	-	463

5.5.1 *Analysis of SWy-2 and STx-1b Montmorillonites using FT-IR and XRD*

These clays had been the subject of baseline studies (Madeova & Komadel, 2001; Chipera & Bush 2001) and the results from those studies regarding FT-IR bands of montmorillonite standard clays SWy-2 and STx-1b are at Table 5.3. The results from this research for the same standard clays are also at Table 5.3 and can be compared. Generally, the previous research *(ibid)* and this research has similar bands with the following exceptions: Swy-2 montmorillonite – band shifts for Al-Al-OH deformation and Al-Mg-OH deformation. Stx-1b montmorillonite - the only band shift was Al-Mg-OH deformation. These band shifts were minor and may reflect that the samples used in this research may have had adsorbed a small volume of atmospheric water before analysis was conducted. However, the overall results were not affected by this. Figure 5.2 shows both montmorillonite spectra with bands in the MIR (1400 cm^{-1} to 400 cm^{-1}). Figure 5.2 shows these bands were: 1040 cm^{-1}; 798 cm^{-1}; 778 cm^{-1}; 620 cm^{-1}; 524 cm^{-1} and 466 cm^{-1}. Other common bands for montmorillonites are Al-Al-OH at 917 cm^{-1}; Al-O-Si at 521 cm^{-1} and Al-Mg-OH at 842 cm^{-1}. Differences between the two clays used in this research are Al-Fe-OH at 885 cm^{-1} for SWy-2 montmorillonite and the mineral cristobalite in STx-1b at 1089 cm^{-1} and 794 cm^{-1}. Both spectra have the band at 842 cm^{-1} for Al-Mg-OH. However, the band is much more pronounced in STx-1b spectrum due to the absence of iron that masks the band in SWy-2 montmorillonite. These band assignments are typical for dioctahedral montmorillonites *(ibid)*. These results cannot differentiate between CEC (section 4.3) such as sodium and calcium ions. However, they do show sheet layer bonds such as silicon, magnesium, aluminium, iron and hydroxyl ions that are found in the tetrahedral and octahedral layers (section 4.3) as well as minerals such as cristalobite and opal.

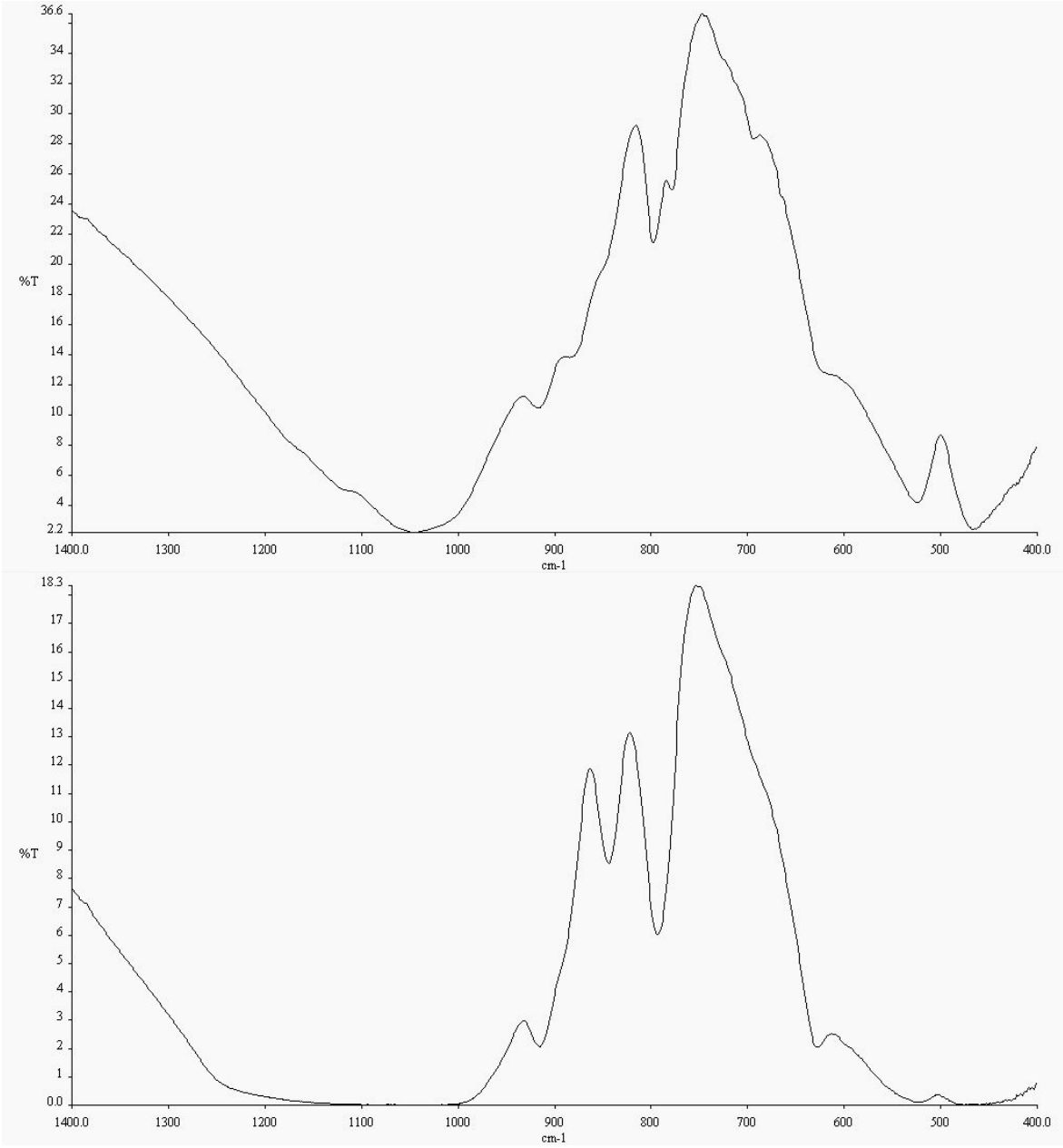

Figure 5.2 Transmission IR Spectra of SWy-2 montmorillonite (top) and STx-1b montmorillonite (bottom)

XRD dimension (*d*) space results for these two montmorillonites are summarised in Table 5.4; and the results are shown in Appendix 14 and they show dioctahedral smectite peak at 11.03 Å for SWy-2 and quartz peaks are at 4.25 Å; 3.33 Å; 3.03 Å and 2.46 Å and 1.82 Å. These peaks confirm that the major phases are dominated by 2:1 layer montmorillonite.

For STx-1b montmorillonite, a large peak observed at 13.54 Å is attributed to hydrated montmorillonite. There are fewer quartz peaks for STx-1b montmorillonite (3.36 Å and 1.82 Å). These peaks are consistent with the baseline investigations by Chipera & Bish, (2001) and confirm that 2:1 layer montmorillonite is the major phase. However, the results in Table 5.4 do not show peaks associated with talc, kaolinite or opal CT which was shown

in the Chipera & Bish (2001) results. However, that study used fine particle fractions (< 2 μm, which allowed for the separation of quartz, feldspar, opal and calcite from the sample. The domination of dioctahedral smectites and quartz with the variable charge suggests that these clays prefer to adsorb slightly polar molecules and this explains why light and medium petroleum compounds are adsorbed and excludes heavy petroleum compounds from a petrol/diesel mixture (1:1 w/w) as discussed in sections 4.7.2.2 & 4.7.2.3.

Having completed the analysis of standard clays the next stage was to analyse Fuller's Earth and limestone.

Table 5.4 d-space results of tested samples analysed by powder X-Ray Diffraction (n = 3)

Major phases from XRD Analysis Measured by *d*-space (Å)	**SWy-2**	**STx-1b**	**Fuller's Earth**	**Limestone (calcite)**	**Mixture Limestone / Fuller's Earth (9:1 w/w)**
Smectite	11.03	13.54	10.27; 6.35; 4.49 and 3.04	-	10.27
Quartz	4.25; 3.33; 3.03; 2.46; 1.82	3.37; 1.82	3.35; 4.25	-	4.25; 3.34; 1.82 and 1.80
Calcite	-	-	3.86; 3.04; 2.49; 2.28 and 2.09	3.05; 2.09; 2.28	3.04; 2.10 and 2.29
Silicon dioxide	-	-	9.13 and 2.47	-	-
unidentified	-	-	-	10.57	-

5.5.2 *Fuller's Earth*

Unlike the two montmorillonites in section 5.5.1, the Fuller's Earth sample was not a standard reference clay and its origin was not known. The infra-red spectrum (Figure 5.3) showed bands which allowed the identification of distinguishing vibrational bands (Table 5.3) and distinguishing phases were identified from XRD diffractogram peaks (Table 5.4).

Si-O stretching was evident at 1200 cm^{-1}; 1060 cm^{-1} and 975 cm^{-1} (Figure 5.4). At 875cm^{-1}, there was a distinctive band that was either Al-Fe-OH or calcite (v_4). Quartz was present as a double band at 798 cm^{-1} and 778 cm^{-1} respectively. The band at 712 cm^{-1} could indicate a calcite band but is also where feldspar vibrates (Farmer, 1974, p. 369). Other bands (522cm^{-1} and 467cm^{-1}) indicate quartz (Table 5.1). These results show that the major bands are indicative of a 2:1 (TOT) layer silicate but may also contain calcite.

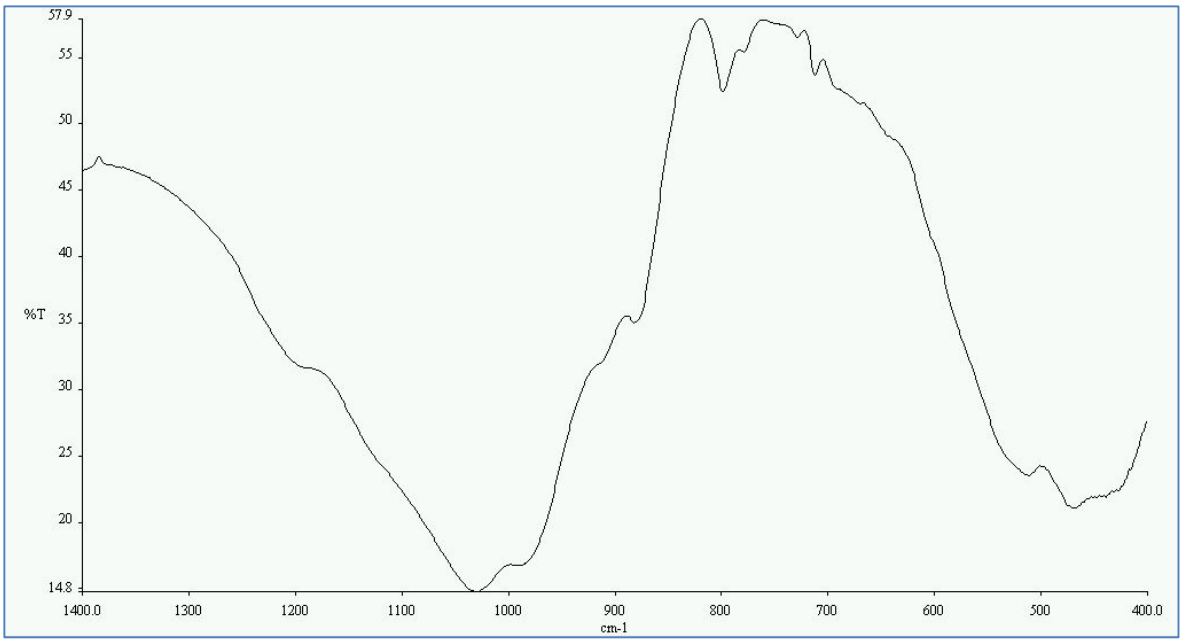

Figure 5.3 Transmission infrared spectrum of a Fuller's Earth, 2% sample in KBr disc

For XRD analysis of Fuller's Earth there was no baseline reference from which to compare results. The major phase assignments are in Table 5.4. The diffractogram at Figure 5.4 is dominated by the sharp tall quartz peak at 3.34 Å and a lesser peaks at 4.26 Å; 2.46 Å and 1.82 Å. The closest match found for the peaks at 10.27Å; 6.33Å; and 4.49Å was palygorskite (Brindley & Brown, 1980, pp. 109-112) from the family of clay minerals known as sepiolite-palygorskite. Many calcite peaks can be found at 3.85 Å; 3.04Å; 2.50Å; 2.28Å; 2.09Å; 1.92Å; 1.88Å and 1.82Å. The Match software (Crystal Impact GbR, 2014) listed the matched phases percentage values: Quartz 43.7 %; calcium carbonate 40.8 % and palygorskite 15.5 %.

These results confirm that Fuller's Earth is dominated by quartz structures and also contains calcite and a different type of clay that belongs to the sepiolite-palygorskite family which is a phyllosilcate clay (section 4.3) composed of 2:1 inverted ribbons. In this clay, the TOT sheets are short and alternating and this causes a twisting effect. Under a

microscope they can be viewed as lathe-like fibres (Brindley & Brown, 1980). The clay has a variable charge similar to 2:1 layer montmorillonites but in this case is due to CEC and water in the TOT cavities *(ibid)*. It is proposed that the combination of quartz and palygorskite contribute a variable charge while the 41% calcite content mitigates the charge slightly (section 4.7.2.1). This would explain why Fuller's Earth range of adsorption extends past the standard montmorillonites to incorporate the adsorption of heptadecane. However, the downside is that the adsorption of fast retention molecules such as ethylbenzene and xylene isomers is not as efficient as the montmorillonites. The overall content of this sample of Fuller's Earth contains different types of clay and minerals and this has also been found in research by (Hawkins, et al., 1986; Hosterman & Patterson, 1992).

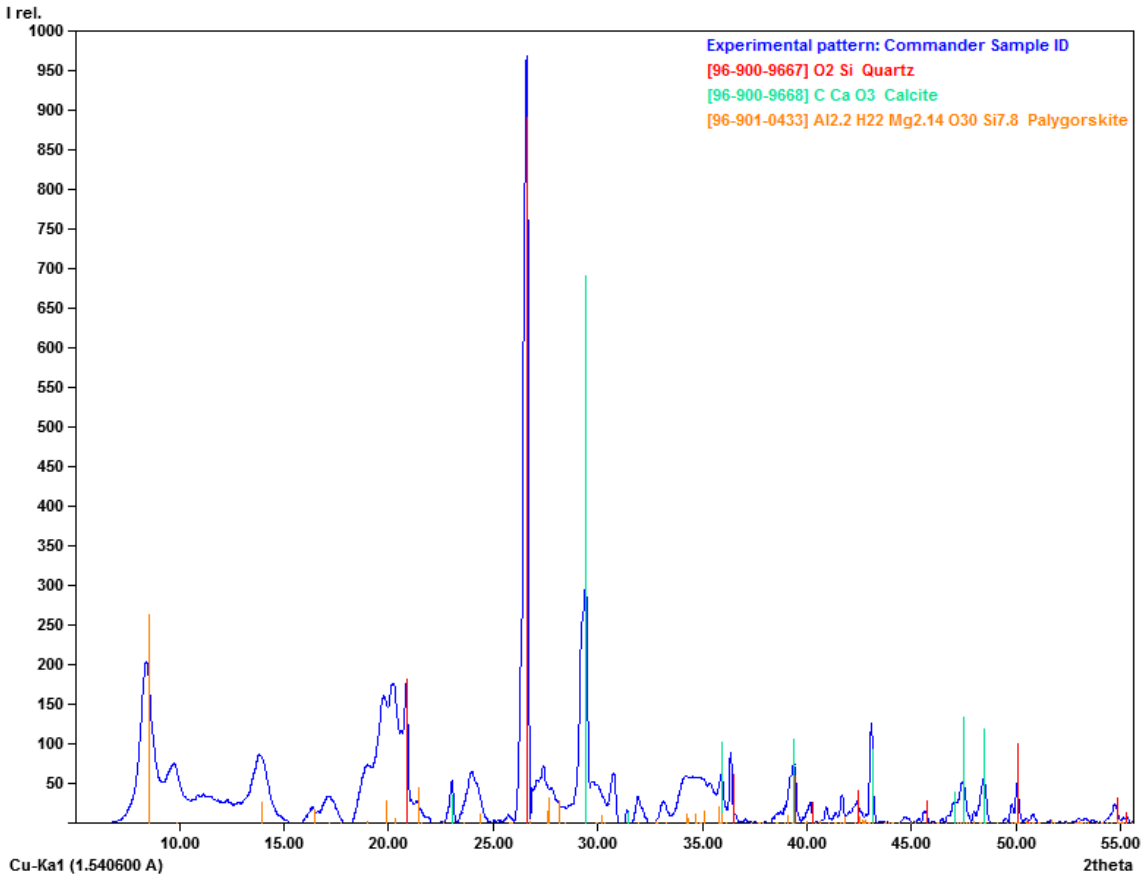

Figure 5.4 XRD powder diffractogram of Fuller's Earth with match lines at major phases

5.5.3 *Limestone*

The transmission infrared spectrum of calcium carbonate was compared with National Institute of Standards and Technology Web Book (2009). Major peak vibrations were recorded at 1420 cm^{-1}; 875 cm^{-1}; 712 cm^{-1} (Table 5.3; Figure 5.5). These bands are typical of calcite and according to Farmer (1974), p. 233 and Sathyanarayana (2004) these wavenumbers indicate the CO_3^{2-} ion vibrations in calcite making it distinguishable from aragonite and this was introduced in sections 2.1.5 & 5.2.2.

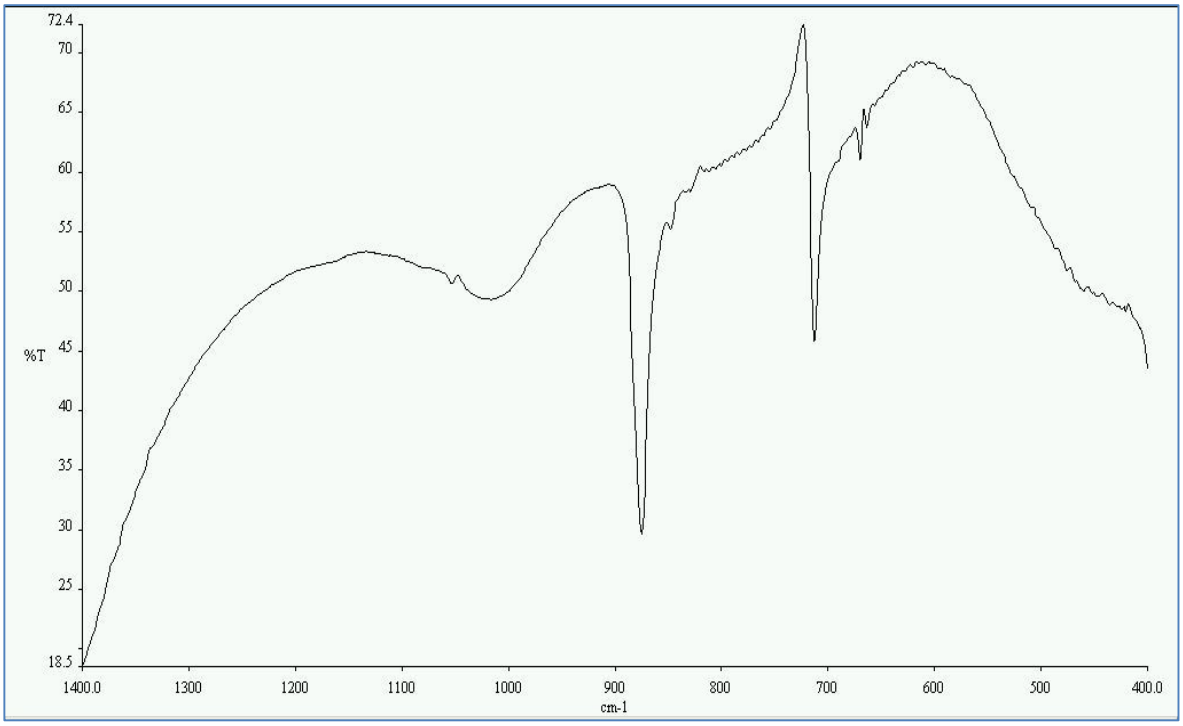

Figure 5.5 Transmission infrared spectrum of powdered limestone 2% sample in KBr disc

The result from the XRD diffractogram (Figure 5.6) was the easiest to interpret of all the samples as the major phases fit the calcite data listed in Brindley & Brown (1980), p. 390. The three largest phases for calcite are: 3.05Å; 2.09 Å and 2.28 Å. Other phases are at 3.86 Å; 2.50 Å; 1.91 Å and 1,87 Å. These results indicate that Garden Lime is almost entirely from a calcite rich, limestone deposit and supports the assumption that this adsorbent can adsorb medium and heavy non-polar molecules as indicated in sections 2.4.1 & 4.7.2.1.

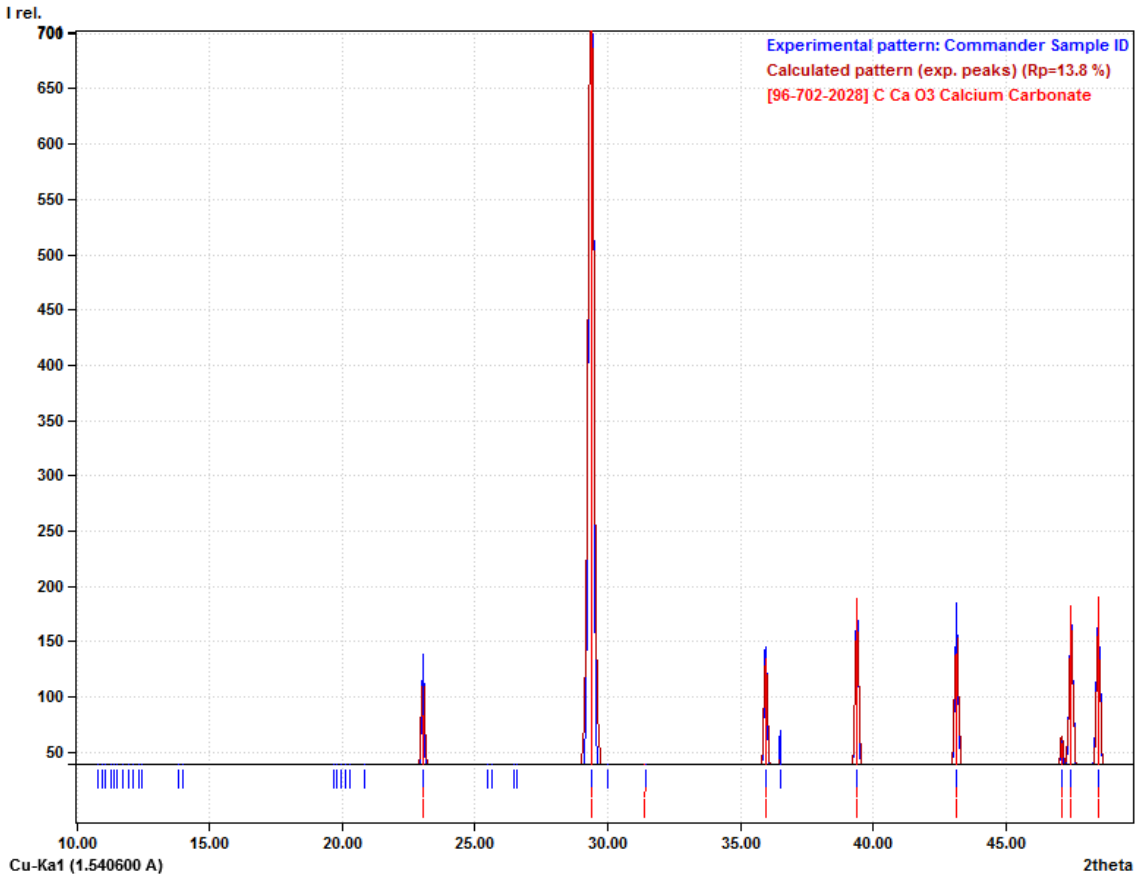

Figure 5.6 XRD powder diffractogram of limestone with matched peaks at major phases

5.5.4 *Adsorbent Mixture Limestone / Fuller's Earth (9:1 w/w)*

The infrared results at Table 5.3 and Figure 5.7 show combined bands of calcite and Fuller's Earth on the spectrum. Si-O (quartz) stretching is evident (1031 cm^{-1}); and deformation of Al-O-Si and Si-O-Si at 521 cm^{-1} and 463 cm^{-1} respectively. The quartz or opal impurity at 798 cm^{-1} is still visible. The dominant bands on the spectrum are the calcite in-bend plane at 875 cm^{-1} and 712 cm^{-1}.which is expected in a 9:1w/w calcite/Fuller's Earth ratio.

This mixture was prepared similar to samples as described in section 5.4.1. Because it is a mixture of a limestone and Fuller's Earth, it was expected to show bands from both substrates, but it was unclear if the bands would shift due to new inter-molecular bonds formation. There was the possibility of one of the adsorbent components interfering with the other and negating any adsorption range benefits of that component.

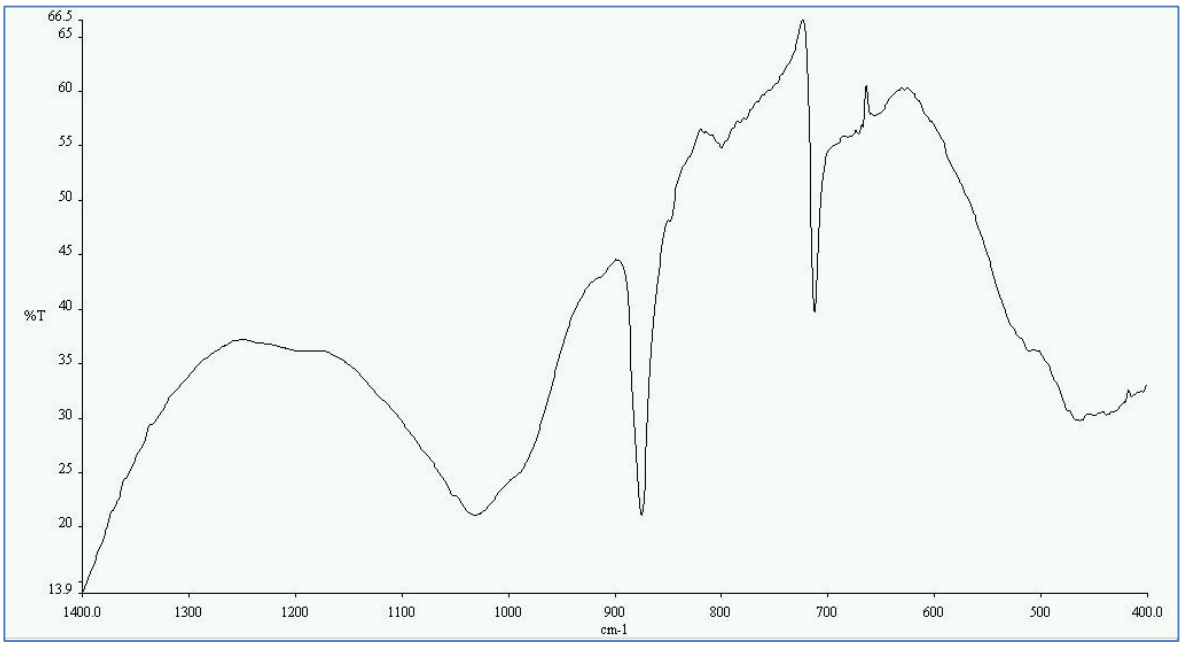

Figure 5.7 Transmission FT-IR spectrum of a limestone/ Fuller's Earth mixture (9:1 w/w), 2% sample in KBr disc

Results of the XRD diffractogram for limestone/Fuller's Earth mixture (Table 5.4 & Figure 5.8) showed a calcite dominant landscape with quartz phases. Calcite phases are listed as: 3.04 Å; 2.10 Å and 2.29 Å. Other phases are at 3.85 Å; 2.50 Å; 1.93 Å and 1,88 Å. Quartz phases are at: 4.25 Å; 3.34 Å; 1.82 Å and 1.80 Å. Mixing Fuller's Earth with limestone did not alter the chemical structure of calcite and Si-O phases, as this would have been observed as a shift in unit cell values (*d*-space value) and would have indicated altered crystalline phases (Chipera & Bish, 2001) and this would have been evident on the diffractogram by a change in the *d*-space value. The results form IR and XRD analysis do not show any change in the chemical structure of the components when mixed. Therefore the charge exerted by the quartz fraction has been diminished which leads to the charge becoming attractive to non-polar molecules which allows the adsorption of heavy alkanes, but it is proposed that enough charge is present from the quartz to attract slightly polar molecules. This would explain the success with the adsorption of both polar and non-polar target compounds in sections 4.7.3.3 and 4.7.4.

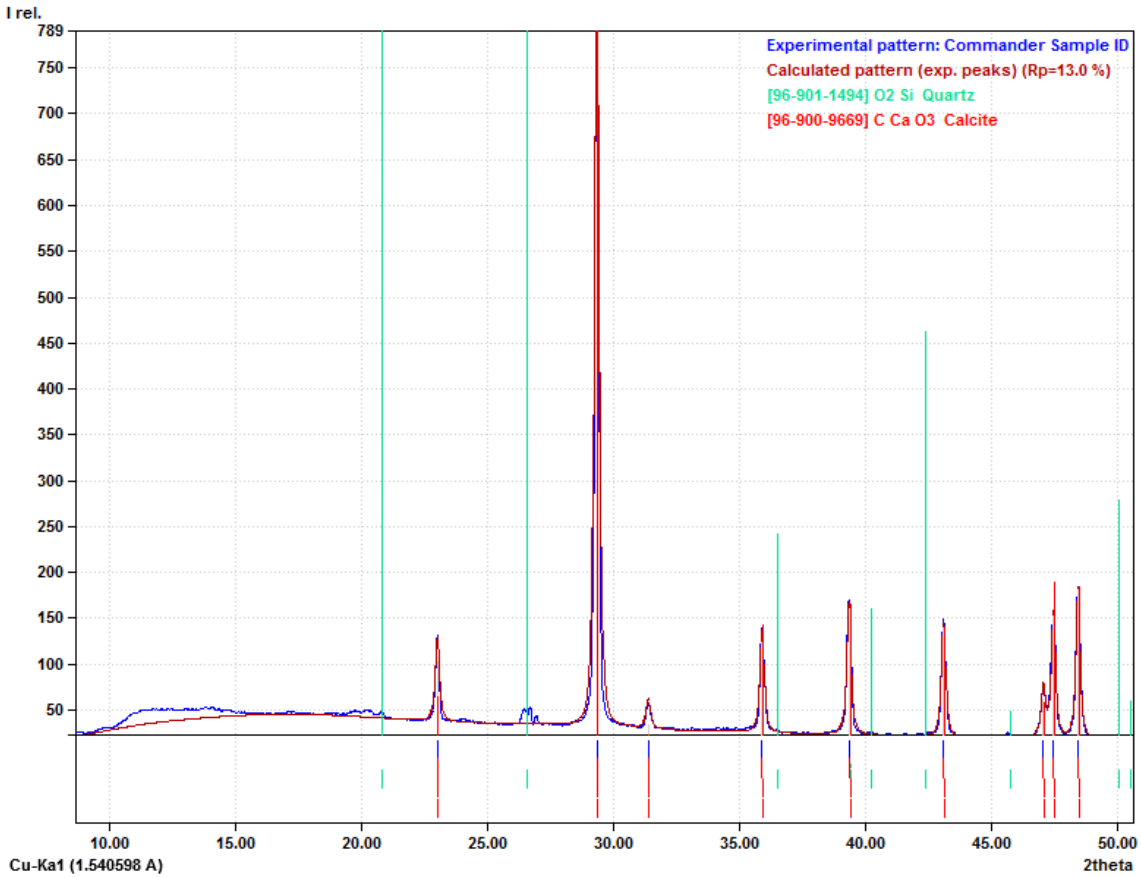

Figure 5.8 Diffractogram of mixture limestone/Fuller's Earth (9:1 w/w) with matched peaks at major phases

5.6 Conclusion

The focus for this part of the study was to characterise the newly created adsorbent mixture limestone/Fuller's Earth (9:1 w/w) and the individual mineral/clay with two different spectroscopic techniques. Fourier Transform Infra-red provided structural information about each adsorbent while X-ray diffraction provided phase information about each adsorbent.

The investigations found that limestone purchased as 'Garden Lime' is predominately composed of the calcium carbonate polymorph calcite. There was no evidence of quartz phases in this sample. However, Fuller's Earth contained major phases of quartz, calcite and palygorskite. The presence of calcite explains the preference of this material to adsorb heavier compounds found in diesel during laboratory adsorption tests (section 4.7.2.4) when compared to the montmorillonites SWy-2 and STx-1b.

The adsorbent mixture (limestone/Fuller's Earth 9:1 w/w) contained major phases of calcite, quartz and palygorskite. This was no evidence of ion exchange in the calcium carbonate lattice when in the adsorbent mixture, as the XRD cell dimensions and infra-red bands were the same as when analysed as a single adsorbent.

Each major component of the mixture is adapted for the adsorption of particular types of molecules and each prefers those molecules and rejects other types. The long chain alkane compounds are preferentially adsorbed to limestone, while the light mass and aromatic compounds are preferentially adsorbed by Fuller's Earth. These findings confirm that the limestone/Fuller's Earth adsorption of a wide range molecule types will be of great benefit to adsorb common ignitable liquids as those liquids contain polar, slightly polar and non-polar compounds. This was confirmed in adsorbent evaluation in Chapters 4 and 6 of this thesis.

Chapter Six

The Blind 'Field Evaluation' of a New Adsorbent

6 Introduction

A mixture of and limestone and Fuller's Earth (10:1 w/w) (section 4.8) was chosen as a new adsorbent for evaluation in a blind field evaluation experiment involving a real compartment fire scene, various ignitable liquids and fire suppression. To be accepted as an adsorbent of common ignitable liquids the new adsorbent mixture had to fulfil the criteria laid out in section 4.5.1. As was the case in section 4.7.4, this evaluation was setup with the analyst having no knowledge of the setup, ignition and suppression of the fire, or if any ignitable liquids were used. The analyst was faced with a cooling fire scene (forty five minutes after fire successful suppression), partially combusted fuels such as furniture, broken window glass and fire debris.

The scene of the fire was a fully furnished compartment supplied and managed by a team from Essex County Fire and Rescue Services (ECFRS) at Ministry of Defence Police and Guard Agency (MDPGA), Wethersfield. The team from ECFRS were instructed by a third party to enable this research to be completed blind.

6.1 The fire scene

The building where the field trial took place at Wethersfield was a pre-fabricated building which was built from individual containers known as units 1–3. The centre unit, Unit 2 (Figure 6.1 and Figure 6.2) was used for the field trial. The compartment dimensions were 4.880 m x 3.005 m x 3.100 m (45.46 m^3). There were 2 PVC framed windows and 1 PVC door. The walls and ceiling were constructed from plaster boards. The skirting boards were made from Medium Density Fibreboard (MDF).

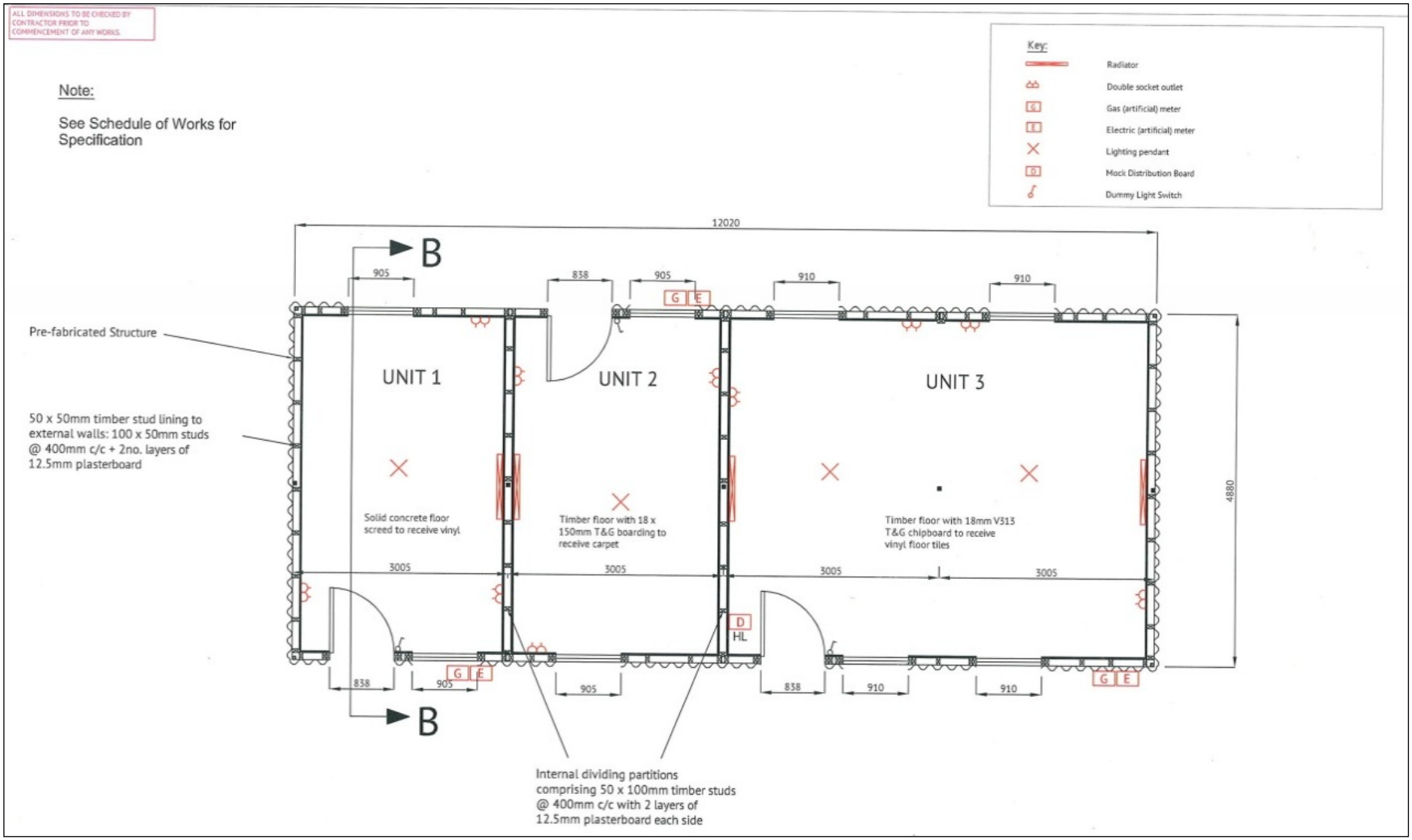

Figure 6.1 A plan view of the compartment fire scene (unit 2), MDPGA Wethersfield

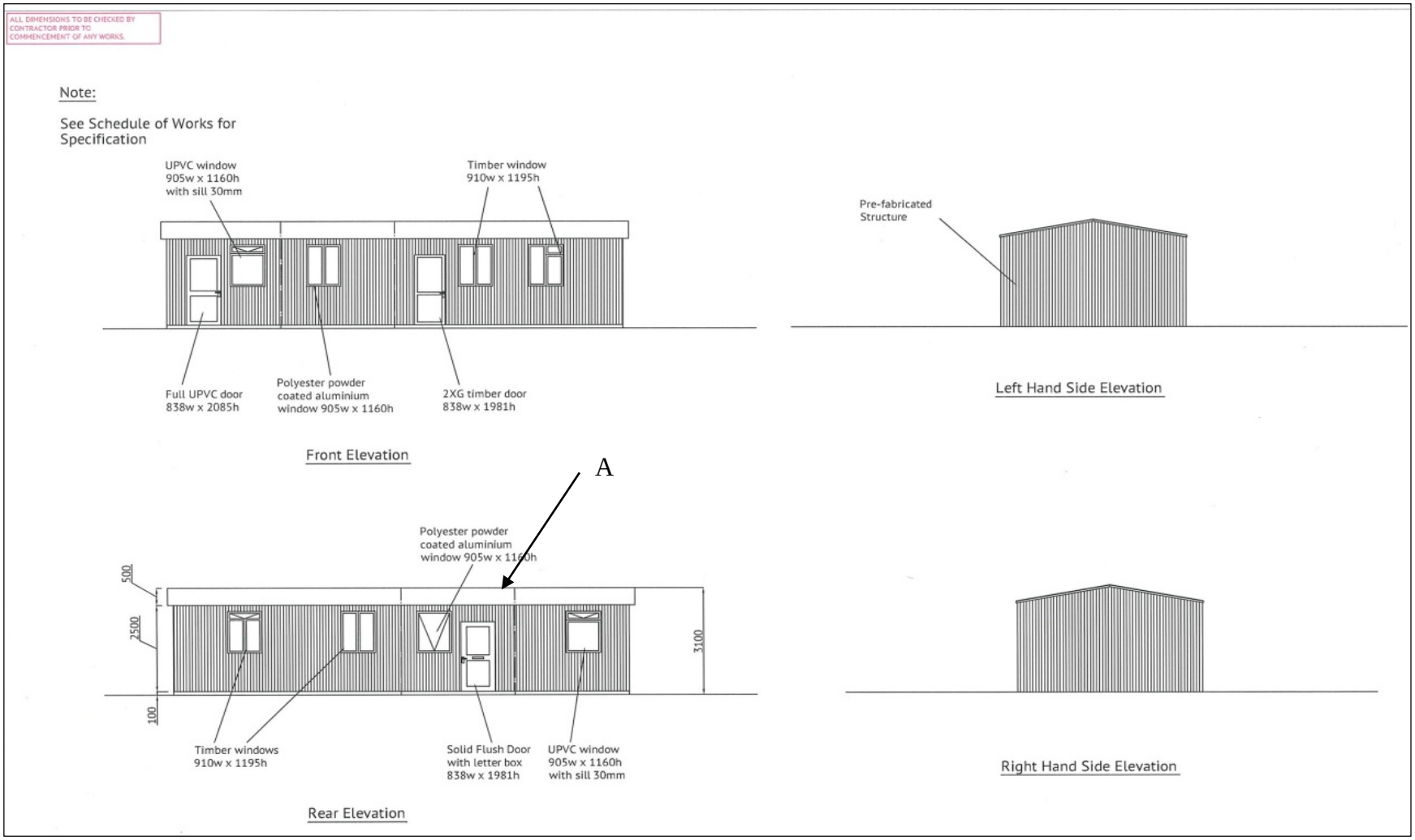

Figure 6.2 An side elevation view of the compartment fire scene

The fuel load of the compartment consisted of the following (Figure 6.3): Single bed with feather down quilt and pillows and shredded paper; carpet flooring; 2 seat sofa; 2 m x 0.6 m x 0.3 m polymer wardrobe; circular wooden table with 2 wooden chairs with leather seats; a book case (0.8 m high) with books and a ceramic bowl containing a gel substance. There was also a filled upright CD/DVD rack. A chair with a coat was close to the foot of the bed and adjacent to the wardrobe.

Figure 6.3 A photograph of the compartment Unit 2 showing furnishing fuel loads prior to ignition

6.2 Setting the fire scene

Ignitable liquids including petrol, diesel, white spirit and alcohol gel were poured onto various surfaces within the compartment and then controlled ignition was initiated by ECFRS personnel. The fire was allowed to progress to flashover and continued until fifteen minutes post flashover. Fire suppression was conducted by trained ECFRS personnel using modern fire fighting methods with water (section 6.6). Figure 6.4 shows the compartment during combustion and Figure 6.5 shows the compartment post combustion and also where ignitable liquids were found. This information was divulged to the analyst and author of this research post-fire and the author was not present at all during the pre-fire or actual fire phases.

Figure 6.4 The combustion of furnishings inside Unit 2 with trained fire fighters in the foreground

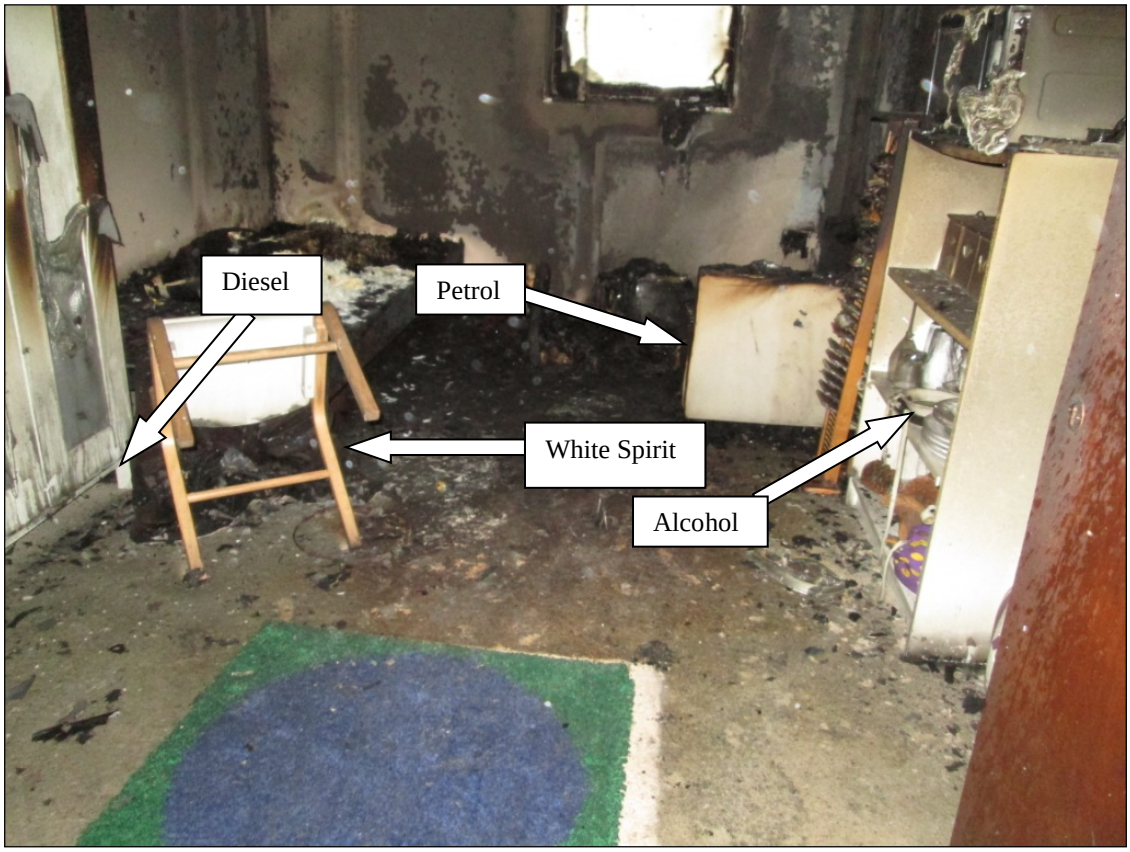

Figure 6.5 Unit 2, the destruction of furnishings post combustion and fire suppression and locations of ignitable liquids found. Identification of ignitable liquids was enabled post-fire

6.2.1 *Deciding where to sample with the adsorbent*

In the laboratory, the adsorbent mixture had been used on paving slabs with success, but at a real fire scene, one is confronted with a range of substrates that might or might absorb, adsorb or not absorb/adsorb ignitable liquid residue. The decision to sample was based on:

a. Where the main combustion had taken place

b. Where there was a strong ignitable liquid like smell in the air

c. On the examination of physical evidence

6.3 Aim and Objectives

The aim of the blind field evaluation was to determine if the adsorbent mixture limestone/Fuller's Earth (10:1 w/w) could adsorb and desorb common ignitable liquid target compounds and allow the positive identification of ignitable liquids. The ratio of limestone was increased from 9:1 w/w to 10:1 w/w from the recommendations from section 4.8.

Furthermore, it was also important to repeat the objectives of short oven time from section 3.9 for headspace adsorption (post olfactory test) using Tenax TA® and to reduce the flow to the column by changing the split flow settings (section 4.8) on ATD-GC-MS to evaluate overloading.

6.4 Materials and Methods

6.4.1 *Materials*

Adsorbent: Mixture of screened limestone/Fuller's Earth (10:1 w/w). Other materials included: Various sizes of Rilsan® polyamide 11 bags and bag ties (WA Products, England; various size DIY paint brushes (Homebase); a plastic dustpan and adhesive bag labels, PPE (Seton, UK) and grinding apparatus (Retsch GmbH) PM100 with 80 mL ZrO_2 jar, and 5 x 20 mm ZrO_2 balls. All other materials used for the blind field evaluation are listed in section 4.6.1.

6.4.2 *Method*

6.4.3 *Adsorbent preparation for use at the fire scene*

The chosen adsorbent mixture of limestone/Fuller's Earth (10:1 w/w) was dehydrated overnight (section 4.6.2.1) and transferred to a 0.5 L plastic bottle with a screw-top lid. The

Retsch grinder was used to grind the adsorbent mixture to a grain size of 63µm (500 rpm x 6 min), and then heated to 90 ^{0}C for 18 hours.

6.4.4 *Fire Scene Method*

The procedure of collecting the adsorbent mixture was identical to the method stated in Section 2.2.2. As a summary, the adsorbent mixture was sprinkled from its container onto the area of interest. A period of 20 minutes elapsed in order for the adsorbent to adsorb volatile compounds it had come into contact with. This may have been ILR or pyrolysis products (section 1.4) or both. A clean paintbrush was used to sweep the adsorbent material into a Rilsan® bag. A brand new paintbrush was used for every collection. Where there was difficulty gaining access to hold a Rilsan® bag open, a dustpan was used to initially collect the adsorbent material and then brushed into a Rilsan® bag. Bags were labelled and marked on the outside, and then placed into another Rilsan® bag. Both inner and outer bags were plasticuffed with a 'swan neck' knot to prevent gas escaping into the atmosphere for later laboratory analysis. A Rilsan bag was also used to capture the compartment air by holding the bag open and then tying the bag with a swan neck knot and double-bagging as a sample of the background air. This was important as any resultant chromatogram from this control would show if any ignitable liquid compounds were still in the gas phase and also act as a background control so that detected compounds could be deducted from sample results. Only adsorbent samples were recovered leaving the substrate behind. This is discussed in section 6.5.

6.4.5 *Laboratory Preparation and Analysis Methods*

These procedures were the same as methods described in sections 3.6.3 & 3.6.4. In addition, preparation included the removal of fire debris from the adsorbent using a pair of stainless steel tweezers. The ATD method is the same as previously described in section 3.6.3 but the inlet and outlet split flow was adjusted to 40 mL/min as discussed in section 4.7.4.5. As a summary, previous testing in this research had indicated that it was easy to overload the detector with adsorbed ignitable liquid compounds and so make identification of target compounds more difficult.

6.5 Results and Discussion

The adsorbent mixture was deployed at various locations in Unit 2 (Table 6.1). Each adsorbent was placed for twenty minutes before being recovered. The mixture was poured from its container until enough material covered the area of interest. At all locations except the left hand side of the sofa, the adsorbent mixture was recovered with a new paintbrush and a Rilsan® bag. On the left side of the sofa, the adsorbent was recovered using a dustpan, paintbrush and Rilsan® bag. The dustpan was only used for this task once. It was placed in the Rilsan® bag along with the paintbrush. All the paintbrushes were placed into the bag they had been used to sweep up the adsorbent mixture so that they were kept separate from other materials to prevent contamination and also they could be analysed if necessary.

After twenty minutes of being deployed, the adsorbent was recovered into Rilsan® bags using disposable paint brushes. Consideration was given to the fact that the use of the paint brush meant that other material would find its way into the bag as well. The recovery of the adsorbent that was in the sofa seat area needed the removal of sofa springs in order to make room for a Rilsan® bag. The removal of a substrate such as carpet is a further step that could offer the investigator more evidence that an ignitable liquid was used. For example, the substrate may reveal char depth (De Haan & Icove, 2013, pp. 289-290) or other information about the story of the fire. In this case, the recovered adsorbent and substrate could then be separately bagged and then examined at the laboratory. Any correlation of identified ignitable liquid in both substrate and adsorbent could strengthen evidence in any conclusion reached. However, the use of an adsorbent is an alternative method of sampling suspected ignitable liquid areas, and is particularly useful to use on areas where the removal of the substrate is complicated, or where areas have limited space for mechanical cutting/digging. In these circumstances the adsorbent is a viable alternative to substrate collection. The decision not to collect substrate was based on the objectives, which was to determine if the adsorbent could adsorb/desorb ignitable liquid compounds at a real fire scene.

The screening procedure described at section 3.4 was undertaken for all samples and only two were found to have a strong smell (Table 6.2). Therefore a recommended oven time of three hours was chosen for these samples (section 3.10) and six hours was chosen for the

remaining samples. Only the bottom end of the adsorbent tube was fully exposed to the headspace vapours. The decision to only expose the bottom end of the tube was based on the preliminary findings which indicated detector saturation (section 3.10).

Table 6.1Adsorbent mixture limestone/Fuller's Earth (10:1 w/w) deployment locations and observations

Location in Unit 2	Summary of Observations	Ignitable Liquid identified by laboratory analysis? (type)	Identified ignitable liquid	Notes
Shoes near door	No smell of IL[1]. Shoes stained and carpet damp. No signs of pyrolysis or charring in this area.	No	none	Figure 6.6
Ceramic soup bowl on table	No smell of IL. Moisture present inside bowl. Heavy soot on bowl and surrounding table. Table intact and no charring. Indicated by ECFRS personnel that no IL used and so used as a background control.	Not applicable	none	Figure 6.8
Corner of bed next to wardrobe	Charring of bed cover, partially combusted shredded paper strips. Possible smell of ignitable liquid similar to diesel.	No	none	Figure 6.10
Foot of bed next to wardrobe	Strong smell similar to diesel, greasy stains on wall next to bed corner. No signs of pyrolysis or charring.	Yes (heavy petroleum distillate)	Heavy petroleum distillate	Figure 6.12
Carpet underneath chair next to bed	Overturned chair with partially melted coat hanging on chair back. Smell similar to diesel. Coat melted onto carpet.	Yes (medium petroleum distillate)	Medium petroleum distillate	Figure 6.14
Corner of pillow on bed	Extensive charring of bed cover. Also charred and partially charred shredded paper strips on bed surface. High concentration hydrocarbons detected by DIM detector.	No	none	Figure 6.16
The Sofa	Left hand side of sofa almost destroyed by burning. Right side of sofa suffered burning but not destroyed. No elevated hydrocarbon concentration levels detected	Yes (petrol)	Petrol	Figure 6.19 Figure 6.20
Bowl on bookcase	Green colour solid jelly-like substance in a cereal bowl on middle shelf of bookcase	Yes (alcohol gel)	Alcohol	Figure 6.22

[1] Ignitable Liquid

Table 6.2 Results of the analysis of all adsorbent mixture samples recovered from Unit 2

Target Compound from ASTM E1618-11 (2011)	Ion used to identify	Adsorbent Mixture Collected Samples							
Description		Shoes near door	Ceramic soup bowl on table	Corner of bed next to wardrobe	Foot of bed next to wardrobe	Carpet underneath chair next to bed	Corner of pillow on bed	The Sofa	Bowl on bookcase
Screen Test – Strong smell?		No	No	Yes	Yes	Yes	No	No	No
Analyst identified as?		No ignitable liquid	No ignitable liquid	inconclusive	Heavy petroleum distillate	Medium petroleum distillate	inconclusive	Petrol	Alcohol
ECFRS identification post analysis		None	None	None	Diesel	White Spirit	None	Petrol	Alcohol Gel
Oven Adsorption Time		6 hours	6 hours	6 hours	3 hours	3 hours	6 hours	6 hours	6 hours
ethanol	43, 45	X	X	X	X	X	X	X	√
Isobutyl alcohol	43	X	X	X	X	X	X	X	√
C_2-alkylbenzenes	91	X	X	√	√	√	X	√	√
C_3-alkylbenzenes	105	X	X	√	√	√	X	√	X
C_4-alkylbenzenes	119	X	X	√	√	√	X	√	X
n-C_9 - n-C_{11}	57	X	X	X	√	√	X	√	X
n-C_{12} - n-C_{15}	57	X	X	X	√	X	X	X	X
indane	117	X	X	√	√	√	X	√	X
C_1-indanes	117	X	X	√	√	√	X	√	X
n-cyclohexanes (C_4-C_5)	83	X	X	X	√	√	X	√	X
Trans-decalin	138	X	X	X	√	√	X	X	X
4,7-dimethylindane	131	X	X	√	√	X	X	√	X
n-cyclohexanes (C_6-C_9)	83	X	X	X	√	X	X	X	X
C_1-naphthalenes	142	X	√	√	√	X	√	√	X
C_2-naphthalenes	156	X	√	√	√	X	√	√	X
2,3,5-trimethylnaphthalene	170	X	X	√	√	X	√	X	X
n-C_{16} - n-C_{18}	57	X	X	X	√	X	√	√	X
Pristine and phytane	57	X	X	X	√	X	X	X	X
n-C_{19} - n-C_{20}	57	X	X	√	√	X	X	√	X
n-C_{21} - n-C_{22}	57	x	x	X	√	X	X	X	X

6.5.1 *Shoes near Door*

The shoes appeared stained and wet (Figure 6.6).There was no sign of combustion on the floor, but the coat hanging above the shoes did show signs of combustion. The results are shown at (Table 6.2). The TIC (Figure 6.7) showed minor peaks at 9.88 minutes; 11.32 minutes and 12.68 minutes. An examination of EICs did not reveal any target compounds of ignitable liquids. The coat was closer to hot gases pushing down from the ceiling during post flash-over so this is to be expected. The temperature at the floor did not exceed 50 ^{0}C (Hadjicostas & Ainger, 2013).

Figure 6.6 Shoes near door with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

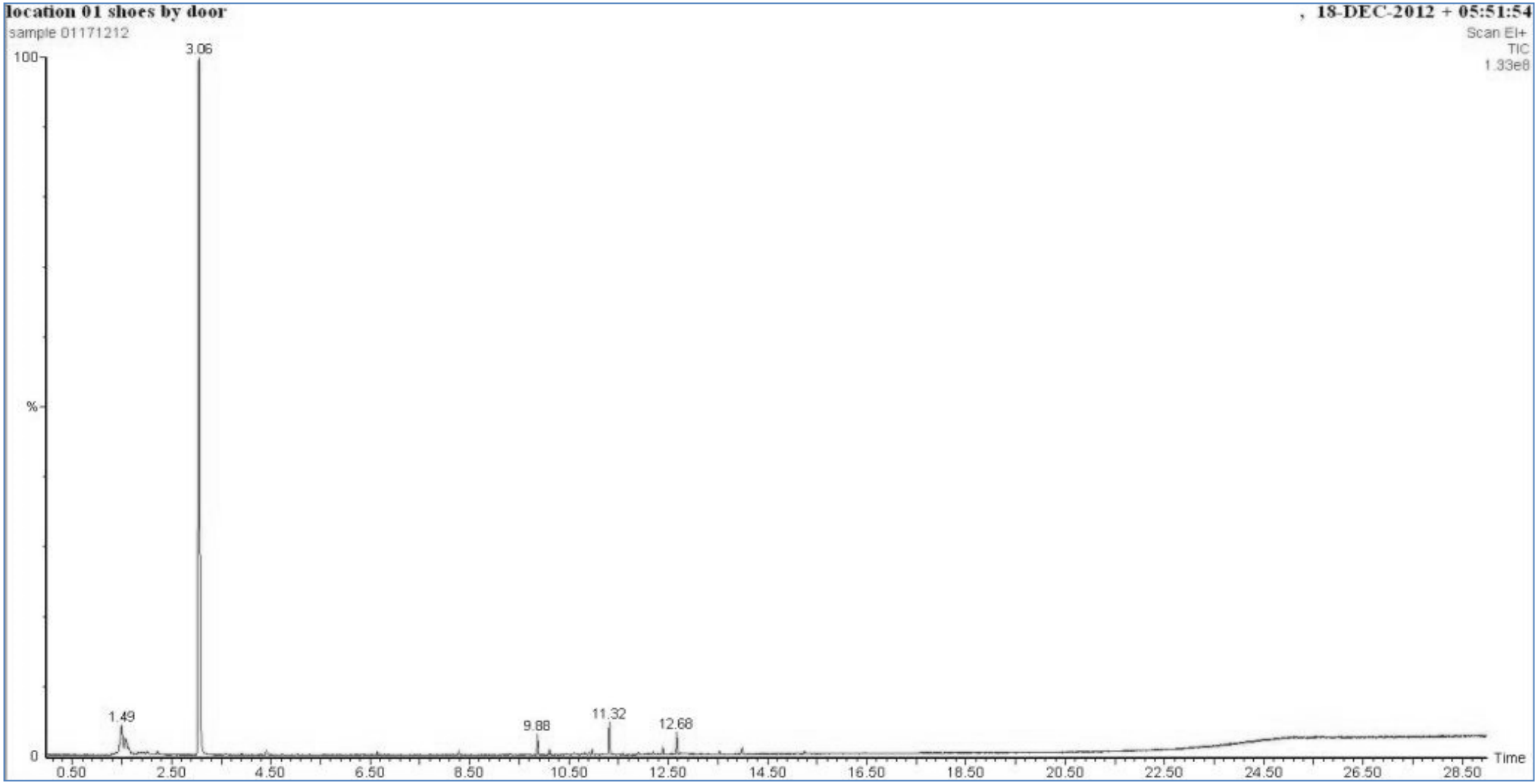

Figure 6.7 TIC of the shoes near door

6.5.2 *Ceramic Soup Bowl on Table*

This area was used as a background control as it was believed that no ignitable liquid had been used in this area. This was indicated by the third party. However, there appeared to be some moisture left in the bowl from fire suppression (Figure 6.8). Although the TIC (Figure 6.9) showed numerous peaks, the target compounds 2-methylnaphthalene, 1-methylnaphthalene and 1,3-dimethylnaphthalene were found using EICs but no other target compounds of ignitable liquids were identified (Table 6.2). These compounds may have originated from gas phase ignitable liquids or precursory gas phase compounds such as those found in plastics (section 1.4.1) Other compounds tentatively identified (due to not having standards for these compounds) included benzaldehyde and acetophenone which are typical combustion products (section 1.4).

Figure 6.8 Ceramic soup bowl on table with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

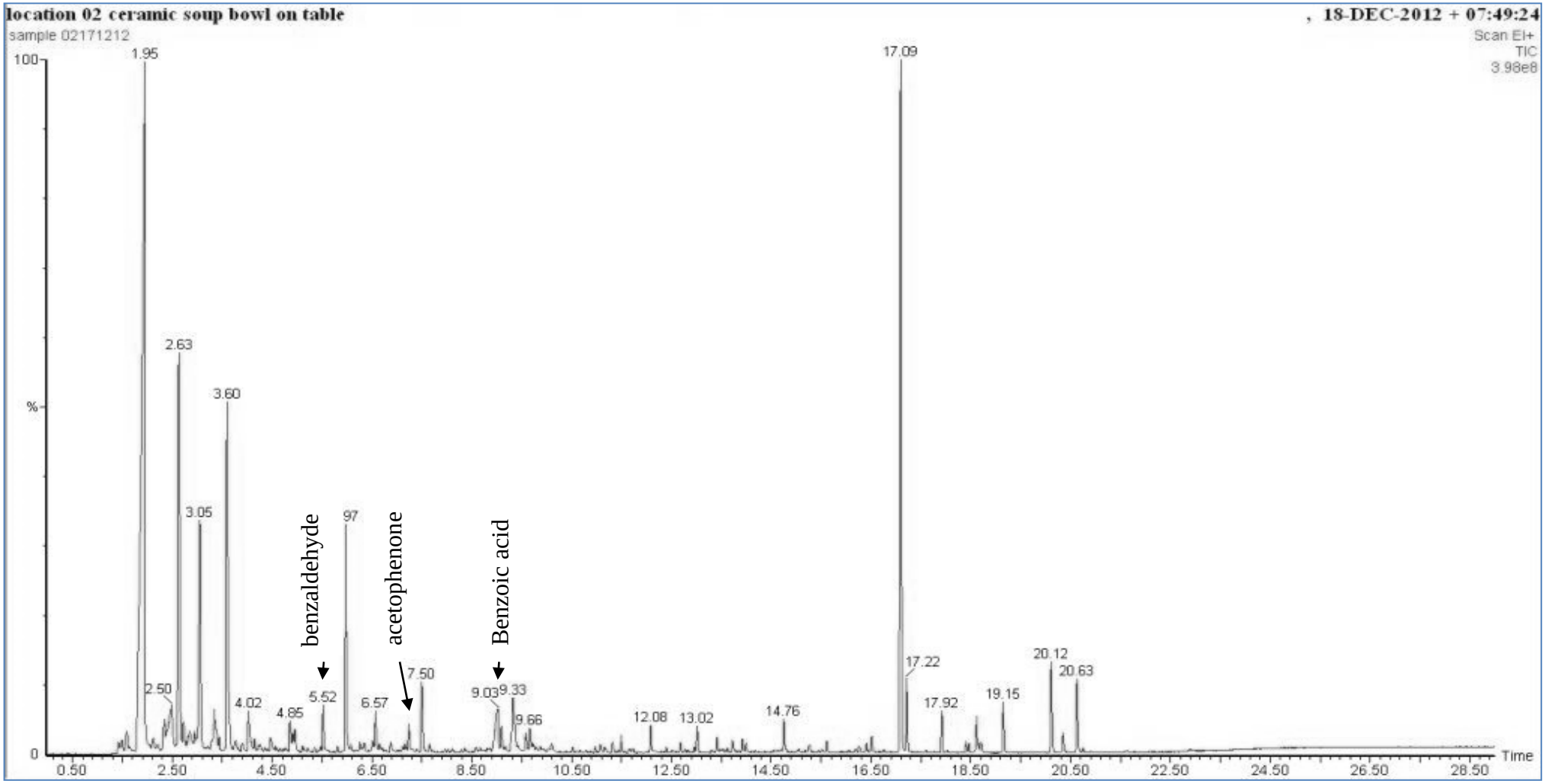

Figure 6.9 TIC of the ceramic soup bowl on table

6.5.3 *Corner of Bed next to wardrobe*

Although the bed cover was charred and partially combusted paper strips littered the top of the bed (Figure 6.10), there were no signs of damage or charring to the wall or medium density fibreboard (MDF) wardrobe next to this spot. Therefore it is unlikely that this was the origin of the fire and it was likely that the hot gas layer was responsible for the combustion of the paper strips. This area was sampled with the adsorbent mixture as a smell of ignitable liquid similar to diesel emanated from this location. The TIC (Figure 6.11) shows many peaks that show no definitive patterns of ignitable liquids (section 1.8.1). However EICs showed that some target compounds of ignitable liquids in this area (Table 6.2). All alkylbenzene compounds, indane compounds and naphthalene target compounds were identified. However, the abundance of these compounds was low indicating the possibility that the compounds had circulated in the room during the fire and settled onto the surface of the relatively untouched bed, rather than having been used in this area (section 6.5.4). With regard to paraffinic products (section 1.4.2), only octadecane was identified from alkane target compounds and there were no cycloalkanes were identified. Because only some target compounds had been identified but not others this sample was marked as inconclusive.

Figure 6.10 Corner of bed next to wardrobe with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

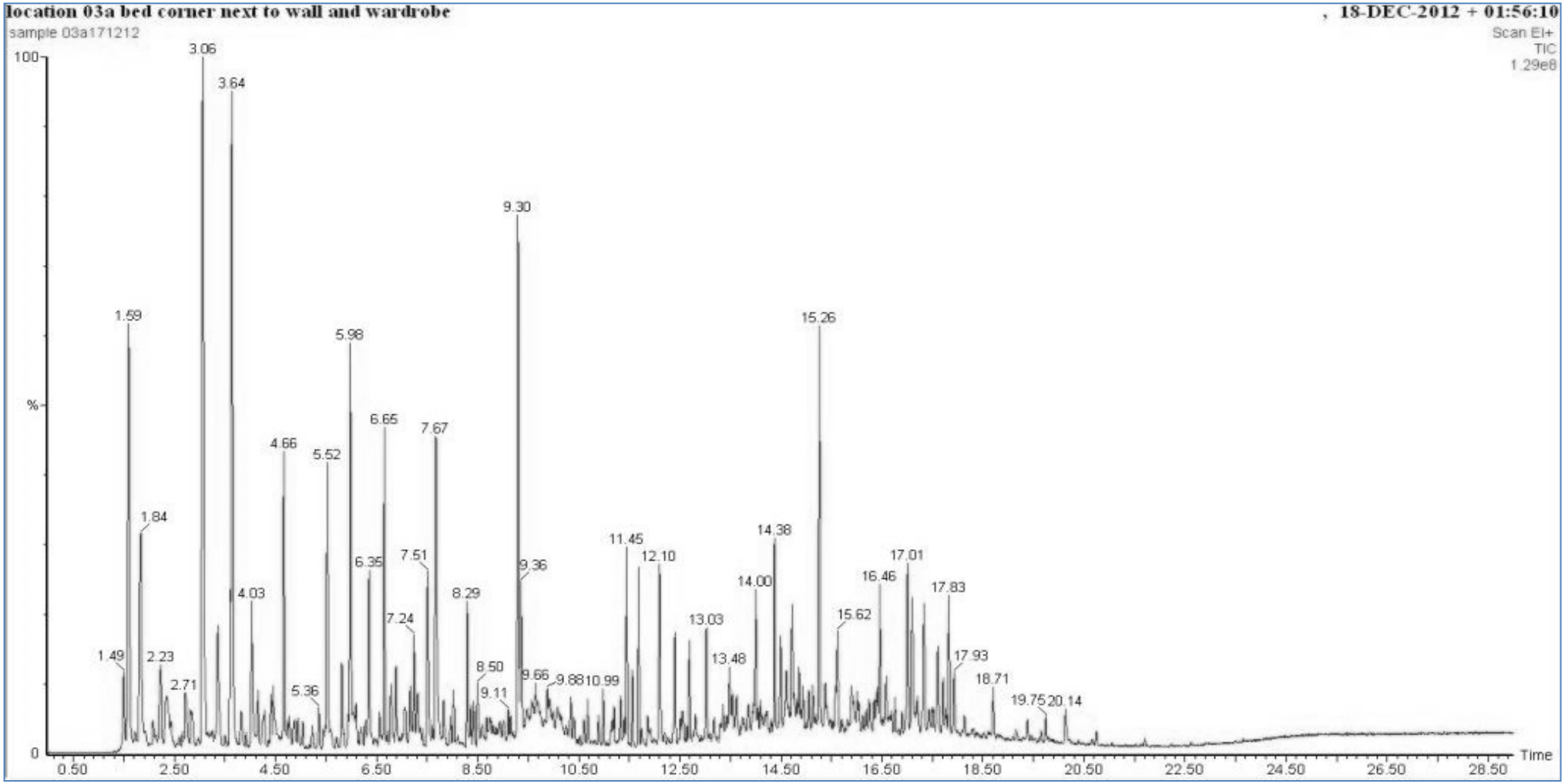

Figure 6.11 TIC of area known as corner of bed next to wardrobe

6.5.4 *Foot of bed next to wall and wardrobe*

This area was below the corner of the bed in the previous section. Greasy stains were noticed on the wall above the skirting board (see arrows on Figure 6.12). The carpeted floor was littered with ash and soot and there was a strong smell similar to diesel at this location. The adsorbent was spread onto the carpet area below the greasy wall stains. The adsorbent was recovered and at that point an odour similar to diesel was detected by sense of smell and the sample was marked for three hours oven time (Table 6.2; section 4.8).

The TIC at Figure 6.13 showed a Gaussian shape spread of peaks with the most abundant peak at 11.69 minutes. EIC analysis revealed all target compounds for diesel had been identified (Table 6.2) and therefore a positive identification of a heavy petroleum distillate was made.

This area is slightly below the area from the previous section where alkylbenzene, indane and naphthalene target compounds were identified on the bed cover. Those compounds are relatively volatile compared to heavier alkane compounds and so could have migrated from the carpet to the top of the bed cover, which supports the theory that there was no ignitable liquid on the bed cover. Post fire it was revealed that diesel had been poured onto the carpet next to the wall.

Figure 6.12 Foot of bed next to wardrobe with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

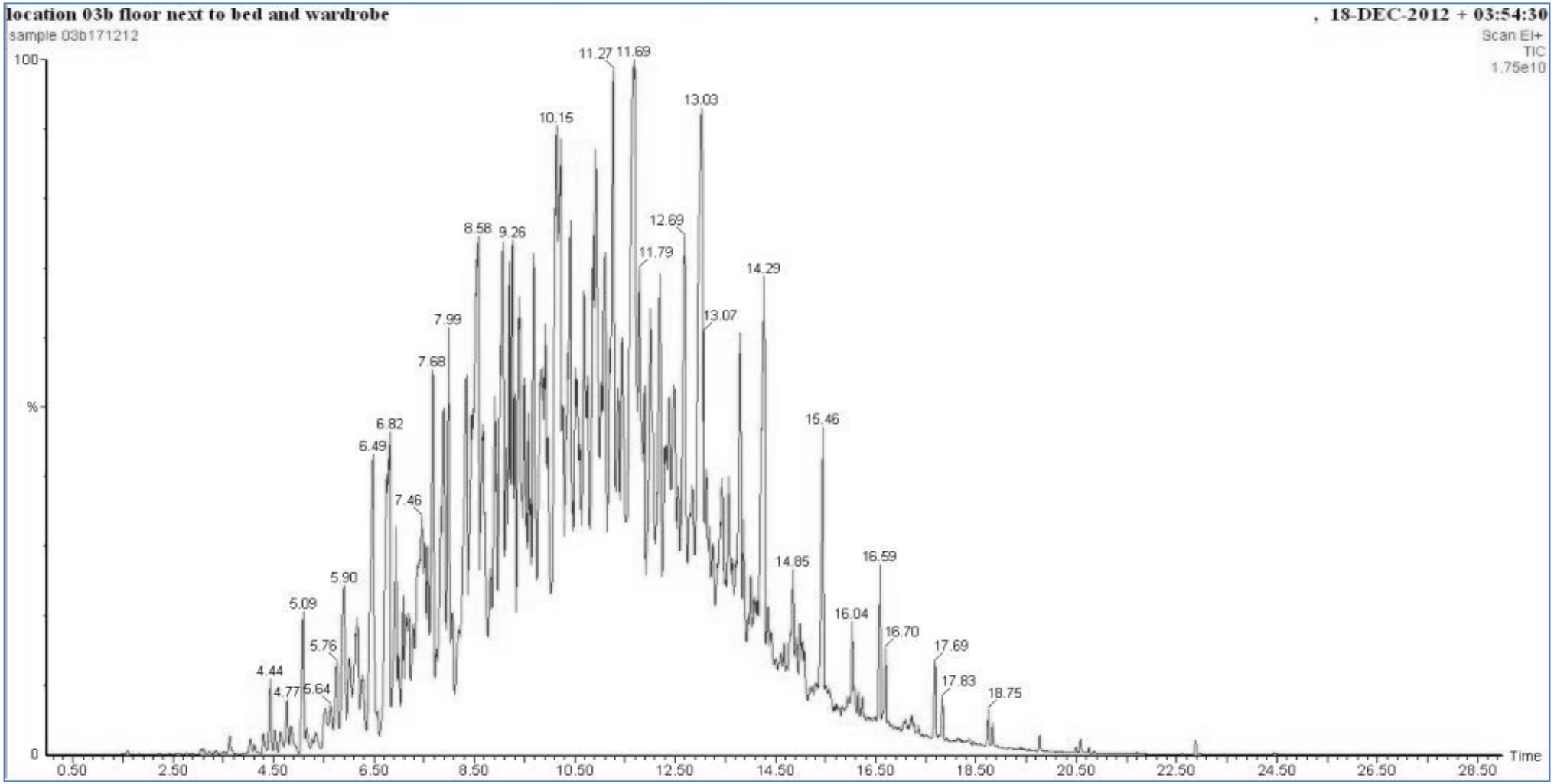

Figure 6.13 TIC of area of floor next to bed and wardrobe

6.5.5 *Carpet underneath chair next to bed*

This area contained an overturned chair with the remains of a coat draped over the back. The coat appeared to have partially melted. The coat was a made from a polyester material (obtained from coat label) that had partially melted onto the carpet below it (Figure 6.14). When the coat was peeled off of the carpet, it showed that the carpet was not charred and there was a smell similar to diesel in the air. Therefore this area was sampled with the adsorbent mixture. The oven time was set to three hours for this sample (Table 6.2).

The TIC showed a narrow Gaussian pattern distribution (5.37 minutes to 8.32 minutes) that resembled a medium petroleum distillate (Figure 6.15). EIC analysis identified ignitable liquid target alkanes from nonane to undecane and target cyclohexanes from butylcyclohexane to pentylcyclohexane as well as *trans*-decalin. Propylcyclohexane was also identified but this compound is not a target compound. Both methylindane target compounds were identified. All alkylbenzene target compounds were identified. There were no naphthalene target compounds identified. All the compounds positively identified show that a medium petroleum distillate was present. Post fire it was revealed that white spirit had been poured into the pocket of the coat hanging over the chair.

Figure 6.14 Carpet underneath chair next to bed with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

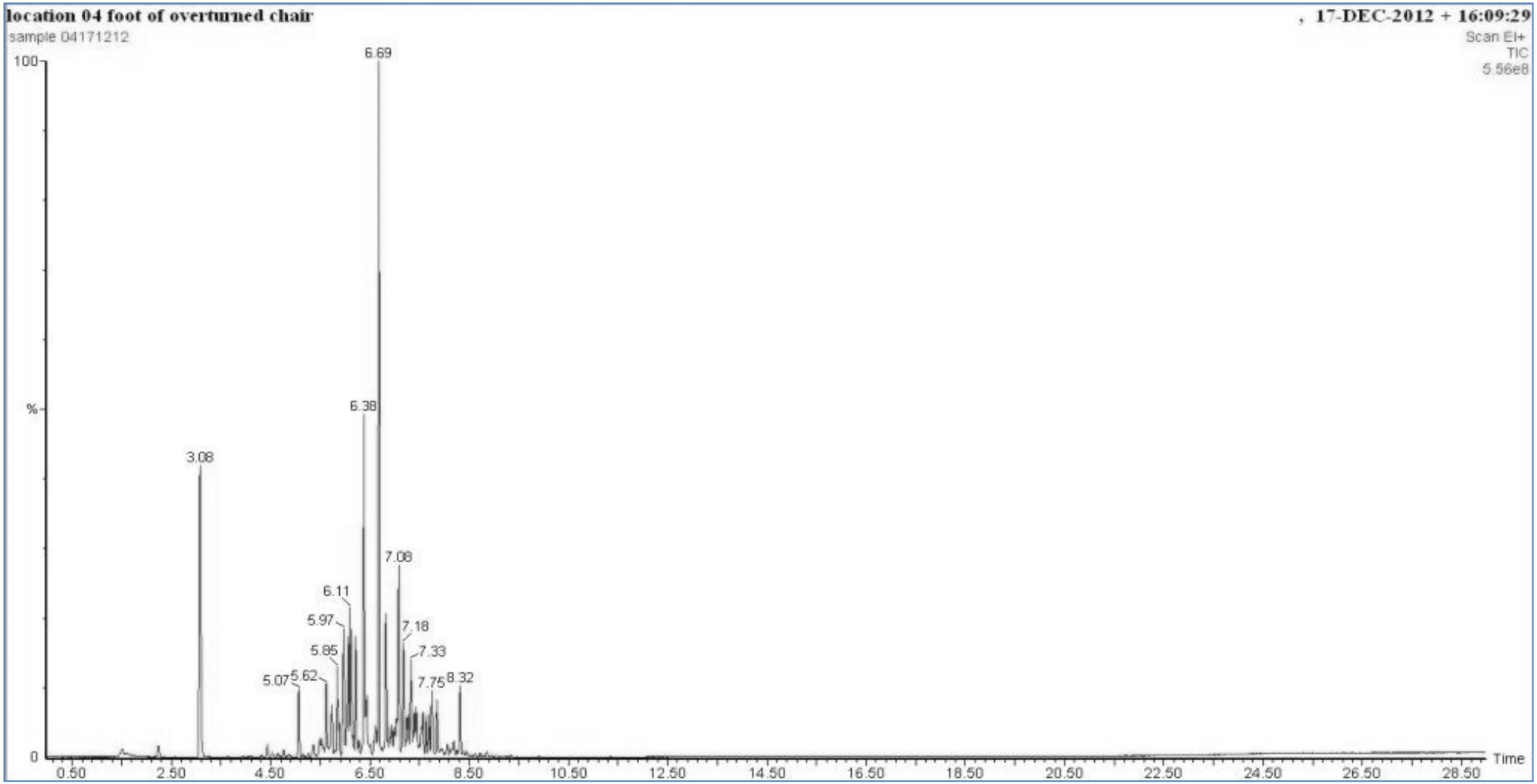

Figure 6.15 TIC of area known as foot of overturned chair

6.5.6 *Corner of pillow on bed*

Extensive charring of the surface of the pillow was evident and many charred or partially charred shredded paper strips were in this area lying on the surface of the bed (Figure 6.16). The adsorbent mixture was sprinkled on the bed and pillow surface in this area. The TIC showed no obvious pattern of ignitable liquids (Figure 6.17). EIC examination showed target compounds hexadecane, heptadecane and octadecane, but there were no other target alkanes or cycloalkanes found (Table 6.2). All naphthalene target compounds were identified (C_1 to C_3) but no other target compounds of any type were identified. These compounds could be the result of combustion products from the pillow or other source but there is not enough evidence to show that there was an ignitable liquid here. Therefore this sample was marked as inconclusive.

Figure 6.16 Corner of pillow on bed with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

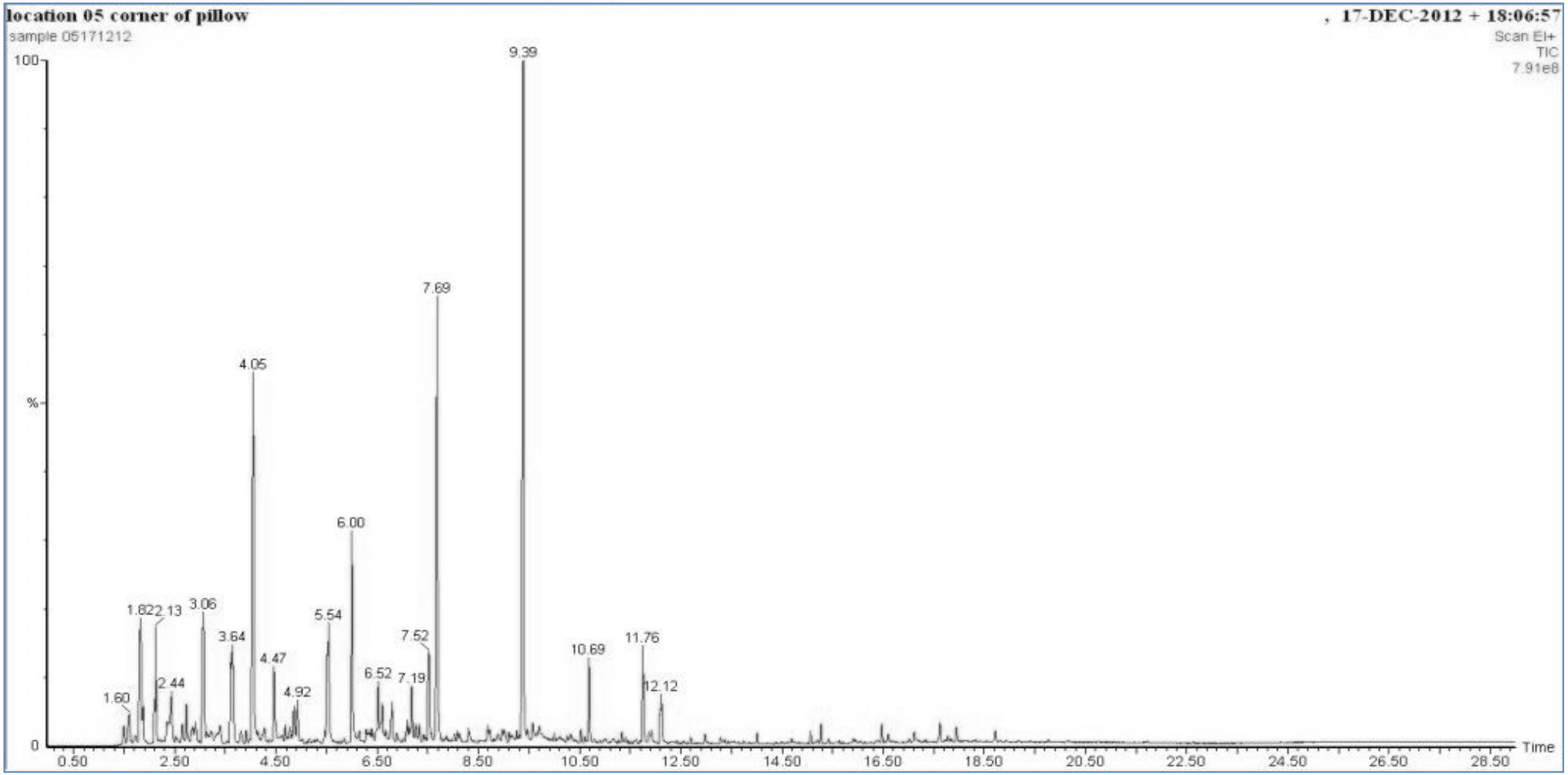

Figure 6.17 TIC of the area known as corner of pillow on bed

6.5.7 *Sofa (front, left and right)*

There was an obvious ‘V’ shape above the sofa on the plasterboard walls. The left side of the sofa was more damaged than the right side. The spalling on the wall above the couch showed that this area had been subjected to a very high temperature (Figure 6.18), but this would be normal if a large fuel load such as a sofa was in this area. The room corner next to the sofa acts as an entrainer of hot gases (De Haan & Icove, 2013, p. 269) and these gases spread across the ceiling where they can ignite other fuels in the room.

Figure 6.18 The area above the sofa with a ‘V’ shape on the plasterboard walls

The area to the right of the window contained what looked like the remains of a sofa. Underneath where the left hand side sofa seat used to be were the remains of the sofa base, with five springs (some of which were detached) and a charred frame. The floor was littered with combusted fabric material.

Figure 6.19 Left hand side of sofa seat with applied adsorbent limestone/Fuller's Earth (10:1 w/w)

The right hand side of the sofa seat did not suffer the same level of destruction as the left hand side. The right side and rear structures were still intact (Figure 6.20). Five springs were still attached to the front of the sofa. The frame had suffered from superficial charring only. On the floor in this area were the remains of combusted fabric and towards the rear was a comparatively un-burnt patch of carpet. The physical evidence such as the 'V' shape patter, plaster spalling and deep charring showed that a high fuel loading had been in this area prior to ignition. This is reason enough to sample this location for possible ignitable liquid use (Hadjicostas, 2013). The adsorbent mixture was sprinkled in front of the couch and in the remains of the left and right seat which was on the floor below each seat (Figure 6.19).

Figure 6.20 Right hand side of sofa seat

The adsorbent mixture was collected and analysed at the laboratory. The results are at Table 6.2; Figure 6.21; Appendix 15 & Appendix 16). The TIC showed known ignitable liquid patterns (section 1.8.1) at early elution times (4.29 minutes to 6.36 minutes) such as ‘the ‘Castle Group’ and the ‘Three Musketeers’. The use of EIC analysis enabled the positive identification of petrol as all target compounds for petrol were identified.

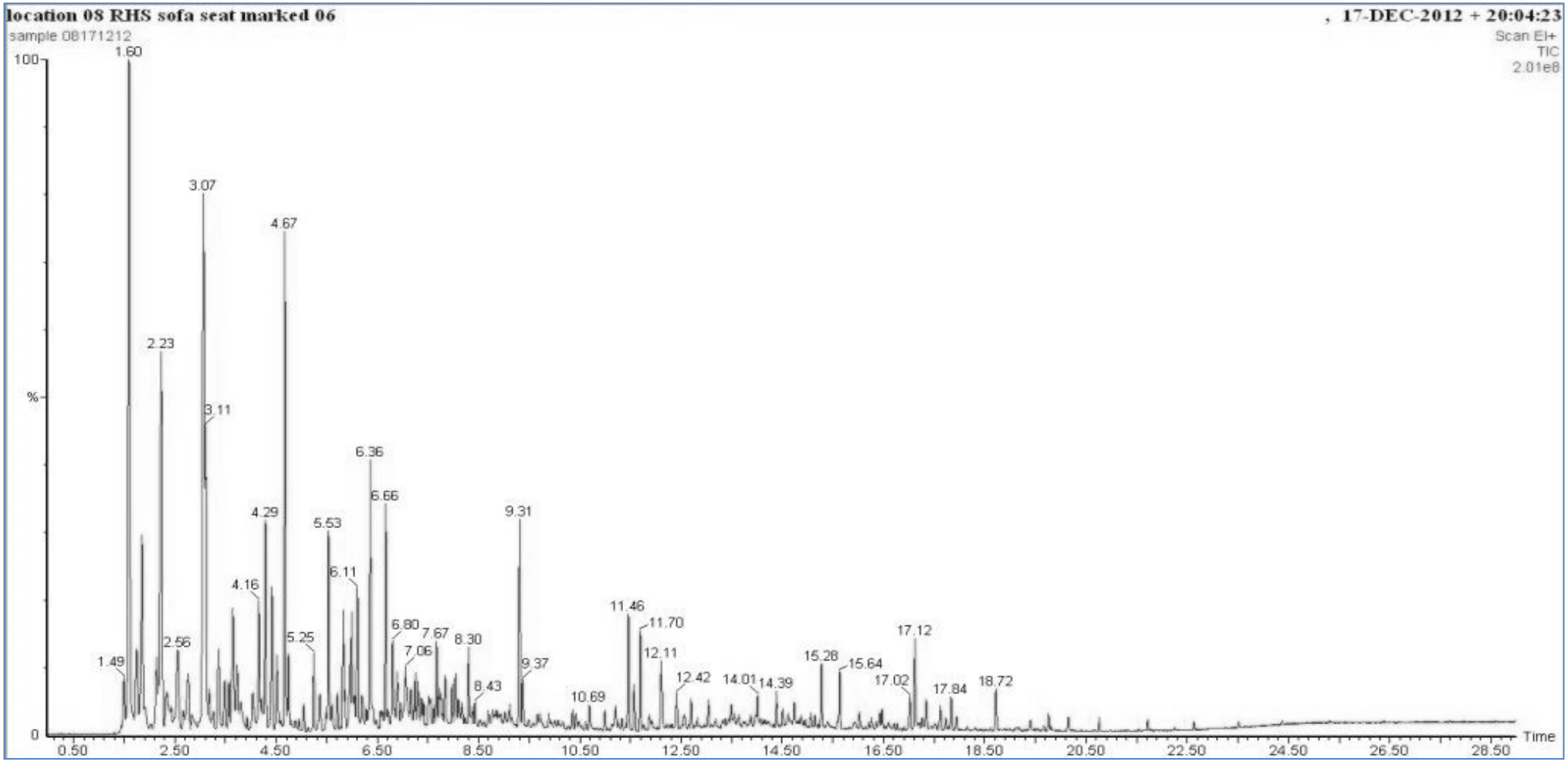

Figure 6.21 TIC of right hand side of the sofa base

6.5.8 *Ceramic bowl on bookcase*

A green coloured gel-like substance was present in the bowl on the bookcase (Figure 6.22). This bowl was situated 430 mm off of the ground on the middle shelf of the bookcase. The bookcase was covered in soot and plastic shelf edges had partially peeled off of the shelves but there was no sign of charring above the bowl and no sign of material fallen to the floor such as a wick. The glassware on the same shelf remained intact and in shape but covered in soot. There was an odour similar to alcohol in this area and so the adsorbent mixture was sprinkled onto the bowl contents covering the green gel-like substance.

The results (Table 6.2) and TIC (Figure 6.23) of this sample showed an abundant peak at 1.5 minutes and another minor peak at 2.0 minutes. EIC analysis enabled the identification of ethanol and isobutyl alcohol using ions 43 and 45. All C_2-alkylbenzene target compounds were also identified. The adsorbent mixture used for the 'bowl on the bookcase' sample was tentatively identified as an alcohol gel as the analyst did not have a positive control of this liquid and so was unable to substantiate the elution of compounds including ethanol and isobutyl alcohol and C_2-alkylbenzenes (Table 6.2).

Figure 6.22 Ceramic bowl on book case that contained a green coloured gel-like substance

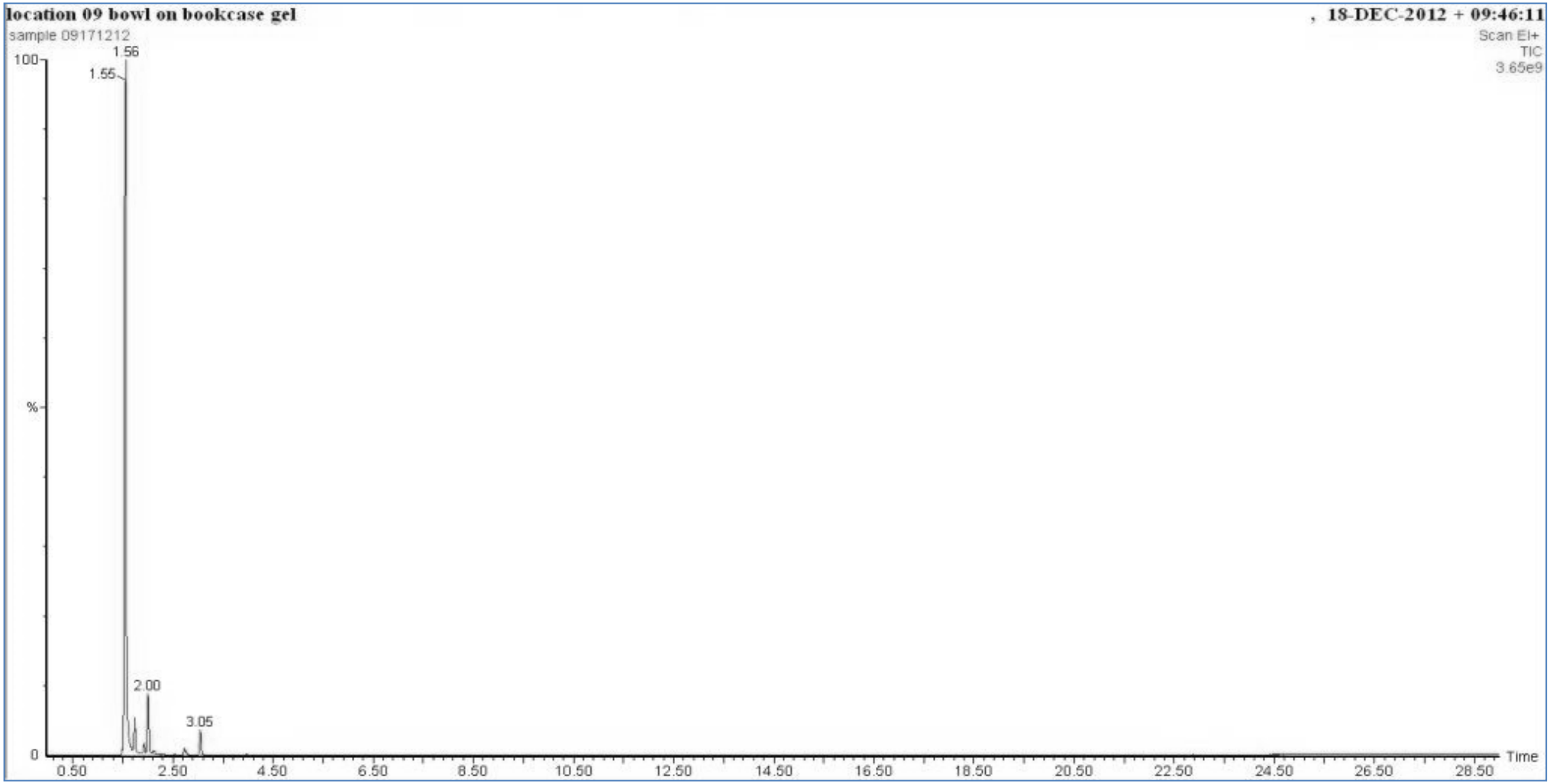

Figure 6.23 TIC of area known as 'bowl on bookcase'

6.6 Further Discussion

The analyst was only present at the scene post fire. According to the lead fire-fighter and 3rd party (Hadjicostas & Ainger, 2013), the fire was allowed to progress complete with a ceiling jet and combustion of other fuels. Water was used to suppress the fire and it was extinguished after fifteen minutes. The fire fighters used a modern technique that used the minimum volume of water necessary (20.0 L) to achieve their aim. It was revealed by the lead officer for the fire investigation unit of ECFRS *(ibid)* that white spirit was poured into the pockets of the coat on the chair for the sample 'Carpet underneath chair next to bed'. A cursory examination of the coat at the scene showed that the bottom portion of the coat (with the pockets) survived but the heat had caused it to stick to the carpet. The adsorbent was applied to where the coat had been and the testing of that sample showed that a medium petroleum distillate had been used (Table 6.2). The cushion and the rest of the sofa ignited with the corner of the wall entraining the fire towards the ceiling (Figure 6.18). At some stage during the fire, the supporting structure under the cushion failed and the cushion dropped to the floor (Figure 6.19 and Figure 6.20). This area was labelled as 'The Sofa' and petrol was identified from laboratory analysis (Table 6.2).

Generally, the mass of adsorbent was not measured but instead was assessed by whether the area of interest was covered sufficiently with at least a single layer of adsorbent. The laboratory test identified a heavy petroleum distillate because of all target compounds for diesel had been identified and this was confirmed by Hadjicostas & Ainger (2013) as being diesel.

Combustion compounds (section 1.4 & Stauffer, et al. (2008), pp. 462-464) such as benzaldehyde, acetophenone and styrene were detected at: The Sofa; ceramic soup bowl on table; bed corner net to wardrobe; corner of pillow on bed and the Sofa. All of these locations were involved in the fire either as a result of direct combustion or in the hot gas layer from the ceiling. These compounds did not interfere with analysis as the use of EIC allowed for the identification of target compounds (section 1.8.1.1).

The ATD inlet and outlet split flow settings had been altered by recommendation (section 4.7.4.1) to 40 mL/min. The chromatograms produced for each sample show that overloading had been reduced so that compounds could be positively identified. Also, the settings indicate that instrument sensitivity has not been compromised by these settings.

6.7 Conclusion

The aims and objectives of this blind field evaluation were fulfilled. The adsorbent mixture (limestone/Fuller's Earth 10:1 w/w) was able to adsorb ignitable liquid residue compounds at a real fire scene from alcohol gel; white spirit; petrol and diesel fuel and subsequently desorb these compounds so that they could be identified using an ATD-GC-MS instrument. The adsorbent does not interfere with analysis, it is easily used being versatile enough to be used on multiple surface types and can easily be collected with bags and brushes. The cost of the adsorbent components is low and on the evidence in this chapter, it is rugged enough to survive real fire scenes including water from fire suppression. Where an ignitable liquid was used the 10:1 w/w limestone/Fuller's Earth mixture was able to adsorb all target compounds and then a positive identification was made using EICs. Even though the ignitable liquids were on different substrates and there was an abundance of precursory and combustion products. It is acknowledged that substrate collection may be carried out in addition to adsorbent collection and is a further step. However, the adsorbent method has shown a considerable advantage over substrate collection in that it can be used to sample from hard surfaces, soft surfaces such as carpets and also awkward or difficult to reach areas.

6.7.1 *Recommendations*

The results from ATD-GC-MS testing (Chapters 3 and 4) and the subsequent evaluation, have shown that the instrument parameters produce repeatable data. Changes were made to the inlet and outlet split as part of the recommendation from preliminary testing (section 4.7.4.5). In this section these changes were implemented and were found to be successful in reducing the volume of sample reaching the detector and causing it to overload. It is now recommended to continue to keep the split flow valve settings at 40 mL/min, but evaluate this change by conducting more tests before concluding that the ATD-GC-MS can cope with case samples that contain high volumes of ignitable liquid residue.

Chapter Seven

7 Conclusion and Future Work

7.1 Conclusion

This research has investigated the use of ad hoc adsorbent materials to collect ignitable liquid residues from fire scenes by UK fire investigators and found that none of them can adsorb all target compounds of petrol and diesel. These materials were tested with an accepted fire debris laboratory analysis method using ACS extraction and GC-MS analysis, and it was found that clay cat litter was able to adsorb ignitable liquid target compounds from petrol but not those from diesel fuel. Garden Lime (limestone) was able to adsorb diesel target compounds but was unable to adsorb light petrol compounds. Other adsorbents such as sand, Tampax®, talc, TENA Lady® and a squeegee device could not adsorb all of these compounds either. This adsorption shortfall shows there is a lack of information in the fire investigation field regarding adsorbent materials and this can jeopardise the identification of target compounds from a fire scene because of the limitations of the adsorbent. Investigators may not be aware that the materials they use to sample fire scenes do not actually work as intended and therefore it becomes difficult for the investigator to arrive at a valid conclusion.

A series of experiments was conducted with various single and mixed adsorbents using Tenax TA® separation and ATD-GC-MS analysis and this culminated in the creation of a clay/mineral mixture that can adsorb a wide range of ignitable liquid compounds from ethanol to docosane. This is the first time that an adsorbent has been reported to be capable of adsorbing such a wide range of compounds and able to be used as a universal adsorbent for common ignitable liquids. The final adsorbent mixture contained limestone and Fuller's Earth (10:1 w/w). This mixture was successful because it has a balanced charge that allows the adsorption of polar molecules such as ethanol, but it can also adsorb heavy non-polar compounds such as docosane. The combined constituent components of this mixture are cheap at £ 8.00/kg (retail price valid 1st Jun 2014) and if the components are packaged in a vacuum pack the adsorbent does not need any pre-deployment treatment such as dehydration in an oven overnight. The adsorbent is easy to use, easy to collect, and does not affect existing fire investigation protocols such as National Fire Protection Association

921 (NFPA) and American Society for Testing and Materials (ASTM E1618-11). It was shown in adsorbent evaluation (Chapter 6) that is not adversely affected by water used in fire suppression.

An ATD-GC-MS was chosen to analyse tested samples, as this instrument uses Tenax TA® adsorbent and is able detect and enable the identification of heavy alkanes such as those found in diesel as well as very light ignitable liquid compounds such as ethanol. The thermal desorber parameters for inlet and outlet split flow initially were set at 10 mL/min but it was found through laboratory tests that the detector can become overloaded with ignitable liquid compounds and therefore identification of target compounds was difficult. The settings were modified first of all to 20 mL/min, and then finally 40 mL/min (Table 7.1). The loss of sample through split valve ratios can lead to a reduction in detector sensitivity, but the final setting does not appear to impact on the non-detection of target compounds and also helps to reduce contamination of the ATD cold trap and GC column.

Another measure was implemented to assist in not overloading the mass spectrometer and that was a reduction in oven adsorption time. Currently sixteen hours has been adopted for both Tenax TA® adsorption and activated carbon strip adsorption as this time span fits into analyst work schedules. However, it was established in this research that optimal adsorption time is between six to nine hours at 90 ^{0}C (Table 7.1) depending on whether there was bulk or trace amounts of ignitable liquid residue detected by preliminary screening. Longer oven times can complicate analysis by raising competition between molecules for adsorption, known as ‘competitive adsorption’. These oven times at 90 ^{0}C enabled the positive identification of all target compounds from a petrol/diesel (1:1 v/v) mixture by using EICs without adverse competitive adsorption and without compromising sensitivity.

Table 7.1 Major achievements of this research

Adsorbent Mixture Component (ratio w/w)	**Preliminary screening**	**Oven time adsorption (Tenax TA®)**	**ATD Split flow valves**	**Characterisation of adsorbent mixture[1]**
Limestone/Fuller's Earth (10:1). Determined by experiment initial ratio 9:1 then adjusted to 10:1 to adsorb heaviest alkanes in diesel. Evaluated at 10:1.	Olfactory or headspace analysis used to determine possibility of ignitable liquids and to prevent detector overload.	Determined optimum adsorption at three to six hours @ 90 ^{0}C depending on preliminary screening result. Statistical analysis determined minor variable adsorption dependent on position in oven.	Tested from 10 mL/min to 40 mL/min. Determined that 40 mL/min should be set for both inlet and outlet set to prevent detector overload	Used Fourier Transform Infrared and X-Ray diffraction to determine structural and phase information about the adsorbent and to identify what minerals were present.

[1] Adsorbent mixture was characterised at 9:1 w/w and not 10:1 w/w (see section 4.8)

The ATD-GC-MS method was tested and evaluated with the aforementioned modified parameters with success. However, more testing still needs to be completed to further evaluate the method in order to ensure that the split-flow parameters are effective at reducing instrument overloading. It is proposed that Tenax TA® and ATD-GC-MS could be adopted by the community as 'The Method' to use for the investigation of ignitable liquid analysis (section 7.2). If adopted, this method may become the future ASTM de-facto method for fire debris analysis using the adsorbent mixture and proposed instrumental settings for ATD-GC-MS.

Fourier Transform Infrared and X-Ray diffraction techniques were used to characterise the mixture components and the adsorbent mixture itself to ascertain information about structure and phase. These techniques revealed that the components were unaltered by mixing them together but the resultant effect was to widen the target compound adsorption preference and so adsorb aromatic and aliphatic compounds in the tested ignitable liquids.

Overall this study is the first systematic study of adsorbents used at fire scenes using an accepted ASTM for fire debris analysis and progressed to the development of a new adsorbent for the collection ignitable liquid residues from fire scenes along with method development of ATD-GC-MS. The limestone/Fuller's Earth mixture (10:1 w/w) adsorbed every ignitable liquid in a field test evaluation ranging from alcohol gel to diesel and this demonstrates that this adsorbent mixture should be used at fire scenes to replace ad hoc adsorbents.

7.2 Future Work

It has been shown in this thesis that sprinkling adsorbents directly onto suspected ILR produces reproducible results and allows the identification of ignitable liquid compounds. Sprinkling adsorbents directly onto ILR involves adsorption through both direct contact and gas vapour adsorption. Future work should include an investigation of into both modes of adsorption. The investigation of the adsorption of gas phase molecules could be achieved by placing the adsorbent in a sieve above the ILR to allow vapour transfer. The mechanisms of transfer could be investigated at each stage of the sampling procedure to determine if adsorption by gas phase yields the same results as by direct contact. If adsorption by gas phase does achieves the same results, it may lead to the design of portable instruments based on GC-MS, that can be used by scene investigators that also

give results at the scene. This would allow the investigator to make an informed decision about the next course of action before the crime scene is closed down.

Although characterisation of the adsorbent was achieved through structural and phase information morphology and elemental analysis with a scanning electron microscope - energy dispersive X-rays (SEM-EDS) would allow better identification of minerals such as feldspar and opal. This research showed that these phases were minor in the mixture but they may influence adsorption by adding or subtracting their charge to the net charge of the mixture. Understanding their role may lead to new mixtures being created for different adsorption roles such as chemical weapons and contaminates.

The ATD-GC-MS showed that it was more than capable of analysing ignitable liquid residues with Tenax TA®. More tests should be undertaken to evaluate real fire debris samples with the parameters and then it is recommended that the method be fully validated and submitted to the American Society for Testing and Materials as a standard method for the investigation of ignitable liquids in fire debris.

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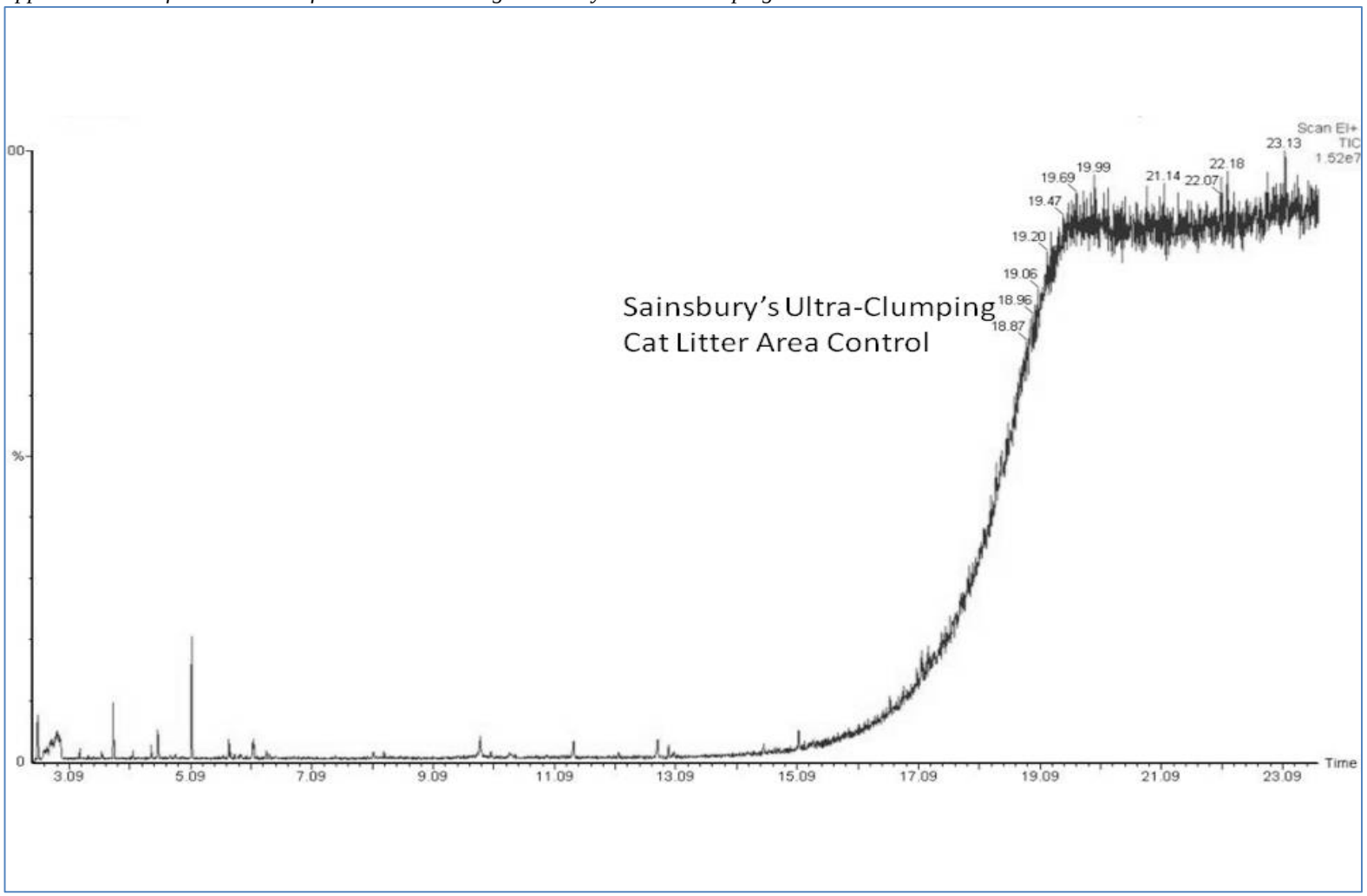
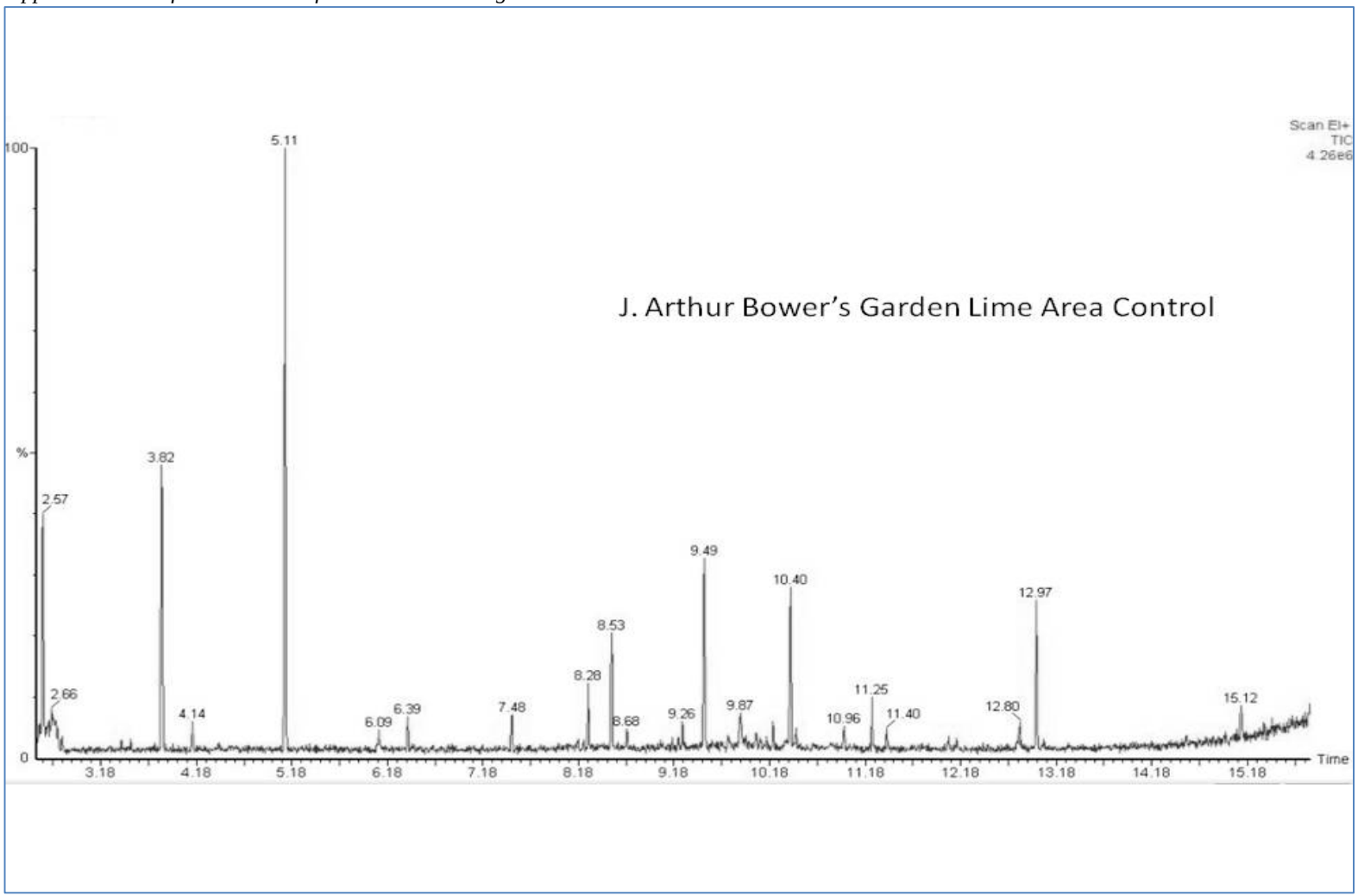
Appendices

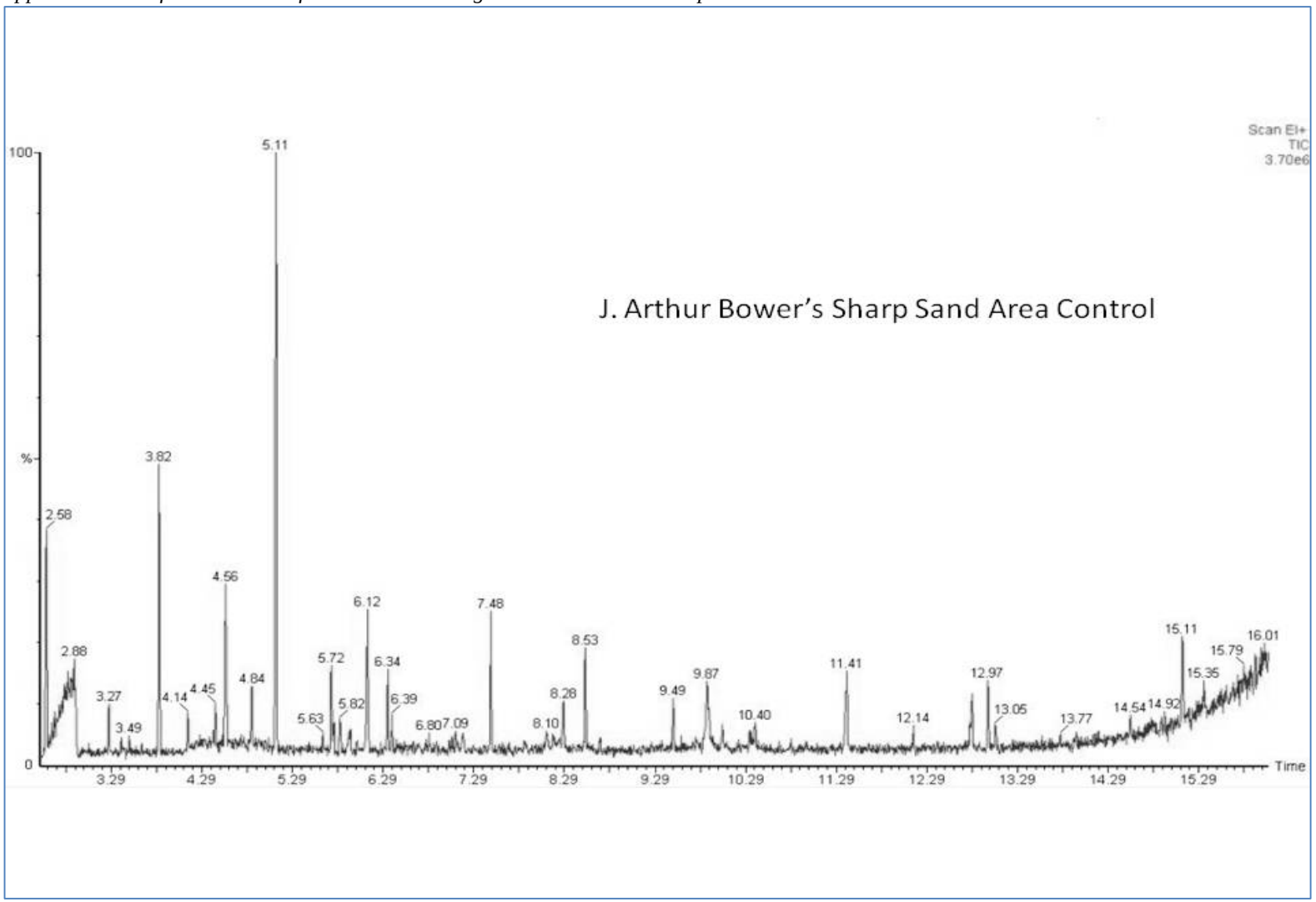
Appendix 1 TIC of area control of Smoke House using Sainsbury's Ultra-Clumping Cat Litter



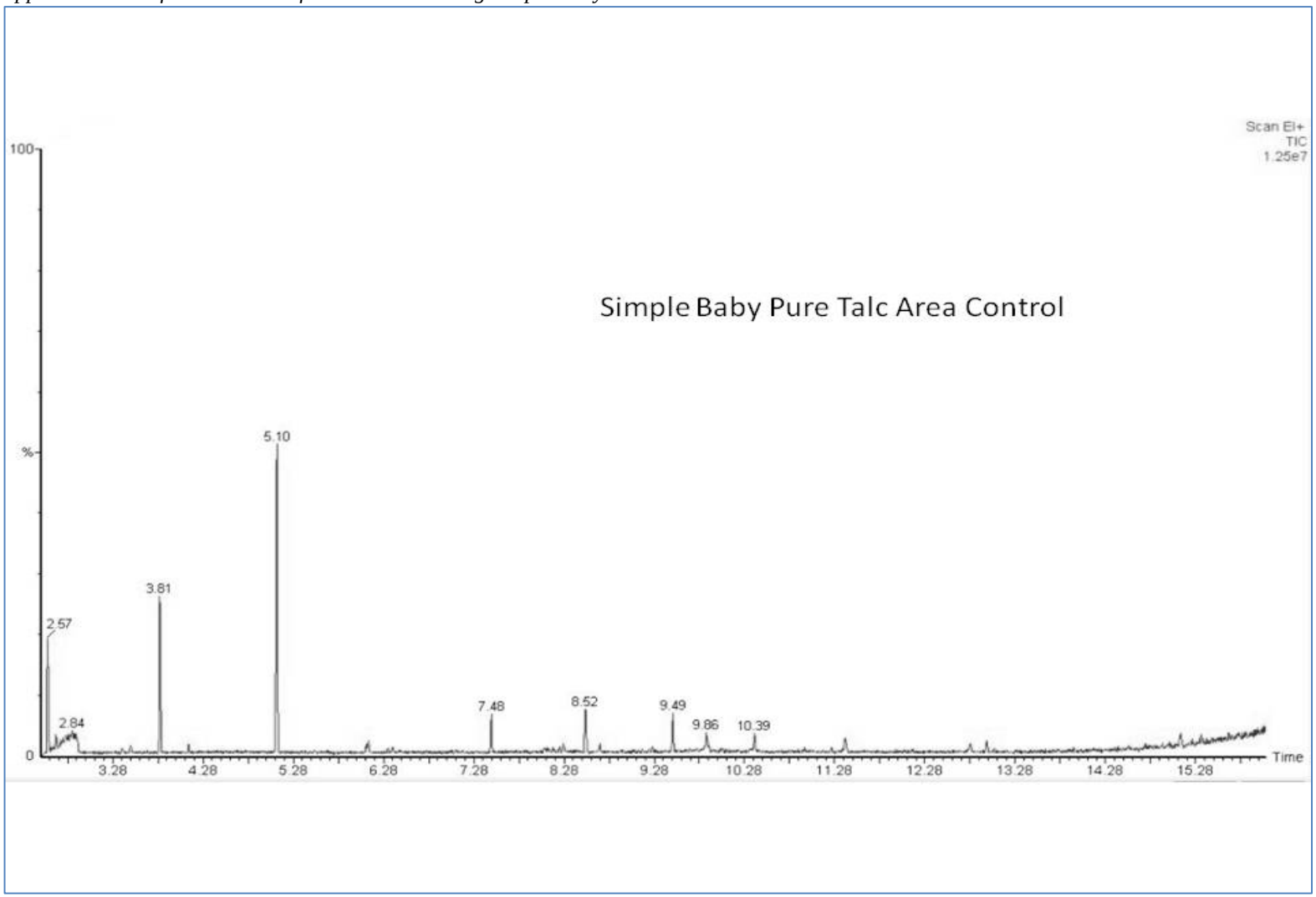
Appendix 2 TIC of area control of Smoke House using J. Arthur Bower's Garden Lime



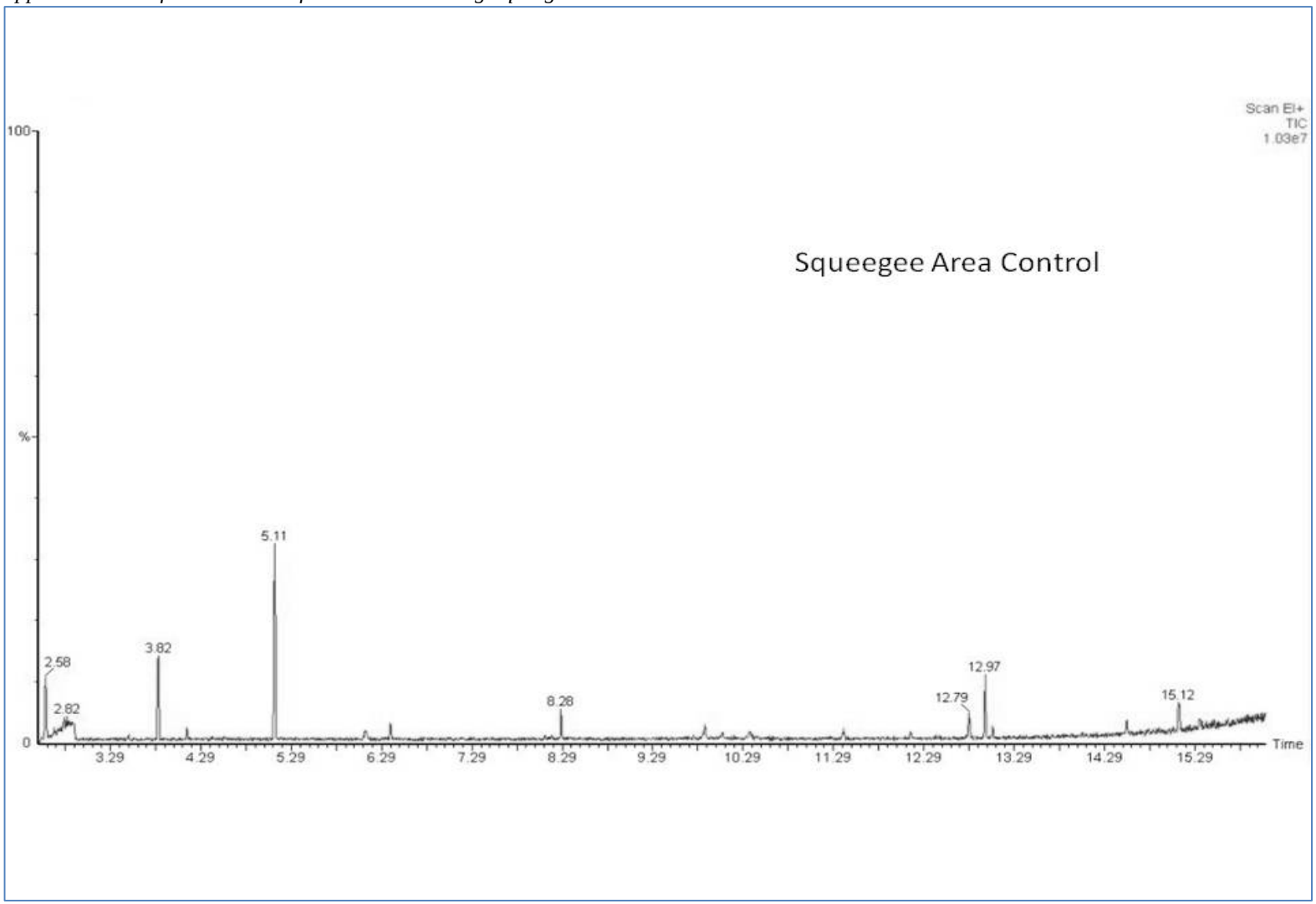
Appendix 3 TIC of area control of Smoke House using J. Arthur Bower's Sharp Sand



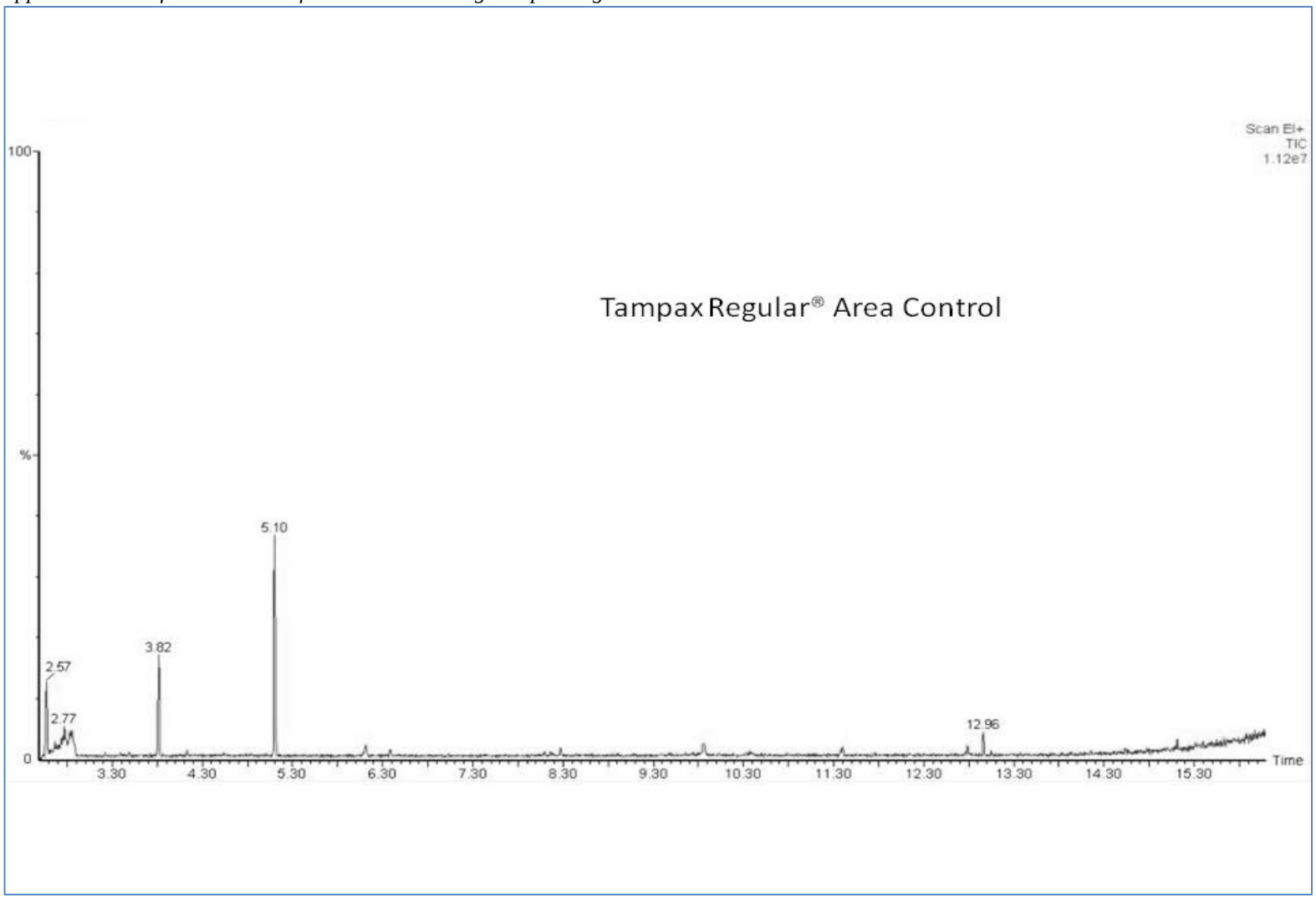
Appendix 4 TIC of area control of Smoke House using Simple Baby Pure Talc



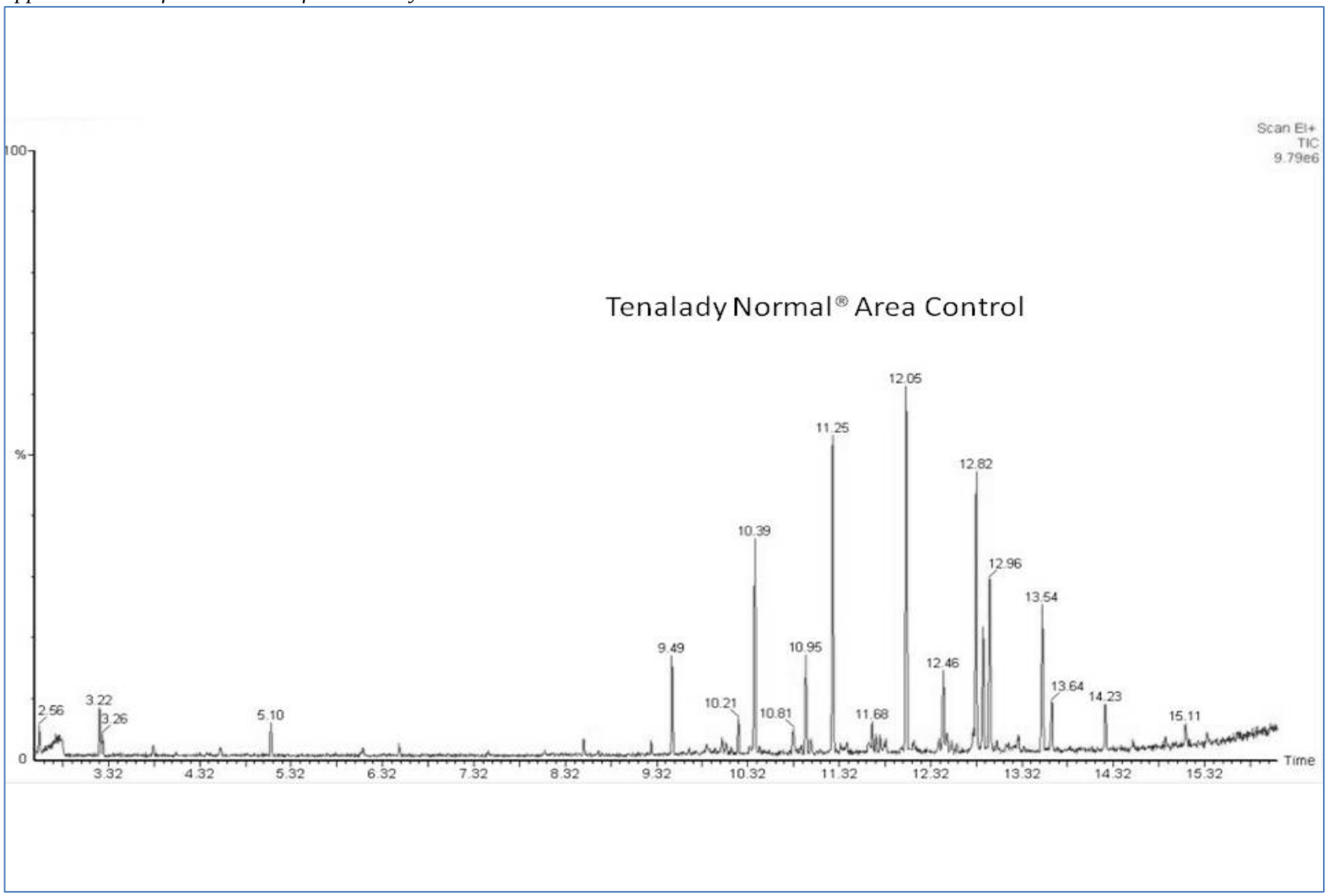
Appendix 5 TIC of area control of Smoke House using Squeegee



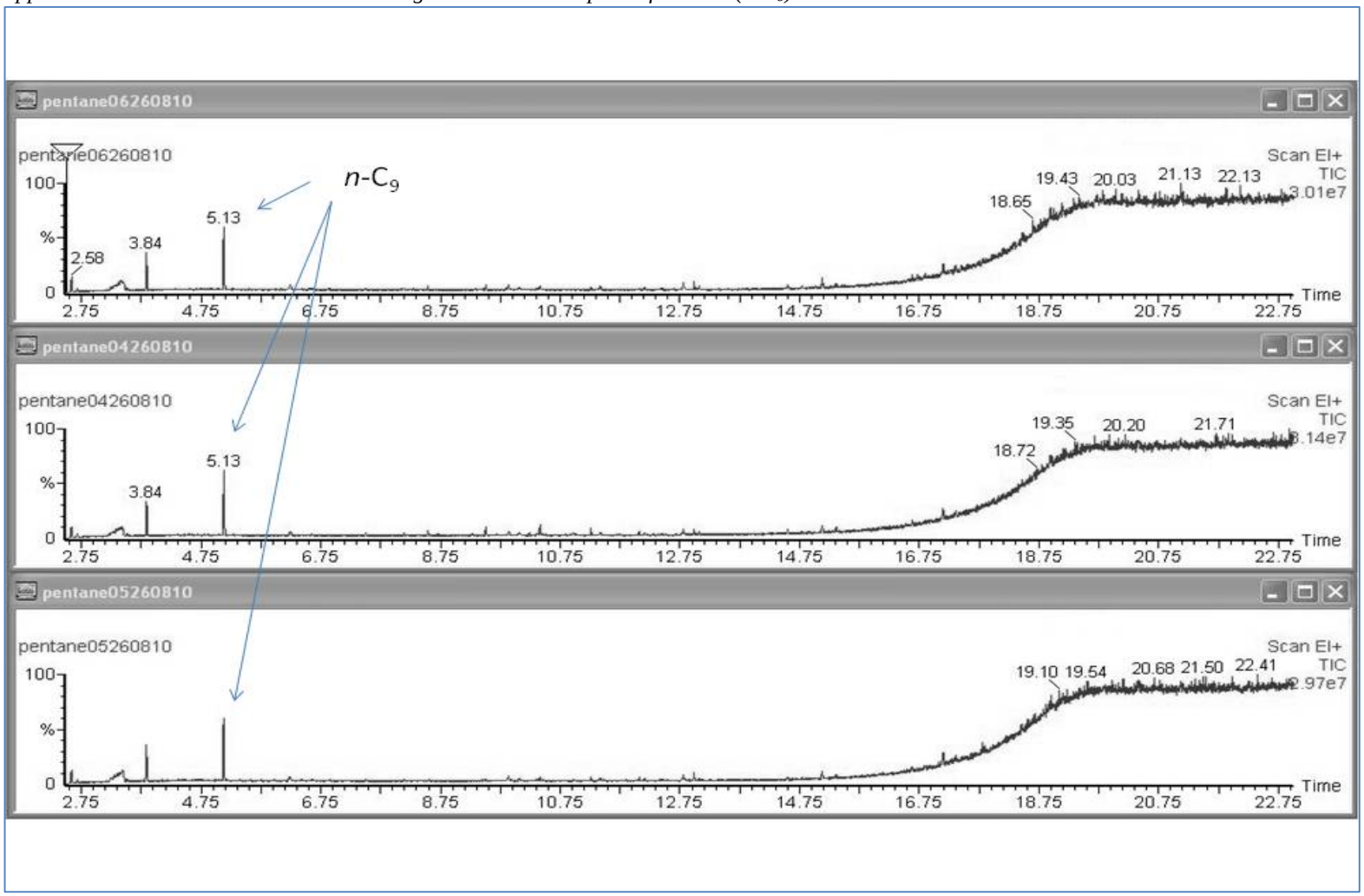
Appendix 6 TIC of area control of Smoke House using Tampax Regular®



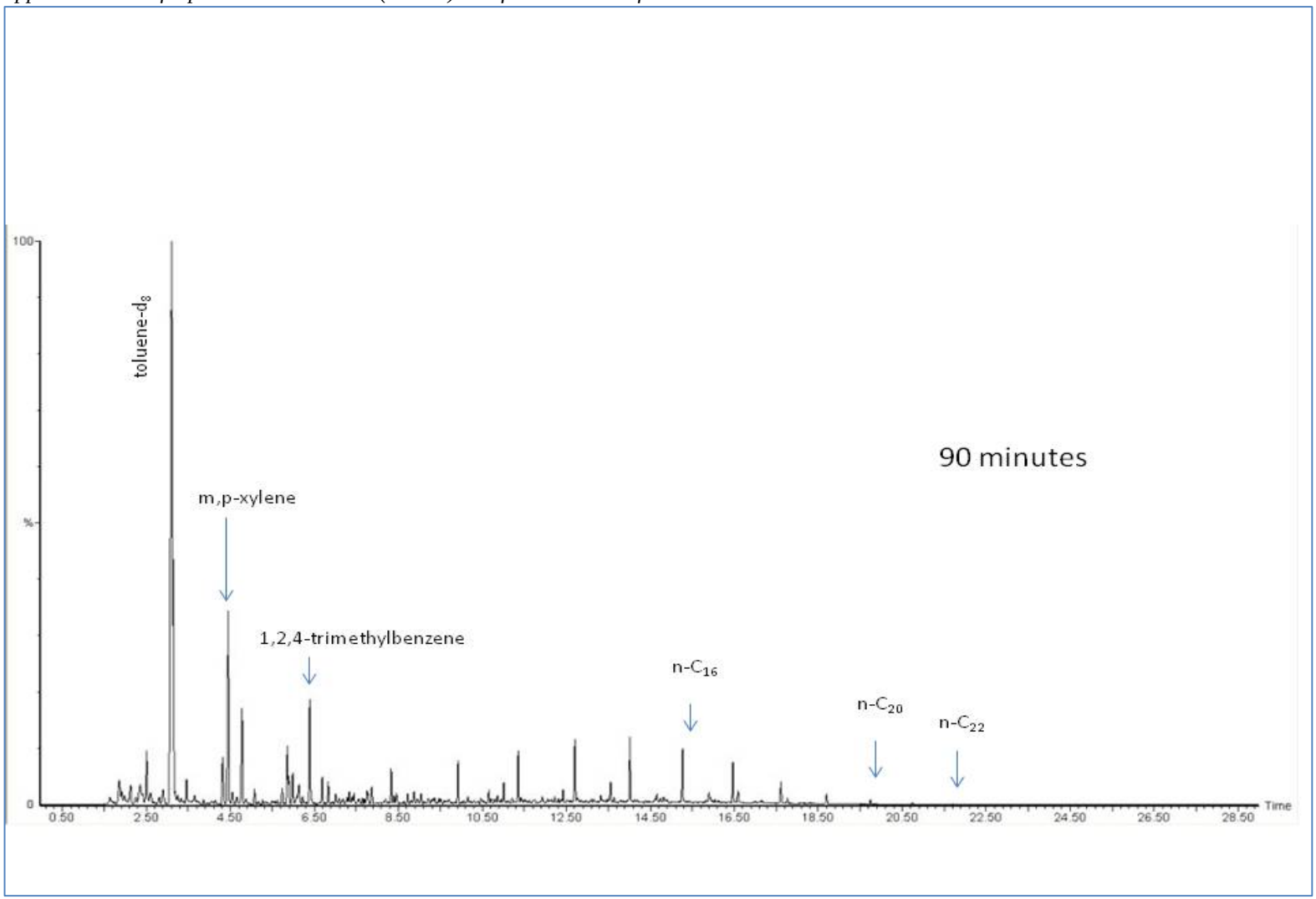
Appendix 7 TIC of area control of TENA Lady Normal®



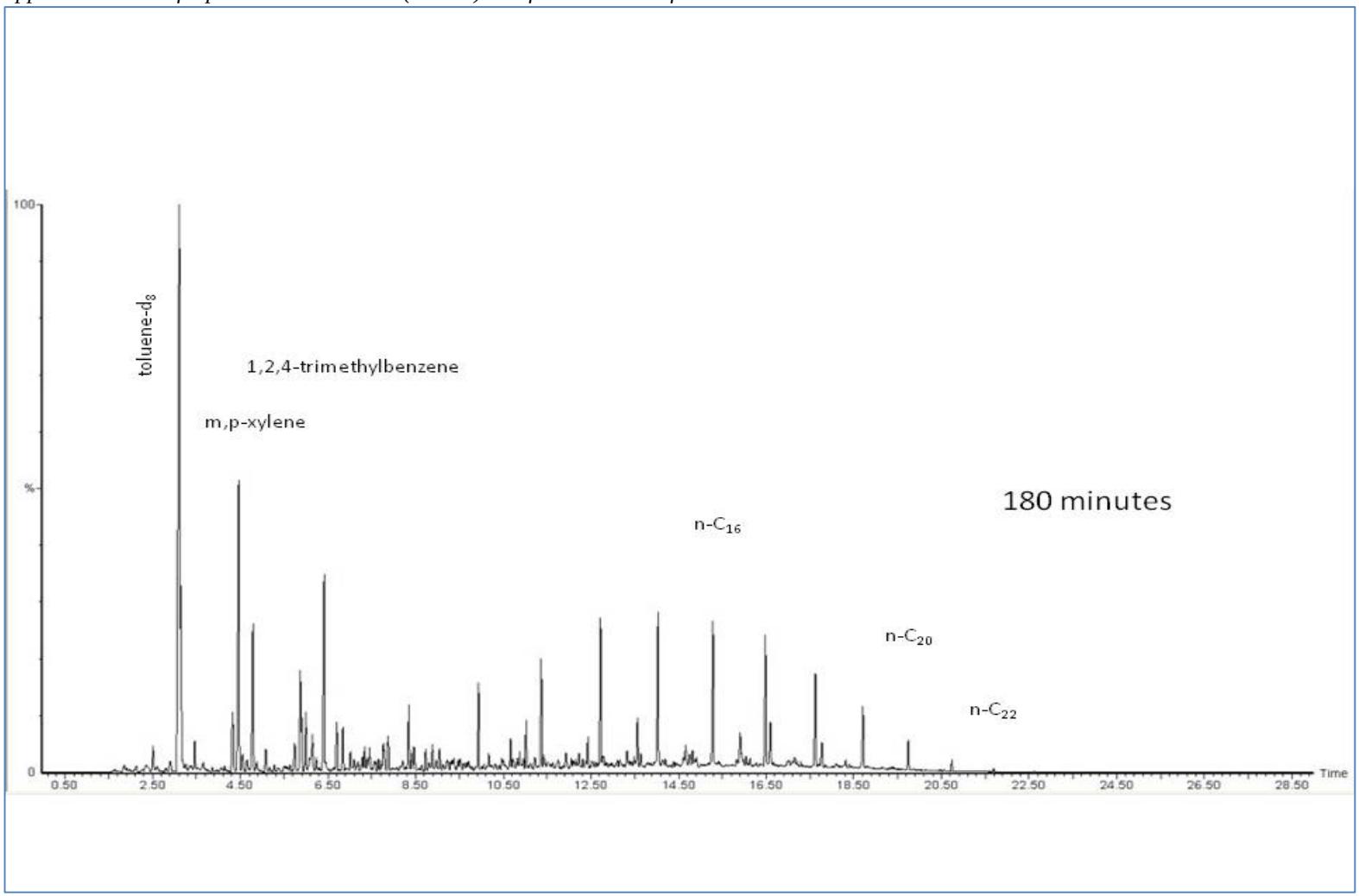
Appendix 8 Pentane blank TICs with showing a contamination peak of nonane (n-C_9)



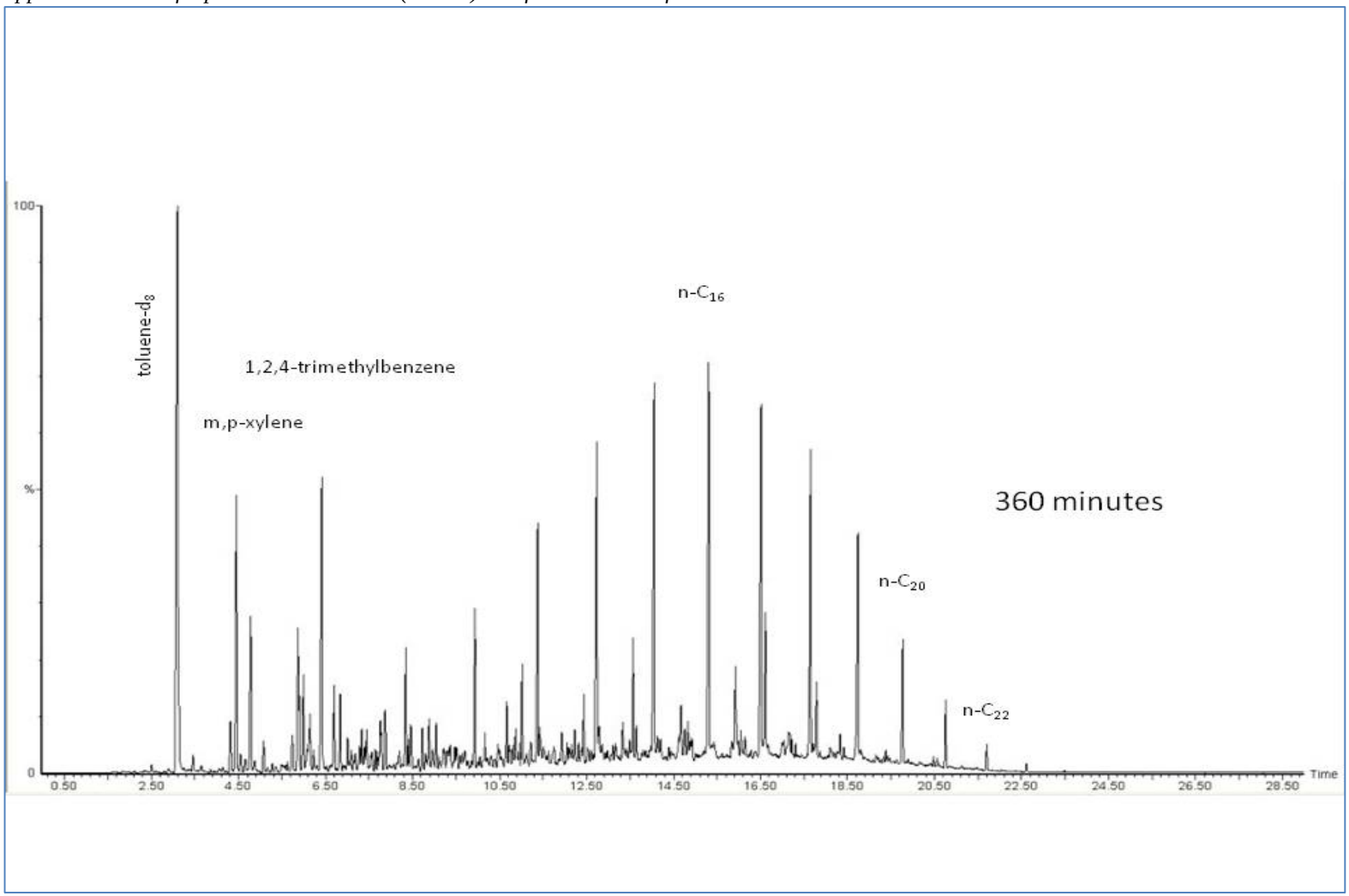
Appendix 9 TIC of a petrol/diesel mixture (1:1 v/v) at a fan oven time of 90 minutes



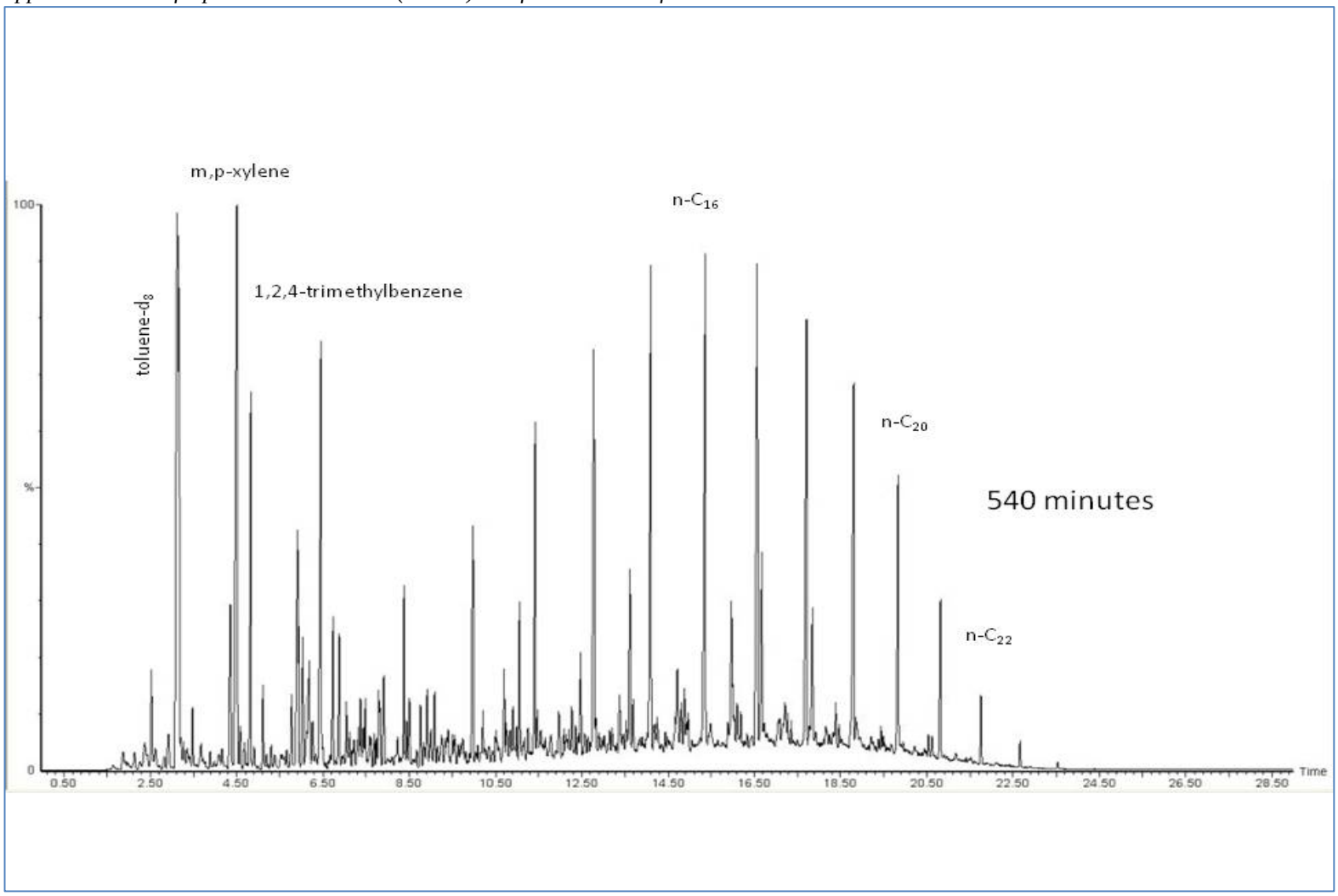
Appendix 10 TIC of a petrol/diesel mixture (1:1 v/v) at a fan oven time of 180 minutes



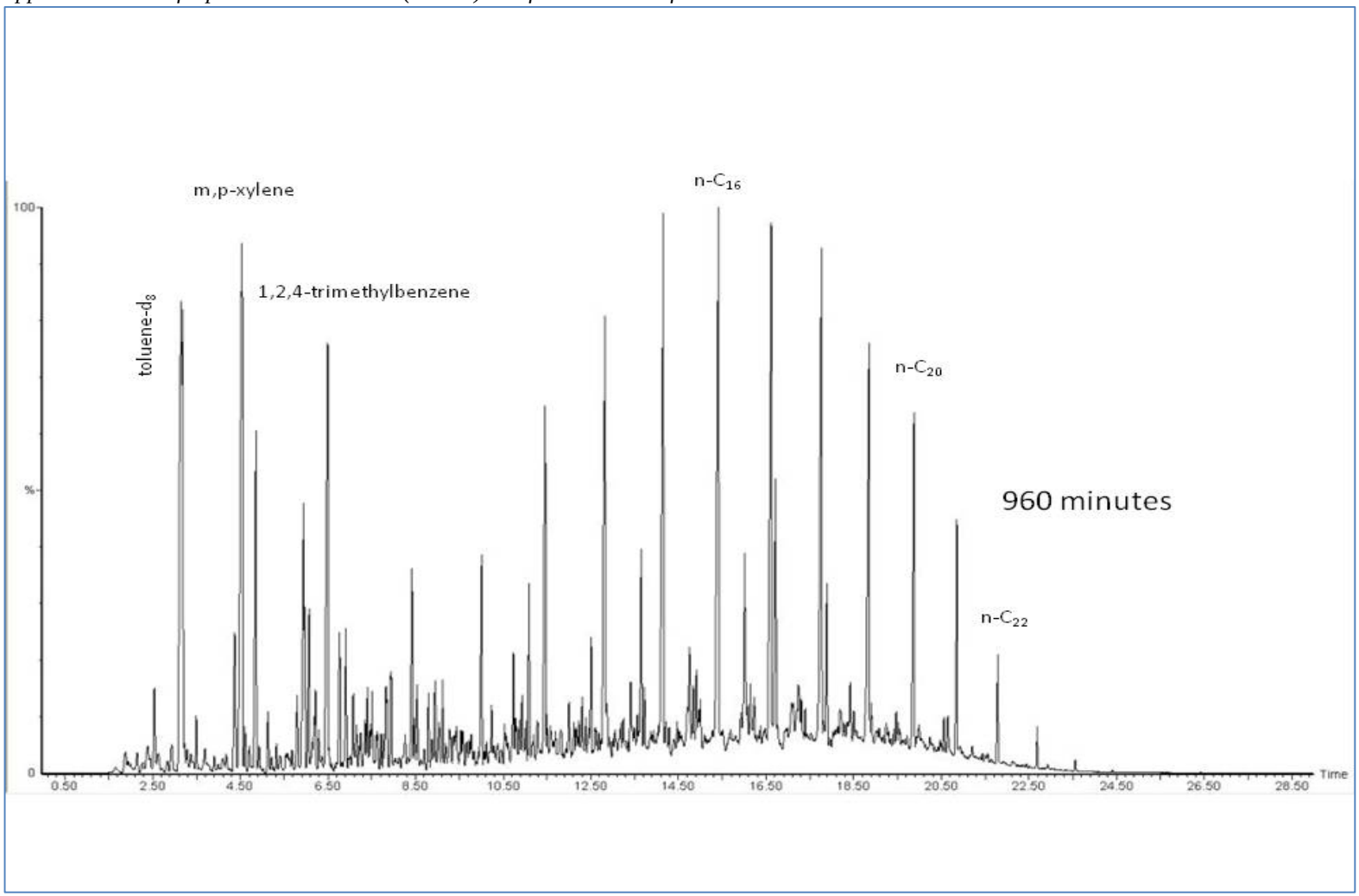
Appendix 11 TIC of a petrol/diesel mixture (1:1 v/v) at a fan oven time of 360 minutes



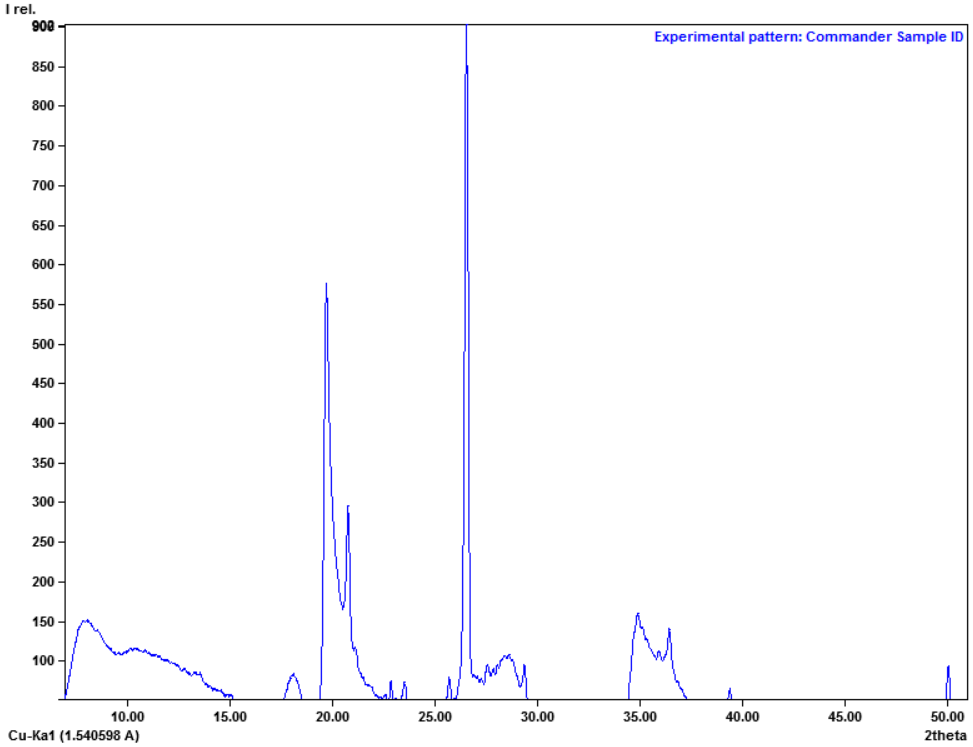
Appendix 12 TIC of a petrol/diesel mixture (1:1 v/v) at a fan oven time of 540 minutes

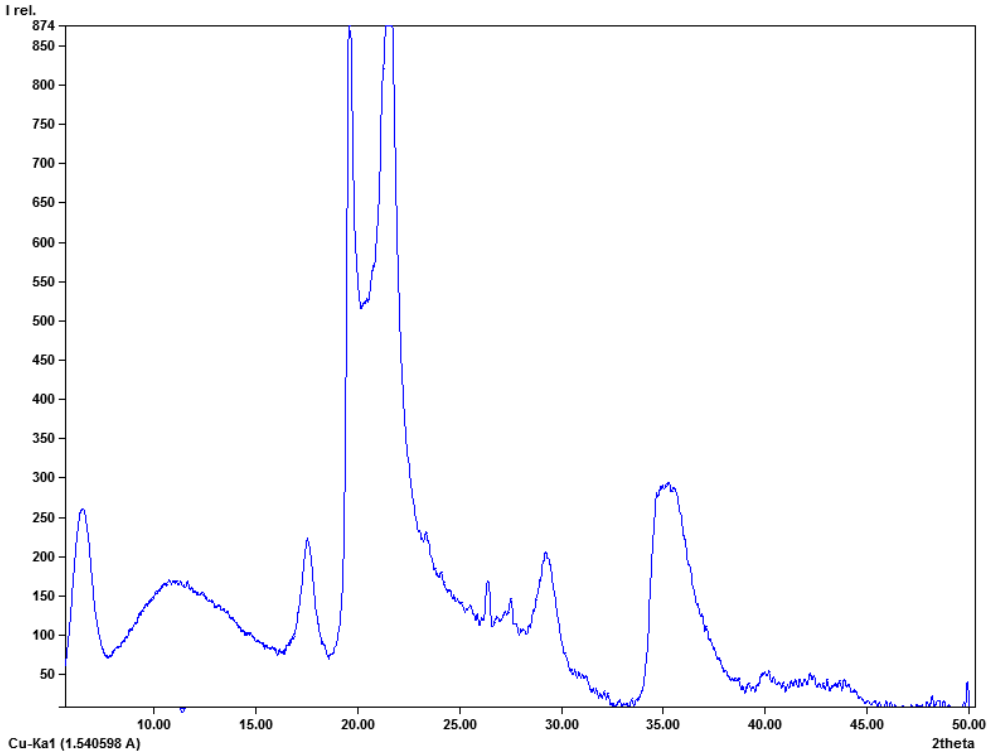


Appendix 13 TIC of a petrol/diesel mixture (1:1 v/v) at a fan oven time of 960 minutes

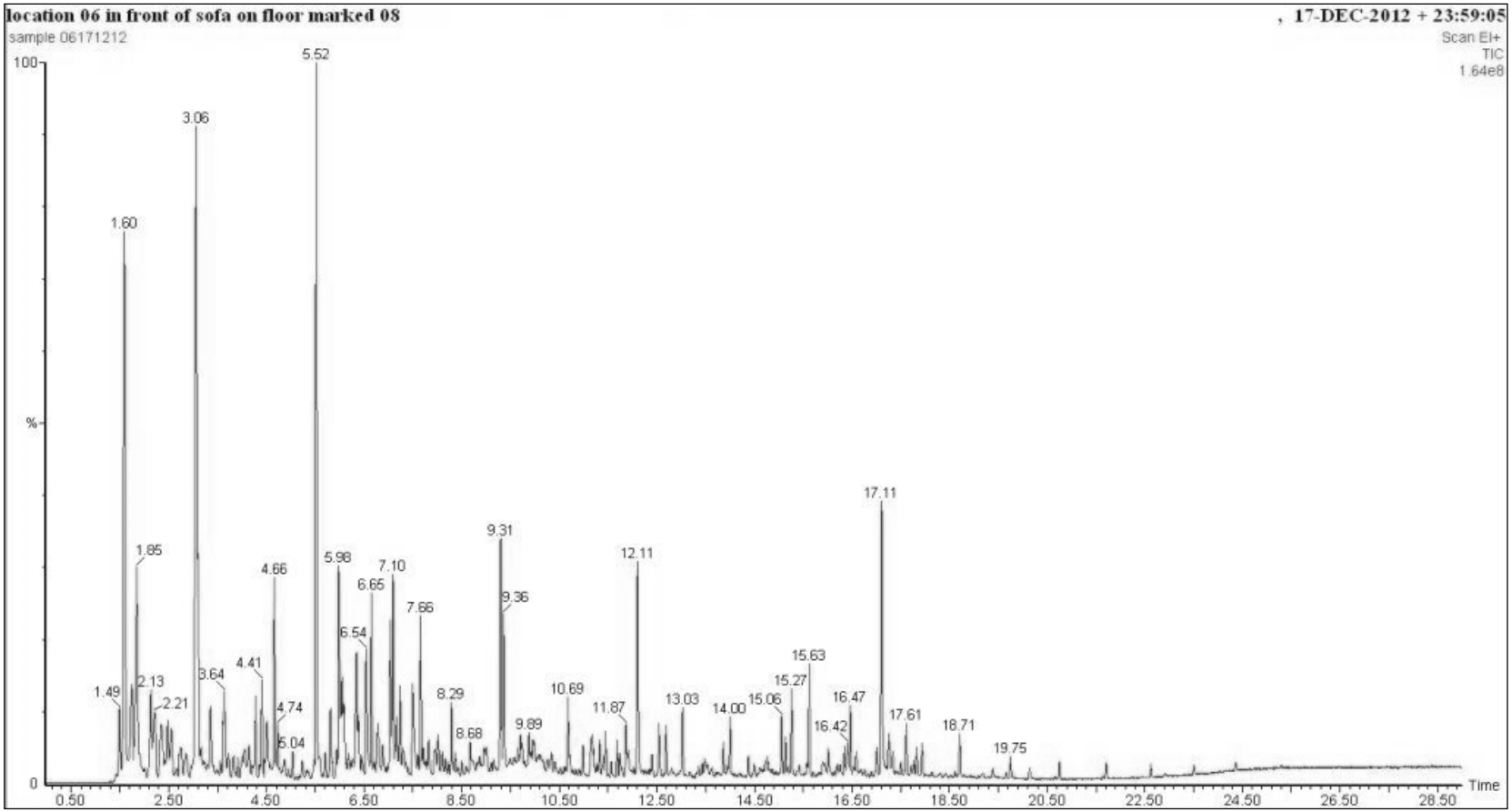


Appendix 14 XRD diffractograms SWy-2 montmorillonite (top) and STx-1b montmorillonite (bottom)

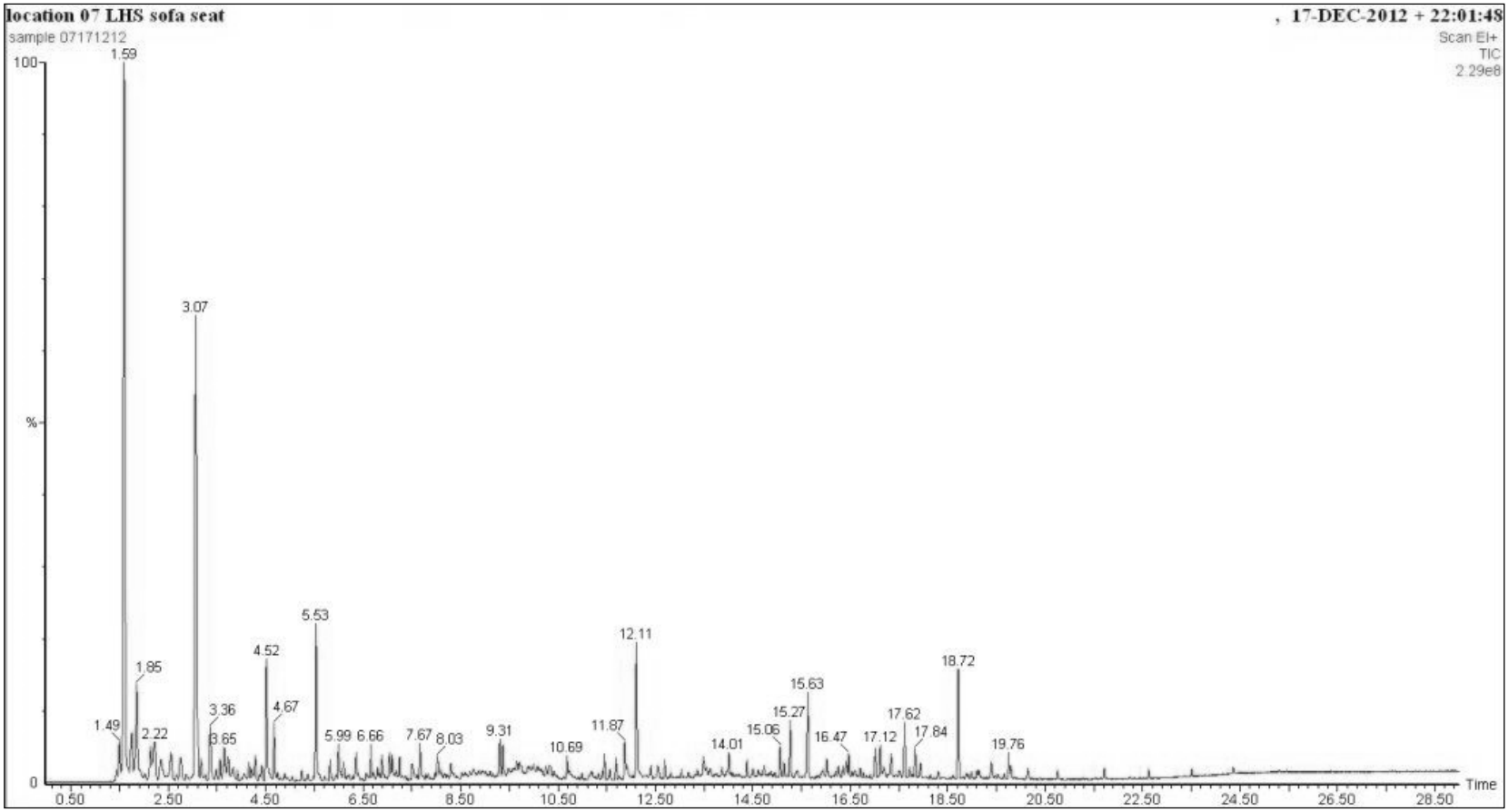




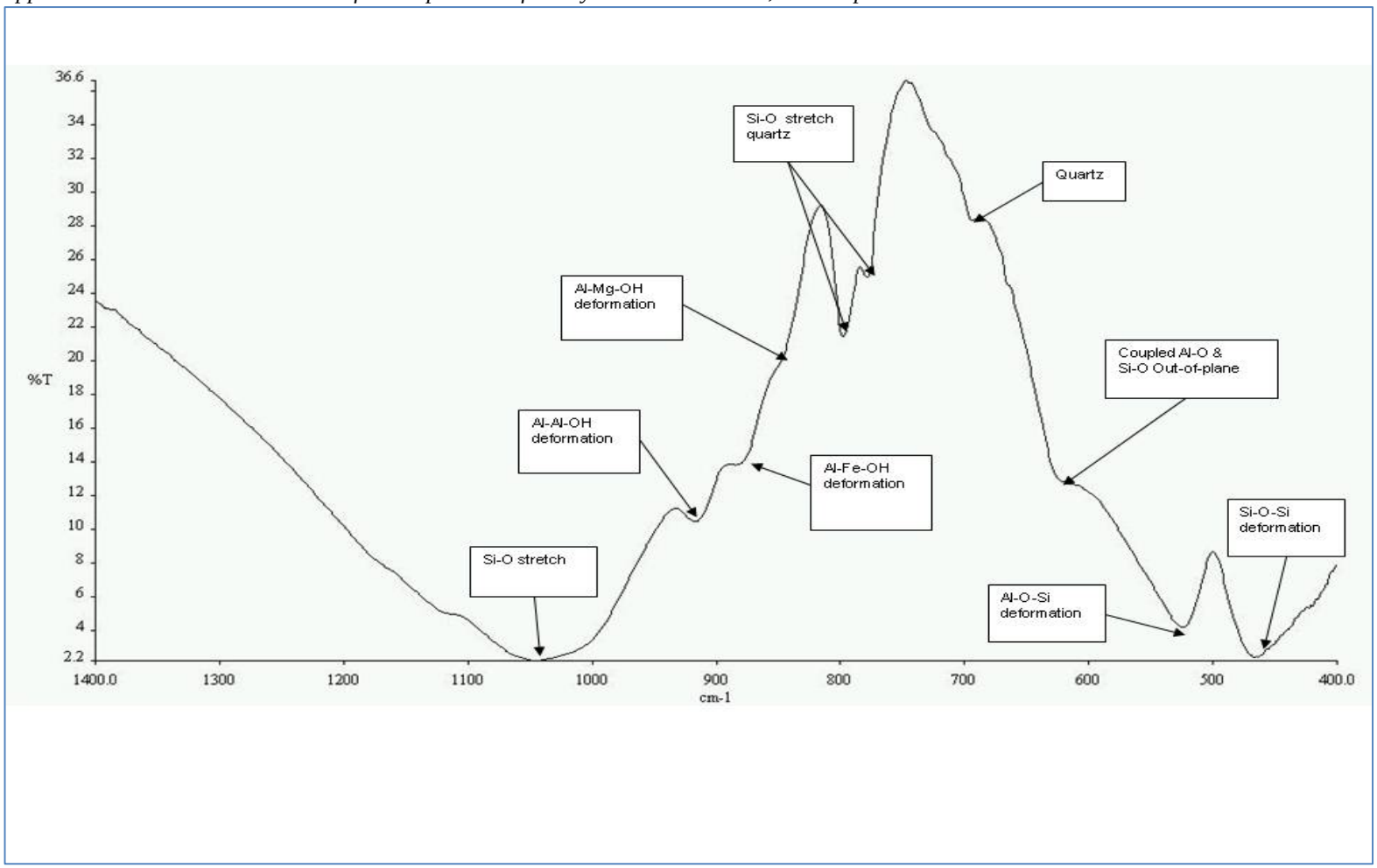
Appendix 15 TIC for area marked 'In front of sofa'



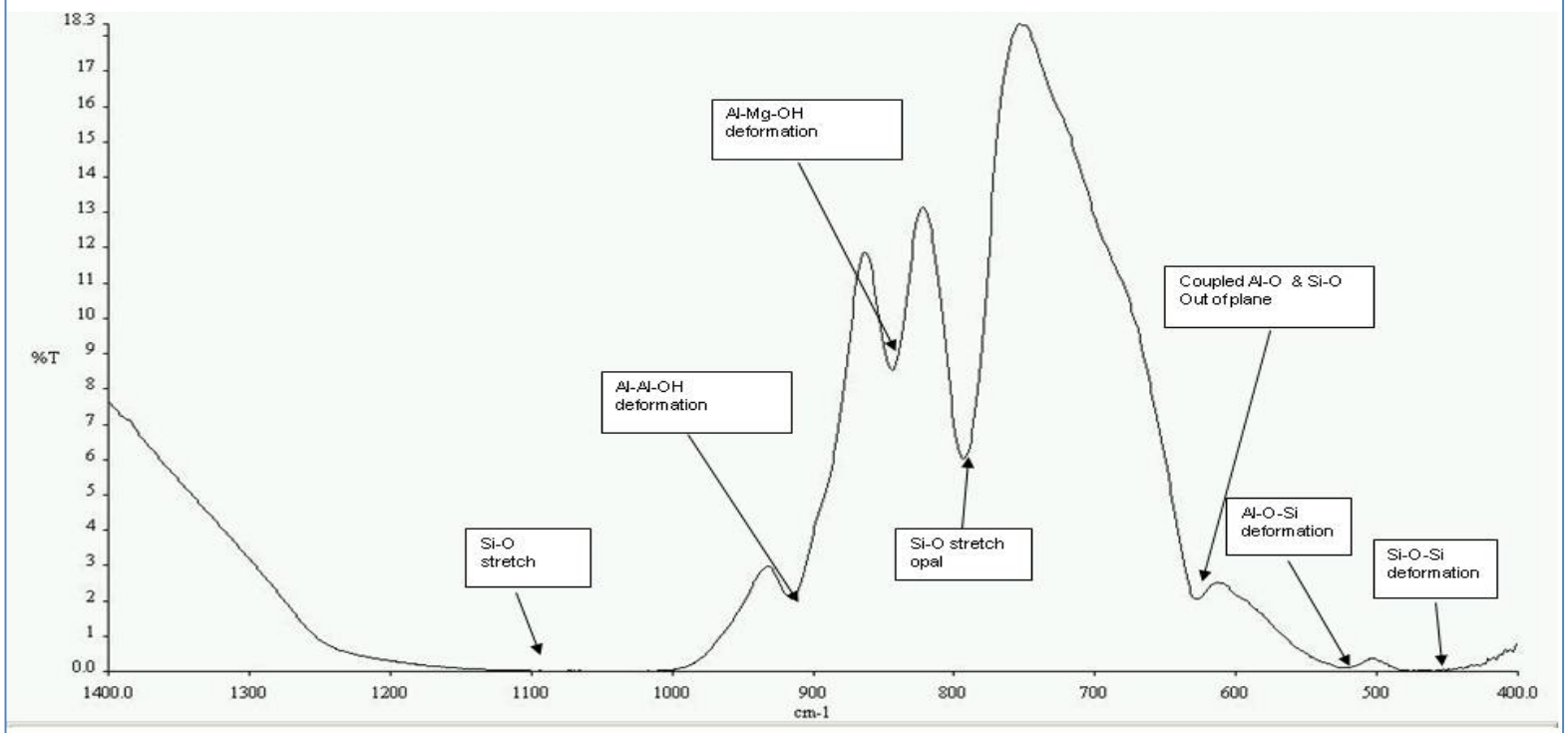
Appendix 16 TIC for area marked 'Left hand side of Sofa'



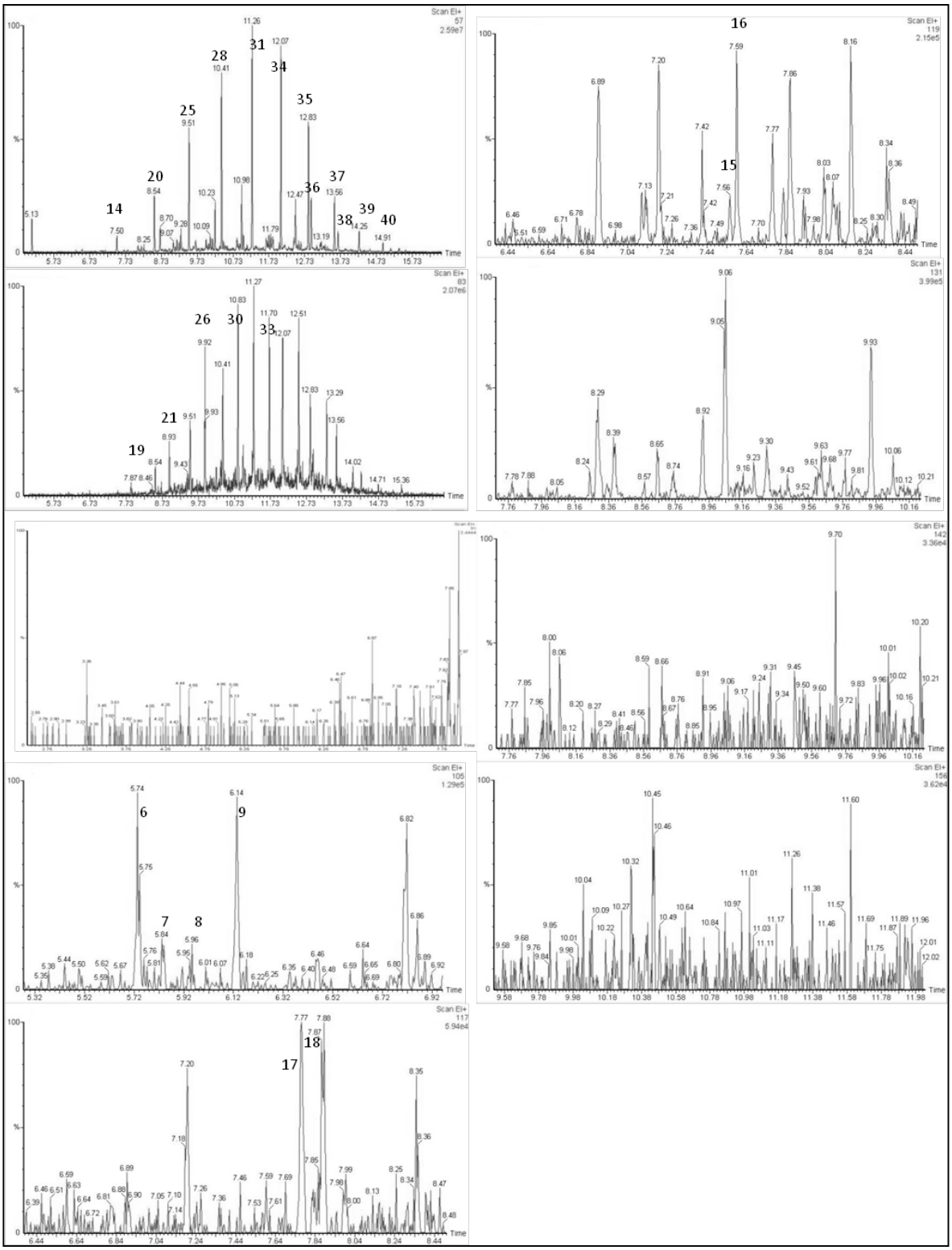
Appendix 17 Percent Transmission infrared spectrum of a SWy-2 montmorillonite, 2% sample in KBr disc



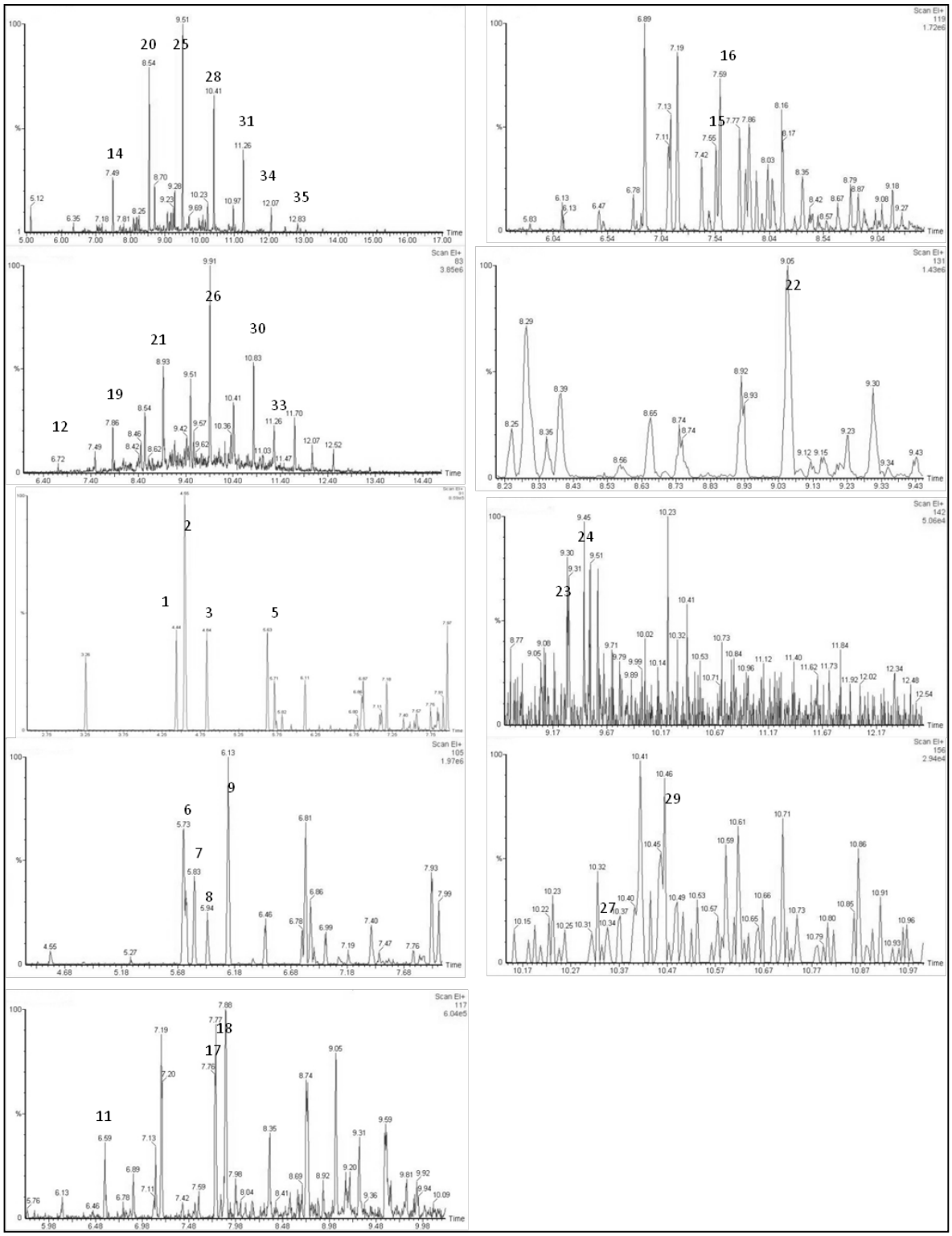
Appendix 18 Percent transmission infrared spectrum of a STx-1b montmorillonite, 2% sample in KBr disc



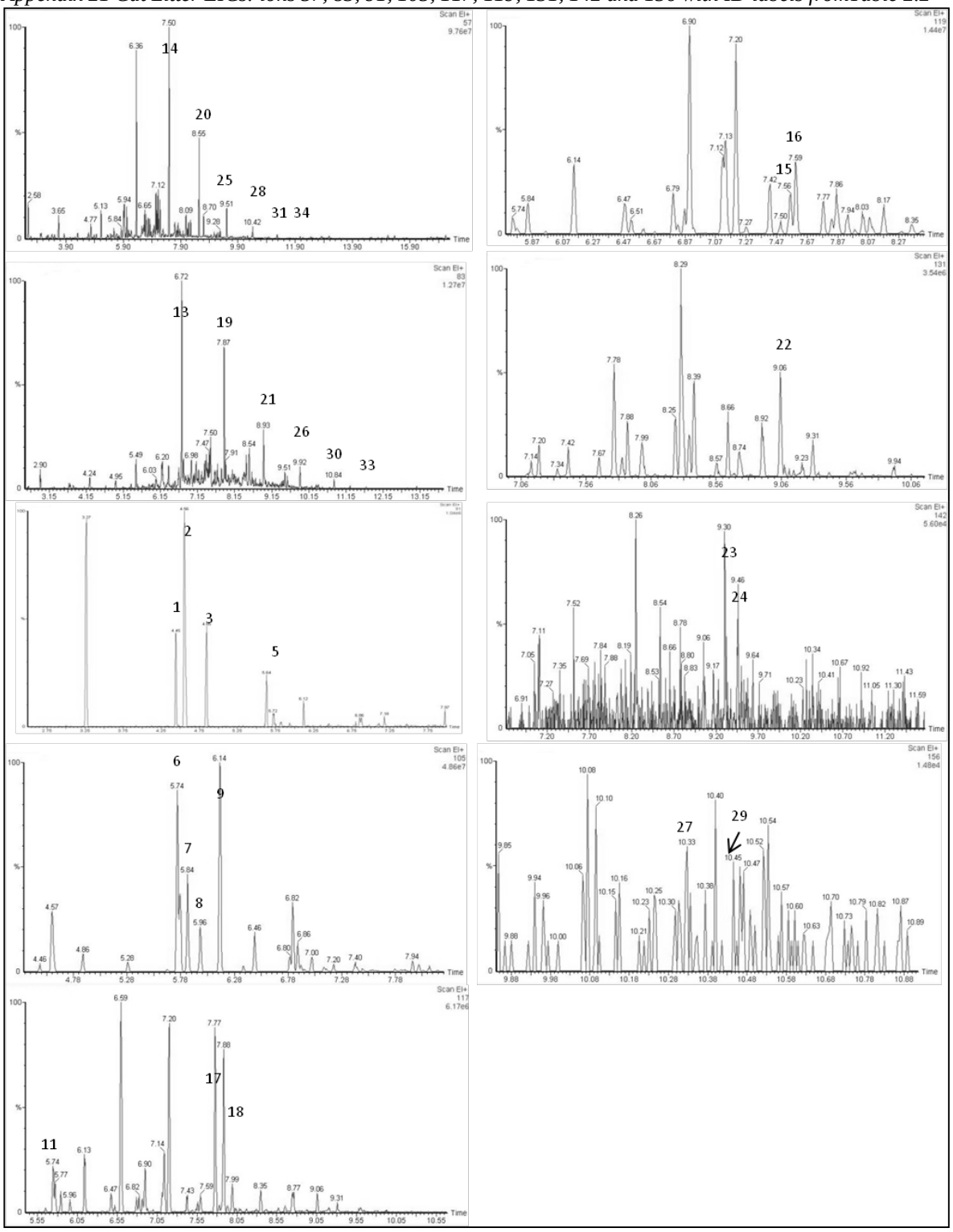
Appendix 19 Garden Lime EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



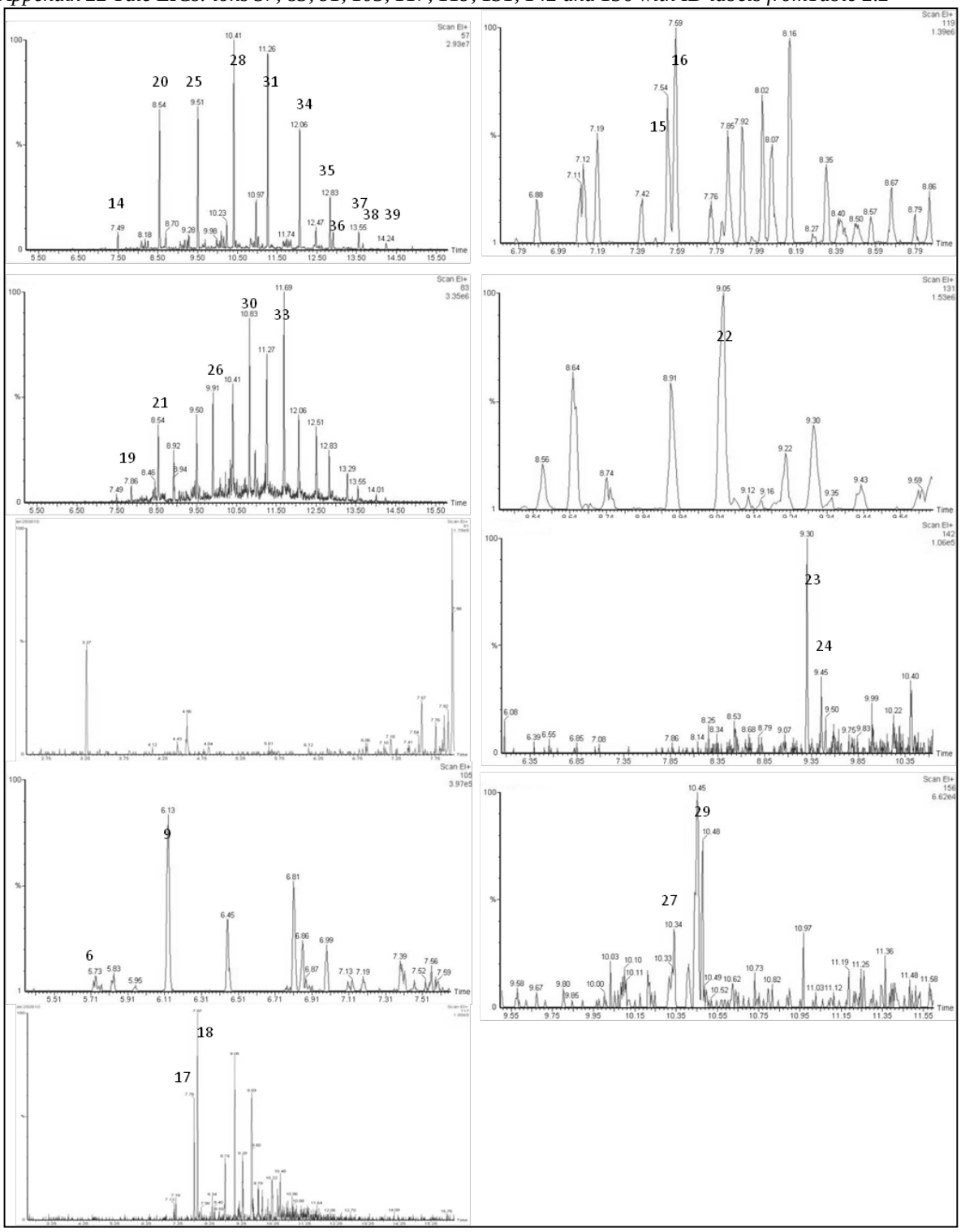
Appendix 20 Sharp Sand EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels from Table 2.2



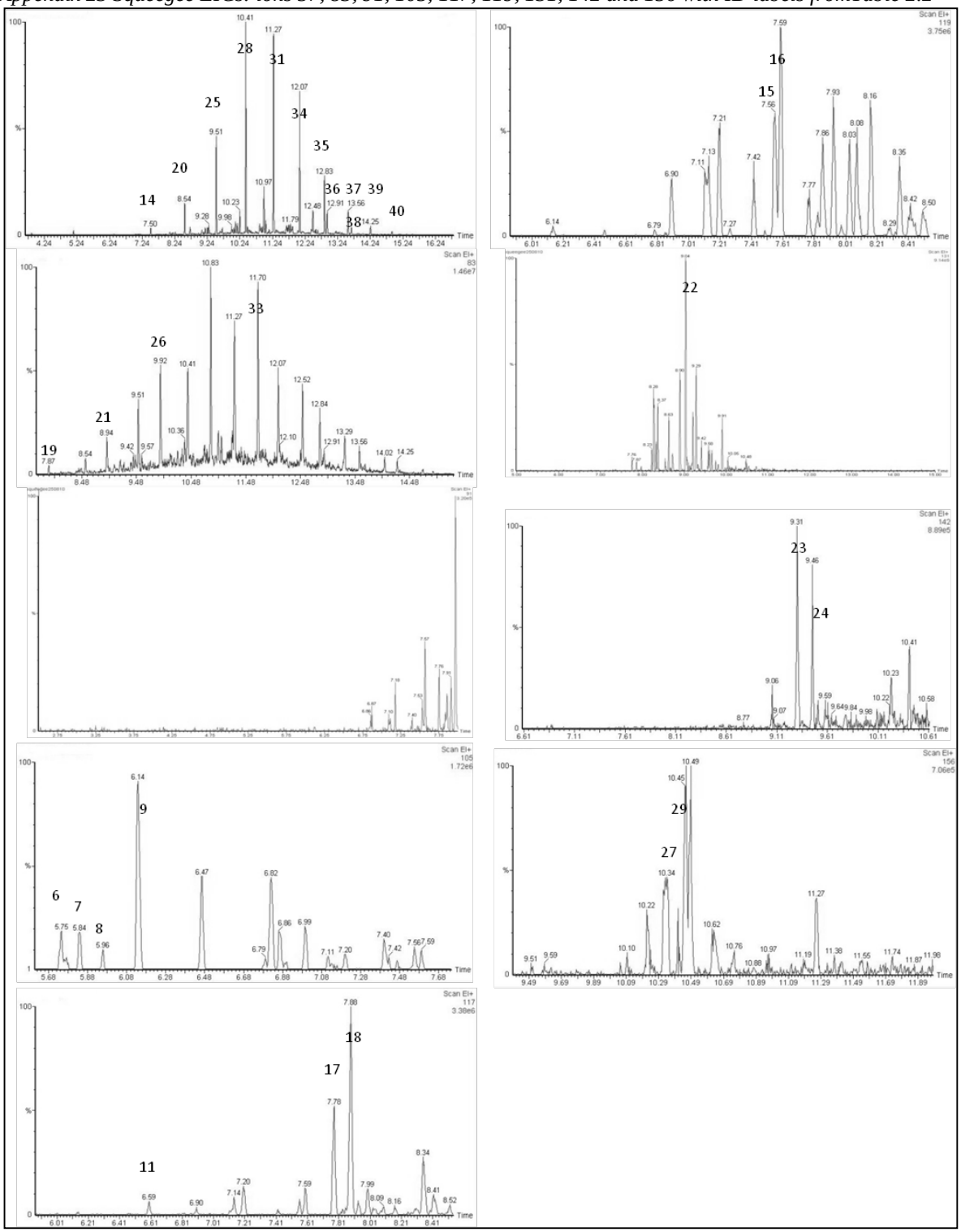
Appendix 21 Cat Litter EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



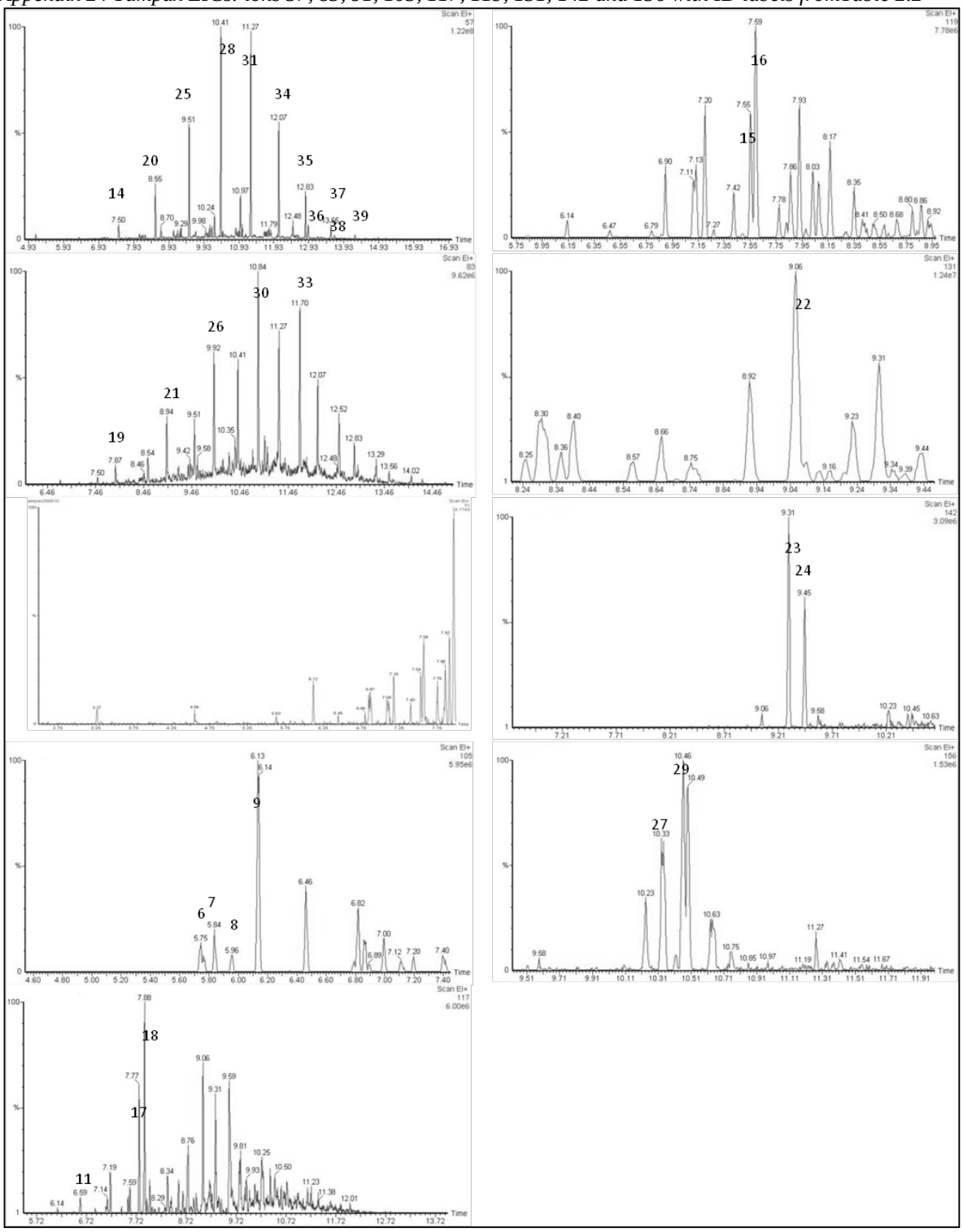
Appendix 22 Talc EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



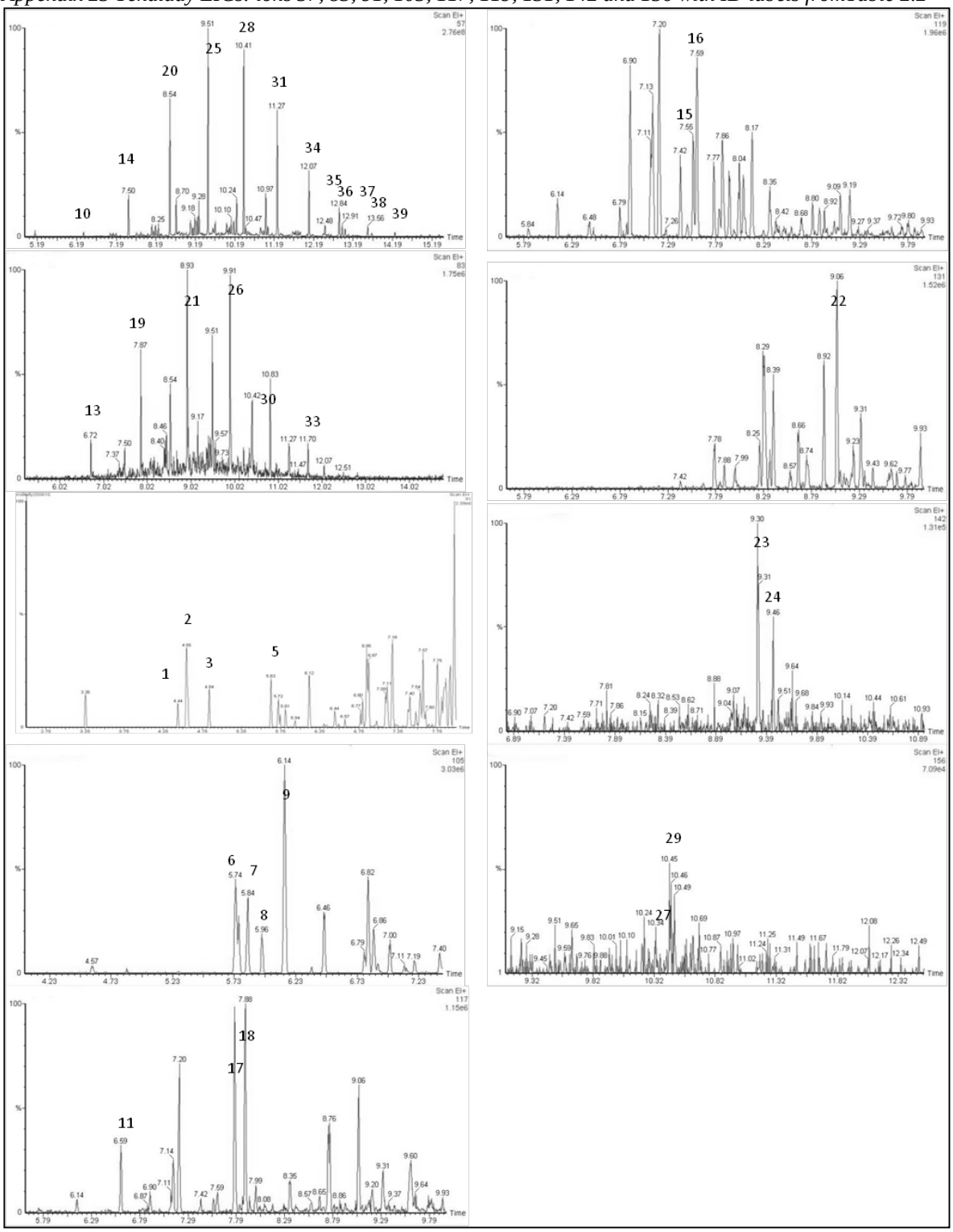
Appendix 23 Squeegee EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



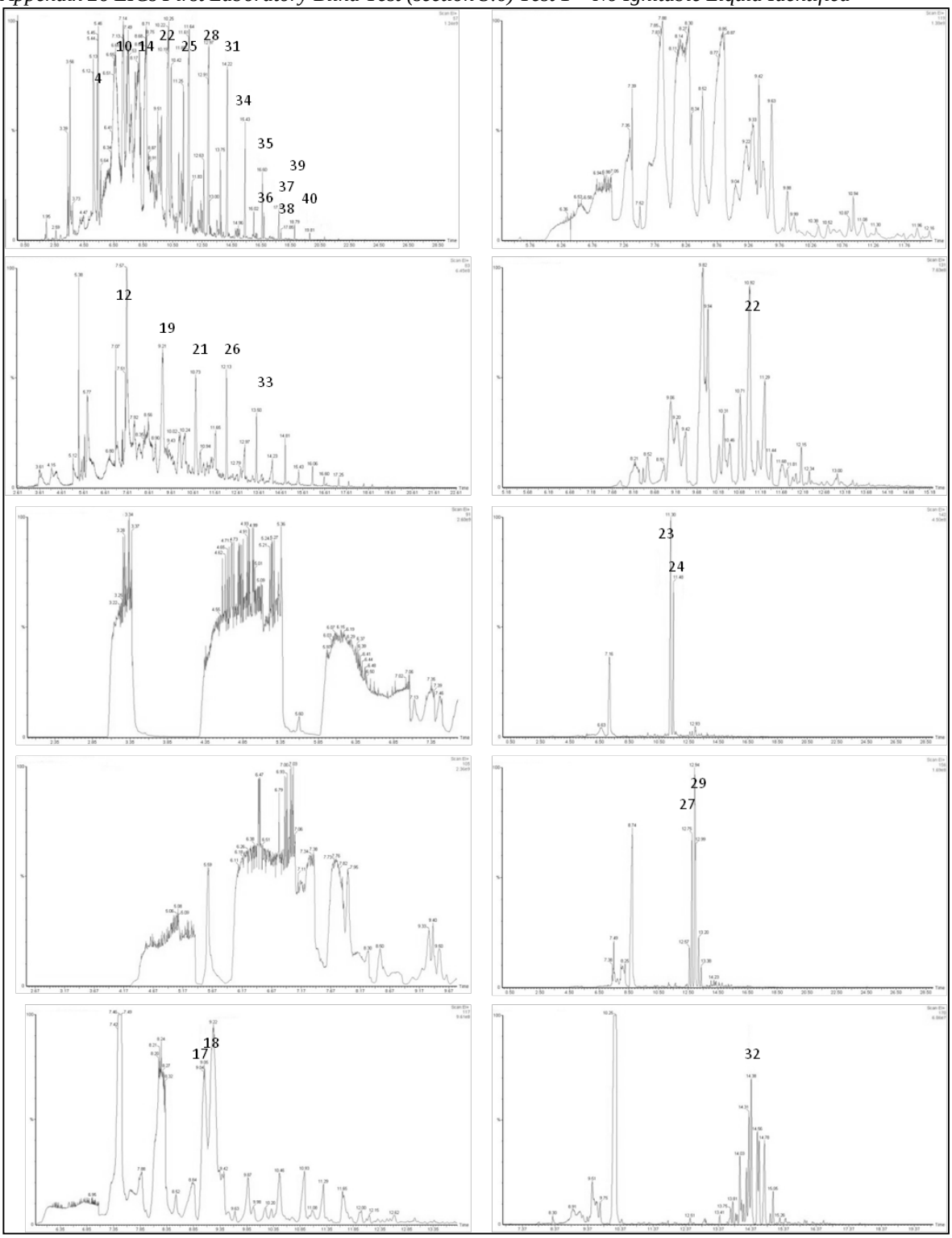
Appendix 24 Tampax EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



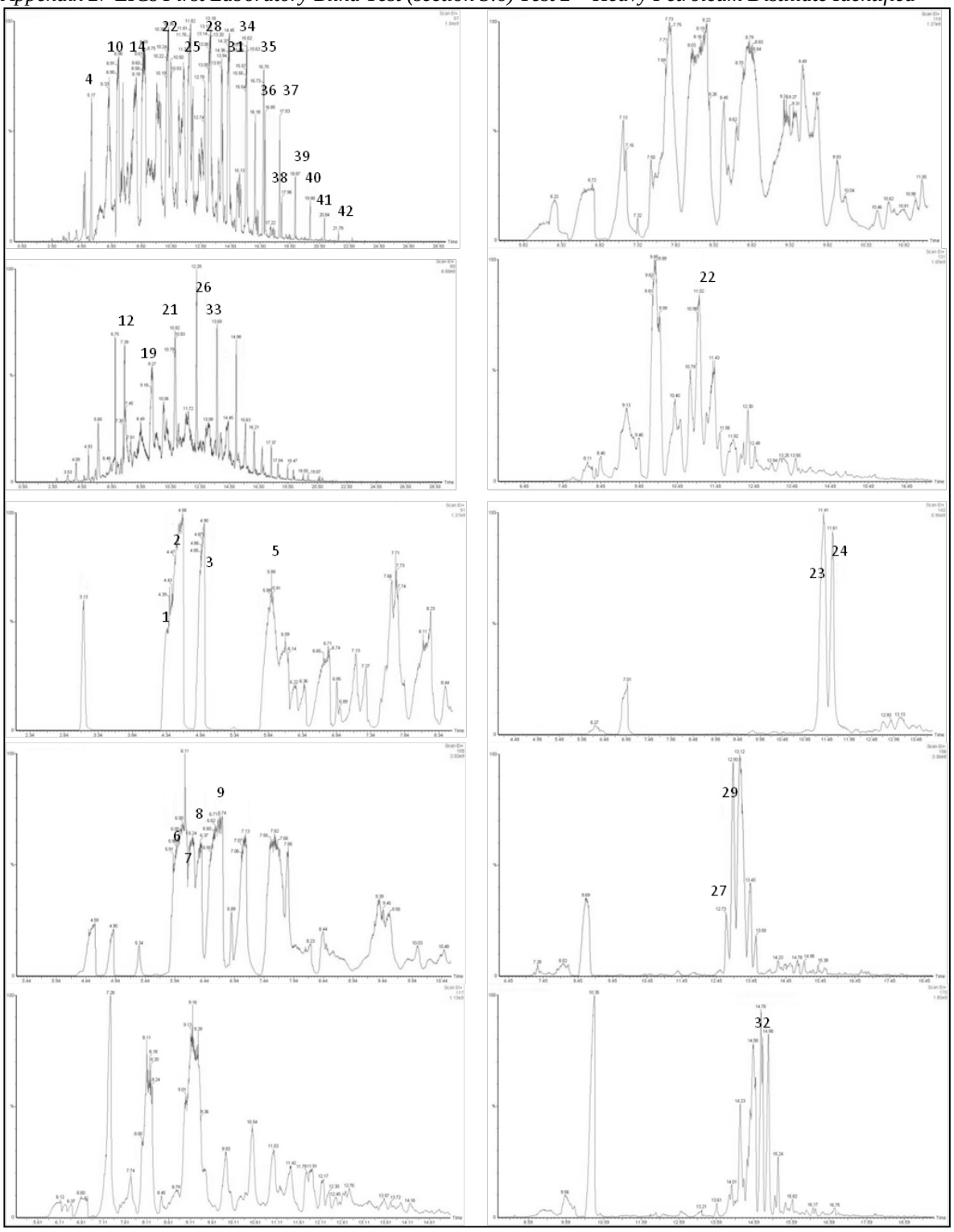
Appendix 25 Tenalady EICs: ions 57, 83, 91, 105, 117, 119, 131, 142 and 156 with ID labels fromTable 2.2



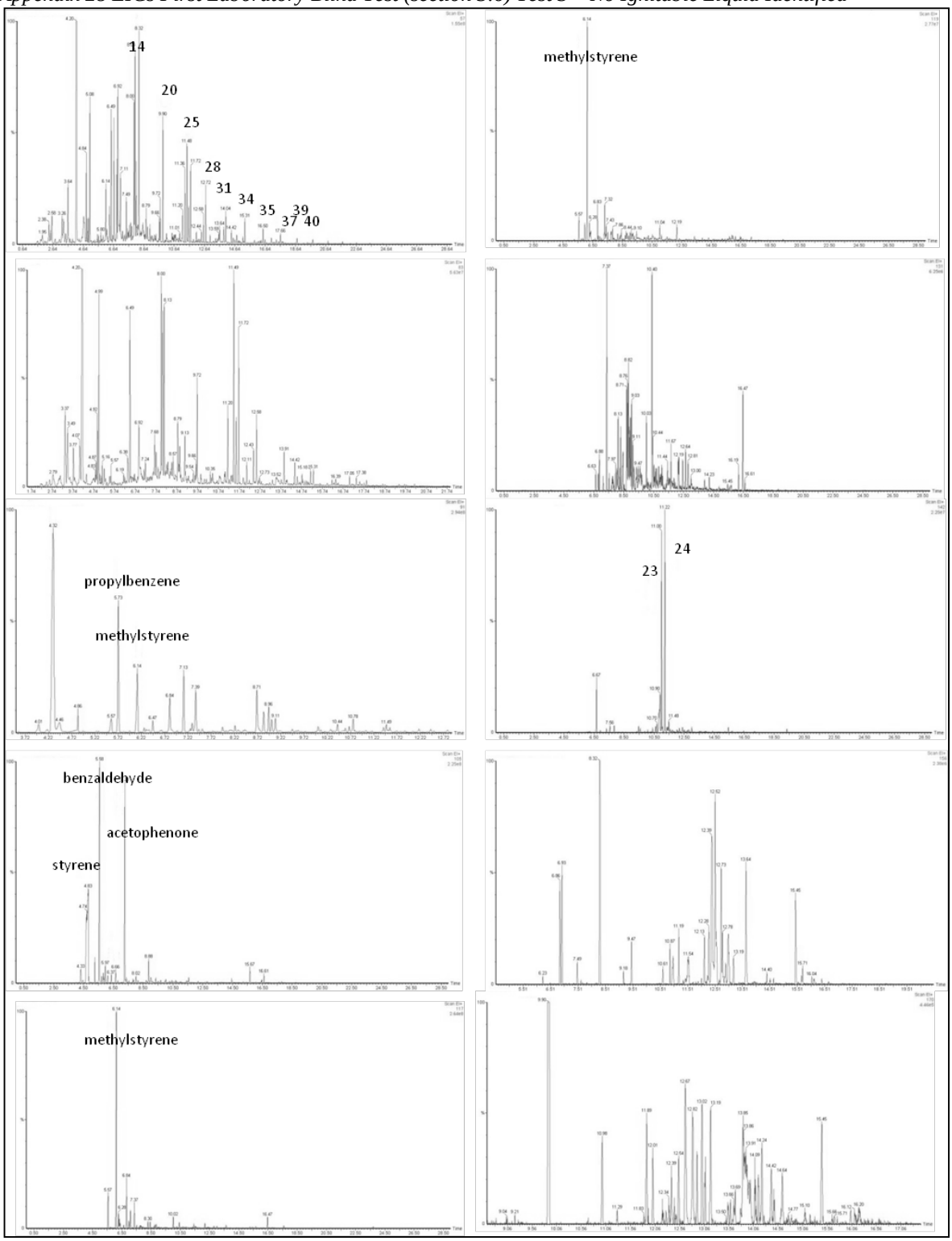
Appendix 26 EICs First Laboratory Blind Test (section 3.6) Test 1 – No Ignitable Liquid Identified



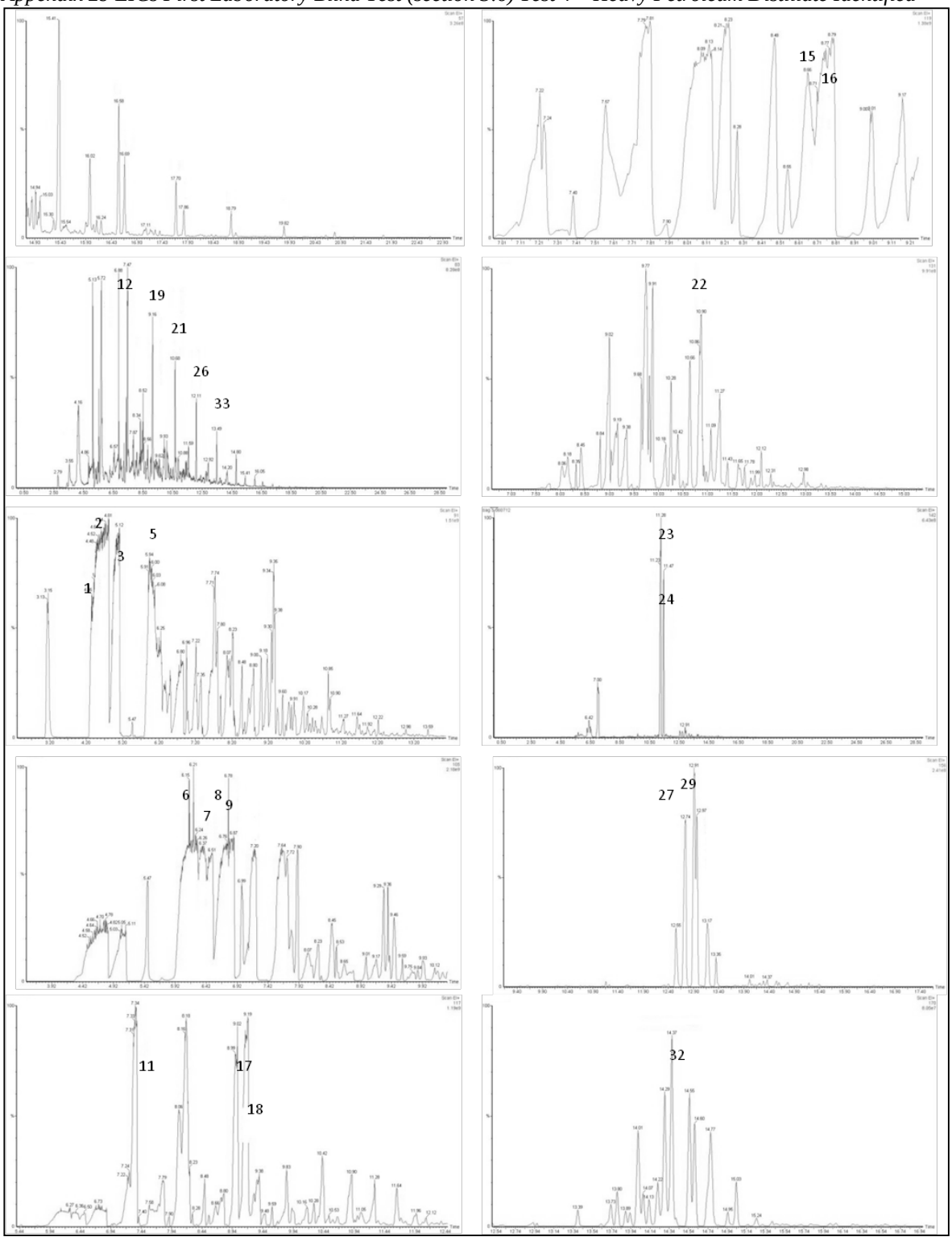
Appendix 27 EICs First Laboratory Blind Test (section 3.6) Test 2 – Heavy Petroleum Distillate Identified



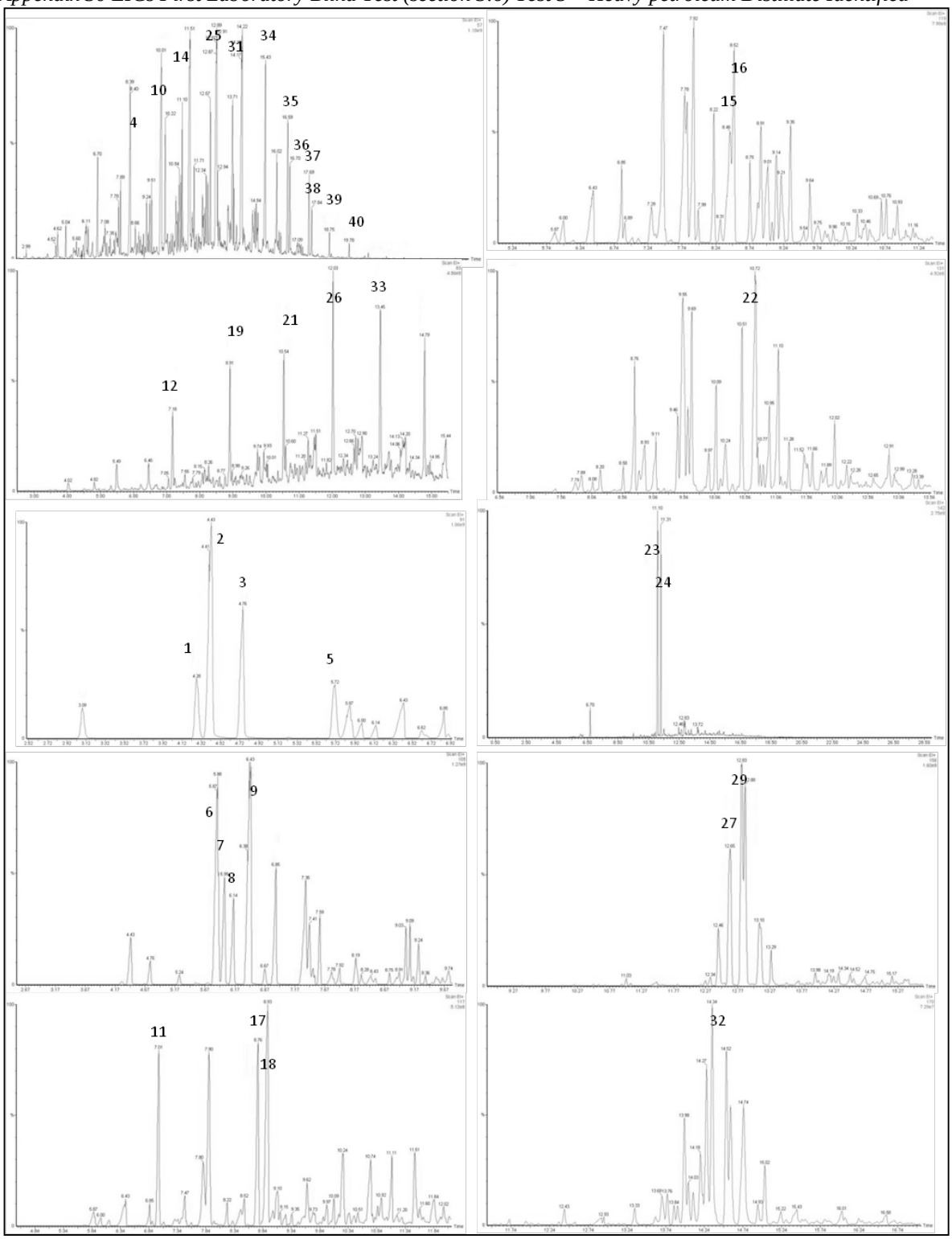
Appendix 28 EICs First Laboratory Blind Test (section 3.6) Test 3 – No Ignitable Liquid Identified



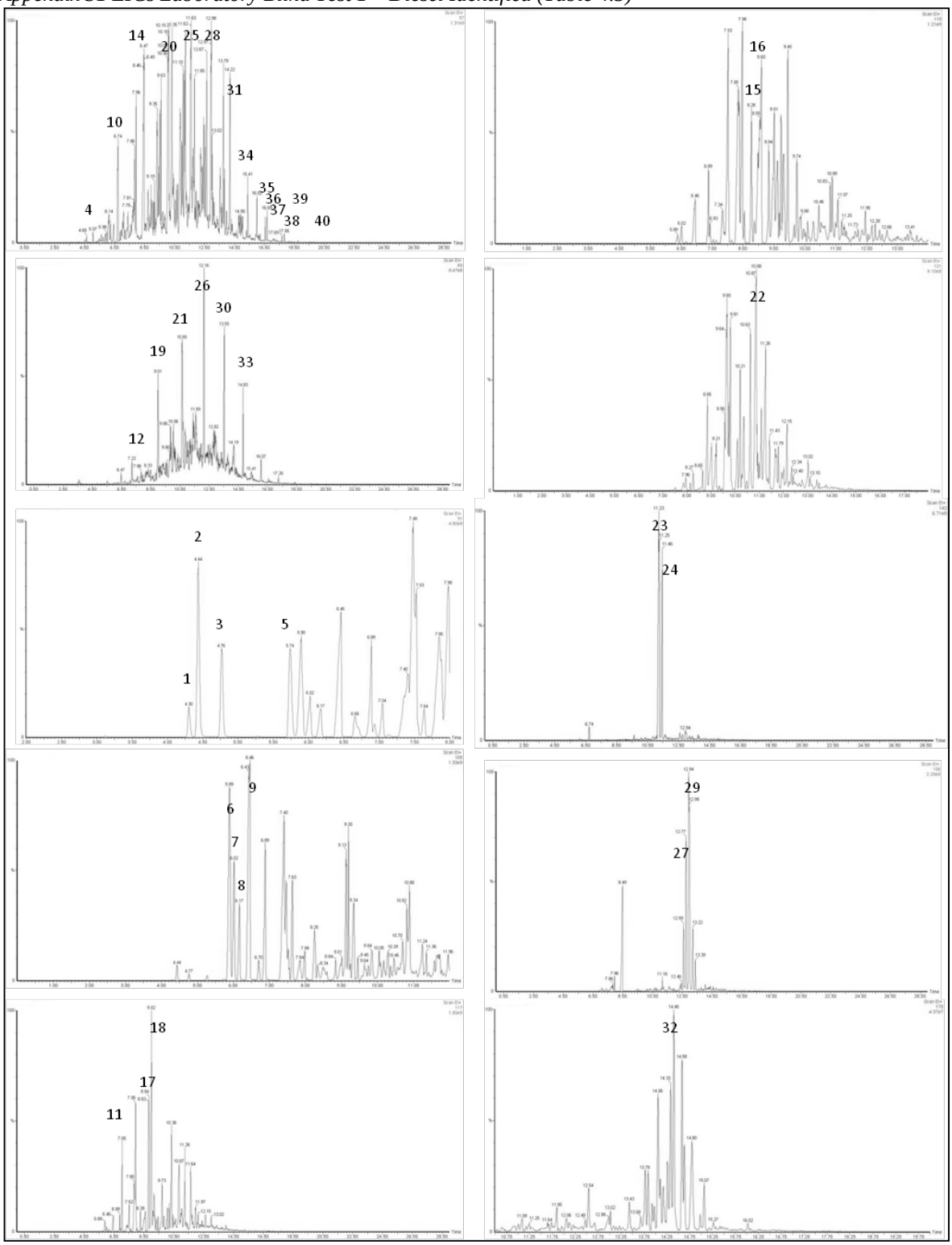
Appendix 29 EICs First Laboratory Blind Test (section 3.6) Test 4 – Heavy Petroleum Distillate Identified



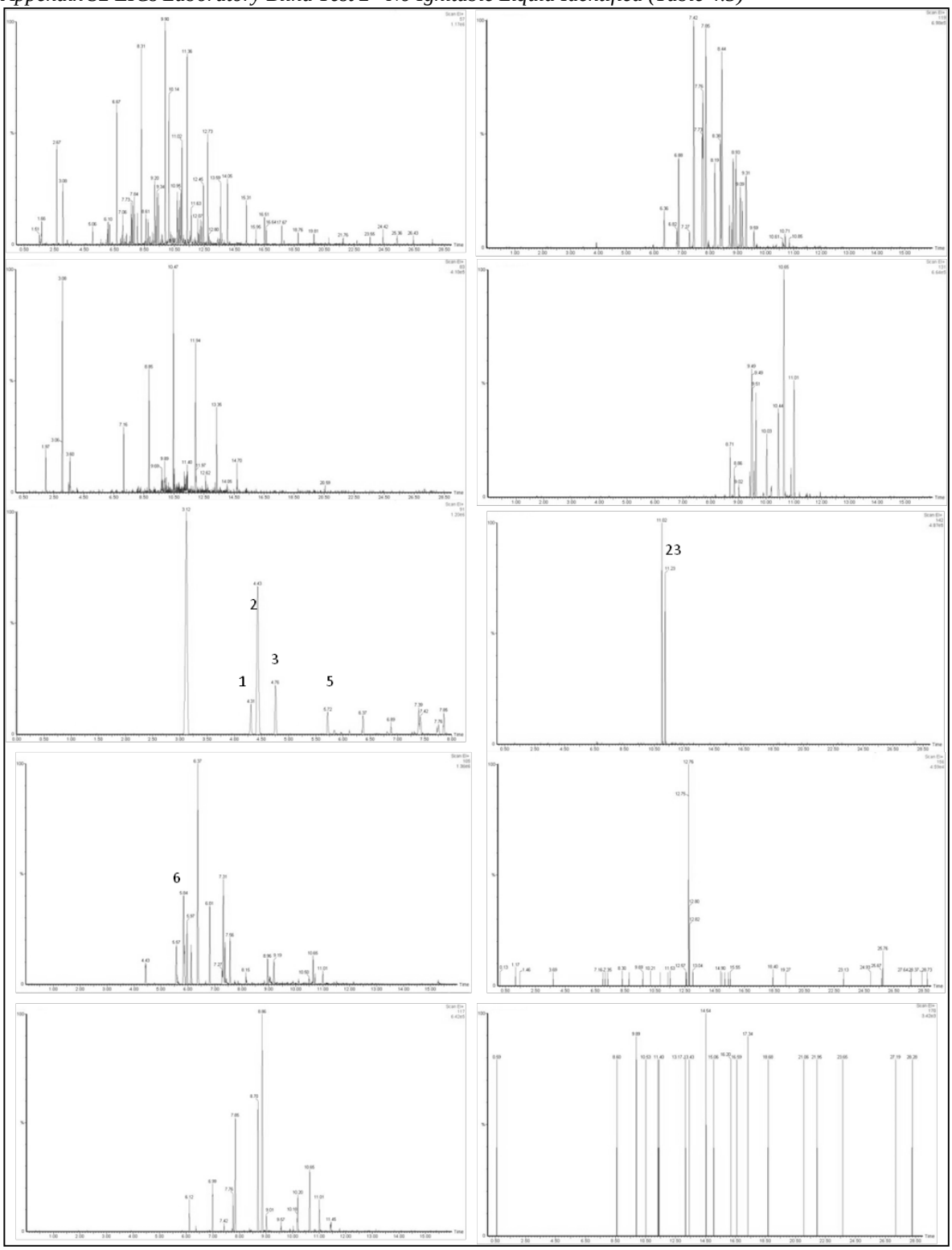
Appendix 30 EICs First Laboratory Blind Test (section 3.6) Test 5 – Heavy petroleum Distillate Identified



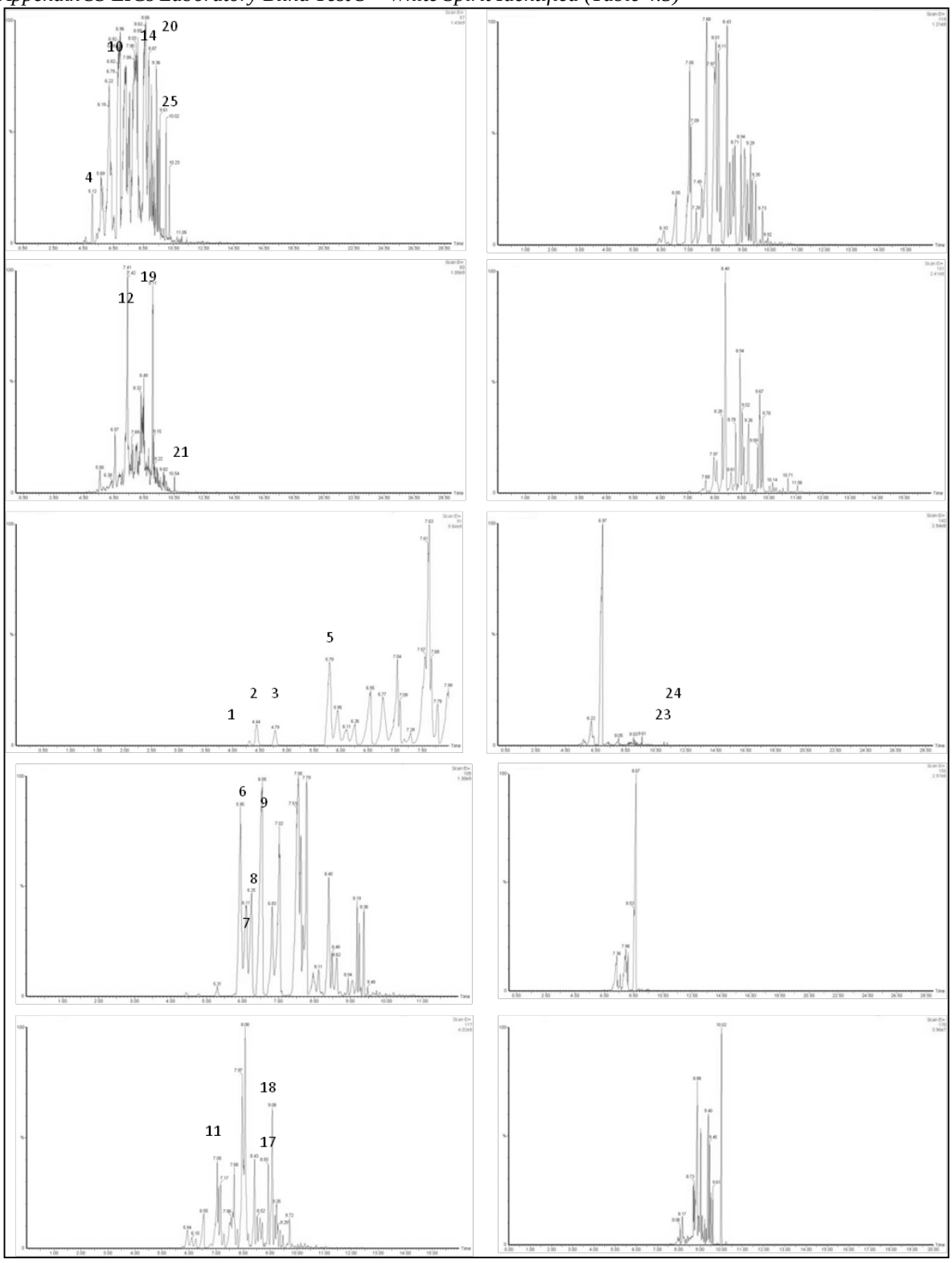
Appendix 31 EICs Laboratory Blind Test 1 – Diesel Identified (Table 4.5)



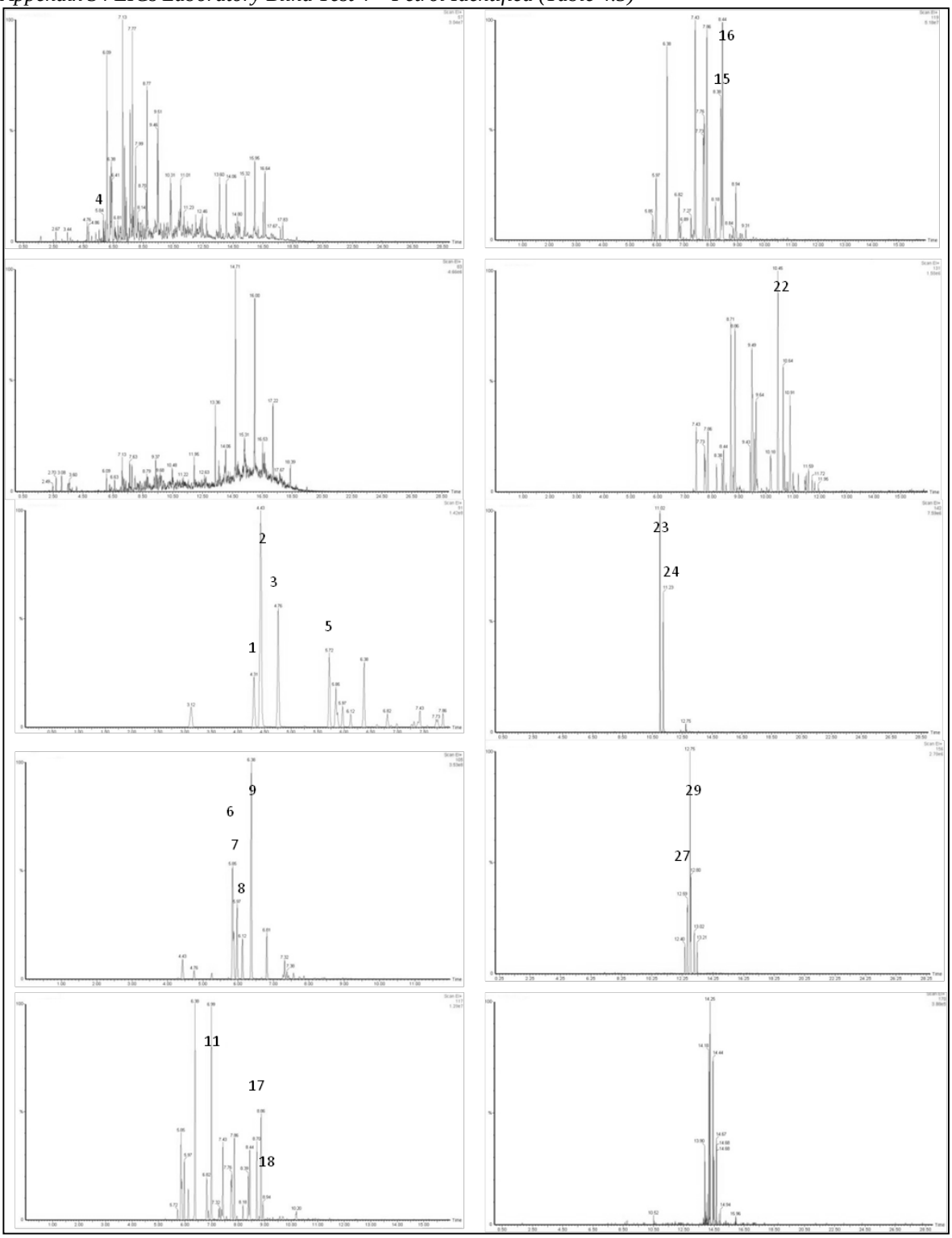
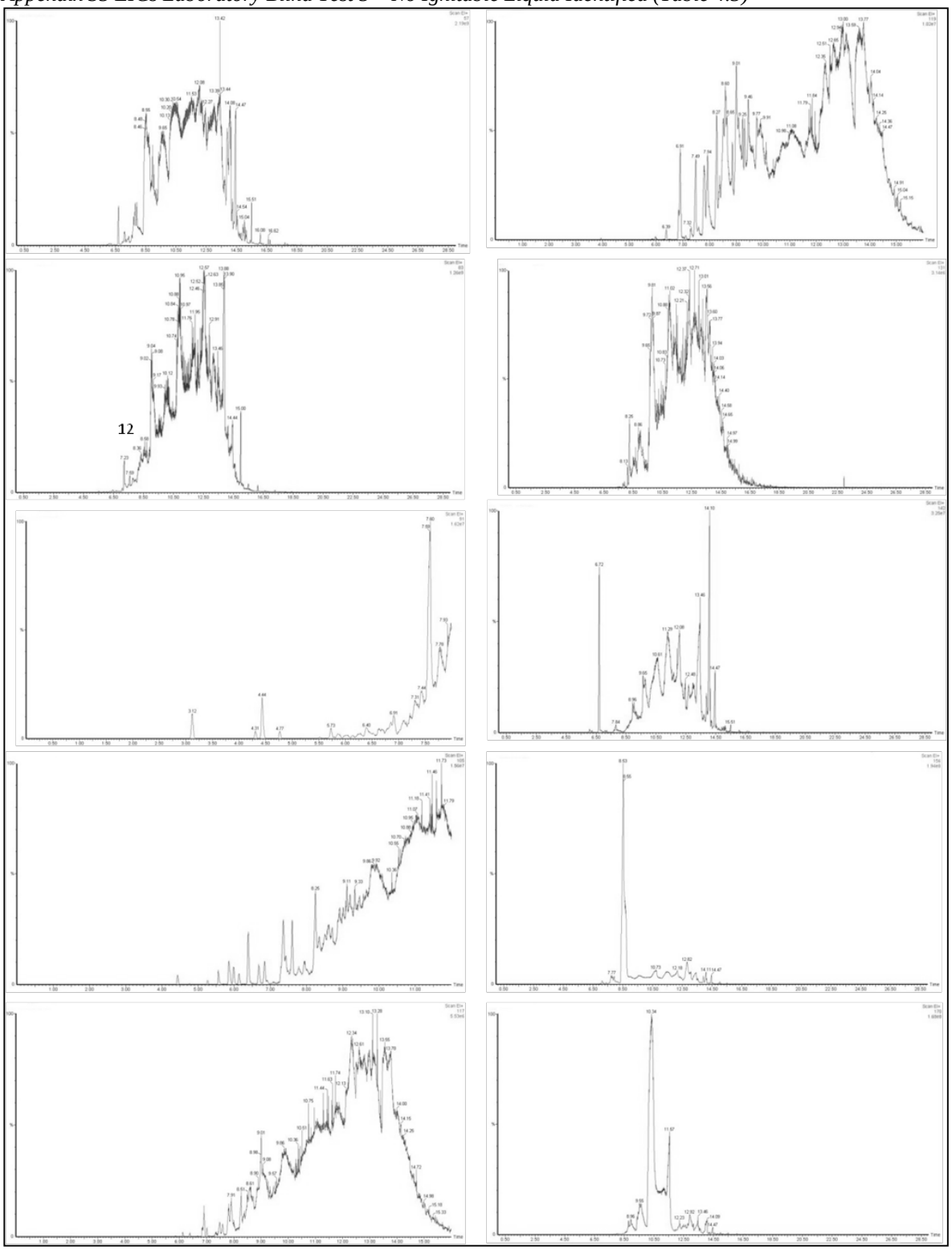
Appendix 32 EICs Laboratory Blind Test 2 –No Ignitable Liquid Identified (Table 4.5)



Appendix 33 EICs Laboratory Blind Test 3 – White Spirit Identified (Table 4.5)



Appendix 34 EICs Laboratory Blind Test 4 – Petrol Identified (Table 4.5)



Appendix 35 EICs Laboratory Blind Test 5 – No Ignitable Liquid Identified (Table 4.5)