



ERASMUS MUNDUS MASTER FORENSIC SCIENCE

MASTER THESIS

FOR OBTAINING THE DEGREE OF
MASTER OF SCIENCE IN FORENSIC SCIENCE

***“Contribution to Portuguese Urban Fire Investigations
– Forensic Fire Debris Analysis”***

WORK PRESENTED BY

STEFANIA OLIVERIO

PRESENTED IN

JULY 2016

TO

INSTITUTO SUPERIOR DE CIÊNCIAS DA SAÚDE EGAS MONIZ



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Certificate of originality

This is to certify that I am responsible for the work submitted in this thesis and that the work is original and not copied or plagiarised from any other source, except as specified in the acknowledgments and in references. Neither the thesis nor the original work contained therein has been previously submitted to any institution for a degree.

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Name:

Date:

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Abstract

Fire scene investigation and fire debris analysis (FDA) are two tightly linked and mutually exclusive key elements of a forensic arson investigation. While the fire scene investigation is performed by a trained fire investigator, FDA is a task undertaken by a fire debris analyst, which is normally a forensic chemist with expert knowledge in analytical chemistry. To solve a case efficiently and successfully, cooperation and information- and knowledge-exchange are necessary, especially since this branch of forensic science is defined as one of the most complex and arduous ones due to the highly destructive nature of fires that severely compromises the integrity of the evidence collected at the crime scene. The task of analysing the fire debris for the detection of ignitable liquid residues (ILRs) is further complicated by the large influence and existence of interfering products. Most ignitable liquids (ILs) are made of hydrocarbons, which are also compounds that have been found in the substrate of common household or construction materials as well as being created during the processes of combustion and pyrolysis.

The purpose of this study was to identify and characterize background, combustion and pyrolysis products of commonly encountered substrate materials in fire scenes in Portugal and observe the effects on ILRs identification by using headspace solid-phase micro-extraction linked to gas chromatography-mass spectrometry (HS-SPME-GC-MS).

The results show that both the background of the substrates and the combustion and pyrolysis products formed during a fire include many compounds that constitute common ILs, such as alkanes and aromatics, that especially in the presence of low amount of ILRs constitute a problem in the conclusive identification of ILs. Even though detailed analysis of the chromatographic and mass-spectral patterns and the combinations of compounds detected in the materials can avoid misinterpretation, in some cases, awareness and knowledge of interfering products is essential.

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Abbreviations

Acronym	Definition
°C	Degree Celsius
ACS	Activated Charcoal Strip
Art.	Article
ASTM	American Society for Testing and Materials
BP	Boiling Point
CO	Carbon monoxide
CO ₂	Carbon dioxide
EIC	Extracted Ion Chromatogram
EIP	Extracted Ion Profile
eV	Electron-Volt
FCT	Faculdade de Ciências e Tecnologia
FDA	Fire Debris Analysis
FID	Flame Ionization Detector
g	Grams
GC	Gas Chromatography
GC-FID	Gas chromatography-Flame ionization detection
GC-IRMS	Gas chromatography-Isotope ratio mass spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
GC-MS/MS	Gas chromatography-tandem mass spectrometry
GCxGC	Comprehensive two-dimensional GC
h	Hour(s)
HCN	Hydrogen cyanide
HP-5	5% Phenyl 95% dimethylpolysiloxane capillary column
HPD	Heavy Petroleum Distillate
HS	Headspace
HSSE	Headspace sorptive extraction
IL	Ignitable Liquid
ILR(s)	Ignitable Liquid Residue(s)
IUPAC	International Union of Pure and Applied Chemistry
L	Liter

LOIC	Lei Orgânica da Investigação Criminal (General Law for Criminal Investigations)
LOPJ	Lei Orgânica da Polícia Judiciária (General law for the scientific police)
<i>m/z</i>	Mass-to-Charge Ratio
MPD	Medium Petroleum Distillate
min	Minutes
μm	Micrometers
mL	Milliliters
MS	Mass Spectrometry
MW	Molecular Weight
NACP	National Authority of Civil Protection
NCFS	National Center of Forensic Science
NFPA	National Fire Protection Agency
NIST	National Institute of Standards and Technology
PAH	Polycyclic Aromatic Hydrocarbon
PDMS	Polydimethylsiloxane
PET	Polyethylene terephthalate
PJ	Polícia Judiciária
PPE	Personal Protective Equipment
ppm	Parts Per Million
PU	Polyurethane
PVAc	Polyvinylacetate
PVC	Polyvinylchloride
RT	Room Temperature
s	Seconds
SIM	Selected Ion Monitoring
SOPs	Standard Operating Procedures
SPME	Solid-phase micro-extraction
SWGFX	Scientific Working Group for Fire and Explosions analysis
TCC	Target Compound Chromatogram
TIC	Total Ion Current/Chromatogram
UNL	Universidade Nova de Lisboa
V	Volt

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1.1 Fire investigation – the main concepts from the scene of the crime to the laboratory examination

What is fire? – From a sociological and evolutionary perspective, fire is one of the most important elements of human evolution. The control of fire around 2.5-1.5 million years ago set an important milestone in civilization, since the main properties of fire – source of heat and light – allowed the hominids to discover cooked food, to survive longer in hostile environments and cold climates and to be able to extend activities such as hunting until after it got dark (James et al., 1989).

From a scientific perspective, fire is defined as an exothermic reaction that involves a combustible substance, also known as fuel, and an oxidizer and that has a reaction rate sufficient to produce thermal energy and light. To start the reaction, an activation energy given by a heat source is necessary. For fire sustainment and propagation, also an uninterrupted chemical chain reaction between the fuel, oxidizer and thermal energy is required. All these principles of fire are represented in what is known as the ‘fire tetrahedron’ (**Figure 1**). If one of the sides is missing, the fire cannot subsist and will be extinguished (Stauffer et al., 2007).

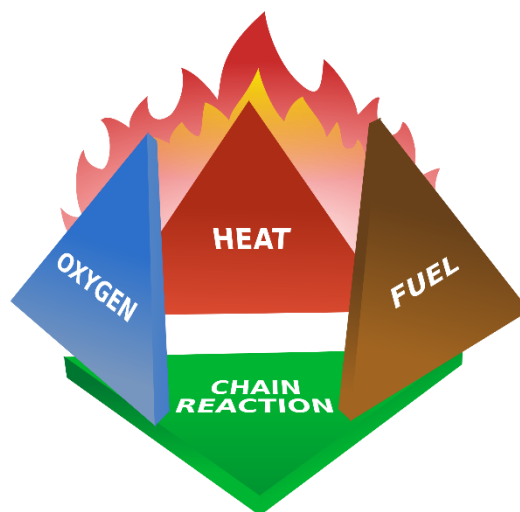


Figure 1: Image of the elements constituting the ‘fire tetrahedron’ (Source: tetraedrodofogopt.svg).

Not only was fire important for the human evolution from a physical point of view, but also from a philosophical one: fire was one of the four classical elements in alchemy and Greek philosophy. It was associated with properties like energy and passion, which challenged and kept the brightest minds of those times, like Plato and Aristoteles, busy for a long period (Frazer, 2013).

Throughout the years the humans evolved rapidly and soon fire was not only used for cooking, heating and lighting purposes, but it's properties were developed negatively to the use as weapons, to harm people and to damage properties, buildings and entire cities during the wars.

Furthermore, in the 19th century during the farming period and later on during the industrialization period, fire continued to be used for destructive purposes. It became popular to deliberately set fire to houses, wildland, crops, cars and other personal belongings.

This phenomenon is known as 'arson' and the person setting the fire is called an 'arsonist' (Redsicker and O'Connor, 1996).

Arson nowadays is a crime and is punished severely in the majority of the countries. Back in the days, however, it was not seen as a crime: not because it was not frequent, but mainly because the population was more scared about crimes against the person, e.g. robberies or murders, than damaged properties. Another reason for the reduced interest by the judicial system for arsonists, at that time, was the insufficient knowledge about fire behaviours and the related inadequacy of evidence to prove responsibility, ensuing unsolved and unpunished cases (Blumberg, 1981).

Fire is a complex chemical process, which implicates a high degree of destruction, resulting in insufficient remains for evidence (De Haan and Ilove, 2011). But throughout the years, the incidence of fires in many countries all over the world grew exponentially to a level that was too high to be tolerated, which resulted in the need for a deeper understanding of the nature of fires, their behaviour, the chemistry and physics behind it and its observable consequences. Therefore, many scientists started showing interest in fires and studying its behaviour. This eventually led to the establishment of 'arson' as a punishable crime. As a result, the development of a fire investigation system was necessary.

Originally, fires were investigated by the same firefighters that were responsible for extinguishing them; it was the easy and convenient option, since they already had enough experience with handling and understanding fires.

However, most of the firefighters were and still are volunteers. This means that the majority was not in possession of a high level of education, even less in a scientific field. Consequently, the efficiency of a complex and challenging investigation such as the fire investigation is limited. Hence, a separation of the duties was required: firefighters to control the fires, fire investigators to investigate them (Lentini, 2009).

A fire investigator is a technical expert who works in a unique field, *'a person with the field experience and technical training necessary to collect and evaluate factual information and identify criminal activity in situations where others perceive only confusion and chaos'* (Redsicker and O'Connor, 1996). He is the one conducting the fire investigation, in which the 'scientific method' is applied to determine the origin, cause and development or spread of a fire.

The 'scientific method' is a principle of investigation used to approach and solve legitimate scientific and engineering problems. Due to the complexity of a fire investigation, which requires an unbiased analysis of the facts by a combination of skills, technology, knowledge and science, the use of a systematic method is recommended. All the steps involved in the 'scientific method' are shown in **Figure 2**:

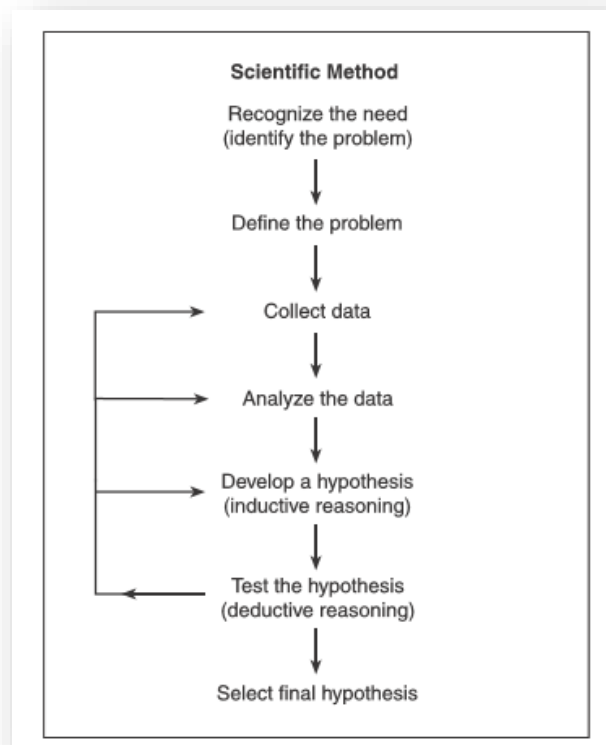


Figure 2: Steps defined in the application of the 'scientific method' according to the NFPA (Source: NFPA-921, 2008 Edition, p. 17, Figure 4.3).

In case of a fire investigation, the problem is defined as the occurrence of a fire. The cause needs to be determined in order to prevent a re-occurrence of the event (National Fire Protection Association, 2008).

A fire investigator is tasked with the determination of the cause and origin of the fire. The primary approach involves the scene examination, followed by collection of data of the event. Moreover, it is necessary to obtain information about previously conducted investigations by other people involved, which implicates: interviewing witnesses, gather information about the history of the property and the area, determine an approximated amount of the fuel load present before the fire occurred and obtain, if possible, photographic and video data of the fire in progress (De Haan and Icove, 2011).

All the data needs then to be analysed. The analysis of the data is an essential step in the fire investigation, since it is the step determining the working hypothesis. It requires a fair amount of knowledge, training, experience and expertise of the fire investigator. Even though this hypothesis needs to be tested against all the data available, it is still important to start with a valid and reasonable hypothesis to not waste time and, more importantly nowadays, money on an illogical proposition. Therefore, a fire investigator with inadequate expertise or knowledge to analyse the data is required to request assistance. This is in order to ensure that the subsequently developed hypothesis is not based on speculation, but on evidence, essential point in cases of arson or insurance fraud argued in a trial.

After appropriate analysis of the data, the development of a hypothesis is necessary, which in a fire investigation includes an estimate of the first fuel, the ignition source, the time for fire growth, spread and the direction of propagation.

This process is also known as 'inductive reasoning' and is mainly based on the observation, collection of data and development of explanations by the fire investigator through his knowledge and expertise.

The following step, called 'deductive reasoning', comprises the testing of the developed hypothesis against all the data available and, if necessary, against new data collected from the scene, witnesses, the literature or other sources. In cases where the available data and the suggested hypothesis are not in accordance, the development of a new hypothesis based on a re-analysis of the data is mandatory. This process must be followed until a final hypothesis can be formulated. Nevertheless, it is paramount to re-test the final hypothesis against all data to ensure that all other possibilities are excluded. The final conclusions can then be reported

with a thorough and clear explanation. However, the possibility exists that none of the formulated hypotheses are in accordance with the examination by 'deductive reasoning'. In those cases, the problem is considered as undetermined (National Fire Protection Association, 2008; De Haan and Icove, 2011).

All personnel involved must follow all the steps involved in this 'scientific method' thoroughly in all fire investigations.

A fire investigation encompasses two different stages:

The first part, which was previously described, involves the fire scene examination to determine the cause, origin and spread of the fire based on the observations made and the data collected. However, in some cases, a second part of fire investigation is required, implicating the laboratory examination of samples recovered from the fire scene when the suspected cause of the fire is arson (Almirall and Furton, 2004a). In case of a fire scene, the laboratory examination is also called 'fire debris analysis' (FDA), which is defined as "the science related to the examination of fire debris samples performed to detect and identify ignitable liquid residues" (Stauffer et al., 2007). It is important to determine whether the fire was set intentionally or was accidental. Collection and analysis of additional evidence for identification of the culprit and proof of the criminal act of arson might be necessary. Furthermore, in those cases, the investigation is established in two distinct parts, which are performed separately and by different types of experts with individual backgrounds and experience. Those experts are then assigned the corresponding examinations (Daeid, 2004). For a fire scene investigator to be able to perform the fire investigation successfully, efficiently and with high level of accuracy, he is required to possess a wide understanding of several major concepts that are necessary to fully understand the dynamics and behaviour of fires. These concepts include (Daeid, 2004; National Fire Protection Association, 2008):

- Main practices and methodologies applied in fire scene and crime scene investigation.
- The basic chemical and physical principles of a fire, its initiation and subsequent behaviour through either combustion or pyrolysis and the necessary conditions for the maintenance of a fire.
- Dynamic of a fire and the factors that affect the speed and direction of propagation.
- Knowledge of types of fuels.
- Relevant properties of materials and their behaviour in a fire.
- Principles of heat transfer.

- Burn and smoke patterns and their interpretation.
- Behaviour of a fire in a compartment compared to an open space.

To obtain the adequate knowledge, proper training and education are required, but also a good literature basis ensuring the state-of-the-art is essential. For fire investigations, several books recorded by experienced fire investigators are available, which summarize all the relevant information, guidelines and tips necessary to perform an impeccable fire investigation. The most renowned and common books are '*Kirk's fire investigation*' by John DeHaan (De Haan and Ilove, 2011), used as the main reference and as a guidance by many fire investigators; the '*Ignition Handbook*' (Babrauskas, 2003), a more modern and recent publication written by fire engineers that gives extensive information about fire dynamics including a discussion about the process of combustion and about the use of accelerants; '*Analysis and Interpretation of fire scene evidence*' (Almirall and Furton, 2004b), one of the most important works that has been written by several of the most known forensic scientists in the field of fire investigations; it provides a wide but detailed foundation applicable not only by the fire scene investigators, but also by the fire debris analysts. Important guidelines have also been provided by the National Fire Protection Agency (NFPA) (National Fire Protection Association, 2008), with detailed and relevant descriptions and definitions.

For FDA, appropriate knowledge and training in the main relevant analytical techniques is required, as well as a wide understanding of the nature of different kinds of materials, including flammable liquids, combustible solids and liquids, their combustion and pyrolysis products. Additionally, for the person responsible for the laboratory examination, a trained forensic scientist, it is indispensable to possess the ability to interpret the results of the analyses and draw the appropriate conclusions. Further details regarding the analytical techniques used for fire investigations are described in chapter **1.4.3**.

The most important literature-work for fire debris analysis was completed by Eric Stauffer and is called '*Fire Debris Analysis*' (Stauffer et al., 2007). This book describes in detail all the processes behind fire debris and the chemical and physical properties of the materials. It also provides an elaborate analysis of the various sample preparation, extraction and analytical techniques applicable in FDA as well as guidelines on how to interpret the data and the background to it, resulting in the most adopted book by fire debris analysts. Additionally, it is constantly updated with the newest relevant and successful advances in research.

1.2 History of fire investigations and the legislature for fire investigations in Portugal

The methodologies applied to approach a fire scene and perform a fire investigation are generally valid and recognized in the majority of the countries all over the world where fire investigations are part of the criminal legislation, even though there are several books and many articles available in the literature that describe different points of view (Sandercock, 2008). However, every country has a different development and a different history of the means, the timing and the reasons fire investigations became part of the legal system and what law-enforcement office is responsible for them.

In Portugal, the first time that arson was considered a criminal act, with resulting punishments, was in the *Act of the 16th September 1886*. With that, Portugal was probably one of the earliest countries in the world to place arson in the legal system. The reasons for that are mainly the morphological and meteorological conditions and the geographical location of Portugal. Those create the right environment for a fire to occur, increasing the probability of incidence of a fire. Indeed, especially in summer, fires represent a big problem in Portugal (Lourenço et al., 2013). A little spark is enough to ignite a very dry branch and with the heat and the currents of dry air present, the growth and spread of a fire is very rapid, making the containment highly difficult (De Haan and Icove, 2011). Therefore, Portugal has been accustomed to fires in the forest and land areas for a long time (Lourenço et al., 2013). Furthermore, many people took advantage of the dry and hot conditions to intentionally set fires and blaming it to the climatic conditions. Without any witnesses, human intervention could not be proven. However, once the numbers of fires started increasing inexplicably, the suspicion was raised to whether there were other reasons than just the climate for the numerous fires that the country suffered from every year. This eventually led to the recognition of the problem of intentionally set fires.

In that period, arson was essentially seen as a crime against the property and punished with high sentences, justified with the defence of private property, which at that time had a high importance compared to the low quality of life of the people. In general, houses, state properties and heritage as well as life, when destroyed by intentional fire, were highly protected and severely punished.

The Act was in vigour until 1982, when through the *Decree-Law n° 400/82, 23rd September*, some articles were added that not only had punishments if the fire caused damage to a person and/or a property, but also if there was the imminent threat or the danger that a damage and/or injury might occur.

Various additions and changes were made in the 90ies and 2000's mainly regarding the competences of the legal authorities.

The currently final modifications were made in 2007, when the Penal Code was modified one more time, with the *Law n° 59/2007, 4th of September*. Its aims were to separate the sentences for forest fires from fires in other spaces due to their differences in cause, motive and extent in the damage, danger and cost they created.

Following are the sentences for all fires except forest fires (Art. 272):

Table 1: List of sentences stated in Art. 272 of the *Law n° 59/2007, 4th of September* for all types of fires (excl. forest fires).

NUMBER	TYPE OF ACTION	TYPE OF DANGER	SENTENCE
1.	Criminal intent	Criminal intent	3 to 10 years
2.	Criminal intent	Negligence	1 to 8 years
3.	Negligence	Negligence	Up to 5 years

Following are the sentences for forest fires (Art. 274):

Table 2: List of sentences stated in Art. 274 of the *Law n° 59/2007, 4th of September* for forest fires.

NUMBER	TYPE OF ACTION	TYPE OF DANGER	SENTENCE
1.	Criminal intent	---	1 to 8 years
2.	Criminal intent	Criminal intent	3 to 12 years
3.	Criminal intent	Negligence	2 to 10 years
4.	Negligence	---	Up to 3 years or fine
5.	Gross Negligence or Negligence	---	Up to 5 years
6.	Criminal intent	---	1 to 8 years
7.	Criminal intent	---	1 to 5 years

As it can be seen, the sentences for the crime of arson in Portugal are relatively high, especially for negligent behaviour, the sentences of which are not much different from the ones for fires set with a criminal intent. Those severe sentences were created as a final way to drastically reduce the numbers of fires and bring the Portuguese population to a higher awareness about fires and their related dangers.

However, mainly responsible for bringing the necessary awareness and sense of responsibility into the Portuguese people are the various law-enforcement-authorities (Carvalho, 2016a).

1.3 Involvement of authorities

In Portugal, there are several authorities involved in the development of a reported fire, their determination of accidental or intentional cause and that are responsible for the communication of information and reports about fires occurring in the country as well as the education of the population on the proper behaviour in cases of fires.

1.3.1 National Authority of Civil Protection

When a fire is reported to the emergency service, the first authority that is informed is the *Autoridade Nacional de Proteção Civil*, or in English *National Authority of Civil Protection* (NACP), which is the main authority in Portugal that monitors all incoming emergencies and assesses the level of severity of the situation. The NACP is responsible for all risk situations in Portugal mainland and their management. It controls all the forces present in the country, fire fighters, police, National Guard, and organizes the distribution of those forces in the various situations.

In cases of a fire, the local firefighters, ambulance, if necessary, and police are sent to the scene to solve the situation. On scene, the firefighters have the main responsibility and are the commanding officers. They assess the situation and decide whether it is necessary to summon other forces. In cases where arson is suspected, a fire investigator needs to be called at the scene, which is responsibility of another authority, the *Polícia Judiciária*, or Scientific Police (Almeida, 2016).

1.3.2 Scientific Police

Currently, fire investigations where human intervention is suspected are part of the competences of the *Polícia Judiciária*, the Portuguese scientific police force, competences which are determined by the *Law 21/2000, 10th August – LOIC* and *Decree-Law A/2000 art. 275, 9th November – LOPJ*.

1.3.3 Insurance companies

Fire insurance is the main risk of an insurance policy for what is internationally known as property, i.e. the insurance of property, and includes what in Portugal is known as ‘IOD’ (Incêndio e Outros Danos) or ‘fire and other damages’ insurances. Their objectives are to guarantee a compensation for the losses that the property of the policyholder suffered because of an accidental fire. Fire insurance is defined as “a compensation: an insured is not allowed to receive more of the exact value of the suffered damages”, therefore, the insurance’s liability limits correspond to the capital and the value of the property declared in the insurance policy.

From the point of view of the policyholder and owner of the insured property, the value of the fire insurance is based on the transfer of responsibility for the losses that result from the occurrence of a fire to an insurance company. Thus, insurance companies need to have a set of rules that allow the correct evaluation of the risks assumed. Those are applied in the risk assessment, defined as a decision-making process based on which the insurer decides to accept a certain risk by taking into account the best evaluation possible of some crucial points: the activity performed in the property, the location, the value of the object, the amount and level of combustible material, the construction type and the protective measures applied to the property.

To determine the cause of an occurred fire and the thereby related decision to whether compensation to the policyholder is required and in what amount, an external fire investigator is tasked with a technical expert report (Carvalho, 2016b).

1.4 Fire Debris Analysis

In a fire investigation, the most important part is considered the fire scene examination and interpretation of fire patterns, since it answers the most important questions relevant from a legislative point of view in determining whether the cause of the fire was intentional, accidental or natural (Daeid, 2004). However, if the fire investigator determines or suspects an intentional cause, it is classified as arson, which is a criminal act for which the responsible person needs to be identified and punished according to the law. Apart from photographic evidence of the fire patterns and damages, usually several samples are collected at the fire scene, to strengthen the case in a court of law. To prove arson, the samples collected need to e.g. be residues of materials that can confirm or contradict the suspected point of origin, the ignition source, the fire behaviour or the reached temperatures during the fires by their chemical properties: if a certain material is suspected to have been ignited and to be the cause of the fire spread, but the flashpoint of the material or the degradation behaviour based on the molecular structure of the material makes it scientifically improbable, it can be ruled out as the ignition source and another source needs to be found. Very common in arson cases is the use of fuels to enhance and speed up the spread of the fire. If the fuels do not undergo a complete combustion during the fire, residues of those fuels, or ignitable liquids (ILs), can be still found and prove the deliberate setting of the fire. Hence, a crucial role for the law-enforcement authorities is also played by the analysis of the fire debris collected at the scene (Almirall and Furton, 2004a; Pert et al., 2006).

Ignitable liquids are liquids that will readily ignite when exposed to an ignition source (Almirall and Furton, 2004c). Also known as combustible materials or fuels, they are frequently found in households because of their common use to generate heat and energy for cooking, but also for transport vehicles, in industries, etc. However, if ignitable liquid residues (ILRs) are found at a fire scene, it is crucial to determine whether their presence is due to common industrial or household-use or the use as a fire accelerant, which will, in most cases, determine whether a fire has been accidental or deliberate. An ignitable liquid can be defined as an accelerant when it is used to increase the speed and spread of a fire to deliberately cause damage and/or harm (Stauffer et al., 2007).

For the proper and efficient analysis of the fire debris evidence collected at the fire scene, there are different steps that need to be followed and requirements that need to be fulfilled.

1.4.1 Sample collection and preparation

In general, fire debris samples are chosen by the fire investigator, based on his analysis and interpretation of the fire scene and the type of evidence required to prove his hypothesis explaining and confirming the events. For fire debris suspected to contain ILRs, one of the main ways used for selection and detection is odour. Since most ignitable liquids have a very strong and characteristic smell, a fire investigator can normally smell the presence of a possible fuel. However, olfaction is a very subjective sense, it can vary based on the climate and the genetic predisposition; it lowers its efficiency with time and the substances smelled, which are usually unknown, can be harmful when inhaled. Therefore, opposed to the human olfaction, the canine olfactory sense is preferred. It is more developed and efficient, being able to reach lower detection levels. In fact, in many countries, like the UK or the US, a trained canine unit for accelerant detection exists: they are widely used for additional assistance during the fire investigations. Even though there have been reported cases where dogs were confusing the smell of a fuel with the smells coming from pyrolysis and combustion products of the materials at the scene, the probabilities of collecting samples that contain ILRs are highly enhanced with the help of canines and thus are an option to consider especially in cases of complex and highly damaged fire scenes.

Since ignitable liquids are mostly highly volatile substances, it is important to collect the samples with consideration of time and to preserve the samples from any loss due to evaporation of the gaseous substances. This is achieved by the use of either glass or metal cans or nylon bags that can be properly sealed. It is based upon the material sampled and the subsequent extraction technique used (Stauffer et al., 2007).

To prepare the sample for analysis, various are the techniques available, from steam distillation to solvent extraction, to passive headspace and dynamic headspace concentration. The choice of the appropriate technique has to consider several factors including a high sensitivity and efficiency of the recovery in a short amount of time, low costs involved and, most importantly, degradation or destroying of the sample must be avoided as much as possible.

Furthermore, the technique is obliged to be able to recover the full range of substances possibly present as an ILR. ILRs are mostly made of hydrocarbons, usually mixtures of aliphatic and aromatic compounds of different complexities comprising a wide hydrocarbon-range.

After evaluation and validation of this variety of methods available, the method identified as the one that fulfils the most requirements is, according to ASTM standards, passive headspace concentration (ASTM E-1412) (Stauffer and Lentini, 2003).

1.4.2 Extraction Techniques

As already mentioned in the previous chapter, a variety of techniques is available for the sample preparation and the extraction of the relevant substances for analysis. Many of them, for instance solvent extraction, steam and vacuum distillation, are traditional methods, which are still approved by ASTM standards (Stauffer and Lentini, 2003). However, they are rarely applied due to their high amount of disadvantages, that include co-extraction of other unrelated compounds, time-consume, high costs, poor sensitivity and high complexity of the resulting data to analyse. Therefore, new techniques were developed to solve the previous issues, which led to the application of the technique known as passive headspace concentration.

Passive headspace concentration involves the thermal release of the volatile components of a sample in the headspace of the sampling container. This is followed by the adsorption and concentration of those substances onto a substrate. The compounds are then desorbed and finally analysed. The main advantages of this technique are the non-destructive nature of the process, low costs, high efficiency and sensitivity, simplicity of use and the possibility of re-analysis without significant loss of the compounds (Waters and Palmer, 1993; Stauffer and Lentini, 2003; Pert et al., 2006). The efficiency of the recovery is mainly dependent on the temperature for heating the container during the adsorption process, which needs to be able to volatilize all relevant components but not degrade the sample. The time of exposure to the adsorbent is also relevant, since it is required to be sufficient for quantification of the compounds but at the same time cost-efficient (Lothridge et al., 1996).

The most common adsorbents used are activated charcoal strips (ACS) and solid-phase micro-extraction (SPME).

The strips are made of activated carbon impregnated onto a polymer substrate, which are then inserted into the heated container containing the sample for extraction. The advantage of ACS is its applicability for the majority of ignitable liquids, having a high affinity for hydrocarbons, as well as being resistant to oxidation and having an adsorptive surface.

SPME is one of the most effective and sensitive extraction techniques. It uses a polymer adsorbent coated onto a silica fibre, which is exposed to the headspace of the sample for adsorption and concentration. Compared to ACS, the desorption is performed thermally and directly into the injection port of the gas chromatograph, which is one of its greatest advantages, since it leads to the highest possible sensitivity as well as eliminating the use of toxic and expensive solvents. However, the size of the fibre limits its lifetime and saturation is reached quickly, which can lead to falsified results in cases of quantification analyses. In addition, depending on the type of polymer used for the fibre, affinities vary for different types of compounds; therefore, the right polymer must be selected for the types of substances that are analysed. The most versatile and common polymer used is polydimethylsiloxane (PDMS) (Stauffer et al., 2007).

1.4.3 Analysis Techniques

After successfully extracting the compounds from the sample, they need to be analysed.

For FDA, the most common used analytical technique due to its higher efficiency, sensitivity and reproducibility and approval by the ASTM (Stauffer and Lentini, 2003), is gas chromatography (GC) in conjunction with a mass spectrometer (MS) or a flame ionization detector (FID). GC-MS is not a novel technique; it has already been available for more than 20 years. In FDA, however, it started to be used routinely only recently due to the advances in development of the technique. Those included increased speed, lower costs and simplicity in use, factors that play an important role for a technique frequently used in a laboratory.

The principle of GC-MS lies in the chromatographic separation of substances into their major components. This is based on their differences in retention times due to different boiling points and polarities, followed by detection after ionization based on their different mass-to-charge ratios (m/z). With a MS detector, not only can the total amount of ions be displayed in the chromatogram, known as total ion chromatogram (TIC), but it is also possible to select certain ions, which might be characteristic for a specific compound or fuel class, known as single ion monitoring (SIM) (Bertsch, 1997). Additionally, the appearance of interfering and background compounds in very complex matrices can be highly reduced by the application of target compound chromatogram (TCC). Here the TICs are scanned for characteristic parent/daughters fragmentation ions that give a pattern specific for an IL class, which can then

be compared to the patterns available in libraries from known substances (Lennard et al., 1995). The ASTM also names GC-FID as one of the analytical methods for FDA. Similar to GC-MS, substances are separated chromatographically and then detected after ionization. With GC-MS, the ions going through the detector can be selected and, therefore, specific mass-to-charge ratios can be analysed. However, FID yields a chromatogram with the total ion count of ions going through the detector. Chromatograms from FDA can be very complex and are similar for many types of fuels, which can only be differentiated by having a closer look at the different hydrocarbon classes and specific ions. Those requirements are fulfilled by GC-MS only, which is therefore preferred to GC-FID.

1.4.4 Interpretation of the data

The main data obtained from both standard techniques, GC-MS and GC-FID, are the TICs, which represent the abundance of all ions passing through the detector at every retention time, for each sample analysed, and the corresponding mass spectrum at each retention time. Through observation and visual inspection of the peak pattern, a trained fire debris analyst is able to determine whether the sample contains ILRs and, if so, which type of IL. The reason for that lies in the chemical and structural properties of ILs.

Petroleum-derived ILs, which are the most common liquids used as accelerants, are complex mixtures of hydrocarbons, which are mainly composed by the following categories of hydrocarbons: alkanes, cycloalkanes and aromatics, which are sub-divided into alkylbenzenes, polynuclear aromatics (or naphthalenes) and indanes. Each of those classes has specific ions that characterizes them due to their different fragmentation of their chemical structure, making the recognition in the mass spectrum possible. A list of the different chemical classes and their characteristic ions is found in **Table 3**.

Table 3: List of the main chemical classes and their characteristic fragmentation ions (Hendrikse et al., 2015).

Compound Family	(Group of) Compound(s)	Fragment ions (m/z)
Alkanes	<i>n</i> -Alkanes, branched alkanes	43, 57, 71, 85,..
	Cycloalkanes	41, 55, 69, 83, 97,..
Aromatics	Toluene	91
	C ₂ -Alkylbenzenes	91, 106
	C ₃ -Alkylbenzenes	91, 105, 120
	C ₄ -Alkylbenzenes	91, 119, 134
	Indane	117
	Methylindane	117, 132
	Naphthalene	128
	Methylnaphthalene	142
Oxygenates	Alcohols	31, 45, 59,..
	Ketones	43, 58, 72, 86
	Acetates	43
	Saturated methyl esters of fatty acids (FAMES)	74, 87
	Single unsaturated FAMES	55, 74, 87
	Double unsaturated FAMES	55, 67

There are various types of petroleum-derived ILs available nowadays, with apparently similar composition. However, having a look at their relative abundance in the various hydrocarbon classes highlights significant differences, which are used to differentiate them. The ASTM developed a classification system for ILs, which is summarized in **Table 4** and is commonly used by the majority of fire debris analysts around the world. To be able to determine the abundances in the different hydrocarbon classes, the TICs are not sufficient; the obtained chromatogram is too complex to be able to extract any information from it. Therefore, through the use of the analysis-software of the mass spectrometer, extracted ion chromatograms (EICs) need to be obtained. EICs are chromatograms, which show the abundance present in the sample of a specific ion. However, for some classes there are multiple specific ions characterizing it. To have an overview of all ions in one class, extracted ion profiles (EIPs) can be created, which summarize the EICs of various ions into one

chromatogram. This helps minimize the data and time needed for evaluation. For that purpose, reference profiles for different compounds and their classes can be found in the literature (Newman et al., 1998; Stauffer et al., 2007), to which the obtained profiles can be compared, allowing the determination of the compound present in the sample (Almirall and Furton, 2004b; Pert et al., 2006).

Table 4: Classification scheme for ILs according to the ASTM standards (Stauffer et al., 2007).

Class	Alkanes	Cycloalkanes	Aromatics (includes indanes)	Polynuclear aromatics
Gasoline	Present, less abundant than aromatics	Present, less abundant than aromatics	Abundant	Present
Petroleum distillates	Abundant, Gaussian distribution	Present, less abundant than alkanes	Present, less abundant than alkanes (Absent in dearomatized distillates)	Present (depending on boiling point range), less abundant than alkanes (Absent in dearomatized distillates)
Isoparaffinic products	Branched alkanes abundant, <i>n</i> -alkanes absent or strongly diminished	Absent	Absent	Absent
Naphthenic paraffinic products	Branched alkanes abundant, <i>n</i> -alkanes absent or strongly diminished	Abundant	Absent	Absent
Aromatic products	Absent	Absent	Abundant	Abundant (depending on the boiling point range)
Normal-alkanes products	Abundant	Absent	Absent	Absent
Oxygenated solvents	-	Composition may vary	Presence of oxygenated	Organic compounds

1.4.5 Sources of interferences

With the use of TICs, EICs, EIPs and TCCs, under normal and ideal conditions, each sample can be assigned to a specific fuel class. However, in most cases, conditions are rarely ideal and there are many changes in these conditions that can alter the chromatographic patterns obtained, making the identification of the compounds in the sample more difficult.

One of the complications can derive from the different evaporation levels of the ILs, due to the loss of material either during the fire itself or after the fire in the period until sample collection. Therefore, the references found in the literature usually have profiles for various evaporation levels available for comparison (Newman et al., 1998; Stauffer et al., 2007).

The loss of signal can be also due to degradation of the sample, which can be of thermal or microbial nature (Turner and Goodpaster, 2012).

Apart from the weathering of the sample, another relevant role in interfering with the chromatographic patterns is played by matrix interferences. Matrix interferences probably are the broadest type of interferences, since there are several sources they can derive from.

The biggest source are inherent interferences, which originate in the sample itself, due to substrate background compounds and combustion and pyrolysis products formed during the fire (Baerncopf and Hutches, 2014).

Combustion is defined as *'a chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or flame'* (National Fire Protection Association, 2008). A solid or liquid that undergoes combustion is slowly decomposing. The volatile and inorganic components of the material evaporate relatively quickly, while the organic ones resist for a longer period before going into the gaseous state.

During a fire, combustion is the most common process occurring, since oxygen is usually present during a fire and necessary to start a fire (see **Figure 1**). However, another process that can occur to a material is pyrolysis.

Pyrolysis is *'a process, by which a solid or liquid undergoes degradation of its chemicals into smaller volatile molecules under heat, without interaction with oxygen or any other oxidants, that is necessary for almost all solids or liquids to burn'* (Stauffer, 2003a). As opposed to combustion, when a material undergoes pyrolysis, it does not react with any oxidant, but it degrades under the effects of heat. However, the more energy is transferred and if an oxidant

is present in the right proportions, a flaming fire can result, in which not the material itself is burning, but the gaseous pyrolysis products released (Stauffer, 2003a).

During a fire, usually both processes occur. This means that in a fire debris sample, products from both are present, which was confirmed in various researches performed on the subject (Lentini et al., 2000; Stauffer, 2001; Cavanagh et al., 2002).

But the type of products formed during those processes are not all the same and varies based on the temperatures reached during the fire, the time it is subject to the processes and, most importantly, the type of material that makes up the substrate.

Thousands of different materials exist, but there are several ones that can be generally found at a fire scene. Those have described in the literature as being the most commonly encountered at fire scenes and mainly include common household items and material used for the construction of buildings.

For walls and partitions, the most common materials used are: masonry, plaster, drywall, wood, cement, concrete and steel.

The most common flooring materials nowadays include the traditional ones like wood, plywood and tiles, but also the more modern but popular synthetic floorings made of polymers such as linoleum, PVC-flooring, nylon carpets and acrylic carpets.

For walls and doors, also the use of wallpapers and paints is common.

Main household items include televisions, sofas, tables, chairs, rugs, paintings, computers, curtains and various materials made of plastic such as bottles, sanitary products and decorative items. The majority of those items are made of polymers: the inside of sofas is made of polyurethane foam, the outside of synthetic textiles like nylon or polyester, tables and chairs are made of wood composites and hard plastics, rugs are made of synthetic fibres or natural materials such as wool or cotton, television and computer cases are made of thermosets, such as Bakelite, curtains are made of acrylic, cotton or polyethylene (Redsicker and O'Connor, 1996; Daeid, 2004; Stauffer et al., 2007; De Haan and Icove, 2011).

All those materials have different chemical structures and therefore a distinct behaviour when subject to heat, releasing different compounds, which can interfere with the signals of an eventually present accelerant in the sample.

The process of pyrolysis and the effects of it on various substrate materials has firstly been described and demonstrated by Stauffer in his article, which is based on the extensive work completed in his master thesis (Stauffer, 2003a). Almirall and Furton continued with the work

on interfering compounds in FDA by determining and characterizing background and pyrolysis products that may interfere in the analysis of fire debris (Almirall and Furton, 2004c). They selected a wide number of common materials encountered on fire scenes in USA, subjected all of them to combustion and some of them to pyrolysis and applied one of the ASTM standards, which is extraction by passive headspace concentration with activated charcoal and analysis by GC-MS. Similarly, a research group in China determined the background components of burned carpet by using SPME and analysis via GC-MS (Li et al., 2013). Another recent study performed on Mauritius islands determined the background and pyrolysis products of materials found on their island with the same methods used by Almirall and Furton in 2004, even though a lower number of samples was selected (Almirall and Furton, 2004d; Jhaumeer-Laulloo et al., 2013).

1.5 Aims and Objectives

Fire investigations and the related fire debris analysis are one of the most complex fields of forensic science. Numerous studies were conducted on the various topics and relevant research areas. However, like all scientific fields, research will never cease and there is always a chance of improvement and development. An area showing a more pronounced absence of consolidated and recognized opinions was identified in the study of interfering products.

The aim of this research is to combine the two parts of a fire investigation by actively going to fire scenes, conducting the fire investigation, collecting relevant samples and performing the analysis of those samples in the laboratory. Additionally, not only samples for the cases are collected, but also samples that are then used to determine and characterize the background, combustion and pyrolysis products of commonly encountered substrate materials, specifically for Portuguese fire scenes.

The extraction method to be evaluated is SPME, due to its large amount of advantages compared to the other methods, which are cost effectiveness, simplicity in use, high sensitivity and, highly important factor nowadays with the advent of an era in the name of 'green chemistry', environmental friendly and non-toxic.

2.1 Methods

2.1.1 Crime Scene Investigation

As already mentioned in the previous chapter, the 'scientific method' is used to approach a crime scene. The method for a crime-related investigation is developed during a cycle, named the 'cycle of investigation', which is based on three key moments.

The first one is the *reasoning*, where the observed scene is analysed by isolating the facts and taking them apart, having as a key tool the application of fundamental questions like "What?, When?, Where?, How?, Who?, Why?". Afterwards, the obtained elements will be subject to correlation by comparing them with the data known by the investigators and the police forces on a plausibility and probability level, using the points of conflict (rule of elimination), the points of doubt and points of agreement (hypothesis) as validation method. It depends on whether the point of doubts are cleared to proceed to the last part of this phase, the *summary*, which has as objective the formulation of the working hypothesis. This is formulated by regrouping the certain points with the objective (known) and subjective (unknown and doubtful) points, assessing, ordering and selecting them based on the priority level and the objectives to meet.

The *reasoning* phase is followed by the phase of *execution*, where the tasks determined in a pre-arranged action plan based on the data obtained from the *reasoning* phase are executed. The last phase is the one of *information*, which consists of the exploration and validation of the certain results obtained from the previous phases.

In some cases, it will be necessary to repeat this cycle until all the possibilities of not obtaining points of agreement are exhausted and the doubts can be substituted by answers through the information obtained. Only then, the elements of proof that consolidate the solution for the investigation are obtained unambiguously.

In the approach to the investigation of urban fires, we need to take into consideration that since those develop in a confined space, they can give rise to false indicators for direction

and path of propagation as well as the ignition area/point, which therefore need to be systematically validated, even though the elements that support them seem very robust.

The 'cycle of investigation' for an urban fire is the following:

Cycle of investigation

- 1) Collection of background information: It is fundamental to an investigator or a team of investigators to possess perfect knowledge of the previous facts concerning the location where the fire occurred, more concretely of what concerns the date (days of the week), hour, location and causes of fires that happened in that area, in order to be able to find connections with the ongoing investigation.
- 2) Identification of the morphology of the burned area: This is fundamental in the approach to the area where the fire occurred; it is based on the delimitation/identification of the main area to be investigated and certain rules required to be chronologically followed:
 - a. Identification of the compartment with higher degree of damage: Here the combustion developed more slowly; therefore, the heat source persisted for a longer period, resulting in an increased amplitude of the damage.
 - b. Identification of the area on the ceiling with the highest degree of damage: Consequence to the reception of heat during a longer period, even though it is of less intensity (quantity of heat); effects of transmission of heat through convection (starting from the layers of hot air – less dense than the cold air which gives the air an ascending movement) are observed.
 - c. Identification of carbonized material at a low level (of height): If encountered, it results from the fact that the heat and consequent propagation developed from the bottom up, for the effects of convection, and from the center to the sides, due to radiation, which leads us to the 'epicenter' of the physical/chemical phenomenon.
 - d. Homogeneity in the carbonization of the combustible material: Results from the path and intensity of the combustion, creating a pattern of carbonization that reflects the development of the fire.

- 3) Application of the main frame of indicators of path and direction of propagation: This set of indicators results from the behaviour of the different materials, combustible or not, to the action of heat produced by the fire when passed by the flames, and consists in identifying in each of them the path of propagation and also the following:
- a. Degree of damage: Allows us to determine the extent of the damage suffered by the materials through the heat received as a consequence of the combustion. This way, we are able to identify how long the materials received heat not only due to the action of heat like e.g. in combustion, which will allow us to determine the speed of propagation in that exact point.
 - b. Burn pattern: It is the set of sequential carbonizations, in the different materials, from levels of lower point with a higher degree of damage (close to the ignition point) to levels of higher point with lower degree of damage (along the path of propagation).
 - c. Exposition/Protection: Allows the determination of the path of propagation through the observation of both sides of an object or material, which can be the aforementioned carbonization or the fixation of soot (resulting from direct impact with the flames), on the side where the combustion is coming from, and protection from the heat and soot on the other side.
 - d. Chipping: Sign observed in organic combustible material such as wood (very thin – up to 6 mm diameter), on the side where the heat was received, as a consequence of the degradation of the material through the action of heat, which dehydrates the material and makes it lose its level of humidity.
 - e. Carbonization models: Different carbonization patterns observed and to interpret in the different materials found at the scene, that allow us to establish the direction of propagation.
 - f. Flaking: Damage observed in the materials as a consequence of the lowering level of humidity, which sequentially degrade the material until it reaches a point called 'alligator skin', which occurs when there is already an advanced level of combustion, where only through the solid part it's about to reach glowing combustion.
 - g. Soot marks: Signs that results from the fixation of the particulates present in the flames, which when impacting a material or object, cool down and fix

themselves on the object, giving us this way the path of propagation of the flames.

- h. Colour of the ashes: It consists in the identification of the different levels of discoloration resulting from the combustion, being sure that the more complete the combustion is, the more clear will the residues be (white being equal to complete combustion).
- 4) Identification of the area/point of origin: This results as an opposite of the path of propagation, in all its different paths, giving that the fire started in one point where the igniting material was located. In this area, we need to identify, simultaneously, the concentric carbonization marks (central ignition point and consequent effects of radiation), marks of complete combustion (due to the long persistency – slow burning), marks of carbonization of material on lower points (low height of flames) and the apex of the 'V'-pattern, consistent with the carbonization point at a low level (due to the transmission of heat).
- 5) Validation of the seat of fire: Obtained by interviewing people who first attended the scene, including fire fighters and eyewitnesses.
- 6) Search of the ignition source: Following the method of looking at the indicators for the path and direction of propagation through the sweeping of the area/point of origin, the identification and collection of the ignition source is required, in case the evidence is present. This can help determine the intention of the person setting the fire through the relation between the quantity of heat applied and the time necessary for the ignition of the combustible material.
- 7) Collection of the testimonies: Moment to collect the personal proof, of all the people able to function as witnesses to the facts.
- 8) Ordering of the material and personal proof: It is the phase of the investigation where the different types of evidence collected are cross-referenced, in order to reconstruct the facts in all its amplitude.
- 9) Determination of the Primary Hypothesis for the cause: It is here that the investigator, in possession of all the facts and data, can conclude the investigation with a central hypothesis for the fire.

- 10) Validation: the investigator or the team of investigators, who will recreate all the facts until before its development and go through them from the beginning of the investigation to the identification of the probable cause, performs the validation.
- 11) Final (probable) cause: After the technical investigation of the location and the recreation of the facts, the final cause can be determined with a high degree of certainty, depending on the level of destruction or the absence of signs that make up the material proof. The word 'probable' is used due to the necessity of further investigations, at the police station, using all the police investigation techniques until the perpetrator is identified.

Evidence collection

With a small, clean shovel, the material selected as evidence is collected and put into a glass can with vacuum cap, which is then closed. The maximum amount of material to be collected is up to 2/3 of the glass can. It is then sealed as evidence and labelled with the date, case number, sample number, location of collection, type of sample and name of collector. Maintenance of the 'chain-of custody' is essential. For cases in which the scientific police is involved, only one samples if collected. However, for insurance companies, collection of two equal but separate samples is required, one to be analysed by the technical expert and another one for the counter-analysis of the ensured.

2.1.2 Fire debris analysis and determination of background, combustion and pyrolysis compounds

The second part of a fire investigation, when arson is suspected or if the cause of the fire is unclear, consists in analysing the samples collected at the fire scene. Following are the steps involved in the FDA:

2.1.2.1 Sample preparation:

Prior to extraction and analysis, the samples, depending on the intended use of its results, are subject to sample preparation

1. Cases: For the evidence collected from the fire scenes for analysis, no further sample preparation is required, since extraction is performed directly from the glass cans the sample is collected into.
2. Pre-burn: Piece of the material is cut and placed into one of the evidence collection glass cans, then sealed.
3. Post-burn: A piece of the material is cut, then, under a fume hood, it is ignited with a propane-lighter while being held with forceps on top of an open glass can and left to burn until 2/3 of the material was burned (is possible) or enough fumes were observed. If no burning signs were observed, the flame was kept on the item for 2 minutes. The material was then placed into the glass can and extinguished by sealing it to remove the oxygen.
4. Pyrolysis: 5 g of the material was cut into very small pieces and inserted into the reactor for pyrolysis. After setting up the instrument, the Nitrogen-flow was set to 10 units, which are equal to 2.060 mL/s, and left for conditioning for 15 minutes. Subsequently, the pyrolysis-programme was started, which was set as follows: 1 h to reach 800°C from room temperature (RT), then hold 800°C for 60 s, then 1 h to cool down to RT. The residue was then collected into a glass can and immediately sealed.

2.1.2.2 Extraction:

For all samples analysed, the extraction technique used is Solid-Phase Micro-extraction (SPME) according to ASTM standard practice E2154-01. The SPME fibre is subject to conditioning in the GC-MS for 30 minutes at 250°C. With a needle and a hammer, a small insertion space is made in the middle of the cap of the glass can containing the sample, which is immediately covered with tape to prevent any substantial loss of material. The glass can is then placed into a water bath preheated at 80°C, the fibre is injected through a septum on top of the previously made insertion space and, once it has been stabilised on a rack, exposed to the headspace for 30 minutes.

2.1.2.3 Analysis:

Analysis of all samples is performed with Gas-Chromatography Mass-Spectrometry (GC-MS) according to ASTM standard practice E1618-01. The conditions are summarized in **Table 5**.

Table 5: summarized list of the GC-MS conditions used in the experiments.

GC-Column	HP-5 MS (30 m x 0.25 mm x 0.25 μm)
Injector	250°C
Injection volume	Manual (SPME fibre)
Splitless mode	
Carrier gas	He at 1.0 mL min ⁻¹
Total flow	13.3 mL/min
Oven temperature program	35°C during 3 min and increase to 310°C at 8°C min ⁻¹ (run time: 39.99 min)
Transfer line	230°C
Ionization	El+ at 70 eV
	Source: 230°C
Multiplier	350 V
Scan	Mass range: m/z 35-200
	Scan time: 3.89 scans/s
	Inter-scan delay: 0.01 s
Detector	280°C

2.1.2.4 Data Analysis:

For each sample, the retention times for all components were recorded. For the identification of the major components, the mass spectrum of each compound was compared against the reference library provided by the GC-MS and the in-house library created in the laboratory through previous analyses. The highest match was chosen as the correct compound.

Additionally, EICs for each of the major ions for the different characteristic hydrocarbon classes were created for compound characterisation and confirmation of the nature of the sample, based on the previously mentioned ASTM E-1618 guidelines.

2.2 **Materials**

2.2.1 *Fire Scene Investigation*

Personal Protective Equipment (PPE) included an overall-suit provided by Prof. António Carvalho, a helmet (3M, Portugal), a mask (3M, Portugal), boots provided by Prof. António Carvalho and latex gloves.

Samples collected from the various fire scenes:

Collected from fire scene 1, north of Portugal:

- 1) Residue of detoxification plaque 1 (**Figure A1**)
- 2) Residue of detoxification plaque 2 (**Figure A2**)

Collected from fire scene 2, central-east of Portugal:

- 1) Wood-imitating flooring (**Figure A3**)
- 2) Laminated cardboard skirting board (**Figure A4**)
- 3) Wall-sustaining wood (**Figure A5**)
- 4) Cement (**Figure A6**)

Collected from fire scene 3, central-west of Portugal:

- 1) Wood from possible point of origin 1 (**Figure A7**)
- 2) Wood from possible point of origin 2 (**Figure A8**)
- 3) Wood from possible point of origin 3 (**Figure A9**)

2.2.2 Determination of background, combustion and pyrolysis products

2.2.2.1 Sample preparation:

2.2.2.1.1 Pre-burn:

Following materials were selected and purchased for the analysis before and after combustion:

Table 6: List of all materials used for the burning experiments and their origin.

Sample Nr.	Sample type	Source
1	Plywood flooring	Collected from fire scene
2	Polyurethane	Collected from fire scene
3	Cement	Collected from fire scene
4	Cork	Leroy Merlin, Lisbon
5	Compressed Wood	Collected from fire scene
6	Vinyl flooring kitchen-use	Leroy Merlin, Lisbon
7	Curtain orange	Leroy Merlin, Lisbon
8	Carpet underlay	Leroy Merlin, Lisbon
9	Carpet red	Leroy Merlin, Lisbon
10	Double-layered carpet black	Leroy Merlin, Lisbon
11	Curtain black	Leroy Merlin, Lisbon
12	Vinyl flooring living room-use	Leroy Merlin, Lisbon
13	Skirting board	Collected from fire scene
14	Wallpaper	Leroy Merlin, Lisbon
15	Gas Pipe	Laboratory 319, Departamento de Quimica, FCT-UNL
16	Wood composite	Leroy Merlin, Lisbon
17	Electric cable with 3 connectors	Leroy Merlin, Lisbon
18	Paint solvent-based	Leroy Merlin, Lisbon
19	Paint water-based	Leroy Merlin, Lisbon

2.2.2.1.2 Post-burn:

For the burning of all the above-mentioned materials, a propane-based lighter by BIC®, straight model, was used.

2.2.2.1.3 Pyrolysis:

For the pyrolysis, a pyrolyser (Respirel, LDA, type VWA) with a constant flow of compressed nitrogen was used. The substrate materials subject to pyrolysis include: double-layered black carpet, cork, black curtain, polyurethane, cement, vinyl flooring for kitchen-use, skirting board, gas pipe.

All samples were placed into 0.5 L glass cans by Bormioli Rocco. The glass can was also subject to extraction and analysis with the same equipment and conditions as for all the other samples. Pictures of all the samples before and after burning are found in **Appendix B**.

2.2.2.2 Extraction and Analysis:

For the extraction of the samples, an SPME fibre (Supelco Inc., Bellefonte, PA, USA), type PDMS 100 µm, non-bonded, with SPME Holder 57330-U and a water bath (Mettler GmbH & Co. KG, Germany) were used.

The analysis was performed via GC-MS, with the instrument by *Agilent Technologies* (Santa Clara, CA, USA), GC type 1909 1S-433E, HP-5MS column, and MS type 5975C VL MSD.

As carrier gas for the GC-MS, helium gas with following characteristics was used:

Table 7: Composition of the helium gas used as a carrier gas for the GC-MS analyses.

Compressed Helium Alphagaz™	Pressure	B 50 charge	B 10 charge	Blocking charge	Square charge	H ₂ O	O ₂	CnHm	Purity
	200 bar	9.1 m ³	1.8 m ³	145.6 m ³	109.2 m ³	< 3 ppm	< 2 ppm	< 0.5 ppm	> 99.999%

2.2.2.3 Data Analysis:

For the analysis of the data obtained, the software provided by the GC-MS producer, Enhanced ChemStation and DataAnalysis, version MSD ChemStation E. 02. 00. 493, Copyright 1989-2008 Agilent Technologies, Inc., was used. TICs and EICs were extracted for visual characterisation of the samples and comparison of their main profile and features with the chromatograms of standard products present in a library by superimposition. The library comprises a collection of the results obtained from the analyses of various products, including inflammable liquids, combustion products, pollutants, synthetic materials, treatment products and adhesives, in different conditions, e.g. direct impregnation, smoked, vapours, slightly flared or heavily burned.

Individual compound identification is achieved by comparison of the mass spectra of the peaks with the GC-MS spectral libraries, which include NIST 98, Wiley 275 and lab-internal database. A compound was reported as identified when, after comparison of the spectral pattern with the standards in the library, the matching scores were equal or higher than 850 (85%). Further confirmation for the identifications was obtained by comparing the MS spectra with the spectra in the NIST Chemical Webbook.

3.1 Fire scene 1 – North

On the 13/02/2016 an industrial fire occurred in the Pavilion 4 of the premises of a poultry farm located near the town Albergaria-a-Velha in the north of Portugal. A worker noticed first signs of smoke coming out of the pavilion around 9:00 am. However, since the previous night the pavilion was detoxified with the use of detoxification blocs, which produced smoke, the worker did not set off the alarm until around 10:00 am, when the worker tried to enter the pavilion and had difficulties doing that together with the entrance doors having an elevated temperature. The firefighters arrived at the scene around 11:00 am, when the fire was already at an advanced stage. . Firefighting measures involved the breaking-off of many of the windows.

Resulting from the advanced stage of the fire found when the firefighters got at the scene, the pavilion showed a high degree of damage throughout the whole space. As a protective measure for the investigators to access the scene safely and without damaging the evidence, hay was distributed on the ground throughout the pavilion.

It was also reported that during the days before the fire, on the 11/02/2016 and 12/02/2016, an electrician did some repair works on the electrical circuits of the building due to a fault.

The fire investigation was performed on the 02/03/2016, with the task to determine the cause and development of the fire.

A full fire investigation report is found in **Appendix C**.

3.2 Fire scene 2 – Centre-East

On the 14/04/2016, a fire occurred in a two-story house located in Peso da Régua. The fire was first noticed around 3:30 PM by a neighbour who saw flames and smoke coming out of the ceiling in the area of the bedrooms. The firefighters were immediately contacted, who arrived around 4:00 PM at the scene, where some local people already were trying to put down the fire with water pumps. However, due to the advanced stage of the fire, their attempts were unsuccessful.

In the events of the fire, the living room, the kitchen, the cellar and the floor beneath were damaged in all its extension due to the deposition of soot. The fire itself was confined to the bedroom area of the house.

The fire investigation was performed after three days, on the 17/04/2016, with the task to determine the cause and development of the fire.

A full fire investigation report is found in **Appendix C**.

3.3 Fire scene 3 – Centre-West

On the 29/05/2016, a fire occurred on the fourth floor, left side, of a building located in the Lisbon neighbourhood of Campo de Ourique. The fire was first noticed around 3:00 AM when the owner of the building, who at that time was sleeping in the bedroom of the involved apartment, heard sounds of falling material. At this point, the flames were at the level of the suspended ceiling, coming from the attic on top of the apartment. The firefighters were immediately called to the scene to put down the fire.

In the events of the fire, the attic where the fire originated suffered total damage and the apartment underneath was partially damaged, to an extent that made the apartment not fit for habitation.

The fire investigation was performed after three days, on the 01/06/2016, with the task to determine the cause and development of the fire.

A full fire investigation report is found in **Appendix C**.

4. RESULTS AND DISCUSSION

All samples were subject to sample preparation as described above (*Materials and Methods*), headspace extraction with SPME and analysis via GC-MS (HS-SPME-GC-MS). The results obtained are described and discussed below.

4.1 Case studies

4.1.1 Case study 1 – North

After collection of two samples at the fire scene 1 (FS1) and transport to the laboratory, following results were obtained after the above-mentioned extraction and analysis techniques (HS-SPME-GC-MS) were applied:

Sample 1

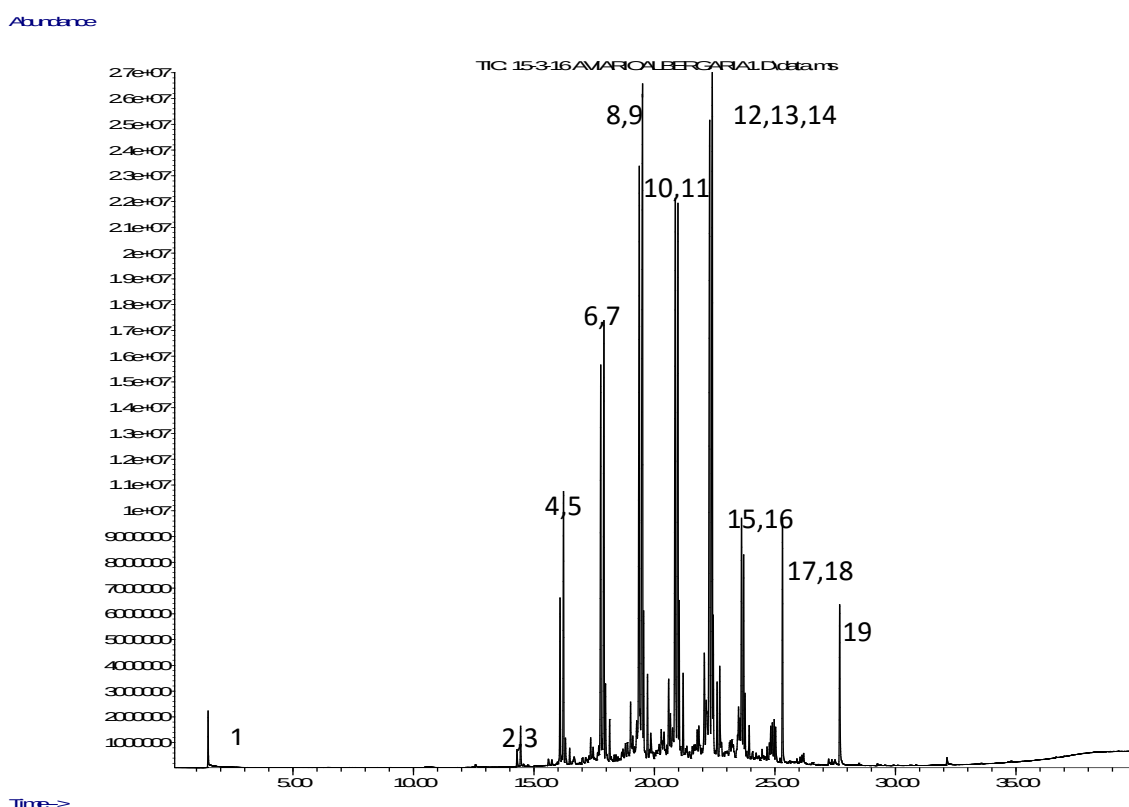


Figure 3: TIC of products produced from the sample 1 collected at *Fire Scene 1*. Peak identities: (1) Carbon dioxide; (2) Dodecene; (3) Dodecane; (4) Tridecene; (5) Tridecane; (6) Tetradecene; (7) Tetradecane; (8) Pentadecene; (9) Pentadecane; (10) Hexadecene; (11) Hexadecane; (12) Decylbenzene; (13) Heptadecene; (14) Heptadecane; (15) Octadecene; (16) Octadecane; (17) Dodecylbenzene; (18) Nonadecane; (19) Octadecanoic acid methylester.

Sample 2

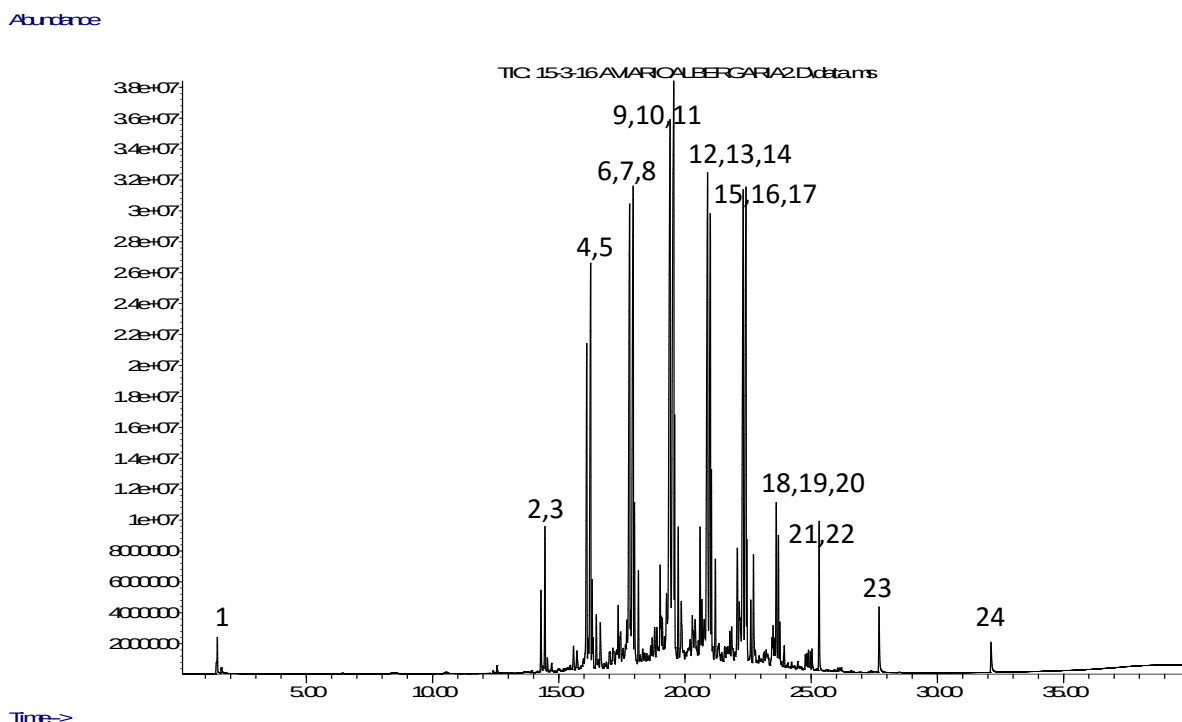


Figure 4: TIC of products produced from the sample 2 collected at *Fire Scene 1*. Peak identities: (1) Carbon dioxide; (2) Dodecene; (3) Dodecane; (4) Tridecene; (5) Tridecane; (6) Heptylbenzene; (7) Tetradecene; (8) Tetradecane; (9) Octylbenzene (10) Pentadecene; (11) Pentadecane; (12) Nonylbenzene; (13) Hexadecene; (14) Hexadecane; (15) Decylbenzene; (16) Heptadecene; (17) Heptadecane; (18) Undecylbenzene; (19) Octadecene; (20) Octadecane; (21) Dodecylbenzene; (22) Hexadecanoic acid methylester; (23) Octadecanoic acid methylester; (24) 1,2-Benzenedicarboxylic acid diisooctylester.

Both samples 1 and 2 show a series of consecutive alkene-alkanes ranging from C₁₂ to C₁₉, which constitute the main pattern of the TICs and highly resemble the profile of a HPD, according to ASTM standards. Additionally, octadecanoic acid methylester was found in both samples, hexadecanoic acid methylester only in sample 2.

According to the manufacturer, the composition of the detoxification blocs includes mainly paraformaldehyde (37%) and stearic acid (percentage not stated). Formaldehyde is a very small molecule and cannot account for the profile obtained from the analysis of the plaques. Stearic acid, however, is a saturated fatty acid with an a chain made of 18 carbon atoms – the IUPAC name is octadecanoic acid – which can create the obtained chromatograms during its gradual decomposition due to the application of heat that results in a scission of the chain into smaller molecules. Formaldehyde has a flashpoint (the lowest temperature at which the vapours of a material will ignite if given an ignition source) of 64°C and makes up 37% of the

bloc. Stearic acid has a flashpoint of 113°C and makes up most of the residual bloc. Hence, a combination of both compounds will have a flashpoint that is close to 100°C and an even higher fire point (the lowest temperature at which the vapour will keep burning after having been ignited and the ignition source has been removed), which is not sufficient to be used as a source to start a fire or maintain a fire. Therefore, the detoxification blocs can be excluded as the ignition source and starting point of the fire.

4.1.2 Case study 2 – Centre-East

After collection of four samples at the fire scene 2 (FS2) and transport to the laboratory, following results were obtained after the above-mentioned extraction and analysis techniques (HS-SPME-GC-MS) were applied:

Sample 1 – Plywood

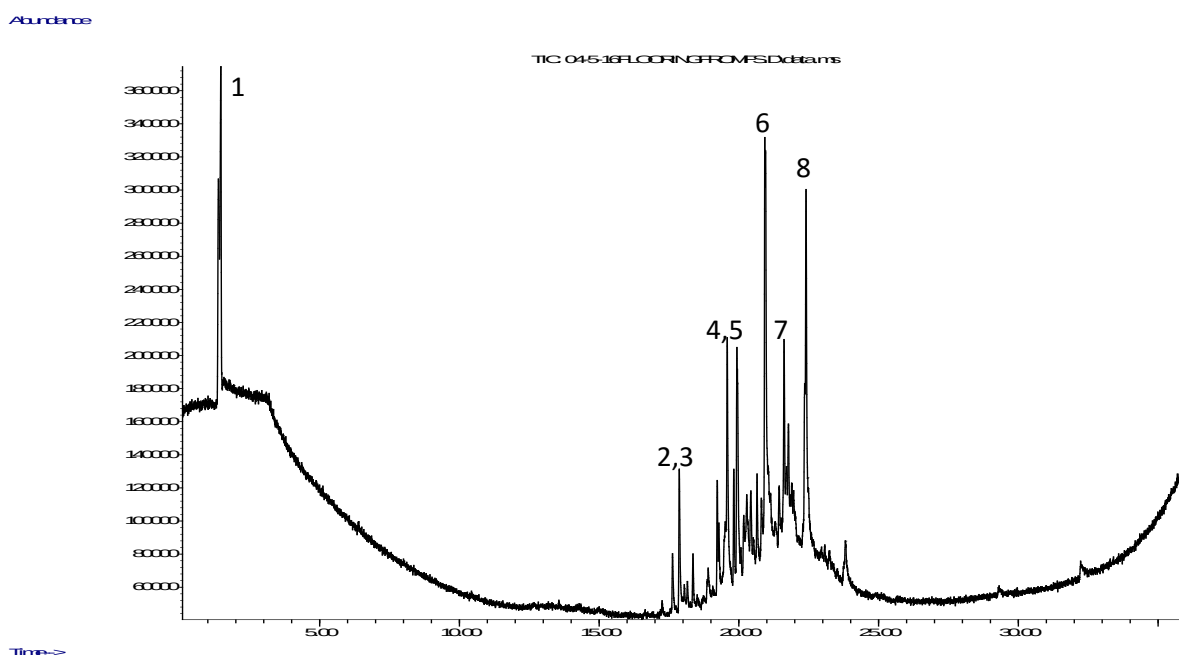


Figure 5: TIC of products produced from the sample 1 collected at *Fire Scene 2*. Peak identities: (1) Carbon dioxide; (2) Naphthalene derivative; (3) Low MW, low BP cyclic hydrocarbon; (4) and (5) Naphthalene derivatives; (6) Hexadecanal; (7) and (8) High MW, high BP hydrocarbon.

Sample 2 – Skirting board

Abundance

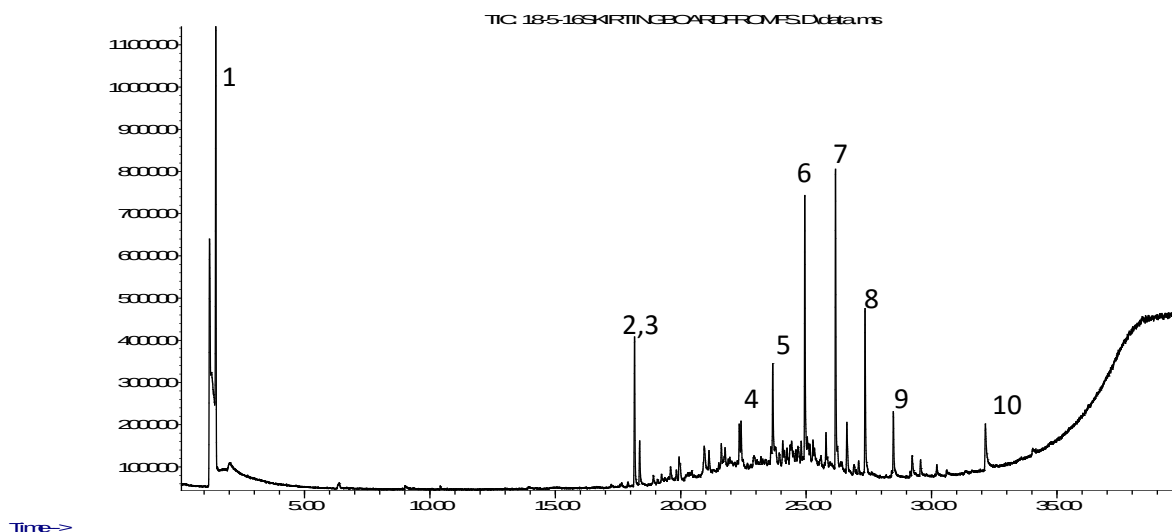


Figure 6: TIC of products produced from the sample 2 collected at *Fire Scene 2*. Peak identities: (1) Carbon dioxide; (2) Longifolene; (3) Naphthalene derivative; (4), (5) and (8) High MW, high BP oxygenated hydrocarbon; (6) and (7) High MW, high BP hydrocarbon; (9) Heptacosane; (10) 1,2-Benzenedicarboxylic acid diisooctylester.

Sample 3 – Wood

Abundance

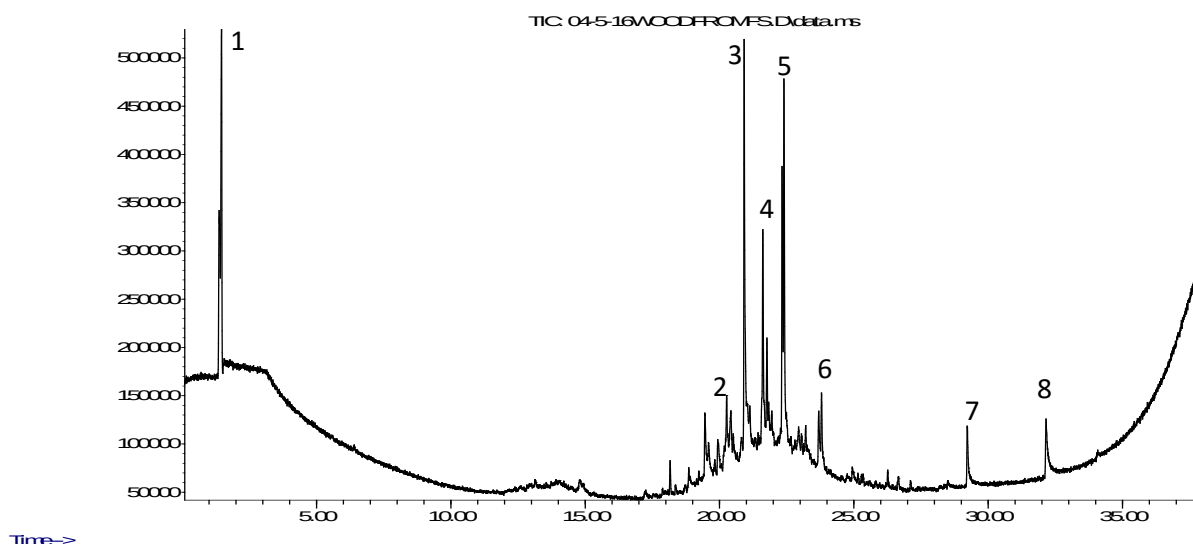


Figure 7: TIC of products produced from the sample 3 collected at *Fire Scene 2*. Peak identities: (1) Carbon dioxide; (2), (4) and (6) High MW, high BP hydrocarbon; (3), (5) and (7) High MW, high BP oxygenated unsaturated hydrocarbon; (8) Phthalic acid butylundecylester.

Sample 4 – Cement

Abundance

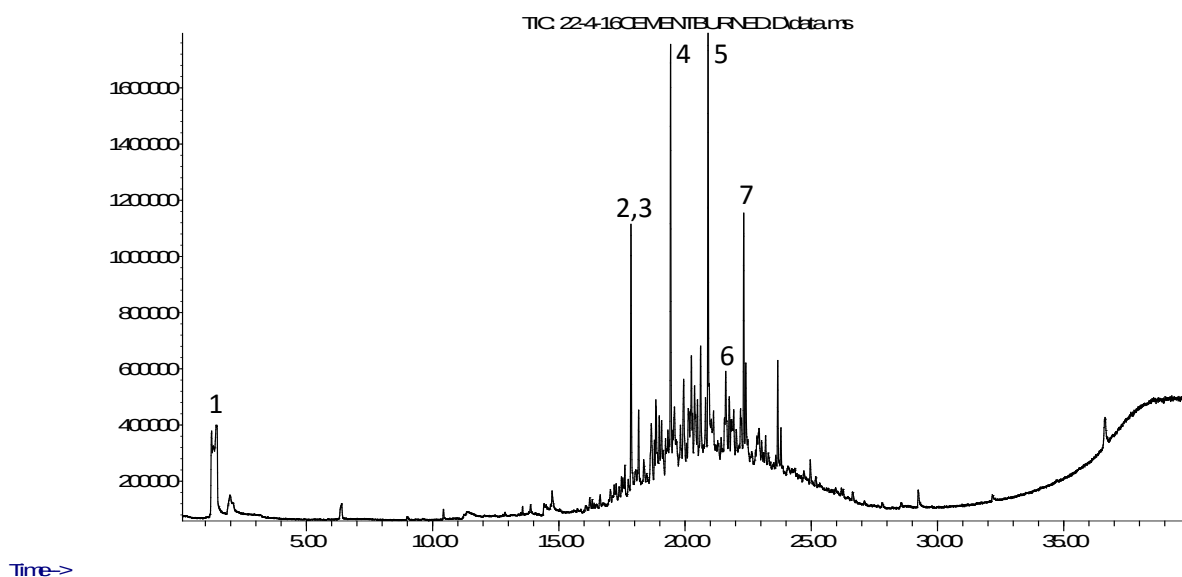


Figure 8: TIC of products produced from the sample 4 collected at *Fire Scene 2*. Peak identities: **(1)** Carbon dioxide; **(2)** and **(3)** Naphthalene derivatives; **(4)-(7)** High MW, high BP hydrocarbon.

All TICs have a similar chromatographic profile, not many compounds are detected. The majority are products resulting from the background and the thermal degradation of the materials. None of the samples contains enough compounds that can constitute an IL according to ASTM standards.

4.1.3 Case study 3 – Centre-West

After collection of three samples and a blank at the fire scene 3 (FS3) and transport to the laboratory, following results were obtained after the above-mentioned extraction and analysis techniques (HS-SPME-GC-MS) were applied:

Blank

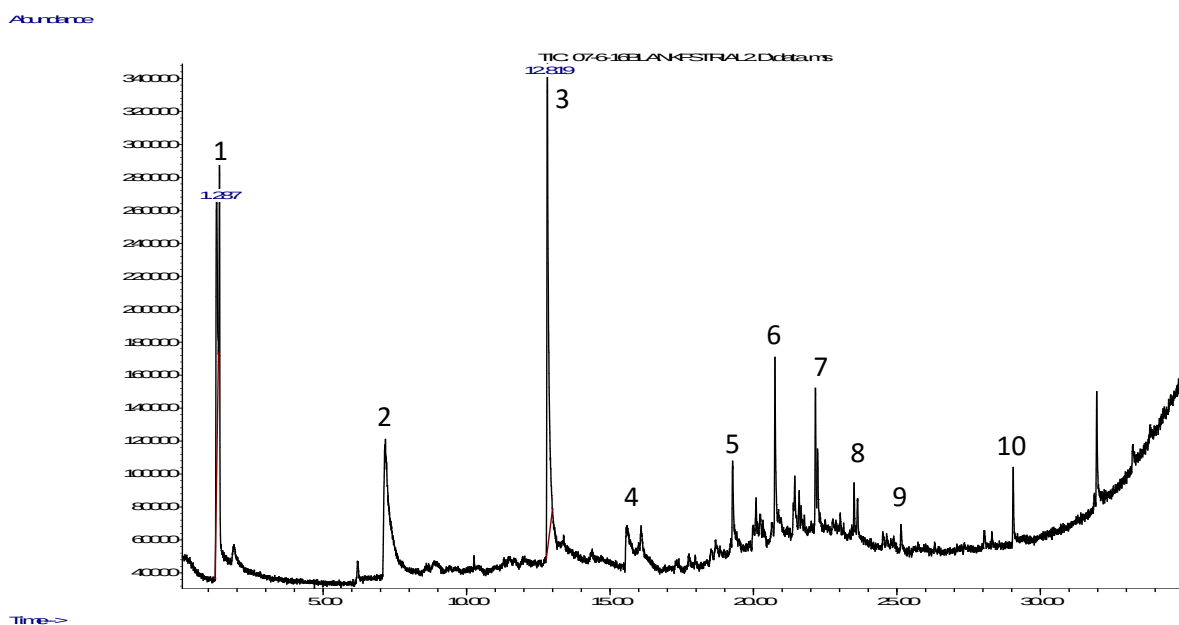


Figure 9: TIC of products produced from the blank sample collected at *Fire Scene 3*. Peak identities: (1) Carbon dioxide; (2) Undecane; (3) Tetradecane; (4)-(7) High MW, high BP hydrocarbon; (8), (9) and (10) High MW, high BP oxygenated hydrocarbon.

Sample 1

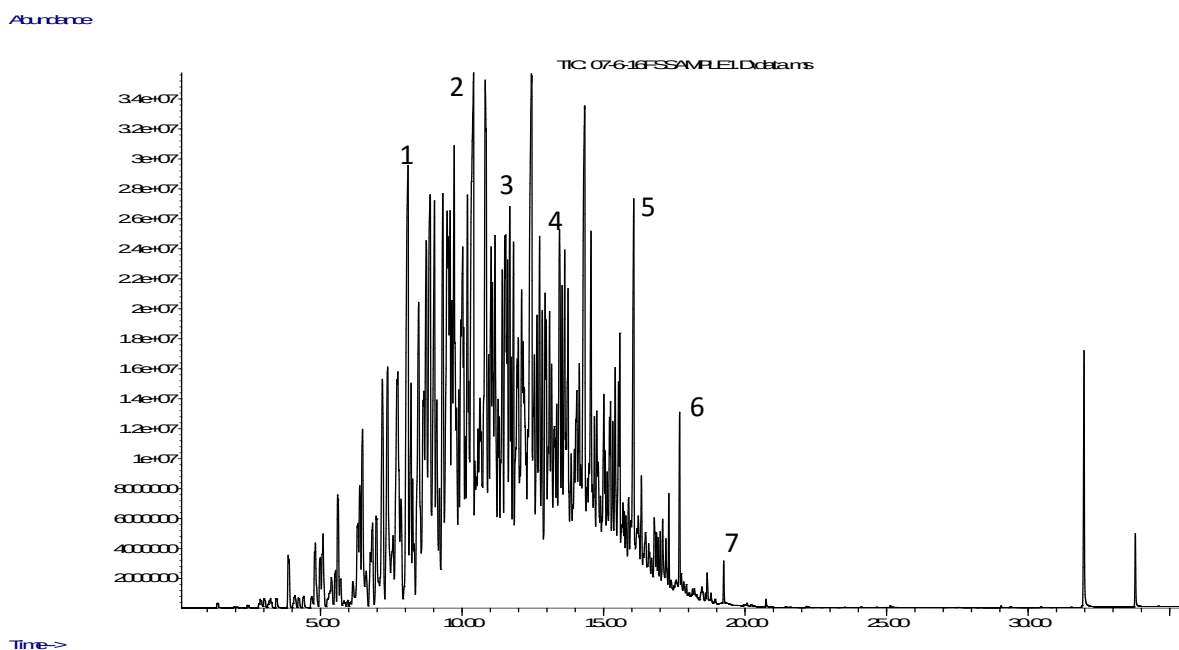


Figure 10: TIC of products produced from the sample 1 collected at *Fire Scene 3*. Peak identities: (1) Nonane; (2) Decane; (3) Undecane; (4) Dodecane; (5) Tridecane; (6) Tetradecane; (7) Pentadecane – a list of all compounds is found in the *appendix* section (**Table D7**).

Sample 2

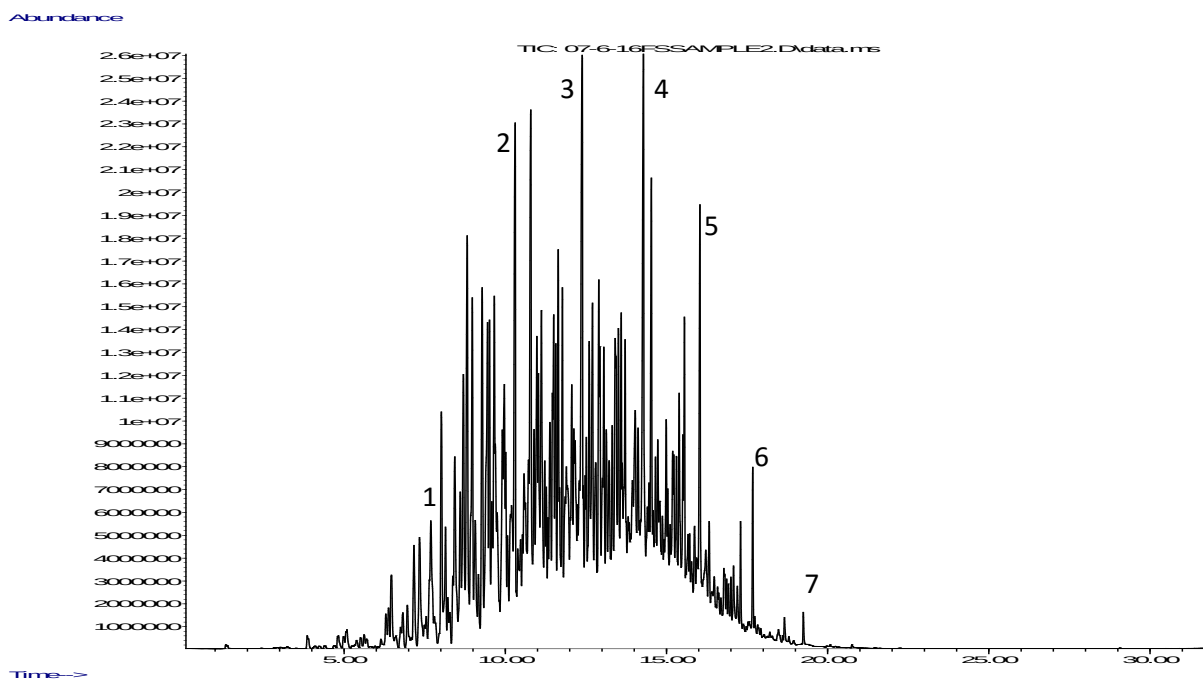


Figure 11: TIC of products produced from the sample 2 collected at *Fire Scene 3*. Peak identities: (1) Nonane; (2) Decane; (3) Undecane; (4) Dodecane; (5) Tridecane; (6) Tetradecane; (7) Pentadecane – a list of all compounds is found in the *appendix* section (**Table D8**).

Sample 3

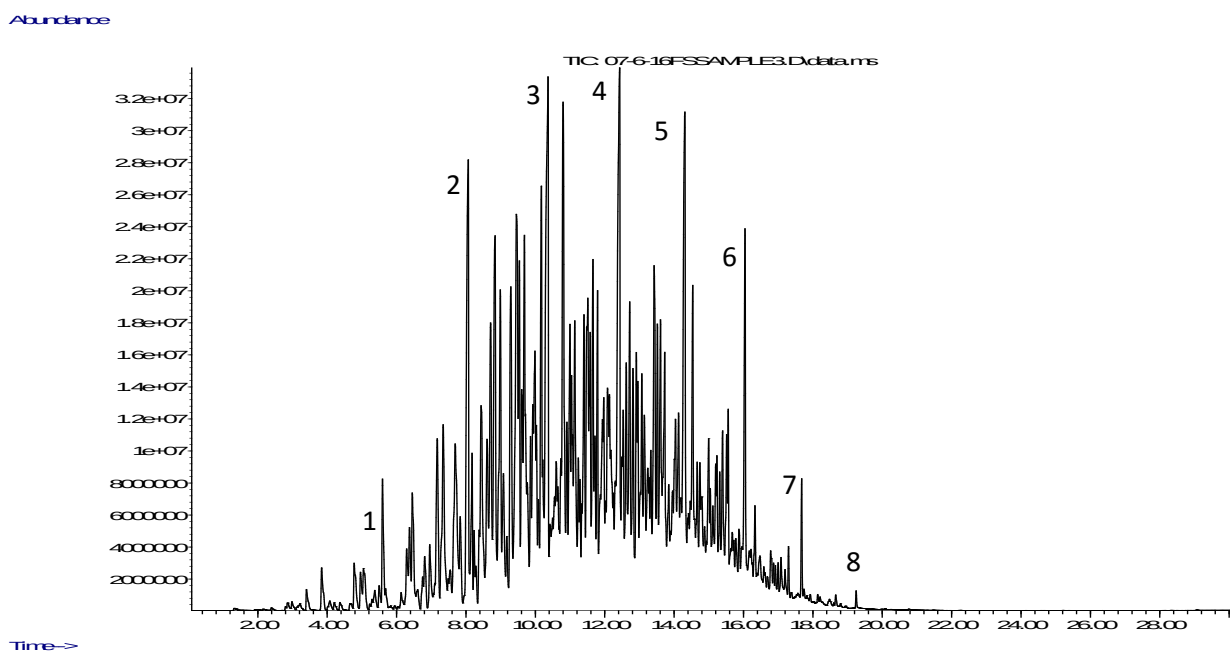


Figure 12: TIC of products produced from the sample 3 collected at *Fire Scene 3*. Peak identities: (1) Octane; (2) Nonane; (3) Decane; (4) Undecane; (5) Dodecane; (6) Tridecane; (7) Tetradecane; (8) Pentadecane – a list of all compounds is found in the *appendix* section (**Table D9**).

By simple visual comparison of the blank sample with the samples from the suspected areas of origin, it can be clearly observed that not only is there a large difference in the abundance of the compounds detected, but also in the amount of substances found and the profiles created. The blank sample merely contains compounds that result from the background of the material and the combustion and pyrolysis occurred during the fire. The other three samples have a very rich profile that resembles that of a HPD and contain various compounds: isoparaffins, consecutive *n*-alkanes in the range of C₉ to C₁₅, C₂-, C₃- and C₄-alkylbenzenes; pristane and phytane, however, are not present. The parameters according to ASTM standard for the identification and confirmation of a HPD include a minimum of five consecutive *n*-alkanes in the range of C₉-C₂₀₊, the abundance of alkanes, presence of cycloalkanes and aromatics and, for diesel, the presence of the doublets C₁₇-pristane and C₁₈-phytane is mandatory. All the parameters are fulfilled by the analysed samples. Additionally, by following the flow-chart presented by Stauffer on page 345 of his book '*Fire Debris Analysis*' (Stauffer et al., 2007), the product identified in the analysed samples is a HPD. Furthermore, comparison of the obtained TICs with the extensive collection of IL profiles obtained by GC-MS analysis provided by Reta Newman (Newman et al., 1998) results in the highest similarity obtained with a kerosene based jet-fuel (Distillate #38 and #41, pp. 174 and 194).

4.2 Determination and characterization of background, combustion and pyrolysis products

19 samples (summarized in **Table 6**) representing the main and most common items found in urban fires were subject to the same sample preparation, extraction and analysis techniques as mentioned in the *Materials and Methods* section. All 19 were analysed before and after burning; eight of them were additionally subject to pyrolysis prior to the procedure. A list of all compounds identified in all the samples before burning, after burning and after pyrolysis can be found in the *Appendix* section, **Tables D12-D57**.

4.2.1 Background products

To determine the background products, all samples were analysed without burning, so that the compounds detected can only be present due to the composition of the material itself, contamination from the manufacturing process or other objects the item came in contact. No

combustion or pyrolysis products can be detected. To exclude interfering products coming from the container used for sampling, an empty container was also subject to the same extraction and analysis technique. The compounds detected are listed in **Table D11**. Among them there are some alkanes and branched alcohols, however in a very low abundance, therefore they can be due to contamination from the manufacturing process and can be neglected. The most significant compounds are 2,6,10-trimethyltetradecane, tributylacetylacrylate and 1,2-benzenedicarboxylic acid diisooctylester. The first one is a C₁₇ saturated isoprenoid hydrocarbon, which has also been found in petroleum (Cason and Graham, 1965), and is usually present due to the manufacturing process. The acrylate is the most abundant peak in the chromatogram (**Figure D1**) and is a substance used as plasticizer. 1,2-Benzenedicarboxylic acid diisooctylester, which is also known as diisooctylphthalate, as implied in the name, is a phthalate. Phthalates are a class of organic compounds mainly used in the industrial production of plastics. Hence, those main compounds detected in the glass can are products derived from the manufacturing process and are not part of the background products found in the materials analysed.

4.2.2 Combustion products

For the determination of products formed in a material due to combustion, all samples were burned with the previously mentioned method in presence of oxygen, thus allowing a combustion reaction to occur. Hereby the compounds detected in the samples are explained by both components of the substrate and the combustion of those.

To determine which compounds were created due to combustion and which ones are part of the material itself, the burned and unburned chromatograms were compared. All chromatograms can be found in the *Appendix* section, **Figures D2-D32**.

4.2.3 Pyrolysis products

To determine what kind of products are formed after pyrolysis of a material found on a fire scene, eight of the 19 samples were selected and were subject to pyrolysis with the conditions mentioned in the *Materials and Methods* section. The compounds detected after analysis represent the products formed through the pyrolysis reaction.

To determine which compounds were created due to pyrolysis and which ones are part of the material itself, the chromatograms of the blank samples are compared to the ones obtained after pyrolysis. The TICs of all pyrolysed samples are found in the *Appendix* section, **Figures D2-D32**.

The eight materials selected for pyrolysis each represent one type of material-class: a carpet made of a combination of synthetic and natural fibre, cork representing all natural materials containing cellulose, a curtain made of polyester, polyurethane, which is one of the most commonly encountered polymers in household items, cement as the base for all walls and an inorganic material, vinyl flooring, one of the most commonly used type nowadays, a skirting board found in the majority of houses and apartments in Portugal, and the gas pipe representing common chlorinated thermosets.

Plywood flooring

The background compounds detected in the plywood sample are mainly copaene, caryophyllene and α -caryophyllene, which are part of the chemical class of terpenes, as well as naphthalenes. Terpenes and oxygenated products are commonly found in wood-based products (Stauffer et al., 2007).

Additional products that are only found in the burned sample are alkanes, cycloalkanes, alcohols and esters. Alkanes, alcohols and esters are oxygenated products that are common combustion products.

In general, the comparison of the TICs of the burned and unburned plywood (**Figure D2**) show that there is a significantly higher abundance for the compounds in the burned sample. This can be due to the fact that the compounds present in wood products have high boiling points and therefore are not yet volatilized at the extraction temperature (80°C).

Noticeable is also that for the burned sample, the spread of the compounds detected is over the whole analysis period, which is very common for interfering products, but not for ILs, where usually depending on whether it is a light (C₄-C₉), medium (C₈-C₁₃), or heavy (C₁₃-C₂₀₊) fuel, the elution order are respectively early, medium or late and confined in a smaller time period based on the number of consecutive hydrocarbons and their boiling points (Stauffer et al., 2007). Hence, in this case there is no possibility of misinterpretation of the chromatogram as containing ILs.

Polyurethane

Polyurethane (PU) is nowadays one of the most common used polymers for coatings and paddings due to its fire-retardant properties and therefore often found in households. Its chemical structure (**Figure 13**) is based on polymer chains linked together by carbamate (urethane) groups, which are obtained by the reaction of a di- or polyisocyanate with polyols. The length of the reactants make up the length of the polymer chains between the urethane groups.

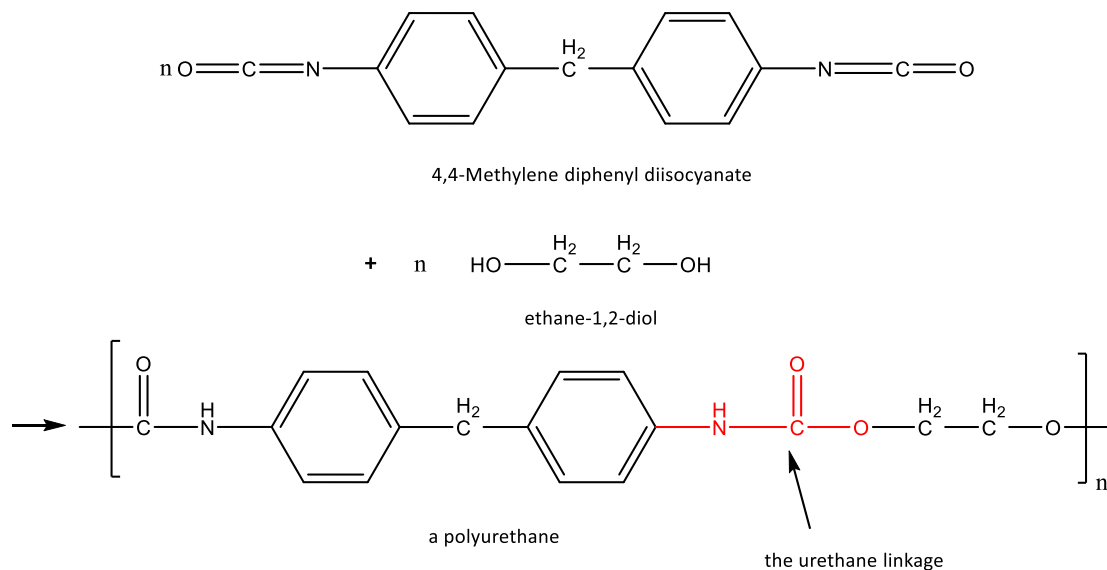


Figure 13: Chemical structures of the reaction of a polyisocyanate with a diol to produce a polyurethane (Source: drawn by Stefania Oliverio via ChemDraw)

Background products found in the PU sample are mainly a few alkanes. PU is not volatile and thermal degradation of PU usually starts at temperatures around 110°C (Levchik and Weil, 2004), which explains the lack of compounds found in the blanks analysis.

However, a large number of products was detected after combustion. Consecutive alkene-alkane in the range of C₆ to C₂₂ are present in what appears like two bell-shaped Gaussian curves (**Figure D3**) in the range of medium (MPD) and high petroleum distillates (HPD). In addition, some aldehydes and alcohols are present. Those products derived from the thermal decomposition of PU.

Thermal decomposition of polymers is different for every polymer. There are three main mechanisms that have been identified as the most common to occur, which are: *random scission*, where the backbone of the polymer is taken apart randomly; *side-group scission*, where the side groups attached to the backbone of the polymer are eliminated; *monomer*

reversion, where the polymer returns to its monomers. Most polymers undergo thermal decomposition through those mechanisms. However, there are also other mechanisms that take place (Stauffer, 2003b). In the case of polyurethane, in the first stage of combustion or pyrolysis, the first compound to be released are hydrogen cyanide (HCN), carbon monoxide (CO) and carbon dioxide (CO₂), which make up the links of the polymer (Levchik and Weil, 2004). What are left once those substances are released are long hydrocarbon chains that undergo random scission. Therefore, based on the length of the monomers used, the alkenes and alkanes are detected.

The pyrolysis similarly shows one bell-shaped Gaussian curve (**Figure D3**), with a boiling point range from C₁₉ to C₂₇, similar to a HPD.

The Gaussian distribution of boiling points of different components that comprise a mixture is distinctive for petroleum products and is a consequence of the fractionation distillation process used in refining (Stauffer et al., 2007). Therefore, the TICs of polymers like PU can be easily confounded with a HPD, especially if additionally, the EICs of the characteristic ions of alkanes and cycloalkanes are observed (**Figures D4 and D5**), which confirm the abundance of alkanes and cycloalkanes. However, as already mentioned before, in the case of the burned sample, the spread of the compound is along the whole elution period, which is not common for ILs, even though it can be argued that an IL is present in the substrate resulting in the detection of both substrate and combustion products.

Cement

Cement is the most common used binding agent in constructions and is mainly made of limestone and clay, two sedimentary, natural rocks, mainly of mineral nature. It is produced at temperatures higher than 1400°C (Taylor, 1997). Hence, one of its main properties is heat-resistance to very high temperatures. In fact, during very destructive and large fires, one of the last standing items are the walls made of cement (De Haan and Icove, 2011).

Therefore, it is not surprising that there are no background, combustion or pyrolysis products detected (**Figure D6**). The compounds found are mostly interferences from the sampling container.

Cork

Cork is a natural plant material derived from the cork tree *Quercus suber* for commercial use (Pereira, 1988). In the world, it is mainly used as a wine-stopper, but in Portugal especially it is very common to have various items like handbags, shoes, wallets, jewellery and many others made of cork (Parsons, 1962). The main components are the biopolymers suberin and lignin and various polysaccharides (Pereira, 1988). Suberin and lignin are both polymer containing mainly aromatics and polyesters (Kolattukudy, 1980; Yang et al., 2007).

Compounds detected in the blank sample (**Figure D7**) are mainly interferences from the sampling container, which include isoparaffins and aldehydes. Among the substances found in the burned material there are various isoparaffins, alcohols and as a main peak 2-(2-butoxyethoxy)-ethanolacetate. Due to the highly complex structure of the polymers cork is made of, when they undergo thermal degradation, the structure decomposes in a variety of hydrocarbons, some of which are more or less volatile. Only the less volatile ones are still detected, since the more volatile ones are released during the burning process. The acetate is also a VOC, which is usually used during the production of composite film preparations for Polyvinylacetate (PVAc). In this case, it might be present due to some contamination from the manufacturing process.

The pyrolysis of cork resulted in no compounds detected. The only material left was carbon, which is expected from plant-derived materials, which are often used for biomass production (Pereira, 1988).

Wood compressed

Wood, similarly to cork, is mainly made of cellulose, lignin and hemicellulose (Eriksson et al., 2012). Therefore, the main compounds expected after analysis are terpenes and oxygenated products (Stauffer et al., 2007). Substances found in the analysis of the blank sample include various alkenes and esters, which are all background compounds derived from the substrate, but also longifolene. Longifolene is a naturally occurring oily hydrocarbon of the class of tricyclic terpenes. It is primarily found in the high-boiling fraction of some resins, especially from pinewood, which are used for production of wood-materials (Zi-yong, 1982). Therefore, the presence of this compound is not surprising and in fact, it confirms that the material analysed is compressed wood mainly made from pine.

The pre- and post-burning profiles seen in the TICs (**Figure D8**) are very similar, the main difference lies in the higher abundance of the compounds in the burned sample, no relevant additional compounds are detected after burning the material, and thus no combustion products are detected after burning of compressed wood.

Vinyl flooring white bathroom/kitchen

Polyvinylchloride is a polymer made of vinyl chloride monomers. Due to its easiness and inexpensiveness in production, but most importantly due to its versatility in use, it is the third most produced polymer in the world after polyethylene and polypropylene (Allsopp and Vianello, 2012). As previously mentioned, it is used for many household items, such as floorings, coatings, decorative items or pipes used for the gas lines.

When undergoing thermal degradation, PVC decomposes in two main stages: the first one consists in the dehydrochlorination, the elimination of hydrochloric acid (HCl) through side group scission (Stauffer et al., 2007), which is a highly toxic substance; the second stage consist of the breakdown of the intermediate compounds produced after the first stage, which are mostly aromatics (Wu et al., 1994; Stauffer, 2003a). In fact, the analysis of the blank sample resulted in the detection of mainly aromatic compounds such as benzoates and phthalates (**Table D26**). The same for the burned sample (**Table D27**), even though the number of compounds detected as well as the abundance were higher, which makes sense given that during the burning, higher temperatures are reached, which release also the compounds with a higher boiling point. The narrow time span the aromatics are found in resemble the profile of a medium aromatic compound. This is confirmed by the EICs of alkanes (**Figure D10**) and aromatics (**Figure D11**), the obtained graphs clearly show the high abundance of aromatics, specifically for ion 105, compared to alkanes (**Figure D10**), alicyclics and olefinics (**Figure 12**).

Curtain orange

Curtains can be made of various materials, from natural ones like silk, to synthetic ones like nylon, acrylics, cotton, polyesters, in different combinations and different proportions (Stauffer et al., 2007). Therefore, it is not easy to interpret the chromatogram obtained from the analysis of a curtain. Nevertheless, it has been proven that even though a mixture of polymers is present, each polymer undergoes thermal degradation at its own mechanism

(Stauffer, 2003a). This means that a chromatogram of a mixture of polymers will be complex and show compounds that belong to all of the present polymers.

In this case, the analysis of the orange curtain resulted in no detection of background components (**Figure D13**), which indicates that the fabric the curtain is made of does not contain highly volatile substances and most likely does not contain volatile functional groups such as chlorine. Given that curtains nowadays are by law supposed to be fire-retardant, it is sensible that no highly volatile components are used for production. After burning, however, a high number of compounds was detected (**Figure D13**), which included aldehydes, branched alcohols, isoparaffins and some aromatics, namely biphenyl and benzylbenzoate. These compounds are most likely products of the thermal degradation of the polymers in the curtain. Aldehydes and alcohols are pyrolytic products common for cotton, while aromatics are products formed during degradation of polyesters like polyethylene terephthalate (PET) (CDS Analytical, 2002), hence the curtain might be a blend of cotton and PET.

The chromatographic profile resembles a medium isoparaffinic product, however, isoparaffinic products are solely made of isoparaffins and do not contain aromatics, which is the case here.

Carpet underlay

Similarly to curtains, carpets can be made of various natural or synthetic materials and can also be either a single or multiple component product. Most monofiber carpets are made of polypropylene, polyester, polyolefin or nylon, multifiber ones are usually blends of nylon with polyolefin, PET or polypropylene in different proportions (Stauffer et al., 2007).

The blank analysis did not result in any significant background components present (**Figure D14**). On the other hand, the analysis of the burned carpet underlay resulted in the detection of a high number of thermal degradation products (**Figure D14**), varying from isoparaffins, aromatics like toluene, styrene, α -methylstyrene, naphthalene and benzene to branched alcohols, alkane and alkenes. This highly complex mixture of substances suggests that the carpet is made of a blend of polymers. Given the absence of amines, nylon is most likely not contained in the carpet, leaning towards a mixture of polyester and polypropylene. In fact, the TIC resembles the TIC obtained from the pyrolysis of pure polypropylene in Stauffer's study (Stauffer, 2003a).

Carpet red

The analysis of pre- and post-burning of the red carpet gave similar results to the carpet underlay. No significant background components were detected, but a high number of thermal degradation products were found, mainly isoparaffins, alkanes, alkenes, alcohols, esters and aromatics like styrene, benzaldehyde and α -methylstyrene. The profile of the burned red carpet (**Figure D15**) shows a similar profile to the carpet underlay (**Figure D15**). However, the isoparaffins appear more abundant and the aromatics less abundant, suggesting a different proportion of polymers in the composition of the material, with a higher percentage of polyester contained in the red carpet and a higher polypropylene percentage in the carpet underlay. The TIC of the red carpet additionally shows a not so developed bell-shaped Gaussian curve, which can be confused for a MPD. However, given the absence of consecutive alkanes, it is possible to distinguish the profile from an IL.

Carpet with plastic layer black

The blank analysis resulted in the detection of two mainly Isoparaffins and *n*-Alkanes (**Figure D16**), which can be accounted for as impurities from the container or the manufacturing process. The post-burning analysis revealed the presence of numerous compounds (**Figure D16**): branched alcohols, isoparaffins, alkenes, esters and many aromatics, such as benzene, ethylbenzene, styrene, benzaldehyde, naphthalene. The combination of those compounds together with the profile of the TIC, which highly resembles the one shown in Stauffer's pyrolysis study (Stauffer, 2003a), indicates that the carpet is mainly made of PVC and the detected substances are all products derived from the thermal degradation of PVC. The pyrolysis of the carpet resulted in the remanence of a few oxygenated, branched and cyclic substances (**Table D36**); most of the constituting compounds have been volatilized during the pyrolytic process.

Curtain black

The analysis of pre- and post-burning of the black curtain resulted in similar TICs (**Figure D17**), with a profile similar to a partial medium to heavy petroleum distillate (C₁₂-C₁₉). In fact, in the background analysis, three consecutive alkanes are detected. The presence of aromatics is also possible in a MPD or HPD according to ASTM standards. Therefore, this profile can be

confounded with a petroleum distillate. The profile is similar to the one previously seen for the orange curtain (**Figure D13**), suggesting a similar composition.

Vinyl flooring living room

This type of flooring is similar to the vinyl flooring used in kitchens and bathrooms, so mainly made of PVC; however, it is stiffer and has an additional decorative layer with wood-imitating design. It is normally bought in plies and installed on the floor by attaching it with the layer of glue present. During its production various solvents and adhesives are used, which contain numerous VOC. Thus, it is not surprising that the analysis of both pre- and post-burning of the sample produced a large number of VOCs. Background components detected include alcohols, aldehydes, alkanes and phthalates. The products derived from the thermal degradation of the flooring consist of various benzoate, phthalate, acetic esters and chlorinated alkanes. Benzoates and phthalates are common precursors to plasticisers (Saillenfait and Laudet-Hesbert, 2005; Monyatsi, 2015; Pivnenko et al., 2016), while acetates are common to be main components of adhesives (Carvalho et al., 2015). The profiles of the TICs of pre- and post-burning (**Figure D18**) are of high similarity, merely the abundance is higher in the burned sample, but the majority of the peaks is concordant, indicating that most compounds are due to the nature of the material and only some are products derived from the decomposition process. Confirming the composition of the flooring to be mainly PVC and adhesives is the fact that the pyrolysed sample shows no significant substance (**Table D41**), meaning that the majority of the products are already evaporated during the process and at the temperatures reached during pyrolysis. From a visual perspective, the TICs obtained have some similarity with a weathered HPD, but the composition does not match a HPD.

Skirting board

The blank analysis resulted in the detection of several high molecular weight alkanes (**Figure D19**), which based on their boiling point range appear as a bell-shaped Gaussian curve. Similarly, the burned sample presents the same bell-shaped Gaussian curve of *n*-alkanes, with an additional bell-shaped curve made of isoparaffins and branched alcohols. Due to the bell-shaped *n*-alkanes, the profile has high similarity with a diesel fuel, even though neat diesel fuels have alkanes in lower molecular weight ranges (they usually start at C₁₃). This can still be explained by weathering, which usually not only lowers the signal, but also removes the

components with lower boiling points, leaving mainly the high molecular weight and therefore high boiling point compounds (Stauffer et al., 2007). The EICs of the alkanes (**Figure D20**), alicyclic, olefinics (**Figure D21**) and alkylbenzenes (**Figure D22**) confirm the high abundance of alkanes in a Gaussian distribution as well as the presence of cycloalkanes and aromatics in lower abundances, which are characteristic for a petroleum distillate such as diesel according to ASTM standards (Stauffer et al., 2007). Thus, this sample can be misinterpreted as an ILR or ILR mixtures. The pyrolysis does not detect any significant substance (**Figure X**), meaning that the components of the material were completely volatilized during the pyrolytic process.

Wallpaper

Nowadays, wall coverings are usually made of either wallpaper or paint. Wallpaper is most commonly produced from paper, PVC or a combination of PVC and some decorative layer on top such as silk, cotton or paper (Stauffer et al., 2007).

From the analysis of the material before burning, a rich chromatogram was obtained (**Figure D23**), which contained various isoparaffins, alkanes, alcohols and the tricyclic terpene longifolene. As previously mentioned, longifolene is obtained from the processing of pine resins, which are also used for the production of paper (Landers et al., 1995).

The post-burning analysis revealed the presence of mainly aromatics (toluene, styrene, and ethylbenzene), isoparaffins and longifolene (**Table D46**), which appeared in a bell-shaped curve similar to a MPD, even though the present aromatics clearly are indicators of products due to thermal degradation. The profiles suggest that the wallpaper is made of a combination of paper with a synthetic material that is not PVC, since there is no clear pattern for PVC as seen in the thermal degradation of the material in the pure state (Stauffer, 2003b).

Gas Pipe

In older buildings, from the 60ies and 70ies for instance, the gas and sewer pipes were mostly made of steel, copper or concrete. But after the discovery of the versatility, anti-corrosive and water- and fire-resistant properties of polymers, the majority of the pipes was produced of plastics, such as high and medium density polyethylene (HDPE, MDPE) (Kiass et al., 2005) and PVC (Nielsen et al., 2008; Allsopp and Vianello, 2012; Lon, 2016). Not only due to its properties and high use, but also because of its reported cases of failure with subsequent spontaneous

ignition of the released gases, which resulted in fires (Babrauskas, 2003; Dryer et al., 2007), pipes are often encountered on fire scenes and are of high interest for the fire investigator. In fact, the anti-corrosive and fire-resistant characteristics of gas pipes has been confirmed in this experiment: no relevant or abundant compounds were detected after the pre- and post-burning (**Figure D24**) analysis of the sample, indicating that the pipes are fire-resistant and do not release any VOC into the lines they are used for.

However, the fire-resistance has its limits at the applied pyrolysis temperatures, since after pyrolysis (**Table D49**), several compounds, which include chlorinated isoparaffins, cycloalkanes, aromatics and esters, are detected in the sample. The profile of the TIC is slightly similar to the profile of a MPD; however, the latter does not contain chlorinated compounds, thus confounding this profile with a MPD is highly unlikely.

Wood composite

High quality wood is a quite expensive material and deforestation nowadays is quite a debated subject due to the global warming problems, which lead timbers and manufacturers of furniture to come up with a cheaper and more eco-friendly alternative. Therefore, the idea of wood agglomerates, or wood composites, was created. A wood composite is a combination of compressed wood material with polymers and adhesives, to recreate the same resistance and strength of wood (Maloney, 1996; Carvalho et al., 2015).

Therefore, it is not surprising that the analysis of the wood composite samples resulted in the detection of a high amount of VOCs. In the blank sample (**Figure D25**), isoparaffins, consecutive *n*-alkanes from C₉ to C₂₇, xylenes, C₃-alkylbenzenes and naphthalenes are detected, most likely originating from the adhesives used in the manufacturing process. In the sample analysed after burning (**Table D51**), phthalates, alcohols, terpenes and alkanes were found. Phthalates are, as already previously mentioned, used as plasticizers, while terpenes and oxygenated compounds are typically found in wood-derived materials (Fernandes et al., 2002; Saillenfait and Laudet-Hesbert, 2005; Stauffer et al., 2007). However, the TIC profiles of the pre- and post-burning (**Figure D25**) show a very distinctive pattern of consecutive *n*-alkanes that has high similarity with a MPD or HPD, with the possible interpretation of weathering of the sample due to the not completely regular-shaped curve. This is also confirmed by observation of the EICs of alkanes (**Figure D26**), alicyclics, olefinics (**Figure D27**) and aromatics (**Figure D28**), which show profiles that are consistent with a mixture of medium

and high petroleum distillate according to the ASTM standards. Therefore, also in this case, there are chances for misinterpretation.

Electric cable with three conductors

The main constituents of a cable are the conductors, the insulation on the inside, the shield, the filler and the jacket insulation on the outer part, all assembled in layers as can be seen in **Figure D29**. The conductors are made of inorganic materials, mostly metals, such as cadmium, bronze, chromium, steel or copper, the same goes for the shield material, which is usually copper, and filler, usually constituted of tinsel wire. Insulations are mainly made of polymers, such as PVC, polyurethane, silicone rubber or polyester (Evans, 2016). Since inorganic material normally does not release any volatiles, the only VOCs detected originate in the insulating material of the cable.

The pre- and post-burning analyses (**Figure D29**) of the cable have high similarity in the profile of the TICs, the abundance being higher in the blank sample.

The blank sample contains mainly isoparaffins, alkanes, alcohols and benzoates, the burned sample contains mainly the same compounds, but fewer and with less abundance.

Paint solvent-based

As already implied in the name, solvent-based paints are mainly made of organic chemical compounds used to dissolve the coloured pigments and make them soluble for application (Yuan et al., 2010). Thus, it is expected that the analysis of solvent-based paint result in the detection of a high amount of VOCs. Indeed, the blank analysis of the paint (**Figure D30**) lead to a high number of VOCs being detected, mainly xylenes, isoparaffins and alcohols, which are all chemical classes that are commonly used as solvents.

The analysis of the paint after burning also revealed the presence of many VOCs, like toluene, ethylbenzene, o- and p-xylene as well as some alkanes and isoparaffins.

The TIC profiles highly resemble the profile of a medium to heavy isoparaffinic product.

In fact, paint poses a high difficulty level to the FDA for the determination of whether ILs are present or not, since it can be misinterpreted as an IL due to the high amount of compounds that match between an IL and the solvents used in paint production.

Paint water-based

Water-based paints, compared to solvent-based paints, do not use organic solvents, but mostly water as a diluent for the colour pigments (Del Amo et al., 2002). Therefore, the analysis of the paint, both pre- and post-burning (**Figure D31**), does not result in the detection of any VOCs, but mainly oxygenated and hydroxylated compounds, such as esters and alcohols. In addition, some alkanes are found in the analyses. The difference between water- and solvent-based paints can clearly be observed in the resulting chromatograms; while the TICs of the solvent-based paint are rich and abundant (**Figure D30**), the TICs of the water-based paint show only a small number of compounds detected, that do not match the composition of an IL.

The main components detected after the analysis of the 19 selected substrate materials, which were subject to burning and pyrolysis, are summarized in the following table (**Table 8**):

Table 8: summarized list of significant background, combustion and pyrolysis compounds detected in the analysis of the selected substrate materials.

Sample type	VOCs in background	VOCs from combustion and pyrolysis
Plywood flooring	Terpenes, cycloalkanes, PAHs, chlorooctadecane	Alkanes, alcohols, phthalates, terpenes
Polyurethane	<i>n</i> -alkanes and alkenes, PAHs	<i>n</i> -alkanes and alkenes, aldehydes, alcohols, isoparaffins
Cement	<i>Not significant</i>	<i>Not significant</i>
Cork	Isoparaffin, benzene and naphthalene derivatives	Isoparaffins, alcohols, 2-(2-butoxyethoxy)-ethanolacetate
Wood compressed	Longifolene, alkenes, isoparaffins	Docosanol
Vinyl flooring kitchen	Dibutylhydroxytoluene, benzoates	Dibutylhydroxytoluene, benzoates, phthalates
Curtain orange	<i>Not significant</i>	Biphenyl, docosanol, benzylbenzoate
Carpet underlay	<i>Not significant</i>	Toluene, styrene, α -methylstyrene, naphthalene, benzene, acetates, isoparaffins
Carpet red	<i>Not significant</i>	2,4-Dimethyl-1-heptene, Styrene, benzaldehyde, α -methylstyrene, acetates, isoparaffins
Carpet double-layered black	Isoparaffins, alkanes	Benzene, 2,4-dimethyl-1-heptene, ethylbenzene, styrene, benzaldehyde, α -methylstyrene, naphthalene, esters
Curtain black	Consecutive <i>n</i> -alkanes, dibutylhydroxytoluene	Biphenyl, docosanol, anthracene derivative, isoparaffins
Vinyl flooring living room	Alcohols, aldehydes, <i>n</i> -alkanes, phthalates, esters	Phthalates, benzoates, chloroalkanes, isoparaffins
Skirting board	High MW <i>n</i> -alkanes	Isoparaffins, alcohols, high MW <i>n</i> -alkanes
Wallpaper	Longifolene, low MW, low BP hydrocarbons, 2,4-dimethylhexane, other isoparaffins, alkanes, alcohols	Toluene, ethylbenzene, styrene, α -methylstyrene, isoparaffins
Gas Pipe	Not significant	Isoparaffins, aromatics, cycloalkane
Wood composite	Cycloalkane, <i>p</i> -xylene, α -pinene, naphthalene, isoparaffins, longifolene, <i>n</i> -alkanes	α -pinene, naphthalene, carophyllene, 1-chlorooctadecane, cedrene, phthalates, <i>n</i> -alkanes
Electric cable with three conductors	Isoparaffins, <i>n</i> -alkanes, benzoates, heterocyclic aromatic compounds	Isoparaffins, <i>n</i> -alkanes, benzoates, 1,1'-(1,4-phenylene)bis-ethanone
Paint solvent-based	Benzoates, xylenes, isoparaffins, vinyl-2-hexanoate	Toluene, ethylbenzene, xylenes, isoparaffins
Paint water-based	α -pinene, β -pinene, limonene, branched esters, <i>n</i> -alkanes, longifolene	Isoparaffins, <i>n</i> -alkanes

Given that all the experiments were conducted in complete absence of ILs, a high amount of VOCs and especially compounds that according to ASTM standards are of interest for IL analysis, which are mainly alkanes, aromatics and oxygenates (Hendrikse et al., 2015), were detected in both the background of the substrate as well as products generated after combustion and pyrolysis.

However, for many of the compounds identified, a trained fire debris analyst is capable of distinguishing the detected products from the possible presence of ILs.

For instance, for the family of wood-derived and cellulose-based materials, such as plywood, cork, compressed wood and cotton, the substances found in the background are common to wood products. Therefore, even though the profiles might resemble the ones of ILs or IL mixtures and various pyrolysis and combustion products are detected, the composition does not entirely match the composition of ILRs.

Also for inorganic material like cement, there are no interfering products found in their analysis, neither pre- and post-burning nor after pyrolysis.

For materials that are a combination of natural and synthetic polymers, like curtains, wood composite or wallpaper, the chromatographic profiles as well as the composition partially resemble the profiles of MPD or HPD and an untrained fire debris analyst might get the impression that an ILR is present in low amounts and is camouflaged by the fire debris matrix. The confusion might arise even more with purely synthetic materials like polyurethane, PVC-based materials, carpets and gas pipes, which all revealed a high number of VOCs, many of them specifically and characteristically present in ILRs, such as toluene, xylenes, C₃-alkylbenzenes and naphthalenes. Also, the TIC profiles have high similarity with HPD with the characteristic bell-shaped Gaussian distribution of *n*-alkanes present in many of them, which can easily bring the fire debris analyst to misinterpret it as an ILR.

But again, most of those mistakes are mainly made by untrained fire debris analysts. An experienced scientist has skills to observe and identify the details that differentiate these profiles from real IL mixtures. For instance, the spreading of the peaks along the chromatogram is highly indicative of whether an IL is present or not: petroleum distillates in the low and medium range have a narrow spread, HPDs are more widely spread, however in general, ILs are never spread all over the chromatogram (Stauffer et al., 2007), which is though the case in most of the observed TICs of synthetic polymer-based materials. Together with the presence of chlorinated compounds, the probability of the presence of ILs is therefore

reduced. The highest interference for ILR determination is given by the solvent-based paint. Since many solvents can be and are used as fire accelerants, the analysis of fire debris that contains paint as a main substrate creates a highly complex matrix that even for a trained fire debris analyst is difficult to interpret.

For the majority of the obtained products, another way of being able to distinguish it from an ILR is the observation of the specific ions, characteristic for a certain class of hydrocarbons. Not only are those ions specific for a hydrocarbon family, but the EIC profiles obtained are usually also different and characteristic for each fuel class, according to ASTM standards. On the one hand, in most of the presented cases that were doubtful, like polyurethane and vinyl flooring, the EICs were able to confirm that the obtained profile does not match with an ILR. On the other hand, however, in some cases, like the skirting board or the wood composite, the EICs resulted in exactly the opposite, raising the possibilities of misinterpretation of the sample as containing an ILR. It is therefore true that the EIC can be helpful in determining whether an IL is actually present or not, but in some cases it is not sufficient.

A different alternative for being able to distinguish the obtained chromatograms is to observe the relative abundance of the profiles and compounds obtained. Most of the substances are exclusively found for the materials that were analysed after burning and in almost all cases; the abundances were significantly higher in the burned samples compared to the blank sample. This confirms that a high amount of products are formed after a material has undergone combustion and pyrolysis, but also highlights the need for the collection of control samples to be able to diminish the interferences affecting the analysis, which was already suggested by the earlier study by Fernandes (Fernandes et al., 2002).

As previously mentioned, fires are highly destructive in nature. Therefore, in most fire scenes the finding of a control sample is very rare. Moreover, if a sample is encountered at the scene, it cannot be assured that it was not contaminated if in proximity of the fire due to the high extent a fire can have. These facts point out even more the need for the creation of a library of substrate materials for fire debris analysts.

However, the methods used for extraction and analysis also require some consideration. As previously described in chapter 1.4.2, ACS and SPME are the preferred extraction methods. Apart from the above mentioned characteristics of ACS, an additional pitfall is that the time for heating and extraction are very high, varying from one to 24 hours depending on the required efficiency, and the desorption involves the use of environmentally toxic and

expensive solvents like carbon disulphide. This makes it a less probable choice as extraction method for laboratories in economically more challenged countries like Portugal.

On the other hand, SPME is the more economic and sensitive extraction technique, and thus preferred. However, it also exhibits some disadvantages that are significant especially for FDA. The extract cannot be re-analysed, since after desorption into the injection port by exposure of the fibre, the sample is completely used. For that purpose, a hybrid technique between ACS and SPME was tested, where the fibre was desorbed with a small amount of solvent instead of direct injection into the port. This led to reduced signal intensities, which however were still sufficient for compound identification (Harris and Wheeler, 2003).

To try to reduce sampling time and increase even more extraction efficiency and sensitivity, a novel method was proposed, which involves pre-concentration of the analytes by using a technique called headspace sorptive extraction (HSSE). This technique uses PDMS stir bars as the enrichment phase and the desorption is carried out thermally and directly into the injection port of the GC. By comparing the results obtained with the ones obtained with SPME, a higher sensitivity was determined as well as a higher sorbent surface of the stir bars, allowing for better data for quantitative analysis (Cacho et al., 2014).

Furthermore, some of the pitfalls of ACS have been tried to be reduced, one of them being the possible mass-loss with the use of ACS during the extraction of the probe from the container and the desorption process as well as the heterogeneity in adsorption. A new method, headspace-mass spectrometry (HS-MS), was applied to simulated fire debris samples and optimized for the thermal desorption of the ACS. Compared to the standard ACS method, this technique has its main advantages in the high speed of the process, the safety for the environment and health and the lower costs involved with the same discrimination power and efficiency as the standard ACS methods (Ferreiro-González et al., 2014).

Regarding the analytical techniques, GC-MS is currently the standard method. However, it still has highly complex chromatograms resulting from the analyses, resulting in the need for development and improvement of the analytical tools available to simplify the interpretation of the data and to make the data validated and acceptable in a court of law (Pert et al., 2006). Comprehensive two-dimensional GC (GCxGC) has been used to characterize, differentiate and identify various types of ignitable liquids and background products in fire debris samples. Through the separation of the analysed compound first by boiling point and then by polarity, a two-dimensional, highly detailed chromatogram is obtained, from which patterns belonging

to ignitable liquids and the ones belonging to pyrolysis and background products can be better differentiated. The detection of weathered ILRs in the presence of pyrolysis products was successfully applied in FDA (Frysiner and Gaines, 2002). Apart from the differentiation capability, comprehensive two-dimensional GC also reduces the signal-to-noise ratio and also the ability of detection and quantification are increased, which are important for forensic analyses.

Another tandem technique, which was initially developed for the characterization of oils and other substances in geological and environmental studies, but has found application potential in FDA, is gas chromatography-isotope ratio mass spectrometry (GC-IRMS). GC-IRMS allows the determination of the carbon and hydrogen isotopic compositions of individual compounds even in a highly complex mixture, which again is relevant for the discrimination of the various compounds present in a fire debris sample. However, this method has not been validated yet and has still to be further studied for it to fulfil the quality assurance guidelines necessary to be admitted in a court of law (Benson et al., 2006; Schwartz et al., 2013).

Other techniques that have been applied to FDA are GC-MS/MS or tandem GC-MS, where a second MS is coupled to the first MS. This allows following the fragmentation pathway of ions that have been previously selected in the first MS. Even though interfering compounds present in the sample might give the same mass as the original parents target ion, for the following fragmentation patterns it is almost impossible to be the same. With this technique, matrix interferences can be highly reduced and the signal-to-noise ratio is decreased. While an increase in sensitivity has been proven for alkylbenzenes and naphthalenes, a loss of sensitivity for alkanes was found. This can be problematic for classes of compounds where differentiation is based on alkanes, such as some types of solvents. Therefore, GC-MS/MS is not yet applicable as a sole technique for FDA but it can be used alongside conventional GC-MS for confirmation of the results (de Vos et al., 2002; Pert et al., 2006; Sandercock, 2008). Especially for differentiation and classification of different ILs, in recent years more and more research groups have focused their studies on the combination of instrumental techniques with statistical methods. Present FDA still relies on visual pattern recognition of the TICs and extracted ion profiles (EIPs) for the definitive identification of ILs and determination of their presence in a tested sample by comparison with a known reference. However, this is mainly based on the retention times obtained during chromatographic separation of specific compounds and the ions obtained from that after mass spectrometric differentiation, which

can vary between different instruments, methods and laboratories where the analyses are carried out, resulting in a significant limitation. Although common GC-MS works well for a small, limited and simple number of samples, it is also very time-consuming for larger data sets. Additionally, the accuracy and quality of the results is highly subjective, depending on the experience and skills of the analyst. Hence the need for a more objective evaluating method of the results, which can be obtained through the application of statistical methods, e.g. by being able to calculate error rates, which reduce subjectivity and gives a confidence level not currently existing in FDA.

Various chemometric methods have been applied to novel techniques such as Raman Spectroscopy (Gonzalez-Rodriguez et al., 2011), GC linked to Differential Mobility Spectrometry (GC-DMS) (Lu and Harrington, 2007), HS-MS (Ferreiro-González et al., 2015) and GC-IRMS (Schwartz et al., 2013), but also for the standard techniques such as GC-MS (Tan et al., 2000; Doble et al., 2003; Sandercock and Du Pasquier, 2004) and GC-FID (Bodle and Hardy, 2007). The majority of those studies resulted in the successful application of chemometric procedures to FDA for classification and identification purposes, with results that are potentially admissible in court and therefore of forensic relevance. Especially for large data sets, statistical methods are more and more becoming of vital importance in FDA, even though there is still margin for improvement, to increase the accuracy of the methods and decrease the number of dependent variables.

The different extraction and analysis techniques lead to differences in the chromatograms obtained that make the comparison between the data unsuitable. As a result, if a library for substrate material is created, it is required for every combination of extraction and analysis methodology employed in FDA.

There are numerous papers that have dealt with the determination of interfering products during the identification of ILs, but most of them all spiked the samples with an IL as a comparison (Dabdoub et al., 1996; Cavanagh et al., 2002; Almirall and Furton, 2004d; Cavanagh-Steer et al., 2005; Baerncopf et al., 2011; Turner and Goodpaster, 2012; Contreras et al., 2013; Jhaumeer-Laulloo et al., 2013; Li et al., 2013). Their focus was mainly on the identification of ILs in the presence of interfering compounds. Only a few papers have performed the analysis of household items with the main goal being the determination of background, combustion and pyrolysis products to understand the processes of pyrolysis and combustion, the effects these processes have on the substrate material and to create a

reference library with these substrates for use by local fire debris analysts (Lentini et al., 2000; Fernandes et al., 2002; Stauffer, 2003b).

Especially for an untrained fire debris analyst, the knowledge and awareness of interference products play an important role in the successful performance of the analyses. It is relatively easy to determine whether an IL is present or not if the chromatographic pattern is as clear as stated in the ASTM standards for each IL class and all the characteristic compounds for an IL are found in the analysed sample. However, fires are highly destructive and never behave the same exact way, thus always creating a different effect on the burned materials, which results in a different and complex matrix of debris found at the scene that modifies the chromatogram obtained after the analysis, making the identification of ILs more difficult. Furthermore, the composition of the materials found in a household, from the construction material to the type of flooring, from the type of wood used for the furniture to the type of decorative materials used, varies significantly from country to country, from one part of the world to another. The reasons for that being several: economic, cultural, political, social, religious, natural. Therefore, it is vital to create an internationally recognized and spread database also for the most common background, pyrolysis and combustion products obtained from the analysis of the most commonly encountered substrates on fire scenes in the various countries. For that not only is there the need for further scientific work, but also a more developed communication network between laboratories and scientists all over the world.

Earlier work came from renowned fire debris analyst Eric Stauffer during his master thesis and his later published and related summary-paper '*Concept of pyrolysis for fire debris analysts*' (Stauffer, 2003b) as well as forensic chemists Almirall and Furton (Almirall and Furton, 2004c), who selected a number of common household products encountered in the United States and analysed them after subjecting them to combustion and pyrolysis. For many of the items analysed, such as carpets, floorings, plywood and materials containing adhesives, the chromatographic profiles obtained are similar to the ones obtained in this work. Furthermore, the main background, combustion and pyrolysis products encountered are also similar, including mainly *n*-alkanes, isoparaffins and many aromatic compounds, most of them being also target compounds of ILs. However, differences between the TICs obtained by the analysis after extraction with ACS and SPME are generally observed for the same materials: the abundance in the TICs obtained with SPME extraction are significantly higher than the ones obtained with ACS extraction (**Figure D32**). This is most likely due to the different extraction

technique and the GC-MS temperature program used: the SPME extraction and the temperature program used in this work show a higher sensitivity for the extraction and detection of volatile compounds from both burned and unburned materials compared to passive headspace adsorption with ACS or Tenax as well as a significantly reduced extraction time.

5. CONCLUSIONS

Fire debris analysis is a crucial part of a fire investigation with a suspected case of arson. Together with the fire investigation performed at the scene, it can be the key point to confirm or contradict that hypothesis by revealing the presence of ILRs in the samples collected at the scene. However, FDA has been known to be a highly complicated branch of forensic science due to the variety and large number of interferences that can be present in the debris matrix. The results obtained from the analyses of 19 unburned and burned substrate materials commonly encountered in the debris of fire cases confirmed the complexity of the matrices fire debris analysts have to face when tasked with the determination of the presence of ILRs. Many of the compounds resulting from the background of the analysed material but also the products obtained due to combustion and pyrolysis processes include various alkanes, such as *n*-alkanes and isoparaffins, and aromatics, such as toluene, alkylbenzenes, and naphthalenes, which are all target compounds of ILs. Through detailed observation of the chromatographic patterns and abundances and comparison of the profiles of characteristic hydrocarbon classes with known standards, a fire debris analyst is able to distinguish the matrix interferences from ILRs in most cases, but not all, depending mostly on their level of training and experience. Especially in cases where the amount of ILRs is small, awareness and knowledge of possible interfering products play an important role.

It is therefore of high importance to create a library of interfering products resulting from different substrate materials of different origins (qualitative and geographical), with different stages of weathering or decomposition and subject to different conditions that most closely resemble a real fire, including mainly combustion and pyrolysis. Analysis of samples from real fire scenes additionally confirmed the presence of many interfering products.

Furthermore, the capability of determination of interfering products is influenced by the extraction and analytical techniques used. The extraction via SPME and analysis via GC-MS (HS-SPME-GC-MS) applied in this work showed a higher sensitivity than results obtained by passive headspace adsorption techniques used in previous studies.

Moreover, for SPME no pre-treatment of the sample is needed and no solvents are used, being more environmental-friendly, cheap and easy, which makes it the preferable method in the current economy- and environment-focused scientific world. The efficiency of the applied method was confirmed by the positive results obtained for one of the cases studied.

6. RECOMMENDATIONS FOR FURTHER WORK

The work done in this study represents only a small part of what is required in this field.

One of the most important points of improvement consists in the use of an extensive set of standards representing the various compounds expected as interfering products that are subject to the same extraction and analysis techniques for the comparative use in compound identification, similarly to what was done by Almirall and Furton in their study (Almirall and Furton, 2004c). This will allow increasing the level of confidence in the methods used as well as the accuracy in compound identification.

Furthermore, to expand the library of substrate materials with their background, combustion and pyrolysis products, great effort must be put into collecting and analysing as many materials as possible in various conditions for the creation of a database, similarly to the one created by the University of Florida and National Center of Forensic Science (NCFS) in cooperation with the Scientific Working Group for Fire and Explosions Analysis (SWGfEX), called *Ignitable Liquid Reference Collection Substrate Database*, but on a more international level.

Moreover, in fire debris analysis, the majority of the samples arriving at the laboratory are samples that have undergone combustion and pyrolysis. However, in most cases those samples are not collected immediately after the fire occurred; depending on when the fire was reported, when the fire fighters got to the scene, were able to secure the fire and the fire investigators went to the scene and collected the samples, there is a significant time delay, in which many light volatiles are lost in the environment and rarely can be collected or detected. Therefore, another important aspect to be investigated is the influence of time between the occurrence of the fire, the extinguishing of the fire and the sample collection for analysis.

Related to time is also the weathering of the sample, which can derive from meteorological conditions, which are different in every region of the world, but also the different fire-fighting agents used that can compromise the integrity and quality of the fire debris. The latter has been recently studied by the research group lead by Contreras (Contreras et al., 2013) specifically for linear alkylbenzenes; however, there is still further work needed.

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Appendix A – Pictures of collection location of Fire Scene Samples

Appendix B – Pictures of substrate materials before and after burning

Appendix C – Full fire investigation reports

Appendix D – Additional tables and figures for results and discussion

Appendix A - Pictures of sample collection location in Fire Scenes

Collected from fire scene 1, north of Portugal:



Figure A1: Residue of detoxification plaque 1.



Figure A2: Residue of detoxification plaque 2.

Collected from fire scene 2, central-east of Portugal:



Figure A3: Wood-imitating flooring.



Figure A4: Laminated cardboard skirting board.



Figure A5: Wall-sustaining wood.



Figure A6: Cement.

Collected from fire scene 3, central-west of Portugal:



Figure A7: Wood from possible point of origin 1.



Figure A8: Wood from possible point of origin 2.



Figure A9: Wood from possible point of origin 3.

Appendix B – Pictures of samples before and after burning

Plywood flooring

Blank



Figure B1: Picture of the plywood flooring before burning.

Post-burn



Figure B2: Picture of the plywood flooring after burning.

Polyurethane

Blank



Figure B3: Picture of the polyurethane before burning.

Post-burn



Figure B4: Picture of the polyurethane after burning.

Cement

Blank



Figure B5: Picture of the cement before burning.

Post-burn



Figure B6: Picture of the cement after burning.

Cork

Blank



Figure B7: Picture of the cork before burning.

Post-burn



Figure B8: Picture of the cork after burning.

Wood

Blank



Figure B9: Picture of the compressed wood before burning.

Post-burn



Figure B10: Picture of the compressed wood after burning.

Vinyl flooring kitchen-use

Blank

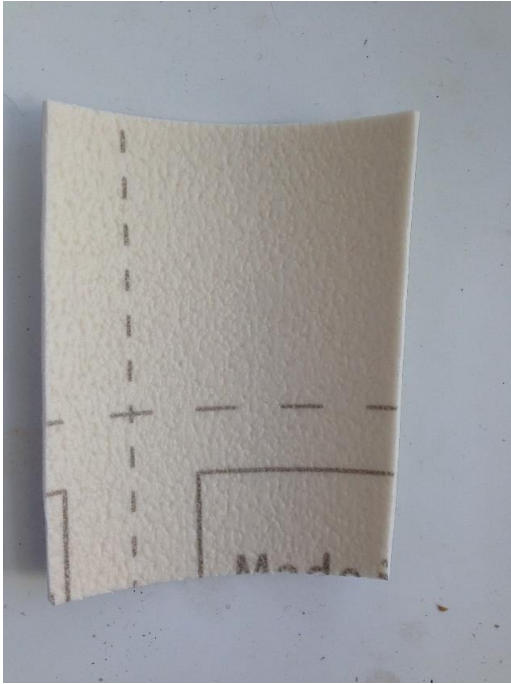


Figure B11: Picture of the vinyl flooring kitchen-use before burning.

Post-burn



Figure B12: Picture of the vinyl flooring kitchen-use after burning.

Curtain orange

Blank



Figure B13: Picture of the orange curtain before burning.

Post-burn



Figure B14: Picture of the orange curtain after burning.

Carpet underlay

Blank



Figure B15 : Picture of the carpet underlay before burning.

Post-burn



Figure B16: Picture of the carpet underlay after burning.

Carpet red

Blank



Figure B17: Picture of the red carpet before burning.

Post-burn



Figure B18: Picture of the red carpet after burning.

Carpet double layer black

Blank



Figure B19: Picture of the double-layered carpet before burning.

Post-burn



Figure B20: Picture of the double-layered carpet after burning.

Curtain black

Blank



Figure B21: Picture of the black curtain before burning.

Post-burn



Figure B22: Picture of the black curtain after burning.

Vinyl flooring living room-use

Blank

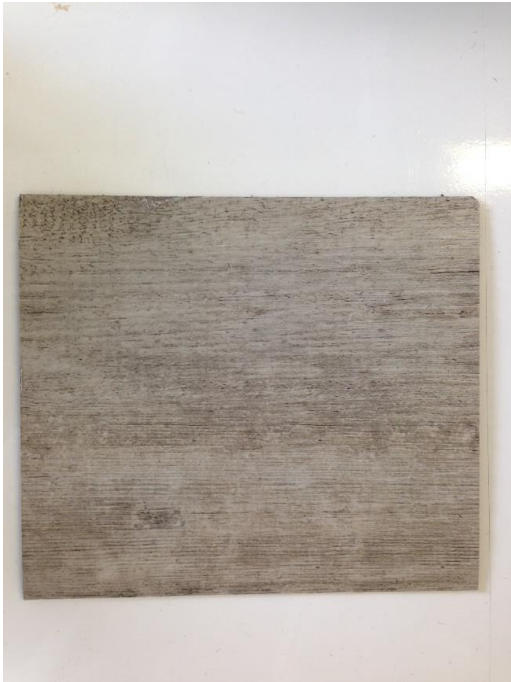


Figure B23: Picture of the vinyl flooring living room before burning.

Post-burn



Figure B24: Picture of the vinyl flooring living room after burning.

Skirting board

Blank



Figure B25: Picture of the skirting board before burning.

Post-burn



Figure B26: Picture of the skirting board after burning.

Wallpaper

Blank



Figure B27: Picture of the wallpaper before burning.

Post-burn



Figure B28: Picture of the wallpaper after burning.

Gas Pipe

Blank



Figure B29: Picture of the gas pipe before burning.

Post-burn



Figure B30: Picture of the gas pipe after burning.

Wood composite

Blank



Figure B31: Picture of the wood composite before burning.

Post-burn



Figure B32: Picture of the wood composite after burning.

Electric cable with three conductors

Blank



Figure B33: Picture of the electric cable with three conductors before burning.

Post-burn



Figure B34: Picture of the electric cable with three conductors after burning.

Paint solvent-based

Blank



Figure B35: Picture of the solvent-based paint before burning.

Post-burn



Figure B36: Picture of the solvent-based paint after burning.

Paint water based

Blank

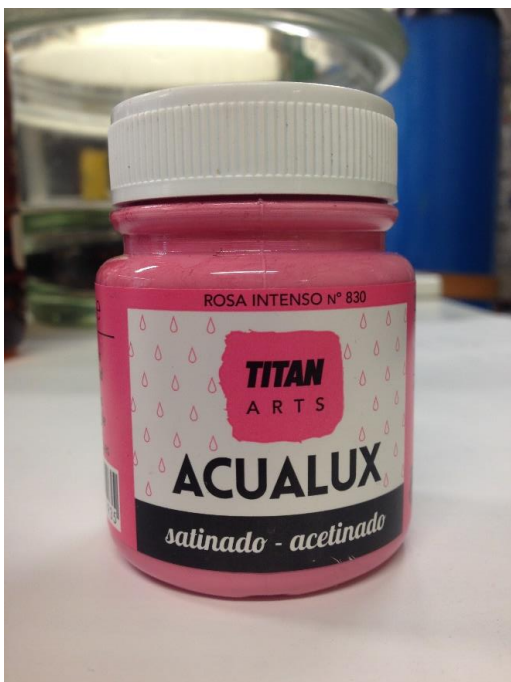


Figure B37: Picture of the water-based paint before burning.

Post-burn



Figure B38: Picture of the water-based paint after burning.

Appendix C – Full fire investigation reports

Technical expertise report – Fire Scene 1 – North

Technical report

The fire scene was approached with an 'outside-to-inside' methodology, resulting in the first observation of the exterior conditions of the damaged building as well as determining the morphology and collecting all relevant background information and witness statements.

The analysis of the exterior of the building showed no major damages on the walls or doors (Pictures 01 to 03), merely soot depositions were observed on the exterior of the back door and back ventilation shafts (Picture 03). Also, the majority of the windows were found lying on the floor outside of the building, whole, with soot depositions above the window frames on the along the whole east wall (Picture 02), indicating that at some point during the fire the pressure build up and the heat removed the windows and the fire and smoke exited the building through those openings. Just with these observations, a general trend of the propagation direction of the fire can be determined as being from south to north (main front door to back door) and from the inside to the outside can be observed, since there is are no major fire damages on the main front door or on the exterior of the pavilion.

From the exterior, the investigation moved to the interior of the pavilion, which showed a high degree of damage in general in the inside of the pavilion (Pictures 04 and 05).

Following the standard scientific method of a fire investigation, the areas with the highest degree of damage were identified first, which were found to be one area in the first part of the pavilion between the 3rd and 7th pillar and another one in the rear part of the pavilion between the 19th and 22nd pillar, in close proximity of the motors regulating the opening and closing of the metal grids (Pictures 04, 05, 08 and 09). The high degree of damage was observed in the absence of the PVC roofs and wood panels, the high carbonization level on the floor, the high oxidation signs on the metal bars as well as high soot depositions on the ceiling above that area (Pictures 04, 05 and 06), sign of convective heat damage, which also shows the direction of propagation to be from the bottom up. Residues of the plastic curtains and the melted lamp (Picture 06) show also a high degree of damage resulting from radiant and convective heat, indicating that the ignition source must have been close as well as that the burning process was slow. Propagation direction again is shown to be from south to north.

However, the damaged area is not that big, since it did not reach the end of the first part of the pavilion (Picture 07), which is intact, meaning that the fire in the first area must have been of a slow rate. On the other hand, the second major damage area is bigger (Picture 09), resulting in high damages on most of the area in the rear part of the pavilion. Here also a propagation direction from south to north can be observed as well as from the bottom up and then from the inside to the outside.

The 'alligator marks' observed at the upper part of the north wall (Picture 42) are a sign of dehydration after a long persisting of high temperatures and smoke, with decreasing damage from the top down, confirming that a hot gas layer reached the end of the pavilion quickly but then stayed there for a prolonged time, with the flames eventually getting closer to the central part (soot on the right ventilation shaft more present than on the left), since signs of convective heat damage can be observed, but no direct contact with the flames.

However, in the rear part of the pavilion, the flames did have direct contact with the ceiling (Picture 49 and 50) with clean burn pattern observed. The areas of clean burn match with the position of the plastic curtains present in the pavilion. Plastic is a highly combustible but not conducting material, therefore the observations can be explained by the flames reaching the curtains, then being stopped in those positions, creating a rise of the flames towards the ceiling and a higher persistence of the flames in those points until the curtains eventually were completely destroyed, liberating the flames again to propagate (towards north) further until the same happened when encountering the next curtain.

Once the major damage areas were identified and the direction and general behavior of the fire were determined, a closer look at the areas was taken to determine the ignition source and the seat of fire. This was done during the second day.

The floor around the second major damage area shows highly combusted and carbonized materials, with still visible residues of the detoxification blocs (Picture 10 and 11). The damage observed on the floor is increasing from west to east (bottom to top of picture) and also the metal bars show a higher degree of oxidation on the top part, indicating a higher proximity to the ignition source, since this damage is caused by high temperatures and direct contact with the flames. The metal bars also show a concentric increasing damage that point towards the area around and underneath the motor (Pictures 12, 15 and 16), indicating a high probability of that point to be the point of origin. The high deformation of the metal bars right in front of the motor indicate a relatively slow heat transfer but at very high temperatures. When having

a closer look at the area in front of the motor, a clean burn pattern can be observed, confirming the high temperature impact and therefore the direct flame contact. The motor shows high degree of damage from the front as well as from underneath (Picture 14 and 25), where melted plastic can be observed, indicating that a dropdown occurred. The dropdown also caused a secondary fire, since damage on the area on the floor and underneath the motor (Pictures 12, 17 and 23) do not match with a fire started in the motor and propagated from there. However, this fire was very small and slow, since the metal bars around that area do not show any signs of damage coming from underneath (Picture 18).

Direction of propagation of the fire starting from the motor and then going concentrically in the surrounding area and the front (west wall) is also confirmed by the less damage observed in the area behind (east) the motor (Picture 20). Removing of the debris underneath the motor (Pictures 27 and 28) does not show any ignitable liquid pattern, confirming that the fire was not caused by an accelerant. The patterns observed around the detoxification bloc (Picture 22) does not match with a fire that started in that point.

A closer look at the motor shows the highest degree of damage between the 2nd and 3rd contacts (Picture 29 and 32), with a 'V-pattern' observable from there and a high damage area of melted material underneath the contacts. Very high oxidative damage can also be observed on the main metal frame of the motor, also indication of high temperature impact for a prolonged period and of direct flame contact.

When moving to the first major damage area, a similar general damage pattern can be observed (Picture 33), with an increasing damage pattern in a concentric way towards the motor. The burn and damage patterns on the metal bars around the motor (Pictures 34-37) indicate a high temperature and direct flame contact right in front of the motor towards the west wall (Picture 35) and then moving upwards and from the inside towards the outside. Deformation of the metal bars right in front of the motor (Picture 36) is higher than in the second major damage area and the height of the bars is lower, indicating a heat transfer for a longer period of time and of high temperatures, without any secondary fires starting, since also no damage in the area underneath the motor can be observed (Picture 40).

Closer look at the motor (Picture 38 and 39) show the highest damage point also between the 2nd and 3rd contact with a 'V-pattern' observable from there, indicating this as another point of origin. Same as for the motor in the second major damage area, the area underneath the

contacts is highly damaged and has melted materials and the metal frame shows strong oxidative damage.

After removal of the debris underneath the motor, no signs of ignitable liquid residues can be observed, confirming that no accelerant was used.

The electrical boxes, located next to the main front door, were also observed (Pictures 46 and 47) with signs of heat damage on the top more than the bottom, however no electrical malfunction or misplaced plug could be observed.

Samples from the detoxification blocs located in both major damage areas (tags #5 and #8) were collected for laboratory analysis.

Laboratory Analysis

The analysis of the detoxification bloc residues did not reveal the presence of any ILR. The components of the blocs were identified as formaldehyde and stearic acid.

Conclusions

The fire originated in two separate points simultaneously, namely between the 2nd and 3rd contact of both motors, due to an electrical overcharge, which was so high that the material could not resist it and the created heat with that speed ignited the material.

However, the fire spread slowly and in a concentric way at first, since the material surrounding the contacts was mainly made of hard plastic, which is a slow degrading material. Eventually the heat generated by the wall towards the west was enough to reach the metal fences and through conduction and convection the PVC grids and eventually the wood panels, in an outward and upward propagation direction.

While the fire in the front part of the pavilion kept a slow propagation rate and stayed relatively small, the plastic material covering the bottom part of the motor in the rear part of the pavilion melted and dropped down, creating a secondary seat of fires, since the floor was covered in hay-like material, which is easily flammable. This drop-down indicates a faster growing fire compared to the one in the front part of the pavilion, which is due to the locations of the ventilation shafts, which were located on the west wall of the pavilion close to the dividing metal fence and in the rear part of the pavilion, creating an air current that speeded

up the fire in the rear part, but did not affect the one in the front part, since the propagation direction was from south to north. This explains the greater damage found in the back part of the pavilion compared to the front part.

The fire grew from the middle of the pavilion outwards and upwards and once it reached the ceiling, the gas layers and flames circulated back, eventually exiting the pavilion through the windows on the sides and the ventilation shafts on the back.

The detoxification blocs were not involved in the ignition of the fire, which was confirmed by the observations that did not match the starting point being there and by the laboratory analyses, which confirmed that the components of the blocs are not able to be ignited by human intervention and thus are not able to generate enough energy to cause the fire.

Taking into account all mentioned before, the fire resulted from an accidental cause from an electrical fault, without any direct human intervention.

Pictures



Picture 01 - Outside view of main entrance – no visible damage or signs caused by the fire.



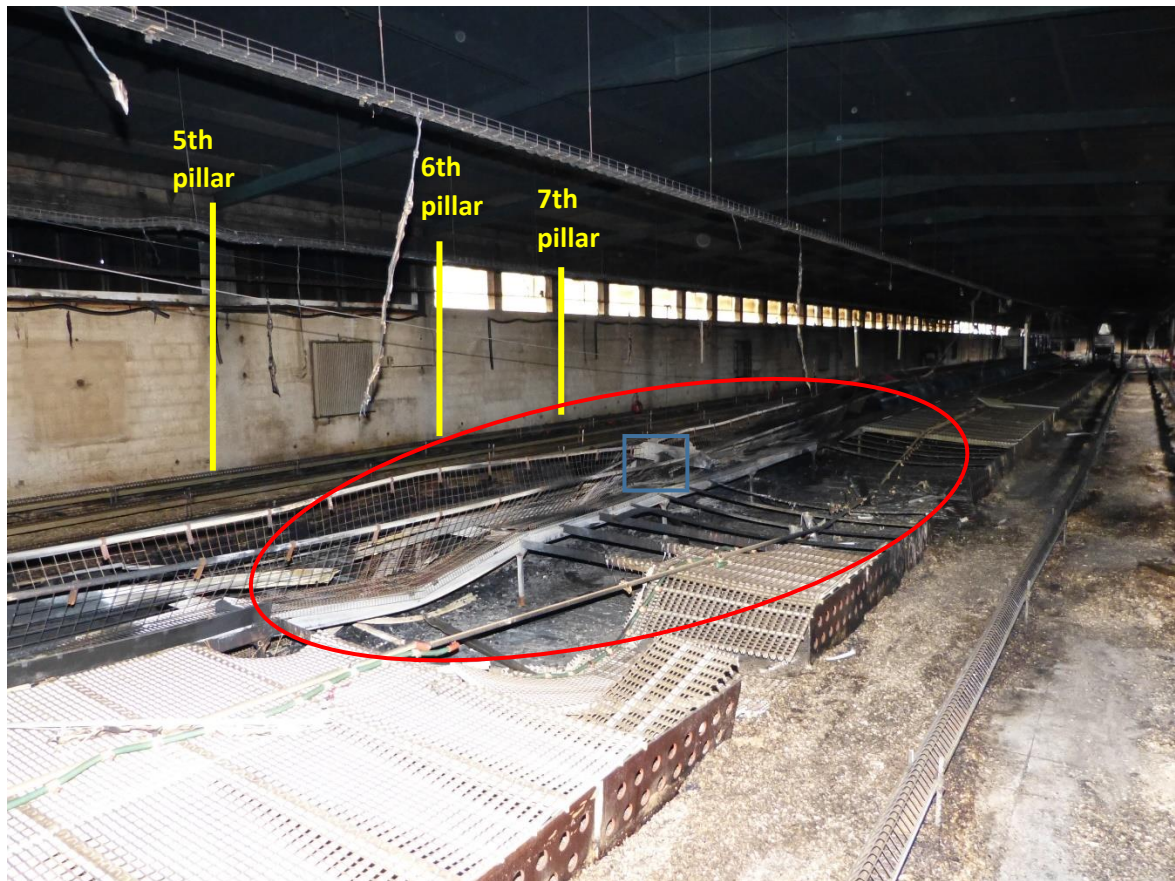
Picture 02 - Outside view of east wall of the pavilion – soot deposition on the top of all window frames, the direction of the flames and smoke coming out of the windows is indicated by the red arrows.



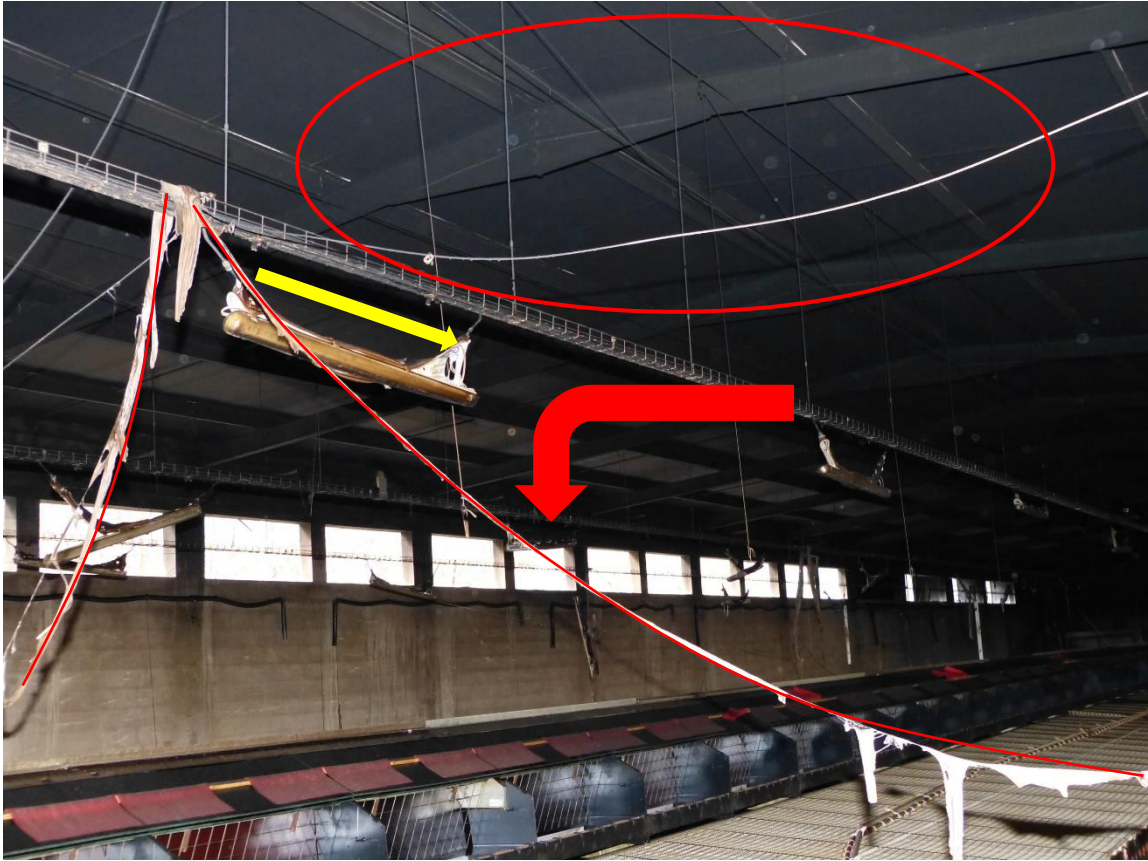
Picture 03 - Outside view of backdoor (north to south) – compared to the front entrance, here there are signs of the fire visible, on top of the main door and on the two top ventilation shafts (orange circles) and on the left one (green circle); darker soot present on the top shafts than the top one, indicating that the smoke and flames were at a high level at the time when they reached the end of the pavilion.



Picture 04 - First major damage area between pillars 3-7– View from left side (west) of the pavilion; the red circle indicates the area with the highest degree of damage, due to the complete absence of the covering fences, high carbonization level of the material and high soot deposition, also the metal bars are highly bent, which indicates a longer persistence of the flames in that area, which is an indication of a slow developing fire; additionally, major damage and soot deposition can be seen on the ceiling and from there the soot deposition level decreases from the middle to the outer part of the building as well as from the upper part of the walls going down, indicating that the fire propagated from the inside towards the outside and that the flames went up in the middle and then were deviated to the sides once they reached the ceiling, which is a typical phenomenon observed in compartment fires; also, one possible point of origin can be the blue squared engine, where the most damage can be seen.



Picture 05 - First major damage area – View from right side (east) of the pavilion; the first area with major damage that is found in the pavilion is marked by the red ellipse – damage on the right side of the motor (blue square) is less than the one on the left side of the motor (see Picture 10), indicating that the fire started and developed from the motor in direction of the west wall.



Picture 06 - Middle area of the pavilion – residues of plastic curtains (red line), lamps increased damage from right to left of the picture (south-north, yellow arrow), convective heat damage can be observed on ceiling (red ellipse), indicating a top-down direction in this part of the pavilion as well as a south to north propagation of the fire.



Picture 07 - Food supply machines – view from south to north, no discoloration or oxidation signs, chicken-houses almost intact (yellow circle) while ceiling shows soot deposition (red circle) signs of direct contact with flames and propagation on top, indicating point of origin further away from there.



Picture 08 - Food Supply machines – View from north to south – soot depositions visible (orange circles), more on the right side (west) than left side (east), also major damage on floor (red bottom ellipse) due to completely absent chicken-house covers, metal bars showing high degree of soot deposition and oxidation and deformation, convective heat signs on ceiling (red top ellipse), residues of curtains on right of picture (green line), indicating that the fire was low on that part of the pavilion but had an upgoing trend when it reached the metal fence, directed more towards the right (west) side.



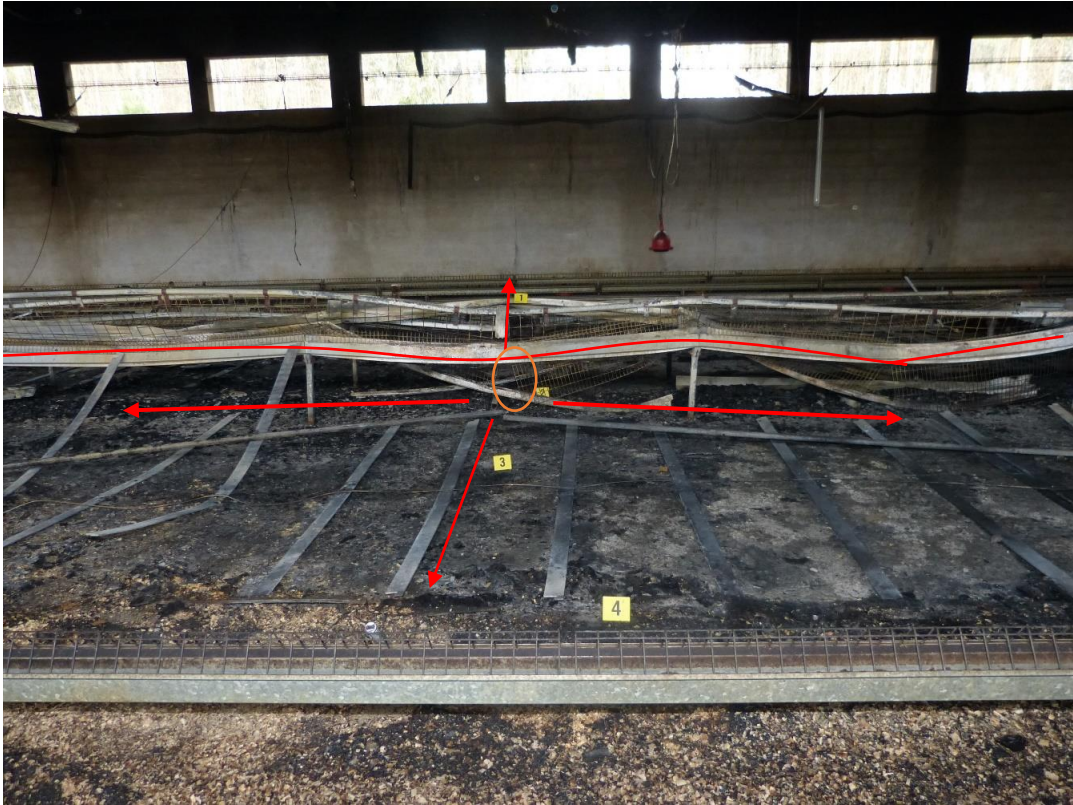
Picture 09 - Rear part of the pavilion – view from south to north, second area with major damage and possible location of second seat of fire; more extensive damage to the chicken-houses, since most of the roofs are completely destroyed, high level of carbonization; high deformation degree of the metal bars and soot deposition and oxidation signs (red ellipse), signs of a long persisting fire in that area, with the fire going upwards – convective heat signs on ceiling – and then from the middle outwards towards the walls; orange circle shows signs of higher degree of damage on the ceiling, indicating direct flame contact and for a longer period of time in that point; also, the deformation of the light bulbs shows signs of radiant heat.



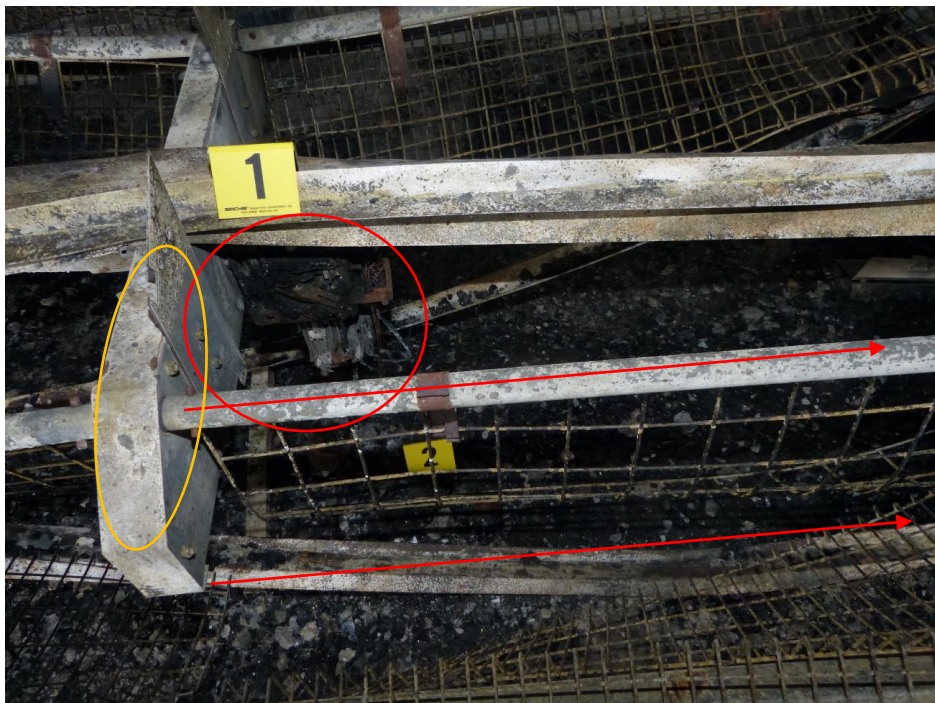
Picture 10 - Tag #6 – residues of detoxification blocs (orange ellipse), possible point of origin; high degree of carbonization and combustion can be observed on the floor, indicating a slowly progressed fire; red circle indicates the breaking point of the metal bars, indicating a long and high heat transfer in that point; the red arrow indicates on the metal bars on the floors an increasing damage and carbonization level from the bottom to the top of the picture (west to east).



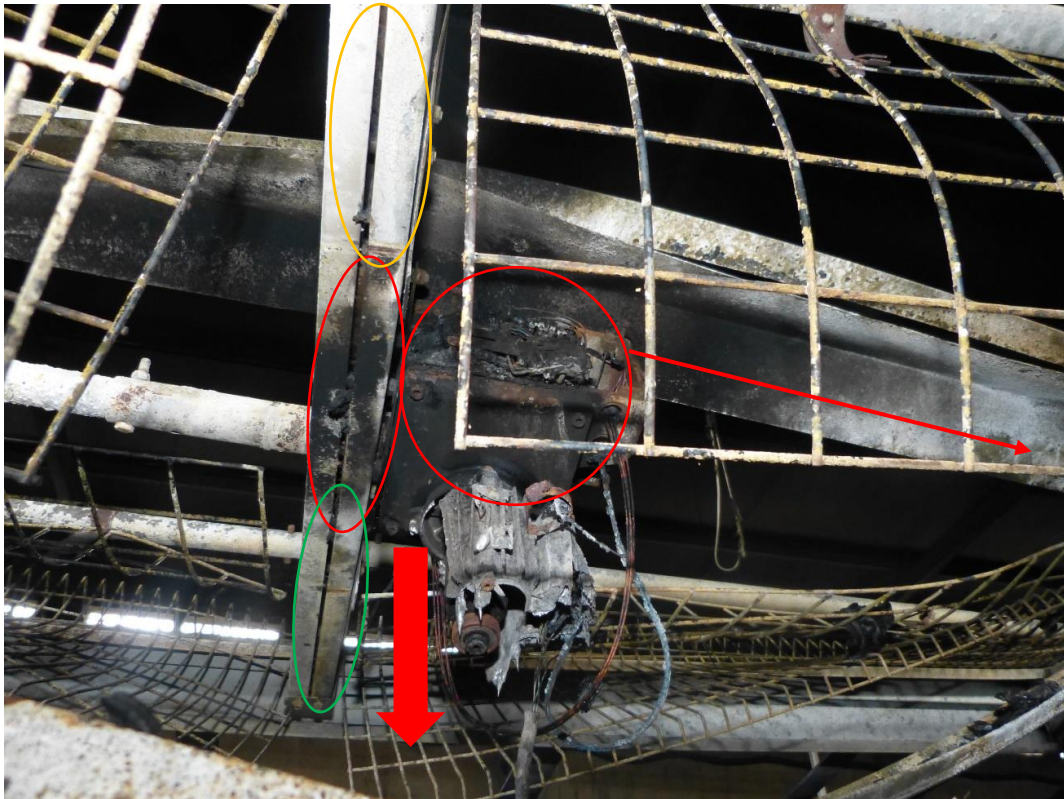
Picture 11 - Tag #5 – residues of second detoxification bloc (red circle) and potential area for point of origin; signs of high exposition levels can be observed on the metal bars (orange ellipse), increasing from the right to the left of the picture (south to north) with signs of oxidation (orange arrow); presence of part of the PVC-roof (green circle) indicates that the fire was not travelling towards that direction, since it otherwise would have destroyed it completely, but it was affected by radiant heat of being in close proximity of the fire.



Picture 12 - Tag # 1-4 – potential seat of fire; high deformation levels of the metal bars can be observed (red lines) and decreasing levels of carbonization in a circular, concentric way (red arrows) from underneath tag #1 (orange circle), giving indication of high probability of that point being the point of origin.



Picture 13 - Tag #1 and #2 – view from above – high levels of destruction and carbonization (red circle) on the engine; high oxidation and exposition signs on the metal bars, with decreasing levels from left to right (red arrow, north to south); high deformation of metal bar on bottom, indicating high temperature impact and the exposition signs indicate direct flame contact; transversal metal bar (orange ellipse) shows a clean burn pattern, indicating a high temperature and long persisting direct contact with the flame, which makes sense if coming from the engine.



Picture 14 - Tag #1 and #2 view from underneath; high deformation and drop-down of plastic from underneath the engine; high levels of soot deposition underneath the engine (red ellipses), indicating a possible second seat of fire coming from underneath; clear protection of metal bar behind the engine (green circle), indicating the direction of the fire from the engine towards the top of the picture (west); clear difference in oxidation and damage levels on top (west) of picture (high) compared to bottom (east) of picture (low), confirming direction of propagation facing west.



Picture 15 - Tag #1 – View from the top, south to north – damage decrease from north to south (orange ellipse), side is clear (red circle), indication of direct flame contact for a prolonged time, while the other side is protected; red arrows show direction of propagation.



Picture 16 - Tag #2 – view from the left side (north to south) – middle horizontal metal bar is protected from this side (green ellipses) – vertical bar in the middle shows decreasing damage/oxidation from south to north, confirming the direction of propagation of the fire.



Picture 17 - Tag #2 – view from the left side (north to south) – metal bar on right of picture shows strong deformation in front of the motor and increasing oxidation from north to south – also, dropdown from melted plastic of bottom motor part – black underneath motor (red ellipse): radiant heat from second fire (blue ellipse).



Picture 18 - View from underneath of metal bar on right side of previous picture – protected area (red ellipse), indicating fire did not come from underneath.



Picture 19 - View of metal bars on left side of pavilion from potential seat of fire south to north – decreasing levels of oxidation and damage from south to north and from east to west, red arrows indicate the increasing level of damage pointing towards one area of origin.



Picture 20 - View from east to west of tags #1-4 – metal bars are still in their original position, even though with levels of soot deposition and damage increasing from west to east; less damaged area than in the area behind (west) tag #1, indicating that the direction of travel of the fires was not towards this direction.



Picture 21 - View from top of tags #1-3, west (top) to east (bottom) – exposition levels on the metal bars are decreasing from tag #1 in the marked directions (red arrows); again, high deformation of metal bars shows exposition to high temperatures for a long time; high levels of carbonization on the floor (tag #3), indicating also a low level fires in that point.



Picture 22 - Tag #3 – detoxification bloc – damage on bars does not coincide with this point as seat of fire, since the damage should have been pointing to the direction of the bloc in a concentric way, but instead the damage is increasing from bottom (west) to top (east).



Picture 23 - Tag #2 view from top, east (top) to west (bottom) – high damage area on floor, signs of low level slow burning.



Picture 24 - View from underneath of central metal bar near tag #1 – direct flame contact in black area (red circle); protection on the left side of the metal bar (green ellipse) and exposition signs on the right (orange ellipse).



Picture 25 - Damage of motor (tag #1) from front.



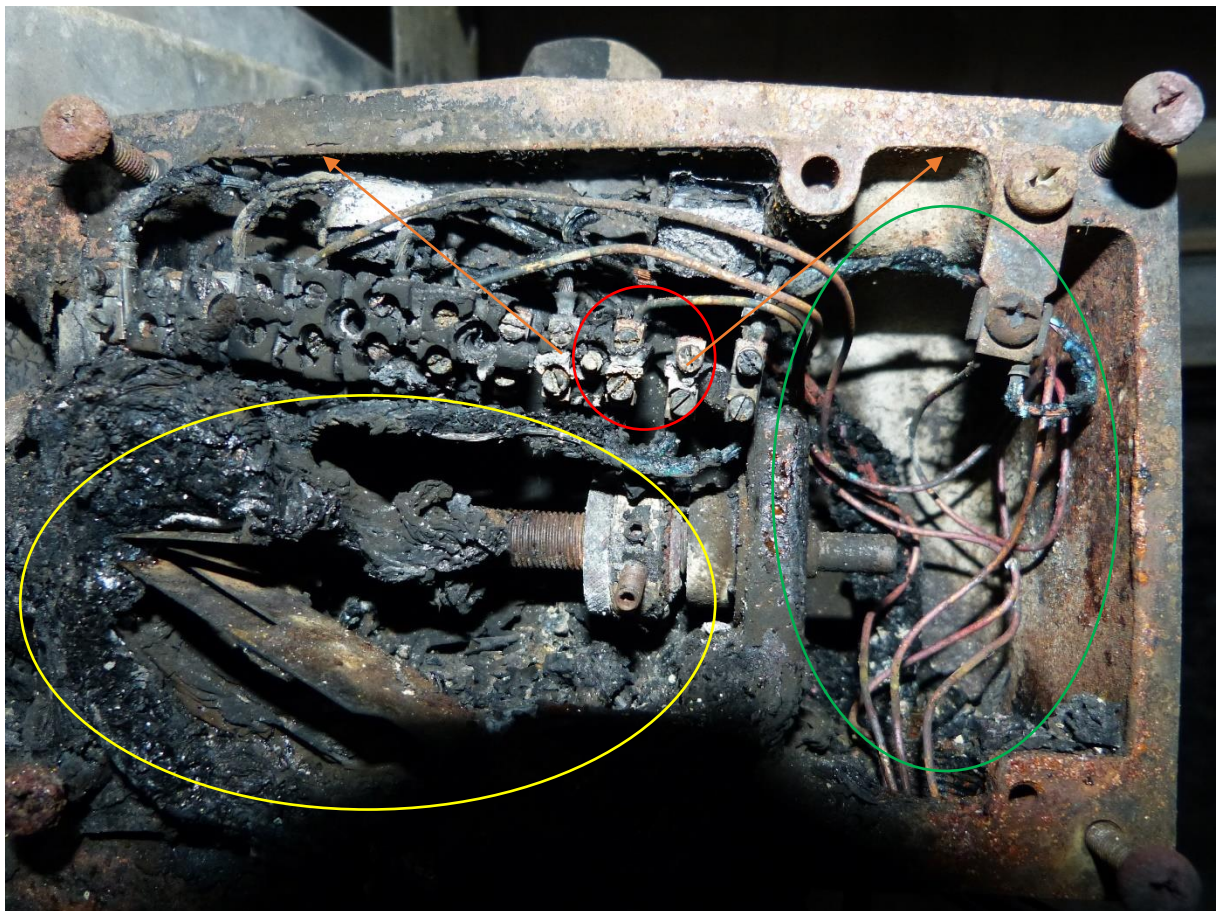
Picture 26 - View of motor (tag #1) from top, west (top) to east (bottom) – transversal metal bar area behind the motor shows signs of protection, but motor shows signs of heat transfer from underneath (black), indicating heat/fire source from underneath.



Picture 27 - View of floor area around tag #2 – completely melted bottom part of the engine (drop-down, orange ellipse); high levels of carbonization, no signs of ignitable liquid residues (red ellipse).



Picture 28 - View of floor area around tag #2 after removal of fire debris – no ignitable liquid residues visible.



Picture 29 - Close up view of motor (tag#1) – area with major damage (red circle) between 2nd and 3rd contact since the plastic of the connections is completely melted away, also from there, V-pattern (orange arrows) can be observed; radiant heat burn area (yellow ellipse); cables on the right of the picture (green area) have the protection completely melted, indication of high temperature impact.



Picture 30 - View of motor (tag#1) from bottom – black area underneath the motor (red ellipse) indicates heat source from underneath; drop-down of plastic underneath the motor (red arrow).



Picture 31 - View from top of part of motor (tag#1) that dropped to floor.



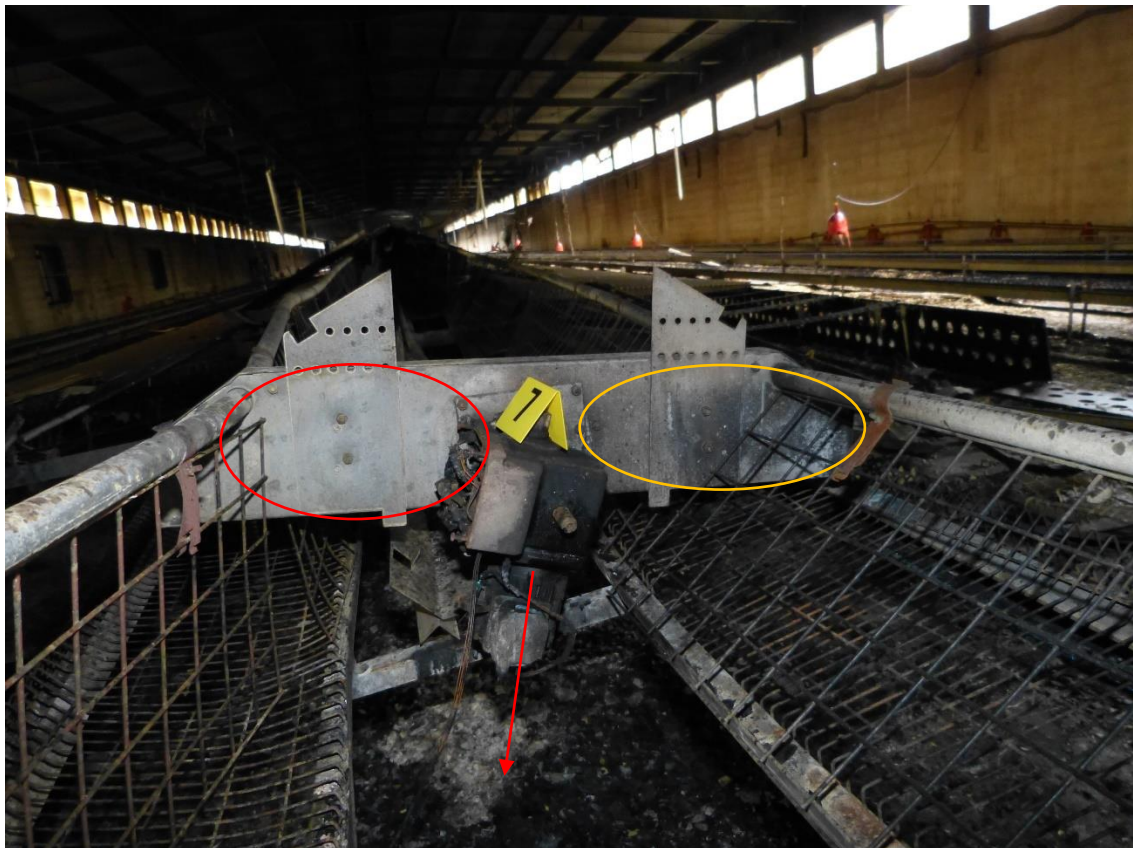
Picture 31 - Close up view of motor (tag#1) from top – point of origin (red circle).



Picture 33 - Tags #7 and #8, view from west (bottom) to east (top) – second potential seat of fire; red arrows indicate the probable direction of propagation of the fire, due to increasing damage levels in a concentric way towards one point (red circle), highest point of deformation of the metal bars, also signs of prolonged exposition to high temperatures, exposition signs are strong; metal bars on the floor show decreasing damage signs from top (east) to bottom (west).



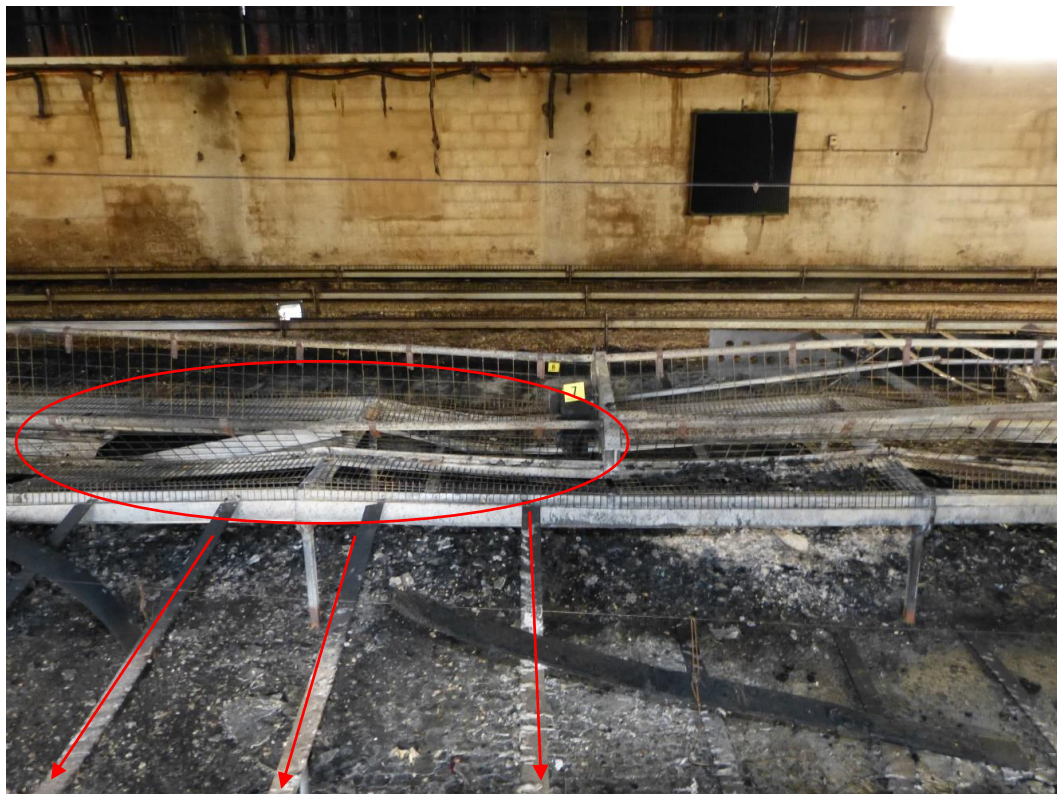
Picture 34 - Tag #7, view from left side (north to south) – increased oxidation level from north to south (green arrow), protected left side of metal bar on left of tag#7 (green ellipse).



Picture 35 - Tag #7, view from right side (south to north) – horizontal metal bar in middle shows clean burn pattern on left side (red circle), soot deposition of right side (orange ellipse), indicating direct flame contact on left side and radiant/convective heat damage on right.



Picture 36 -View of left side of tag #7 from bottom – high deformation of metal bars (red lines) on the right side (west) of the picture compared to the left side (east), indicating propagation direction towards west and not east from the motor (blue ellipse); increased oxidation levels of metal fence towards the motor (green arrow), pointing to the point of origin.



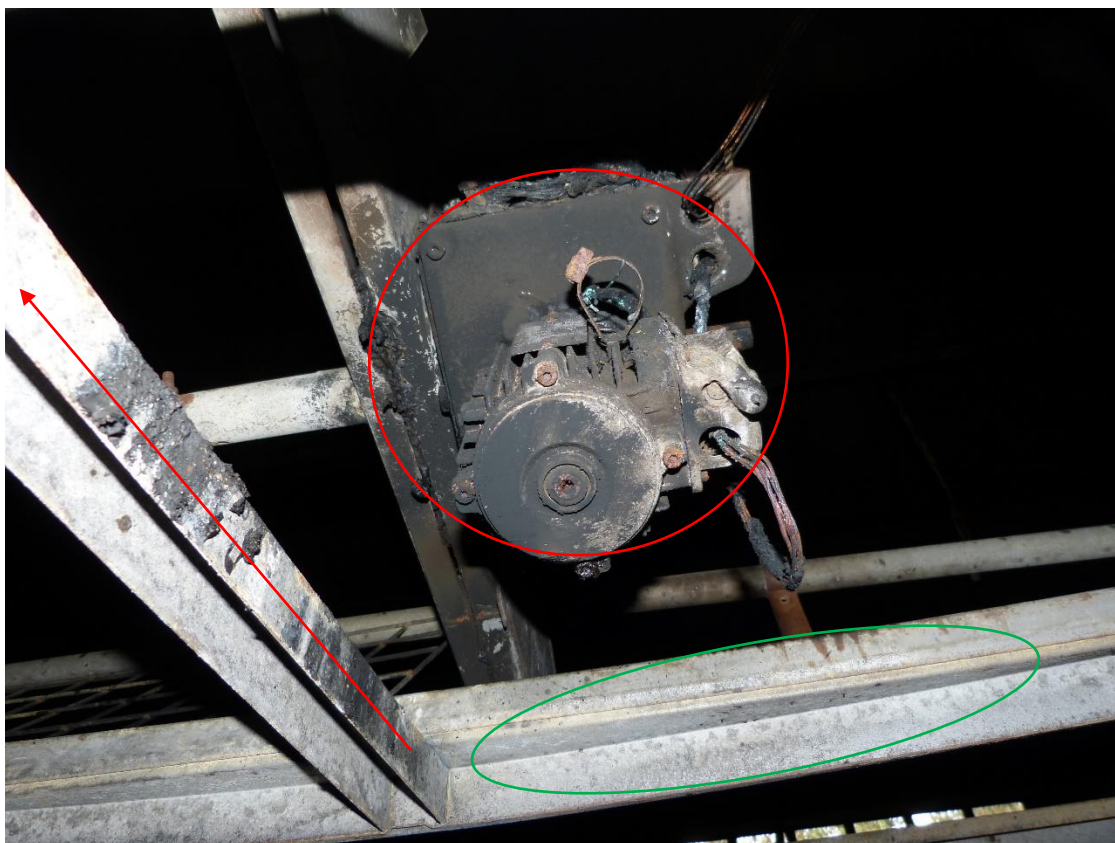
Picture 37 -View from back of tag #7 and #8 – metal bars show decreasing damage inside to outside, metal grids show more damage and deformation on south side of tag#7 than north side.



Picture 38 - Close up view of motor (tag#7) – highest degree of damage between 2nd and 3rd contact (red circle), from there V-pattern can be observed on the levels of damage; radiant heat damage on the part below the contacts (orange ellipse).



Picture 39 -Close up view of motor (tag#7) II – high oxidation levels on the upper right side but higher damage levels on the lower left side, indicating that the fire started there, but then traveled downwards.



Picture 40 -View from underneath of motor (tag#7) – high soot deposition levels underneath the engine, showing convective heat damage (red circle); decreasing damage from there outwards (red arrow); protected area behind the motor (green ellipse).



Picture 41 -View of floor underneath motor (tag#7) – no visible signs of presence of ignitable liquids (orange ellipse).



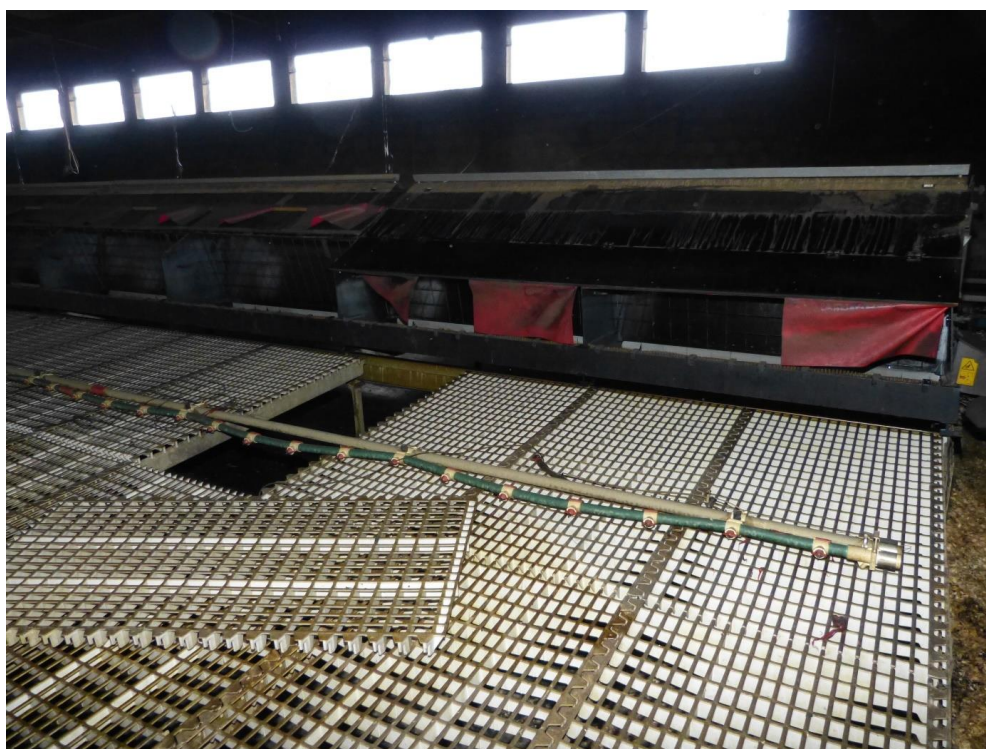
Picture 42 -Corner of west and north walls – alligator marks (orange ellipse), signs of dehydration after a long persistence of high temperatures and smoke; decreased damage from up to down and from right (east) to left (west).



Picture 43 - View of rear part of pavilion – damage on ceiling (red circle) coincides with a direct flame contact for a longer period of time, which is due to the presence of curtains in those points (orange lines), which worked as a barrier for the fire, until the curtain was melted and the fire could 'carry on'.



Picture 44 - Ceiling in rear part of the pavilion, view from east to west – close up view of Picture 49.



Picture 45 - Chicken houses without damage – open (left) and closed (right) positions of 'doors', PVC grids, pump with water supply (green).



Picture 46 - Electrical box – red rectangles mark the areas repaired by the electrician.



Picture 47 - Electrical box 2 – timer.



Picture 48 - Residues of fumigation plaque.

Technical expertise report – Fire scene 2 – Central-East

Technical report

At the beginning of the investigation, the morphology and reconstitution of the damaged area were determined, using an approach from the least to the most damaged area, from a more general to a more detailed perspective, in order to identify the zone where the combustion had its origin.

During the protocol procedures, first the outside of the property was observed. Thus, it was found that the combustion was in the defined area on the right side of the upper floor corresponding to the bedroom area (Picture 01).

The remaining facades did not exhibit any damage due to its remoteness from the starting point of the fire (Picture 02).

During the analysis in the delimiting facades of the area of the rooms, including the insured's son's bedroom, it was found that the fire acted on the window structures as a result of the heat transferred by hot air currents downwards (Picture 03).

On the right side, where the rooms of the child and the couple's main bedroom were located, a total destruction of the coverage was observed, however two types of damages along the façade were noticed.

In the window of the first room and the access door to the hallway, a destruction of high amplitude and intensity is visible, corresponding to a smoke-control zone, indicating the action of heat in an already advanced stage of the fire.

However, the opposite side – couple's bedroom- showed a carbonization circumscribed with low intensity but persistence in time. The observed low exit of the smoke from the room is consistent with the breaking of glass in a late stage of the fire, since the heat received gradually over an extended period of time prevented the establishment of an early phenomenon of thermal shock, characteristics that occur close to the point of origin (Pictures 04 and 05).

The observation of the damage on this window allowed us to conclude that the right side of the aluminum frame – observed from the front of the window- showed a destruction level confined to a small section, which coincides with the reception of heat slowly from a heat source located on that side of the room and at a lower level (Pictures 06 and 07).

Inspection of the other facilities of the house showed that there was a low level of general damage, confirming that the soot deposition downwards resulted solely from the heat transmission effect by hot air flows (Picture 39).

The effect of smoke-exit was particularly evident in the dining room because of its contiguity to the hallway that leads to the bedrooms (Picture 08).

In the frame of the access door to that hallway, effects of heat accumulation in a downward direction were found. Similarly, the observation of ceiling of the room above this zone resulted from the effect of hot air flow that persisted for a longer time-period, resulting in the complete breakdown of the original paint (Picture 09).

The hallway showed damage in a downward manner due to the effects of the convection currents in the smoke extraction process. A higher concentration of damage was observed through those convection currents rather than through the direct action of the flame resulting from the spread, which is because there are no furniture and objects that would allow a continuous combustion at lower levels in space.

Concomitantly, the storage area, the son's childhood bedroom and the bedroom currently used by the son showed damage resulting from the heat released by the fire that already broke out, which lit up and ignited the various combustible materials that made up all the room (Picture 10).

Through the analysis of the access door to the master bedroom, it was possible to identify deeper charring marks on the left (side of the door hinges) –frontal observation from the corridor towards the room-, rather than on the other side.

This damage is due to a greater exposure in time of the material of that side, to the action of heat downwardly along the corner as a result of the position of the door in that moment (open) (Picture 11).

The identification and evaluation of morphological damage at the level of the mentioned room showed that there was a total destruction of the false ceiling -PVC- and the roof structure.

The walls exhibited a similarity, in what the degree of damage is concerned, due to the combination of the generated calorific power and, after the bulging of the upper structures, which occurred due to oxygenation of the space which promoted the destruction of the outer wall layer, which is in greater depth in the section at the head of the bed due to the closeness to the initial heat source (Picture 12).

Further in the investigation, it was found that the wardrobe was in damaged atypically and with a "V"-shape pattern, with the greatest concentration of damage on the right side of it and from a lower level next to the corner, in line with the transmission of heat by radiation (Picture 13).

However, by observing this area, traces on the table supporting the TV -type LCD- and DVD-player, were observed, which exhibited charring in a downward pathway (Picture 14).

After removal of combustion residues was possible to recover the DVD player (which was not connected) and the TV, which also evidenced a homogeneous destruction due to the hot air from an external heat source (Pictures 15, 16 and 17).

By observing the area in front of the bed, it was found that the faces of the feet exposed to this area showed a low degree of damage, indicating protection against the development of heat (Picture 19).

In contrast, the plug and the electrical extension cable with four inputs - which were attached the TV power chips and a mobile phone charger - showed greater oxidation of its upper section.

After reconstitution of that area and the conditions present before the fire occurred, it was determined that the structures and electrical and electronic components described above were damaged following the spread of the fire, creating a secondary fire.

In addition to identifying the location of this secondary focus, it was also confirmed that no ignitable liquid was spill on the pavement, due to the evidence and analyzed patterns after removal of the debris around that area. It can be seen that the parquet floor was protected, which would not occur if ignitable liquid was poured on it (Picture 18).

Through the examination of the window and in accordance with data from the external facade, according to the degree of damage and carbonization marks in its structure, it was possible to determine the direction of propagation of the fire from one area close to the wall next to the headboard of the bed (Pictures 20 and 21).

After removal of fire debris and the reconstruction of the area of higher degree of damage, the interpretation of the traces indicated a convergence of the effects of heat coming from the area corresponding to the left side of the headboard.

Focusing on the inspection of the table next to the bed and the structures around it, it was found that the interior of the table exhibited areas of low degree of damage compared to the right side, where the degree of carbonization observed was maximum, coinciding with the

transmission of heat slowly and downwards from the top. Similarly, the bed frame and spring mattress exhibited a high degree of punctual discoloration and in depth in the section exposed to the side (Photo 22) for having received heat slowly, coinciding with what observed in the initial area of propagation.

On the floor between the bed and the bedside table traces of an alarm clock that was usually on the right side on the top of that table were recovered, which coincided with the starting point of the fire (Picture 23).

The alarm clock was connected to the triple extension cable, which was plugged into the wall plug behind the headboard of the bed where also the lamp was plugged in.

The remaining residues of the clock with its electronic circuit board and circuit board of the display, were impossible to reconstruct, since they were made of plastic and were found as one melted item.

From the analysis of these components, it was determined that the sign of electronic components had received heat from the outside, with a homogeneous, contrary to the printed circuit board of the display, which exhibited damage coinciding with localized heat, resulting in failure of one of the elements. This caused an unusual overheating over a large period of time, giving rise to a combustion that sequentially lead to the spread to other structures and materials in the house (Pictures 24-28).

Finally, for validation purposes, we proceeded to the analysis of electrical board, which was located in the dining room, that showed damage only as a result of the hot air effects in a downward path due to being located far from the area of the fire.

Thus, through the systematic application of the general behavior of the fire, it was determined that the fire originated in an electronic component – the alarm clock – which due to the failure of one of its components went into overheating, reaching the auto-ignition temperature and then bursting into flames. The flames, which were generated slowly and were of low intensity, propagated in a systematic way to the top of the bedside table and subsequently to other surrounding materials and thereby started the fire that caused this case.

Laboratory Analysis

The analysis of the samples collected at the scene, which were analysed via HS-SPME-GC-MS, did not reveal the presence of any ILRs but merely combustion, pyrolysis and background products.

Conclusions

This fire was due to an accidental cause for malfunctioning of an electronic component of a clock / alarm in the master bedroom, without any outer human responsibility.

This conclusion is obtained from the technical inspection carried out at the site, specifically, the identification of the different degrees of damage and the sense of direction and spread of the fire that allowed us to determine their starting point, which is at the level of the top of the bedside table on the left side of bed, where the alarm clock was originally placed and was powered by electrical current from the power strip attached to the socket located behind the headboard of the bed. The laboratory analysis additionally confirmed that the corner next to the wardrobe, which was a possible candidate as a point of origin due to the fire patterns observed on the wardrobe, was not a starting point of the fire due to the absence of ILRs.

In this scenario, in which combustion is found confined to a point, it was concluded that the fire began in the printed circuit board of the display for a potential failure in one of its electronic components, which would result in overheating over a range of time, generating combustion, albeit slow in the initial phase, in line with a low intensity heat point.

This fire then will gain amplitude with sequential ignition of other materials, such as the cotton tablecloth and other synthetic materials, propagating towards the other areas in proximity and igniting them.

As outlined above, we are facing a case in which the ignition resulted from an accidental situation, without human intervention in any way, produced by a fault in an electrical component.

Pictures



Picture 01 – Outer view of the house where the fire occurred: damages were only recorded in the area where the bedrooms were located.



Picture 02 – No damages were observed in the other parts of the house.



Picture 03 – View from outside of the window to the son’s childhood bedroom – damage with a propagation direction downwards (red arrow).



Picture 04 – On the side with access to rooms, two different types of damage are identifiable. In the window of the son's room, as well as the coverage area above a resultant destruction due to a sequential propagation in great amplitude of the available materials –wood and synthetics – is observed, consistent with the distance to the starting point, due to the increased the temperature generated by hot air flows –yellow arrows.

Comparatively, on the opposite side – master bedroom - , the similar structures show a more limited degree of damage, particularly to the window level, where a lower rate of smoke exit is observed. This comes from the action of heat from a slow combustion, which affected the molecular structure of glass progressively, avoiding its abrupt breaking, as opposed to what happened in the son bedroom window – red arrows.

The destruction of the cover above this division was another factor that prevented a high damage the facade, allowing the smoke extraction to occur directly in a vertical way.



Picture 05 – In detail the contrast between the destruction observed along the front window of the son's (-II-) and couple's (-III-) bedroom, identifying a sense of clear spread in the latter resulting from a combustion point located at a lower level on the right side –red arrow. On the contrary, in the corridor area and the son's bedroom window, the marks are the result of a heat accumulation in downward direction and in greater range, consistent with a fire already spreading.

After breaking the window glass, as the roof had not collapsed here, smoke extraction of hot air changed direction to being vertical –yellow arrows (Picture II).





Picture 06 – The master bedroom window shows, albeit to a lesser extent, a higher concentration of the damage on the right side of the aluminum frames –yellow frame-, in line with the incidence of a low heat source with intensity but slowly – red arrows - from a point below and located on that side.



Picture 07 – Lower part of the window, confirming the direction of propagation.



Picture 08 – General view of the dining room and access to the corridor leading to the bedroom area – damage observed on the ceiling – red arrow and in a downward direction - yellow arrow.



Picture 09 – In detail the damage to the ceiling –red circle - and the door frame of the access door to the corridor to the rooms -which was closed- showing the carbonization of the material downwards in the course of propagation of combustion –red arrows - in consequence of the convection currents.



Picture 10 – In the corridor uniformity in the degree of damage is observable, confirming that the heat transfer occurs mainly by the upper area - full destruction of the false ceiling and cover- it is possible to see greater protection areas at a low level with the presence of the original paint on the walls and the preservation of the central heating.



Picture 11 – Access door to the master bedroom. Major destruction of the doorjamb on the wall opposite to the window is observable.

This derives from a higher accumulation of hot air downwardly and over a longer time period, due to the door being open at the time of the start and spread of the fire-red arrows. The same type of damage is observable on the radiator, which is located behind the bedroom door.

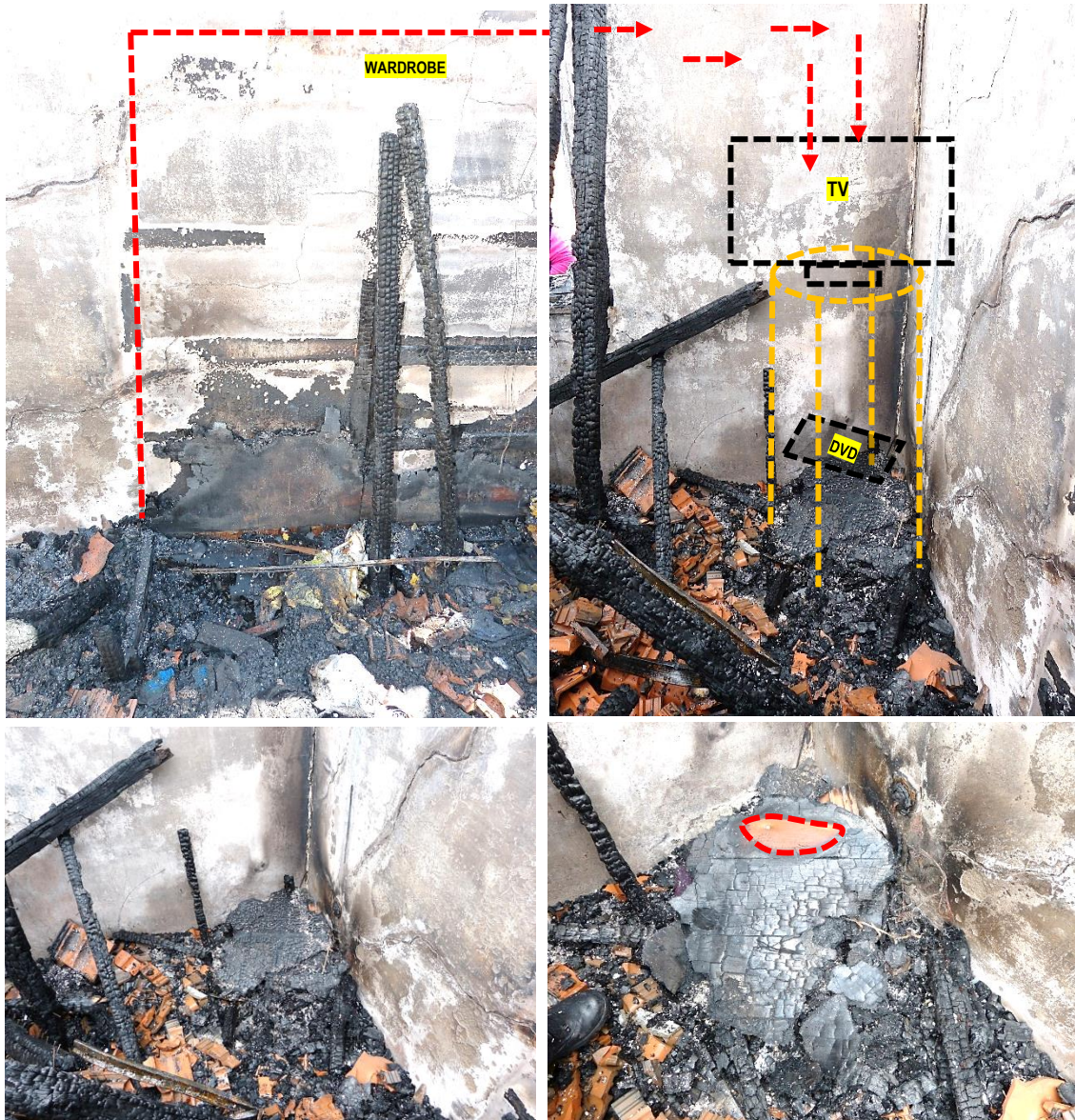
It's confirmed that this is the room where the fire had its origin.



Picture 12 – Overview of the room where the fire started. To be noticed, a greater depth in the degree of damage can be observed, particularly on the wall at the bedside, consistent with proximity to the initial heat source. In the wardrobe leaning against the opposite wall, the damage occurred in the downward direction by the effect of convection currents – red line.



Picture 13 – Observing the heat transfer along the wall where the closet is located, a degree of atypical damage is seen, with a higher degree of carbonization on the left side and starting from a low level, as well as a damage in "V"-shape, resulting from heat received by radiation from the combustion of table, which was covered with a cloth, that supported the TV and DVD –secondary fire-.



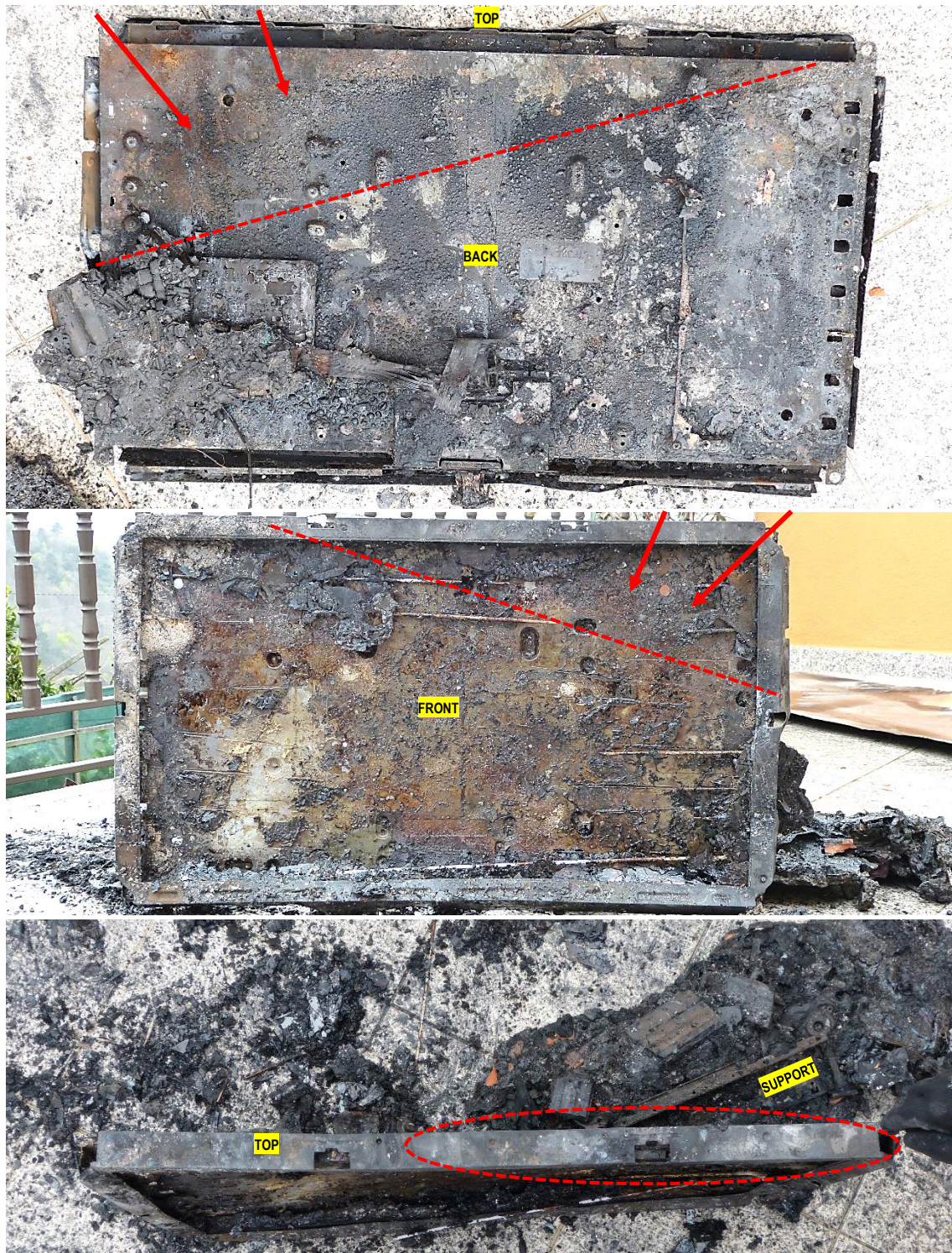
Picture 14 – Corner of the area, where remains of the table are found (orange lines to simulate the location), that show on the top a protected zone, coinciding with the position of the "foot" of the TV –red circle- which indicates a consumption of the structures in a downward direction red arrows.



Picture 15 – In the same area the DVD player was recovered, which was disconnected and located on a shelf below the top of the table and showed a similar damage concerning the degree and direction –red arrow.



Picture 16 – TV recovered in the debris, which had fallen in front of the table. Underneath the device -due to melting- a section of the false ceiling was identified, which fell on the floor due to the heat received by the spread of the fire before the fall of the TV.



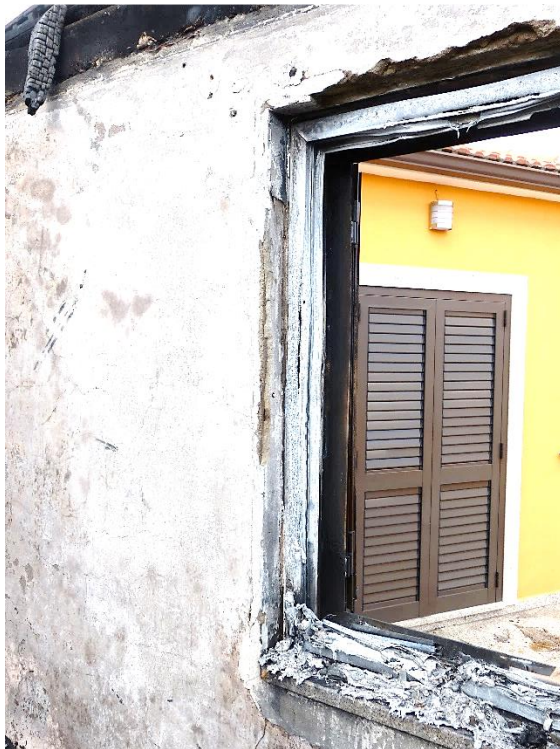
Picture 17 – View of the TV, with observation of the direction of propagation being from outside to inside and from the right side (direction of observation) upwards, which has a high level of oxidation due to the exposure to convection currents. This indicates that the heat source was located on the opposite side.



Picture 18 – Detailed view of the floor where the table was located (see previous photos). After removing the debris, there was the absence of any damage to the floor level, which allows us to exclude that a fire started at that point, especially with the use of an ignitable liquid as a fire accelerant.



Picture 19 – Perspective of the couple's bed, metal frame, identifying different degrees of damage. In the horizontal bar and the support feet a low degree of oxidation on the face exposed to the wardrobe and the table is observable, confirming their remoteness from the initial point of combustion on the head, where a higher degree of damage is visible.



Picture 20 – Concomitantly with the observed on the outer face, the inner window had a greater concentration of damage on the left side –red arrows, consistent with exposure to heat for a longer time interval.

The wall around the window reflects a high degree of destruction, with the total consumption of their outer layer present there as a result of fuel load, consisting of synthetic material – curtains.



Picture 21 – Headboard. High degree of damage along the whole length of the wall above the bed, particularly on the left side, where the destruction of the plaster denotes an area of greatest and heterogeneous damage, consistent with the position of the bedside table in line with the incidence of a direct source of heat for a longer time period.



Picture 22 – Overview of the area with higher degree of damage - the high damage to the chair results from the heat received directly by the emissions of the starting point of the fire, which led to the subsequent light-up of the chair .On the side of the table exposed to the chair and in its interior some areas of protection are observed, determining the development of combustion from an higher area, at a level around the top of the table.



Picture 23 – On the floor between the bed and the bedside table debris of the alarm clock that was originally located on the right side of the table top, coincident with the area of start of fire were recovered.

The clock was connected to the power strip plugged into the wall socket, along the headboard, along with the lamp power plug.

The total destruction of case of the alarm clock and some of the components did not allow the reconstitution of it.

However, due to the observed marks and indicators, it can be concluded that the combustion is developed from a source of low intensity and punctual heat over a large period of time.

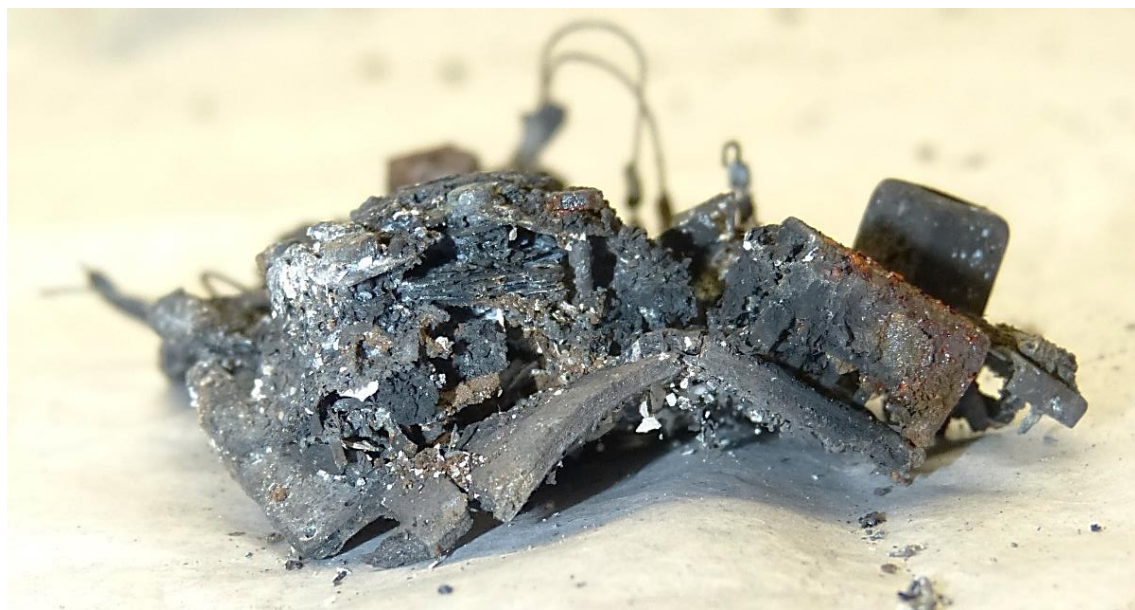




Picture 24 – Detailed view of the remains of the electrical components belonging to the alarm clock after cleaning of the fire debris. Homogeneous damages can be observed, which result from the reception of an external heat source.



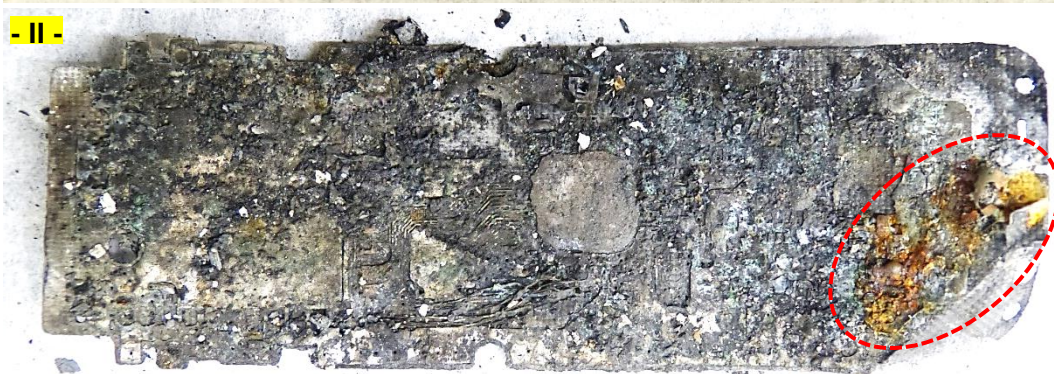
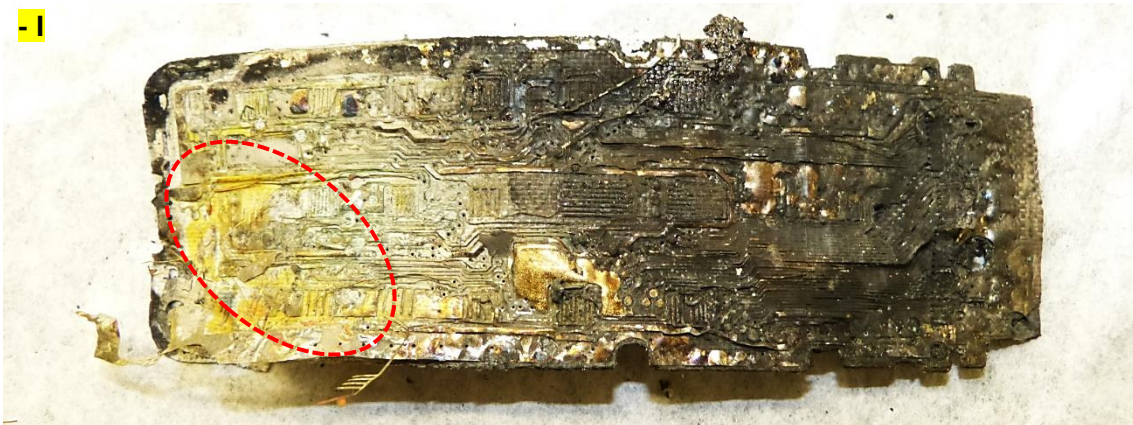
Picture 25 – Same, from other angle.



Picture 26 – Same again, from other angle.



Picture 27 – Detailed view of the back part of the internal electrical components.



Picture 28 – Circuit board, view from the front (I) and back (II). Due to the higher degree of damage observable – higher oxidation and discoloration of the material due to reception of heat during a longer period of time – it is possible to determine the ignition point – red circle – resulting from an overheating of a faulty electrical component.

Technical expertise report – Fire scene 3 – Central-West

Technical report

This investigation work was greatly hampered by the inaccessibility to areas that would prove to be of great importance, in particular in the areas of the upper floor -attic- which would later be determined as being where the fire started.

These areas showed a clear instability resulting from the complete combustion of the wood material and contractions of the materials after exposure to the elevated temperatures of the fire.

However, we were able to collect information about the composition and materials located in the zone with the help of the owner of the building, which we ratified with the remains of the materials still available.

In the development of the technical inspection, we determined the morphology of and reconstituted the damaged area, using an approach from the least to the most damaged area, from a more general to a more detailed perspective, in order to identify the zone where the combustion had its origin.

According to this methodology, absence of damage - internally and externally – was observed on the entire length of the facades. This indicates that the origin of the fire is at the upper floor of the building, the smoke and heat movement developed vertically after the collapse of the ceiling (Pictures 01).

The access door to the apartment –fourth floor, left side- was analysed based on the locking points - bolts, locks and security chain. No signs or traces of forced entry were observed (Pictures 02 and 03).

Concerning the damages, on the inside of the fourth floor apartment there was only one area that was identified as having been affected by the fire, namely the ceiling of the dining room, which was located along the left side, just below what was later identified as the starting point No. 3 (Picture 04) in the attic.

In this area, a limited degree of damage was seen, particularly to the ceiling level, where the consumption of the main structure holding the ceiling was observed. In contrast, the support beams (slab) of the flooring and the ceiling attachments showed a protected area on a low level, which indicates that the heat propagated downwards from the upper floor.

Further on during the investigation of this area, the extent of the damage observed evidenced a circumscribed and heterogeneous section where the degree of carbonization was high, consistent with the proximity to a source of heat resulting from a point of origin (Pictures 05 and 06). A sample was collected in this area – tag #3 – for laboratory examination.

Moving on to the inspection of the upper floor (attic), it was observed that the division of ladder that gave access to the upper floor generally had a high degree of damage in amplitude and homogeneous in terms of wall and roof structures, coinciding with the reception of heat at an advanced stage of the fire, where the speed and the intensity were higher.

The examination of the wood coating on top of the handrail of the staircase showed that the horizontal section has received heat from the front. In contrast, the adjacent vertical section, showed a higher carbonization side opposed to its counterpart, which were clearly produced by the hot air flow coming from two different directions of two, indicating that they originated from two separate points (Pictures 07 and 08).

Observing the degree of damage to the top of the staircase, made of wood, where the skylight was located, specifically on the side exposed to this part, a high degree of damage was identified on the main facade exposed to the right side of the building. Additionally, the morphology of the damage was in "V"-shape, indicating that heat reception was through radiation and direct action of the flames (Picture 09).

Similarly, the door that gave access to the main part of the attic had a similarity in the degree of damages, showing a homogenous carbonization on both sides of the frame, again supporting the theory of two distinct directions of propagation of the heat (Picture 10).

On the wall exposed to the main area of the attic, where this door is located, the destruction of the outer layer due to heat reception in high amplitude was observed.

In contrast, in the corner on the opposite side of the door destruction marks of the plaster located upwardly were observed, which resulted from the spread of fire by radiation and by direct action of the flames over a longer period of time.

The wall had signs of a similar spread of the fire, coinciding with the transmission of heat by the downward movement of the convective air flows (Picture 11).

On the right wall, different destruction marks were identified. Half of the masonry shows a breakdown of the material in a downward direction, as a result of receiving heat from the fire that was already spreading. On the other part of the wall, well-distributed and fragmented

plaster layers located above the false ceiling, were found, indicative of the incidence of a heat source during an extended period, coming from the main facade (Picture 12).

Simultaneously, by observing the "slope" of the cover in that area, a greater destruction of the beams ("studs") exposed to the sidewall was observed, as a result of heat accumulation resulting from an upward movement of the hot air coming from the side adjacent to the corner (Pictures 13 and 14).

On the floor, a destroyed area with a circular morphology was identified –marked with the tag #1 - as a result of combustion in depth. The cover in that area, located on the extremity close to the main façade, mainly had a damage resulting from the annealing of the material due to combustion in its initial phase, consistent with an abnormally high volatilization rate compared to the expected volatilization of wood, which indicates the application of an ignitable liquid used as a fire accelerant. A sample from this area – tag #1 – was taken for laboratory examination.

Note that, with the structure of the floor and the ceiling being homogeneous relative to the material that constitute it - wood – one would expect charring with similar characteristics as to the degree of damage observed, due to the heat transfer capacity and the propagation being more intense in an upward direction.

Thus, marks of complete carbonization were identified on the pavement of the floor with a circular morphology and a sense of downward propagation, in both the wooden beams of the slab as well as in the non-combustible materials from the wall of the main facade. Therefore, two opposite directions of propagation were found in this point, one ascending from the floor and another one of high intensity but in a descending direction, consistent with the use of an ignitable liquid, which will have been absorbed into the wood and, simultaneously, infiltrated the spaces between the boards to a lower level.

* * *

Continuing the examination of the area, a geometry and morphology of destruction in a "V"-pattern was found in the structure of the wooden box below the skylight, consistent with the action of heat received at upwardly from a point in close proximity but at a low level (Picture 15).

Following the same methodology, a similar damage to the wood structure delimitating the storage area (Picture 16) was found (tag #2), showing a heat-convergence area on the left

side, determining the existence of a second outbreak of fire in the attic, specifically from a section of the floor adjacent to what was identified as the first point of origin (Picture 17).

The type of damage observed is consistent with the pouring onto the floor of a liquid product with great capacity for volatilization and combustion, which had the function of enhancing the combustion in its early stages (Photo 25). A sample was taken for laboratory examination.

* * *

On detailed examination of the electrical switchboard, which was disabled, no trace of an ignition point was found, but it showed a degree and sense of carbonization consistent with sources of heat from the area in front (Picture 18).

The interpretation of the marks indicated a third point of origin in storage area (tag # 3), more specifically, on the floor near the corner formed by the walls of the left side and the masonry. In this place there was no suitable combustible material nor any means capable of generating heat that somehow could function as activation energy to the system and cause combustion, so we can infer that energy had to be transported to the site (Picture 19).

Thus, it is concluded that in this area a combustion must have started with the pouring and ignition of a liquid product with high calorific value and easy volatilization used as a fire accelerant (Picture 20).

Considering the lack of combustible material in the whole attic area, it would not be possible with a common source of heat to cause combustion in three different points without the use of an accelerant.

Supporting this *modus operandi* are the traces of carbonization in depth on the sides of the beams that constituted the "slab", which result from the infiltration of a liquid fuel that would also deposit on the structure of the partition underneath it.

That the ignition occurred on the floor of the attic and not inside the lower floor of the dining room is confirmed by the missing soot deposition on the ceiling and the walls of the rooms, indicating that smoke infiltrations on the roof of the lower floor (fourth) already existed before the second fire started.

Another common indicator found in the three ignition points, was the absence of any source of heat or energy that could somehow trigger the pyrolysis process of the combustible material and the consequent inflammation and subsequent combustion.

Regarding the type of combustible material available, it was the wood that made up most of the structure of the building, which was probably around 80 years old and therefore had a very low level of humidity, which is a contributing factor to the increased speed of propagation.

Laboratory Analysis

The analysis of the collected samples, which was performed via HS-SPME-GC-MS, confirmed the presence in all three suspected points of origin of a Heavy Petroleum Distillate (HPD), specifically kerosene used as a jet fuel.

Conclusions

This fire was due to the pouring of a liquid product with the ability to enhance and accelerate combustion in its early stages in three different locations on the attic, which was confirmed and identified by the laboratory analysis as kerosene used as jet fuel.

After application of the accelerant, this would seep down into the space between the floor of the attic and the ceiling of the lower floor, which then would ignite these parts and allows a widespread combustion at various levels throughout the wood structure.

Any electrical cause was excluded, due to the existing installation and the location of the light bulbs. Thus, no other type of anomaly can be seen as the cause of the fire, also because the nature of that type of anomaly does not coincide with the observed traces.

It also needs to be pointed out that the points of origin are located in opposite corners of the attic area, two next to right side of the main facade and another one on the left side of the facade, which creates a convergence of convection currents from the different point of origin and the accumulation of greater heat concentration along the ridge in the stairwell of the area, with a consequent increase in the speed of propagation.

There were no signs of forced entry on the doors and windows of the room, a situation confirmed by the owner, which confirms that no one besides the owner and related people had access to the area. As outlined above, we are facing a fire where the ignition resulted from an intentional situation by those who had access to the area and who transported an ignitable liquid to the site and applied an external heat source at three different points.

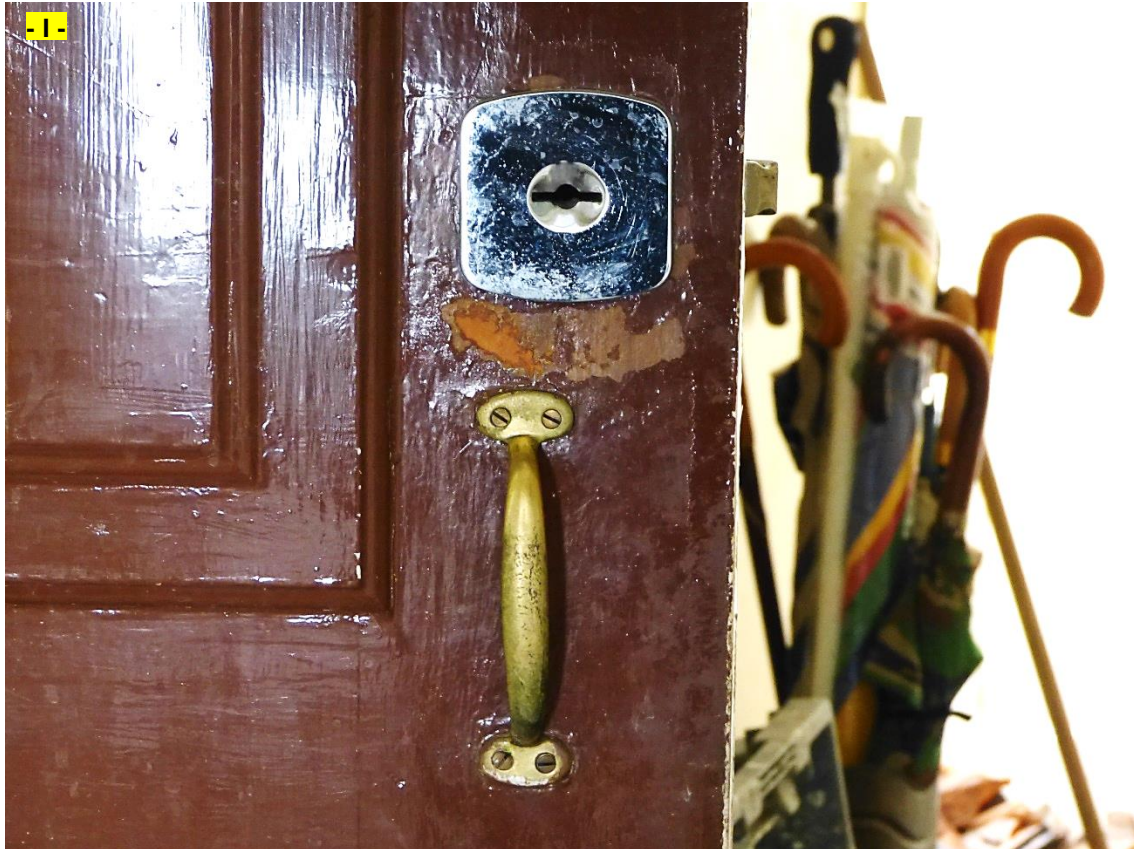
Pictures



Picture 01 – View of the damaged building from the outside; to note that all the facades of the apartment in question – delimited by the red line – do not show any signs of damage.



Picture 02 – Main door of the damaged apartment – outside view.



Picture 03 – Detailed view of the lock from the outside (I), the main frame (II) and the connecting part on the other side of the door (III) – no signs of forced entry.



Picture 04 – View of the apartment’s entrance hall, where it is observed that there is no damage from the spread of fire, except at the level of the area in the living room corresponding to the damaged area in the attic, which resulted from collapse of the false ceiling, indicating the development of the fire from the top floor -attic-.



Picture 05 – Inside of the dining room, observing a degree of complete destruction of the ceiling and the main wooden structure between the floors. Accordingly, it appears that the lower face is protected, consistent with heat acting downwards from an upper level, the attic. This damage is particularly visible at the corner, where it is limited and the degree of carbonization of the structures is higher, resulting from its proximity to a circular point of origin – red circle. Yellow circle indicates tag#3, where a sample was collected for laboratory analysis.



Picture 06 – In the roof area it is possible to observe a converging carbonization area along the support beams near the corner -red circle-, which results from the proximity to a point of origin. The absence of a greater extent of damage throughout the room, in particular by soot-fixation, arises from the rupture of the ceiling, which allowed the smoke of a small secondary fire outbreak to exit upwards.



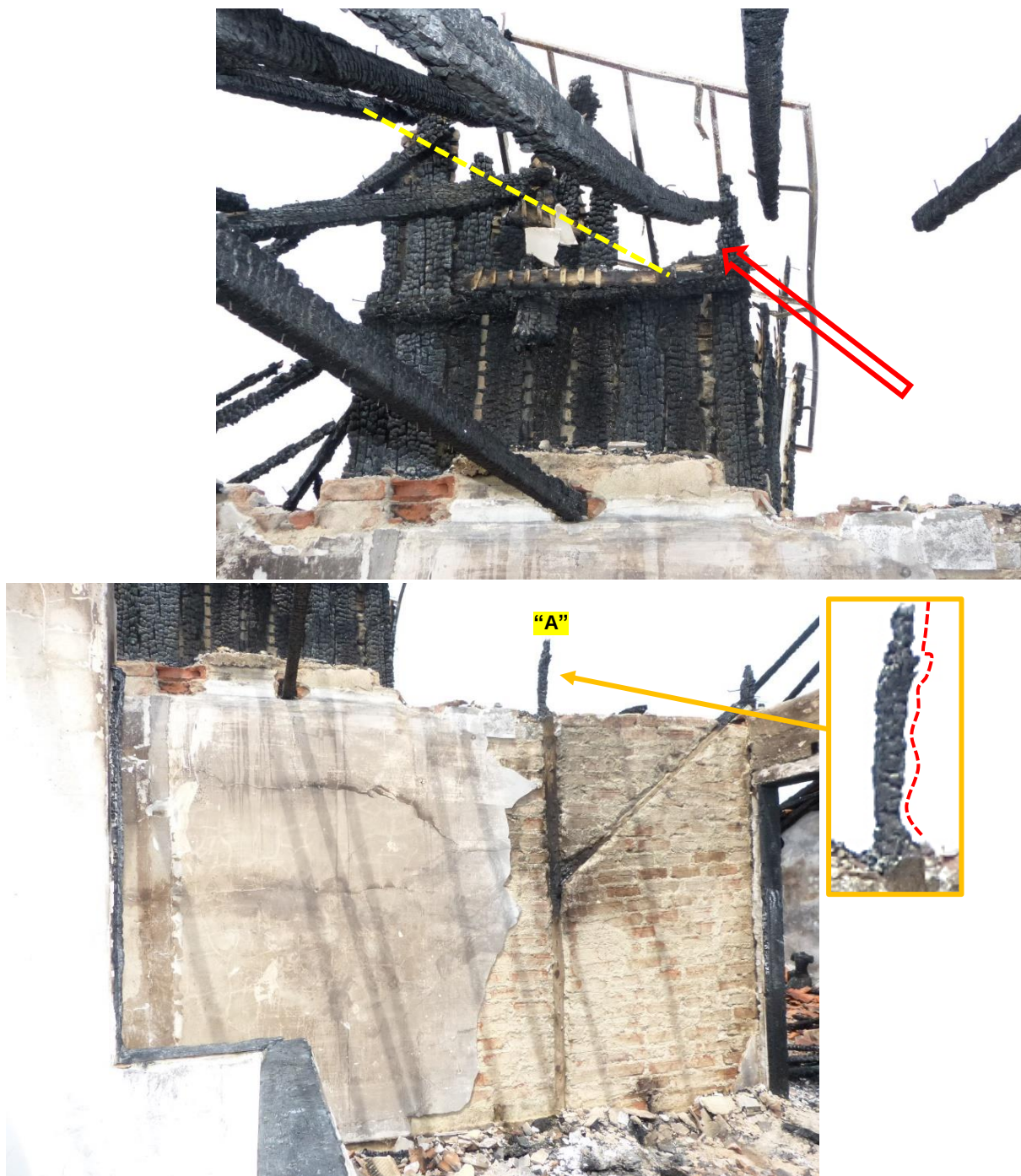
Picture 07 – Area of the attic with access to the stairs to the apartment. Especially on the balcony damage indicators of both directions of propagation are visible, meaning they originate from opposite points.

This phenomenon is particularly evident in the balcony, where you can see the profile of trim wood displays different carbonization levels. In the horizontal part, coming from a point located on the front side –red arrows- and vertically, resulting from the heat transmitted by convection from the side –blue arrows-. Consequently, damage from heat sources located on opposite sides are observed.

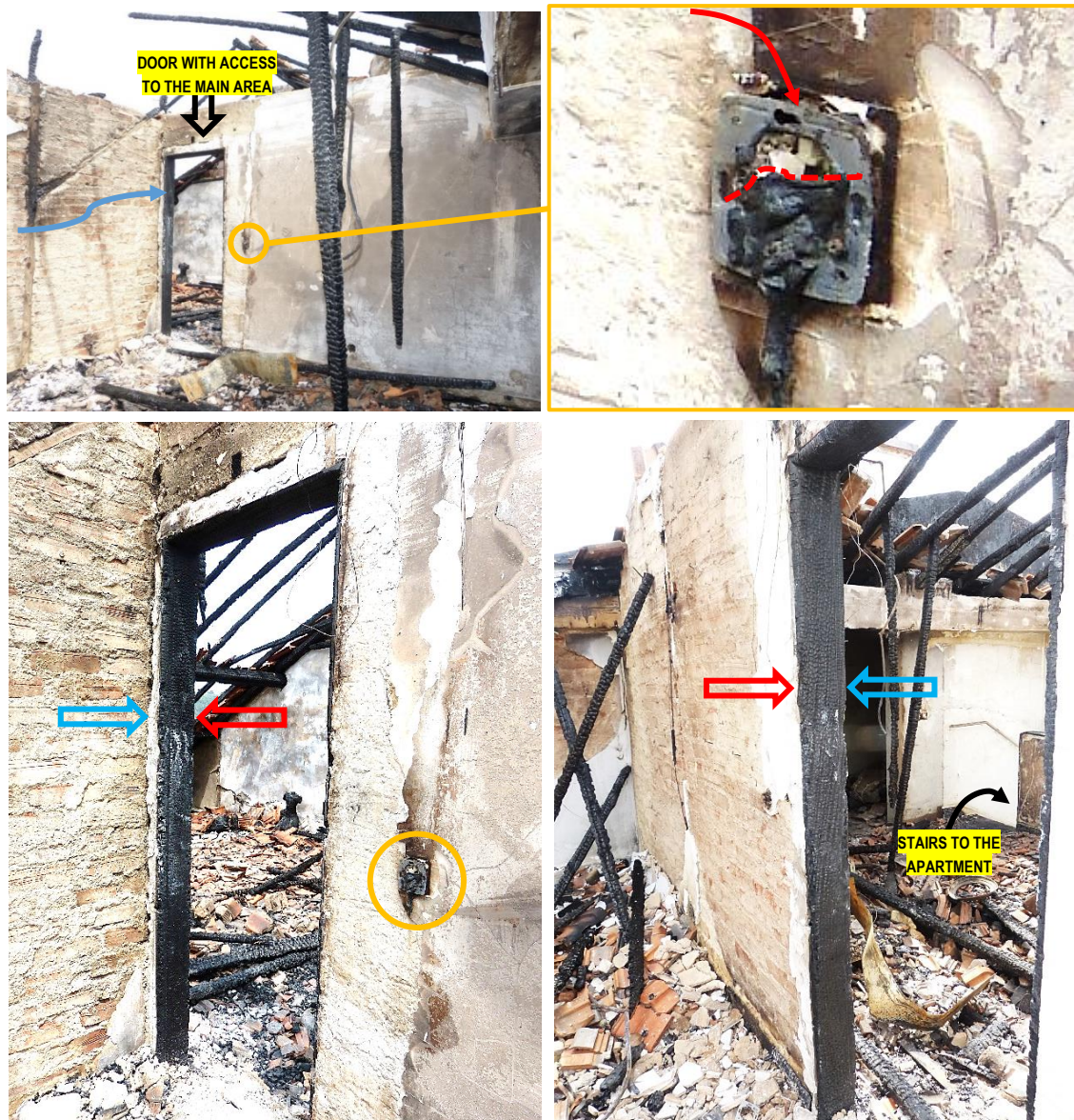


Picture 08 – Detailed view confirming the divergence of the damage present on the wooden balcony, identifying both directions of propagation of the fire in the sections of the horizontal and vertical profiles –red and blue arrows..

These indicators allow us to conclude the existence of spreads from two fires located on opposite sides of the attic.



Picture 09 – Appearance of the level of carbonization on the structure of the ladder-box supporting the skylight, which identifies a higher consumption of the right side (side facing the front right side) - relative to the left sense of observation- with a damage in "V"-pattern , due to transmission of heat by radiation and by direct action of the flames upwards, with the direction of propagation being shown by the red arrow, from the front side of the right side. Concomitantly the "A" pillar presents a similarity in the degree of damage reported –red line-, due to the same direction of propagation.



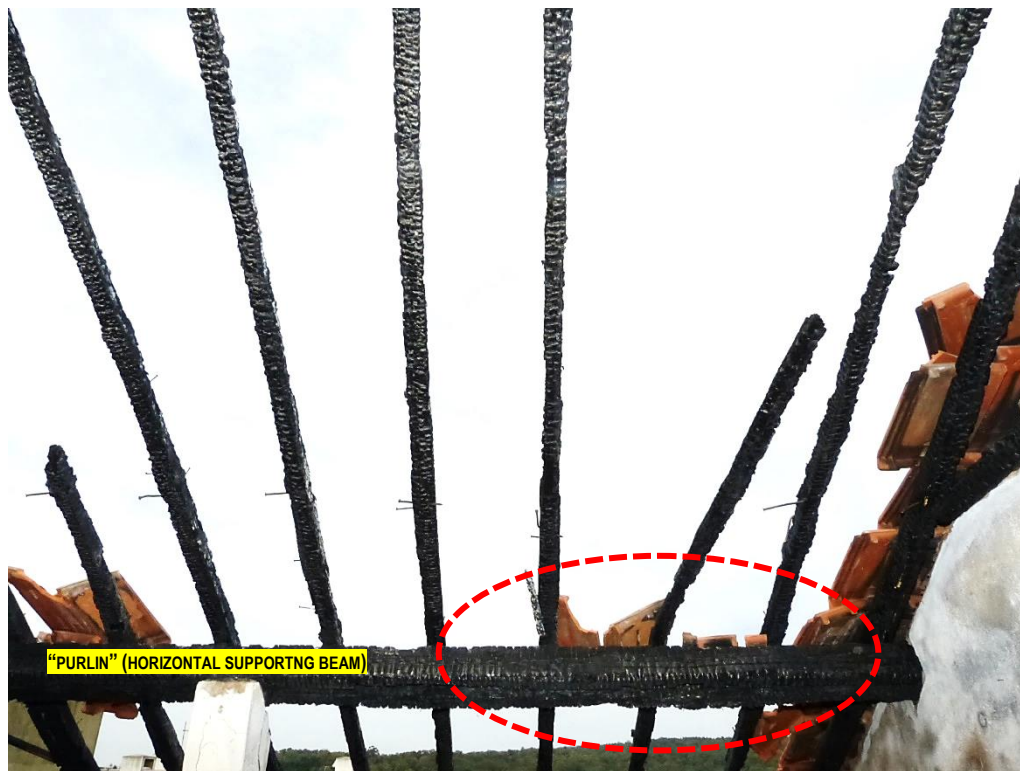
Picture 10 – Door delimiting the hall at the top of the stairs to the lower floor and the large attic area. On both sides of the door-jamb a homogeneous morphology of the damages is observed, identifying a symmetrical carbonization level on the trim structure, indicative of two directions of propagation of fire from two separate sides -red and blue vectors. On the switch next to the face of the exposed door to the room / hall with access to the stairs a higher consumption of its components is visible downwards, consistent with the transmission of heat by convection, showing their distance from one of the points of origin –red line-.



Picture 11 – View of the back wall showing damages in amplitude starting from a higher level, consistent with the reception of heat during an advanced stage of the combustion, in which the fire was already in propagation – red arrows – resulting from the development of a fire originating on the opposite side – main facade.



Picture 12 – In the upper area of the room there has been a complete consumption of the false ceiling and an intensive destruction of the coverage (the "Rafters"). This damage is particularly visible in the "Rafters" and "slats" of the structure that exhibit a greater concentration of damage on the front right section of the building –red circle. Also observable are damages resulting from convection currents –in the orientation from the main façade to the back wall, red arrows-, consistent with the direction of propagation from a separate point of origin.



Picture 13 – In detail, seeing that the structures of the "rafters" exhibit charring marks in greater depth close to the "purlin" horizontal support beams- red circle- resulting from longer exposure to the action of heat –red arrows- from a point of origin at a lower level.



Picture 14 – By observation of the tiles, protected areas at the top can be observed –yellow arrows, compared to the side (surface) facing the floor, which has soot depositions from direct contact with the flames, confirming the upward direction of propagation of the fire as well as the development of combustion, with an increasing amplitude of the damage directly proportional to a point of origin on the bottom of the beam located on the main facade of the building – tag #1.



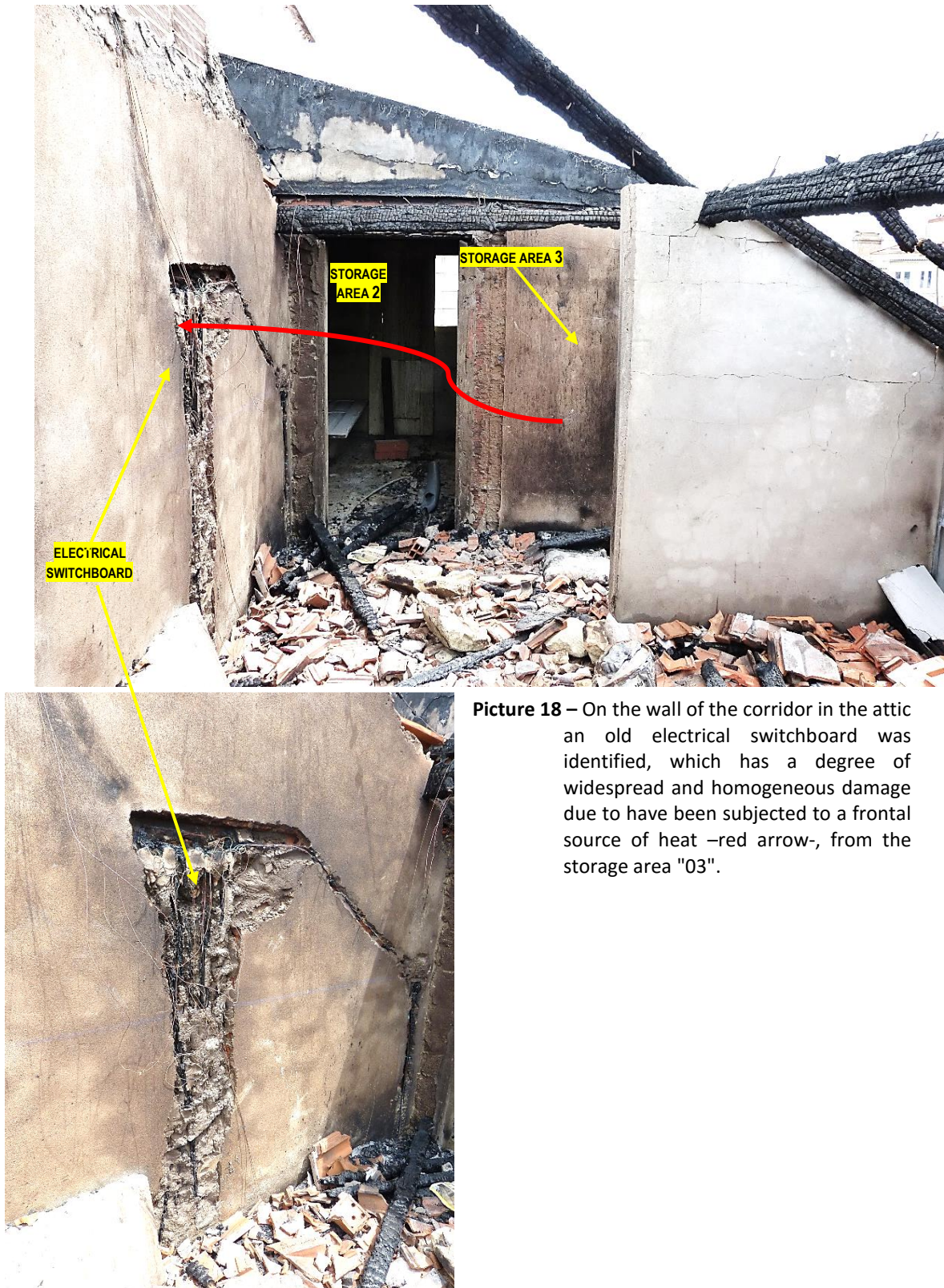
Picture 15 – Perspective of the remaining area. In the structure of the stairwell-box "A" and the masonry pillar damage in a "V"-pattern can be observed, which results from the exposure to direct action of heat transmitted by radiation for an extended period of time from a second point of origin –tag #2 - present on the right side –red arrow-, on the main facade and one level below the window - B -.



Picture 16 – In the adjacent space (towards facade on the left side) charring of the structure of the delimiting area was observed in an upward direction –red arrow- consistent with the incidence of a heat source- tag #2, which was close but at a lower level on the right side –red circle-.



Picture 17 – Na estrutura da caixa de escada onde assentava a clarabóia, contrariamente ao verificado nas faces expostas ao primeiro e segundo pontos de início (vide Fotos 11 e 22) foi identificado numa das faces um dano pontual -círculo a tracejado vermelho- resultante da acção do calor de uma propagação proveniente de um terceiro foco de incêndio -vector a vermelho-, razão pela qual o movimento dos fluídos de ar quente protegeram a zona de canto da parede e da estrutura da caixa de escada. Esse localizava-se do lado oposto dos anteriores na zona entre as fachadas lateral esquerda e a de tardoz.



Picture 18 – On the wall of the corridor in the attic an old electrical switchboard was identified, which has a degree of widespread and homogeneous damage due to have been subjected to a frontal source of heat –red arrow-, from the storage area "03".



Picture 19 – Perspective of the area along the corner between the walls of the facades on the left side and the building's outer masonry.

The degree of damage to the structure of the wooden beams in the corner is higher than those observed in the remaining space of the room, in addition to showing a downward development, suggesting a third point of origin in that corner – red circle.





Picture 20 – Detailed view of the corner-area, where a heterogeneous damage in depth and downwards from the floor with a rounded shape is observed. This type of damage results from the combustion of fire accelerant in the initial phase, which was poured on the floor, allowing it to seep into the floor to develop a combustion at low level, in addition to allowing a spread in the initial phase of considerable intensity due to the evaporation capacity of the material used. It can also be observed that the combustion started in an area above the floor and below the roof structure, since a reduced damage of the sealing material of the curbs can be seen. The total combustion of the pavement in a circumscribed area downwards would lead to the partial destruction of the ceiling of the dining room in the lower floor, located right below the ignition point (see pictures 07 and 08).

Appendix D – Results: additional tables and figures

Case studies

a) Case study 1 – North

Sample 1

Table D1: List of all compounds detected from the analysis of sample 1 collected at Fire Scene 1, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS1 Sample 1			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,47	Carbon dioxide	44	-
14,3	Dodecene	55, 41, 69, 83, 111	<i>n</i> -Alkene
14,45	Dodecane	57, 43, 71, 85	<i>n</i> -Alkane
16	Tridecene	55, 41, 69, 83, 111	<i>n</i> -Alkene
16,2	Tridecane	57, 43, 71, 85	<i>n</i> -Alkane
17,75	Tetradecene	55, 83, 41, 69, 111	<i>n</i> -Alkene
17,9	Tetradecane	57, 71, 43, 85	<i>n</i> -Alkane
19,3	Pentadecene	55, 83, 41, 69, 111	<i>n</i> -Alkene
19,5	Pentadecane	57, 71, 43, 85	<i>n</i> -Alkane
20,58	Nonylbenzene	83, 41, 57, 204	Aromatic
20,83	Hexadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
20,95	Hexadecane	57, 43, 71, 85	<i>n</i> -Alkane
22,06	Decylbenzene	93, 41, 218, 67, 133	Aromatic
22,3	Heptadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
22,4	Heptadecane	57, 71, 43, 85	<i>n</i> -Alkane
23,48	Undecylbenzene	92, 41, 232, 69, 133	Aromatic
23,56	(1-methyldecyl)-benzene	105, 232, 55, 79	Aromatic
23,6	Octadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
23,8	Octadecane	57, 71, 43, 85	<i>n</i> -Alkane
24,7	Hexadecanoic acid	97, 43, 71, 149	Carboxylic acid
24,8	Dodecylbenzene	92, 56, 246, 133	Aromatic
24,9	Nonadecane	57, 43, 71, 85	<i>n</i> -Alkane
25	Heptadecanone	43, 57, 71, 97, 124	Aldehyde
25,3	Hexadecanoic acid methylester	74, 87, 43, 143, 97	FAME
27,8	Octadecanoic acid methylester	74, 87, 43, 143, 97	FAME

Sample 2

Table D2: List of all compounds detected from the analysis of sample 2 collected at Fire Scene 1, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS1 Sample 2			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,45	Carbon dioxide	44	-
14,28	Dodecene	55, 41, 69, 83, 111	<i>n</i> -Alkene
14,45	Dodecane	57, 43, 71, 85	<i>n</i> -Alkane
16,05	Tridecene	55, 41, 69, 83, 111	<i>n</i> -Alkene
16,2	Tridecane	57, 43, 71, 85	<i>n</i> -Alkane
16,6	Decanoic acid methylester	74, 43, 87, 105, 143	FAME
17,35	Heptylbenzene	92, 176, 43, 67	Aromatic
17,75	Tetradecene	55, 83, 41, 69, 111	<i>n</i> -Alkene
17,9	Tetradecane	57, 71, 43, 85	<i>n</i> -Alkane
19	Octylbenzene	92, 190, 57	Aromatic
19,38	Pentadecene	55, 83, 41, 69, 111	<i>n</i> -Alkene
19,5	Pentadecane	57, 71, 43, 85	<i>n</i> -Alkane
20,6	Nonylbenzene	83, 41, 57, 204	Aromatic
20,86	Hexadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
21	Hexadecane	57, 43, 71, 85	<i>n</i> -Alkane
22	Decylbenzene	93, 41, 218, 67, 133	Aromatic
22,3	Heptadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
22,4	Heptadecane	57, 71, 43, 85	<i>n</i> -Alkane
22,7	Methyltetradecanoate	74, 87, 43, 143, 199	FAME
23,48	Undecylbenzene	92, 41, 232, 69, 133	Aromatic
23,61	Octadecene	55, 83, 97, 69, 41	<i>n</i> -Alkene
23,68	Octadecane	57, 71, 43, 85	<i>n</i> -Alkane
24,77	Octadecanal	97, 43, 57, 71, 123	Aldehyde
24,83	Dodecylbenzene	92, 56, 246, 133	Aromatic
24,98	Nonadecane	57, 43, 71, 85	<i>n</i> -Alkane
25	Heptadecanone	43, 57, 71, 97, 124	Aldehyde
25,3	Hexadecanoic acid methylester	74, 87, 43, 143, 97	FAME
27,7	Octadecanoic acid methylester	74, 87, 43, 143, 97	FAME
32,1	1,2-Benzenedicarboxylic acid diisooctylester	149, 57, 279, 113	Phthalate

b) Case study 2 – Centre-East

Sample 1 – Plywood flooring

Table D3: List of all compounds detected from the analysis of sample 1 collected at Fire Scene 2, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS2 Sample 1 - Plywood			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,41	Carbon dioxide	44	-
17,6	Naphthalene derivative	40, 105, 161	PAH
17,8	Low MW, low BP cyclic hydrocarbon	40, 93, 83, 69	Cycloalkane
19,2	Naphthalene derivative	40, 161, 105, 79	PAH
19,5	Naphthalene derivative	40, 105, 204	PAH
20,9	Hexadecanal	40, 71, 57, 97	Aldehyde
21,5	High MW, high BP hydrocarbon	40, 57, 71, 97	Isoparaffin
22,4	High MW, high BP hydrocarbon	40, 57, 71, 97	Isoparaffin

Sample 2 – Skirting board

Table D4: List of all compounds detected from the analysis of sample 2 collected at Fire Scene 2, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS2 Sample 2 - Skirting board			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,33	Carbon dioxide	44	-
18,15	Longifolene	40, 91, 161, 119, 189	Tricyclic terpene
18,35	Naphthalene derivative	40, 91, 69, 133	PAH
21,61	High MW, high BP oxygenated hydrocarbon	40, 57, 71, 85, 97	Alcohol
23,65	High MW, high BP oxygenated hydrocarbon	40, 57, 71, 85, 97	Alcohol
24,95	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
26,17	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
27,35	Heptacosane	57, 43, 71, 85	<i>n</i> -Alkane
28,48	High MW, high BP oxygenated hydrocarbon	40, 57, 71, 207	Alcohol
32,1	1,2-Benzenedicarboxylic acid diisooctylester	44, 207, 149, 70, 104	Phthalate

Sample 3 – Wood

Table D5: List of all compounds detected from the analysis of sample 3 collected at Fire Scene 2, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS2 Sample 3 - Wood			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
20,9	High MW, high BP hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
21,7	High MW, high BP oxygenated unsaturated hydrocarbon	40, 83, 57	Alkene-Alcohol
22,3	High MW, high BP hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
23,67	High MW, high BP oxygenated hydrocarbon	40, 57, 85	Alcohol
23,7	High MW, high BP hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
29,2	High MW, high BP oxygenated hydrocarbon	40, 185, 129, 207	Carboxylic acid
33,3	Phthalic acid butyl undecyl ester	40, 207, 149	Phthalate

Sample 4 – Cement

Table D6: List of all compounds detected from the analysis of sample 4 collected at Fire Scene 2, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS2 Sample 4 - Cement			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
17,87	Naphthalene derivative	40, 91, 69, 133	PAH
18,15	Naphthalene derivative	40, 91, 69, 133	PAH
19,42	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
20,9	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
21,6	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
22,3	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin

c) Case study 3 – Centre-West

Table D7: List of all compounds detected from the analysis of sample 1 collected at Fire Scene 3, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS1 Sample 1			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
4,8	Methylheptane	57, 43, 70, 99	Isoparaffin
5,6	2,4-Dimethylhexane	43, 85, 57, 71	Isoparaffin
6,3	Methyloctane	43, 57, 71, 85, 113	Isoparaffin
6,48	Trimethylcyclohexane	111, 57, 71, 83, 41	Cycloalkane
7	Ethylhexane	43, 84, 57	Isoparaffin
7,18	Methyloctane	43, 57, 71	Isoparaffin
7,37	Low MW, low BP hydrocarbon	57, 43, 98	Isoparaffin
8	Nonane	57, 43, 71, 85, 128	<i>n</i> -Alkane
8,62	Low MW, low BP unsaturated hydrocarbon	57, 43, 71, 105, 81	<i>n</i> -Alkene
8,8	2,3-Dimethyloctane	57, 71, 43, 113	Isoparaffin
9	Low MW, low BP unsaturated hydrocarbon	57, 71, 43, 98, 125	Isoparaffin
9,3	Medium MW, medium BP oxygenated hydrocarbon	57, 71, 43, 84, 125	Alcohol
9,5	Methylnonane	57, 43, 71, 85	Isoparaffin
9,7	Medium MW, medium BP unsaturated hydrocarbon	57, 71, 41, 81, 112	<i>n</i> -Alkene
9,8	1,2,3-Trimethylbenzene	105, 119, 57, 81, 41	Aromatic
9,9	1-Ethyl-2-methylbenzene	105, 119, 77, 55	Aromatic
10,1	1,2,4-Trimethylbenzene	105, 119, 77, 39	Aromatic
10,3	Decane	57, 43, 71, 85	<i>n</i> -Alkane
10,7	1,3,5-Trimethylbenzene	105, 71, 43	Aromatic
11,7	1-Methyl-2-propylbenzene	105, 134, 71, 43	Aromatic
12,4	Undecane	57, 43, 71, 85	<i>n</i> -Alkane
14,3	Dodecane	57, 43, 71, 85	<i>n</i> -Alkane
14,5	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
15,57	High MW, high BP hydrocarbon	57, 71, 43, 113, 85	Isoparaffin
16	Tridecane	57, 71, 43, 85	<i>n</i> -Alkane
17,68	Tertridecane	57, 71, 43, 85	<i>n</i> -Alkane
19,24	Pentadecane	57, 71, 43, 85	<i>n</i> -Alkane
31,9	Di- <i>n</i> -octylphthalate	149, 57, 279, 113	Phthalate

Table D8: List of all compounds detected from the analysis of sample 2 collected at Fire Scene 3, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS3 Sample 2			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,4	Carbon dioxide	44	-
7,18	Methyloctane	43, 57, 71, 85	Isoparaffin
7,9	1,2,3-Trimethylcyclohexane	91, 55, 97, 73	Cycloalkane
7,97	Nonane	57, 43, 85, 71	<i>n</i> -Alkane
8,8	2,6-Dimethyloctane	57, 71, 43, 113	<i>n</i> -Alkane
9,4	Low MW, low BP unsaturated hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
9,5	Methylnonane	57, 43, 71, 85	Isoparaffin
9,6	1,2,3-Trimethylbenzene	105, 119, 81, 57, 39	Aromatic
9,8	1-Ethyl-3-methylbenzene	105, 69, 41, 119	Aromatic
10,1	1,2,4-Trimethylbenzene	105, 69, 41, 119	Aromatic
10,3	Decane	57, 43, 71, 85	<i>n</i> -Alkane
10,77	Methyldecane	71, 57, 43, 105	Isoparaffin
12,36	Undecane	57, 43, 71, 85	<i>n</i> -Alkane
14,28	Dodecane	57, 43, 71, 85	<i>n</i> -Alkane
14,52	2,6-Dimethylundecane	57, 71, 43, 98	Isoparaffin
15,55	High MW, high BP hydrocarbon	57, 71, 43, 113, 85	Isoparaffin
16	Tridecane	57, 43, 71, 85	<i>n</i> -Alkane
17,67	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
19,24	Pentadecane	57, 71, 43, 85	<i>n</i> -Alkane

Table D9: List of all compounds detected from the analysis of sample 3 collected at Fire Scene 3, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS3 Sample 3			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,4	Carbon dioxide	44	-
3,87	Methylcyclohexane	83, 55, 41, 99	Cycloalkane
5,6	Octane	43, 85, 57, 71	<i>n</i> -Alkane
7,18	Methyloctane	43, 57, 71, 85	Isoparaffin
7,26	p-Xylene	91, 57, 105	Aromatic
7,3	2,5-Dimethylheptane	57, 43, 41, 98	Isoparaffin
7,7	1-Ethyl-2-methylcyclohexane	97, 55, 125, 71	Cycloalkane
7,83	o-Xylene	91, 105, 55	Aromatic
8	Nonane	57, 43, 85, 71, 128	<i>n</i> -Alkane
9,4	1-Ethyl-3-methylbenzene	105, 57, 43, 119	Aromatic
9,62	1,3,5-Trimethylbenzene	105, 119, 71, 41	Aromatic
9,8	1-Ethyl-3-methylbenzene	105, 119, 77, 39	Aromatic
10,1	1,2,4-Trimethylbenzene	105, 119, 77, 39	Aromatic
10,3	Decane	57, 43, 71, 85	<i>n</i> -Alkane
10,8	Tetramethyldecane	71, 105, 57, 43	Isoparaffin
12,1	1-Methyl-4-(1-methylethyl)-benzene	119, 69, 91, 41	Aromatic
12,4	Undecane	57, 43, 71, 85, 156	<i>n</i> -Alkane
14,3	Dodecane	57, 43, 71, 85, 156	<i>n</i> -Alkane
14,52	2,6-Dimethylundecane	57, 71, 43, 98, 133	Isoparaffin
16	Tridecane	57, 71, 43, 85, 141	<i>n</i> -Alkane
17,68	Tetradecane	57, 71, 43, 85, 145	<i>n</i> -Alkane
19,23	Pentadecane	57,71,43,85	<i>n</i> -Alkane

Table D10: List of all compounds detected from the analysis of blank sample collected at Fire Scene 3, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

FS3 blank			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,38	Carbon dioxide	44	-
7,2	Undecane	43, 57, 71, 209	<i>n</i> -Alkane
12,9	Tetradecane	40, 57, 71	<i>n</i> -Alkane
15,6	High MW, high BP hydrocarbon	40, 43, 57, 71, 85	Isoparaffin
19,27	High MW, high BP hydrocarbon	40, 43, 57, 71, 85	Isoparaffin
20,7	High MW, high BP hydrocarbon	40, 43, 57, 71, 85	Isoparaffin
22,1	High MW, high BP hydrocarbon	40, 43, 57, 71, 85	Isoparaffin
23,47	High MW, high BP oxygenated hydrocarbon	40, 43, 57, 71	Alcohol
23,6	High MW, high BP oxygenated hydrocarbon	40, 43, 57, 71	Alcohol
29,05	High MW, high BP oxygenated hydrocarbon	40, 43, 185, 206, 128, 259	Carboxylic acid

2) Determination and characterization of background, combustion and pyrolysis products

Glass can blank

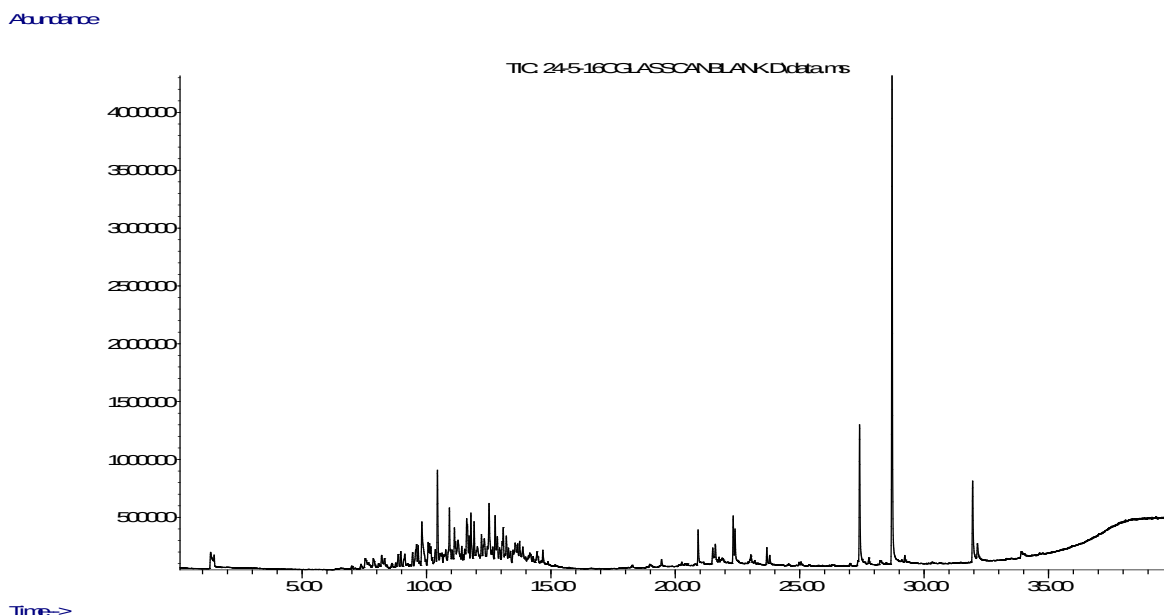


Figure D1: TIC of products produced from the analysis of the glass container as a blank.

The compounds that were extracted and analysed from the empty glass can are shown in **Table D11**.

Table D11: List of all compounds detected in the analysis of the glass container used for sample collection, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Retention time t [min]	Compound	Major ions [m/z]	Chemical family
1,39	Carbondioxide	44	-
10,4	Decane	57, 85, 39, 111, 142	<i>n</i> -alkane
20,9	Nonadecane	57, 85, 39, 111, 207	<i>n</i> -alkane
21,6	High MW, high BP hydrocarbon	40, 71, 149, 97	Isoparaffin
27,4	Decanoic acid dibutylester	241, 185, 41, 98, 125, 69	Ester
28,7	Tributylacetylcitrate	185, 129, 43, 259, 157	Ester
31,9	1,2-Benzenedicarboxylic acid diisooctylester	149, 55, 104, 207	Phthalate

Plywood flooring

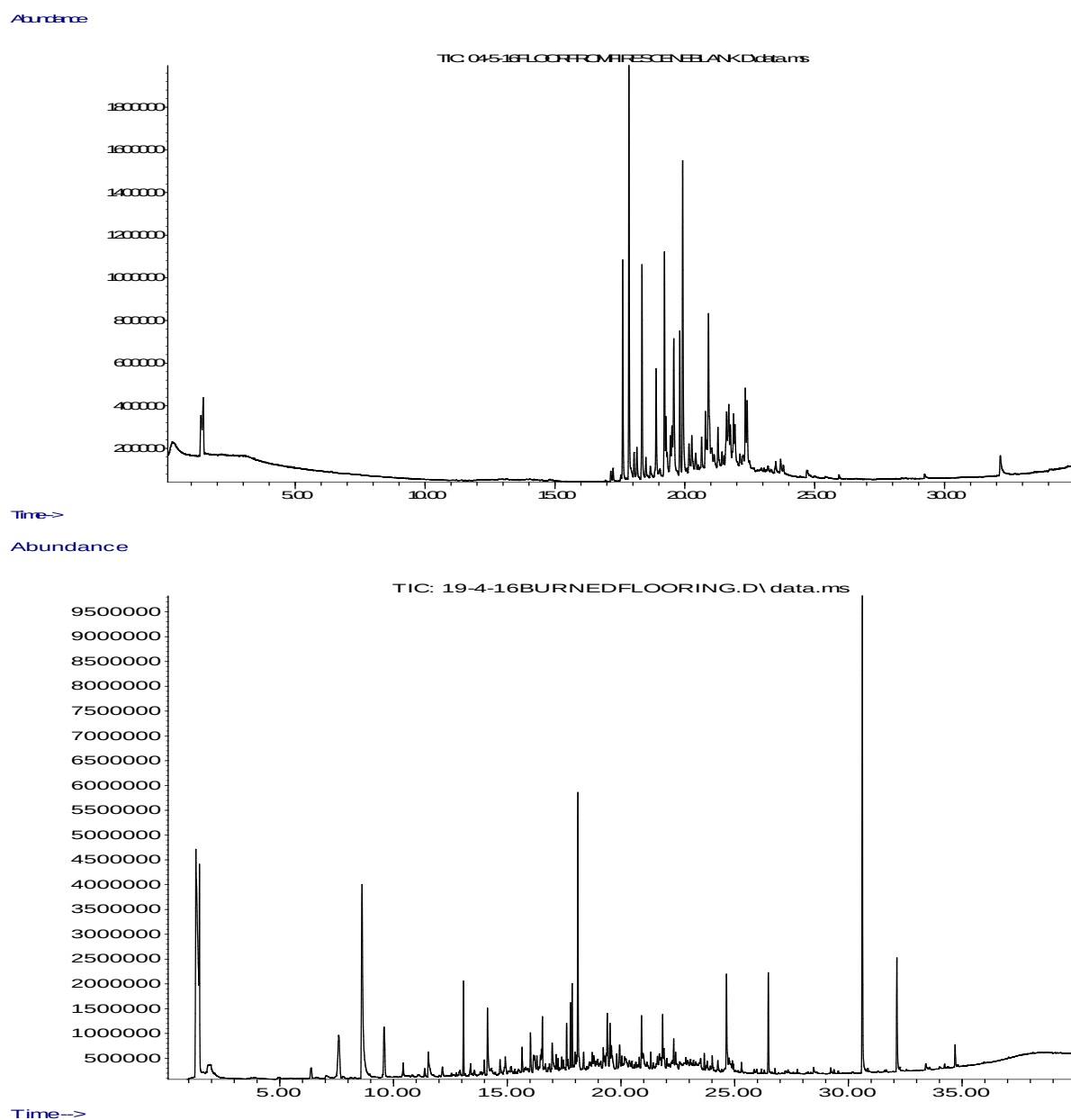


Figure D2: TICs of products produced from the analysis of the burned (bottom) and unburned (top) plywood flooring.

The compounds found in the analysis of the plywood flooring before and after burning are listed in **Tables D12** and **D13**.

Table D12: List of compounds found in the analysis of plywood flooring before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,526	Carbondioxide	44	-
17,61	Copaene	119, 161, 105, 93, 40	Cyclic terpene
17,86	High MW, high BP cyclic hydrocarbon derivative	93, 67, 41, 121, 147	Branched cycloalkane
18,34	Caryophyllene	93, 133, 41, 69	Bicyclic terpene
18,89	α -Caryophyllene	93, 40, 131, 67	Bicyclic terpene
19,21	Naphthalene derivative	161, 105, 40, 79, 133	PAH
20,91	1-Chlorooctadecane	57, 85, 39, 105	<i>n</i> -alkane
32,15	1,2-Benzenedicarboxylic acid diisooctyl ester	44, 149, 207, 70	Phthalate

Table D13: List of compounds found in the analysis of plywood flooring after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
8,68	Low MW, low BP hydrocarbon	57,83,37	Isoparaffin
14,12	Medium MW, medium BP oxygenated hydrocarbon	57,43,83,113	Aldehyde
17,61	Copaene	119,161,93,40	Cyclic terpene
18,3	Carophyllene	40,69,133,105	Bicyclic terpene
24,6	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	149,57,104	Phthalate
30,59	Hexanedioic acid, bis(2-ethylhexyl) ester	129,57,83	Ester
32,15	1,2-Benzenedicarboxylic acid, diisooctyl ester	149,57,113,207	Phthalate

Polyurethane

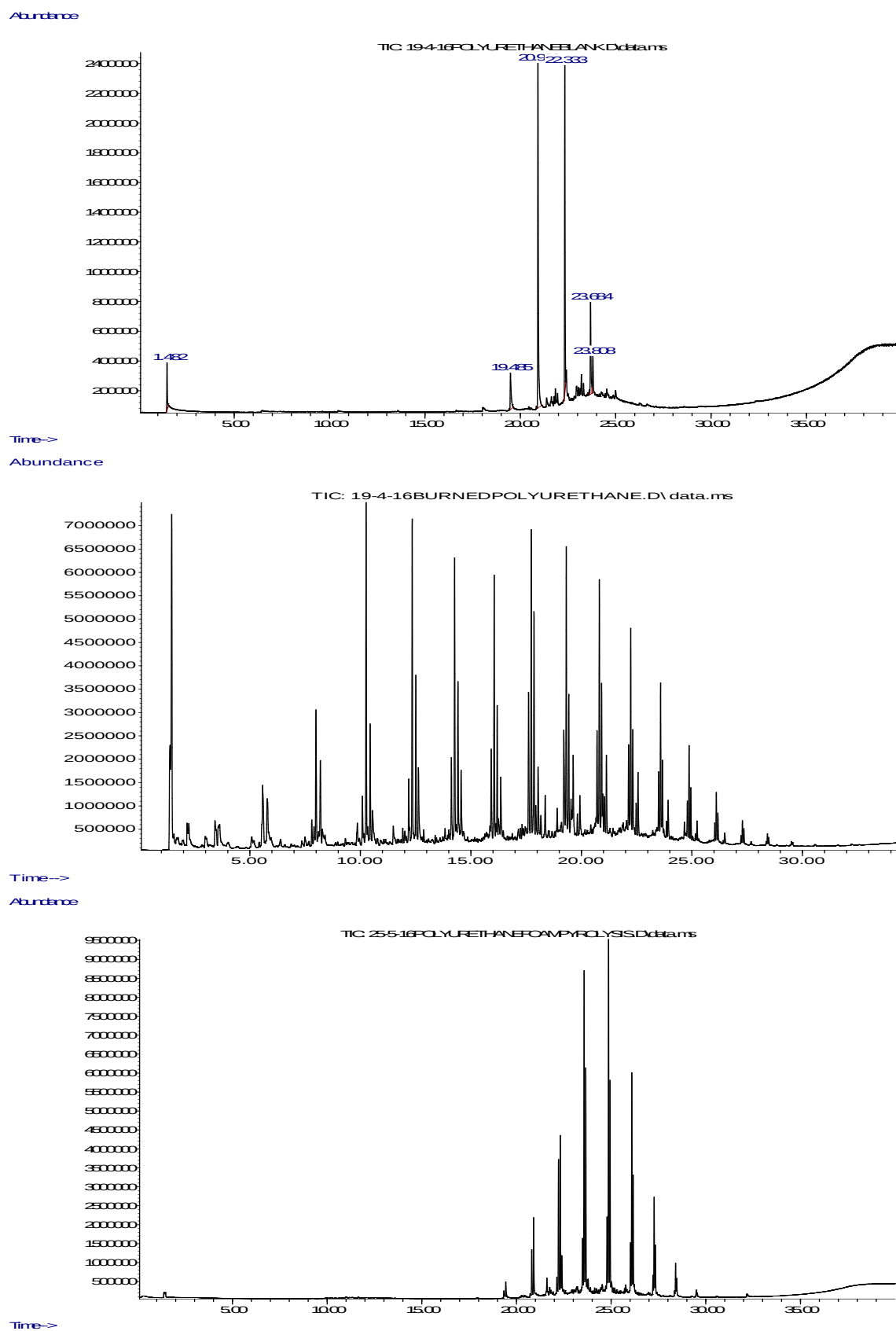


Figure D3: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) polyurethane.

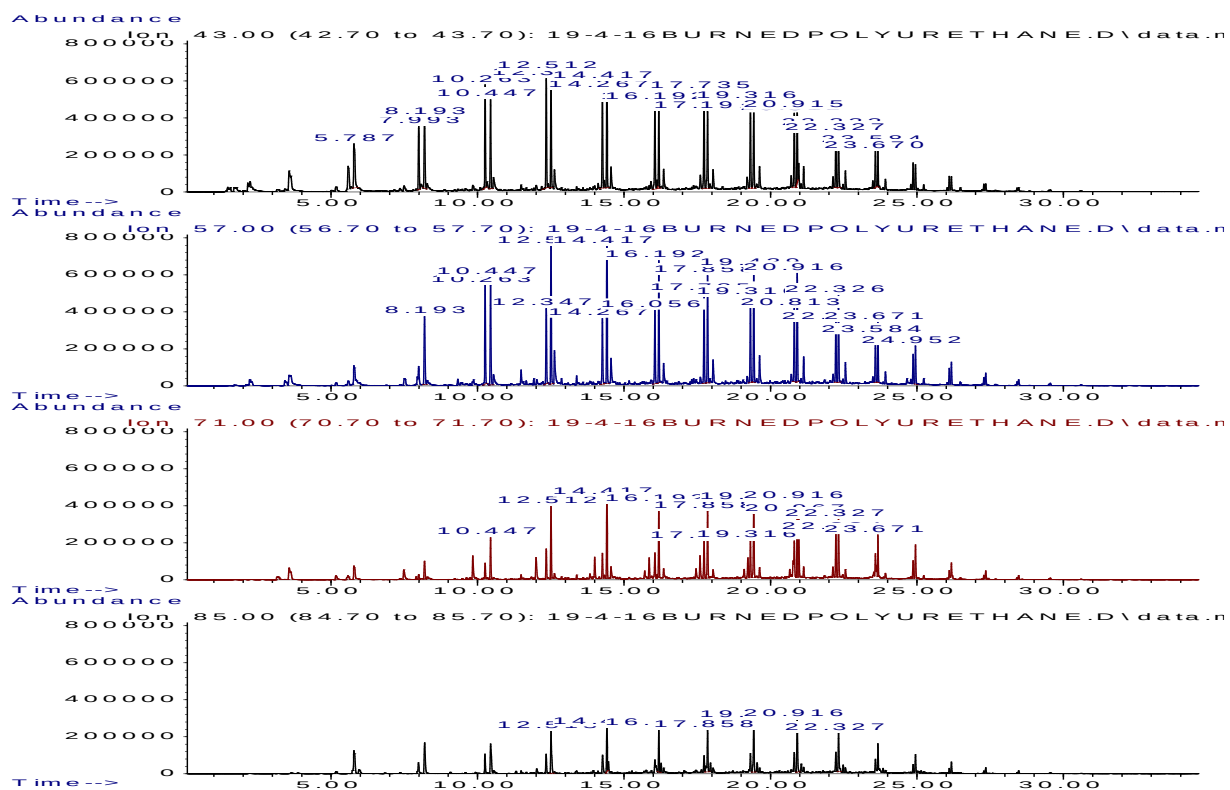


Figure D4: EICs for alicyclics and olefinics, ions 55,69 and 83, produced from the analysis of the burned polyurethane.

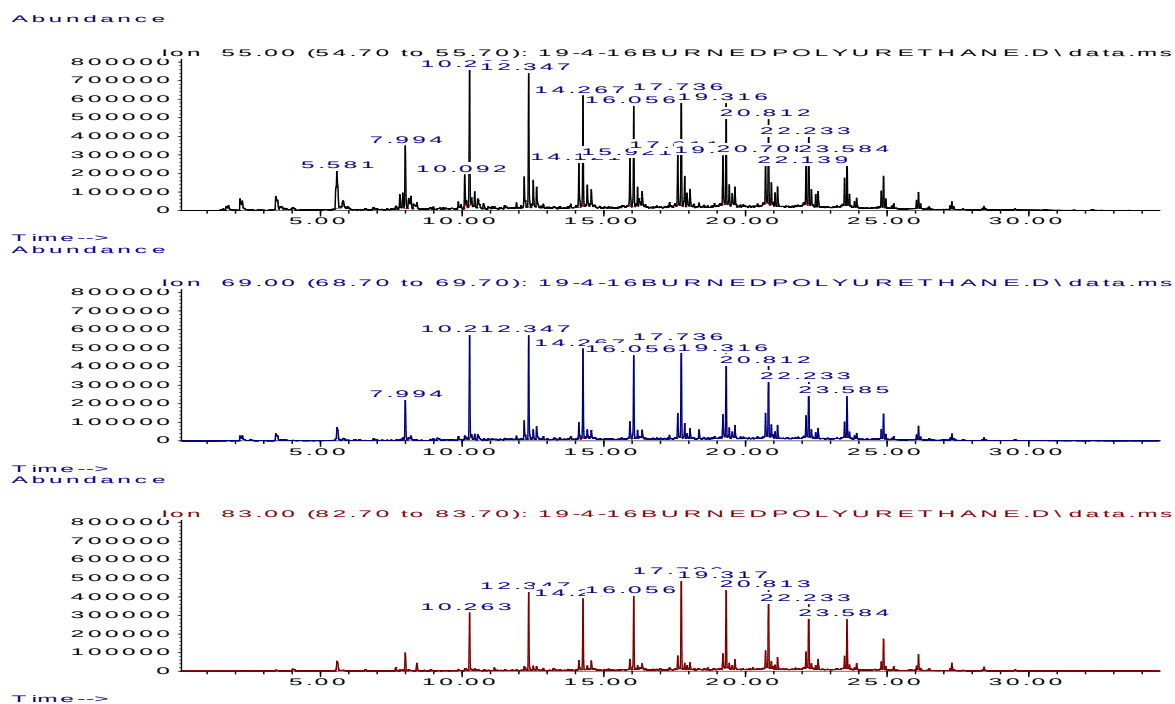


Figure D5: EICs for alkanes, ions 43, 57, 71 and 85, produced from the analysis of the burned polyurethane.

The compounds found in the analysis of the polyurethane foam before and after burning and after pyrolysis are listed in **Tables D14, D15** and **D16**.

Table D14: List of compounds and retention times found in the analysis of polyurethane before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
19,43	Tetradecane	40,71,99	<i>n</i> -alkane
20	Hexadecane	57,85,43	<i>n</i> -alkane
22,33	Heptadecane	57,85,43	<i>n</i> -alkane
23,63	High MW, high BP hydrocarbon	57,43,85,111	Isoparaffin
23,8	Octadecane	57,85,43	<i>n</i> -alkane

Table D15: List of compounds and retention times found in the analysis of polyurethane before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
5,57	Octene	55,83,71	Alkene
5,81	2,4-Dimethylhexane	43,57,85,67	isoparaffin
9,85	Low MW, low BP hydrocarbon	56,69,41,83	isoparaffin
10,1	1,9-Decadiene	55,41,67,81,110	Alkene
10,26	Decene	55,43,69,83	Alkene
10,44	Decane	57,43,71,85	<i>n</i> -Alkane
12,24	Undecene	55,43,69,83	Alkene
12,61	Undecane	57,43,71,85	<i>n</i> -Alkane
14,12	1,11-Dodecadiene	55,41,81,96,109	Alkene
14,27	Dodecene	55,43,59,83,125	Alkene
14,44	Dodecane	57,43,71,85	<i>n</i> -Alkane
16,04	Tridecene	55,43,59,83,111	Alkene
16,19	Tridecane	57,43,71,85	<i>n</i> -Alkane
17,73	Tetradecene	55,43,59,83,111	Alkene
17,85	Tetradecane	57,43,71,85	<i>n</i> -Alkane
19,9	Naphthalene derivative	161,119,204,40,91,69	Polycyclic aromatic hydrocarbon (PAH)
20,8	Hexadecene	55,43,59,83,111	Alkene
20,9	High MW, high BP hydrocarbon	57,43,71,85	isoparaffin
21,13	Tetradecanal	57,43,82,109,138,168	aldehyde
23,8	Nonadecane	57,43,71,85	<i>n</i> -Alkane
23,9	Octadecanal	44,57,82,96,109	Aldehyde
26,1	Docosene	55,43,83,97,111	Alkene

Table D16: List of compounds and retention times found in the analysis of polyurethane after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,43	Carbon dioxide	44	-
20,8	Hexadecanol	55,69,83,97,111	Alcohol
22,2	1-Heptadecanol	55,69,83,97,111	Alcohol
22,4	2,6,10-Trimethyltetradecane	57,71,43,85,113	isoparaffin
23,57	Nonadecene	55,83,97,111,139	Alkene
23,6	Nonadecane	57,71,43,85,113	<i>n</i> -Alkane
24,85	Decene	55,83,97,111,139	Alkene
24,9	Decane	57,71,43,85,113	<i>n</i> -Alkane
26,1	Eicosane	57,71,43,85,113	<i>n</i> -Alkane
27,2	Heneicosene	55,83,97,111,125	Alkene
27,34	Heneicosane	57,71,43,85,113	<i>n</i> -Alkane
28,4	Docosene	55,83,97,111,125	Alkene
28,47	Heptacosane	57,71,43,85,113, 207	<i>n</i> -Alkane

Cement

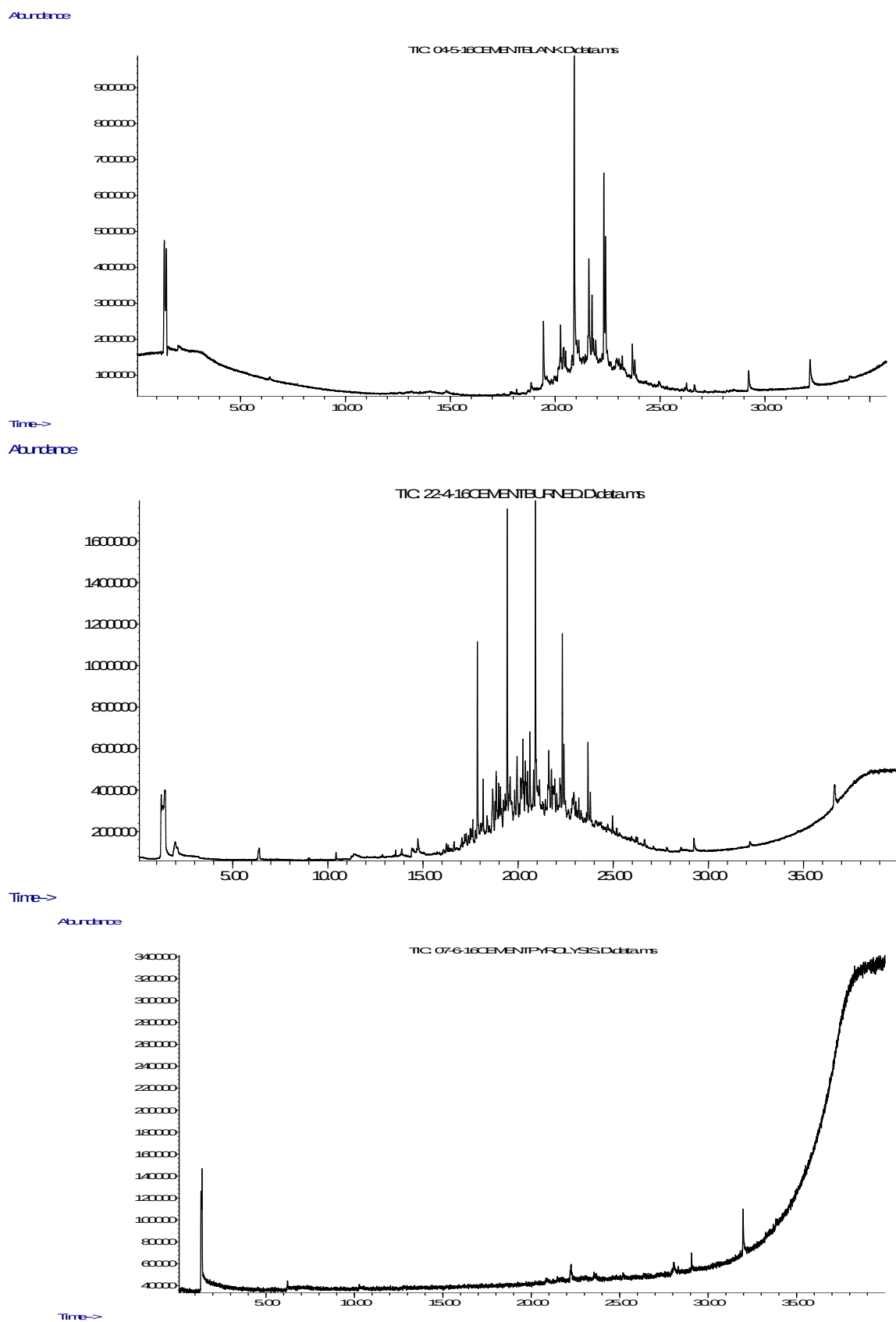


Figure D6: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) cement.

The compounds found in the analysis of cement before and after burning and after pyrolysis are listed in **Tables D17, D18 and D19**.

Table D17: List of compounds and retention times found in the analysis of cement before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
19,45	Trimethyltetradecane	57, 43, 85, 111	isoparaffin
20,92	Nonadecane	57, 43, 71, 85, 111	<i>n</i> -Alkane
21,75	Hexadecenal	40, 83, 55, 109	Aldehyde

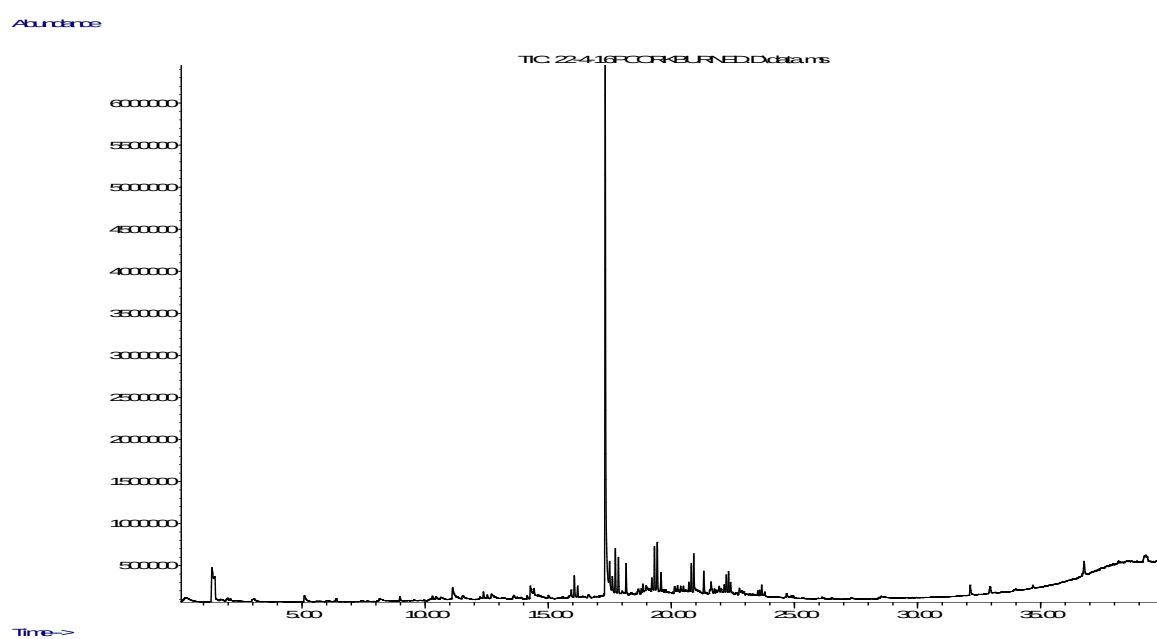
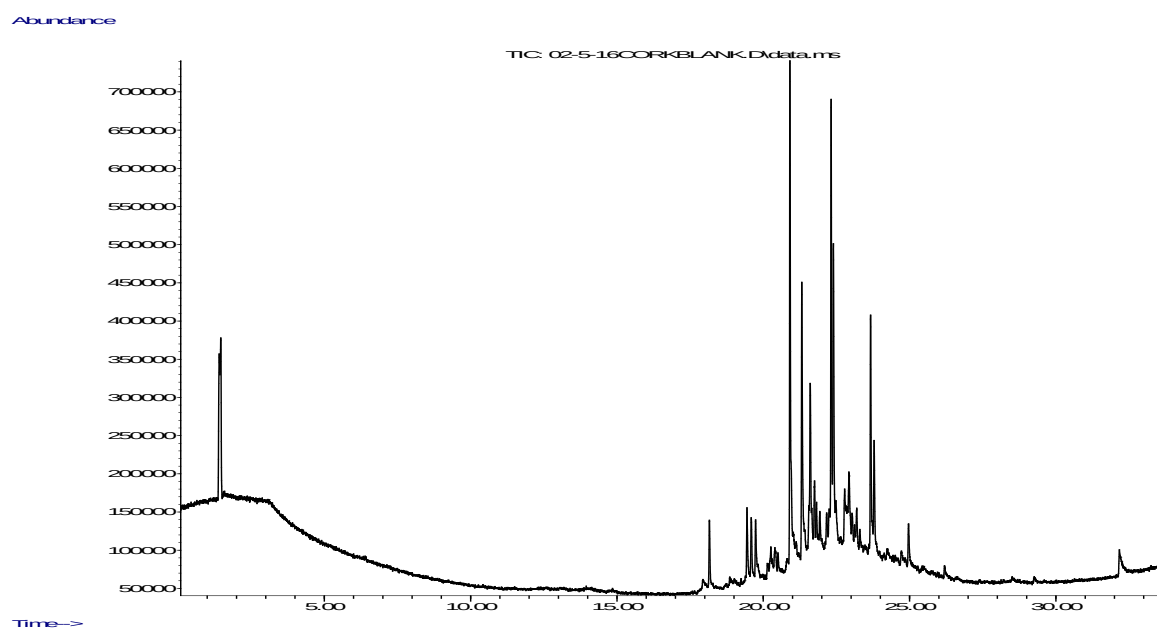
Table D18: List of compounds and retention times found in the analysis of cement after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
17,87	Naphthalene derivative	57, 43, 71, 85, 161, 107, 189	PAH
19,42	High MW, high BP branched hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
20,9	High MW, high BP branched hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
21,6	High MW, high BP branched hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
22,3	High MW, high BP branched hydrocarbon	57, 43, 71, 85, 111	Isoparaffin
23,65	<i>tert</i> -Hexadecanethiol	57, 41, 69, 85, 111, 207	Isoparaffin

Table D19: List of compounds and retention times found in the analysis of cement after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-

Cork



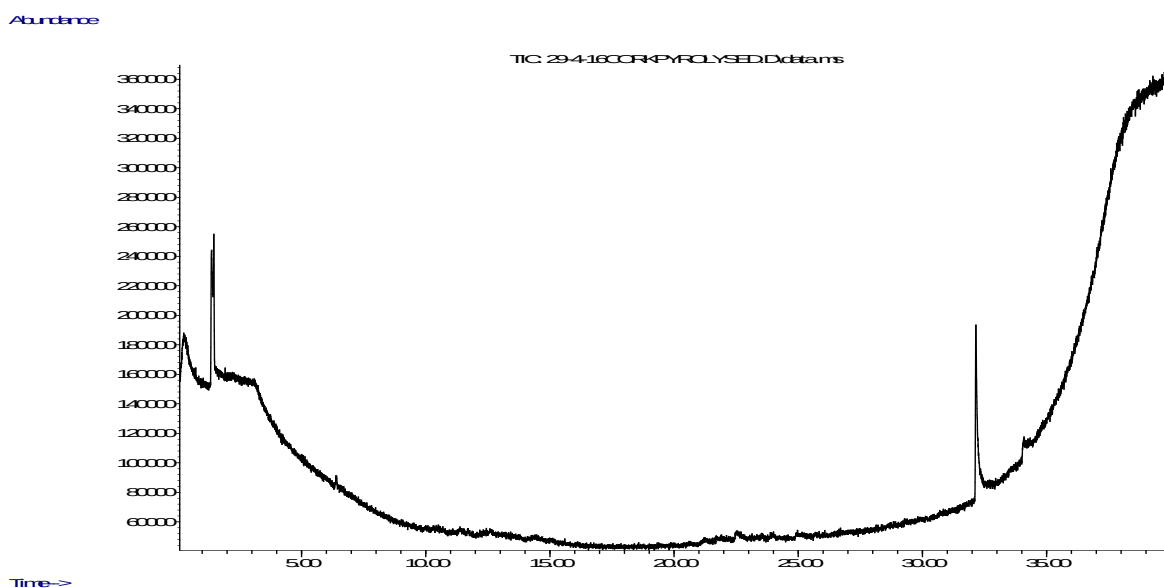


Figure D7: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) cork.

The compounds found in the analysis of cork before and after burning and after pyrolysis are listed in **Table D20**, **D21** and **D22**.

Table D20: List of compounds and retention times found in the analysis of cork before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
18,15	Benzene derivative	40, 91, 161, 107, 133	Aromatic
19,45	Hexadecanal	40, 57, 71, 85	Aldehyde
19,6	Naphthalene	40, 108, 161, 57	PAH
20,92	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
21,6	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
22,3	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
22,4	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
23,6	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin

Table D21: List of compounds and retention times found in the analysis of cork after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
17,4	2-(2-butoxyethoxy)-ethanolacetate	87, 57, 43	Acetate ester
19,1	1,12-Tridecadiene	40, 55, 81, 109	Alkene
19,2	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
19,4	High MW, high BP branched hydrocarbon	57, 43, 71, 85	Isoparaffin
19,6	Naphthalene derivative	40, 105, 161, 85, 204	PAH
20,7	High MW, high BP branched hydrocarbon	40, 55, 69, 95	Alkene

Table D22: List of compounds and retention times found in the analysis of cork after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-

Wood compressed

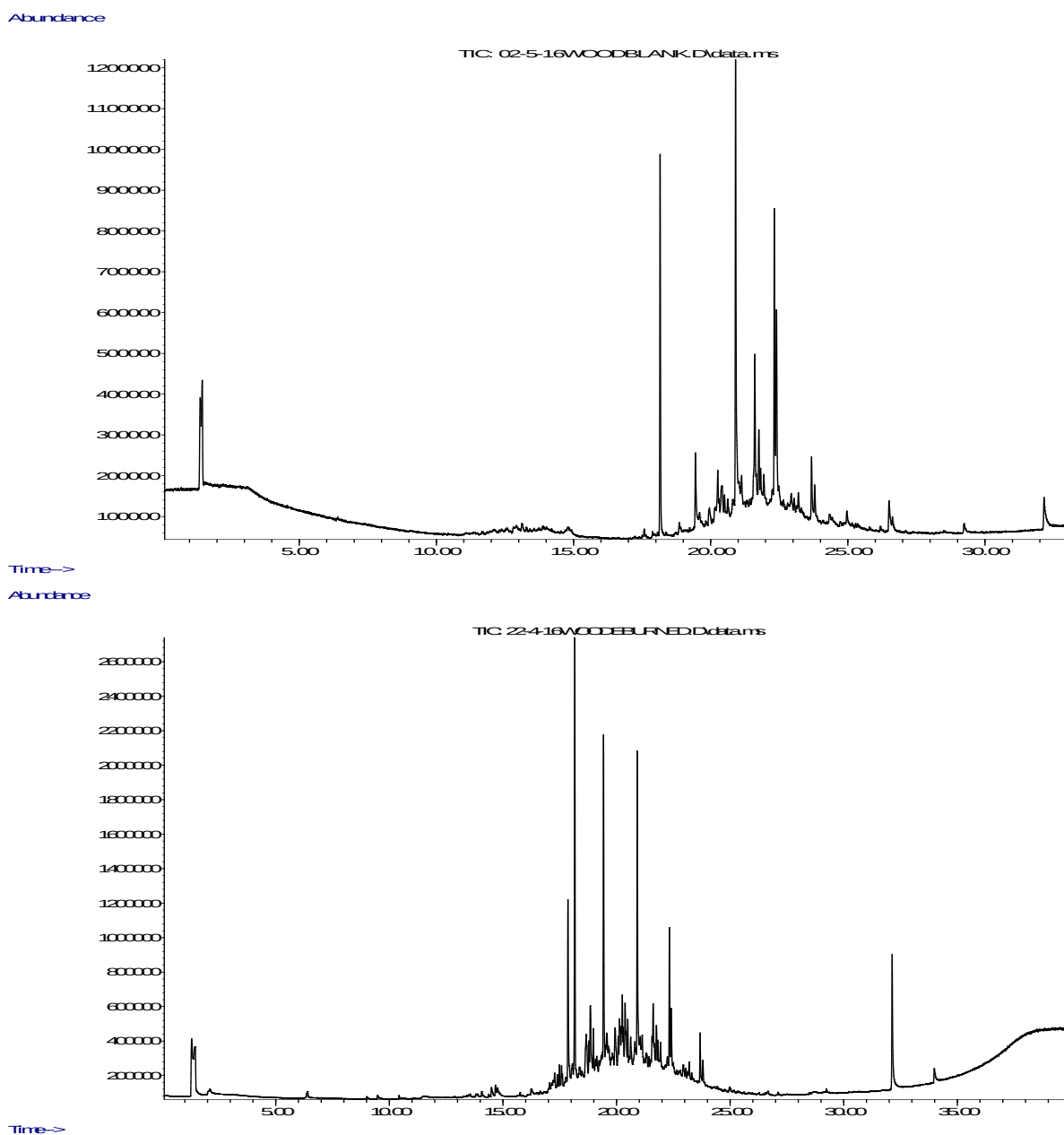


Figure D8: TICs of products produced from the analysis of the burned (bottom) and unburned (top) compressed wood.

The compounds found in the analysis of wood before and after burning are listed in **Tables D24** and **D25**.

Table D24: List of compounds and retention times found in the analysis of compressed wood before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
18,1	Longifolene	40, 161, 91, 107, 133, 189, 67	Tricyclic terpene
19,4	High MW, high BP hydrocarbon	40, 57, 71, 85, 97	Alkene
20,9	High MW, high BP hydrocarbon	57, 71, 43, 85, 97	Isoparaffin
21,6	High MW, high BP hydrocarbon	57, 71, 43, 85, 97	Isoparaffin
22,3	High MW, high BP hydrocarbon	57, 71, 43, 85, 97	Isoparaffin
22,4	High MW, high BP hydrocarbon	57, 71, 43, 85, 97	Isoparaffin
23,7	High MW, high BP hydrocarbon	40, 57, 71, 85, 97	Alkene
32,2	1,2-Benzenedicarboxylic acid, diisooctyl ester	40, 149, 207, 57, 70	Ester

Table D25: List of compounds and retention times found in the analysis of compressed wood after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
17,87	High MW, high BP hydrocarbon	57, 43, 71, 85, 161	Isoparaffin
18,1	Longifolene	91, 161, 41, 119, 189, 67	Tricyclic terpene
19	High MW, high BP hydrocarbon	57, 43, 71, 85, 111, 183	Isoparaffin
19,4	Nonadecane	57, 43, 71, 85	<i>n</i> -Alkane
20,93	High MW, high BP hydrocarbon	57, 43, 71, 85, 111, 183	Isoparaffin
21,75	Docosanol	40, 57, 83, 111	Alcohol
22,3	High MW, high BP hydrocarbon	40, 57, 83, 111	Isoparaffin
33	1,2-Benzenedicarboxylic acid, diisooctyl ester	149, 44, 70, 207, 104	Phthalate

Vinyl flooring white bathroom/kitchen

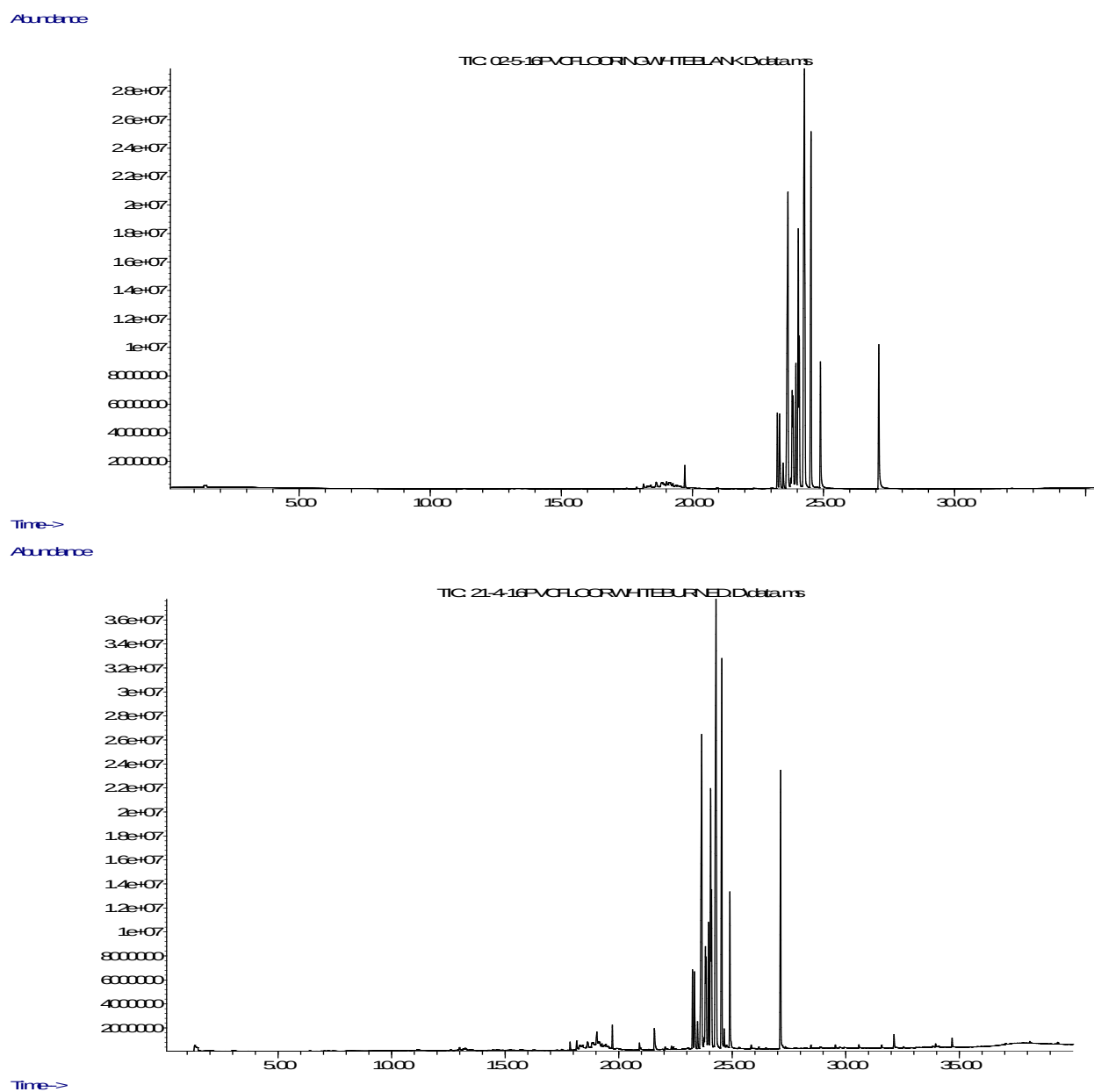


Figure D9: TICs of products produced from the analysis of the burned (bottom) and unburned (top) white PVC flooring.

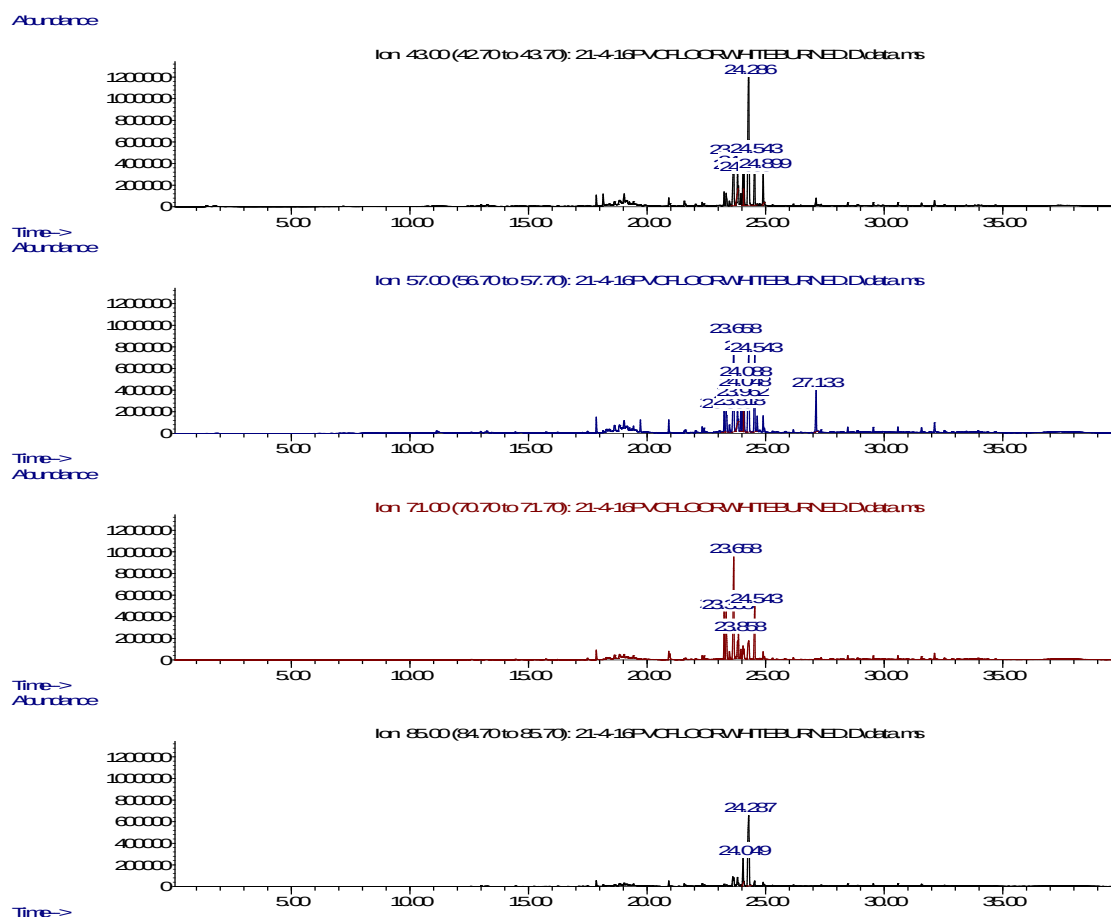


Figure D10: EICs for alkanes, ions 43, 57, 71 and 85, produced from the analysis of the burned vinyl flooring.

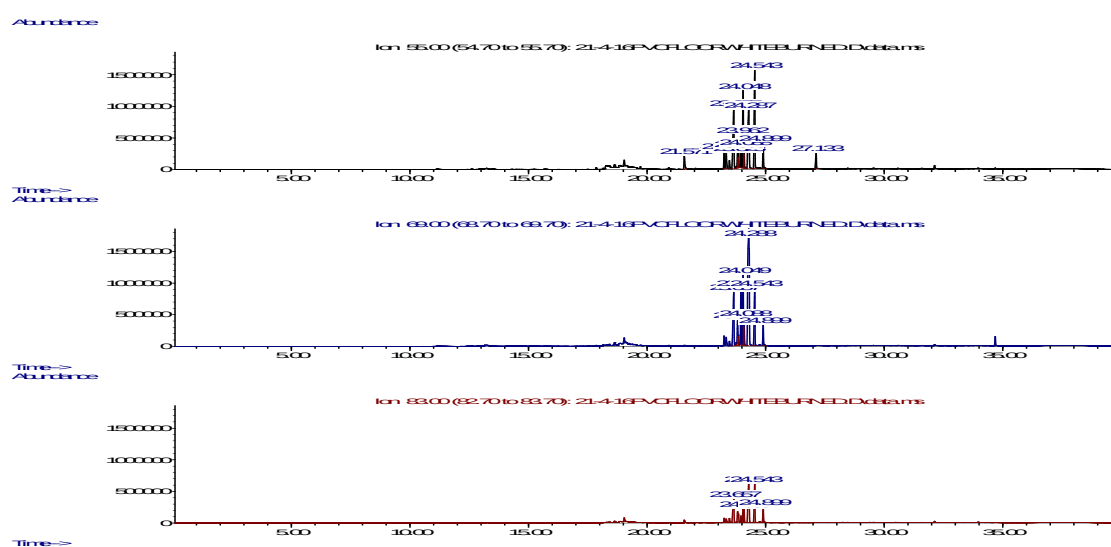


Figure D11: EICs for alicyclics and olefinics, ions 55, 69 and 83, produced from the analysis of the burned vinyl flooring.

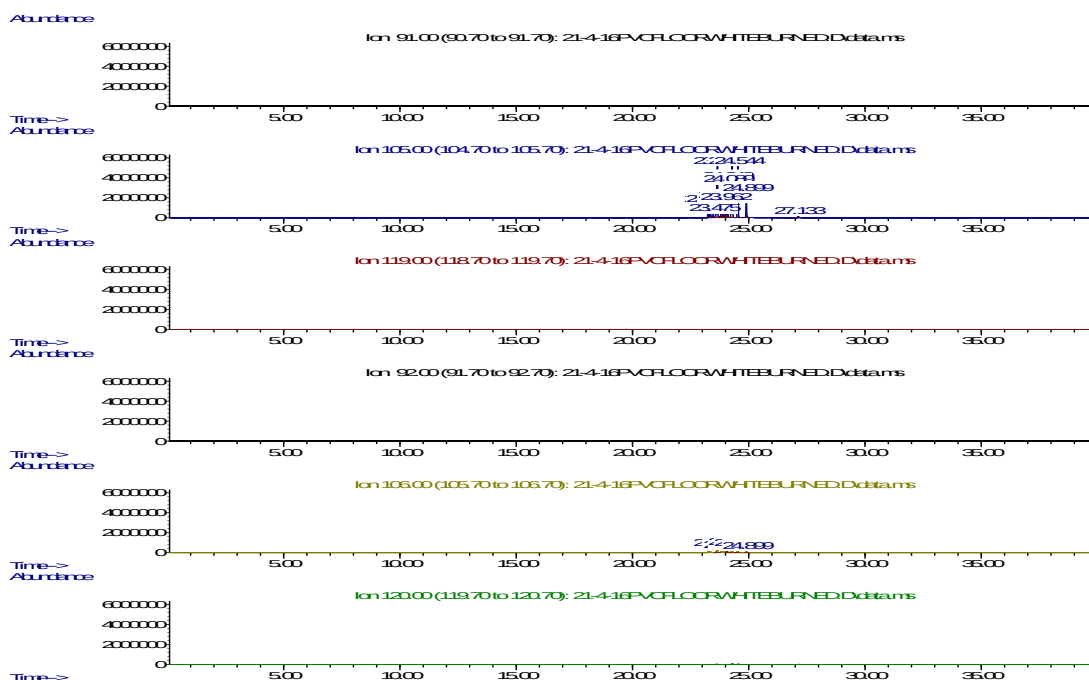


Figure D12: EICs for aromatics (alkylbenzenes), ions 91, 105, 119, 92, 106 and 120, produced from the analysis of the burned vinyl flooring.

The compounds found in the analysis of white vinyl flooring before and after burning are listed in **Tables D26** and **D27**.

Table D26: List of compounds and retention times found in the analysis of vinyl flooring for kitchen use before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
19,7	Butylated Hydroxytoluene	205, 220, 57, 145	Aromatic
23,2	Benzoate derivative	105, 70, 123, 41	Aromatic Ester
23,46	Benzoate derivative	105, 70, 125, 41	Aromatic Ester
23,6	Benzoate derivative	105, 70, 123, 41	Aromatic Ester
23,9	Benzoate derivative	105, 70, 123, 41	Aromatic Ester
24	Benzoate derivative	105, 70, 123, 41	Aromatic Ester
24,2	Benzoate derivative	105, 70, 123, 41	Aromatic Ester
27,1	1,4-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	167, 205, 223, 149, 56	Phthalate

Table D27: List of compounds and retention times found in the analysis of vinyl flooring for kitchen use after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
19,7	Butylated Hydroxytoluene	205, 220, 57, 145	Aromatic
21,58	High MW, high BP oxygenated hydrocarbon	173, 55, 99, 129	Ester
23,25	Benzoate derivative	105, 70, 41, 127	Aromatic Ester
24	Benzoate derivative	105, 77, 133, 41	Aromatic Ester
24,2	Benzoate derivative	105, 133, 77, 41	Aromatic Ester
24,8	Benzoate derivative	133, 105, 77, 41	Aromatic Ester
27,1	1,4-Benzenedicarboxylic acid bis(2-methylpropyl) ester	208, 187, 55, 104	Phthalate
32,1	1,2-Benzenedicarboxylic acid diisooctyl ester	149, 57, 43, 71, 83, 207	Phthalate

Curtain orange

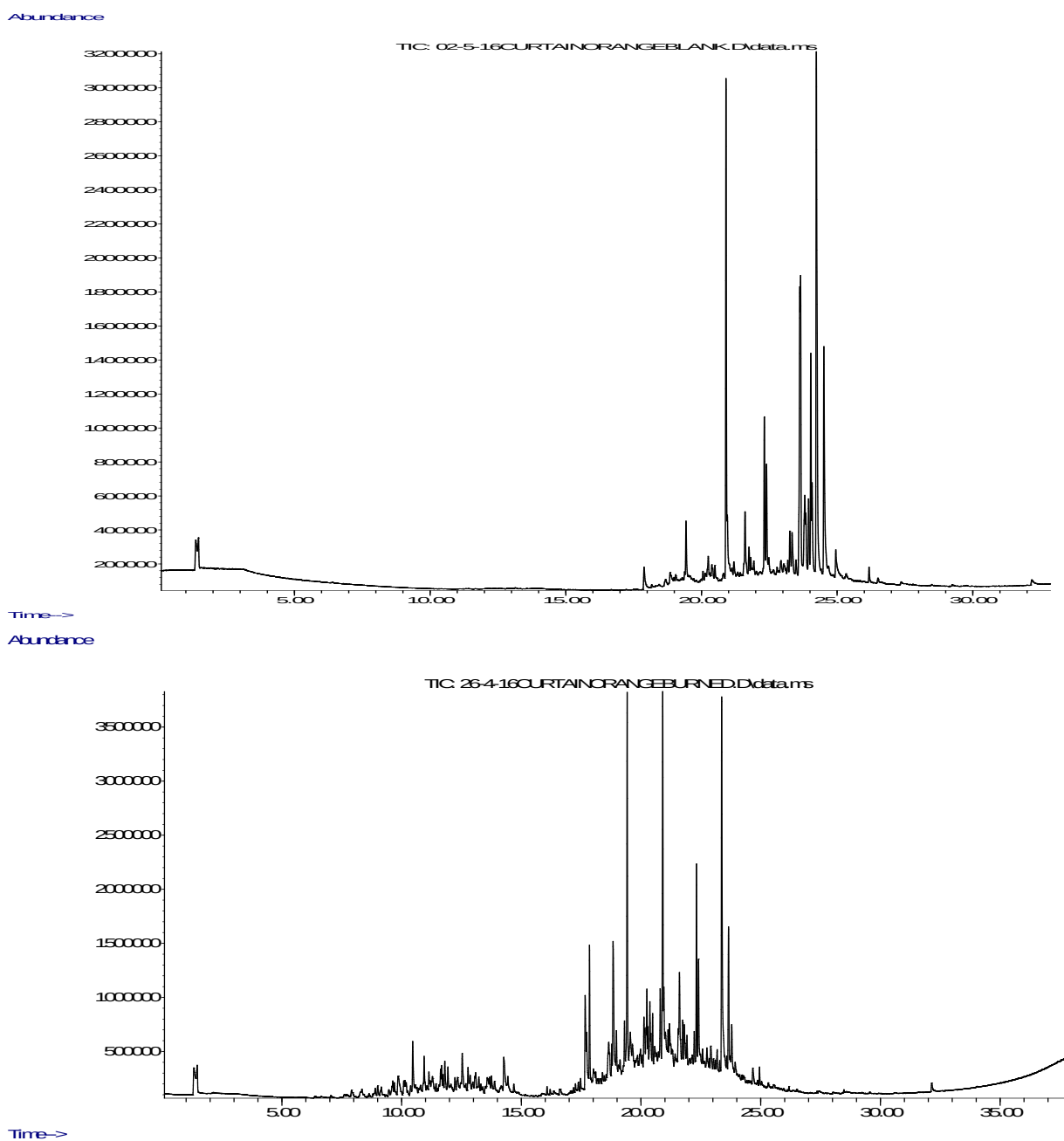


Figure D13: TICs of products produced from the analysis of the burned (bottom) and unburned (top) orange curtain.

The compounds found in the analysis of the orange curtain before and after burning are listed in **Tables D28** and **D29**.

Table D28: List of compounds and retention times found in the analysis of orange curtain before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
No peaks			

Table D29: List of compounds and retention times found in the analysis of orange curtain after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
17,69	Biphenyl	154, 76, 40, 115	Aromatic
17,85	Tetradecane	57, 43, 71, 85, 154	<i>n</i> -Alkane
18,97	High MW, high BP hydrocarbon	43, 57, 71, 85, 111, 168	Isoparaffin
19,4	High MW, high BP hydrocarbon	57, 71, 43, 85, 152	Isoparaffin
20,7	Docosanol	57, 43, 71, 83, 97, 111, 165	Alcohol
20,9	Hexadecane	57, 71, 43, 85, 166	<i>n</i> -Alkane
21,6	High MW, high BP hydrocarbon	57, 43, 71, 85, 111, 177	Isoparaffin
22,3	Nonadecane	57, 71, 43, 85	<i>n</i> -Alkane
23,4	Benzylbenzoate	105, 97, 77, 51, 212	Aromatic
23,8	High MW, high BP hydrocarbon	57, 71, 43, 85, 178	<i>n</i> -Alkane

Carpet underlay

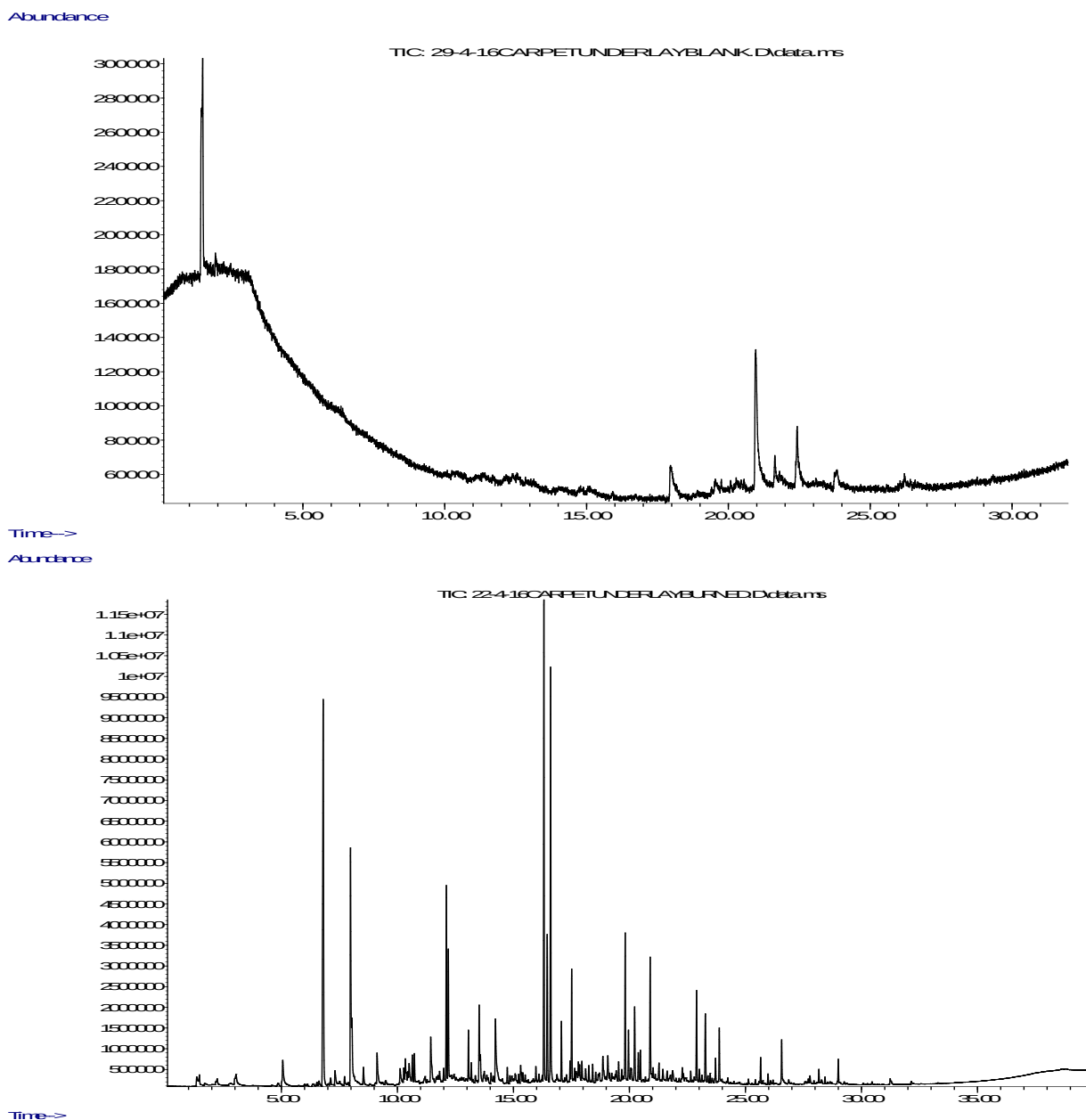


Figure D14: TICs of products produced from the analysis of the burned (bottom) and unburned (top) carpet underlay.

The compounds found in the analysis of the carpet underlay before and after burning are listed in **Tables D30** and **D31**.

Table D30: List of compounds and retention times found in the analysis of the carpet underlay before burning with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
20,9	High MW, high BP hydrocarbon	40, 57, 85	<i>n</i> -Alkane
23,3	High MW, high BP hydrocarbon	40, 57, 71	<i>n</i> -Alkane

Table D31: List of compounds and retention times found in the analysis of the carpet underlay after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
5,06	Toluene	91, 40, 70	Aromatic
6,79	2,4-Dimethyl-1-heptene	43, 70, 57, 85, 126	Isoparaffin
8,02	Styrene	104, 78, 51	Aromatic
10,1	α -Methylstyrene	118, 40, 78, 58	Aromatic
12,1	High MW, high BP hydrocarbon	69, 43, 57, 81, 111	Isoparaffin
14,35	Naphthalene	128	PAH
16,4	High MW, high BP hydrocarbon	69, 43, 57, 83, 111	Isoparaffin
17,06	Eicosene	69, 43, 57, 83, 125	Alkene
17,5	Eicosyne	69, 57, 83, 109, 41	Alkyne
19,9	Acetic acid ester derivative	69, 57, 43, 83, 111	Ester
23,85	Acetic acid ester derivative	69, 57, 43, 83, 111	Ester
25,65	High MW, high BP hydrocarbon	69, 83, 57, 109, 41, 173	Isoparaffin

Carpet red

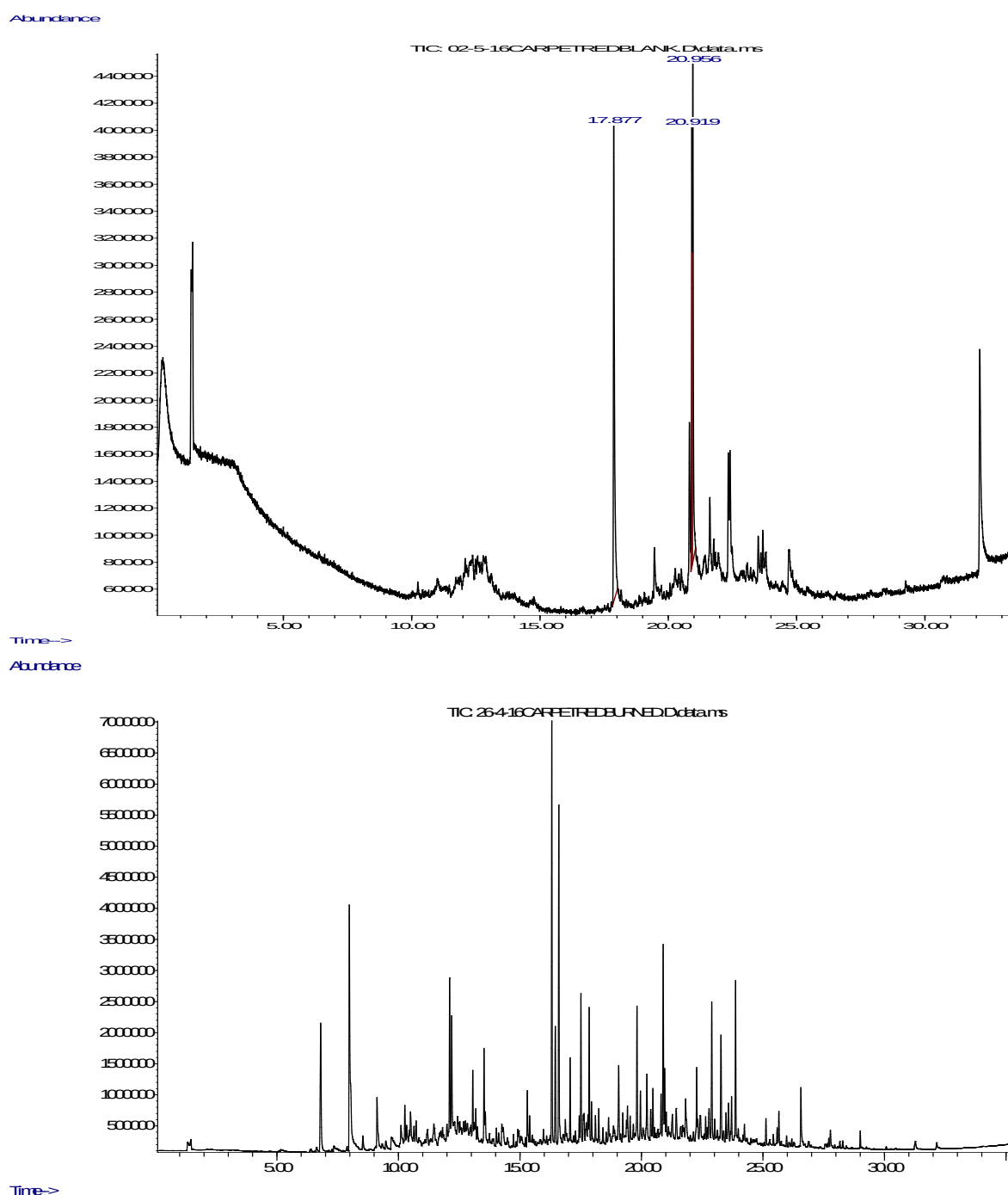


Figure D15: TICs of products produced from the analysis of the burned (bottom) and unburned (top) red carpet.

The compounds found in the analysis of the red carpet before and after burning are listed in **Tables D32** and **D33**.

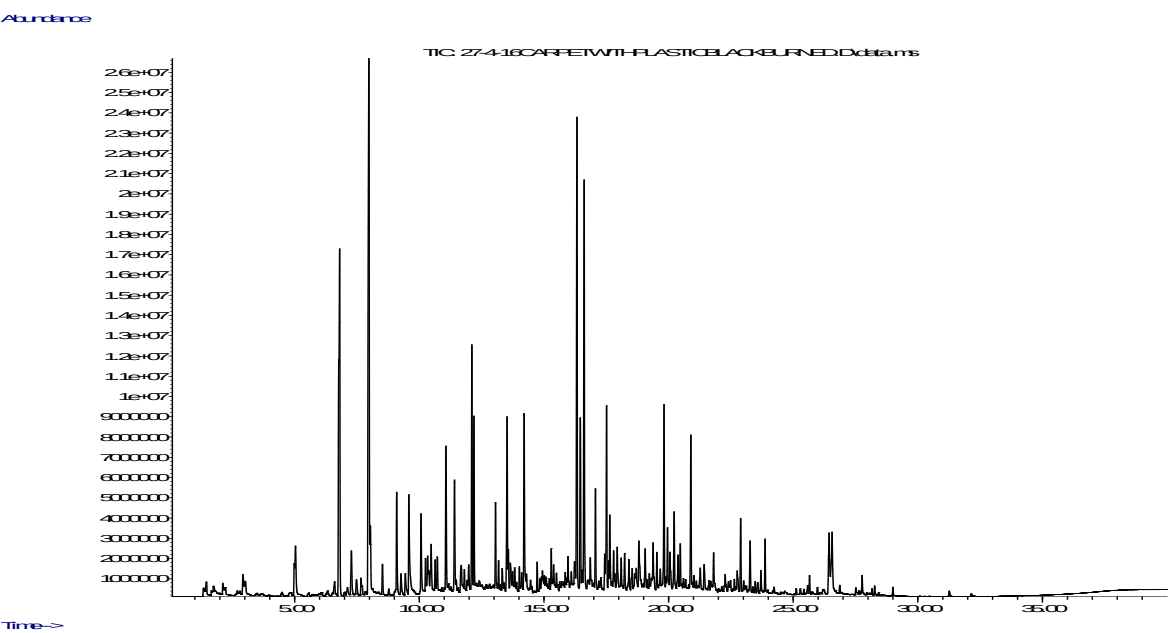
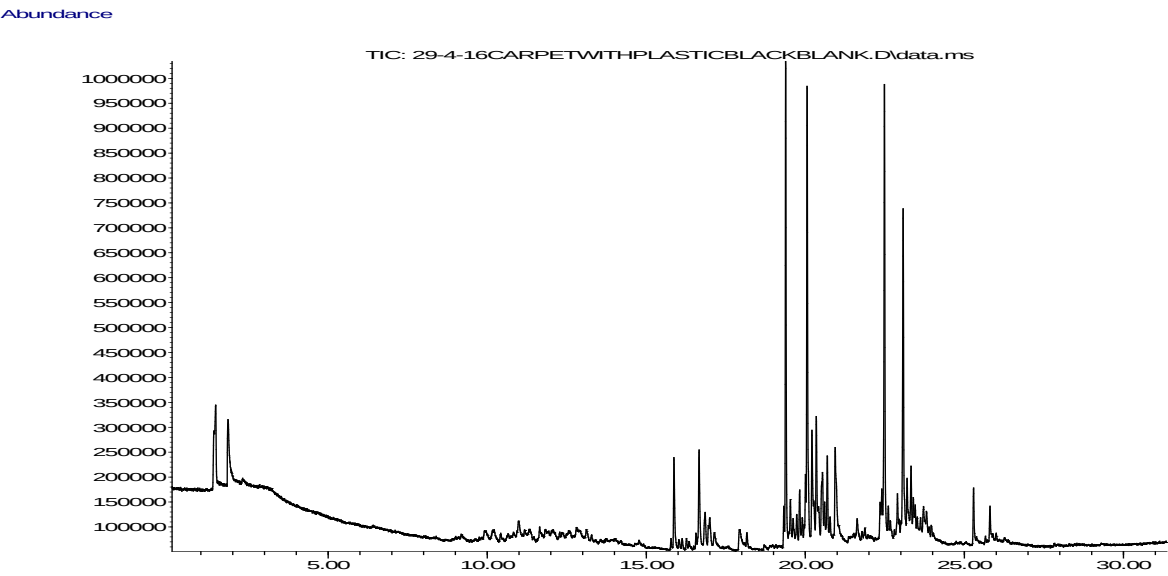
Table D32: List of compounds and retention times found in the analysis of the red carpet before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,43	Carbon dioxide	44	-
17,89	Tetradecane	43, 57, 71, 85	<i>n</i> -Alkane
20,8	High MW, high BP oxygenated hydrocarbon	40, 57, 69, 97	Ester
20,95	High MW, high BP oxygenated hydrocarbon	71, 40, 57, 97	Ester
32,2	Didodecyl phthalate	40, 149, 207	Phthalate

Table D33: List of compounds and retention times found in the analysis of the red carpet after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
6,79	2,4-Dimethyl-1-heptene	43, 70, 57, 126	Branched alkene
8,01	Styrene	104, 78, 51	Aromatic
9,74	Benzaldehyde	105, 77, 40	Aromatic
10,11	α -Methylstyrene	118, 40, 105, 77	Aromatic
12,1	High MW, high BP hydrocarbon	69,43, 57, 71, 111	Isoparaffin
16,3	High MW, high BP hydrocarbon	69, 43, 57, 71, 111	Isoparaffin
17,05	Acetic acid ester	69, 43, 57, 71, 111	Ester
17,5	Eicosyne	69, 57, 71, 109, 41	Alkyne
17,35	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
20,89	High MW, high BP oxygenated hydrocarbon	69, 83, 57, 109, 41	Branched acetate
23,9	High MW, high BP oxygenated hydrocarbon	69, 83, 57, 109, 41	Branched acetate

Double-layered carpet black



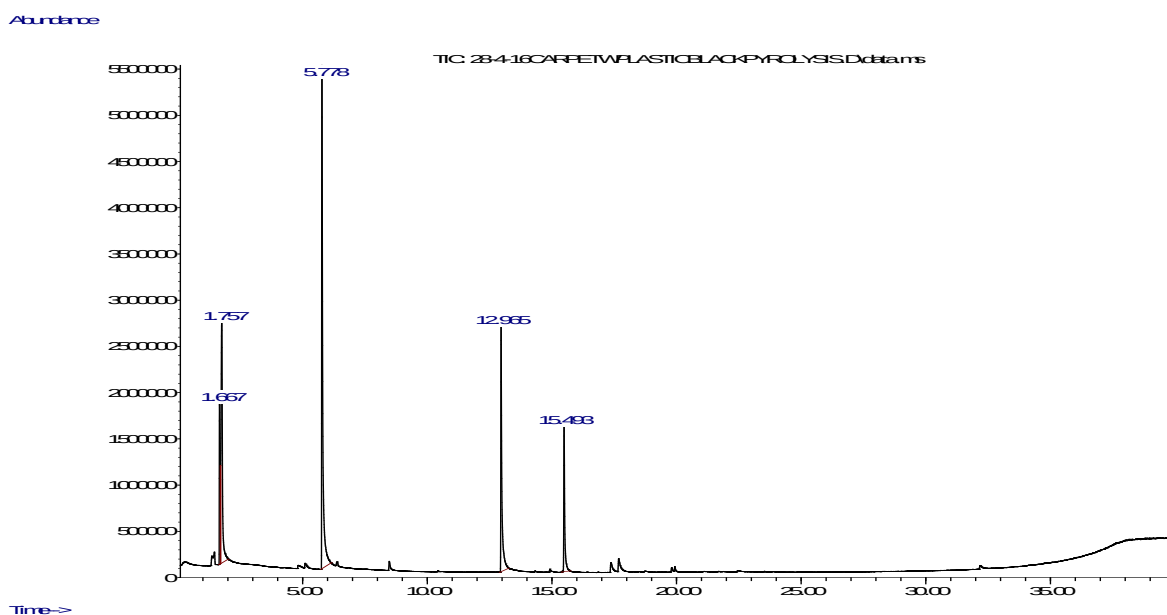


Figure D16: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) double-layered black carpet.

The compounds found in the analysis of the black carpet with additional plastic layer before and after burning and after pyrolysis are listed in **Tables D34, D35** and **D36**.

Table D34: List of compounds and retention times found in the analysis of the black double-layered carpet before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,43	Carbon dioxide	44	-
15,86	High MW, high BP hydrocarbon	40, 57, 71, 85, 113	Isoparaffin
16,66	High MW, high BP hydrocarbon	40, 57, 71, 85, 99	Isoparaffin
19,37	High MW, high BP hydrocarbon	57, 71, 43, 85, 99, 127	<i>n</i> -Alkane
20,21	High MW, high BP hydrocarbon	71, 40, 57, 85, 99, 127	Isoparaffin
22,5	High MW, high BP hydrocarbon	57, 71, 85, 43, 99, 127	<i>n</i> -Alkane
23,1	High MW, high BP hydrocarbon	40, 43, 57, 71, 85, 99	Isoparaffin
23,3	High MW, high BP hydrocarbon	40, 43, 57, 71, 85, 99	Isoparaffin

Table D35: List of compounds and retention times found in the analysis of the black double-layered carpet after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

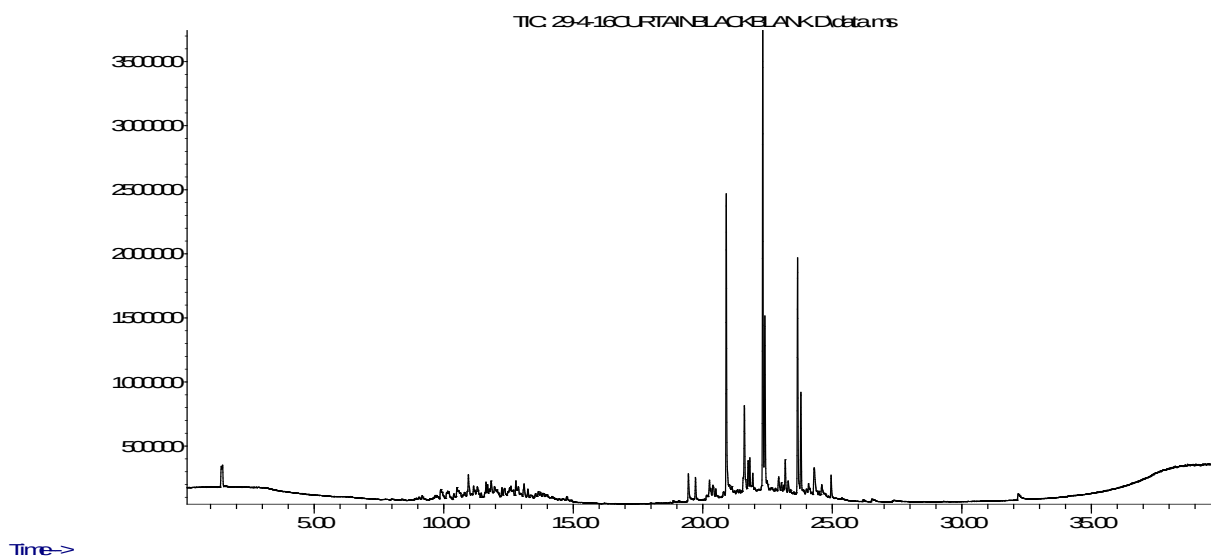
Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,39	Carbon dioxide	44	-
2,95	Benzene	78, 40, 55	Aromatic
6,78	2,4-Dimethyl-1-heptene	43, 70, 57, 85, 126	Isoparaffin
7,27	Ethylbenzene	91, 111, 51	Aromatic
7,98	Styrene	104, 75, 51	Aromatic
9,59	Benzaldehyde	105, 77, 51	Aromatic
10,1	α -Methylstyrene	118, 105, 78, 51	Aromatic
13,05	High MW, high BP oxygenated hydrocarbon	69, 43, 85, 125, 97	Branched alcohol
14,2	Naphthalene	128	PAH
16,4	Eicosene	69, 43, 71, 57, 111, 154	Alkene
17,06	High MW, high BP oxygenated hydrocarbon	69, 43, 57, 71, 125, 97	Ester
19,8	High MW, high BP oxygenated hydrocarbon	69, 57, 43, 71, 111, 153	Ester
22,8	High MW, high BP oxygenated hydrocarbon	69, 57, 43, 71, 111, 153	Ester
23,2	High MW, high BP oxygenated hydrocarbon	69, 57, 43, 71, 111, 153	Ester

Table D36: List of compounds and retention times found in the analysis of the black double-layered carpet after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,4	Carbon dioxide	44	-
1,66	Acetone	43, 58	Ketone
1,75	Acetone	43, 58	Ketone
5,77	Low MW, low BP hydrocarbon	83, 55, 97, 43	Isoparaffin
12,96	Medium MW, medium BP hydrocarbon	82, 138, 39	Isoparaffin
15,4	4-Acetyl-3-carene	43,135,178,105,77	Bicyclic Terpene

Curtain black

Abundance



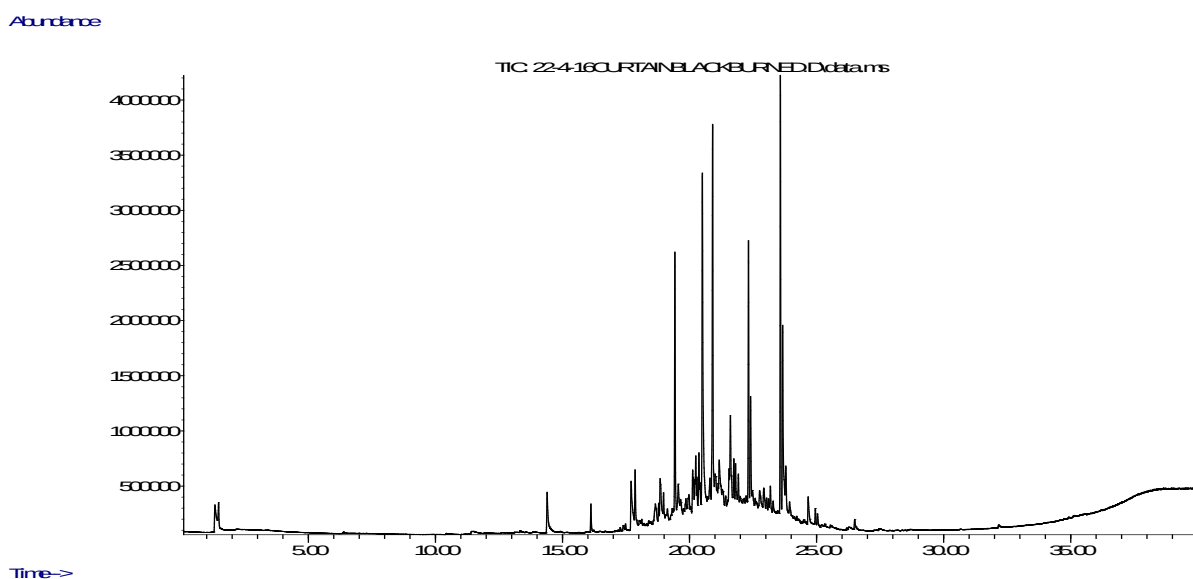


Figure D17 TICs of products produced from the analysis of the burned (bottom) and unburned (top).

The compounds found in the analysis of the black curtain before and after burning and after pyrolysis are listed in **Tables D36, D37** and **D38**.

Table D36: List of compounds and retention times found in the analysis of the black curtain before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,43	Carbon dioxide	44	-
19,44	High MW, high BP hydrocarbon	40, 57, 71, 85, 97	Isoparaffin
19,72	Butylated Hydroxytoluene	40, 205	Aromatic
20,63	Hexadecane	57, 71, 85, 113	<i>n</i> -Alkane
21,6	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	<i>n</i> -Alkane
22,32	Heptadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
22,4	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	<i>n</i> -Alkane
23,6	Nonadecane	57, 71, 43, 113	<i>n</i> -Alkane
23,8	High MW, high BP hydrocarbon	57, 71, 85, 43, 113	<i>n</i> -Alkane

Table D37: List of compounds and retention times found in the analysis of the black curtain after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,39	Carbon dioxide	44	-
17,7	Biphenyl	154, 40, 76, 115	Aromatic
18,79	High MW, high BP hydrocabron	57, 43, 71, 85, 154	Isoparaffin
19,4	Hexadecane	57, 43, 71, 85	<i>n</i> -Alkane
20,92	Nonadecane	57, 71, 43, 85, 166	<i>n</i> -Alkane
21,6	High MW, high BP hydrocabron	57, 71, 43, 85, 113	Isoparaffin
22,32	Nonadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
23,58	Heptadecanal	55, 83, 97, 43, 111, 139	Aldehyde
23,66	Anthracene derivative	178, 57, 85, 152	PAH

Table D38: List of compounds and retention times found in the analysis of the black curtain after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbondioxide	44	-
8,9-14,9	Impurities from glass can		
20-24	High MW, high BP hydrocarbons	57, 71, 43, 85	Isoparaffins
32,1	1,2-Benzenedicarboxylic acid diisooctylester	149, 57, 43, 71, 83, 207	Phthalate

Vinyl flooring kitchen-use

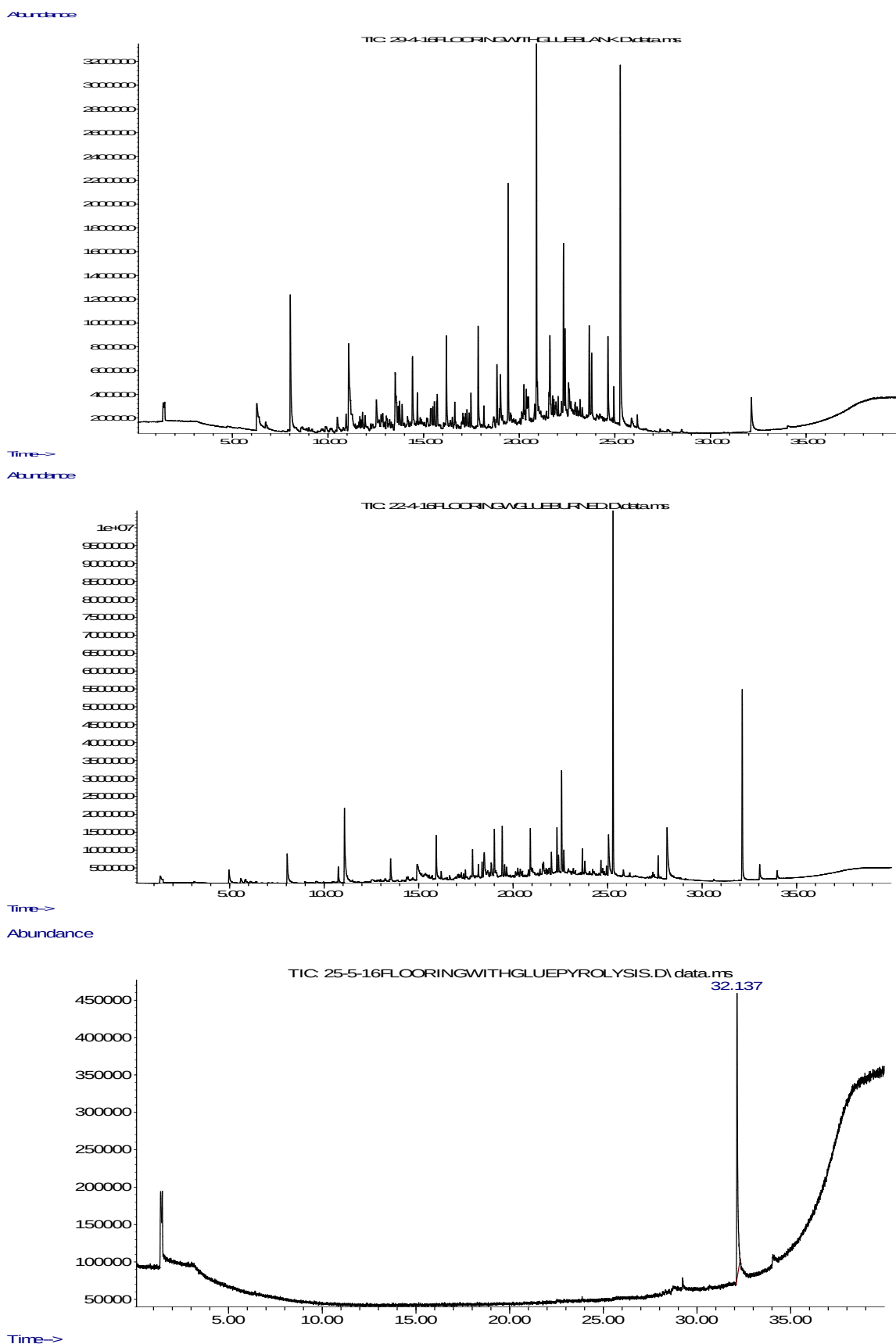


Figure D18: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) vinyl flooring for kitchen use.

The compounds found in the analysis of the linoleum flooring before and after burning and after pyrolysis are listed in **Tables D39, D40** and **D41**.

Table D39: List of compounds and retention times found in the analysis of the vinyl flooring for living room use before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
8,06	Cyclohexanone	55, 43, 98, 69	Cycloalkane
11,15	Low MW, low BP oxygenated hydrocarbon	57, 41, 71, 83	Branched alcohol
12,55	Low MW, low BP oxygenated hydrocarbon	57, 41, 71, 85	Aldehyde
13,5	Medium MW, medium BP oxygenated hydrocarbon	43, 70, 57, 113	Ester
14,4	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
14,67	2,6-Dimethylundecane	57, 43, 71, 85, 98	Isoparaffin
16,1	Tridecane	57, 43, 71, 85, 112	<i>n</i> -Alkane
17,85	Tetradecane	57, 43, 71, 85, 112	<i>n</i> -Alkane
18,84	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
19,4	Pentadecane	57, 43, 71, 85, 147	<i>n</i> -Alkane
20,8	Hexadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
22,3	Heptdecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
23,67	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
24,65	Phthalic acid butyl tetradecyl ester	149, 57, 104, 223	Phthalate
32,11	Di- <i>n</i> -octylphthalate	44, 149, 70, 207, 104	Phthalate

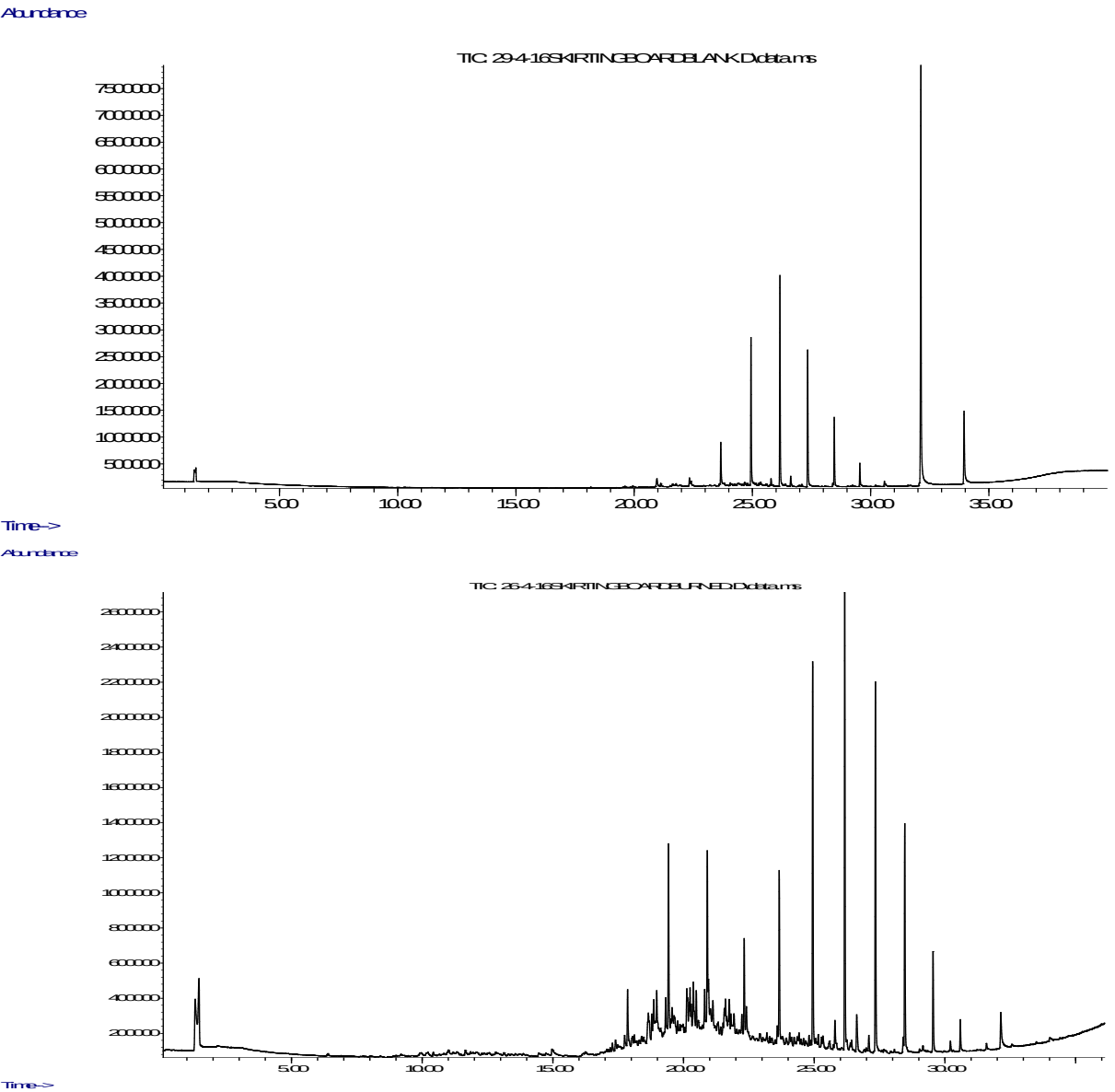
Table D40: List of compounds and retention times found in the analysis of the vinyl flooring for living room use after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,41	Carbon dioxide	44	-
11,1	2-Ethyl-1-hexanol	57, 41, 71, 83	Branched alcohol
13,5	Medium MW, medium BP oxygenated hydrocarbon	43, 70, 112	Ester
15,9	6,6-Dimethyl-Bicyclo[3.1.1]hept-2-ene-2-ethanol	105, 40, 91, 79, 133	Bicyclic terpene
17,8	High MW, high BP hydrocarbon	57, 43, 71, 85, 154	Isoparaffin
19	Chlorododecane	57, 91, 43, 69, 105	Chloroalkane
19,4	High MW, high BP hydrocarbon	57,43, 71, 85, 147, 281	Isoparaffin
20,9	High MW, high BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
22,05	Chlorotetradecane	57, 43, 91, 71, 105	Chloroalkane
22,32	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
22,6	Benzoate derivative	105, 70, 41	Aromatic ester
23,65	High MW, high BP hydrocarbon	57, 71, 43, 85, 111	Isoparaffin
24,65	Phthalate derivative	149, 40, 57, 104	Phthalate
25,25	Hexadecanoic acid methylester	74, 87, 43, 143, 227	FAME
32,1	1,2-Benzenedicarboxylic acid diisooctylester	149, 57, 104, 279	Phthalate

Table D41: List of compounds and retention times found in the analysis of the vinyl flooring for living room use after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
32,15	Di-n-octylphthalate	44, 149, 70, 207, 104	Phthalate

Skirting board



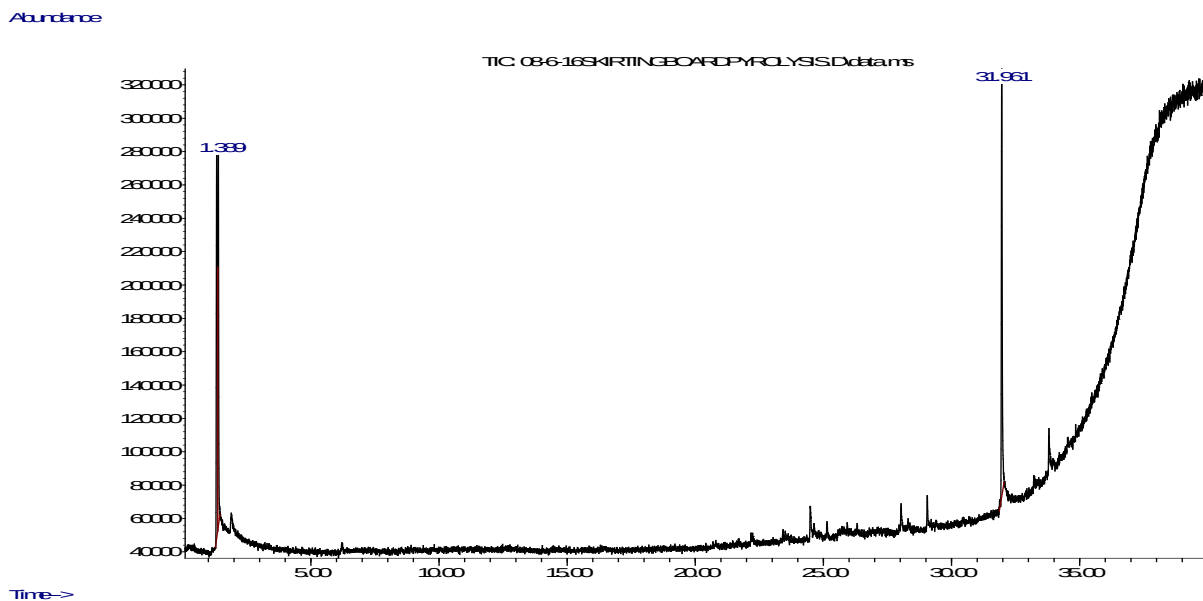


Figure D19: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) skirting board.

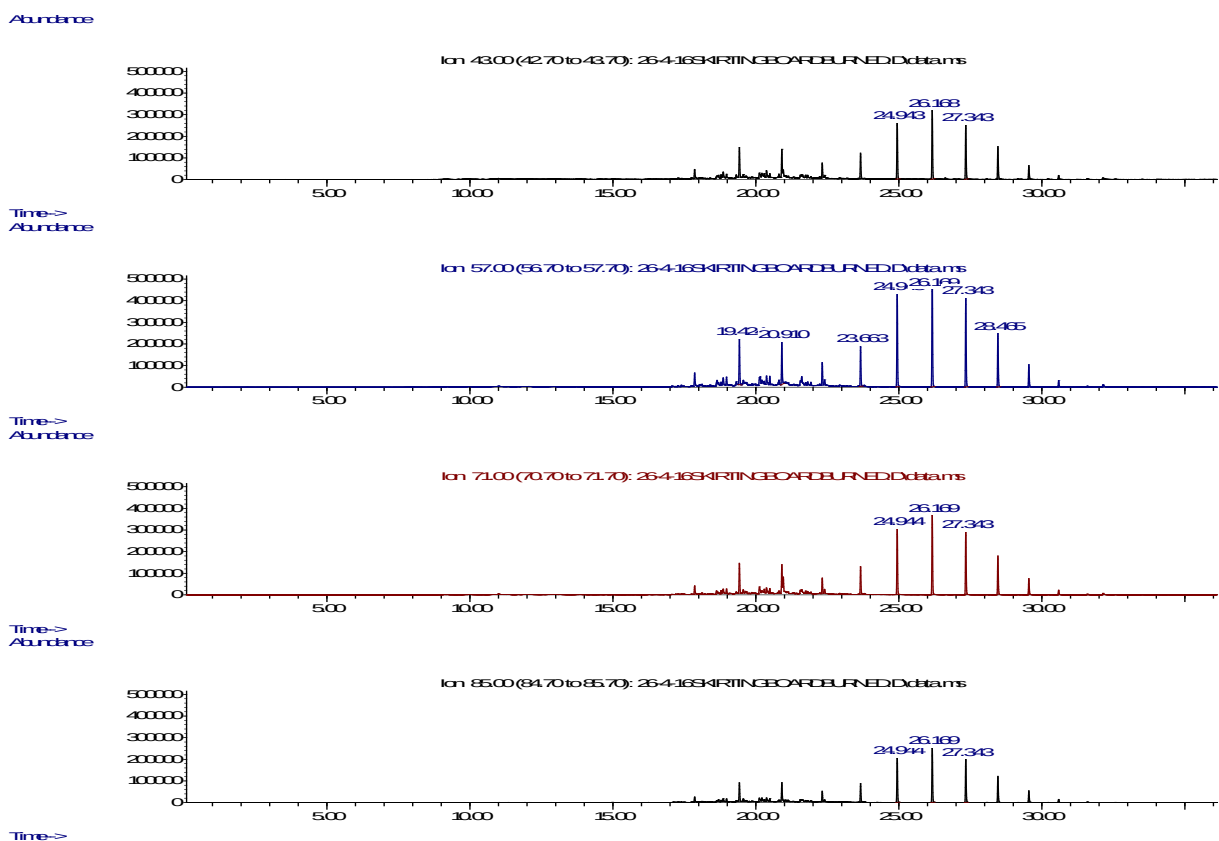


Figure D20: EICs for alkanes, ions 43,57,71 and 85, produced from the analysis of the burned skirting board.

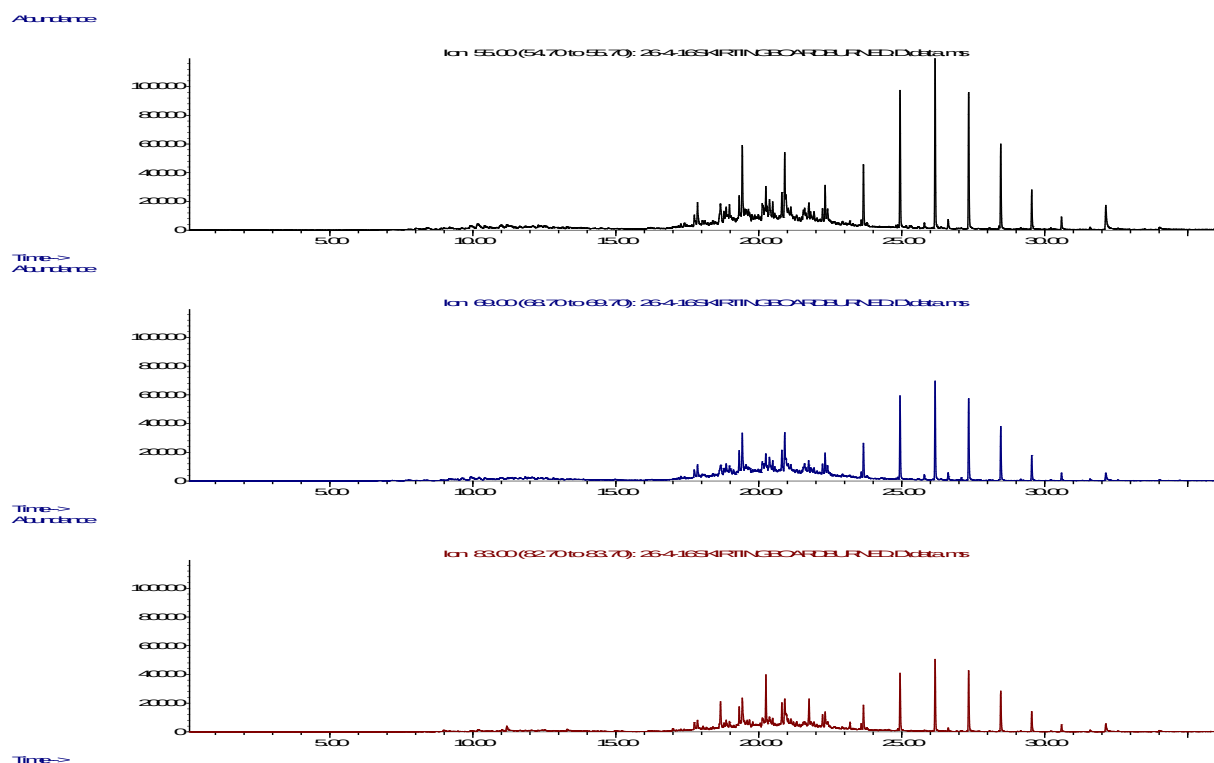


Figure D21: EICs for alicyclics and olefinics, ions 55, 69 and 83, produced from the analysis of the burned skirting board.

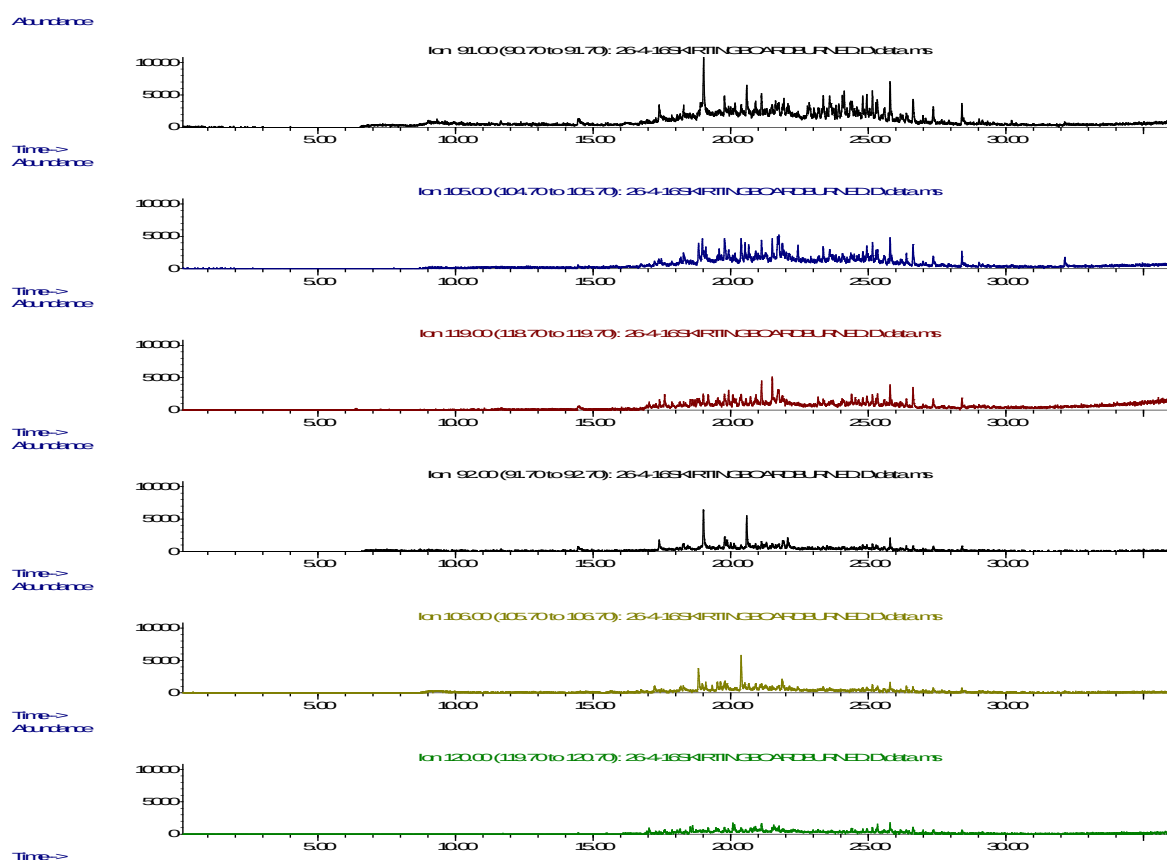


Figure D22: EICs for aromatics (alkylbenzenes), ions 91, 105, 119, 92, 106 and 120, produced from the analysis of the burned skirting board.

The compounds found in the analysis of the skirting board before and after burning and after pyrolysis are listed in **Tables D42, D43** and **D44**.

Table D42: List of compounds and retention times found in the analysis of the skirting board before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
23,65	Nonadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
24,95	Decane	57, 71, 43, 85, 113, 141	<i>n</i> -Alkane
26,15	Eicosane	57, 71, 43, 85, 113, 141	<i>n</i> -Alkane
27,34	Heneicosane	57, 71, 43, 85, 113, 141	<i>n</i> -Alkane
28,45	Heneicosane	57, 71, 43, 85, 113, 141	<i>n</i> -Alkane
29,5	Heptacosane	57, 71, 43, 85, 207, 113	<i>n</i> -Alkane
33,1	1,2-Benzenedicarboxylic acid diisooctylester	149, 57, 104, 276	Phthalate

Table D43: List of compounds and retention times found in the analysis of the skirting board after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
17,85	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
19,4	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
20,9	High MW, high BP hydrocarbon	57, 43, 71, 85, 99	<i>n</i> -Alkene
22,2	High MW, high BP oxygenated hydrocarbon	40, 57, 69, 83, 97, 125	Branched alcohol
22,34	High MW, high BP hydrocarbon	57, 71, 43, 85, 97	Isoparaffin
23,6	Octadecane	57, 71, 43, 85, 113	<i>n</i> -Alkene
24,95	Nonadecane	57, 71, 43, 85, 113	<i>n</i> -Alkene
26,15	Eicosane	57, 71, 43, 85, 113	<i>n</i> -Alkene
27,3	Heneicosane	57, 71, 43, 85, 113	<i>n</i> -Alkene
30,3	Heptacosane	57, 71, 43, 85, 113	<i>n</i> -Alkene
32,1	Diisooctyl phthalate	44, 149, 207, 70, 104	Phthalate

Table D44: List of compounds and retention times found in the analysis of the skirting board after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,36	Carbon dioxide	44	-
32	Di- <i>n</i> -octylphthalate	44, 149, 70, 207, 104	Phthalate

Wallpaper

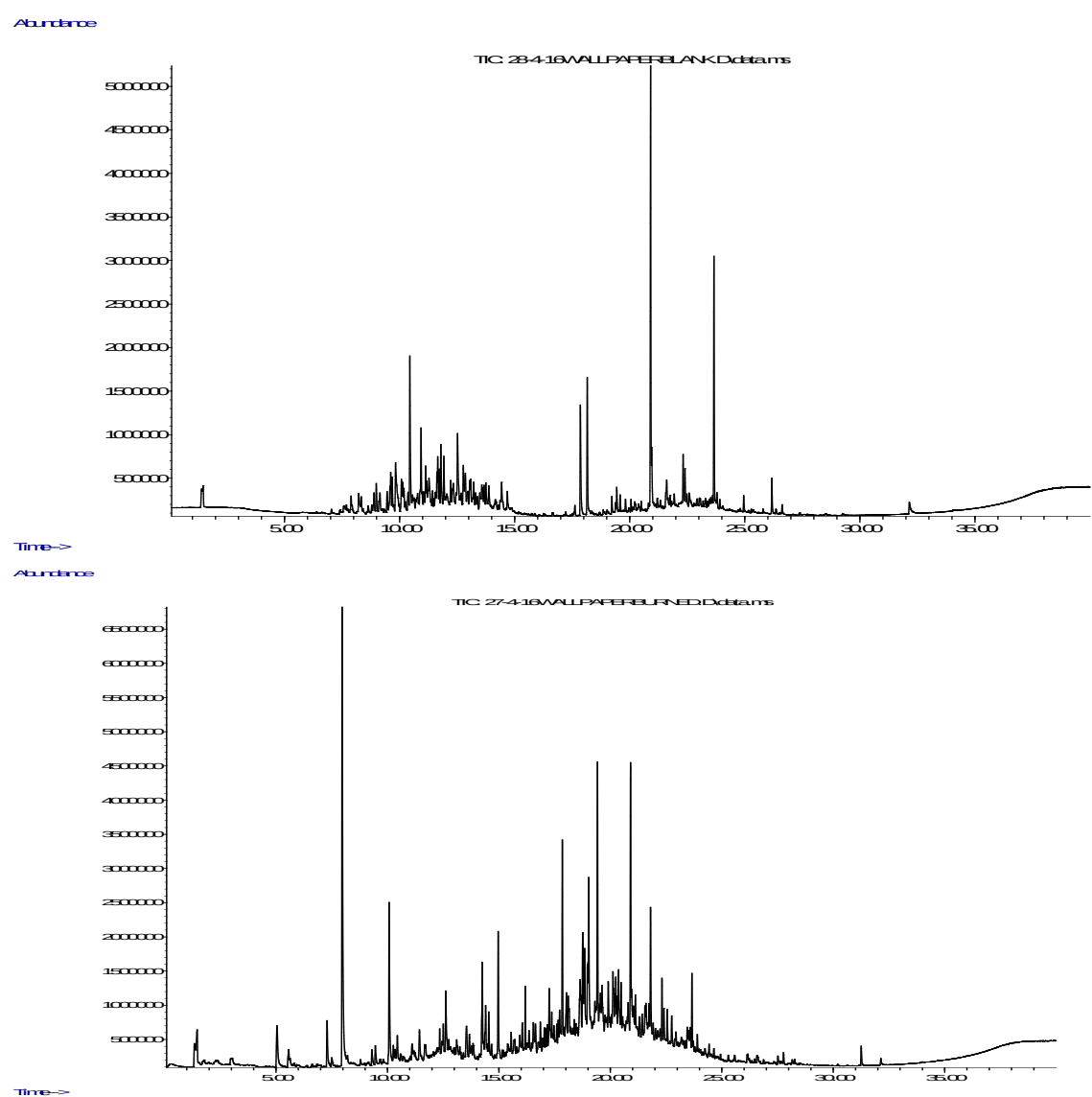


Figure D23: TICs of products produced from the analysis of the burned (bottom) and unburned (top) wallpaper.

The compounds found in the analysis of the wallpaper before and after burning are listed in **Tables D45** and **D46**.

Table D45: List of compounds and retention times found in the analysis of the wallpaper before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
7,8	Low MW, low BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
8,25	2,4-Dimethylhexane	40, 43, 57, 85, 105	Isoparaffin
8,35	Low MW, low BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
8,95	Low MW, low BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
9,61	Low MW, low BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
9,65	Low MW, low BP hydrocarbon	57, 43, 71, 85, 113	Isoparaffin
10,4	Decane	57, 43, 71, 85	<i>n</i> -Alkane
10,9	Low MW, low BP hydrocarbon	71, 57, 43, 113, 85	Isoparaffin
11,1	Low MW, low BP cyclic hydrocarbon	83, 55, 97, 140	Cycloalkane
11,6	Low MW, low BP hydrocarbon	57, 43, 85, 71, 111	Isoparaffin
12,8	Low MW, low BP oxygenated hydrocarbon	57, 43, 71, 81, 99, 149	Aldehyde
17,8	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
18,1	Longifolene	161, 91, 107, 41, 55, 119, 189	Tricyclic terpene
20,8	Hexadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
22,3	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
22,4	Heptadecane	57, 71, 43, 85, 109, 113	<i>n</i> -Alkane
23,6	Octadecane	57, 71, 43, 85, 109	<i>n</i> -Alkane
24,9	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin

Table D46: List of compounds and retention times found in the analysis of the wallpaper after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
5,05	Toluene	91 ,40, 55	Aromatic
7,28	Ethylbenzene	91, 109, 40, 65	Aromatic
8	Styrene	104, 78, 51	Aromatic
10,1	α -Methylstyrene	118, 104, 78, 51	Aromatic
12,63	Medium MW, medium BP oxygenated hydrocarbon	57, 40, 81, 109	Aldehyde
14,25	Medium MW, medium BP oxygenated hydrocarbon	128, 55, 69, 83	Ester
14,4	Medium MW, medium BP hydrocarbon	57, 43, 71, 85, 138	Isoparaffin
14,55	Decanal	57, 43, 41, 70, 82, 112	Aldehyde
16,1	High MW, high BP hydrocarbon	57, 43, 71, 85, 131	Isoparaffin
17,85	Nonadecane	57, 43, 71, 85, 131	<i>n</i> -Alkane
18,8	High MW, high BP hydrocarbon	57, 43, 71, 152, 85	Isoparaffin
19,4	High MW, high BP hydrocarbon	57, 43, 71, 85, 131	Isoparaffin
21,8	1,1'-(1,3-propanediyl)bis-benzene	92, 196, 104, 57	Aromatic
22,3	High MW, high BP hydrocarbon	57, 43, 71, 85, 131	Isoparaffin

Gas Pipe

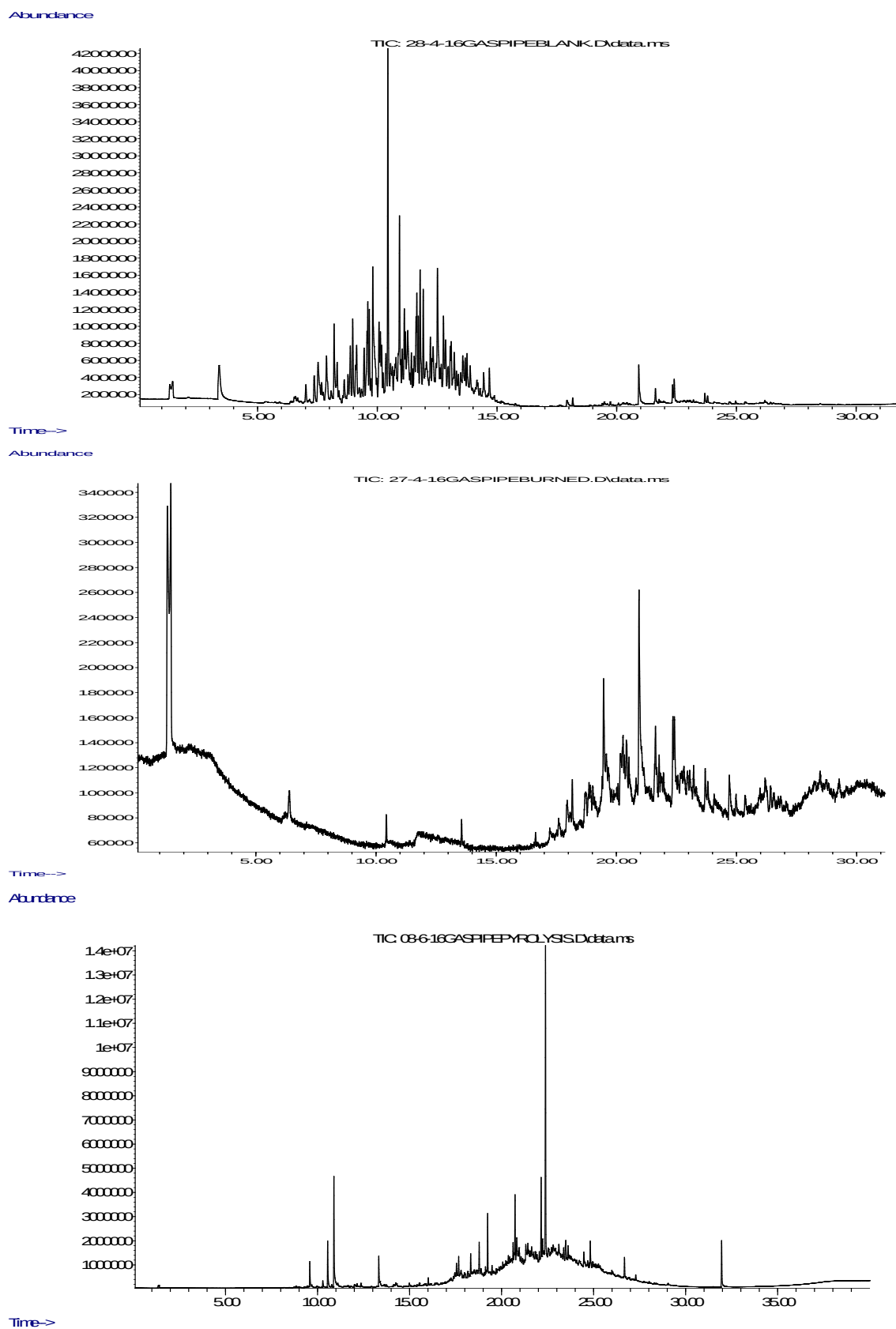


Figure D24: TICs of products produced from the analysis of the burned (middle), unburned (top) and pyrolysed (bottom) gas pipe.

The compounds found in the analysis of the gas pipe before and after burning and after pyrolysis are listed in **Tables D47, D48** and **D49**.

Table D47: List of compounds and retention times found in the analysis of the gas pipe before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
No Peaks			

Table D48: List of compounds and retention times found in the analysis of the gas pipe after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,37	Carbon dioxide	44	-
19,47	High MW, high BP hydrocarbons	40, 57, 71, 97, 206	Isoparaffin
20,95	High MW, high BP hydrocarbons	40, 57, 71, 83, 97, 207	Isoparaffin
21,6	High MW, high BP hydrocarbons	40, 57, 71, 97, 207	Isoparaffin

Table D49: List of compounds and retention times found in the analysis of the gas pipe after pyrolysis, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-pyrolysis			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
9,58	Low MW, low BP cyclic hydrocarbon	55, 71, 41, 83, 112	Cycloalkane
10,56	Low MW, low BP hydrocarbon	57, 43, 99	Isoparaffin
10,88	Low MW, low BP hydrocarbon	57, 43, 71, 83	Isoparaffin
13,3	Medium MW, medium BP oxygenated hydrocarbon	43, 70, 57, 83, 112	Ester
18,31	Diphenylmethane	167, 91, 40, 65	Aromatic
18,78	Hexadecanoic acid ethylester	57, 88, 101, 131	Ester
19,3	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
20,7	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
22,1	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
22,4	Benzoate derivative	105, 70, 41	Aromatic ester
31,9	Di- <i>n</i> -octylphthalate	149, 57, 104, 279	Phthalate

Wood composite

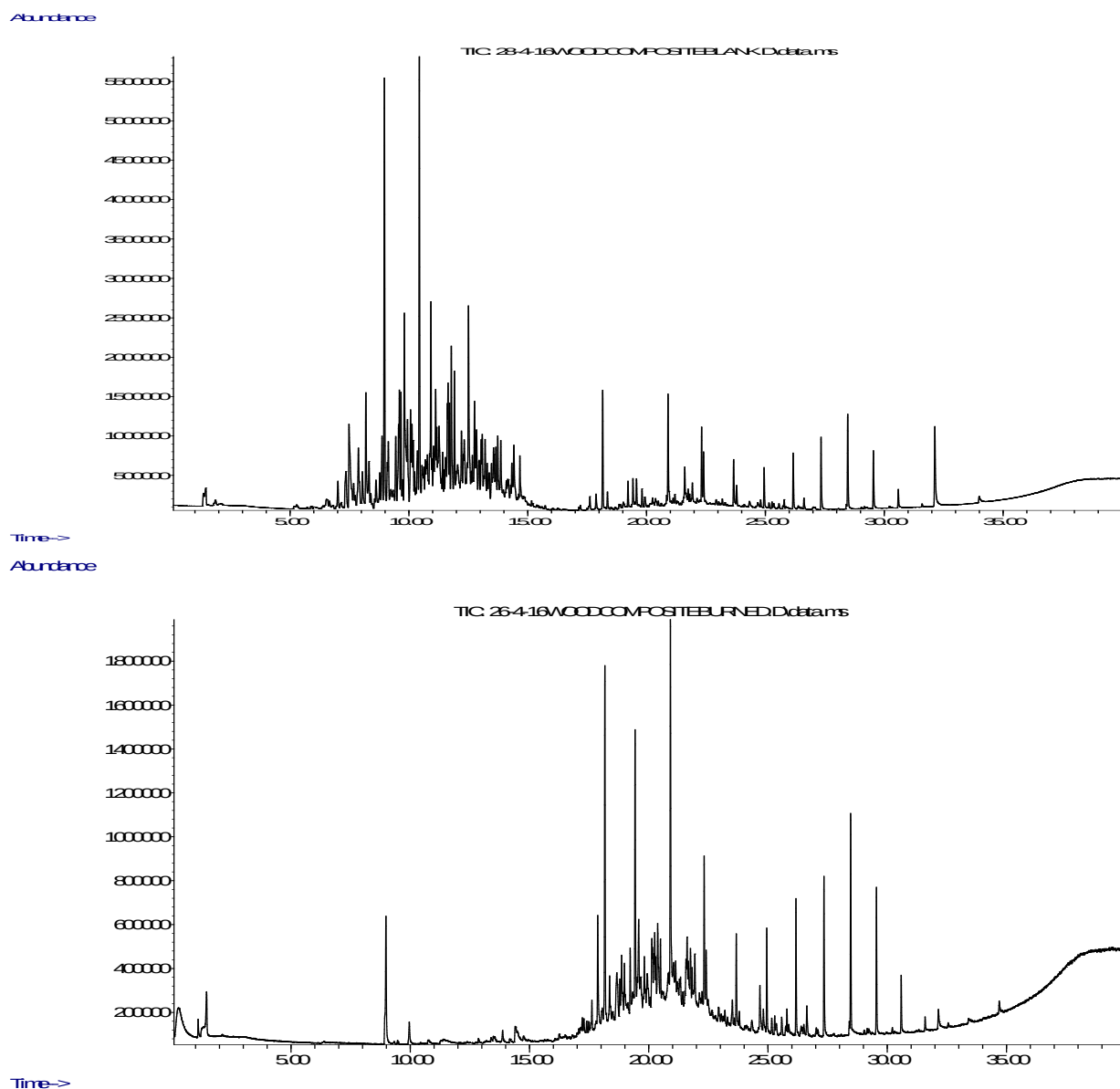


Figure D25: TICs of products produced from the analysis of the burned (bottom) and unburned (top) wood composite.

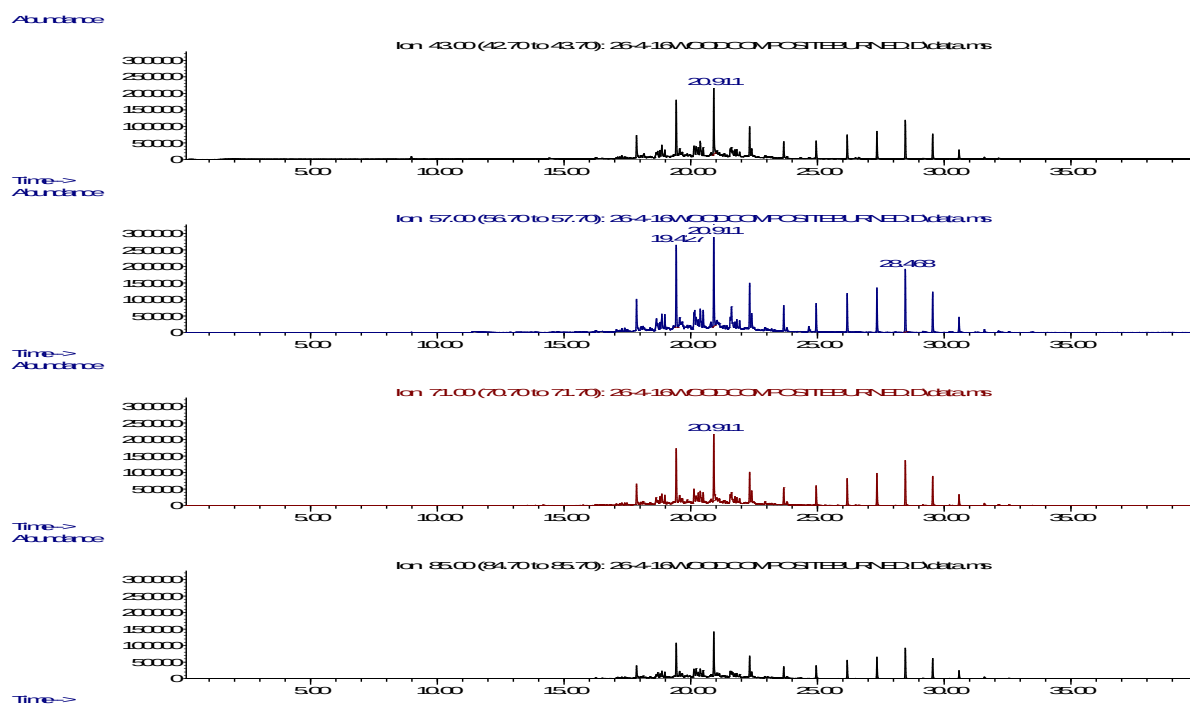


Figure D26: EICs for alkanes, ions 43, 57, 71 and 85, produced from the analysis of the burned wood composite.

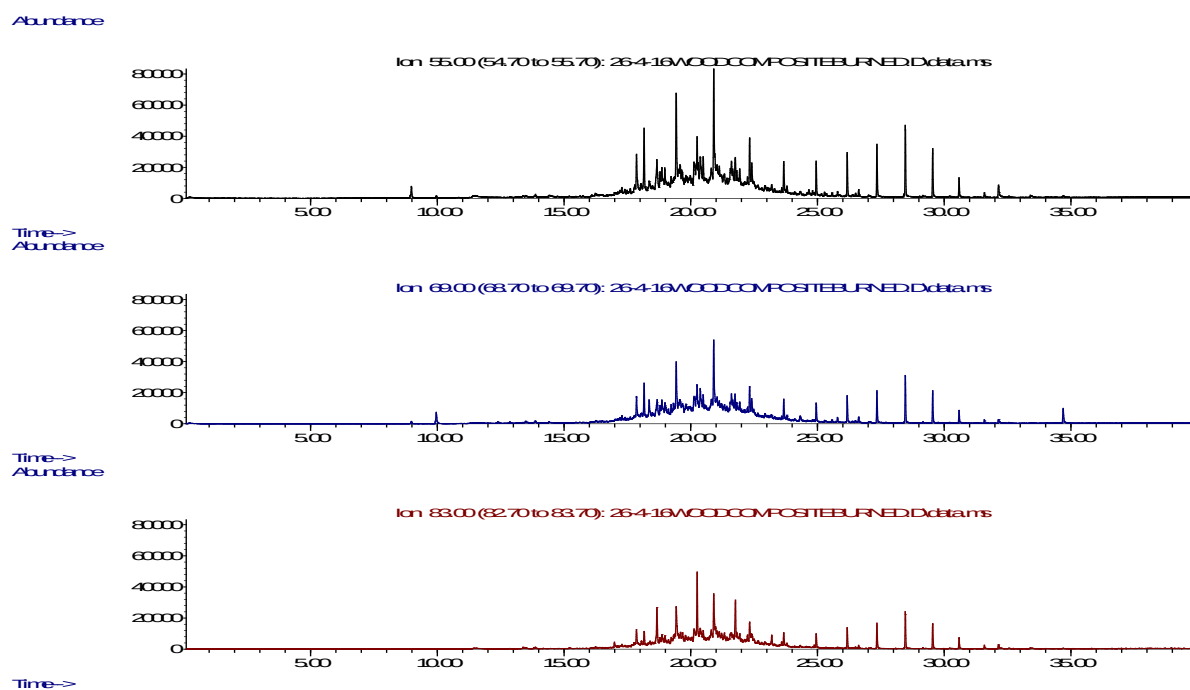


Figure D27: EICs for alicyclics and olefinics, ions 55, 69 and 83, produced from the analysis of the burned wood composite.

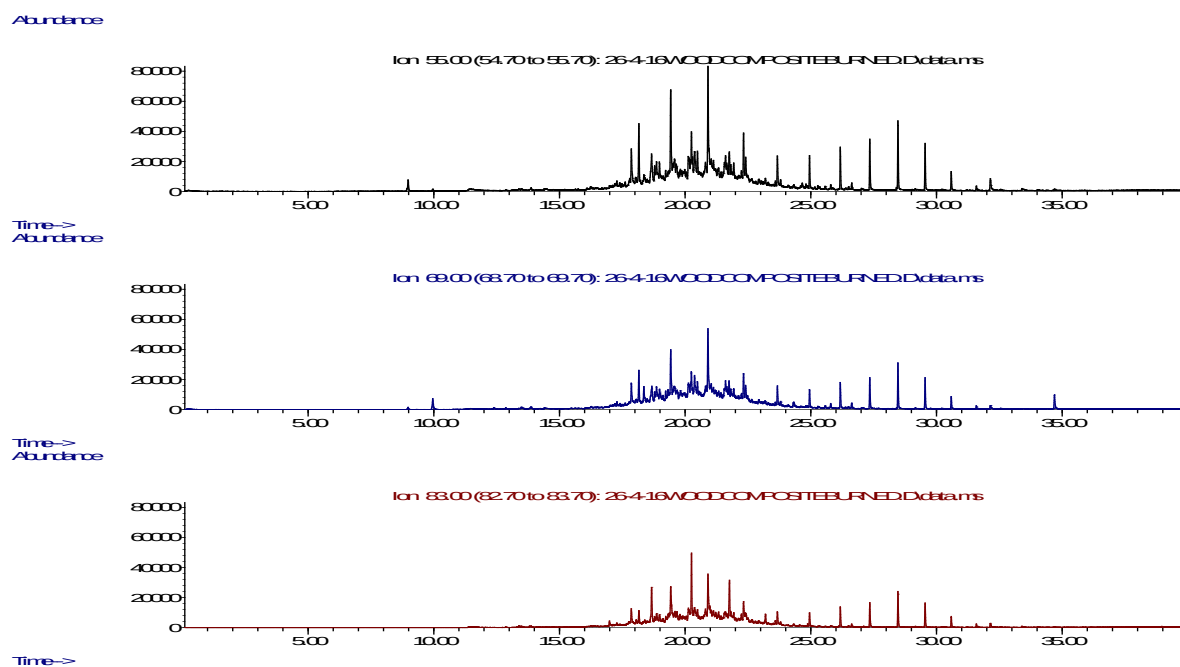


Figure D28: EICs for aromatics (alkylbenzenes), ions 91, 105, 119, 92, 106 and 120, produced from the analysis of the burned wood composite.

The compounds found in the analysis of the wood composite before and after burning are listed in **Tables D50** and **D51**.

Table D50: List of compounds and retention times found in the analysis of the wood composite before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,4	Carbon dioxide	44	-
7	Low MW, low BP cyclic hydrocarbon	111, 69, 40	Cycloalkane
7,35	Low MW, low BP hydrocarbon	43, 57, 71, 91	Isoparaffin
7,48	p-Xylene	91, 105, 40, 65	Aromatic
7,87	Low MW, low BP cyclic hydrocarbon	97, 55, 126	Cycloalkane
8,1	Nonane	57, 43, 85, 128	n-Alkane
8,9	α-Pinene	93, 78, 57, 39, 121	bicyclic terpene
9,1	Medium MW, medium BP hydrocarbon	57, 43, 71, 98, 125	Isoparaffin
9,4	Medium MW, medium BP hydrocarbon	57, 43, 71, 91	Isoparaffin
9,6	Medium MW, medium BP hydrocarbon	57, 43, 71, 98	Isoparaffin
9,8	Medium MW, medium BP hydrocarbon	57, 71, 85, 43, 112, 142	Isoparaffin
10	Medium MW, medium BP cyclic hydrocarbon	97, 55, 140	Cycloalkane
10,4	Decane	57, 43, 71, 85, 142	n-Alkane
10,9	Medium MW, medium BP hydrocarbon	71, 57, 43, 113	Isoparaffin
11,1	Medium MW, medium BP cyclic hydrocarbon	83, 55, 140	Cycloalkane
11,6	Naphthalene derivative	138, 67, 95, 41	PAH
11,6	Medium MW, medium BP hydrocarbon	57, 43, 85, 71, 111	Isoparaffin
11,9	Medium MW, medium BP hydrocarbon	71, 57, 43, 112	Isoparaffin
12,5	Undecane	57, 43, 71, 85	n-Alkane
12,7	Naphthalene derivative	81, 152, 95, 55	PAH
12,8	High MW, high BP hydrocarbon	57, 43, 71, 85, 113, 149	Isoparaffin
18,1	Longifolene	161, 91, 189, 119, 41	Tricyclic terpene
19,2	Naphthalene derivative	161, 105, 41, 79, 133, 204	PAH
19,4	High MW, high BP hydrocarbon	57, 71, 43, 85	Isoparaffin
19,5	Naphthalene derivative	105, 161, 40, 204, 81	PAH
20,9	Hexadecane	57, 71, 43, 85	Isoparaffin
21,6	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
22,3	Heptadecane	57, 71, 43, 85	n-Alkane
23,6	Octadecane	57, 71, 43, 85	n-Alkane
24,9	Nonadecane	57, 71, 43, 85	n-Alkane
26,1	Eicosane	57, 71, 43, 85	n-Alkane
27,3	Heneicosane	57, 71, 43, 85	n-Alkane
28,4	Docosane	57, 71, 43, 85	n-Alkane
29,5	Tetracosane	57, 71, 43, 85	n-Alkane
30,5	Heptacosane	57, 71, 43, 85, 207	n-Alkane
32,1	1,2-Benzenedicarboxylic acid diisooctylester	149, 57, 279, 207	Phthalate

Table D51: List of compounds and retention times found in the analysis of the wood composite after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,44	Carbon dioxide	44	-
8,96	α -Pinene	93, 140, 77, 121	Bicyclic terpene
17,61	Naphthalene derivative	40, 105, 161, 81	PAH
17,87	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
18,65	High MW, high BP oxygenated hydrocarbon	40, 57, 71, 97	Aldehyde
19,2	Naphthalene derivative	40, 161, 105, 69, 133, 204	PAH
19,42	Nonadecane	57, 43, 71, 85	<i>n</i> -Alkane
19,81	High MW, high BP polycyclic hydrocarbon	40, 161, 69, 105, 204	PAH
20,1	High MW, high BP hydrocarbon	57, 71, 43, 85, 111	Isoparaffin
20,5	High MW, high BP hydrocarbon	57, 43, 85, 99, 111	Isoparaffin
22,32	High MW, high BP hydrocarbon	57, 43, 71, 85, 99, 111	Isoparaffin
23,67	High MW, high BP hydrocarbon	57, 43, 71, 85, 99, 111	Isoparaffin
24,67	1,2-Benzenedicarboxylic acid butyloctyl ester	149, 40, 104, 78	Phthalate
24,95	High MW, high BP hydrocarbon	57, 43, 71, 85	Isoparaffin
26,2	High MW, high BP hydrocarbon	57, 71, 43, 85, 113, 207	<i>n</i> -Alkane
27,35	High MW, high BP hydrocarbon	57, 71, 43, 85, 113, 207	<i>n</i> -Alkane
28,48	High MW, high BP hydrocarbon	57, 71, 43, 85, 113, 207	<i>n</i> -Alkane
29,55	High MW, high BP hydrocarbon	57, 71, 43, 85, 113, 207	<i>n</i> -Alkane

Electric cable with three conductors

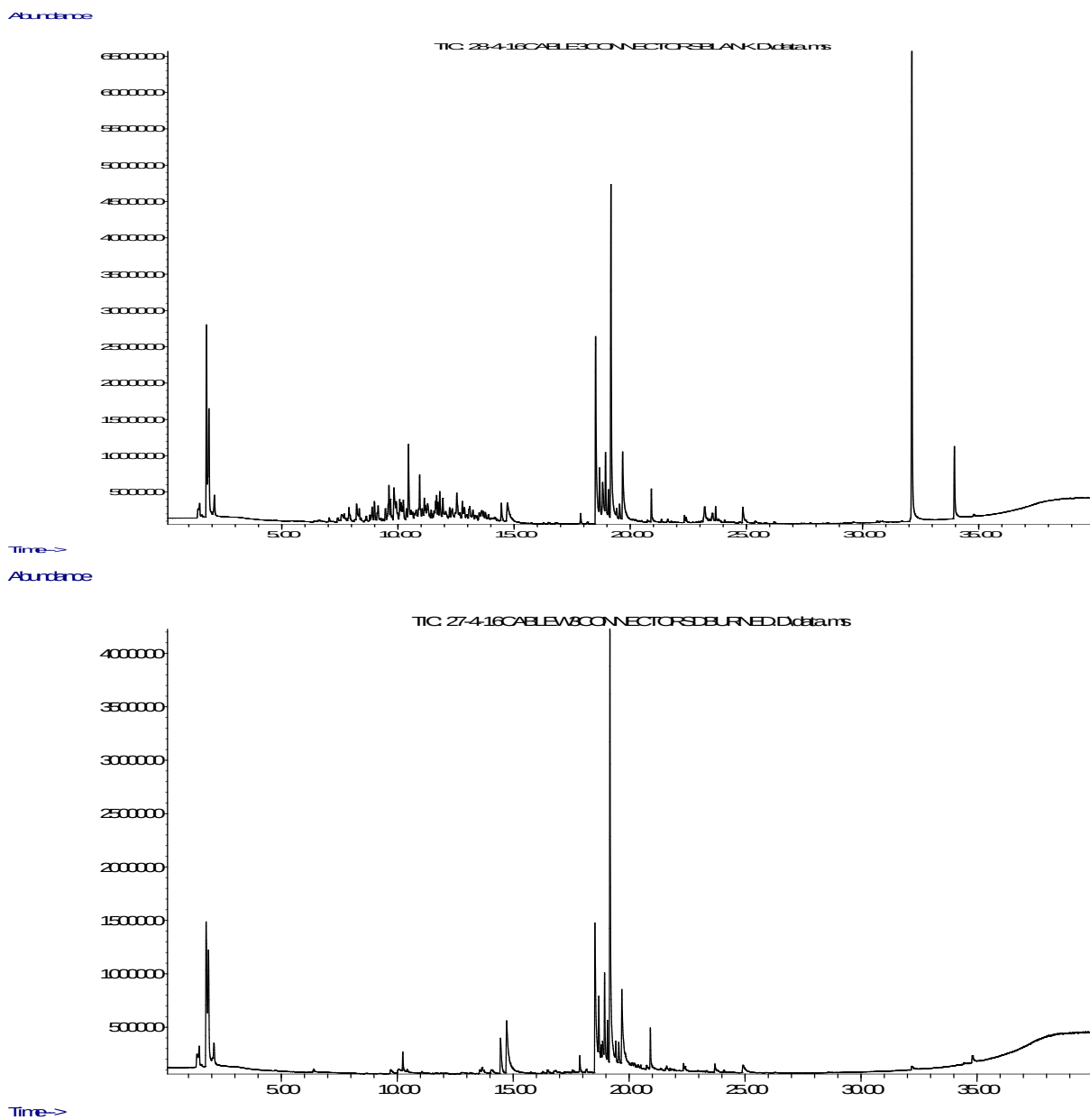


Figure D29: TICs of products produced from the analysis of the burned (bottom) and unburned (top) electrical cable with three conductors.

The compounds found in the analysis of the cable with there conductors before and after burning are listed in **Tables D52** and **D53**.

Table D52: List of compounds and retention times found in the analysis of the electric cable with three conductors before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
1,78	Acetone	43, 59	Ketone
10,45	Decane	57, 43, 71, 85, 142	<i>n</i> -Alkane
10,9	Medium MW, medium BP hydrocarbon	71, 57, 43, 113	Isoparaffin
18,67	2,4-Dimethylquinoline	157, 115, 40, 142	Heterocyclic aromatic compound
18,94	Naphthol derivative	158, 43, 128, 91, 179	Heterocyclic aromatic compound
19,6	High MW, high BP oxygenated cyclic hydrocarbon	145, 163, 43, 115, 91	Aromatic
20,9	Hexadecane	57, 43, 71, 85, 113, 147	<i>n</i> -Alkane
23,2	1,2-Benzenedicarboxylic acid diisooctylester	40, 149, 57, 70, 167, 104	Phthalate
24,85	Benzoate derivative	40, 105, 77, 140	Aromatic

Table D53: List of compounds and retention times found in the analysis of the electric cable with three conductors after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
1,78	Acetone	43, 59	Ketone
14,47	Medium MW, medium BP oxygenated hydrocarbon	71, 40, 57, 127	Branched alcohol
14,75	Medium MW, medium BP hydrocarbon	43, 57, 71, 97, 140	Isoparaffin
18,55	1,1'-(1,4-phenylene)bis-Ethanone	147, 91, 43, 119	Aromatic
18,7	2,4-Dimethylquinoline	157, 40, 115, 91, 63	heterocyclic aromatic compound
18,95	Napththol derivative	158, 43, 128, 91, 179	heterocyclic aromatic compound
19,2	Benzoate derivative	145, 43, 115, 91, 65	Aromatic
20,91	Hexadecane	57, 43, 71, 85, 147	n-Alkane

Paint solvent based

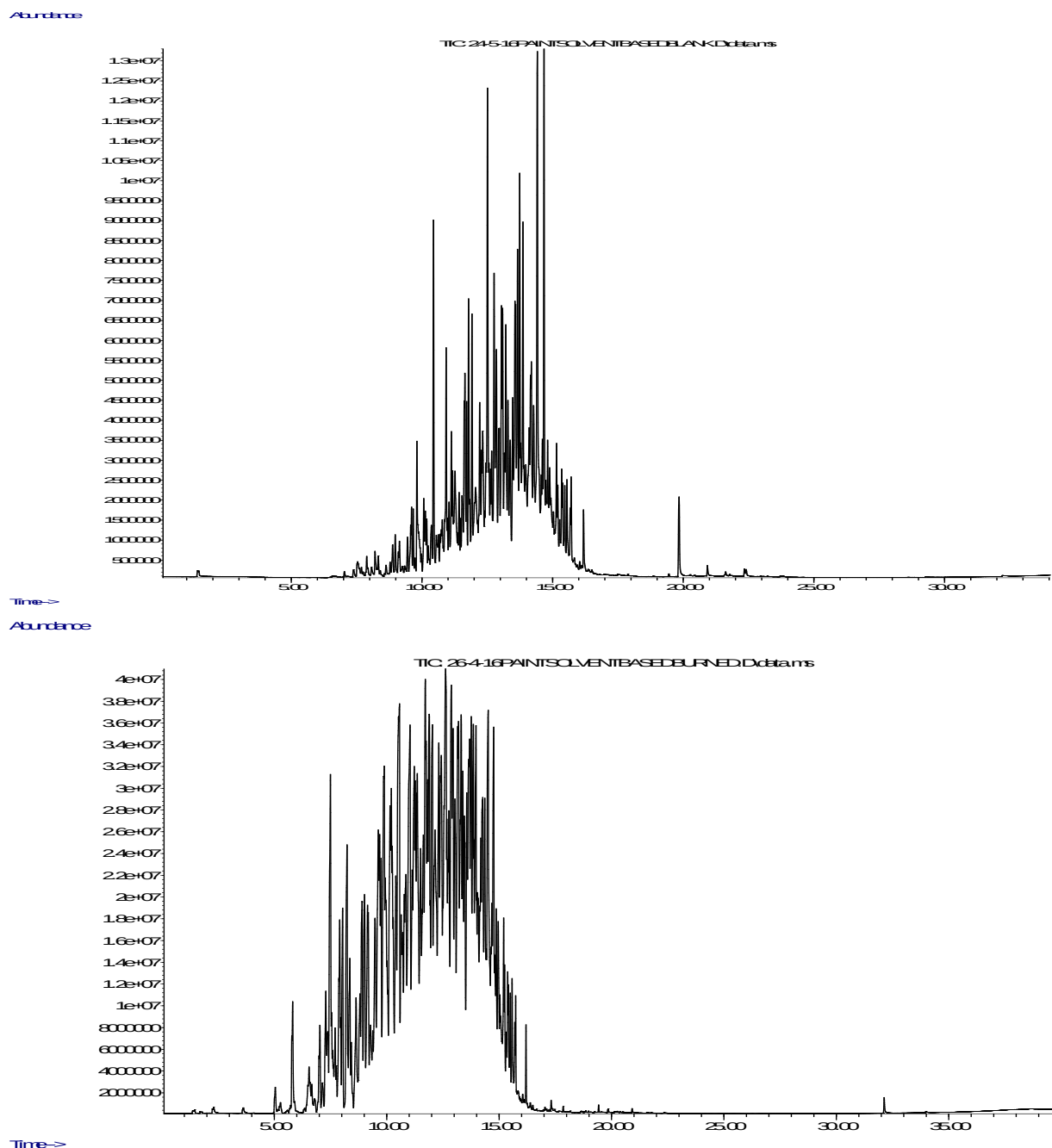


Figure D30: TICs of products produced from the analysis of the burned (bottom) and unburned (top) solvent-based paint.

The compounds found in the analysis of the solvent-based paint before and after burning are listed in **Tables D54** and **D55**.

Table D54: List of compounds and retention times found in the analysis of the solvent-based paint before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
7,39	Benzoate derivative	40, 91, 71, 07	Aromatic Ester
7,6	p-Xylene	91, 40, 104, 69, 207	Aromatic
8,1	o-Xylene	91, 40, 104, 207	Aromatic
8,2	Low MW, low BP oxygenated hydrocarbon	43, 57, 85, 67, 16	Branched alcohol
9,8	Low MW, low BP hydrocarbon	57, 85, 71, 43, 112, 142	Isoparaffin
11,25	Low MW, low BP oxygenated hydrocarbon	57, 71, 85, 127	Branched alcohol
11,9	Low MW, low BP oxygenated hydrocarbon	57, 71, 85, 128	Branched alcohol
12,5	Low MW, low BP oxygenated hydrocarbon	57, 43, 71, 85, 111	Branched alcohol
13,05	Medium MW, medium BP hydrocarbon	57, 71, 43, 85, 127	Isoparaffin
13,7	Medium MW, medium BP hydrocarbon	57, 43, 71, 85, 138	Isoparaffin
14,4	Dodecane	57, 43, 71, 85	n-Alkane
19,8	High MW, high BP oxygenated hydrocarbon	57, 43, 127, 99	Ester

Table D55: List of compounds and retention times found in the analysis of the solvent-based paint after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,42	Carbon dioxide	44	-
5	Toluene	91, 65, 39	Aromatic
7,27	Ethylbenzene	91, 105, 51	Aromatic
7,45	p-Xylene	91, 105, 51	Aromatic
8	o-Xylene	91, 105, 51	Aromatic
8,1	Nonane	57, 43, 85, 71	<i>n</i> -Alkane
9,65	Medium MW, medium BP hydrocarbon	57, 43, 71, 98	Isoparaffin
9,83	Medium MW, medium BP hydrocarbon	57, 85, 41, 142	Isoparaffin
10,06	Medium MW, medium BP cyclic hydrocarbon	69, 111, 57, 41, 140	Branched Cycloalkane
10,35	Medium MW, medium BP cyclic hydrocarbon	69, 57, 111, 41, 140	Branched Cycloalkane
10,5	Decane	57, 43, 71, 85, 142	<i>n</i> -Alkane
11,63	Medium MW, medium BP oxygenated hydrocarbon	57, 43, 71, 83, 125, 154	Branched alcohol
11,95	Medium MW, medium BP oxygenated hydrocarbon	69, 43, 95, 126, 152	Branched alcohol
12,6	Medium MW, medium BP oxygenated hydrocarbon	57, 43, 71, 85, 156	Branched alcohol
14,5	Medium MW, medium BP oxygenated hydrocarbon	57, 43, 71, 85, 170	Branched alcohol

Paint water based

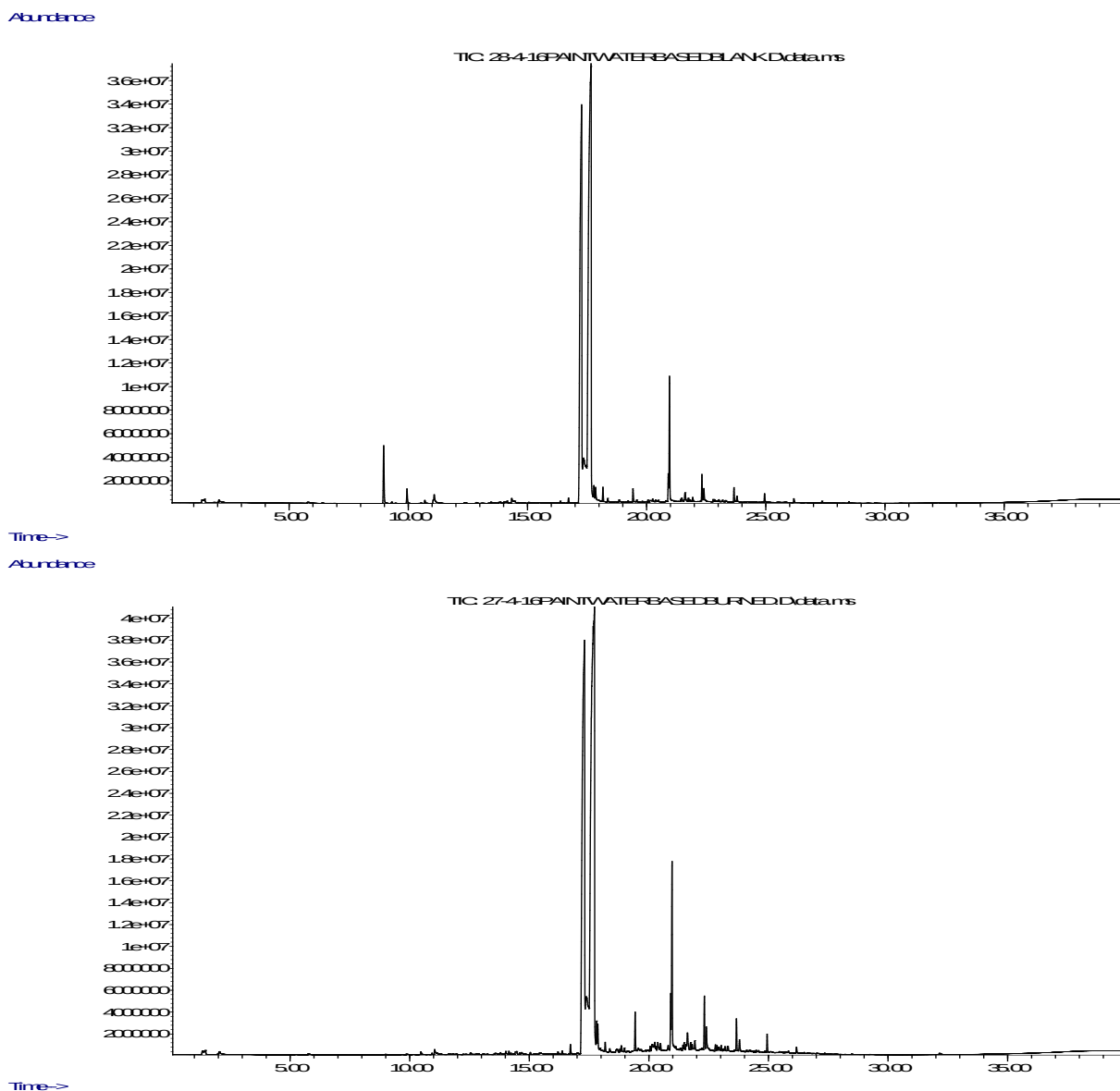


Figure D31: TICs of products produced from the analysis of the burned (bottom) and unburned (top) water-based paint.

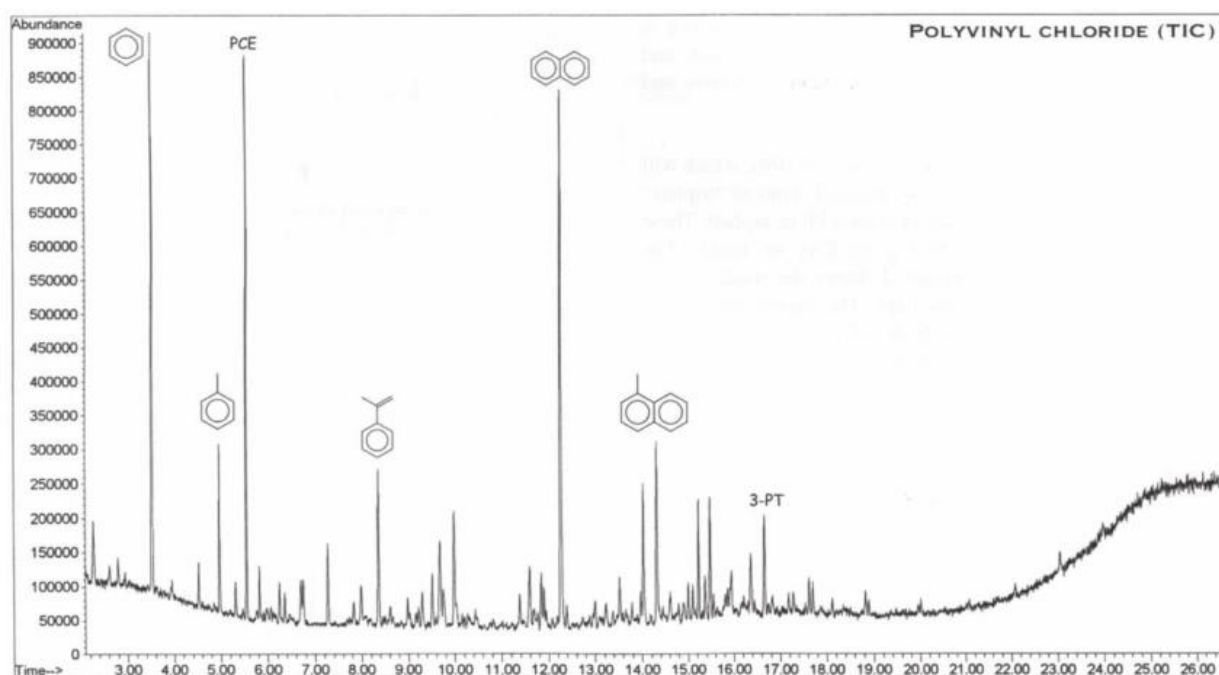
The compounds found in the analysis of the water-based paint before and after burning are listed in **Tables D56** and **D57**.

Table D56: List of compounds and retention times found in the analysis of the water-based paint before burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

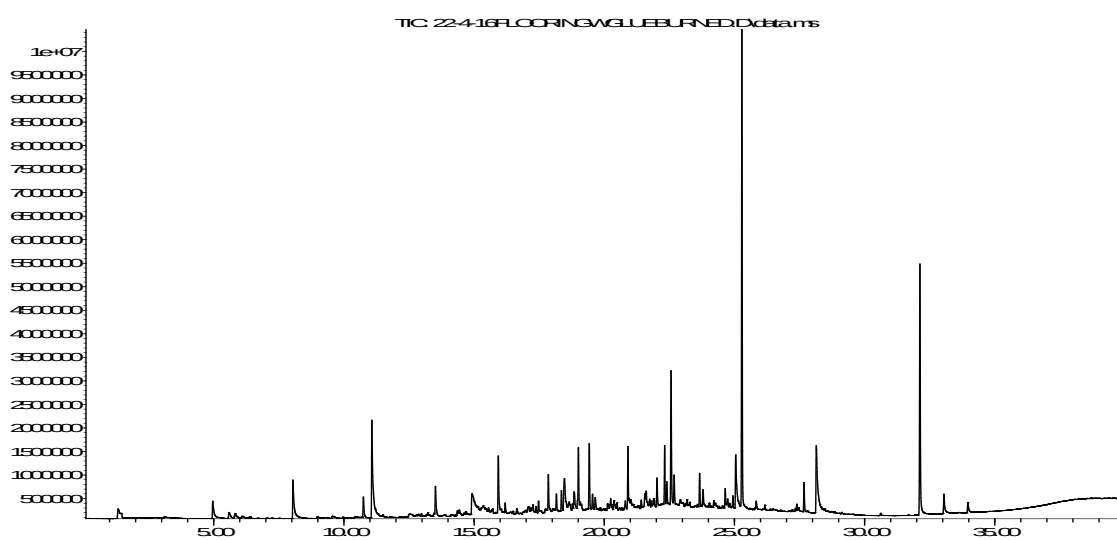
Pre-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,39	Carbon dioxide	44	-
8,97	α -Pinene	93, 91, 77, 41, 67	Bicyclic terpene
9,94	β -Pinene	93, 41, 69, 91, 121	Bicyclic terpene
11,08	Limonene	68, 93, 67, 40, 121	Terpene
17,2	High MW, high BP oxygenated hydrocarbon	71, 43, 83, 98, 143	Ester
17,6	High MW, high BP hydrocarbon	71, 85, 57, 43, 173	Isoparaffin
17,78	High MW, high BP oxygenated hydrocarbon	56, 71, 43, 89	Ester
17,86	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
18,17	Longifolene	161, 91, 41, 119, 189	tricyclic terpene
19,42	Pentadecane	57, 43, 71, 85	<i>n</i> -Alkane
20,9	Hexadecane	57, 71, 43, 85	<i>n</i> -Alkane
22,31	Heptadecane	57, 71, 43, 85	<i>n</i> -Alkane
22,4	High BP, high MW hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
23,66	Octadecane	57, 71, 43, 85, 113	<i>n</i> -Alkane
23,7	High BP, high MW hydrocarbon	57, 71, 85, 43, 99, 113	Isoparaffin

Table D57: List of compounds and retention times found in the analysis of the water-based paint after burning, with indication of retention time, full name, major ions in decreasing order of intensity and chemical family.

Post-burning			
Retention time t [min]	Compound	Major Ions [m/z]	Chemical Family
1,38	Carbon dioxide	44	-
17,3	High MW, high BP hydrocarbon	71, 43, 85, 98, 143	Isoparaffin
17,65	High MW, high BP hydrocarbon	71, 85, 57, 43, 173, 143	Isoparaffin
17,85	Tetradecane	57, 43, 71, 85	<i>n</i> -Alkane
18,15	Longifolene	161, 91, 41, 119, 189	Tricyclic terpene
19,4	Pentadecane	57, 71, 43, 85	<i>n</i> -Alkane
20,85	Hexadecane	57, 71, 43, 85	<i>n</i> -Alkane
20,96	High MW, high BP hydrocarbon	71, 43, 111, 159	Isoparaffin
22,31	Heptadecane	57, 71, 43, 85	<i>n</i> -Alkane
22,4	High MW, high BP hydrocarbon	57, 71, 43, 85, 113	Isoparaffin
23,67	Nonadecane	57, 71, 43, 85	<i>n</i> -Alkane
23,8	Octadecane	57, 71, 43, 85, 99, 113	<i>n</i> -Alkane
24,95	Nonadecane	57, 71, 43, 85, 99, 113	<i>n</i> -Alkane
26,1	Eicosane	57, 71, 43, 85, 99, 113	<i>n</i> -Alkane



Abundance



Time-->

Figure D32: TIC obtained after burning PVC, taken from Stauffer's *"Concept of pyrolysis for fire debris analysts"* (Stauffer, 2003a) (top) compared to the TIC obtained for burned vinyl flooring in this work (bottom): the abundance is significantly higher in the bottom TIC (10000000) compared to the top TIC (900000).