

Sources of interference in fire debris analysis

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Introduction

Apparition of gas chromatography

The first article demonstrating the application of gas chromatography (GC) to fire debris analysis was published by Lucas in 1960 [1]. This marked the beginning of modern fire debris analysis. Prior to that, ignitable liquid residues (ILR) were analysed using rather unreliable methods [2–6].

Question about identification of ILR

The apparition of GC in fire debris analysis did not initially bring any doubts regarding the identification of ILR. It was not until eight years later, in 1968, that the first article questioning the identification of recovered compounds as originating from an ignitable liquid was published [7]. Ettling and Adams raised the issue of interference from substrate materials when they stated: ‘For example, it is known that some hydrocarbons may be produced by pyrolysis of wood.’ However, they also observed that the residues from burned wood, paper, and textiles are distinguishable from ignitable liquids.

Since then, several other authors have performed and published research on this topic. In 1976, Clodfelter and Hueske published an article comparing pyrolysis products with different ‘accelerants’ such as gasoline, diesel fuel, kerosene or jet fuel [8]. They concluded that the chromatograms of burned substrates are readily distinguishable from the chromatograms of the ignitable liquids tested.

In 1978, Thomas warned fire investigators about the necessity of collecting control samples when submitting fire debris samples to the laboratory for analysis [9]. He stated ‘... not all hydrocarbon vapors come from flammable liquids. [...] These hydrocarbons may also be detected by the GC but should not be confused by the analyst with any of the more common flammable liquids.’

Apparition of mass spectrometry

The next important step toward the modern analysis of fire debris is the implementation of mass spectrometry (MS) after separation by GC. In 1982 and 1983 Smith presented gas chromatography–mass spectrometry (GC–MS) as a valuable tool in discriminating ILR from pyrolyzates [10,11]. He reported the presence of styrene and low-boiling alkylbenzenes as arising from pyrolysis of styrene-containing polymers.

In 1984, Howard and McKague reported a case in which charred carpet presented a pattern very similar to the one offered by gasoline, but concluded that it was due to the pyrolysis products (PyP) [12]. They used both gas chromatography–flame ionization detection (GC–FID) and GC–MS to identify several aromatic products.

The same year, Stone and Lomonte discussed false positives in fire debris analysis and related a case report made by Nowicki in which an ‘accelerant’ was produced by the burning of flooring [13,14]. They stated that often turpentine is detected in wood samples, which is due to PyP. They also related a case where a naphtha or diesel was found in fire debris, which again was produced by the pyrolysis of the substrate. They recommended GC–MS versus GC alone to decrease the number of false positives.

In 1988, DeHaan and Bonarius produced the first complete study on PyP [15]. They offered a valuable set of solutions to discriminate between PyP and ILR.

Bertsch presented an interesting study in 1994 describing PyP released by burned carpet and carpet padding [16]. He showed the presence of styrene, methylstyrene, small amounts of aromatics and high presence of naphthalenes and methylnaphthalenes. He used the extracted ion profiles to discriminate PyP from ignitable liquids based on the ratios of the different isomers.

Keto, in 1995, advocated the use of extracted ion chromatograms in order to help identify ILR in the presence of contaminated arson debris [17]. He cautioned, ‘Another hazard is that petroleum like isomer profiles may not originate from petroleum distillates at all.’

In 1996, Kurz *et al.* tested accelerant canines’ ability to discriminate between PyP and ILR [18]. They concluded that PyP generated by burning substrates contained common substances to the ones present in gasoline, which can distract the canines.

In 1997, Tranthim-Fryer and DeHaan presented an identification of PyP of carpet and underlay that resulted in false positive alerts for accelerant detection canines [19].

In 1998, Lentini demonstrated the difference between PyP from tar materials (asphalt) found in smoke condensates and heavy petroleum distillates [20].

In 2000, Lentini, Dolan, and Cherry presented a study on petroleum-laced background and demonstrate that petroleum-based products are inherently present in samples prior to burning [21].

In 2002, Cavanagh, Du Pasquier, and Lennard presented an evaluation of the background contamination of carpet subjected to exposure to external environment for a certain amount of time [22]. They advised the use of comparison samples.

The same year, Fernandes presented an article comparing burned and unburned substrates [23].

Misconception about ‘pyrolysis products’

It is very often encountered throughout the literature and analytical reports that the main difficulty in fire debris analysis is the presence of PyP and that these products interfere with the proper identification of ignitable liquids. Pyrolysis products are usually blamed as the

sole source of interferences in fire debris samples. This concept is wrong, or at least, it is potentially poor verbiage.

Pyrolysis products are only a portion of the products that are released by a burned substrate that will interfere with ILR recovery and identification. Very few authors have realized that phenomenon throughout their publications [16,21–24]. However, the distinction between the different sources has never been reliably demonstrated. Lentini, Dolan, and Cherry successfully demonstrated the existence of background products in different substrates as did Cavanagh, Du Pasquier, and Lennard [21,22].

This chapter covers the sources of interference in fire debris analysis. First, the concept of interfering products in fire debris analysis is introduced and explained. Second, the different sources of interfering products are presented one by one and thoroughly explained. Finally, some practical cases are presented and analysed. This should allow the reader to put into practice the concepts learned in this chapter as well as those in Chapters 5 and 6. The understanding and knowledge of the concept of interfering products will improve the analysts' skills.

Concept of interfering products

In the field of fire debris analysis, the term 'interfering products' is defined as 'the set of products found in a sample that interfere with the proper identification of ignitable liquids residues' [24]. It is possible to distinguish three categories of products originating from a substrate that will interfere with ILR recovery and analysis.

The three categories are

- Substrate background products (SBP)
- Pyrolysis products (PyP)
- Combustion products (CoP).

By applying the rules of a substrate's composition, manufacture, contamination, and combustion, it is possible to easily understand the different categories of interfering products released.

Figure 7.1 is a schematic representation of the sequence of events that a substrate undergoes during a fire accelerated with an ignitable liquid poured onto a substrate.

Pre-fire phase

Let's consider a substrate, such as a nylon carpet. This substrate contains SBP as explained later in the chapter. A liquid, such as gasoline, is poured onto the substrate. Through gravitational and capillary forces, part of the liquid will travel downward and into the deep layers of the substrate. It will get adsorbed onto the surface of the substrate and the excess will create a puddle of liquid. Also, with enough liquid and time, it will eventually reach the wood or concrete under the carpet. Part of the liquid will also evaporate at a rate depending on the physical properties of the liquid and the environmental conditions.

Ignition phase

Ignition occurs and the vapours above the liquid catch fire. Heat is released due to the combustion process. If the liquid has formed a puddle, the radiant heat will first affect the

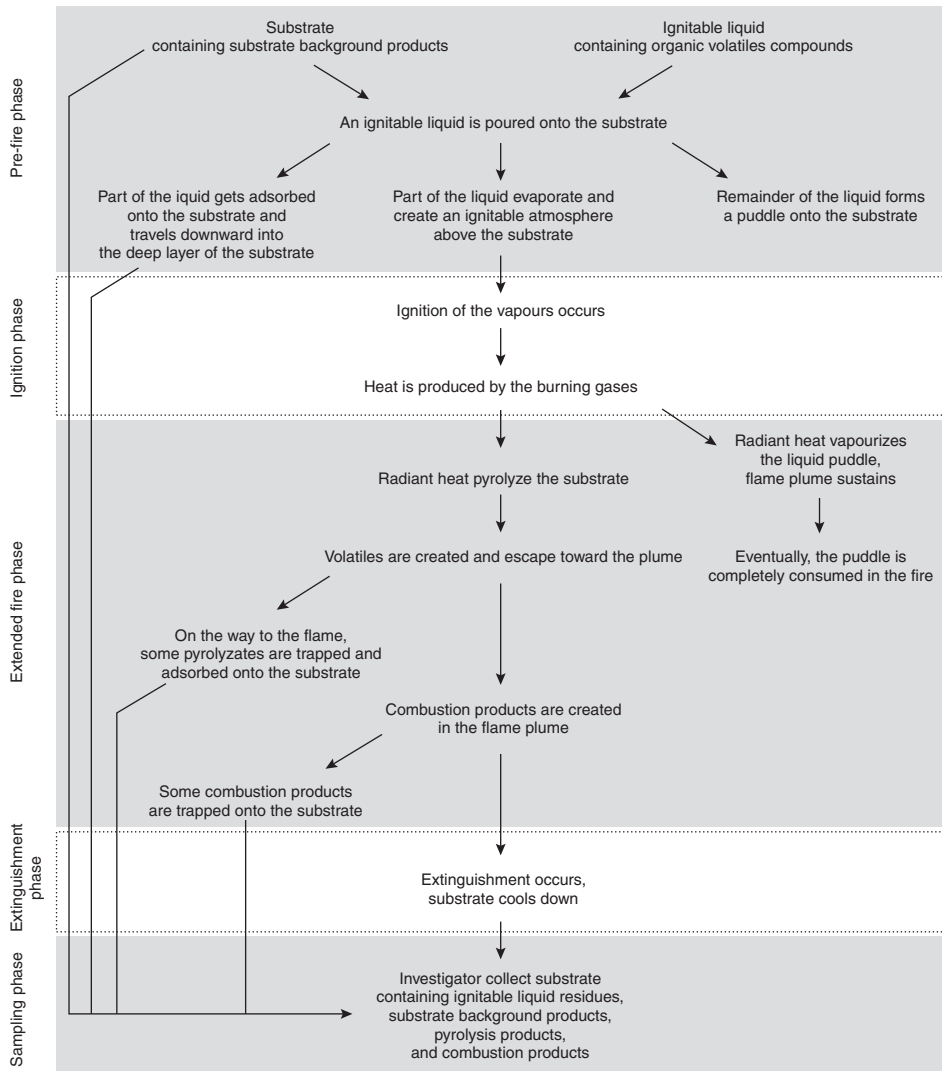


Figure 7.1 A schematic representation of the sequence of events during a fire accelerated with an ignitable liquid poured onto a substrate

evaporation of the liquid. This creation of vapours will feed the fire and eventually, the puddle will disappear.

Extended fire phase

The radiation will also heat the substrate onto which the liquid was poured. Since solids do not burn, they must first transform into gas. The substrate can use different phase transformation pathways, as shown in Figure 7.2. However, the most common pathway, and most pertinent in the scope of this chapter, is the pyrolysis of the substrate. While the

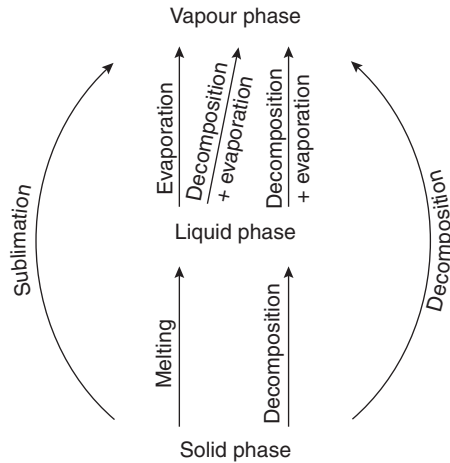


Figure 7.2 Phase transformation pathways

phenomenon of pyrolysis will be explained in detailed later in the text, it can be briefly stated that flammable volatiles are created by the thermal decomposition of the substrate. Due to buoyancy, they will rise to the plume of the flame and sustain the fire. On the way to the plume, it is suspected that some volatiles get trapped onto the carbonized substrate.

Extinguishment phase

At any time during the fire, extinguishment can happen. The fire can self-extinguish by running out of fuel or oxygen, or it can be put out by an external act. This can be accomplished by reducing the oxygen, decreasing the energy of the system, or separating the fuel from the oxygen and/or energy source [25].

Sampling phase

When the fire investigator works the fire scene, he/she will develop a hypothesis regarding the origin and cause of the fire. Eventually, in this case, a sample of the carpet will be collected and submitted to the forensic laboratory for fire debris analysis [26]. The sample collected contains ILR from the gasoline poured, as well as SBP, PyP, and CoP.

Different sources of interfering products

The different sources of interfering products are shown in Figure 7.3.

Substrate background products

This category includes all the products (usually petroleum based) that are already adsorbed onto the surface of the substrate prior to burning that will interfere in the analysis of fire debris. It is possible to distinguish three different sub-sources from which these products originate, as shown in Figure 7.3.

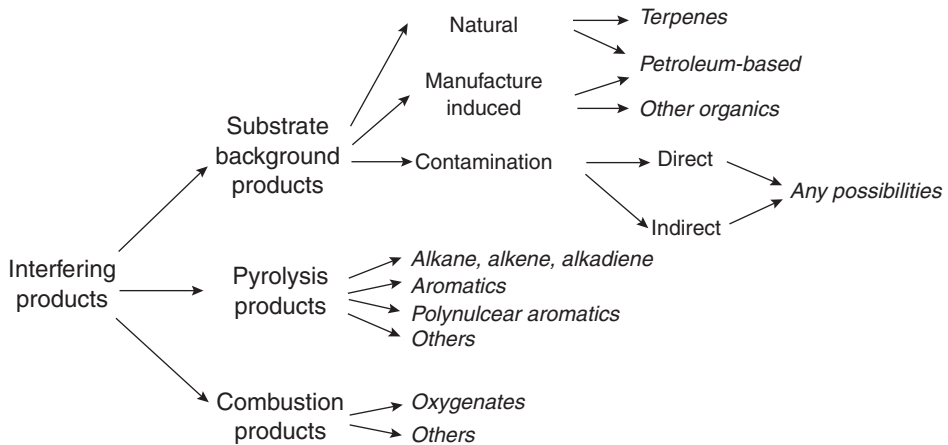


Figure 7.3 Different sources of interfering products

Natural

There can be some natural background present in the raw material of the substrate. As an example, some rubbers contain some high-boiling point hydrocarbons. Also, it is very well-known that some woods contain terpenes as part of their natural background [27,28].

Manufacture induced

The manufacturing and/or finishing process may also involve the use of products that will stay adsorbed onto the substrate and later interfere with ILR identification. Examples of such products are solvents used in the manufacturing process for different purposes [29]. Another known example is the use of kerosene in the printing industry as a solvent for the ink [21].

Contamination

It is very simple to imagine that contaminations of any substrates can occur naturally and accidentally every day. These contaminants can be further classified in two different groups:

Direct contact when there is an established contact between two objects or two surfaces. This is known in forensic sciences as The Principle of Exchange from Locard: ‘tantôt le malfaiteur a laissé sur les lieux les marques de son passage, tantôt, par une action inverse, il a emporté sur son corps ou sur ses vêtements les indices de son séjour ou de son geste’ [30]. While this principle was expressed as describing the exchange of material and traces between the author of a crime and the crime scene, it can be very easily adapted to a regular contaminating situation. As an example, a shoe walking on gasoline traces at a gas station will leave contamination on the floor mat of the vehicle by direct contact. This has been successfully demonstrated by Cavanagh, Du Pasquier, and Lennard [22].

Indirect contact when the contamination is brought to the substrate by aerial transportation. An example of such contamination is the use of positive-pressure ventilation

systems at fire scenes. A study made by Lang and Dixon shows that it was possible that gasoline vapours could contaminate some substrates inside a house through the use of a positive pressure ventilation fan [31]. On the other hand, Koussiafes, using different conditions, did not observe that phenomenon [32].

Pyrolysis products

The second most important category of products is represented by the PyP released by the substrate when subjected to heat. Pyrolysis can be defined as ‘a process, by which a solid (or a 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.’ [24]

While pyrolysis is a process that produces many different chemicals and that is highly influenced by environmental conditions as well as by the nature of the substrate involved, it commonly follows three main degradation mechanisms; random scission, side-group scission, and monomer reversion [33,34]. Other peculiar mechanisms have also been identified, but are of less interest to the fire debris analysts.

Random scission

This first mechanism involves the random breaking of the polymer’s backbone (C–C bond) [35]. Figure 7.4 shows the random scission of polyethylene. This scission results in the

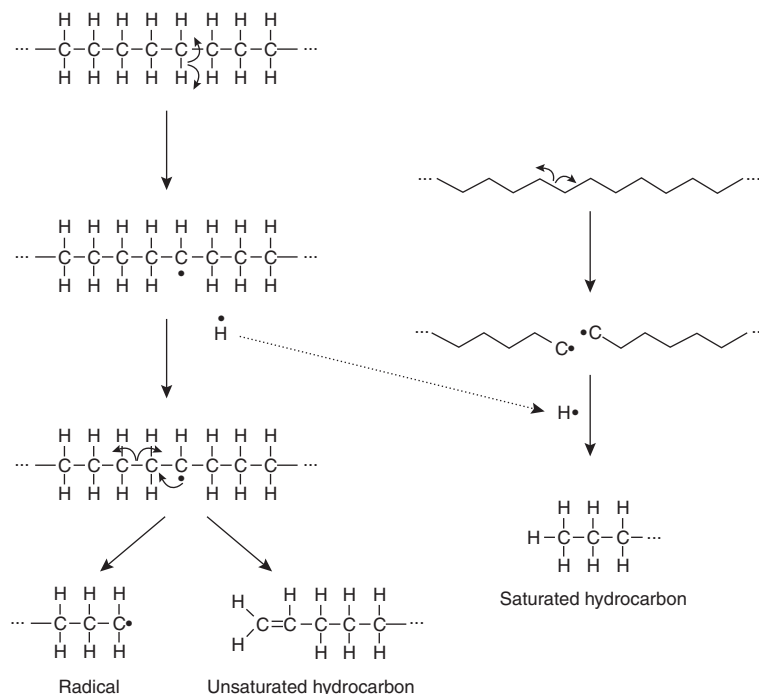


Figure 7.4 Random scission of polyethylene

production of series of alkanes, alkenes, and alkadienes of different lengths. The chromatographic result of such PyP is shown in the previous chapter in Figure 6.24 with the example of polyethylene.

Side-group scission

This mechanism involves the breakage of side groups away from the backbone chain [36]. Hence, the backbone becomes polyunsaturated and undergoes a rearrangement into aromatics, as shown in Figure 7.5 with the example of polyvinylchloride.

The products from this type of pyrolysis include a wide variety of aromatics ranging from benzene to C4- or C5-alkylbenzenes, including an even greater variety of polyaromatic hydrocarbons.

Monomer reversion

This last common degradation mechanism is probably the least interesting to fire debris analysts. The polymer simply unzips and, therefore, reverts to its monomeric version, as shown in Figure 7.6 with the example of an acrylate polymer. This produces usually one compound that is very predictable when the polymer structure is known [37]. The monomeric reversion, itself, does not usually interfere too much with the identification of ILR, because it presents only one peak that is typically not common to an ignitable liquid.

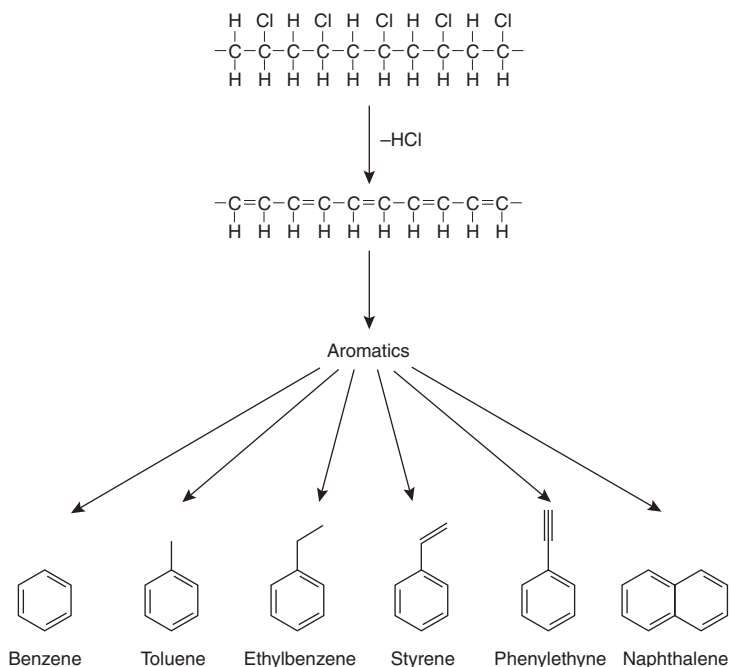


Figure 7.5 The mechanism of side-group scission and rearrangement into aromatics

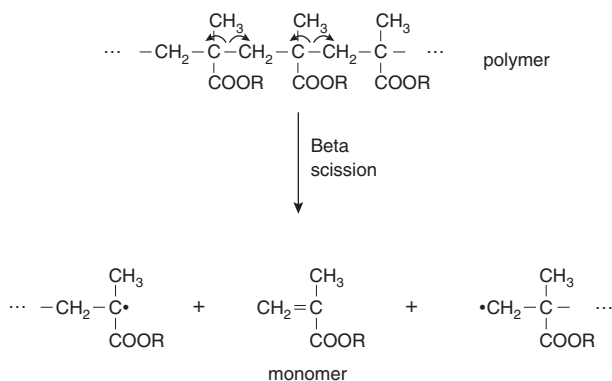


Figure 7.6 The reversion of polymeric to monomeric form

Pyrolysis involving multiple degradation mechanisms simultaneously

As shown previously, degradation mechanisms are pretty straightforward and simple to apply. Pyrolysis products can be predicted and are well defined for a given polymer. However, nature being nature, it is much more complicated than that. As a matter of fact, very few polymers undergo pyrolysis using only one degradation mechanism. Commonly, two or more mechanisms will occur simultaneously.

So, how is it possible to determine which polymer undergoes which pyrolysis mechanisms? Simply put, it is by following the law of the weakest bond. The weakest bond in the polymer will usually break first and consequently determine the mechanism. Unfortunately, parameters, such as rate of temperature rise, will slightly change the bond breakage order in some instances. However, by looking at bond dissociation energy, it is possible to understand the products released by different polymers [38].

Figure 7.7 shows a schematic representation of different polymers placed according to their degradation mechanisms.

Figure 7.8 shows a list of some of the most commonly encountered polymers in a typical household environment. Each polymer is presented with its chemical structure, its main pyrolysis degradation mechanism(s), and the typical PyP released.

The careful study of this table should allow any scientist to get accustomed to the kind of polymers encountered in fire debris analysis. The knowledge of polymer structure will help to improve the understanding of the subsequent PyP, and should improve greatly the interpretative skills of the scientist.

Combustion products

Combustion is a very complex phenomenon and is often described as a chain reaction. Some authors have shown very complex mechanisms of reaction [25,39]. Thus, different products can be released during combustion according to the conditions in which it occurs. If the conditions are ideal, the combustion will be complete and CoP will be completely oxidized and reduced. With most organic polymers, the ultimate CoP produced will be CO₂ and H₂O. However, when the oxidizer is present by default, it will lead to other products that are not completely oxidized or reduced, referred to as products of incomplete combustion.

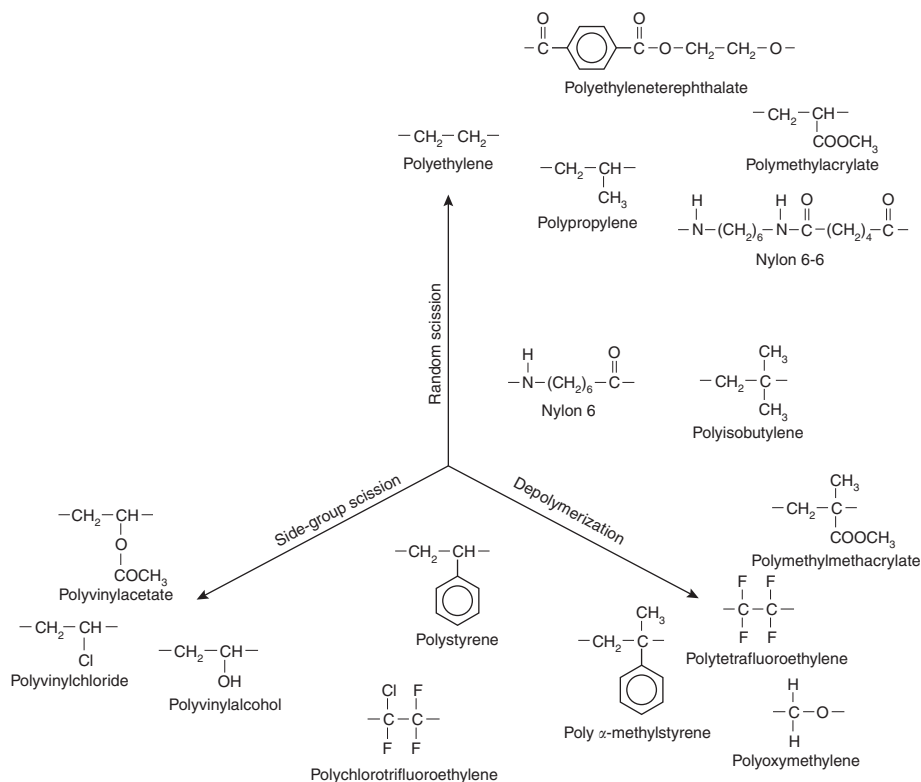


Figure 7.7 A schematic representation of polymers according to their degradation mechanisms

The best example describing these incomplete CoP is shown with smoke condensates. They mainly contain polyaromatic hydrocarbons as described in the literature [40,41]. Differentiation between combustion and PyP is primarily based on the fact that PyP do not result from oxidation reactions, while CoP do. While this concept is disputable, particularly with the definition of some pyrolysis processes, it is beyond the scope of this chapter to adequately present the differences [42]. It is interesting to note that the recent revision of the ASTM standard E 1618 now integrates the wording ‘pyrolysis and combustion products’ in its section 11.2.1, while it presented only ‘pyrolysis products’ in the previous edition [43,44].

Knowledge of polymers and interfering products

Almost any substrate can contain SBP inherent to its composition. On the other hand, PyP are almost exclusively produced by polymers. Nevertheless, polymers constitute most of the raw material used in household items. Hence, it is important for the fire investigator and the fire debris analyst to know the different polymers found among fire debris.

The following is a list of the most commonly encountered polymers and their common applications [45,46]. Their structures are shown in Figure 7.8.



	Chemical structure	Degradation mechanism	Pyrolysis products
<i>Polyolefins</i>			
Polyethylene	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	random scission	<i>n</i> -alkanes <i>n</i> -alkenes <i>n</i> -alkadienes
Polypropylene	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	random scission	branched alkanes branched alkenes branched alkadienes
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	random scission monomer reversion	branched alkanes branched alkenes branched alkadienes
<i>Styrene polymers</i>			
Polystyrene		monomer reversion side-group scission	styrene aromatics
Poly α -methylstyrene		monomer reversion	α -methylstyrene
<i>Vinyl polymers</i>			
Polyvinylchloride	$\begin{array}{c} \text{Cl} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	side-group scission	aromatics chlorinated compounds
Polyvinylidenechloride	$\begin{array}{c} \text{Cl} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{Cl} \end{array}$	side-group scission	aromatics chlorinated compounds
Polyvinylidene fluoride	$\begin{array}{c} \text{F} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{F} \end{array}$	side-group scission	aromatics fluorinated compounds
Polytetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	monomer reversion	tetrafluoroethylene
Polyvinylacetate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{C}=\text{O} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	side-group scission	aromatics acetic acid
Polyvinylalcohol	$\begin{array}{c} \text{OH} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	side-group scission	aromatics
<i>Acrylate polymers</i>			
Polymethylacrylate	$\begin{array}{c} \text{COOCH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	random scission	methanol oxygenated compounds
Polymethylmethacrylate	$\begin{array}{c} \text{COOCH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	monomer reversion	methylmethacrylate

Figure 7.8 A list of some common polymers, their chemical structure, degradation mechanisms, and pyrolysis products

	Chemical structure	Degradation mechanism	Pyrolysis products
<i>Polyamides</i>			
Nylon 6		random scission accompanied by cross-linking	oxygenated compounds
Nylon 6-6		random scission accompanied by cross-linking	oxygenated compounds
<i>Polyesters</i>			
Polyethyleneterephthalate		random scission (of the CO bonds)	oxygenated compounds
Polyethylenaphthalate		random scission (of the CO bonds)	oxygenated compounds
Polybutyleneterephthalate		random scission (of the CO bonds)	oxygenated compounds
<i>Polycarbonates</i>			
		side-group scission	aromatics chlorinated compounds
<i>Polyurethanes</i>			
		monomer reversion random scission	isocyanides oxygenated compounds
<i>Rubbers</i>			
Polybutadiene		monomer reversion (followed by dimerization)	butadiene alkenes
Polyisoprene		monomer reversion (followed by dimerization)	dipentene alkenes
SBS		monomer reversion random scission	butadiene alkenes aromatics
Polychloroprene		side-group scission	aromatics
<i>Polyacrylonitriles and copolymers</i>			
Polyacrylonitrile		side-group scission	aromatics
SAN		side-group scission random scission	aromatics
<i>Cellulose</i>			
		random scission of the CO bonds	oxygenated compounds

Figure 7.8 (Continued)

Polyolefins

Polyethylene (PE)

This is the simplest polymer. It is constituted by the repetition of an ethylene group. Sometimes, it is referred to low density (LDPE) or high density polyethylene (HDPE). This depends on the degree of branching between two chains. The more branching, the lower the density. HDPE is much stronger than LDPE, and is therefore used to make highly resistant fibres, sheets, or objects. For example, PE is used to manufacture grocery and rubbish bags, plastic boxes such as Rubbermaid®, buckets, hoses, shampoo bottles, children's toys, car gas tanks, and even some small backyard shelters. It is also used for the insulation of electrical wiring.

Polypropylene (PP)

When a methyl group is added to one of the carbons of the repetitive unit in PE, PP is obtained. PP is a very versatile polymer, used both as a plastic and as a fibre. Typical objects made of PP are dish-washer resistant food containers, some plastic parts in vehicles (garnitures, HVAC duct, etc.), one-time use objects, and plastic parts in electronic apparatuses. Also, as a fibre it is used to manufacture indoor–outdoor carpets. Most of the outdoor carpets are made of PP, since it does not absorb water.

Polyisobutylene (PIB)

When two methyl groups are attached to one of the carbons in PE, PIB is obtained. This is an elastomer that is also often classified as a rubber. The main quality of PIB is the fact that it is airtight. This is why it is used for the inner liner of tires and basketballs.

Styrene polymers

Polystyrene (PS)

The repetitive element is styrene, which is obtained by substituting a phenyl group for a hydrogen in the repetitive element of PE. This is the second most common plastic among the household items. It is used to make computer housings, model cars, plastic parts of all kinds of appliances, one-time use cutleries, toys, CD cases, keys on a keyboard, and moulded parts inside a vehicle. Perhaps, more widely known is polystyrene foam, which is used with great versatility. Examples of such use are drinking cups, packing material for protection during shipping, and building material.

Vinyl polymers

Polyvinylchloride (PVC)

When a chlorine atom replaces a hydrogen in the repetitive element of PE, PVC is obtained. PVC is used nearly everywhere in the household. PVC is widely used to make objects that need to resist to water. Water pipes, vinyl siding, vinyl car tops, linoleum floor, raincoats, and shower curtains are some examples of the use of PVC. It is also very resistant to fire, due to the fact that when it pyrolyses, the chlorine atoms released inhibit combustion. Thus, PVC burns very badly and can barely sustain a flame by itself.

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Polyvinylidenechloride (PVDC)

By replacing both hydrogens attached to the same carbon in PE with chlorine atoms, polyvinylidenechloride is obtained. PVDC is the plastic wrap that is used to wrap food. A brand name of PVDC is Saran[®].

Polyvinylidene fluoride (PVDF)

When the two hydrogens from one of the carbon in PE are replaced with two fluorine atoms, it becomes polyvinylidene fluoride. PVDF offers excellent resistance to heat and electricity, which makes it a good material to insulate electrical wires. It is mainly used on wires that get hot, such as the ones inside a computer or other electronic apparatuses, when PE is not a suitable material. It is also used on wires in airplanes because it is fireproof. Since it offers good UV radiation resistance, it is blended with PMMA (see later) to make outside windows. Its chemical resistance is also excellent, which makes it a material of choice for bottles or containers to store chemicals.

Polytetrafluoroethylene (PTFE)

When the four hydrogens of PE are replaced with four fluorine atoms, it becomes PTFE, also known by the brand name Teflon[®]. Since it has the property of not sticking to anything, it is used to make nonstick cooking pans. It is also used to treat carpets and fabrics (such as Gore-Tex[®]) to make them stain resistant. It is also a well-accepted substance by the human body, and this is why some artificial body parts are made of PTFE.

Polyvinylacetate (PVAc)

When one of the hydrogen atoms in PE is replaced by an acetate group, it becomes PVAc. PVAc is well spread throughout the household items, however, it is not very well known. It is used to make adhesives, such as wood glues. Also, paper and textiles often have coatings made of PVAc, which make them shiny. PVAc is also one of the constituents forming the latex in acrylic latex paints.

Polyvinylalcohol (PVA)

By replacing a hydrogen atom in the repetitive element of PE by an alcohol group, it becomes PVA. It is used with polyethyleneterephthalate (PET) to make bottles for carbonated beverages. Carbon dioxide can easily go through PET, but not through PVA. By creating a sheet of layers of PET and PVA, a strong bottle that retains carbon dioxide is obtained.

Acrylate polymers

Polymethylmethacrylate (PMMA)

PMMA has a slightly more complicated structure and is shown in Figure 7.8. It is a clear plastic. Its main use is known as Plexiglass[®], which replaces glass as it is shatterproof. It is used in a great variety of applications, such as hurricane-proof windows, and vehicle headlights. It is also used to make surfaces of hot tubs, shower units, and sinks. Indeed, counter

tops that need to be resistant to heat are made of PMMA, usually mixed with an aluminium oxide. This is not to be confused with Formica[®], which is a melamin-formaldehyde resin. Latex paints contain PMMA. Finally, it is used as an additive to oils and lubricants, since the addition of PMMA decreases the viscosity of these fluids.

Polyamides

Nylon 6

The structure of Nylon is shown in Figure 7.8. Nylon is probably the most common polymer used as a fibre. It is mainly used to make clothing and carpets. However, it is also used to make ropes, straps, bags, and parachutes.

Nylon 6-6

While there is a structural difference between Nylon 6 and Nylon 6-6, there is almost no difference in the physical properties. Nylon 6-6 was first invented and patented by DuPont[™], so other manufacturers had to invent Nylon 6.

Polyesters

Polyethyleneterephthalate (PET)

PET is a repetitive element made of a terephthalate and an ethylene group, as shown in Figure 7.8. One very common application of this polymer is the shatterproof plastic bottles for beverages (used with PVA for carbonated drinks). It is also used to make some plastic jars. Usually items made of PET are not reusable, simply because the sterilization procedures involve temperatures too high for PET. It would melt and become too soft to keep its shape. PET is also used as a fibre to make some clothing.

Polyethylenenaphthalate (PEN)

PEN has a similar structure to PET, with a naphthalate group in lieu of the terephthalate group. PEN has a much higher glass transition temperature, which means it is much more resistant to high temperature than PET. This is why it is used in mixture with PET to create reusable bottles and jars.

Polybutyleneterephthalate (PBT)

PBT has a similar structure to PET with a butylene group in lieu of the ethylene group. It is used in the same kinds of applications as PET.

Polycarbonates

There are a couple of important polycarbonates, the most important of which is polycarbonate of bisphenol A. Its structure is shown in Figure 7.8. It is a clear plastic used to make shatterproof windows, lightweight eyeglass lenses, and some vehicle headlights.

Polyurethanes

There are several different polyurethanes, and the general structure is shown in Figure 7.8. These polymers are the most versatile and can be found as foam, fibres, paints, elastomers, or adhesives. A well-known polyurethane is Spandex[®]. It is used to make fabric that stretches, such as sport clothes. Polyurethane polymers are also used to manufacture the foam inside upholstered furniture such as couches and padded chairs, and other foams such as carpet padding, synthetic sponges, and material used for the soft insides of stuffed animals.

Rubbers

Polybutadiene (PBD)

PBD is formed of a monomer with two carbon-to-carbon double bonds. This polymer is one of the first synthetic elastomers developed. It is used as a rubber in a great variety of parts, because it resists cold temperatures better than some other polymers. It is used to manufacture hoses, belts, gaskets, and other car parts. It is also used as a copolymer in order to make tire tread. Among its uses as a copolymer, the most important is poly(styrene–butadiene–styrene), also known as SBS (see later).

Polyisoprene (PIP)

PIP has a slightly more complicated repetitive element as shown in Figure 7.8. As a matter of fact, PIP is natural rubber. It was originally extracted from the Hevea tree. It is used to manufacture tires following vulcanization. Objects commonly known to contain rubber, such as boots, cushioning, or rubber parts in a vehicle, have polyisoprene. Also, the sides of a tire are usually made out of PIP. It is also used to isolate electrical wiring and to make flexible elastic bandages, or rubber bands.

Poly(styrene–butadiene–styrene) (SBS)

SBS is a block copolymer that is made of a mixture of polystyrene and polybutadiene. It is also called hard rubber, since it has the rubbery aspect from PBD, but has been hardened due to the addition of PS. It is typically used for tire treads, shoe soles, or other items where durability is important.

Polychloroprene (PC)

By replacing one of the hydrogens attached to a central carbon in PIP with a chlorine, polychloroprene is obtained. It is better known as Neoprene[®] on the market. It is a rubber or elastomer and it is very resistant to oil. It is typically used to make wet suits for scuba diving.

Polyacrylonitriles and copolymers

Polyacrylonitrile (PAN)

When a nitrile group is substituted for a hydrogen in the repetitive unit of PE, polyacrylonitrile is obtained. It is not widely used alone. Although, it is used as a precursor to make carbon fibres, it is primarily used as a copolymer as shown next.

Poly(acrylonitrile-co-vinylchloride)

When PAN is mixed with PVC, a flame-retardant polymer is obtained. It is often used as a fibre, usually called modacrylic.

*Poly(acrylonitrile-co-methylacrylate) and
Poly(acrylonitrile-co-methylmethacrylate)*

When PAN is mixed with PMA or PMMA, another polymer is obtained. This is used mostly as a fibre for acrylic clothing.

Poly(styrene-co-acrylonitrile) (SAN)

This is a simple copolymer of PS and PAN. It is used as a plastic.

Poly(acrylonitrile-co-butadiene-co-styrene) (ABS)

This copolymer presents a much more complicated structure. As a matter of fact, it is a polybutadiene chain with SAN chains grafted onto it. It is used to manufacture moulded parts such as the bumpers of a car. It is a very light-weight plastic.

Cellulose

Cellulose is a natural polymer made of repeating units of glucose, as shown in Figure 7.8. It is the constituent of wood, paper, and cotton. It is used in an enormous variety of applications, such as clothing, books, furniture, etc.

Interfering products found in household items and their prediction

It is possible to partially predict interfering products according to the substrate studied. These predictions are, of course, to be taken with great caution. This exercise requires a lot of practical training that cannot be obtained through the reading of a book chapter. It is a self-taught experience that can be done very easily at the laboratory. The best way to do this is to obtain samples representative of fire debris samples that do not contain any ignitable liquids. This can be achieved by asking the fire investigator to bring back samples from fire scenes that are known not to contain ILR, or to obtain unburned samples and burn them at the laboratory.

If it gets very difficult to predict interfering products in some instances, it should be possible to understand and justify their presence. Again, the experience of looking at negative samples will allow the scientist to get accustomed to recognizing the interfering products at the earliest stage.

Prediction of substrate background products

While it is very difficult to predict contamination (subclass of SBP), the analyst will likely be able to find out what kind of natural and manufacture induced background are present. This was shown in some examples previously described. Understanding the concept of how

the object or material is manufactured should allow the analyst to have an idea about the kind of products involved.

Prediction of pyrolysis products

All these polymers will be very likely to undergo combustion in a regular house fire, since the highest ignition temperature is around 500°C.

Pyrolysis products are a category that is pretty easy to predict, at least in a qualitative manner. However, there are many parameters that influence the creation of pyrolysis products.

Figure 7.8 also presents the different mechanisms of pyrolysis according to the polymer. Also, the second column shows the typical pyrolysis products encountered. By knowing the chemical structures of the polymers present in the fire debris analysed and by understanding which pyrolysis mechanisms applies to these particular polymers, it is possible to predict some of the resulting products. For a more detailed explanation of this approach, the reader is referred to another article written by the author [38].

Also, the scientist should be aware of the great variety of different polymers that can constitute a single object. For example, when referring to a nylon carpet, one should be mindful that the carpet fibres are made of nylon, but that the backing is probably made of polybutadiene and another natural fibre made of cellulose. Also, the carpet probably lies on a carpet pad made of polyurethane. Thus, the fire debris suddenly contains four different polymers, providing four different sets of pyrolysis products.

Prediction of combustion products

The literature does not contain any studies that address the exact differences between pyrolysis and combustion products in fire debris analysis. However, it seems that this category is relatively restricted and that most of the combustion products are oxidized version of pyrolysis products. Hence, these products are usually not similar to those found in ILR. Therefore, this category is not of much concern to the fire debris analyst.

Differentiation between SBP and PyP/CoP

In order to demonstrate the difference between SBP and PyP/CoP, identical unburned and burned substrates were extracted and analysed. Thus, it is possible to superimpose the two chromatograms obtained and isolate SBP from pyrolysis and combustion products. The three following chromatograms are examples of such results. It is advised to perform this kind of analysis with some of the most common items such as carpets, wood, and upholstery. This will help the analyst to quickly recognize the sources of the different products.

Polyester carpet

In Figure 7.9, it is possible to observe the difference between the chromatograms of unburned (blue line) and burned (red line) polyester carpet. Methyl isobutyl ketone (2.6 min), a C₉ branched alkene (4.1 min), ethylbenzene (4.5 min), styrene (5.2 min), benzaldehyde (6.9 min), 2-ethyl-1-hexanol (9.3 min), naphthalene (13.8 min), cyclopentylbenzene (14.8 min) and some C₁₅ branched alkenes (16–17 min) are produced by the pyrolysis and combustion

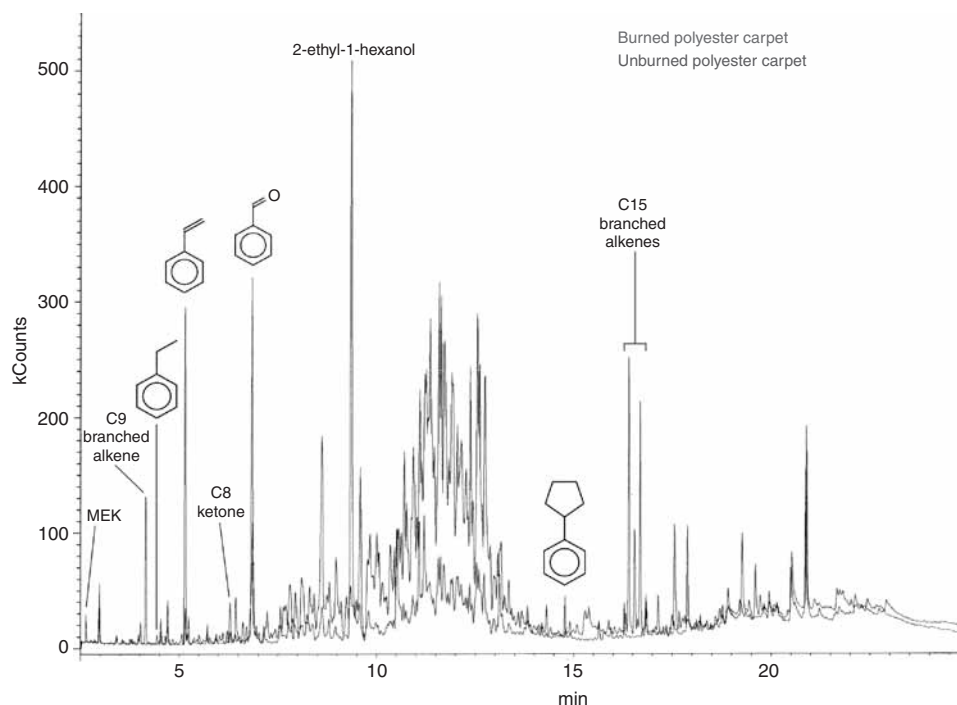


Figure 7.9 The chromatograms of burned and unburned polyester carpet (see Colour Plate I)

of the carpet. In this instance, toluene (3.0 min) is present in higher concentration in the unburned than in the burned sample. On the contrary, benzaldehyde is present in higher concentration in the burned sample than in the unburned one. Finally, it is possible to observe the same stack of aliphatics between 8 and 15 min (C10 to C13) in both chromatograms, showing that they are SBP.

Newspaper

A newspaper was extracted unburned (blue line) and burned (red line) as shown in Figure 7.10. Furaldehyde (3.9 min), ethylbenzene (4.5 min), phenylethyne (4.8 min), styrene (5.1 min), α -methylstyrene (7.6 min), benzofuran (8.0 min), indene (9.8 min), methoxyphenol (11.3 min), naphthalene (13.8 min) and methoxymethylphenol (14.1 min) are produced by the burning process of the newspaper. This is very consistent with the degradation process of cellulose. The heavy petroleum distillate pattern recovered toward the end of the chromatogram comes from the substrate background and has already been described in the literature by Lentini, Dolan, and Cherry [21].

Wood

An example of substrate that does not present a difference between the unburned (blue line) and the burned (red line) stage is yellow pine wood as shown in Figure 7.11. No extraneous peaks were produced in this instance with the burning of the substrate. The two chromatograms are very similar. As expected, most of the peaks are terpenes.

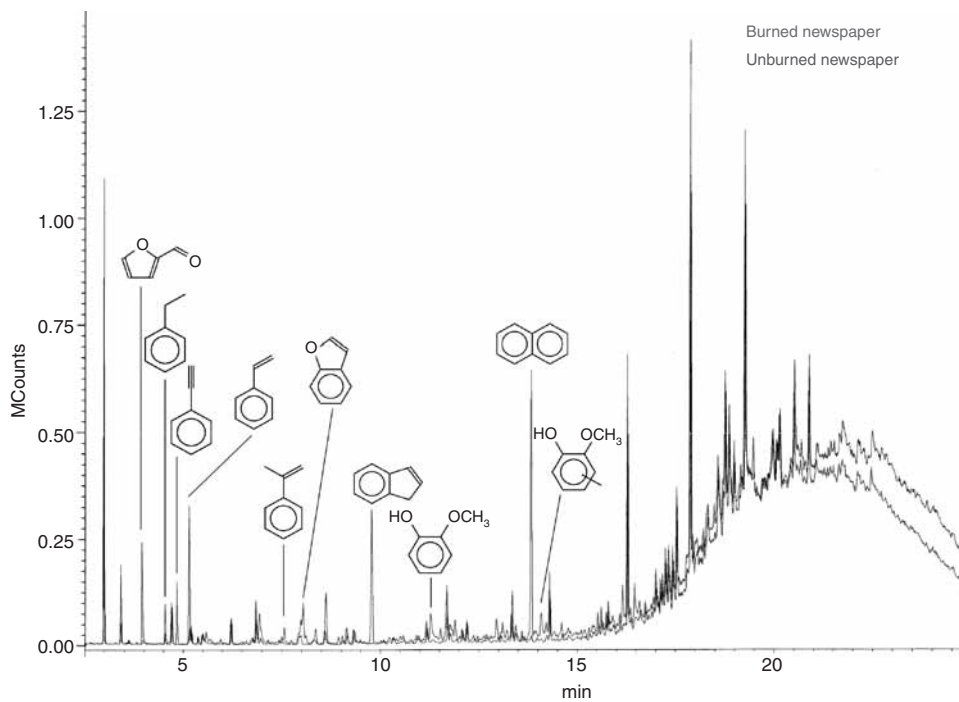


Figure 7.10 The chromatograms of burned and unburned newspaper (see Colour Plate II)

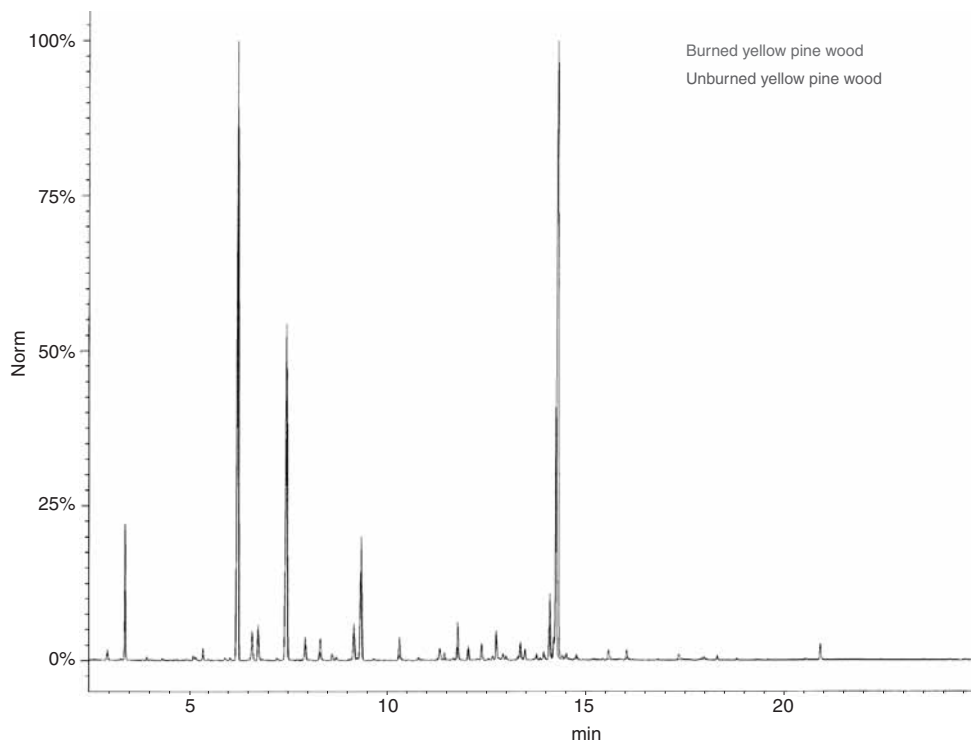


Figure 7.11 The chromatograms of burned and unburned yellow pine wood (see Colour Plate III)

Practical examples of interpretation of chromatograms and identification of sources of interferences

The following chromatograms were obtained from real samples that were analysed by the author. The data collected were interpreted using the information delivered in Chapters 6, and 7 of this book.

The purpose of this exercise is to train the investigator/analyst to look beyond the regular pattern of the possible ILR and to try to understand the sources of the different interfering products. By knowing the nature and the origin of interfering products, the interpretation of the chromatogram is simplified and, more important, the conclusion reached is much more certain.

All samples were extracted using passive headspace concentration according to ASTM standard E 1412-00 [47] at 90°C for 12–16 h on activated charcoal strip (ACS). The ACS was then desorbed using 0.5 mL of diethyl ether spiked at 100 ppm with tetrachloroethylene (PCE) as an internal standard. The extract was analysed on a Hewlett-Packard 6890-5973 GC-MS.

Before presenting the five cases, the reader is invited to look at Figures 7.12–7.15. Figure 7.12 shows the total ion chromatogram (TIC) of 75% evaporated gasoline, and the extracted ion profiles for the aromatic content are shown in Figure 7.13. The TIC of a heavy petroleum distillate ranging from C9 to C15 is shown in Figure 7.14 and the extracted ion profiles for both its aliphatic and aromatic contents are shown in Figure 7.15. These chromatograms can be compared to the case chromatograms for reference.

In Figure 7.13, the different ions represent the following groups of molecules: ion 105 for C2- and greater alkylbenzenes, ion 119 for C3- and greater alkylbenzenes, ion 117 for indan, ion 131 for substituted indans, ion 142 for methylnaphthalenes, and ion 156 for dimethyl- and ethylnaphthalenes.

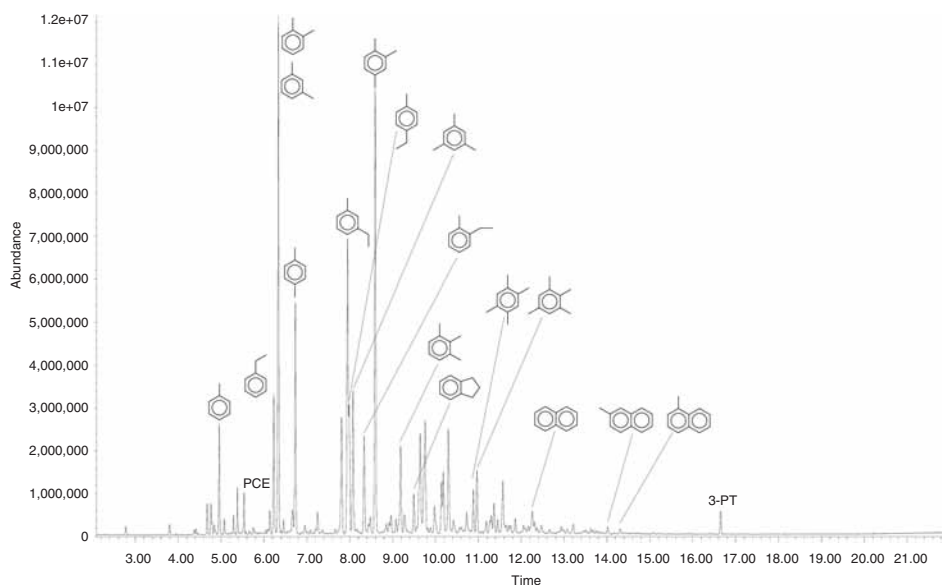


Figure 7.12 The TIC of 75% evaporated gasoline

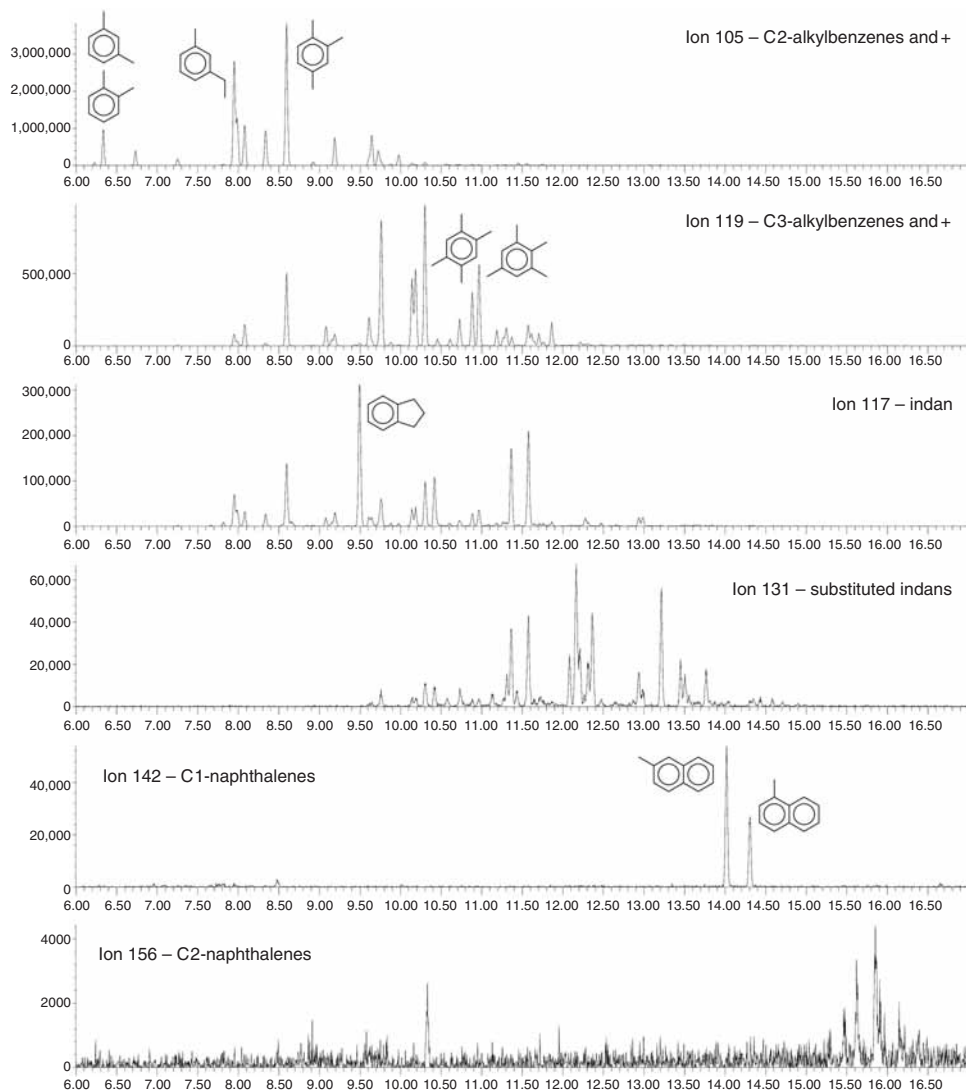


Figure 7.13 Extracted ion profiles for aromatic content in gasoline

In Figure 7.15, the different ions represent the following groups of molecules: ion 55 for alkenes, ion 57 for alkanes, ion 83 for cycloalkanes, and ion 105 for the aromatic compounds.

Case 1

This sample is a piece of carpet of unknown composition, collected from the floor of the room of origin of a house fire. Figure 7.16 shows the TIC of the extract.

At first sight, there is no obvious ignitable liquid pattern. It is possible to distinguish a few peaks between 5 and 9 min, followed by a little ‘hump’ between 10 and 13 min, a group of three peaks around 14 min, and finally a big peak around 19.5 min.

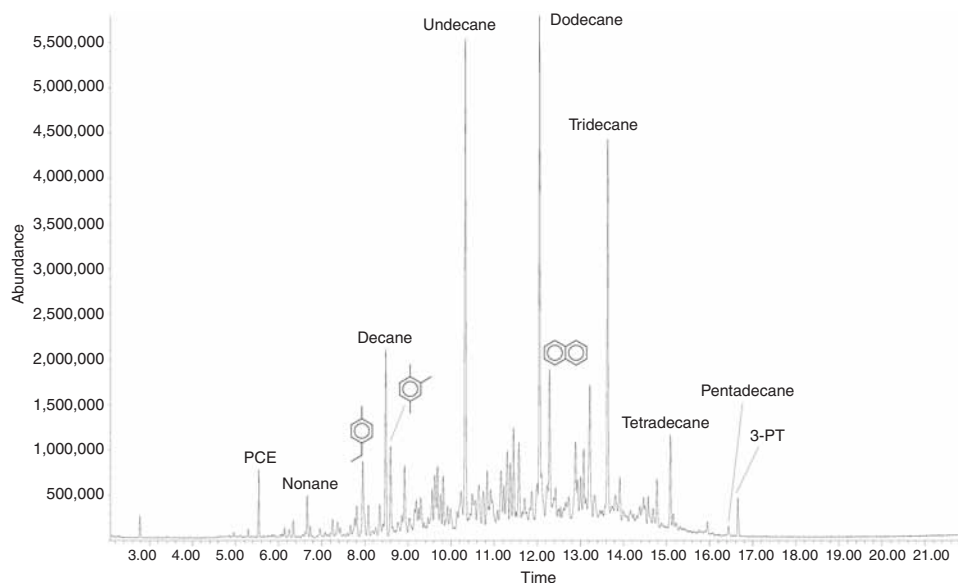


Figure 7.14 The TIC of a heavy petroleum distillate ranging from C9 to C15

The set of three peaks around 14 min is typical of carpet and are branched alkenes. They are found in a lot of different carpet samples, as shown previously in Figure 7.9.

In some instances, the little ‘hump’ can be confusing and might lead the analyst to think that a medium petroleum distillate is present. However, very often, the absence of a distinctive pattern of straight alkanes allows the rapid elimination of the presence of an MPD. This can be easily shown by extracting ions 55, 57, and 83, as presented in Figure 7.17. Furthermore, when looking at the individual peaks and identifying them using the mass spectral library, it is possible to quickly realize that most of these peaks are unsaturated and, therefore, unlikely to come from an ignitable liquid. As shown previously in the chapter, the hydrocarbon ‘hump’ around C10–C15 is often found as SBP in carpet sample.

Hence, the time span from 10 to 14 min was attributed to interfering products. The early eluting peaks in the chromatogram can be rapidly identified through a library search; 2,4-dimethyl-1-heptene (5.9 min), styrene (6.7 min), benzaldehyde (8.0 min), α -methylstyrene (8.3 min), and acetophenone (10.0 min) are all pyrolysis and combustion products. They do not originate from an ignitable liquid. Even 1,2,3-trimethylbenzene (8.6 min) can be produced by pyrolysis.

The final step consists in extracting ion profiles for aromatics. In this case, it did not reveal the presence of any ILR.

Case 2

This sample comes from a house fire. The fire was deliberately set and showed three separate areas of origin. Use of ignitable liquids was suspected due to the burn patterns. This is one of the samples collected by the author and analysed at the laboratory. It encompasses the remains of a trailer of unknown material that was used to spread the fire throughout the attic.

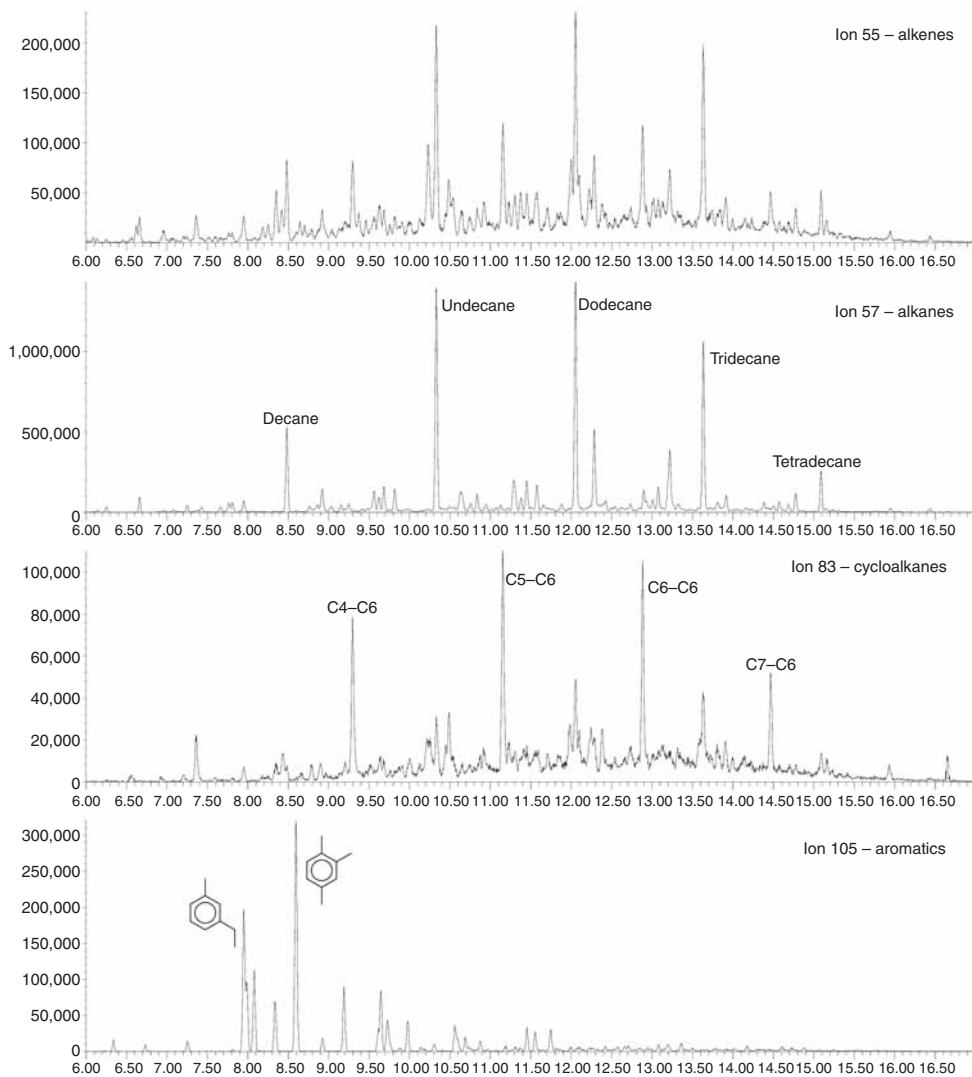


Figure 7.15 The extracted ion profiles for aliphatic and aromatic contents of the heavy petroleum distillate

Figure 7.18 shows the TIC of the extract. At first sight, it is possible to distinguish two patterns; an early-eluting one between 4 and 8 min, and a nice bell-shape pattern, of less intensity, between 8 and 18 min.

When the ions 55, 57, 83, and 105 are extracted, as shown in Figure 7.19, the pattern is immediately clearer. Again, without a close examination of the bell-shape pattern between 8 and 18 min, one would tend to conclude that there is a heavy petroleum distillate. However, a closer look at the pattern shows that there are doublets of peaks in the 55-window, which is indicative of pyrolysis products or polyethylene or asphalt. In this instance, the presence

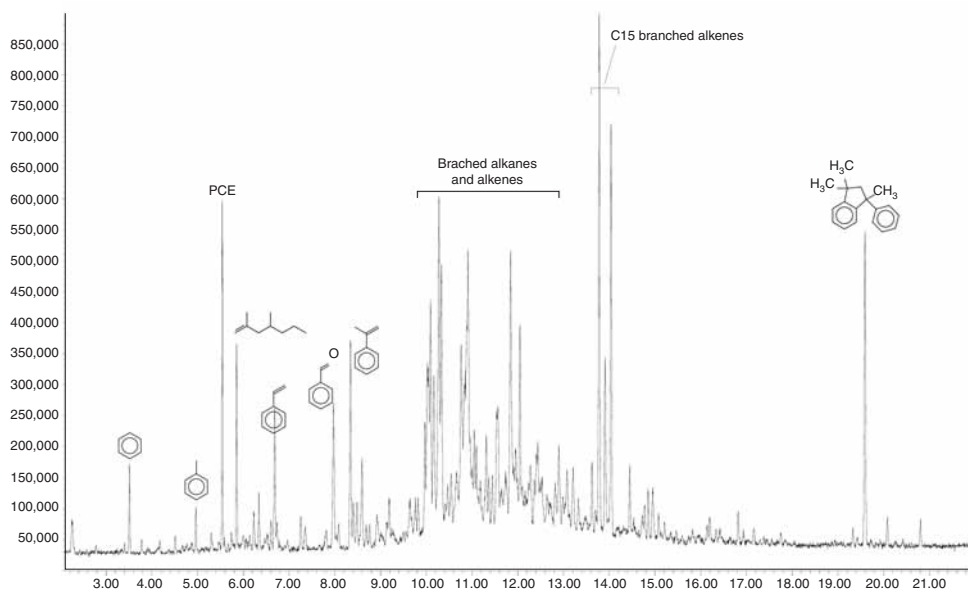


Figure 7.16 The TIC of the extract of a carpet sample obtained from a house fire (Case 1)

of doublets of peaks instead of triplets would suggest that it would originate from asphalt rather than polyethylene [20]. Also, the cycloalkanes in the 83-window do not originate from the pyrolysis of polyethylene [38]. All these elements suggest that the series of peaks from 8 to 18 minutes do not originate from an ignitable liquid.

When a closer look is taken at the early-eluting pattern, it is possible to distinguish a strong signal in the 57-window, which is almost perfectly mirrored in the 55-window. A library search of the different peaks in that region shows the presence of the following compounds: 2-methylhexane (3.5 min), 3-methylhexane (3.6 min), *n*-heptane (4.0 min), 2-methylheptane (4.9 min), 3-methylheptane (5.0 min), *n*-octane (5.3 min), 2,6-dimethylheptane (5.7 min), 2,3-dimethylheptane (6.1 min), 3-methyloctane (6.3 min), and *n*-nonane (6.7 min).

These products are not generated by the pyrolysis of polymers, and are not found in such quantity in substrate background. The presence of a light petroleum distillate ranging from C7 to C9 is, therefore, established.

In this instance, the study of the extracted ion profiles for the aromatic products did not reveal any pertinent data.

Case 3

This sample comes from the front driver's floorboard of a burned American car. It is extremely common for fire investigators to sample the floorboard of a vehicle when arson is suspected. The reasons behind that is the fact that most arsonists will basically spill an ignitable liquid throughout the seats of the vehicle and make a trailer on the floorboard up to the door, where they can light it in a safely manner. When the vehicle sustains the subsequent fire, all the upholstery and filling materials of the seats will often be completely consumed, and, usually, the only remaining debris is on the floorboard.

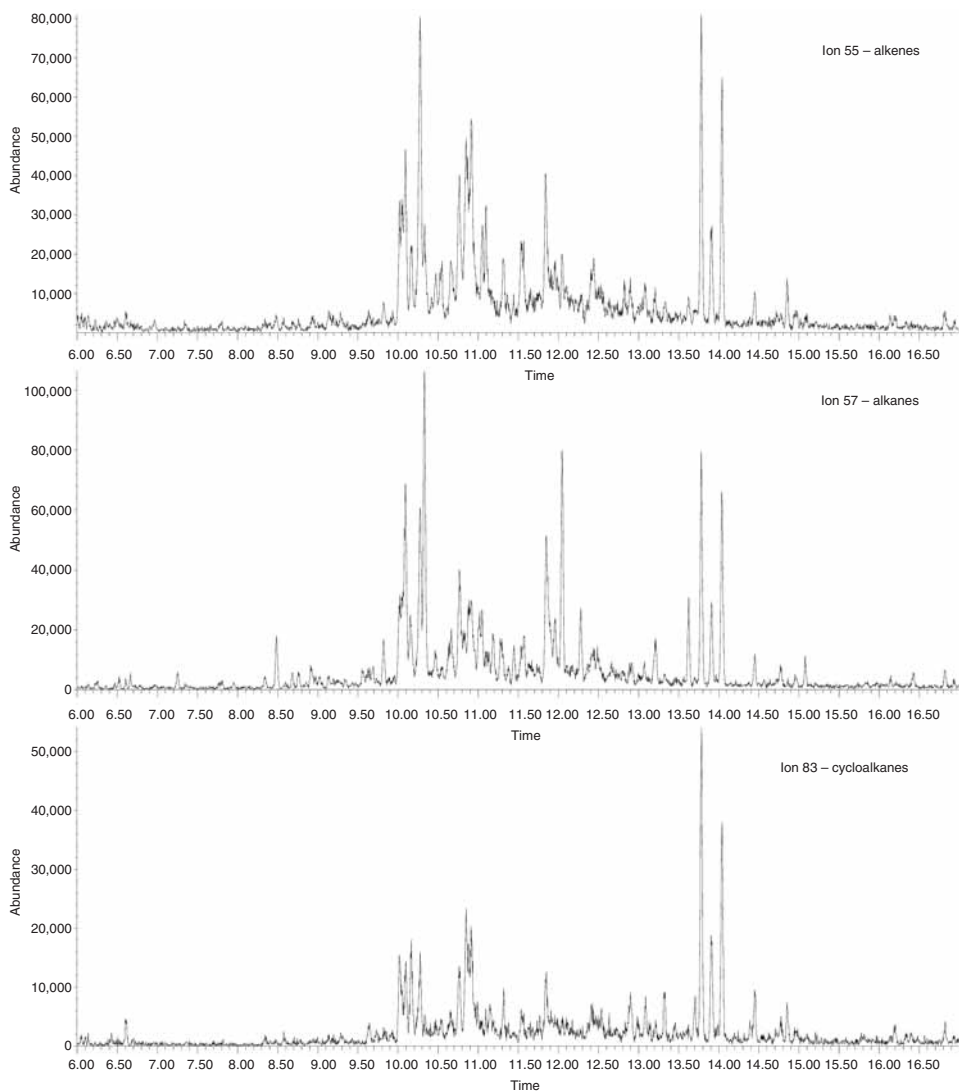


Figure 7.17 Extracting ion profiles of ions 55, 57, and 83 of the sample in Case 1

If the fire was not intense or long enough to completely burn out the floorboard, this kind of sample will usually contain a lot of interfering products. This is due to the fact that it encompasses the carpet as well as any objects that fell on the floor at some point in the fire. So, in considering the composition of the interfering products, one must take into account not only the complex composition of the carpet, but also the composition of fallen objects, which could include ABS, polystyrene and many other polymers. Therefore, these kinds of samples could include a wide collection of aromatic compounds led by the high presence of styrene and α -methylstyrene.

Figure 7.20 shows the TIC of the sample's extract. There are very few peaks and there is no obvious pattern of ignitable liquid.

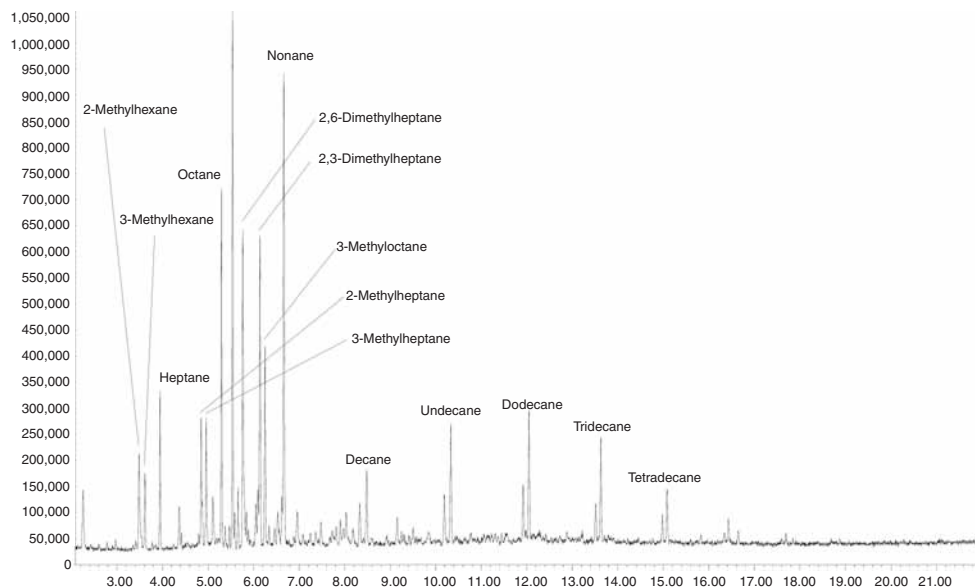


Figure 7.18 The TIC of the extract of sample from a house fire (Case 2)

It is possible to distinguish toluene (5.0 min), ethylbenzene (6.2 min), styrene (6.7 min), α -methylstyrene (8.4 min), and naphthalene (12.3 min). Indeed, there are other compounds such as methylheptene (5.9 min), phenol (8.1 min), and tetradecanediol (10.2 min). All these compounds are interfering products originating from the different polymers constituting the passenger compartment of the vehicle.

Even when no obvious pattern is present, it is necessary to extract the ion profiles and confirm the presence or support the absence of ILR. Figure 7.21 shows the extracted ion profile for the ions 105, 119, 117, 131, 142, and 156.

In the 105 window, it is possible to notice that most of the C2-alkylbenzenes are present. Even if the styrene peak slightly masks the pattern, the ratios are not similar to the ones presented by the gasoline profile shown in Figure 7.13.

In the 119 window, it is possible to distinguish the weak signal given by most of the C3-alkylbenzene, but again in the wrong ratios.

The 117 and 131 windows, while mostly hidden by the tall α -methylstyrene peak, present very few indans and methylindans, common to the aromatic content of petroleum distillates. By taking a particular look at the 131 window, it is possible to realize that the peak ratios are not at all consistent with those of common petroleum products. When referred to Figure 7.13 it is possible to see that the proportions in between ions are not appropriate either.

The 142 window, representing the methylnaphthalenes, is very useful. In all petroleum distillates, the 2-methylnaphthalene (14.0 min) is greater than the 1-methylnaphthalene (14.3 min). If this ratio is inverted, it means that there is a contribution from the pyrolysis of the substrate. In this case they are equally great and indicate that they might originate from the pyrolysis process rather than an ILR. However, it is important to note that an inversion of this ratio does not mean that an ILR is not present; the methylnaphthalenes from an ILR could be present in addition to those produced from the substrate resulting in a skewed proportion.

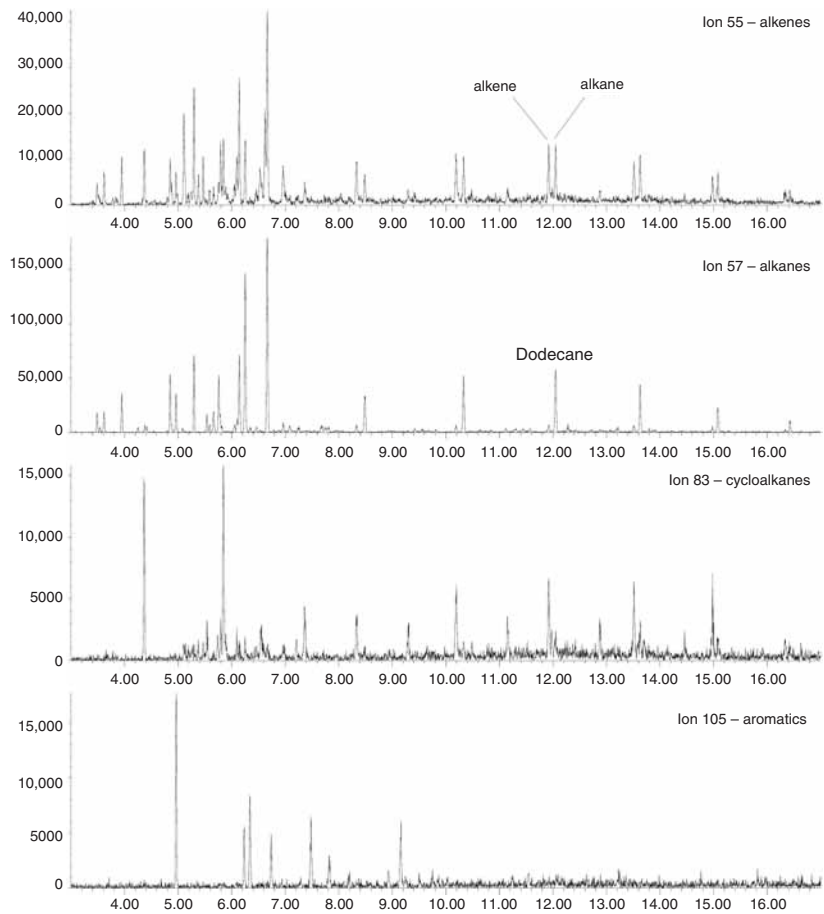


Figure 7.19 Extracted ion profiles of ions 55, 57, 83 and 105 of the sample in Case 2

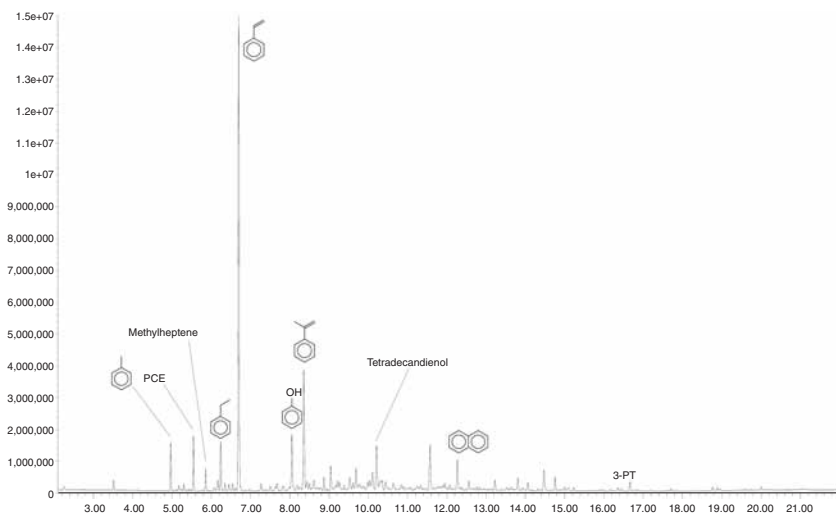


Figure 7.20 The TIC of the extract of a sample from a burned American car (Case 3)

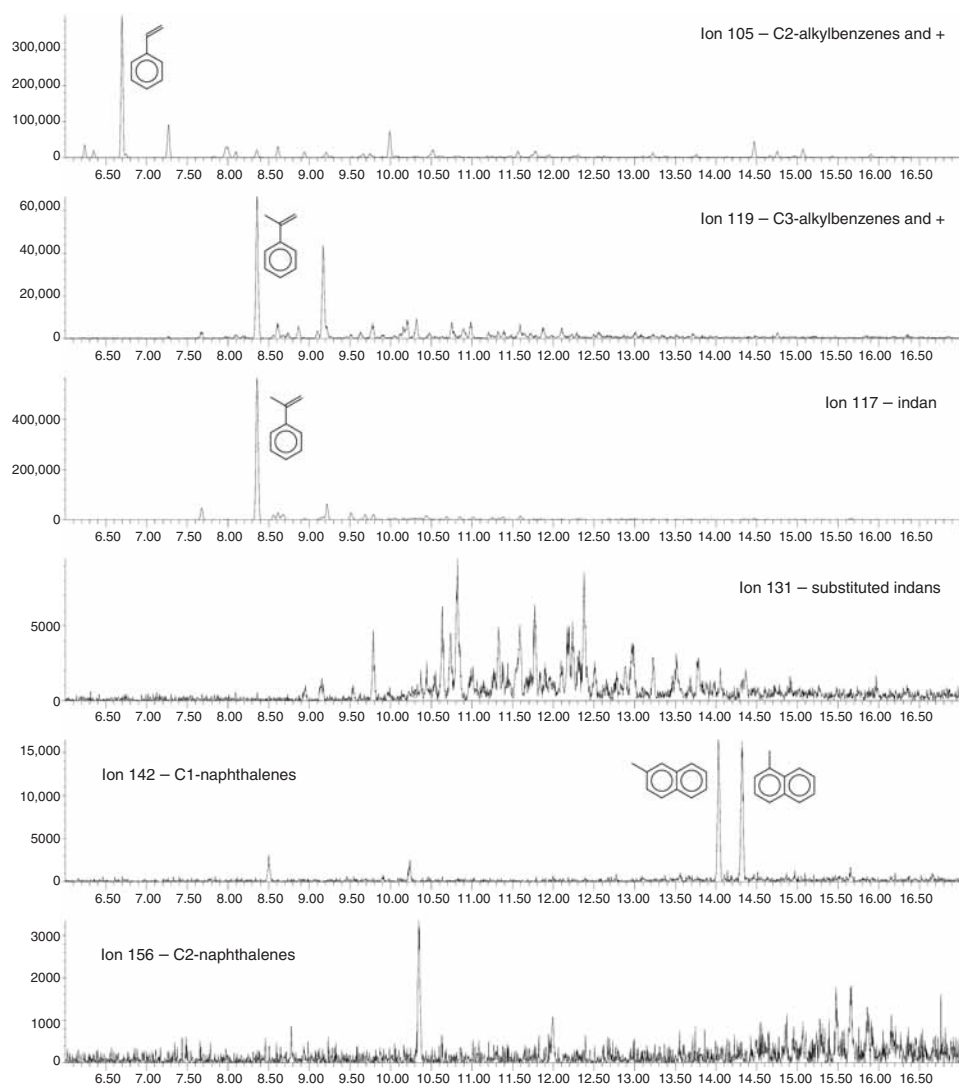


Figure 7.21 Extracted ion profiles for the ions 105, 119, 117, 131, 142, and 156 of the sample in Case 3

Finally, it is barely possible to distinguish any of the dimethyl- and ethylnaphthalenes in the 156 window. The extracted ion profile of ions 55, 57, and 83 did not reveal any ILR pattern. Therefore, it is possible to conclude that this sample failed to reveal the presence of any ILR. It solely contains interfering products typical of the polymers found in the passenger's compartment of a car.

Case 4

This sample consists of a piece of burned carpet removed from the room of origin of a house fire.

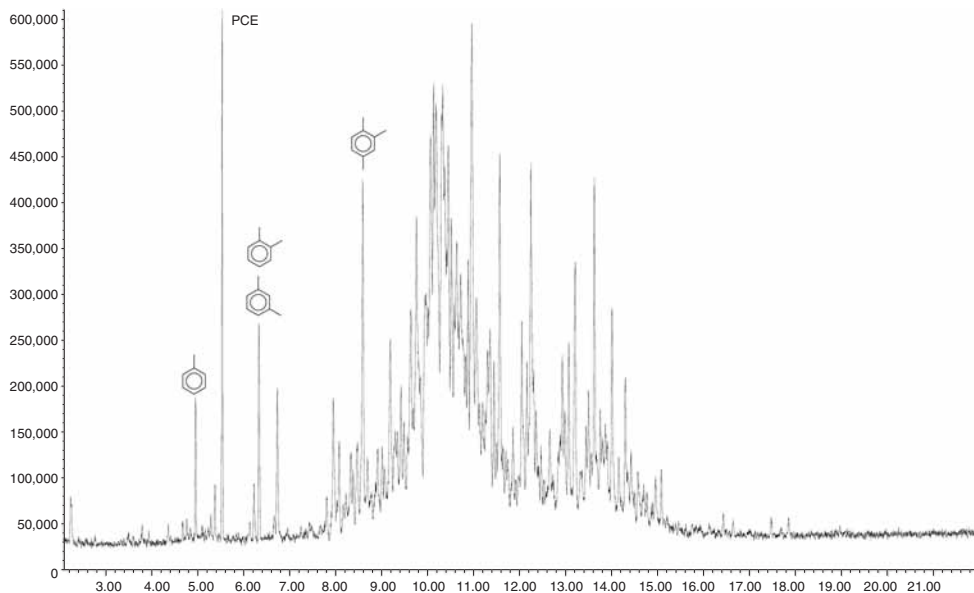


Figure 7.22 The TIC of the extract from a sample of burned carpet from a house fire (Case 4)

Figure 7.22 shows the TIC of the extract. At first sight, it is possible to distinguish a few peaks between 5 and 7 min, followed by a big “hump” between 8 and 16 min. While this hump is wider than the one presented in Figure 7.16, it is totally expected in a carpet, and is very likely made of branched alkanes and alkenes.

When the extracted ion profiles of ions 55, 57, and 83 are studied, it is possible to notice two distinct patterns, as shown in Figure 7.23. The first one is between 8 and 11.5 min and is represented by the typical hump found as SBP in most carpet. The 55 and 83 windows are very similar and the 57 window is weak and does not present any logical patterns.

By contrast there is an evident pattern of straight alkanes starting at 12.1 min with *n*-dodecane, followed by *n*-tridecane (13.6 min), and *n*-tetradecane (15.2 min). Indeed, the cycloalkanes are just pointing out, as seen in-between the *n*-alkanes in the 83 window.

The extracted ion profiles presented in Figure 7.24, present a very clear pattern of aromatics that is matching the pattern shown in Figure 7.13.

The pattern shown by the sample was not generated solely from interfering products there are ILR contributing to this pattern. A very strong signal of that evidence is that the ratio of the methylnaphthalenes peaks at 14.0 and 14.3 min; 2-methylnaphthalene is greater than 1-methylnaphthalene, which is highly indicative of the presence of ILR.

The much greater aromatic content compared to the aliphatic content indicates that the pattern originates from weathered gasoline rather than a medium petroleum distillate.

Case 5

This sample is constituted of burned paper and tape that were removed from the room of origin of a house fire. Figure 7.25 shows the TIC of the extract. The chromatogram presents a familiar pattern, but there are a large number of extraneous peaks. Some of the greatest

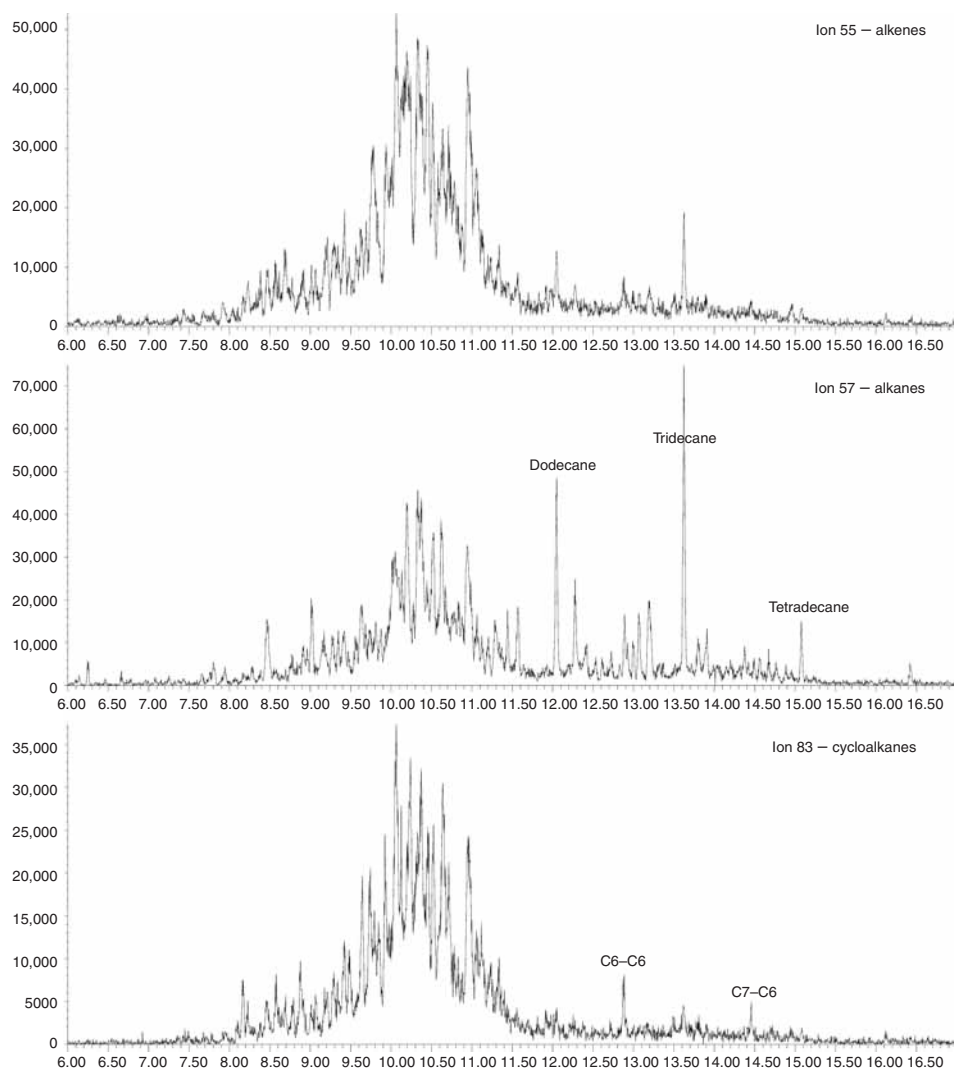


Figure 7.23 Extracted ion profiles of ions 55, 57, and 83 of the sample in Case 4

peaks are 1-butanol (3.4 min), propylene glycol (4.4 min), toluene (5.0 min), hexanal (5.3 min), furfural (5.8 min), ethylbenzene (6.2 min), *m*- and *p*-xylenes (6.3 min), *o*-xylene (6.7 min), 3-ethyltoluene (8.0 min), methylheptanol (8.3 min), 1,2,4-trimethylbenzene (8.6 min), cyclohexane (9.13 min), *d*-limonene (9.2 min), 3-furanmethanol (10.8 min), and two substituted propanoic acids at 14.7 and 15.0 min.

The presence of oxygenated compounds such as furfural, furanmethanol, butanol, hexanal, etc. is not surprising. Since the substrate is paper, it is expected to obtain these kinds of pyrolysis products. Also, there is tape present in the sample. The housing of the tape is probably made of polystyrene and the tape itself of polyester, as seen previously. This contributed

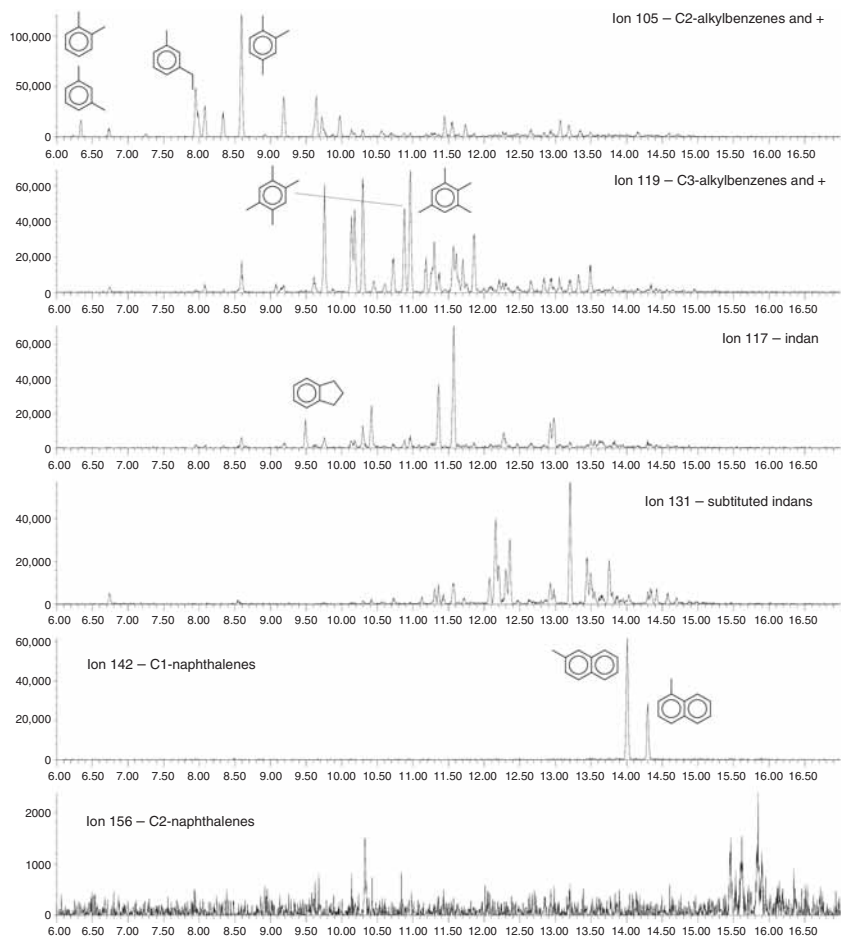


Figure 7.24 Extracted ion profiles of ions 105, 119, 117, 131, 142, and 156 of the sample in Case 4

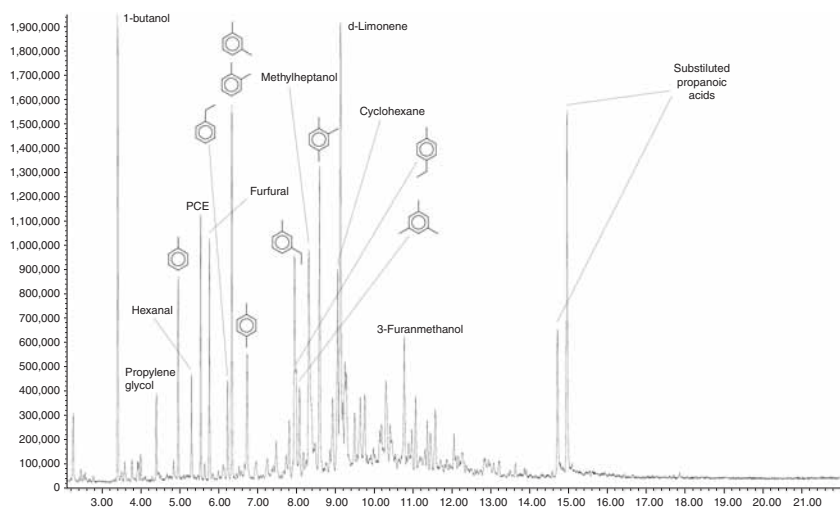


Figure 7.25 The TIC of the extract of a sample of burned paper and tape from a house fire (Case 5)

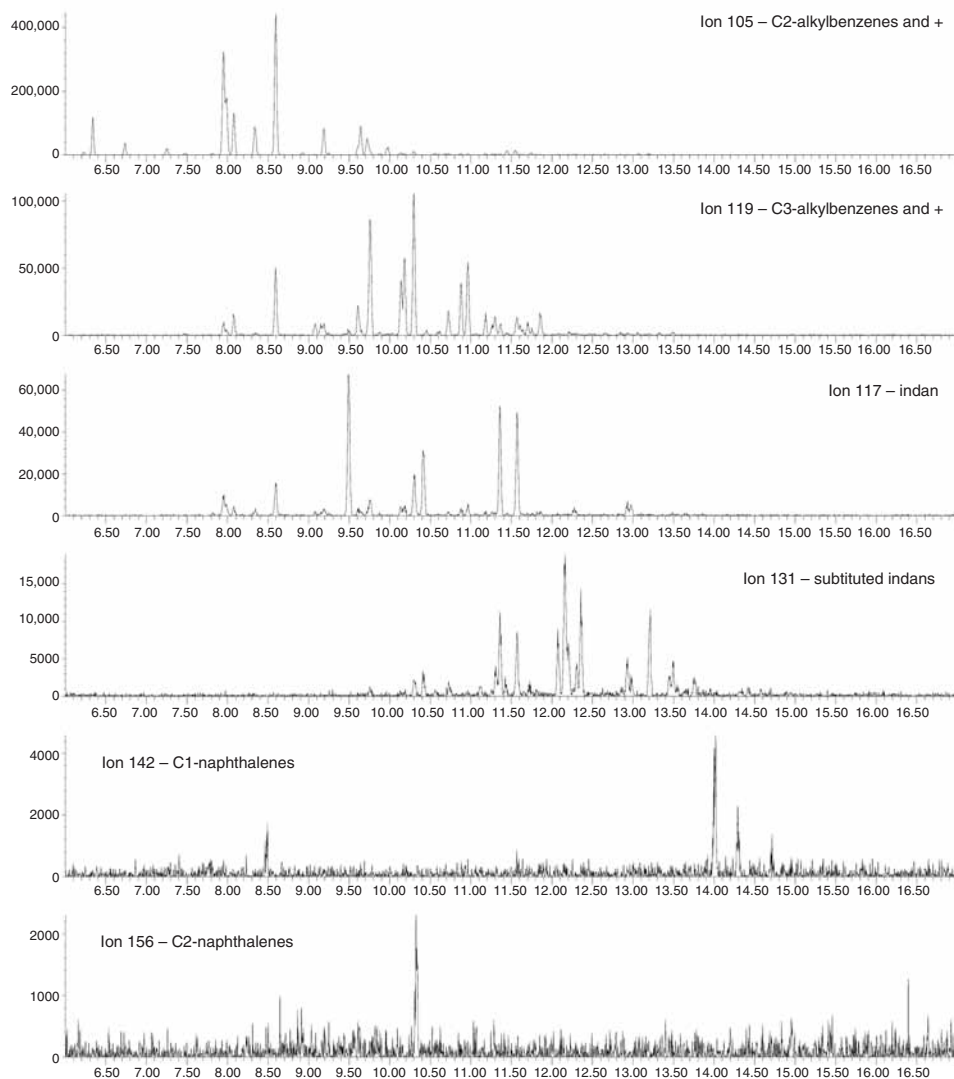


Figure 7.26 Extracted ion profiles for the ions 105, 119, 117, 131, 142, and 156 of the sample in Case 5

slightly to the pyrolysis products content, however styrene and α -methylstyrene are very small peaks.

By contrast the strong presence of certain aromatic compounds such as 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and some other C2 and C3-alkylbenzenes, should catch the attention of the scientist and will require more investigation. Figure 7.26 shows the extracted ion profiles for the ions 105, 119, 117, 131, 142, and 156.

When compared to Figure 7.13, it is obvious that the pattern of all these ions is perfectly matching, with the exception of ion 156, in which the expected peaks are absent in the

sample. This is encountered with some gasolines. In this instance, the presence of weathered gasoline in the sample does not cause any doubt.

Conclusion

The complicated part of fire debris analysis is the interpretation of the chromatograms. This interpretation is difficult due to the facts that ignitable liquids encompass hundreds of different compounds, and that their patterns are modified by weathering and other degradation mechanisms occurring in the sample. Also, interfering products in the substrate that are analysed simultaneously with the compounds of interests can cause great complications.

These interfering products originate from three sources. First, there are the substrate background products (SBPs) that can be divided in natural products, manufacture induced products, and contamination (direct and indirect). Second, there are the pyrolysis products, produced by the burning polymers that comprise most common substrates. Finally, there are the combustion products, created by the oxidation of pyrolysis products and poor burning conditions.

Substrates submitted to fire debris analysts for ILR recovery and identification are complex in the sense that they are made of multiple different polymers, partially burned, and naturally contaminated by their everyday use.

When levels of ignitable liquids are high among a substrate, there is very little doubt about the identification of such ILR. However, when the levels get low enough to start being confused with the background, it becomes very difficult to render a conclusion.

By knowing the substances as well as the chemistry of the polymers that are used in everyday life and that are submitted to the laboratory as fire debris, it is possible to better understand the kind of products that are encountered in negative samples.

This chapter not only presented the basis of understanding such concepts, but it also provided a few examples of real samples typical of those encountered every day in the laboratory. Hopefully, the reader would have grasped the concepts explained and understood the examples. It would require several books such as this one to go over most of the substrates and to present every kind of possible situation. This is not the purpose of this chapter. However, it has presented enough of the basic concepts and ideas for the fire debris analyst to start studying 'blank' substrates with another view and to get more accustomed to these products.

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