

Concept of pyrolysis for fire debris analysts

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This paper introduces the mechanisms of pyrolysis to fire debris analysts. Pyrolysis products are produced during the combustion of substrates that are submitted to forensic laboratories for ignitable liquid residues recovery. These products, among others, create interferences and complicate the interpretation of chromatograms. Pyrolysis follows certain rules, depending mainly on the substance involved. These mechanisms are presented and illustrated with practical examples of burned substrates analyzed according to ASTM standards. Bond dissociation energies represent an important factor in the route taken by a polymer to produce pyrolysis products. These are presented, as well as the structures of some polymers commonly encountered in fire debris. The understanding of these concepts should improve the interpretation of fire debris chromatograms.

Le but de cet article est d'introduire le mécanisme de pyrolyse aux analystes traitant des débris d'incendies. Les produits de pyrolyse se créent durant la combustion de matrices qui sont soumises aux laboratoires forensiques pour la recherche de résidus de liquide inflammable. Ces produits, parmi d'autres, créent des interférences et compliquent l'interprétation des chromatogrammes. La pyrolyse suit certaines règles qui dépendent principalement de la substance impliquée. Ces mécanismes sont présentés et illustrés avec des exemples pratiques de matrices brûlées et analysées selon les standards ASTM. Les énergies de dissociation de liaisons représentent un facteur important dans le chemin pris par un polymère pour produire des produits de pyrolyse. Ceux-ci sont présentés, ainsi que les structures de certains polymères que l'on rencontre fréquemment dans les débris d'incendie. La compréhension de ces concepts devrait améliorer l'interprétation des chromatogrammes provenant de débris d'incendie.

In diesem Bericht werden Brandrückstandsanalytikern die Mechanismen der Pyrolyse vorgestellt. Pyrolyseprodukte werden während der Verbrennung von Materialien erzeugt, die kriminaltechnischen Laboratorien zum Nachweis von Brandbeschleunigern vorgelegt werden. Diese Produkte erzeugen unter anderem Störungen und erschweren die Auswertung von Chromatogrammen. Die Pyrolyse folgt bestimmten Regeln, die hauptsächlich von den jeweiligen Substanzen selbst abhängig sind. Diese Mechanismen werden vorgestellt und anhand von Beispielen aus der Praxis der Analyse verbrannter Substrate entsprechend den ASTM-Richtlinien erläutert. Dissoziationsenergien chemischer Bindungen stellen einen wichtigen Faktor auf dem Weg vom Polymer zu seinen Pyrolyseprodukten dar. Diese werden ebenso vorgestellt wie die Strukturen einiger Polymere, die häufig in Brandrückständen vorgefunden werden. Ein Verständnis dieser Konzepte sollte zu einer besseren Interpretation der aus Brandrückständen erhaltenen Chromatogramme führen.

El propósito de este trabajo es introducir los mecanismos de pirólisis a los analistas de residuos de incendios. Los productos de pirólisis se producen durante la combustión de sustratos que son enviados a los laboratorios forenses para la recuperación de residuos de líquidos combustibles. Estos productos, entre otros, crean interferencias y complican la interpretación de los cromatogramas. La pirólisis sigue determinadas reglas dependiendo fundamentalmente de la sustancia de que se trate. Se presentan estos mecanismos y se ilustran con ejemplos prácticos de sustratos quemados analizados según los standards ASTM. Las energías de disociación de enlaces representan un factor importante para determinar la ruta seguida por el polímero para producir sus productos de pirólisis. Se presentan éstos así como las estructuras de algunos polímeros que se encuentran con mayor frecuencia en los residuos de incendios. El entendimiento de estos conceptos puede ayudar a interpretar mejor los cromatogramas de residuos de incendios.

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Key words Forensic science, pyrolysis, ignitable liquid, gas chromatography, fire debris analysis, polymer, thermal degradation.

Introduction

Fire debris analysis is possibly one of the most complicated fields of forensic science. While the extraction of ignitable liquid residues (ILR) from debris and the chromatographic analysis are relatively simple procedures, the interpretation of results requires very advanced skills. This is due, at least in part, to the presence of interfering products in the residues analysed [1–5]. These products can mask the pattern of the compounds of interest and render the interpretation of chromatograms extremely difficult in some instances. Recent research has shown that these interfering products originate from multiple sources [6]. One source is the substrate background products [7,8]. Another source is the pyrolysis products released by the burning substrate [2,9].

The understanding of phenomenon behind the analyses performed is essential in the interpretation of data. Unfortunately, in the field of fire debris analysis, there is often a lack of understanding of certain concepts, notably the concept of pyrolysis that occurs during a fire. While one knows that pyrolysis products are present in fire debris samples, it is not always obvious how these products are created and how they appear. More recently, an article dealing with the study of pyrolysis products in fire debris proved that some basic concepts are indeed not understood [10].

The purpose of this paper is to introduce to fire debris analysts the basic principle of pyrolysis and to present the processes by which it occurs. Furthermore, it will present practical examples of samples analysed at the laboratory using standard ILR extraction procedures.

Definition of pyrolysis

There are numerous variations of the definition of pyrolysis [11–13]. The following definition integrates the various descriptions [6]:

“Pyrolysis is 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.”

From this definition, it is possible to deduce and infer the following statements:

1. Pyrolysis is defined as the decomposition of a material into simpler compounds by the action of heat alone.
2. The pyrolysis process does not imply a reaction between an oxidant and a reducing agent. It is merely decomposition of a material subjected to heating, without involving any other substances.
3. The more heat that is provided (energy transferred), the faster the pyrolysis will occur and eventually, if an oxidant (oxygen) is present in the correct proportion, a flaming fire will result.

4. In the flaming fire, it is not the combustible solid/liquid that is burning, but the gaseous pyrolysis or evaporation products released by the combustible substrate.

5. The non-flaming (glowing) fire is a peculiar case in which the combustion reaction occurs at the solid surface, and depends on a variety of factors that are not discussed in this paper.

6. The only solids that do not undergo pyrolysis prior to burning are the solids that undergo sublimation [13].

While pyrolysis typically takes place between 500 and 800°C, three other levels are usually considered [14]: from 100 to 300°C, the phenomenon is usually defined as thermal degradation rather than pyrolysis; between 300 and 500°C, it is a mild pyrolysis; above 800°C, it is a vigorous pyrolysis.

Materials and methods

Samples of pure polymers (polyethylene, polypropylene, polyvinyl chloride, polystyrene, and cellulose (paper)) were ignited using a propane torch until they sustained flaming combustion and were allowed to burn about two minutes. They

Table 1 Separation and analysis parameters.

Separation	Type	Passive headspace concentration
	Container	One-quart paint lined (polyester) can (Ribelin Sales, Austell, GA, USA)
	Adsorbant	1/3 of an activated charcoal strip (app. 6 x 8 mm) (Albrayco Labs, Cromwell, CT, USA)
Conditions	Elution	16 hours at 87°C
		0.5 ml of diethyl ether spiked with 100 ppm of tetracholorethylene (PCE)
Column	Type	Hewlett-Packard HP-5 (5% diphenyl methyl siloxane)
	Dimensions	30m x 0.25mm x 1.00µm
Mobile phase	Carrier gas	Helium
	Flow rate	1 ml/min (flow electronically controlled)
Injection	Type	Liquid/Autosampler Splitless
	Volume injected	1 µl
Temperatures	Injector	250°C
	Column	55°C for 2 min
		20°C/min to 115°C for 2 min
		10°C/min to 285°C for 2 min
		Total run 26.5 min
Mass Spec	Transfer line	280°C
	Quadropole	150°C
	Source	230°C
	Scanning range	33-400 amu
	Solvent delay	2.00 min
	Sampling	3.92 scans/sec

were extinguished with less than 10 ml of deionised water using a spray mist. This procedure has previously been shown to produce enough products representative of the pyrolysis of the polymers [6]. Also, the qualitative reproducibility of the results obtained has been verified and determined to be excellent [6].

Figure 1 Random scission mechanism (example of polyethylene).

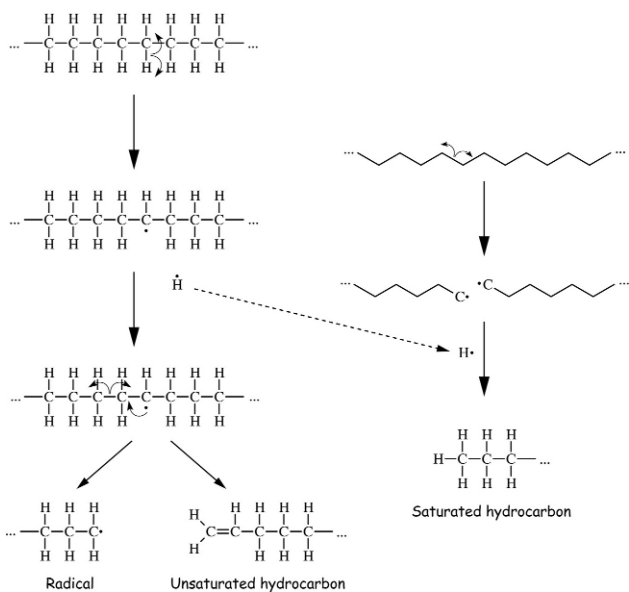


Figure 3 Extracted ion profiles of ions 55, 57 and 83 of burned polyethylene between 6 and 20 min (n-alkanes are marked from C₉ to C₁₇). Note the absence of cycloalkanes in the ion 83 window between the n-alkanes as well as the absence of pristane after C₁₇.

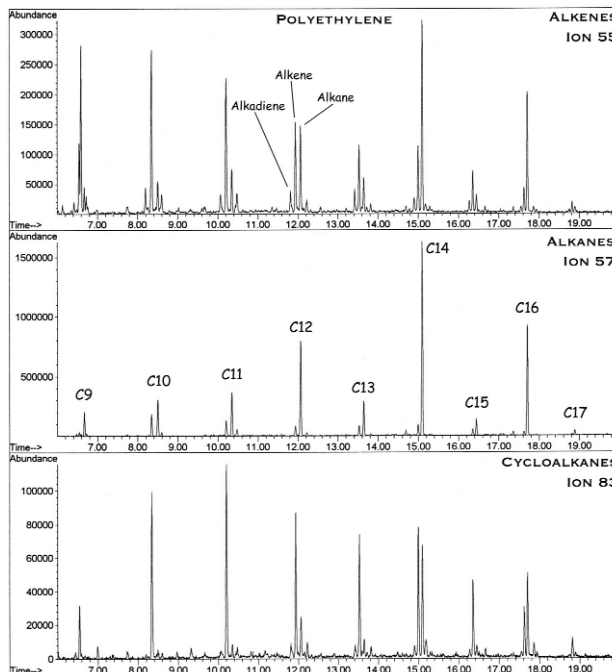


Figure 2 Total ion chromatogram of burned polyethylene (n-alkanes are marked from C₈ to C₂₀, PCE and 3-PT represent the internal standards).

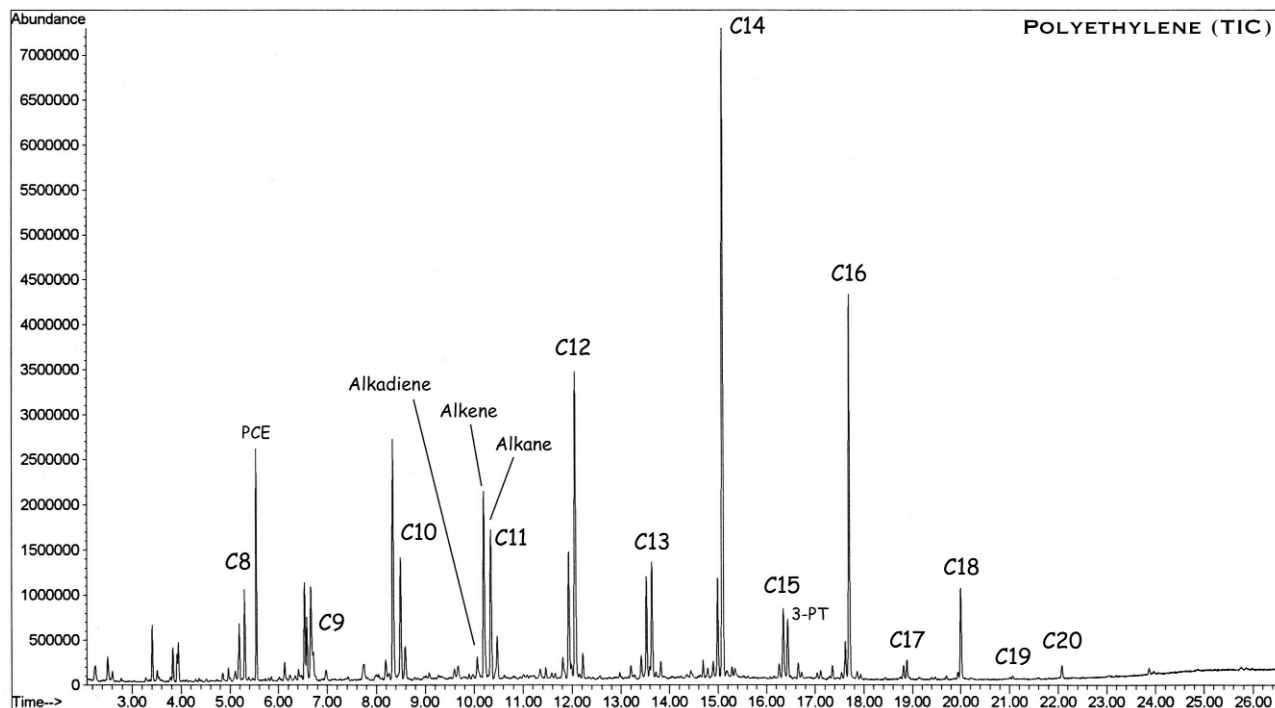
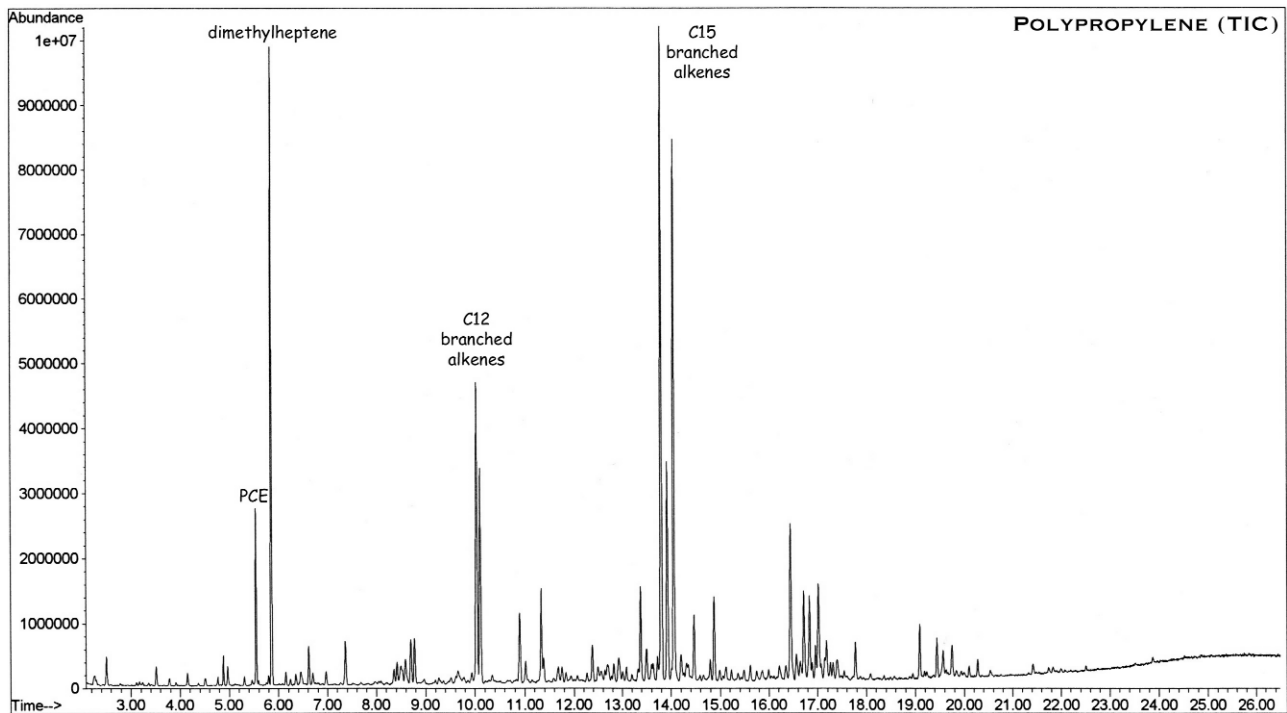


Figure 4 Total ion chromatogram of burned polypropylene, which consists of groups of peaks representing branched alkanes, alkenes and alkadienes (PCE represents the internal standard).



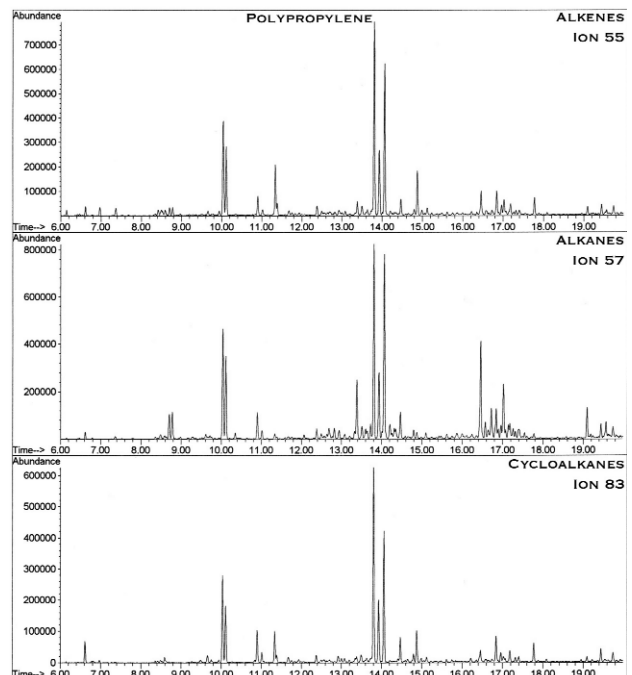
When a substrate is freely burned, most of the pyrolysis products released by the substrate will be fuelling the flame. However, part of them will get adsorbed onto the substrate. This is why they are later recovered during the extraction procedure. Freely burning substrate is not totally representative of “pure” pyrolysis since combustion products will be produced too and not all the pyrolysis products are recovered. On the other hand, it is very representative of the pyrolysis products obtained in real-world fire debris.

Samples were extracted using passive headspace concentration according to ASTM standard practice E1412 and analysed by gas chromatography-mass spectrometry according to ASTM standard guide E1618 using a Hewlett-Packard 6890-5973 gas chromatograph-mass spectrometer (GC-MS) [15–17]. Prior to adsorption step, each sample was spiked with a first internal standard (20 µl of a 2.5% 3-phenyltoluene in diethyl ether). This allows the verification of the extraction process. A second internal standard, tetrachloroethylene (PCE), is dissolved in the desorption solvent, diethyl ether, at 100 ppm. This allows the verification of the injection in the GC-MS. Details of the separation and analysis procedures are presented under Table 1.

Process of pyrolysis

Pyrolysis of polymeric material commonly occurs using different mechanisms of degradation. They are described as follows:

Figure 5 Extracted ion profiles of ions 55, 57 and 83 of burned polypropylene between 6 and 20 min. Note the absence of n-alkanes in the ion 57 window in comparison with Figure 3.



Random scission

The backbone of the polymer is broken apart randomly since all the C–C bonds are of the same strength [12, 18]. As shown in Figure 1, the hydrocarbon chain is randomly broken and resulting products will be of the form of alkanes, alkenes, and alkadienes of smaller sizes.

This kind of scission is typical of polyethylene (PE), which will lead to the formation of the well-documented series of “triplets” of peaks found in chromatograms of burned PE or asphalt. These “triplets” usually range from C₆ to C₂₅ or more. The chromatogram presented in Figure 2 shows the results of the analysis of burned polyethylene bags. The triplets are readily distinguishable and the greatest peak is C₁₄ (15.1 min). In this instance, the distribution of the series of triplets neither follows the typical bell-shaped pattern sometimes observed with the pyrolysis of tar material, nor is it even [6,19]. In addition, it is possible to detect the presence of very small extraneous peaks adjacent to the triplets. While the PE analysed is known as HDPE (high density polyethylene), which means it is not branched, there is probably a very low concentration of branched polymer, which would explain these peaks [20].

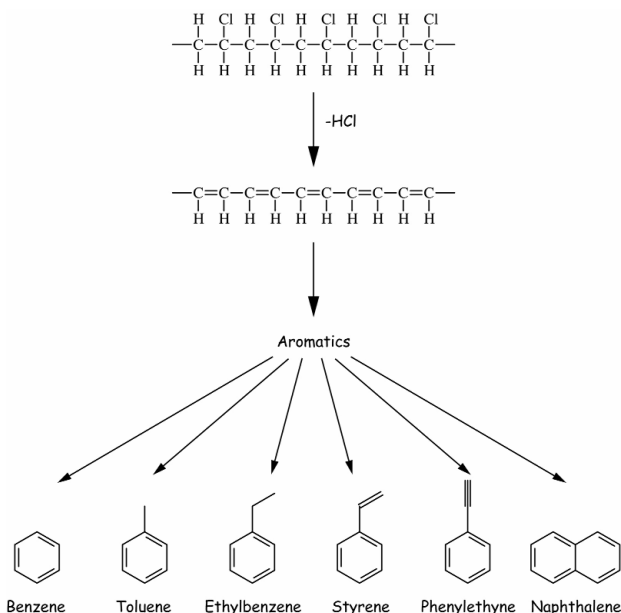
Figure 3 represents the extracted ions 55 (indicative of alkenes), 57 (indicative of alkanes) and 83 (indicative of alkenes and cycloalkanes) of the chromatogram between 6 and 20 minutes. Notice that the alkene and alkadiene peaks are greater in the 55 profile than in the 57 profile, where the alkanes are the greatest. Indeed, the 83 profile shows that the cycloalkanes are not present (they would occur between the n-alkanes), since they are not generated during the pyrolysis process. The absence of cycloalkanes in pyrolysis products has been reported by Lentini [19].

Figure 4 shows another example of a polymer undergoing random scission. Polypropylene (PP) is similar to PE, except that it possesses branched methyl groups along its backbone, which seriously complicates the chromatogram. Every other carbon in the chain is tertiary, since it holds a methyl group. The repetitive sequence is less obvious than the “triplets” of PE, but does exist and each oligomeric group vary by three carbons [21, 22]. This is explained by the fact that the scission of the carbon chain occurs predominantly between the tertiary and the secondary carbon [23]. Figure 5 shows the extracted ions 55, 57 and 83 between 6 and 20 minutes. There is a total absence of n-alkanes due to the substituted methyl groups.

Side Group Scission (a.k.a. side group elimination or chain-stripping)

In side group scission, the groups attached to the side of the backbone are cleaved and the resulting backbone becomes polyunsaturated (polyene). Figure 6 shows the side group scission of polyvinyl chloride (PVC). The pyrolysis yields to the conjugated double bond backbone. Therefore, the formation of aromatic compounds is relatively straightforward from that point. The conjugated chain will break randomly at a C–C bond, yielding to aromatic compounds such as benzene, toluene, ethylbenzene, styrene and naphthalene [12, 24]. Degradation of PVC has been documented to start at about 250°C and HCl

Figure 6 Side group scission mechanism (example of polyvinyl chloride).



commonly represents more than 95% of the volatiles produced [13, 23].

Similar polymers that differ only by their side groups, such as polyvinyl acetate, undergo this kind of scission [25–27]. The resulting pyrolysis products are very similar or identical since the backbone is the same once the side groups are eliminated.

The chromatogram shown in Figure 7 represents burned PVC pipes. The main peaks are benzene (3.5 min), toluene (5.0 min), α -methylstyrene (8.4 min), naphthalene (12.3 min), and 1-methylnaphthalene (14.3 min).

Figure 8 shows the extracted ions 91, 105 and 104 of the chromatogram displayed in Figure 7. In the 91 window, note the presence of ethylbenzene (6.2 min), m,p-xylenes (6.3 min), o-xylene (6.7 min). In the 105 window, note the presence of cumene (7.3 min) and in the 104 window, note the presence of styrene (6.7 min) and 1,2,3,4-tetrahydro-naphthalene (11.8 min). All these products are generated by the pyrolysis of pure PVC.

Figure 9 shows the extracted ions 77, 91 and 104 between 3 and 9 min of the PE chromatogram shown previously. This shows that even aromatic products such as benzene (3.5 min), toluene (5.0 min), ethylbenzene (6.2 min), m,p-xylenes (6.3 min), o-xylene (6.7 min), styrene (6.7 min) and α -methylstyrene (8.4 min) are produced by the pyrolysis of polyethylene. Rearrangements occurred during the pyrolysis in the gas phase in between the ions and free radicals produced. Short straight chains of hydrocarbons (C₆–C₈) eventually rearrange forming aromatic products, which appear at low levels in the chromatogram. Likewise, the presence of these products has been observed to a certain extent in the pyrolysis of polyurethane [28].

Figure 7 Total ion chromatogram of burned polyvinyl chloride (PCE and 3-PT are internal standards).

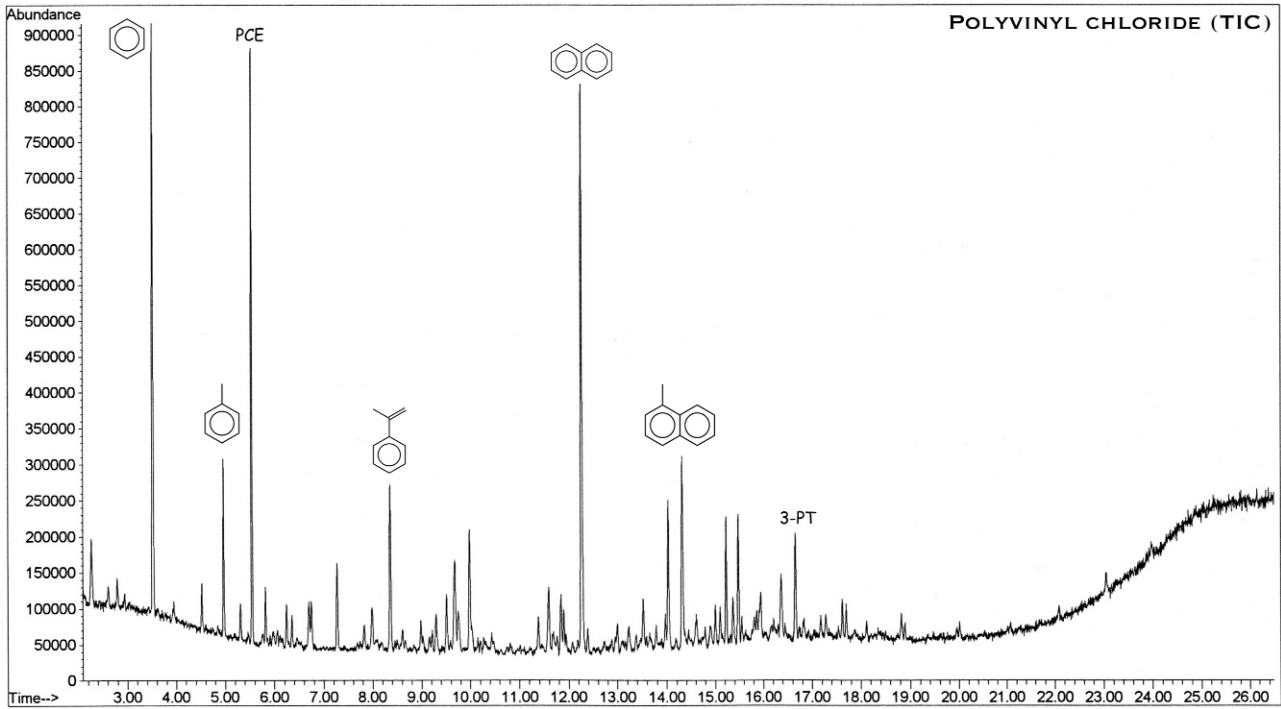


Figure 8 Extracted ion profiles of ions 91, 105 and 104 between 4 and 12 minutes of burned polyvinyl chloride.

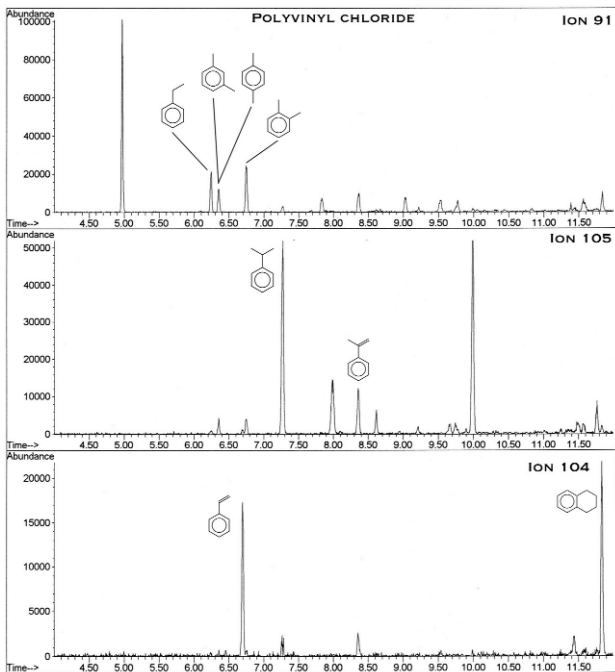


Figure 9 Extracted ion profiles of ions 77, 91 and 104 between 3 and 9 minutes of burned PE. The presence of aromatics, while at low level, is irrefutable.

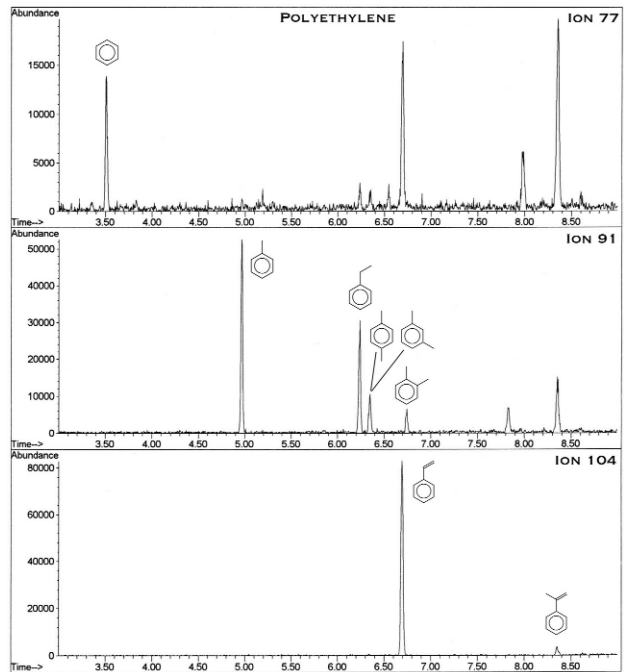
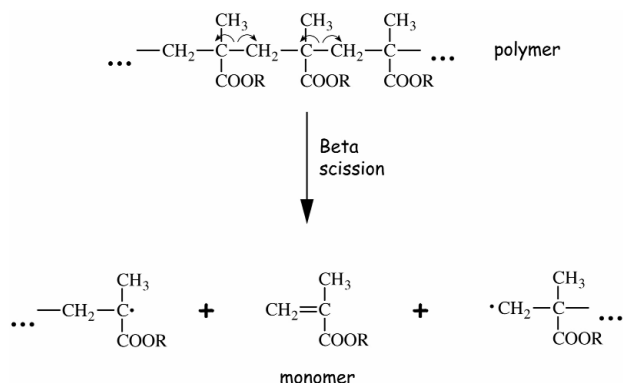


Figure 10 Monomer reversion mechanism (example of polymethylmethacrylate [where R=CH₃]).



Monomer reversion (a.k.a. depolymerisation or unzipping)

The polymer simply returns back to its monomeric version [12, 29]. This can be shown with the example of polymethylmethacrylate (PMMA) in Figure 10. Other polymers known to undergo almost exclusively monomer reversion are polytetrafluoroethylene (PTFE), poly α -methylstyrene and polyoxymethylene [13].

Figure 11 represents the chromatogram of burned polystyrene (PS) obtained from compact disc cases. As shown, the major peak is styrene (6.7 min), since PS undergoes significant depolymerisation; however, the presence of other aromatics

originating from a side group scission route followed by rearrangement is also evident. Toluene (5.0 min), ethylbenzene (6.2 min), phenylethyne (6.4 min), α -methylstyrene (8.4 min), indene (9.7 min), naphthalene (10.5 min), 2-methylnaphthalene (14.0 min), 1-methylnaphthalene (14.3 min), biphenyl (15.2 min), diphenylmethane (15.9 min) and bibenzyl (17.2 min) are all present. In this instance, there is an evident amount of polyaromatic hydrocarbons (PAH). This is explained by the fact that monocyclic aromatic hydrocarbons (as well as n-alkanes) have been reported to be precursors or intermediates of PAH [30].

Table 2 presents a list of polymers and their yields by percent of weight of monomer. The higher the yield, the more likely the polymer undergoes monomer reversion. If the polymer exclusively undergoes monomer reversion, the expected chromatogram should contain one peak and is usually not an issue in fire debris analysis. However, only a few polymers yield a value of 100%, while the others undergo other mechanisms such as random scission or side group scission simultaneously during the pyrolysis process. As shown, polyethylene, which breaks down primarily by random scission yields only 0.1% of monomer.

Other mechanisms and rearrangements

The three degradation mechanisms described above are common in polymeric material. However, other mechanisms, particularly rearrangements in the pyrolysis of natural and synthetic polymeric materials, as well as other organic compounds, have been extensively described in the literature [14, 31].

Figure 11 Total ion chromatogram of burned polystyrene (PCE and 3-PT are internal standards).

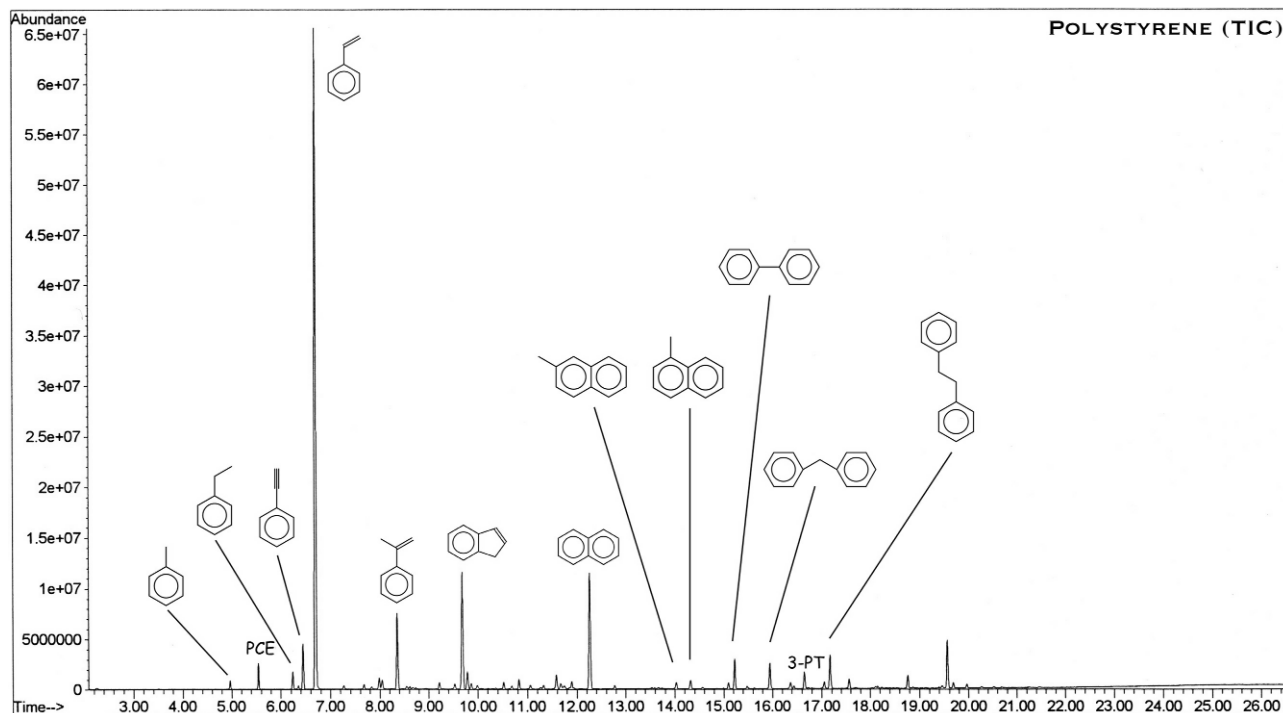


Figure 12 Some commonly encountered polymers and their approximate classification according to the degradation mechanism undertaken.

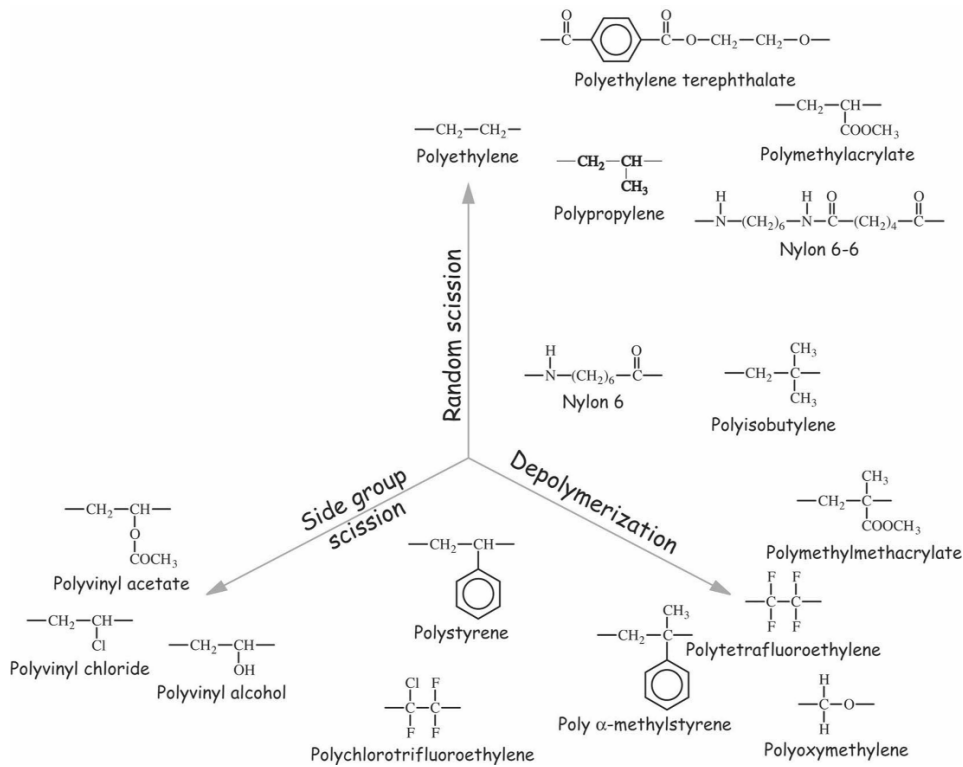


Figure 13 Total ion chromatogram between 2 and 18 minutes of burned paper (cellulose) (PCE and 3-PT are internal standards).

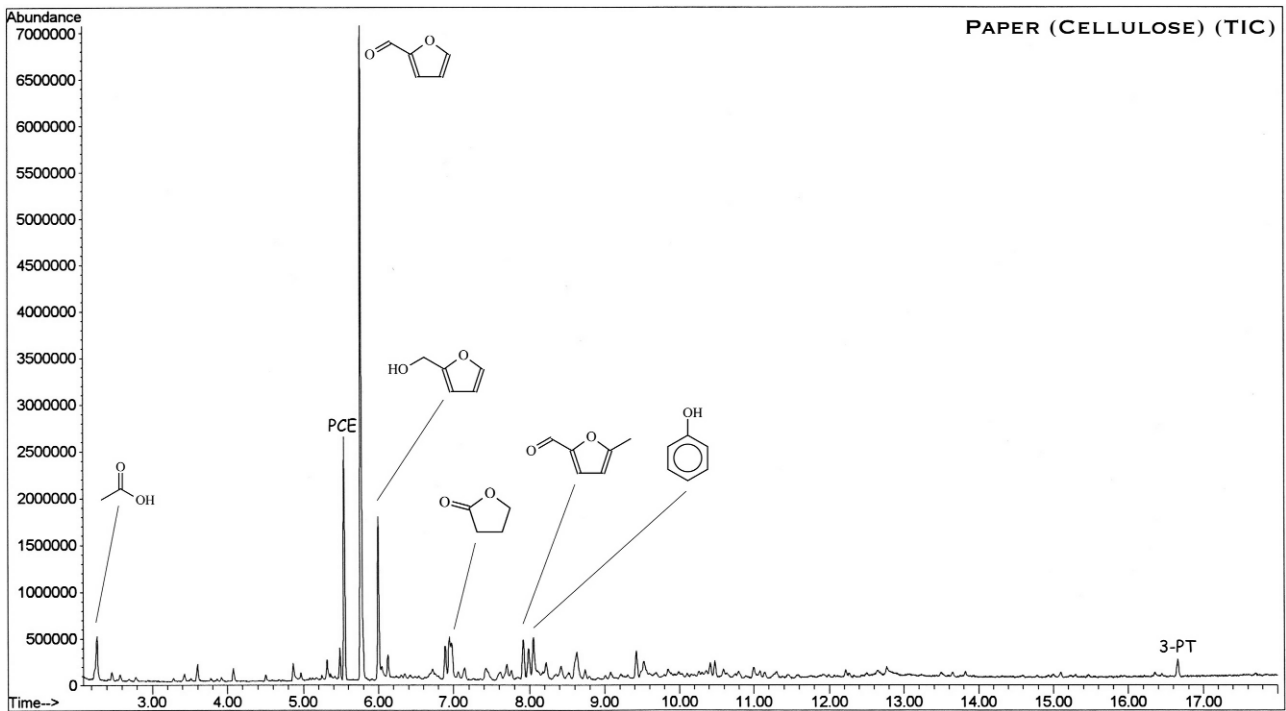


Table 2 Yield of monomer during the pyrolysis of some organic polymers in a vacuum (in percent of total volatilized). Source: Madorsky [23].

Polymer	Temperature [°C]	Yield [%]
Polyethylene	393-444	0.03
Polypropylene	328-410	0.17
Polymethylacrylate	292-399	0.7
Polyisobutylene	288-425	18.1
Polystyrene	366-375	40.6
Polychlorotrifluoroethylene	347-415	25.8
Polymethylmethacrylate	246-354	91.4
Polytetrafluoroethylene	504-517	96.6
Poly α -methylstyrene	259-349	100
Polyoxymethylene	<200	100

A fourth pyrolysis mechanism, less pertinent in this instance but described in the literature, is known as cross-linking and char formation [32]. As the polymer undergoes pyrolysis, more cross-linking occurs within the molecules, which strengthens the product and creates only a small amount of volatile products [33]. Typical substrates undergoing this route are polyacrylonitriles or phenolic resins [13, 32].

Other mechanisms, combined with rearrangements and variations in the parameters influencing pyrolysis (such as temperature, rate of heating, presence of oxygen, hydrogen, nitrogen or water), will significantly complicate chromatograms [34]. The study of these mechanisms is beyond the scope of this paper.

Determination of a degradation mechanism

Bond dissociation energies

A polymer does not always undergo only one of the pyrolysis routes previously discussed. Often, multiple routes are taken simultaneously [32]. The type of reaction is partially determined by the strength of the bonds in the molecule. The bond that is the most easily thermolysed or broken will be favoured [33]. Average bond dissociation energies (D) for some carbon bonds are presented in Table 3 [35].

These values need to be taken with a grain of salt. They are average values and they need to be adjusted according to the molecule in which the bond is studied, notably with the substitution of carbon atoms. The difference can be up to $\pm 10\%$ [35]. However, some basic observations can be drawn from the table.

As seen previously, PVC will typically undergo a side group scission and that is confirmed by the lower energy (C–Cl) of 330 kJ/mol compared to the energy (C–C) of at least 350 kJ/mol.

With the example of PE, it is obvious that the C–H bond with an energy of 410 kJ/mol will be less likely to break compared to the C–C bond even with the highest energy of 380 kJ/mol. Therefore, random scission takes place, yielding to a series of alkanes, alkenes and alkadienes of different sizes.

Table 3 Average bond dissociation energies for some common carbon bonds. Source: McMurphy and Fay [35].

Bond	Energy [in kJ/mol]
C–I	240
C–S	260
C–Br	270
C–N	300
C–Cl	330
C–O	350
C–C	350–380
C–H	410
C–F	450
C=C	611
C=O	732
C≡C	835

Finally, in the case of PMMA, there are different kinds of bonds in the polymer. Again, C–H (410 kJ/mol), C=O (732 kJ/mol) are unlikely to cleave first. The competition will be held between the remaining C–O bond (350 kJ/mol) and C–C bonds (about 350 kJ/mol). In this case, it is the C–C bond at the quaternary carbon that cleaves first and yields to the monomer reversion mechanism.

Parameters influencing route of pyrolysis

As seen previously, there are several parameters that will influence the production of pyrolysis products with a given polymer. One of the most important parameters is the temperature at which the pyrolysis occurs. For example, polyethylene will yield 0.03% of monomer at 500°C, 5.5% at 800°C and 26.4% at 1200°C [23]. The higher the temperature, the smaller the radicals and molecules produced. Indeed, poly α -methylstyrene yields 100% of monomer at 500°C, 88.5% at 800°C and only 37.7% at 1200°C [23]. In this case monomer reversion takes place mostly at temperature below 500°C. With higher temperatures, other bonds will break simultaneously, yielding to other free radicals. Commonly, the temperature influence is more significant from a quantitative perspective than in a qualitative perspective. As a general rule, the higher the temperature, the smaller the molecules. Thus, the ratio highly volatile compounds/poorly volatile compounds usually increases with the temperature. While the proportions change, the pyrolysis products are very similar.

The substitution of one or more hydrogen atoms with a CH₃ group will affect considerably the stability of the polymer and its degradation mechanism. As shown in Table 2, polystyrene yields 40.6% of monomer and when the hydrogen in the α position is replaced with a CH₃ group, the yield increases to 100% as shown with poly α -methylstyrene. This is due to the presence of a quaternary carbon in the latter [23]. The same phenomenon can be observed between polymethylacrylate (0.7%) and polymethylmethacrylate (91.4%) or between polypropylene (0.17%) and polyisobutylene (18.1%). Hence, a highly

Table 4 Some commonly encountered pyrolysis products in fire debris analysis – three most important ions are presented in the last column. The base peak ion is highlighted in bold and the molecular ion peak is underlined. Sources: NIST [40] and Merck [41].

Compound	CAS	Formula	MW [amu]	BP [°C]	Ions
Random scission					
Alkanes	–	C_xH_{2x+2}	–	–	57, 71, 85
Alkenes	–	C_xH_{2x}	–	–	55, 69, 83
Alkadienes	–	C_xH_{2x-2}	–	–	55, 69, 83
Side group scission and polyene chain breakdown					
Benzene	71-43-2	C_6H_6	78.11	80	78 , 51, 50
Toluene	108-88-3	$C_6H_5CH_3$	92.14	111	91 , <u>92</u> , 65
o-Xylene	95-47-6	$C_6H_4(CH_3)_2$	106.17	144	91 , <u>106</u> , 105
m-Xylene	108-38-3	$C_6H_4(CH_3)_2$	106.17	139	91 , <u>105</u> , 106
p-Xylene	106-42-3	$C_6H_4(CH_3)_2$	106.17	138	91 , <u>105</u> , 106
Ethylbenzene	100-41-4	$C_6H_5CH_2CH_3$	106.17	136	91 , <u>106</u> , 51
Styrene	100-42-5	$C_6H_5CH=CH_2$	104.15	146	104 , 103, 78
Phenylethyne	536-74-3	$C_6H_5C\equiv CH$	102.13	142	102 , 76, 50
α -Methylstyrene	98-83-9	$C_6H_4C(CH_3)CH_2$	118.18	164	118 , 117, 103
Indene	95-13-6	$C_6H_4CH=CHCH_2$	116.16	182	116 , 115, 63
Naphthalene	91-20-3	$C_{10}H_8$	128.17	218	128 , 127, 92
1-methylnaphthalene	90-12-0	$C_{10}H_7CH_3$	142.20	242	142 , 141, 105
2-methylnaphthalene	91-57-6	$C_{10}H_7CH_3$	142.20	241	142 , 141, 105
Biphenyl	92-52-4	$C_6H_5C_6H_5$	154.21	255	154 , 153, 152
Cellulosic materials					
2-Furaldehyde	98-01-1	$C_5H_4O_2$	96.08	162	96 , 95, 39
2-Furanmethanol	98-00-0	$C_5H_6O_2$	98.10	170	98 , 41, 81
5-Methyl-2-furancarboxaldehyde	620-02-0	$C_6H_6O_2$	110.11	186	110 , 109, 43

substituted carbon atom (tertiary or quaternary) is usually a point of instability and the chain will most likely break there.

The presence of a benzene ring in the backbone of a chain usually enhances its stability due to the resonance. The presence of a double bond might decrease the strength of the adjacent bonds since it increases the substitution of the atom. Finally, the presence of an oxygen in the backbone lowers the thermal stability, since the C–O bond has a lower strength than the C–C bond.

Polymer structures

When the polymer is known, the forensic scientist can use the bond dissociation energies and the basic aforementioned rules as a tool for a rapid estimation of the types of mechanisms that will occur during the pyrolysis process. Figure 12 presents some commonly encountered polymers approximately placed according to their favoured degradation mechanisms. It is possible to briefly analyse the structure, and by attributing the proper bond dissociation energies to the molecules, the degradation mechanism can usually be predicted.

PE and polyethylene terephthalate (PET) will mostly undergo random scission, as described in the literature [36]. However, PET mostly cleaves in small molecules such as CO, CO₂, and

CH₂CHO. On the other hand, it will produce very small amounts of complex oxygenated aromatics, which usually do not interfere with fire debris analysis.

PVC, polyvinyl acetate, and polyvinyl alcohol will undergo side group scission [25].

PS will undergo some depolymerisation and some side group scission, while poly α -methylstyrene will undergo almost complete depolymerisation.

Nylon 6 will undergo some random scission as well as some depolymerisation, which will present a certain amount of caprolactam, which is the starting monomer [13, 37]. On the other hand, nylon 6–6 (as well as other nylons) will undergo mainly random scission at the quaternary Cs and cyclic rearrangements leading to small compounds such as CO₂ and H₂O as well as cycloalkenes, cyclopentanone and substituted, cyclohexanone and substituted, and complex aromatic nitriles [37].

As shown in Figure 13, cellulosic materials will characteristically produce 2-furaldehyde (5.8 min), 2-furanmethanol (6.0 min), and 5-methyl-2-furancarboxaldehyde (7.9 min). Other pyrolysis products are acetic acid (2.3 min),

butyrolactone (7.0 min) and phenol (8.1 min). Pyrolysis products of different cellulosic materials such as cotton, paper and wood might present important variations, but will almost always present the three first products previously described. For example, wood has been shown to produce numerous molecules, which would be difficult to predict [38, 39].

Table 4 presents a short list of some the most frequently encountered pyrolysis products in fire debris analysis, along with their mass spectral characteristics [40, 41]. By extracting base peak ions (in bold), it is possible to quickly pinpoint these products within the chromatogram and facilitate the interpretation.

Discussion

Pyrolysis is a straightforward process that may lead to the production of a very complex pattern of products depending not only on the substance undergoing pyrolysis, but also on the conditions at which pyrolysis occurs (temperature, pressure, presence of additional reactants, etc.) [34].

Some substrates can be composed of multiple compounds, which will undergo pyrolysis simultaneously. Fortunately, according to Moldoveanu, the pyrolysis of composite materials can be considered as independent pyrolysis of each, which will slightly reduce the problem of prediction of pyrolysis products [14]. When the theory of pyrolysis is applied to a certain polymer, the prediction of resulting pyrolysis products is possible, but not always obvious. It would be optimistic to predict every single pyrolysis product of a material. After estimating which kind of pyrolysis products are expected from a certain substrate, the most reliable way to determine which are really produced is to conduct repetitive trials.

Easier interpretation with knowledge of the polymers

When performing fire debris analysis, the analyst can usually take the opportunity to have a close look at the evidence. This step is recommended and, with experience, the forensic scientist can predict what kind of products, inherent to the substrate, will be present in the chromatogram.

Interpretation of the results is always easier when the interfering products observed are justified by the nature of the substrate. However, one must also be careful of not disregarding a compound based on the mere fact that it is a common pyrolysis product. This is particularly true when the composition of the substrate is totally unknown.

A very interesting website (<http://www.psrc.usm.edu/macrog/>) called "The Macrogalleria: a cyberwonderland of polymer fun," will be of great assistance to the determination of the polymeric nature of objects encountered in the everyday life. While the website unfortunately does not provide any pertinent information regarding the degradation mechanisms of the polymers, the information regarding the structure of polymers and where they are found is invaluable. Then, basic rules and concepts introduced previously can be applied and a prediction of the pyrolysis products expected can be made.

Creation of a database of pyrolysis products

Polymers analysed in this study were pure and mostly free of substrate background products. Therefore, they are not the most representative of the profiles encountered with objects such as carpet, upholstery, wood and other substrates typical of fire debris. However, they fulfil the goal of this article by illustrating pyrolysis degradation process. The pyrolysis process is influenced by several parameters that are not controlled in a free-burning fire. Therefore, the resulting chromatograms might present significant variations, but should still be in accordance to the routes of degradation.

It is important to keep in mind that pyrolysis products constitute only part of the interfering products found in fire debris samples. It would be useful for fire debris analysts to create a database of pyrolysis and interfering products along with the database of ILR that should already be in the analyst's library. Obtaining samples of substrates is very easy, inexpensive and the preparation of the samples for analysis is not labour intensive. This would permit analysts to possess a library of "clean" samples and compare their pyrolysis and interfering products to "real world" samples.

Collecting and analysing a comparison sample

It is recommended to collect a comparison or reference sample from a fire scene when fire debris samples are collected for ILR recovery and analysis [11]. A comparison sample consists of the same substrate than the original sample, but that does not contain any ignitable liquids. If possible, the comparison sample should be unburned. Hence, the fire debris analyst can have a good idea of the material involved. Then, the comparison sample can be burned and analysed, which will provide a good representation of the content of interfering products. This will greatly help in understanding the origin of the different products recovered from the original sample.

Conclusion

Pyrolysis products are part of the interfering products found in fire debris samples. Their presence complicates the interpretation of chromatograms and might lead to a false positive. Likewise, a false negative result can be reached by not knowing what these products are and thus, disregarding compounds originating from an ignitable liquid. In order to better understand these products, the best exercise remains in creating a database of known burned substrates, followed by an in-depth study. Likewise, the collection and analysis of a comparison sample can be of great help to the forensic scientist. The theory and examples presented should improve the analyst's understanding of the process of pyrolysis and its implications for interpreting GC-MS data.

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References

- 1 **Bertsch W.** Volatiles from carpet: a source of frequent misinterpretation in arson analysis. *Journal of Chromatography A* 1994; 674: 329–333.
- 2 **DeHaan JD and Bonarius K.** Pyrolysis products of structure fires. *Journal of the Forensic Science Society* 1988; 28(5–6): 299–309.
- 3 **Clodfelter RW and Hueske EE.** A Comparison of Decomposition Products from Selected Burned Materials with Common Arson Accelerants. *Journal of Forensic Sciences* 1976; 22(1): 116–118.
- 4 **Smith RM.** Arson Analysis by Mass Chromatography. *Analytical Chemistry* 1982; 54(13): 1399A–1409A.
- 5 **Keto RO.** GC/MS Data Interpretation for Petroleum Distillate Identification in Contaminated Arson Debris. *Journal of Forensic Sciences* 1995; 40(3): 412–423.
- 6 **Stauffer E.** Identification and Characterization of Interfering Products in Fire Debris Analysis. Master's thesis. Miami: Florida International University, 2001.
- 7 **Lentini JJ, Dolan JA and Cherry C.** The Petroleum-Laced Background. *Journal of Forensic Sciences* 2000; 45(5): 968–989.
- 8 **Cavanagh K, DuPasquier E and Lennard C.** Background interference from car carpets – the evidential value of petrol residues in cases of suspected vehicle arson. *Forensic Science International* 2002; 125: 22–36.
- 9 **Tranahim-Fryer DJ and DeHaan JD.** Canine accelerant detectors and problems with carpet pyrolysis products. *Science & Justice* 1997; 37(1): 39–46.
- 10 **Fernandes M, Lau C and Wong W.** The effect of volatile residues in burnt household items on the detection of fire accelerants. *Science & Justice* 2002; 42(1): 7–15.
- 11 **DeHaan JD.** *Kirk's Fire Investigation*. Fourth edition. Upper Saddle River, NJ: Prentice Hall, 1997.
- 12 **Wampler TP.** Analytical Pyrolysis: An Overview. In: Wampler TP, ed. *Applied Pyrolysis Handbook*. New York: Marcel Dekker, 1995: 1–29.
- 13 **Drysdale D.** *An Introduction to Fire Dynamics*. Chichester: John Wiley and Sons, 1985.
- 14 **Moldoveanu SC.** Analytical Pyrolysis of Natural Organic Polymers. In: *Techniques and instrumentation in analytical chemistry*. Elsevier: Amsterdam, 1998.
- 15 **American Society for Testing and Materials.** ASTM E 1412–00 Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal. *Annual Book of ASTM Standards* 2001; 14.02: 431–433.
- 16 **American Society for Testing and Materials.** ASTM E 1618–01 Standard Test Method for Identification of Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography–Mass Spectrometry. *Annual Book of ASTM Standards* 2002; 14.02.
- 17 **Newman RT, Dietz WR and Lothridge K.** The Use of Activated Charcoal Strips for Fire Debris Extractions by Passive Diffusion. Part 1: The Effects of Time, Temperature, Strip Size, and Sample Concentration. *Journal of Forensic Sciences* 1996; 41(3): 361–370.
- 18 **CDS Analytical, Inc.** *Degradation Mechanisms – Random Scission* 2000.
- 19 **Lentini JJ.** Differentiation of Asphalt and Smoke Condensates from Liquid Petroleum Distillates Using GC/MS. *Journal of Forensic Sciences* 1998; 43(1): 97–113.
- 20 **CDS Analytical, Inc.** *Pyrolysis GC of High and Low Density Polyethylene* 2002.
- 21 **CDS Analytical, Inc.** *Pyrolysis/GC of Polyolefins* 2002.
- 22 **CDS Analytical, Inc.** *Capillary GC of Polyolefin Pyrolysates* 2002.
- 23 **Madorsky SL.** Thermal degradation of organic polymers. In: Mark HF and Immergut EH, ed. *Polymer reviews*. Vol 7. New York: John Wiley & Sons, 1964.
- 24 **CDS Analytical, Inc.** *Degradation Mechanisms – Side Group Elimination* 2000.
- 25 **Hrdina KE et al.** Defect formation during binder removal in ethylene vinyl acetate filled system. *Journal of Materials Science* 1999; 34: 3281–3290.
- 26 **Scalarnone D and Chiantore O.** The use of Py–GC–MS for identification of the polymeric constituents in artworks, museum and collectible design objects. *Modern Materials Conservation* 2001; August(4): 12.
- 27 **Price DM, Hourston DJ and Dumont F.** Thermogravimetry of Polymers. In: Meyers RA, ed. *Encyclopedia of Analytical Chemistry*. Chichester: John Wiley & Sons, 2000: 8094–8105.
- 28 **Tristan-Rochaix V.** Étude de la combustion lente par calorimétrie différentielle à balayage: Vérification pour le bois et extension aux mousses en polyuréthane. Thesis dissertation. Lausanne: Institut de police scientifique et de criminologie. 1997.
- 29 **CDS Analytical, Inc.** *Degradation Mechanisms – Depolymerization* 2000.
- 30 **Quintana Sancho A.** Effect of temperature on the formation of PAH and n-alkanes during pyrolysis. 6th Annual EuroFlam Seminar 1999. IJmuiden, NL.
- 31 **Flynn JH and Florin RE.** Degradation and Pyrolysis Mechanisms. In: Liebman SA and Levy EJ, ed. *Pyrolysis and GC in Polymer Analysis*. New York: Marcel Dekker, 1985: 149–208.
- 32 **Simmons RF.** Fire Chemistry. In: Cox G, ed. *Combustion Fundamentals of Fire*. San Diego: Academic Press, 1995: 403–473.
- 33 **Wall LA.** Pyrolysis of Polymers. In: Wall, LA, ed. *The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials*. Washington: National Bureau of Standards, 1972: 47–72.
- 34 **Irwin WJ.** *Analytical Pyrolysis A Comprehensive Guide*. New York: Marcel Dekker, 1982.
- 35 **McMurry J and Fay RC.** *Chemistry*. Second edition. Upper Saddle River: Prentice Hall, 1998.
- 36 **Pinorini MT.** La suie comme indicateur dans l'investigation des incendies. Thesis Dissertation. Lausanne: Institut de police scientifique et de criminologie 1992.
- 37 **CDS Analytical, Inc.** *A Comparison of Nylons by Pyrolysis GC* 2000.
- 38 **Faix O, Meier D and Fortmann I.** Thermal degradation products of wood — Gas chromatographic separation and mass spectrometric characterization of monomeric lignin derived products. *Holz als Roh- und Werkstoff*, 1990; 48: 281–285.
- 39 **Faix O, Meier D and Fortmann I.** Thermal degradation products of wood – A collection of electron-impact mass spectra of monomeric lignin derived products. *Holz als Roh- und Werkstoff*, 1990; 48: 351–354.
- 40 **National Institute of Standard and Testing.** NIST chemistry webBook. <http://webbook.nist.gov/chemistry>, accessed performed on August 1, 2002.
- 41 **Merck & Co.** *The Merck Index*. 13th edition. Whitehouse Station: Merck Research Laboratories, 2001.