Review

Introduction to pyrolysis–capillary gas chromatography

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Abstract

By breaking large molecules into characteristic smaller fragments, analytical pyrolysis extends the use of gas chromatography to the analysis of polymeric materials, including natural polymers such as cellulose as well as synthetics. An understanding of the chemistry involved permits interpretation of the information present in these molecular fragments, with application to polymer and copolymer microstructure in addition to routine identification and quality control. Whether microfurnace, Curie-point or resistively heated filament, the pyrolysis device must be interfaced efficiently to the gas chromatograph to make use of the resolving power afforded by capillary columns. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Pyrolysis; Polymers

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1. Introduction

The two most fundamental questions to be asked when evaluating the hyphenated technique of pyrolysis–capillary gas chromatography (Py–capillary GC) are, "What are the benefits that pyrolysis brings to chromatography?" and "How does *capillary* GC benefit the pyrolysis?" Pyrolysis has been used for decades as an analytical technique, predating GC even, and interfaced as well directly to mass spectrometers and to Fourier Transform (FT) IR instruments. But the ability to use GC to separate and analyze the products made when a substance is pyrolyzed has made Py–GC a powerful combination

for material characterization. As will be shown in the examples section of this review, Py–GC is used routinely to analyze complex substances such as tire rubber, textiles, dried paint, glue, paper coatings, petrochemical sources, plant materials, coal, bacteria, and, of course, the whole range of synthetic polymers.

The simple answers to the two questions posed above are, "Pyrolysis permits GC analysis of things that the GC cannot do by itself", and "High resolution capillary analysis helps untangle the wide mix of compounds made when some materials are pyrolyzed". Gas chromatographs are designed to separate and analyze compounds which may be made volatile and pass through a column, but were never intended to be applied to the large molecules found in polymeric materials like polyethylene or cellulose. Pyrolysis creates volatiles from these materials, but may make so many compounds that interpretation requires high resolution separation first. The combination of pyrolysis with capillary GC, then, allows the analyst to use a routine tool such as a gas chromatograph to examine a much wider range of sample materials in detail sufficient to make difficult discriminations.

2. How does pyrolysis work?

Pyrolysis is defined as the breaking apart of large molecules into smaller ones using only thermal energy [1]. The way a large molecule behaves at elevated temperature is, of course, dependent on the relative strengths of the bonds which hold the molecule together. Much of the degradation is the result of free radical reactions initiated by bond breaking, and the products of these reactions reflect molecular structure, stability of the free radical, substitution and internal rearrangements. It is important to recognize that a large molecule will break apart in a characteristic way, and that another sample of the same material heated to the same temperature will behave exactly the same way, making an analysis of the degradation products a reproducible way to study the original macromolecule.

The thermal degradations experienced by polymers are generally grouped into three categories [2] for ease of study, namely chain scission [3–5], side-group scission [6–8] and unzipping [9,10]. In chain scission, the bonds holding the polymer backbone together are broken, creating smaller fragments which still consist of connected monomers. Polypropylene [11], for example, degrades to produce branched hydrocarbons including the dimer, trimer, tetramer and pentamer of propylene, as shown in Fig. 1. (The instument parameters relating to Figs. 1 and 2,4–7 are given in Table 1). Side-group scission occurs when the bonds attaching substituents to the polymer chain are weaker than the bonds in the polymer backbone, so the side groups are split off, leaving the altered chain to break apart at a higher temperature. Polyvinylchloride is a good example of this. When pyrolyzed, it produces HCl by eliminating the side-groups, then makes aromatics from the remaining chain [12] (see Fig. 2). Unzipping refers to a third behavior in which a polymer reverts almost entirely to monomer. The methacrylates degrade this way, [13] so polymethyl methacrylate will produce methyl methacrylate monomer, and little else.

At any temperature sufficient to break bonds the molecule will begin to degrade, but at relatively low temperatures the degradation may be too slow to be analytically useful. At very high temperatures the molecule may be subjected to so much energy that it degrades too extensively, creating only very small (and frequently nonspecific) products. The key in analytical pyrolysis is to select a temperature at which a macromolecule is degraded to produce a wide array of products, but quickly enough to be compatible with GC. Pyrolyzers are capable of heating to temperatures as high as 1400°C, but most analytical work is done using setpoints between 500 and 800°C.

3. Pyrolyzers

There is a fairly wide array of instruments available commercially for performing pyrolysis [14], most of which are designed primarily for use with gas chromatographs. Whether these are single sample analyzers or autosampling systems [15,16] with multiple positions, they generally use one of three heating techniques. Microfurnaces [17–19] provide a constantly heated, isothermal pyrolysis zone into
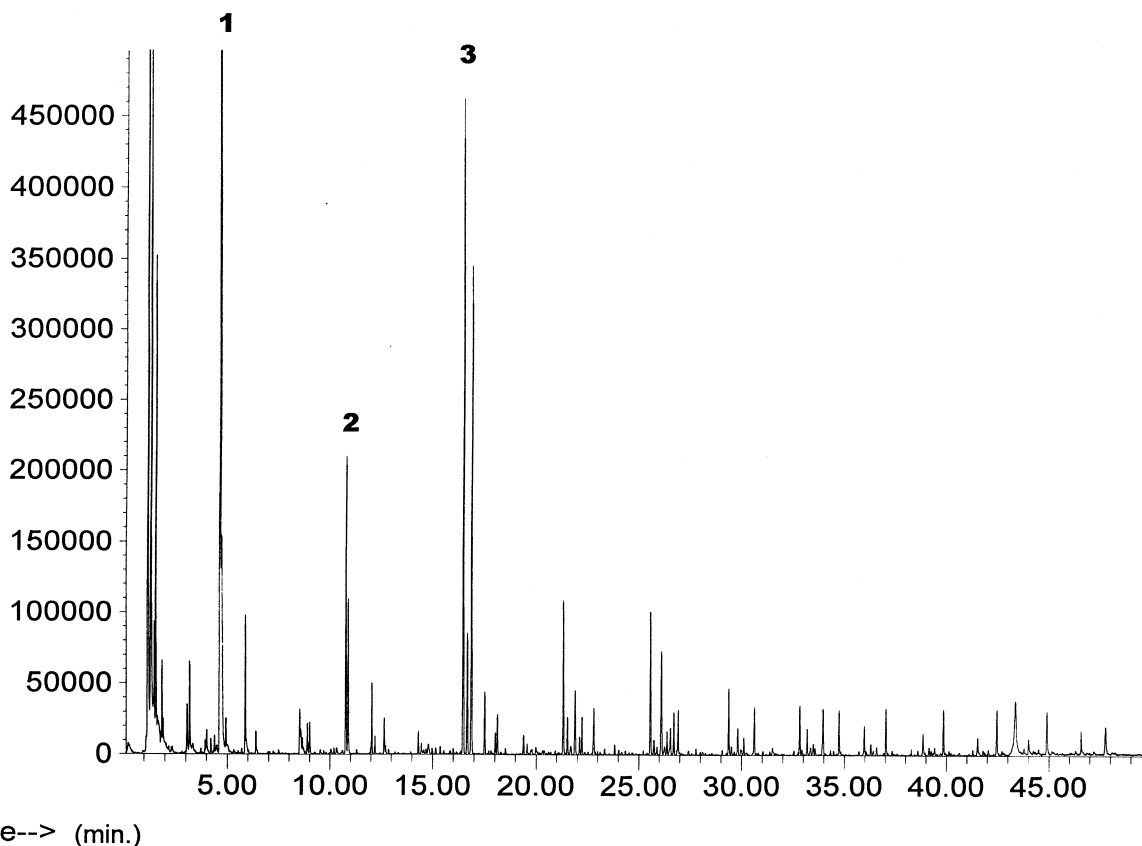
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Fig. 1. Pyrogram of polypropylene. Peak 1=propylene trimer (dimethylheptene), 2=propylene tetramer, 3=propylene pentamer. For conditions, see Table 1.

Table 1
Instrument parameters for Figs. 1 and 2,4–7

Pyrolyzer:	CDS Analytical Model 2500
Pyrolysis setpoint:	750°C for 20 s
Interface oven:	300°C
Gas chromatograph:	Hewlet–Packard 6890
Column:	30 m×0.25 mm HP-5
Carrier:	He
Pressure:	5.9 p.s.i. (1 p.s.i.=6894.76 Pa)
Split:	75:1
Oven program:	40°C for 2 min, then 6 C°/min to 295°C
Detector:	Mass selective detector

which samples are introduced by a liquid syringe, solid plunger syringe or in a little cup. Curie-point pyrolyzers [20] apply the sample to a piece of ferromagnetic metal which is inserted into the pyrolyzer cold, then heated rapidly through induction of current using a high frequency coil. Depending on the alloy of metal used, when it reaches a characteristic temperature (the Curie-point of that metal) no more current can be induced, so the temperature stops at that point. Filament style pyrolyzers [21–23] use a piece of resistive metal (frequently platinum) with a wide temperature range and circuitry capable of causing the filament to heat to a programmed temperature at a controllable rate.
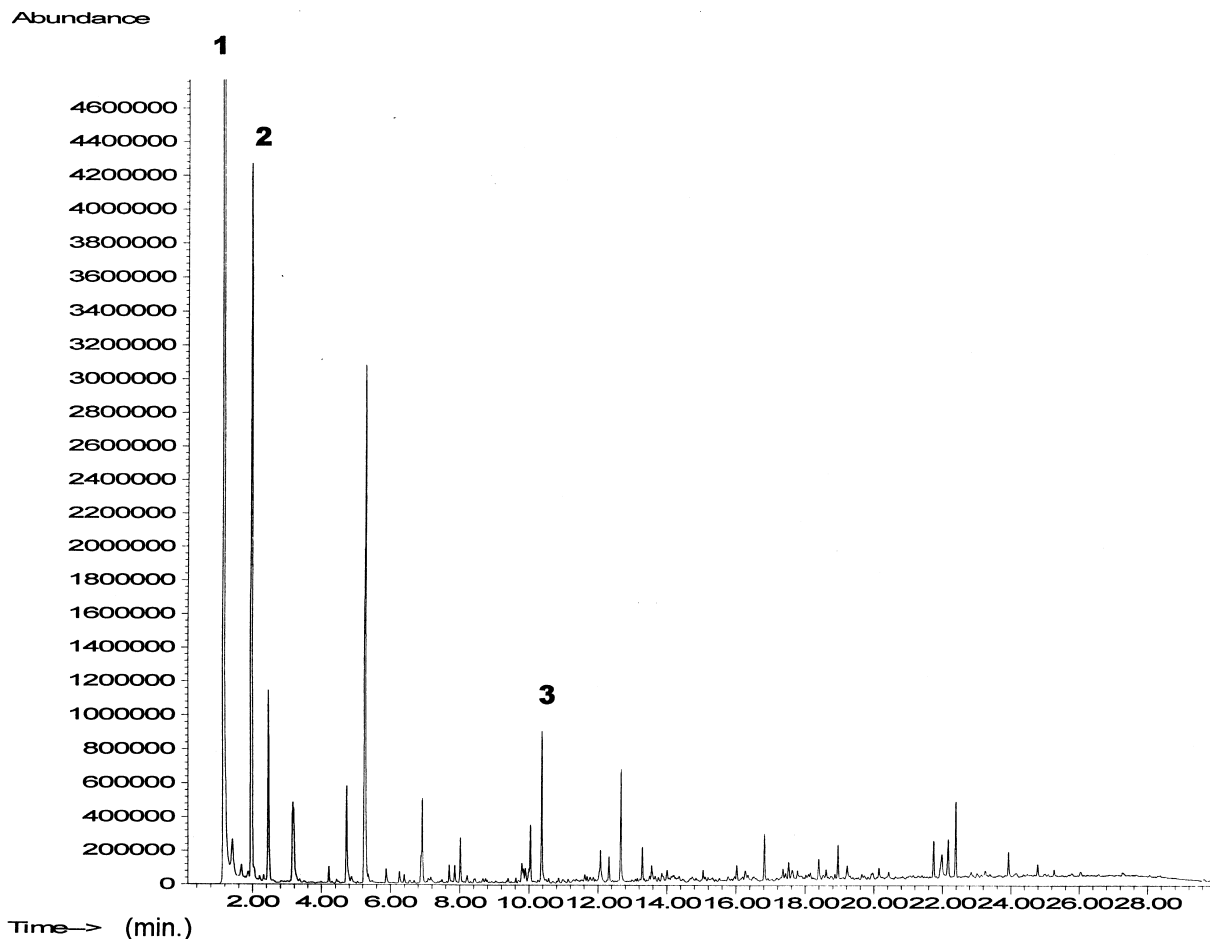
Fig. 2. Pyrogram of polyvinylchloride. Peak 1=HCl, 2=benzene, 3=naphthalene. For conditions, see Table 1.

4. Pyrolysis–capillary GC

The benefits of analyzing pyrolysis products (the pyrolysate) using capillary column chromatography instead of packed columns are the same as for any other application, i.e., the increased resolution reveals more peaks, separating compounds which coeluted previously and providing more information about the sample. This is particularly useful in studying polymers which degrade by chain scission, since these pyrolysates may contain hundreds of peaks. Further, it is frequently the case that compounds important in making discriminations among polymers may produce only small peaks, relative to the larger peaks produced from backbone segments. For example, it is easy to tell polyethylene from

polypropylene by the overall pattern in the pyrolysis chromatogram (pyrogram). But analysis of the small peaks between the oligomers in polyethylene conveys a great deal of information regarding the density and specific comonomer used in preparing different polyethylenes.

From the point of view of the chromatography, the pyrolyzer is just the sample introduction device, taking a solid material and preparing it for analysis by GC. Capillary chromatography in particular places some significant requirements on the behavior and use of the pyrolyzer if it is to take advantage of the resolving power of the capillary column. Particularly for front-end resolution, the sample must be delivered to the column inlet in as tight a plug as possible. Most GC pyrolysis accessories are inter-

faced at the injection port of the GC, requiring that the GC column flow be brought out from the injection port, go through the pyrolyzer and then back into the injection port. This arrangement introduces more volume, surface area and additional fittings, none of which are going to make the injection port more efficient than it is on its own. Consequently the parameters used in the pyrolyzer must be set with chromatographic performance in mind as well as the desired degradation of the sample. Specifically, the sample should leave the pyrolyzer and enter the injection port as rapidly as possible to prevent band broadening. Several things are required for this.

1. The sample should be heated as rapidly as possible. The pyrolysate enters the injection port already volatilized from the pyrolyzer (not in solution as from a syringe). If the sample is heated slowly, or to a temperature at which degradation is slow, the volatiles will travel to the column over a finite time which may make peaks too broad to achieve the resolution needed for the analysis. From a chromatographic standpoint, the sample should be heated instantaneously, and many pyrolyzers come close to that, since they can heat the pyrolysis zone at rates in the thousands of degrees per second, reaching setpoint in milliseconds.

2. The sample should be very small. This achieves several things. First, it ensures that the capacity of the column will not be exceeded, so good resolution is possible. Second, it means that the sample will degrade completely and rapidly. Even at high temperatures and fast heating rates, a large sample will degrade more slowly than a small sample in the same pyrolyzer, again causing peak broadening. To achieve the fast heating rates needed, the mass of the pyrolysis zone must be very small, and large samples exceed the ability of the pyrolyzer to transfer energy. Further, the larger the sample, the more likely it is to experience temperature gradients through it, meaning that different portions of the sample are pyrolyzing at different temperatures, making reproducibility difficult. Many analysts limit their sample size to 10–100 μg.

3. The pyrolyzer should have a small internal volume. This prevents expansion of the volatiles into unswept areas, reduces the contact between analytes and hot surfaces and makes it possible to transfer the pyrolysate compounds away from the high temperature zone (where secondary pyrolysis could take place) and into the column efficiently.

4. Interfacing should be minimal. In general, the analytical pyrolyzer is a separate device from the GC, and the two must be interfaced to work together. The transfer zone between the pyrolyzer and the GC injection port should be kept hot to prevent condensation, and as short as possible to reduce surface area and volume. Some analysts actually feed the capillary column inlet through the interfacing up to the pyrolysis zone to eliminate dead volume.

5. Carrier flow through the whole system should be reasonable. The use of an injection port with a splitter and a relatively high split ratio is important for good resolution. Besides all the usual reasons analysts use split injections with capillaries, there are some additional considerations when interfacing a pyrolyzer. First, many analysts cannot or will not limit their sample to 100 μg, so capacity is an issue. Secondly, despite efforts to minimize size, addition of a pyrolyzer must add volume to the sample path, and a rapid carrier flow helps compensate for the additional volume. Thirdly, the faster the flow, the more quickly the pyrolysate compounds are removed from the high temperature zone, minimizing secondary pyrolysis reactions.

The diagram of a typical pyrolysis interface for GC shown in Fig. 3 presents many of these considerations. The GC carrier gas has been disconnected from the normal injection port inlet and routed up into the pyrolysis interface. The connection usually used to bring flow into the injection port has been capped to prevent sample loss. The interface is heated and insulated in a housing which sits directly onto the injection port of the GC to eliminate cold spots. An eight-port valve is incorporated to permit placing the pyrolysis probe on-line and off-line from the GC column, and a purge flow is added to remove air from the system before placing the pyrolyzer on-line. This both reduces the chance of oxidizing the sample when it is pyrolyzed, and protects the analytical instrument, especially mass spectrometers, from intrusion of air into the system.
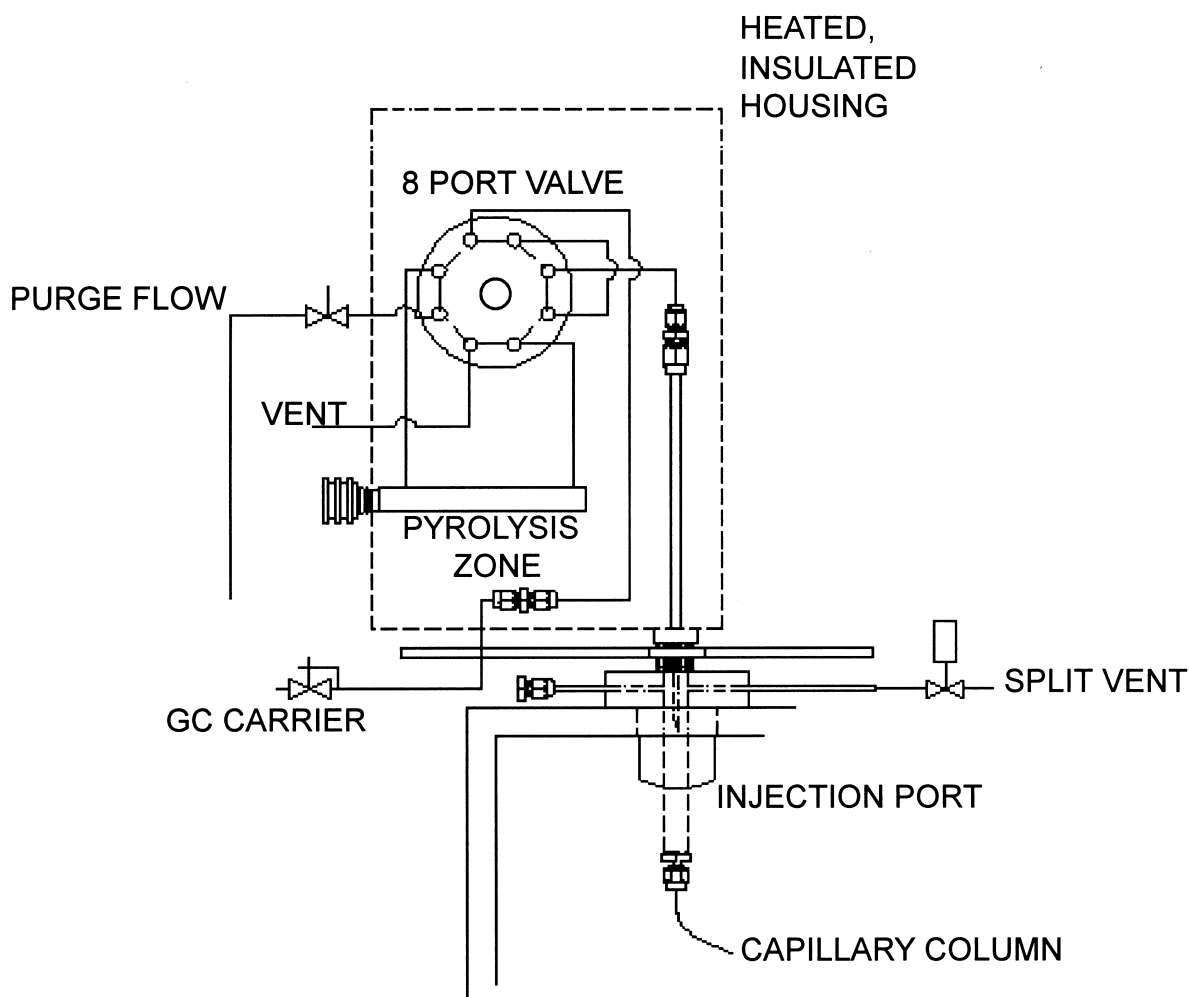
Fig. 3. Interface for connecting a pyrolyzer to the injection port of a gas chromatograph.

It is sometimes necessary for a particular experiment to compromise the above operating conditions. For example, small samples may be seen as nonrepresentative because of a problem with homogeneity, so a larger sample is required. Low heating rates and/or temperatures may be important to studying the kinetics of a material, so product evolution may be slow. Sensitivity may be an issue, so low split ratios are desired. In these cases, some compensation must be made in order to provide good analytical results. Greatly increasing split flows helps cope with larger samples, as does increasing the size of the pyrolysis heater. For slow product evolution, low sensitivity or slow product transfer to the column,

cryogenic focusing onto the column prior to analysis is helpful in regaining resolution.

5. Applications and examples

The range of materials analyzed using Py–capillary GC is extensive, mostly because so many things which people use routinely are made of polymers. Whether it is clothing fibers, appliance bodies, office materials, paint, varnish, furniture coverings, carpet or food containers, almost everything people come into contact with is either made from or coated with a polymeric material. This includes synthetics such

as polyethylene or polyester, and natural polymers, including cellulose (wood, cotton, paper) and proteins (wool, silk, food). This section will list various kinds of laboratories using Py–capillary GC to analyze materials with some examples of the kinds of samples being studied. The categories are very general, and there is considerable overlap in the materials studied by specific laboratories. For example, copolymers using styrene and acrylics are used in paints, photocopy toners and paper coatings, and may be studied in forensic laboratories, paint laboratories, paper laboratories or general polymer laboratories. The applications included here have been selected specifically to include capillary GC as the analytical device. For a broader review of pyrolysis techniques in general, see the excellent paper by Blazso [24].

5.1. Art materials

Museum laboratories are frequently interested in the kinds of organic materials used in producing a work of art, including pigments, glues, binders, varnishes and paints. A review of pyrolysis techniques applied to art and archeology was published by Shedrinsky et al. [25]. The kinds of natural resins used in preparing varnishes has received considerable attention [26], including a study by Jorrit et al. [27] of an early 20th century nonterpenoid varnish used on an oil painting. Interest has also been shown in the authentication of amber objects, and the differentiation of Baltic and nonBaltic ambers [28,29]. Baltic ambers contain succinic acid, which appears in the pyrogram as succinic anhydride, shown in the pyrogram in Fig. 4. The organic materials used as binders in art media have also been assayed, including protein-based binders such as egg and casein found in Renaissance tempera paints [30], as well as nonprotein binders [31].

5.2. Biological samples

Py–GC has been applied to the study of biological materials for more than two decades. In fact, a thorough review with nearly 150 references was published in 1979 by Gutteridge and Norris [32]. Much of the work has been done in an effort to identify and differentiate microorganisms, such as

the work by Smith et al. [33] who found a chemical marker for distinguishing Group A and Group B streptococci, and by Abbey et al. [34] who were able to distinguish nontypable strains of *Klebsiella pneumoniae*. Analysis has not been limited to contemporary materials. Navale [35] has studied cell wall constituents of archaebacteria, identifying compounds referred to as "chemical fossils". Tissues of Iron Age bodies preserved in bogs have been analyzed by Stankiewicz et al. [36] for comparison with contemporary human tissue in an effort to understand the mechanism of preservation. Nor is work limited to whole cells, since other biological materials, including enzymes [37], steroids [38] and bone marrow from patients suffering leukemia [39] have been assayed using Py–GC.

5.3. Environmental

Although a great deal of the analysis of environmental samples involves the determination of volatile organics such as solvents in water and soil samples, there is a need to assay nonvolatiles as well. Bruchet et al. [40] reported on precursors of trihalomethanes which include biopolymers suspended in water samples. Because it is designed to handle such small samples, Py–GC has been found well suited to the analysis of particulate contaminants in both air and water samples. Voorhees et al. [41] used pyrolysis to study airborne particulates collected at a highway tunnel. The origin of the particles found in nearshore sediments has been studied by Pulchan et al. [42] who incorporated simultaneous methylation by adding tetramethylammonium hydroxide to the sample before heating. Likewise, Ishiwatari et al. [43] have looked at "sinking particles" from the northern Pacific and categorized the pyrolysis products according to possible source, including protein, carbohydrate and lipid. In an interesting application Matney et al. [44] even looked at airborne particles collected from the air of a space shuttle during a mission to determine the origin of the particles.

Other applications of pyrolysis in environmental studies include the investigation of polymer recycling efforts, including used automobile tires and the complex mixture of polymers resulting from the shredding of old automobiles [45,46].
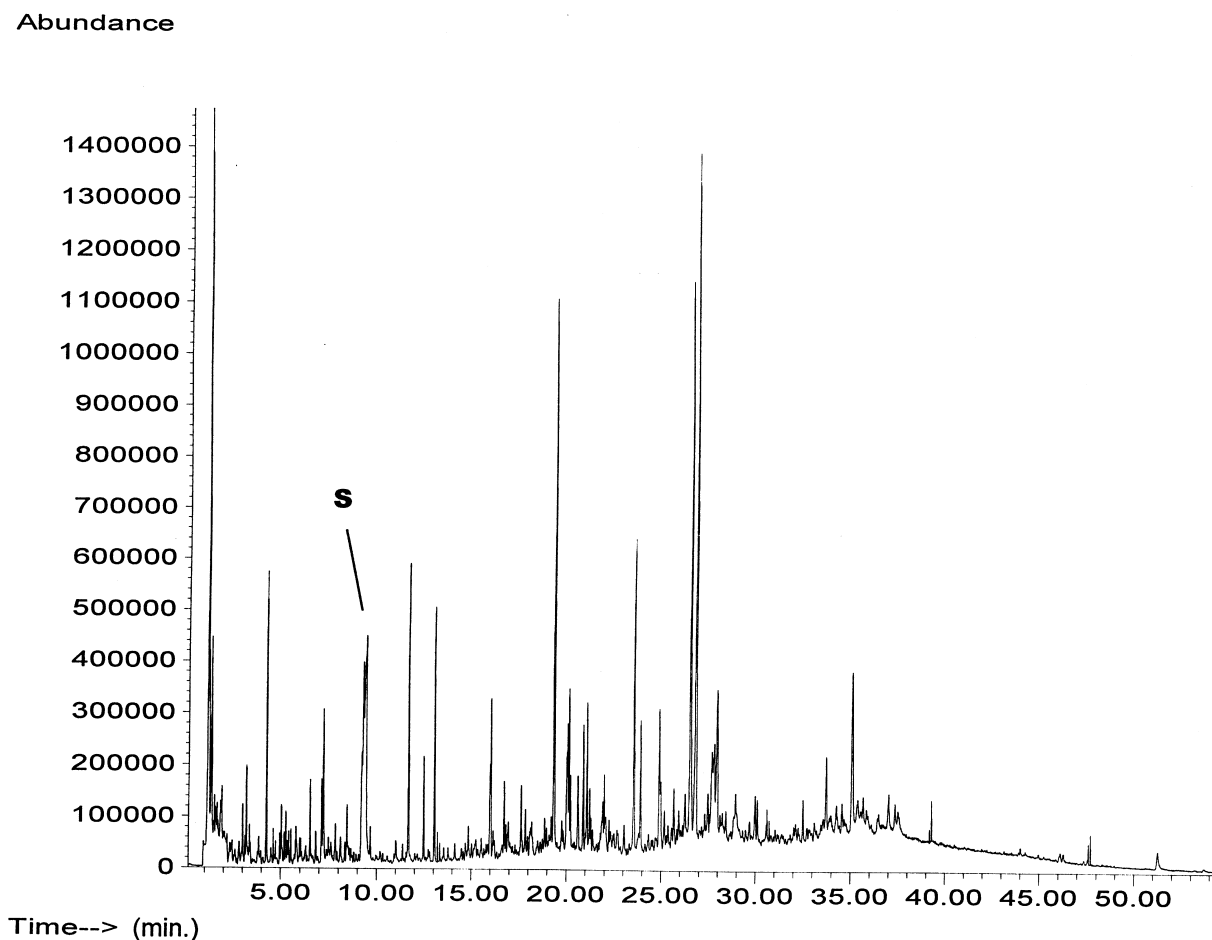
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Fig. 4. Baltic amber pyrolysis, showing presence of succinic anhydride (s). For conditions, see Table 1.

5.4. Food and agriculture

Plant and animal materials are routinely analyzed by Py–GC since the proteins, polysaccharides and other complex molecules involved in these materials present interesting analytical challenges. Fats and oils, including beef fat, peanut oil, soybean oil and ten other samples were examined by Nazer et al. [47] who were able to differentiate all the samples. Huyghues-Despointes and Yaylayan [48] have used Py–GC to study sugar chemistry, while the artificial sweetener aspartame has been examined by Galletti et al. [49] in both sweetener packets and diet soft drinks. The ability of pectin to gel depends on the degree of methylation, which has been investigated by Aries et al. [50] using both Py–MS and Py–GC–

MS. Hashimoto et al. [51] used pyrolysis to differentiate among various herbs and spices, looking at both the thermally desorbed oils and the pyrolysis products resulting from the nonvolatile parts.

From the agricultural point of view, work is being done on two general fronts—agricultural products like animal feeds and soil chemistry. Materials like lignin, tannins and carbohydrates in forages and maize hybrids have been studied by Reeves and Francis [52] and Galletti et al. [53] providing information capable of differentiating among varieties of the same plant, as well as studying product composition. With regard to soils, considerable work is being done in examining the soil organic mater, including humus, by both Py–MS and Py–GC–MS [54]. Ceccanti et al. have differentiated mature and

immature soil organic matter based on specific peaks in the pyrograms, including furfural, phenol and benzene [55]. Kotra and Hatcher [56] have investigated the insoluble aliphatic material found in peat, with an interest in identifying the origin of these materials.

5.5. Forensic

In the forensic laboratory, the most extensive use of pyrolysis is probably in the investigation of paint fragments recovered from accident scenes. Automobile paint [57] of course may be studied for composition in both forensic and other analytical laboratories, when looking at formulation, stability

and competitor products. To that end a quality control method based on Py–GC–MS for resin-modified paints has been demonstrated by Wilcken and Schulten, using principal component analysis [58]. A pyrogram of a recent automobile paint is shown in Fig. 5.

In addition to paint samples, forensic laboratories have been successful in evaluating other kinds of nonvolatile evidence, such as fibers. Almer [59] examined 95 polyacrylonitrile-based fibers, including 63 acrylic and 22 modacrylic, and was able to classify them into nine groups for the acrylics and six groups for the modacrylics. Adhesive tapes (both the polymer tape and the adhesive) have been extensively analyzed. In an interesting study by
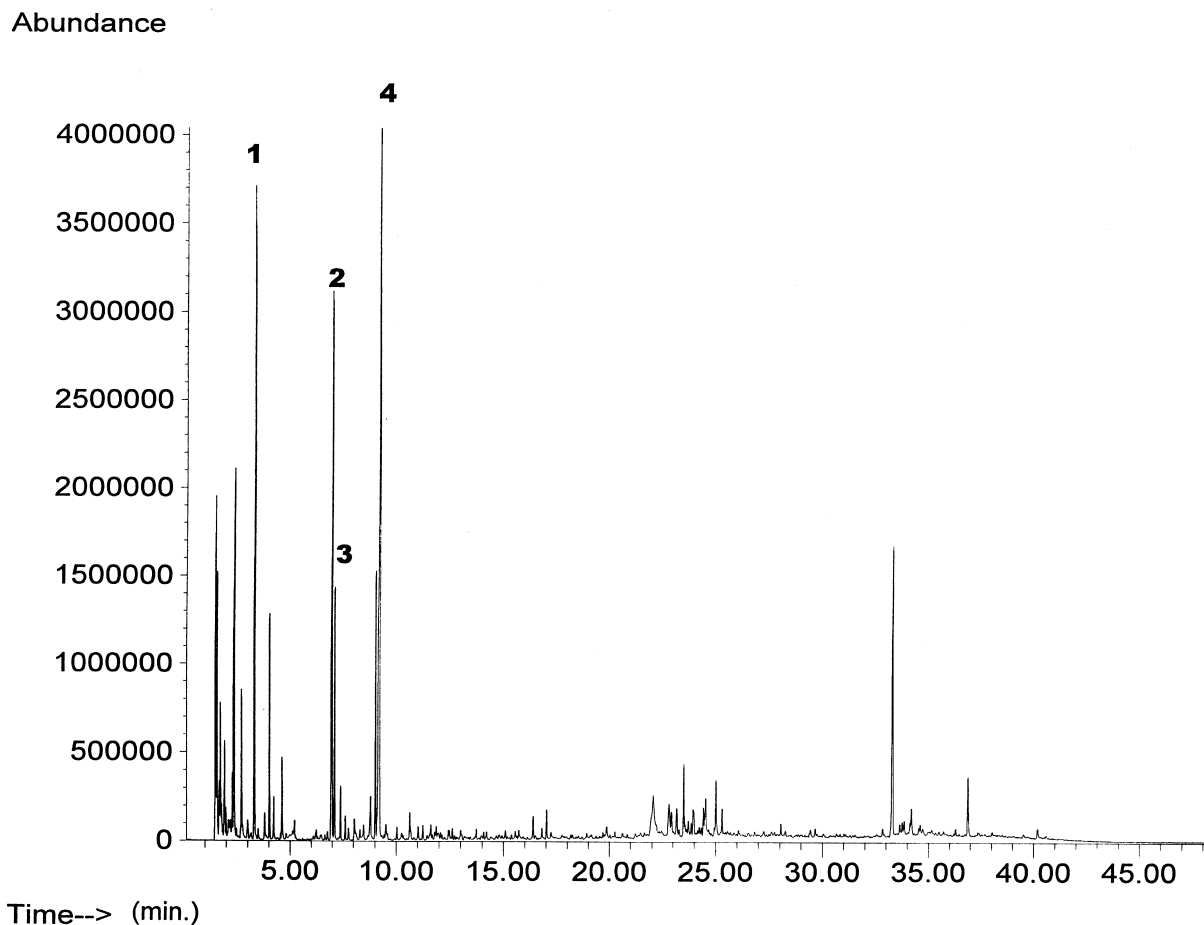

Fig. 5. Pyrogram of automobile paint. Peak 1=methyl methacrylate, 2=styrene, 3=butyl acrylate, 4=butyl methacrylate. For conditions, see Table 1.

Bakowski et al. [60] of adhesives used to make explosive devices, pyrograms were averaged creating a library of composite spectra for 91 commercially available materials, then using the MS data system to identify unknowns. Drugs and their metabolites have also been investigated, including hashish [61] to determine source and the conjugated metabolites of antipyrine in urine [62]. Mitsui et al. [63] have applied pyrolysis to the study of narcotics as alkaloid salts, after extraction from human urine.

5.6. Geochemistry and fuel sources

Petrochemical related materials represent a class of substances studied by pyrolysis even before GC was invented. Investigations today using Py–GC involve several categories, including biological materials seen as precursors, classification and ranking of fuel source and the analysis of coal and related materials. Seeley et al. [64] describe an analytical system employing Py–GC with atomic emission detection to assay sediments and coals, looking specifically at carbon, nitrogen, sulfur, oxygen, phosphorous, arsenic and selenium, obtaining data which help measure the evolutionary stage of the sample. Stankiewicz et al. [65] examined cuticles from fossil invertebrates, which they divided into two classes, those which produced aromatics and those which produced aliphatics. Kerogens—the insoluble constituent found in fuel sources—have benefited from study by pyrolysis since they are very difficult to assay by other means. Systems for classifying kerogens based on the pyrolysis results have been suggested by analysts, including Horsfield [66] and a technique using a polymeric internal standard by Larter and Senftle [67]. Fig. 6 shows an example of what a kerogen looks like when pyrolyzed, with a wide distribution of long-chain hydrocarbons making a repeating pattern of peaks.

Coal studies include the analysis of the organic material itself, as in the study of subbituminous coal by Christiansen et al. [68] and that characterizing vitrinite concentrates from a coal sample with particular attention paid to the significance of phenols [69]. Further, the production of sulfur compounds from coal during pyrolysis has been reported by Almen et al. using a system of simultaneous Py–GC with both flame ionization (FID) and flame photo-

metric detection systems [70], and suggestions for classification of coals by Py–GC–MS–NPD–FID have been made by Bonfanti et al. [71].

Mention must be made of some extraterrestrial applications of pyrolysis. Kotra et al. [72] discuss Viking spacecraft data from Mars suggesting the presence of volatile-rich materials, which were approximated in the laboratory. More recently, the study of organic matter found in meteorites [73] resulted in the proposal of a polycyclic aromatic molecular model for the basis of the organic compounds observed.

5.7. Synthetic polymers

This very broad category includes materials used in a wide array of products, including plastics, rubbers, coatings and composites. These materials may be comprised of homopolymers or of copolymers, and both classes of polymeric materials have been studied extensively using Py–GC. Ohtani et al. [74] have provided numerous examples of the power of high resolution GC to reveal microstructural information about polyolefins, including stereospecific sequencing in polypropylene. For an idea of what polypropylene looks like when pyrolyzed, refer to Fig. 1. Duncan [75] has demonstrated a Py–GC–IR–MS system for the analysis of polybutadiene, and other polyolefins, especially polyethylene, [76] and chlorinated polyethylene [77] have been characterized as well. Oguri et al. report an approach for the analysis of condensation polymers, especially polyesters using thermal and methylation steps [78]. A thermally cured polyimide (Matrimid 5292; Ciba-Geigy) was studied by Galipo et al. [79] determining that the curing process could be followed by monitoring specific pyrolysis products.

More challenging is the analysis of copolymers. These systems can be comprised of different analogs of the same monomer type, such as a copolymer involving several acrylic monomers [80] or include different monomeric materials. The composition and microstructure of styrene–methyl methacrylate copolymers have been assayed by Wang and Smith [81], and Wang et al. report similar analyses for styrene–butyl acrylate copolymers as well [82]. The paint analysis shown in Fig. 5 provides a good example of how styrene–acrylic copolymers behave
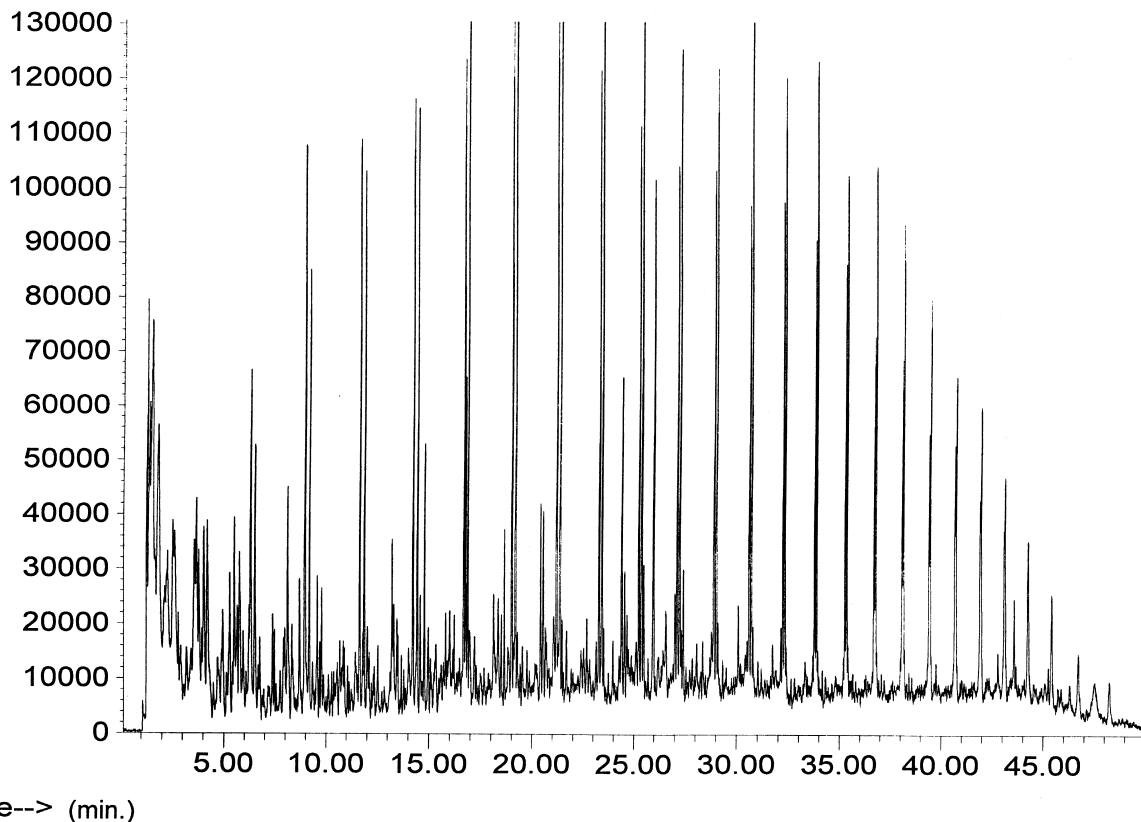
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Fig. 6. Pyrogram of a kerogen. Double peaks are pairs of long-chain normal alkanes and alkenes. For conditions, see Table 1.

when pyrolyzed. Each of the four main monomers used—styrene, methyl methacrylate, butyl acrylate and butyl methacrylate—appear as an easily identifiable peak. A Py–GC–FT-IR–FID system is applied to the analysis of butadiene–acrylonitrile copolymers by Weber [83], obtaining good sensitivity using samples of 1 mg. Other copolymer systems studied include an ABS (acrylonitrile–butadiene–styrene)–alpha methyl styrene copolymer [84] and a material consisting of 1% polyacrylamide in polyvinyl alcohol [85].

Rubbers, both natural and synthetic, comprise a class of materials subjected to considerable analysis. Phair and Wampler [86] have reported an overview of Py–GC–MS results for a wide variety of rubber and rubber-like materials, including polyisoprene, polybutadiene, styrene–butadiene copolymers and polydimethylsiloxane. The presence of fillers in rubber, specifically carbon black, has been investigated by Matheson et al. [87] who report that even the presence of substantial filler has little effect on the ability of Py–GC to identify the rubber polymers. The rubber sample pyrolyzed for Fig. 7 reveals monomers for both isoprene and butadiene, (as well as dimers for both) even though it contained a substantial amount of carbon black filler. Other filled polymer systems have been studied as well, including fiber–epoxy composites [88].

The above citations provide just a brief overview of the kinds of work being done in a few general
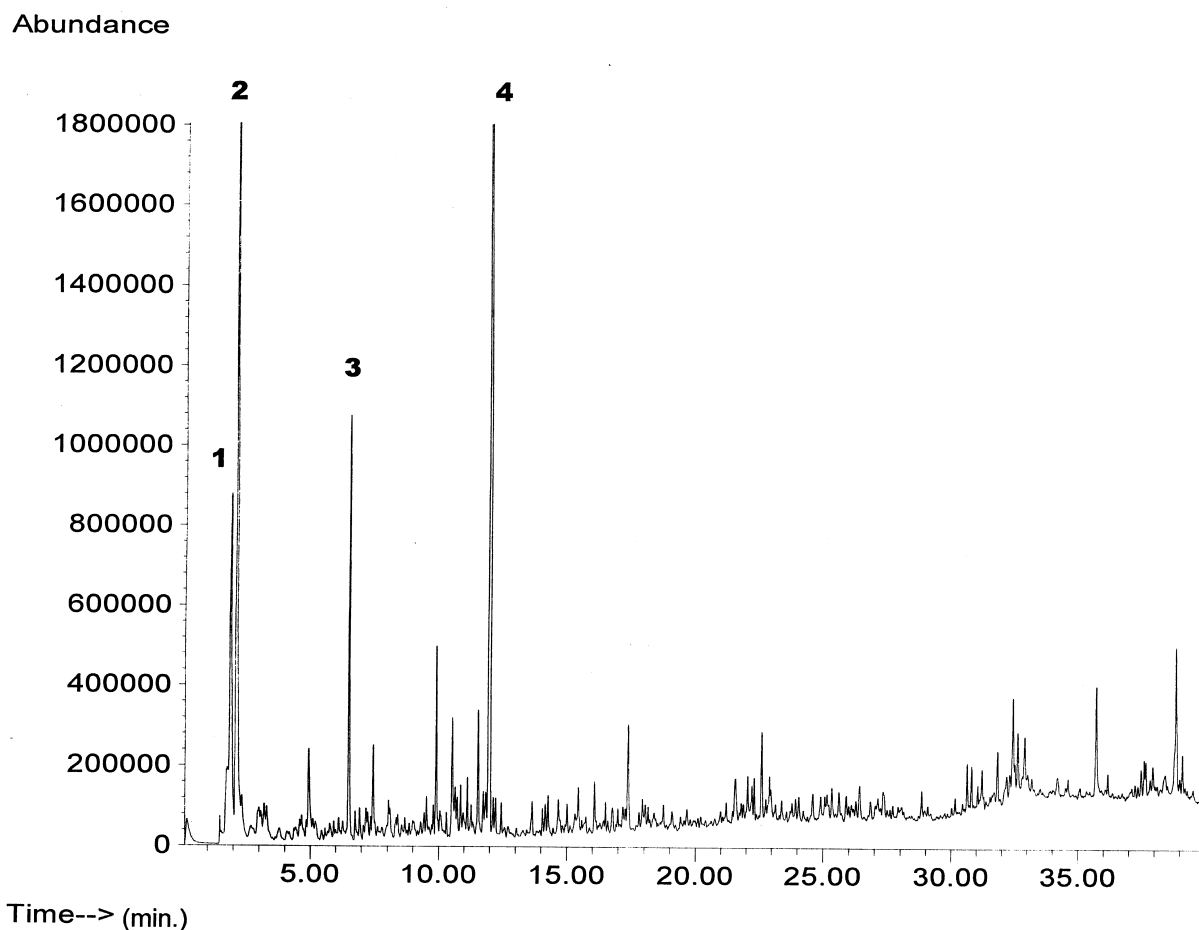
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Fig. 7. Isoprene–butadiene rubber pyrolysis. Peak 1=butadiene, 2=isoprene, 3=butadiene dimer, 4=limonene (isoprene dimer). For conditions, see Table 1.

categories, but analytical Py–GC is being applied to an ever increasing range of materials. Some interesting examples not included in the above categories show work on human hair [89], ink and paper [90], needles from pine trees [91] and polymeric dye transfer inhibitors in laundry detergents [92]. As the world of everyday products grows to include more and more polymeric materials, Py–GC will be increasingly relied upon to analyze them.

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