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# Introductory Chapter: Analytical Pyrolysis-Gas Chromatography/Mass Spectrometry of Polymeric Materials

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## 1. Analytical pyrolysis

According to the International Union of Pure and Applied Chemistry (IUPAC) recommendation, analytical pyrolysis (Py) is defined as the characterization in an inert atmosphere of a material or a chemical process by a chemical degradation reaction(s) induced by thermal energy [1]. Thermal degradation under controlled conditions is often used as a part of an analytical procedure, either to render a sample into a suitable form for subsequent analysis by gas chromatography (GC), mass spectrometry (MS), gas chromatography coupled with the mass spectrometry (GC/MS), with the Fourier-transform infrared spectroscopy (GC/FTIR), or by direct monitoring as an analytical technique in its own right [2]. Analytical pyrolysis deals with the structural identification and quantitation of pyrolysis products with the ultimate aim of establishing the identity of the original material and the mechanisms of its thermal decomposition. The pyrolysis temperatures of 550–1400°C are high enough to actually break molecular bonds in the molecules of the solid sample, thereby forming smaller, simpler volatile compounds. Depending on the amount of energy supplied, the bonds in each molecule break in a predictable manner [3]. By the measurement and identification of the fragments, the molecular composition of the original sample can often be reconstructed [4].

Analytical pyrolysis technique hyphenated to GC/MS has extended the range of possible tools for the characterization of synthetic polymers and copolymers. This technique has been used extensively over the last 30 years as a complementary analytical tool used to characterize the structure of synthetic organic polymers and copolymers, polymer blends, biopolymers, and natural resins. Pyrolysis-GC/MS is a destructive analytical technique. Typical fields of interest and application are polymer identification by comparison of pyrograms and mass spectra with known references, qualitative analysis and structural characterization of copolymers, determination of the microstructure of polymers, determination of the polymers steric structure, investigation of thermal stability of polymers and copolymers, determination of residual monomers and solvents, volatile organic compounds (VOCs) as well as additives in polymers [5].

Pyrolysis method allows for the direct analysis of very small solid or liquid polymer/copolymer sample amounts (5–200 µg) and eliminates the need for time-consuming sample preparation (pretreatment) by performing analyses directly on the sample. The essential requirements for the apparatus in analytical pyrolysis are reproducibility of the pyrolysis temperature, rapid temperature rise, and accurate

temperature control. Depending upon the heating mechanism, pyrolysis systems have been classified into two groups: the continuous-mode pyrolyzer (furnace pyrolyzer) and pulse-mode pyrolyzer (flash pyrolyzer), such as the heated filament, Curie-point, and laser pyrolyzer. The pyrolysis unit (pyrolyzer) is connected directly to the injector port of a gas chromatograph.

Once the polymer/copolymer sample has been pyrolyzed, volatile fragments are swept from the heated pyrolysis unit by the carrier gas (helium) into the gas chromatograph. The volatile pyrolysis products (pyrolyzate) are chromatographically separated by using a fused silica capillary column, according to the boiling points and the affinity of analytes to the stationary phase (internal capillary column wall coating). The detection technique of the separated compounds is typically mass spectrometry (MS). The substances detected by the mass spectrometry are subsequently identified by the interpretation of the obtained mass spectra, by using mass spectra libraries (e.g., NIST/EPA/NIH, Wiley, MPW, Norman Mass Bank, m/z Cloud), or by using reference substances.

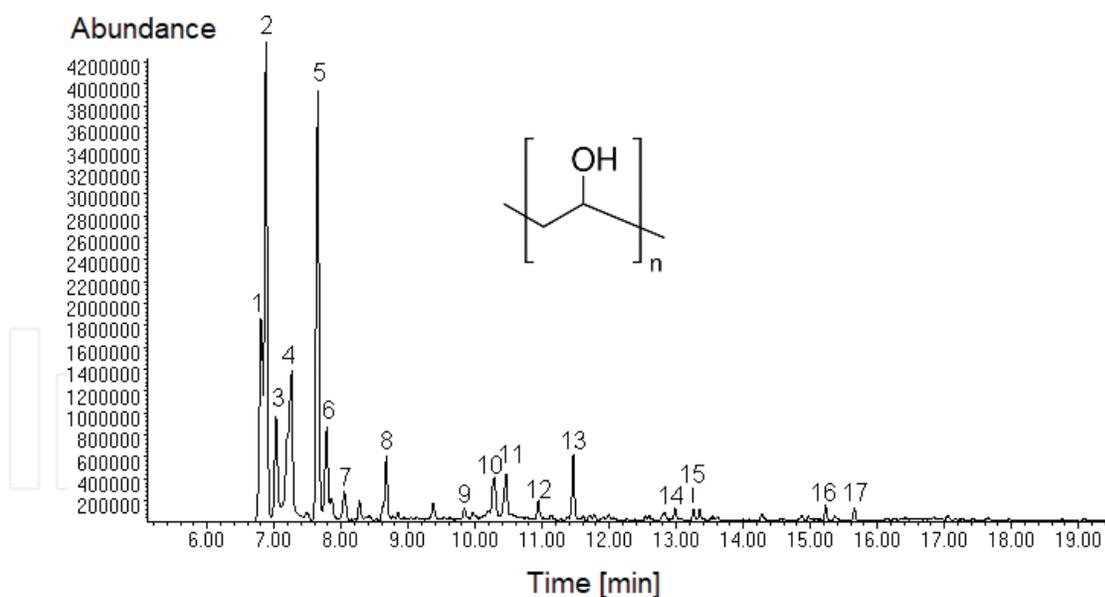
Pyrolysis-GC/MS can be applied to research and development of new materials, quality control, characterization and competitor product evaluation, medicine, biology, and biotechnology, geology, airspace, and environmental analysis to forensic purposes or conservation and restoration of cultural heritage. These applications cover analysis and identification of polymers/copolymers and additives in components of automobiles, tires, packaging materials, textile fibers, coatings, adhesives, half-finished products for electronics, paints or varnishes, lacquers, leather, paper or wood products, food, pharmaceuticals, surfactants, and fragrances.

## 2. Example of application: characterization of poly(vinyl alcohol) by pyrolysis-GC/MS

Poly(vinyl alcohol) (PVA) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing poly(vinyl acetate) in ethanol with potassium hydroxide [6]. PVA is produced commercially from poly(vinyl acetate), usually by a continuous process. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. PVA is an odorless and tasteless, translucent, white- or cream-colored granular powder. It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. PVA is divided into two classes—partially hydrolyzed PVA and fully hydrolyzed PVA. Partially hydrolyzed PVA is used in food as a moisture barrier film, for food supplement tablets, and for dry food with inclusions that need to be protected from moisture uptake. Poly(vinyl alcohol) has various applications in the food industries as a binding and coating agent. PVA protects the active ingredients from moisture, oxygen, and other environmental components while simultaneously masking their taste and odor. This polymer is used as a water-soluble film useful for packaging. An example is the envelope containing laundry detergent in “liqui-tabs.” PVA is used also as packaging material for dishwasher tabs.

### 2.1 Experimental

Approximately, 200 µg of poly(vinyl alcohol) sample was cut out with a scalpel and inserted into the bore of the pyrolysis solids-injector, without any further preparation, and then placed on the quartz wool of the quartz tube of the furnace pyrolyzer *Pyrojector II*<sup>TM</sup> (SGE Analytical Science, Melbourne, Australia) with the plunger. The pyrolyzer was operated at a constant temperature of 700°C. The pressure of helium (99.999 v/v%) carrier gas at the inlet to the furnace was 95 kPa.



**Figure 1.**  
 Pyrolysis-GC/MS chromatogram of PVA at 700°C. For the analytical conditions, see experimental and reference [5].

Peak No.	Retention time $t_R$ (min)	Pyrolysis product
1	6.81	Cyclopropane
2	6.88	Acetaldehyde
3	7.00	Methylbutene
4	7.26	Acetic acid
5	7.65	2-Butenal (crotonaldehyde)
6	7.78	Benzene
7	8.05	Acetic acid anhydride
8	8.68	Toluene
9	9.84	Ethylbenzene
10	10.28	Styrene
11	10.46	2,4-Hexadienal
12	10.95	2-Cyclohexen-1-one
13	11.47	Benzaldehyde
14	13.00	Propenylbenzene
15	13.26	Acetophenone
16	15.23	Dihydronaphthalene
17	15.68	Naphthalene

For the analytical conditions, see experimental and reference [5].

**Table 1.**  
 Pyrolysis products of PVA at 700°C.

The pyrolyzer was connected to a 7890A gas chromatograph with a series 5975C quadrupole mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) operated in electron impact ionization (EI) mode. The fused silica capillary column 60 m long, 0.25 mm I.D. with DB 5-MS stationary phase, film thickness 0.25  $\mu\text{m}$  was used (J&W Scientific, Folsom, CA, USA). The GC/MS analytical conditions were described in detail in another publication of the author [5]. GC/MS data were

processed with the *ChemStation* software (Agilent Technologies) and the *NIST 05* mass spectra library.

## 2.2 Results and discussion

**Figure 1** shows the pyrolysis-GC/MS chromatogram of PVA at 700°C. The pyrolysis products identified by using the *NIST 05* mass spectra library are summarized in **Table 1**.

As shown in **Figure 1** and **Table 1**, pyrolysis of poly(vinyl alcohol) produces a series of aldehydes (acetaldehyde, crotonaldehyde, 2,4-hexadienal, benzaldehyde) and aromatic hydrocarbons. This is the result of the formation of double bonds by the elimination of H<sub>2</sub>O from the PVA macromolecules (dehydration), followed by the breaking of the carbon chain with or without cyclization. The side-group scission occurs when the side groups attached to the backbone are broken away, resulting in the backbone becoming polyunsaturated. A two-step degradation mechanism begins with the elimination of H<sub>2</sub>O from the polymer chain leaving a polyunsaturated backbone that, upon further heating, produces the characteristic aromatics. This is similar to the degradation mechanism seen in poly(vinyl chloride) (PVC), in which hydrogen chloride (HCl) is first stripped from the polymer, which creates multiple double bonds, eventually producing aromatics [7].

## 3. Conclusion

Analytical pyrolysis-GC/MS proved to be a valuable hyphenated technique for the analysis and identification of synthetic organic polymeric materials. This technique allows the direct analysis of very small sample amounts (5–200 µg) without the need of time-consuming sample preparation. Pyrolysis-GC/MS can be applied to research and development of new materials, quality control, as well as characterization and competitor product evaluation. Pyrolysis-GC/MS allows the confirmation of the source of a failed product, the identification of contaminants causing failure, the competitive analysis, as well as overcoming a problem in product development or quality control [5].

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