

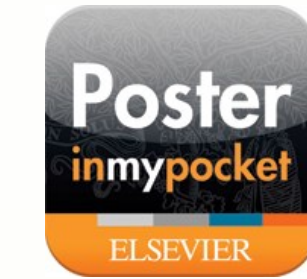
# Analytical pyrolysis beyond fingerprinting techniques



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## Introduction

Analytical pyrolysis has long been used for analysis of non-volatile substances, but mainly as a fingerprinting technique. Through better understanding of the thermal degradation process, and by using a pyrolyzer capable of exploiting the possibilities, it is possible to extract much more information of the processed sample.

Quantitative analysis is an obvious example, but there are more methods to choose from. It is possible to analyse different fractions separately by pyrolysing the same piece of sample at different temperatures, each giving a separate pyrogram. By studying formation rates of pyrolysis products it is possible to get information of the binding energy, and for example to differ between a co-polymer and a mixture of polymers. And with a pyrolyzer capable of extremely short heating pulses, in the order of 10 milliseconds, it is even possible to make a separate analysis of surface coatings or of the different layers in a laminate.

## Background

Pyrolysis is the degradation of a substance by thermal energy in an inert atmosphere. The process generally follows a first-order reaction, that is the degradation, or alternatively the formation of pyrolysis products, is proportional to the amount of sample that has not reacted yet. The result is a curve that is decreasing exponentially, as shown in figure 1.

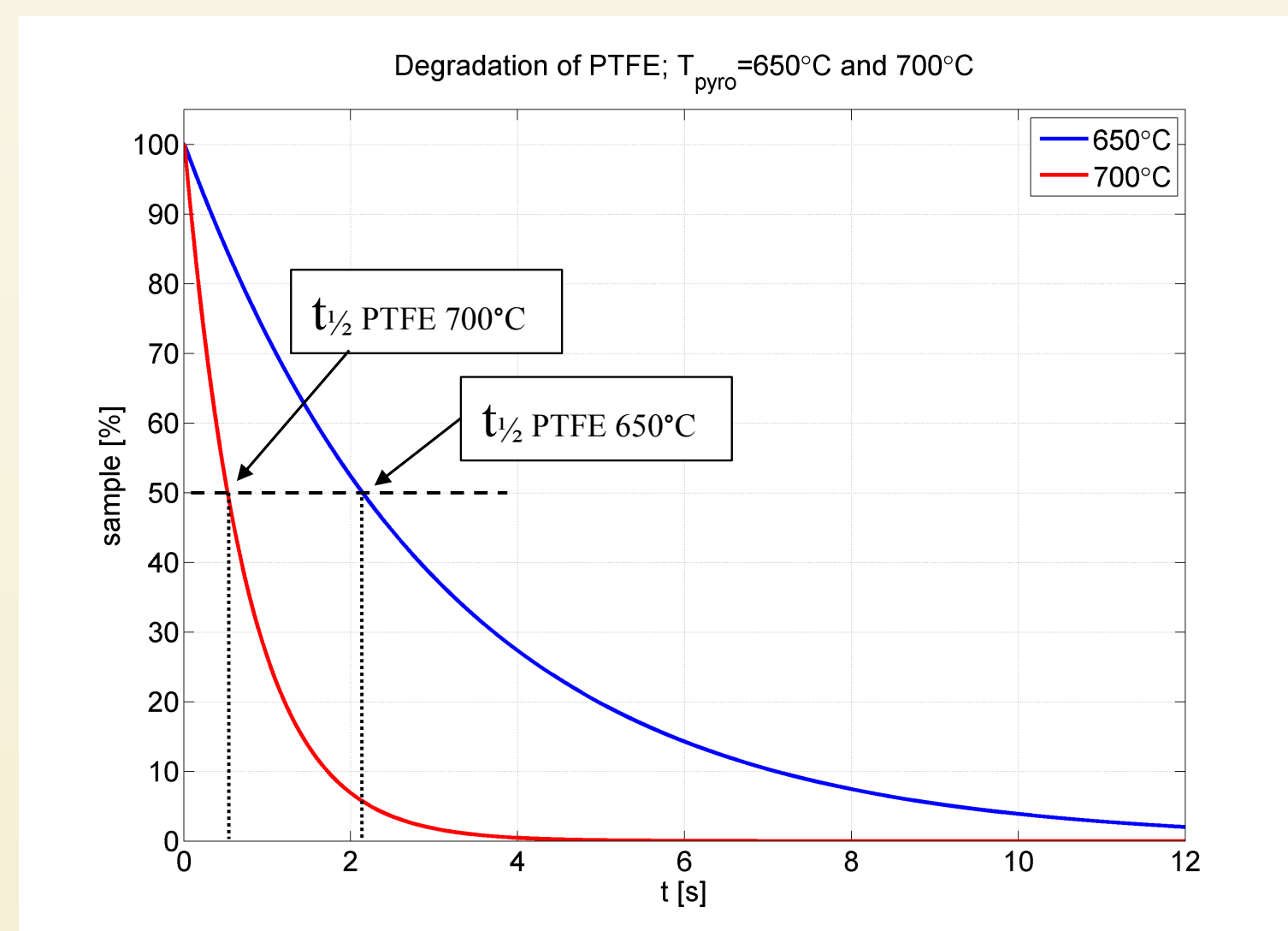


Figure 1. The degradation of PTFE, polytetrafluoroethylene, at 650°C and 700°C. Data from figure 2.

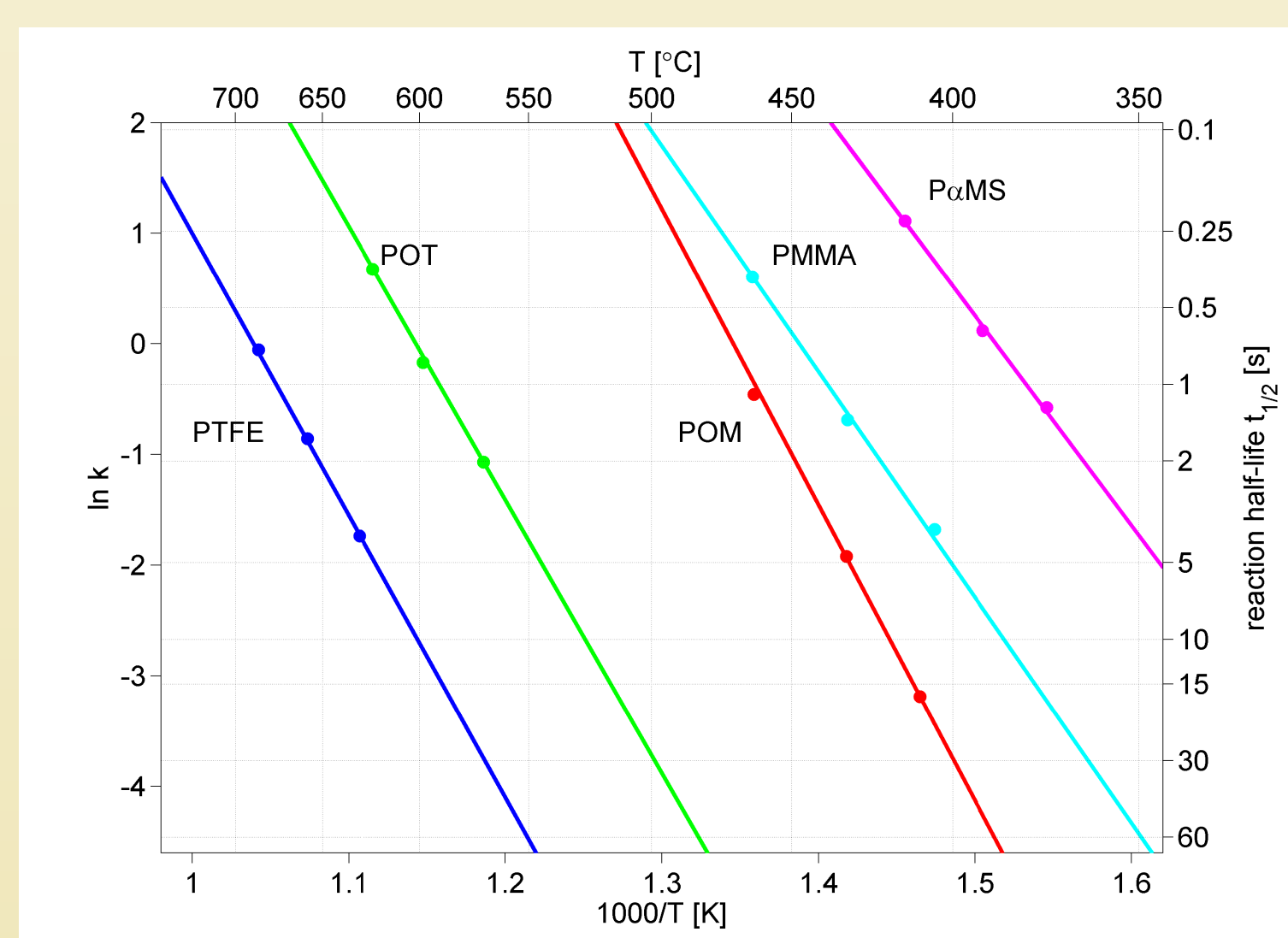


Figure 2. Arrhenius plot of pyrolysis of 5 polymers: PTFE = poly(tetrafluoroethylene) POT = poly(octylthiophene) POM = poly(oxymethylene) PMMA = poly(methyl methacrylate) PaMS = poly(a-methylstyrene). Formation of monomers. Experimental data from [1].

The following observations can be made from the Arrhenius plot, figure 2:

- In order to get a **well-defined pyrolysis temperature** it is important to have a very rapid temperature increase. A slow rise in temperature will cause the substance to be pyrolysed gradually, at different temperatures.
- In order to get a **well-defined pyrolysis temperature** it is important to have a the same temperature throughout the sample. This implies small sample sizes.
- In order to **stop** the pyrolysis of the sample it is important to have a very rapid cooling, and to decrease the temperature well below the pyrolysis temperature.

With a pyrolyzer that fulfils these requirements it is possible to extend the methods of analytical pyrolysis **beyond the fingerprinting techniques** that ordinary, isothermal pyrolysis offer. The Pyrola filament pyrolysers were developed with this in mind, figure 3. The temperature rise time to reach temperatures up to 1400°C is only 8 milliseconds. The following paragraphs describe the methods developed by Pyrol AB to take advantage of these possibilities: sequential pyrolysis, fractionated pyrolysis and pyrotomy.

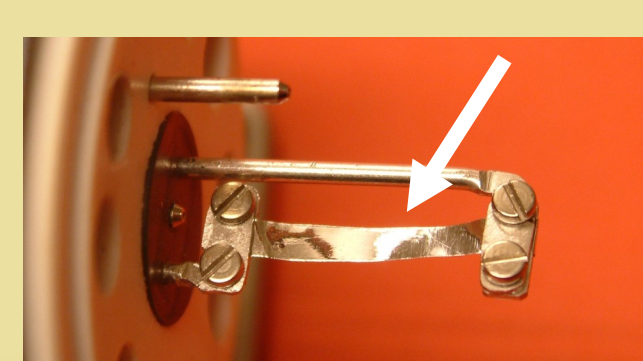


Figure 3. In a filament pyrolyser the sample is placed directly on a filament, which is heated resistively, i.e. by applying a electrical current. The filament has an indentation to keep the sample in place when analysing solid samples.

## Sequential pyrolysis

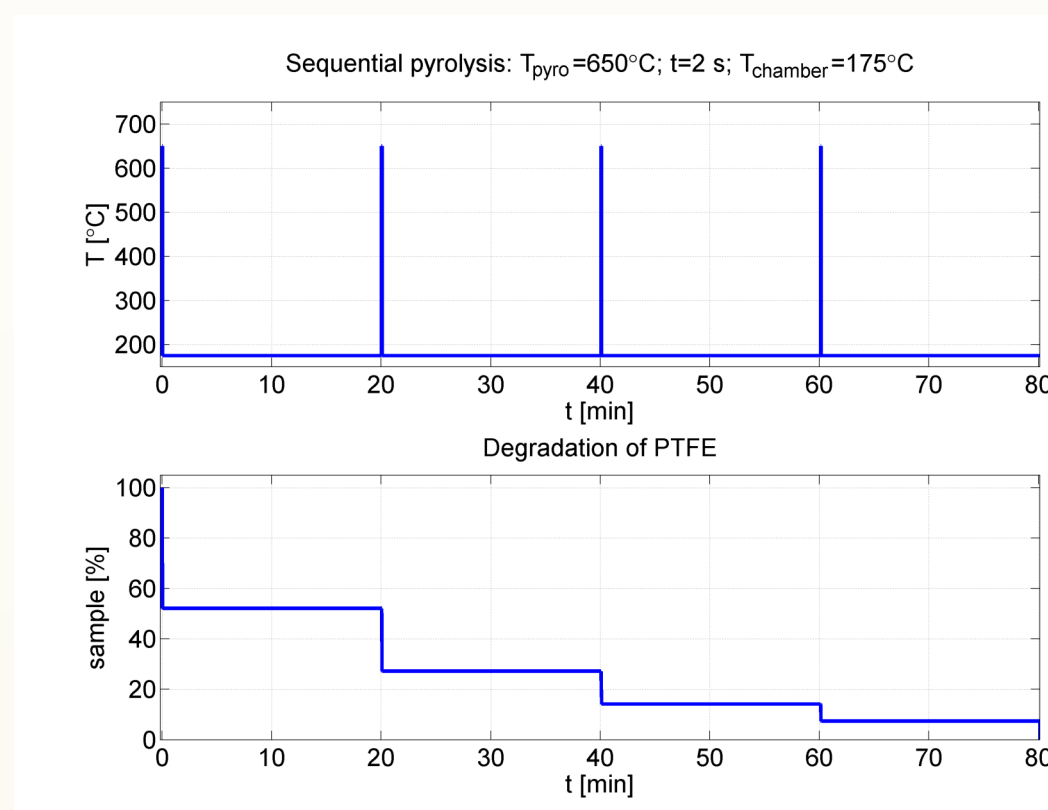
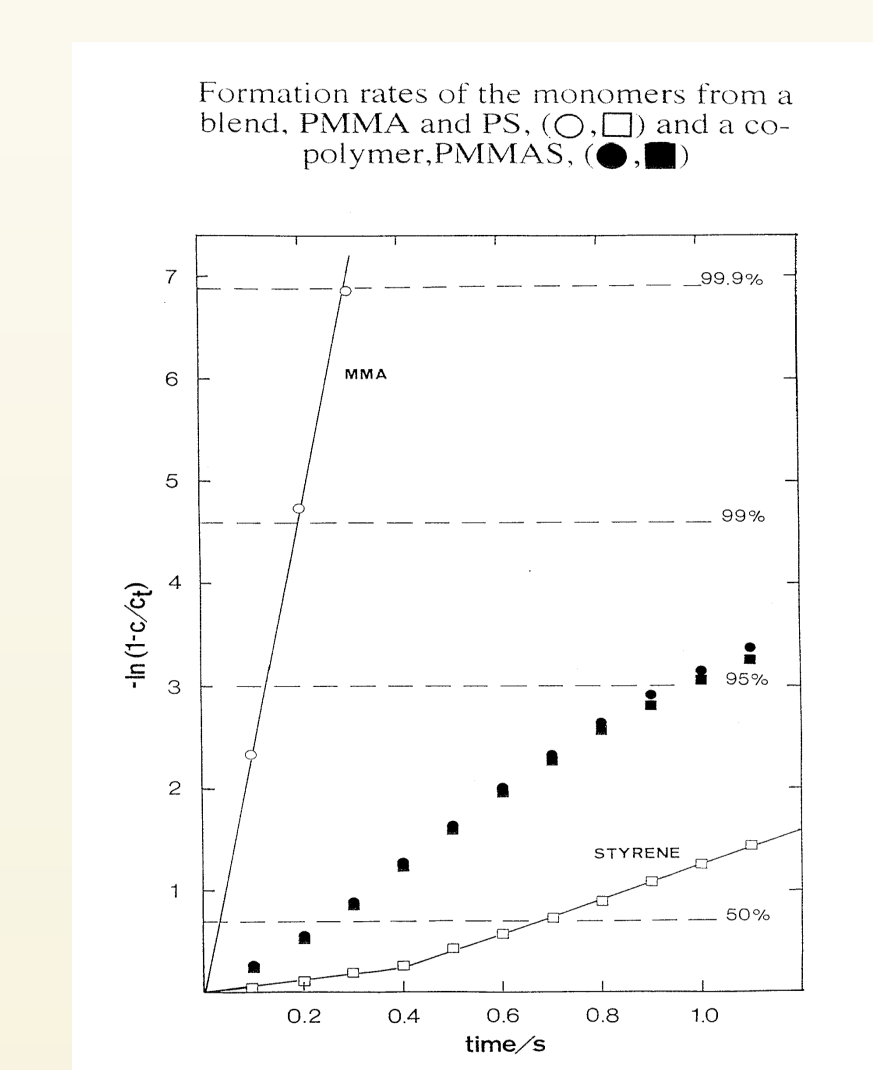


Figure 4. Temperature time profile at sequential pyrolysis, with heating pulses of 2 s. The degradation of PTFE.



By very precise control of the pyrolysis temperature and extremely fast temperature pulses, it is possible to do a partial pyrolysis of the sample at each step. This is **sequential pyrolysis**, defined in the IUPAC recommendations [2] as:

*A pyrolysis in which the same initial sample is repetitively pyrolysed under identical conditions.*

The formation rates of pyrolysis products are obtained by adding the peak areas of the individual pyrograms. An example is shown in figure 5, where formation rates are used to distinguish between a blend and a copolymer with the same constituent monomers.

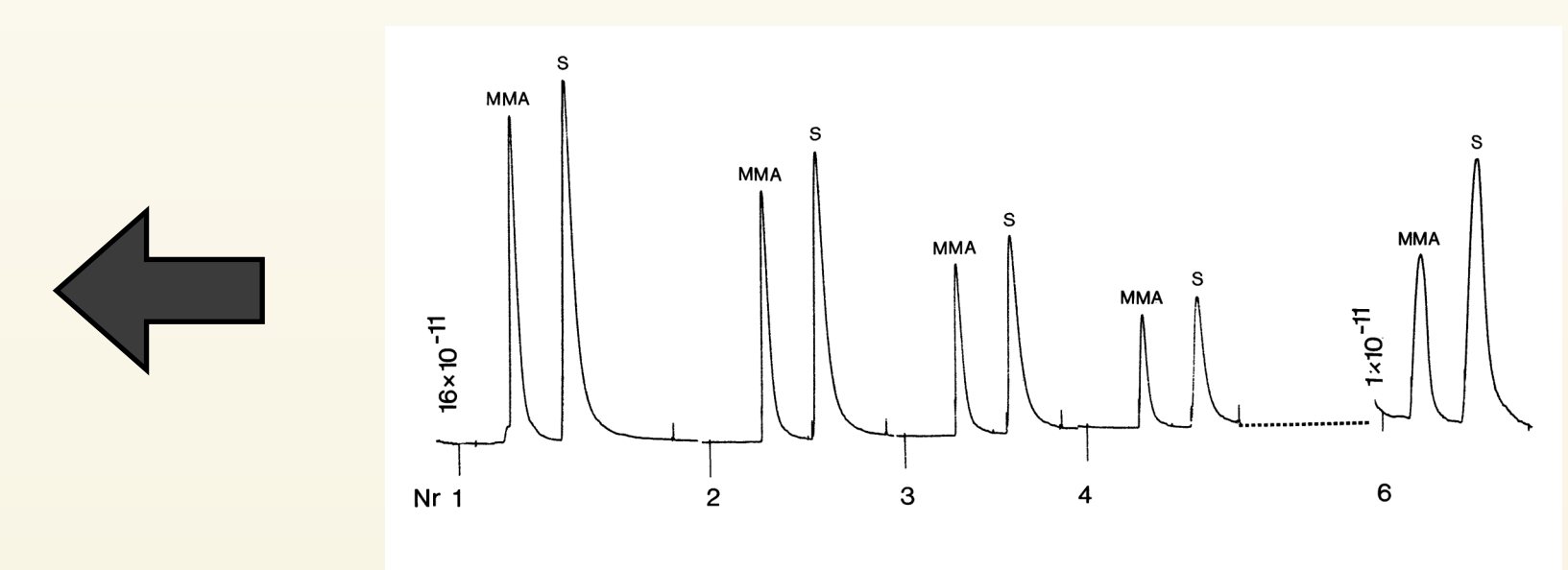


Figure 5. Formation rates of monomers determined by sequential pyrolysis. By studying formation rates it is possible to distinguish between a blend and a co-polymer. From [3].

## Fractionated pyrolysis

With the same temperature profile as in figure 4, but with higher pyrolysis temperatures in each consecutive step, the method is called **fractionated pyrolysis**, IUPAC recommendations [2]:

*A pyrolysis in which the same sample is pyrolysed at different temperatures for different times in order to study special fractions of the sample.*

With a rapid cooling the thermal degradation stops between the pyrolysis pulses, and the result is clean pyrograms at each pyrolysis temperature, ideal for complex samples. An example is shown in figure 6, the fractionated pyrolysis of two different toners for laser printers.

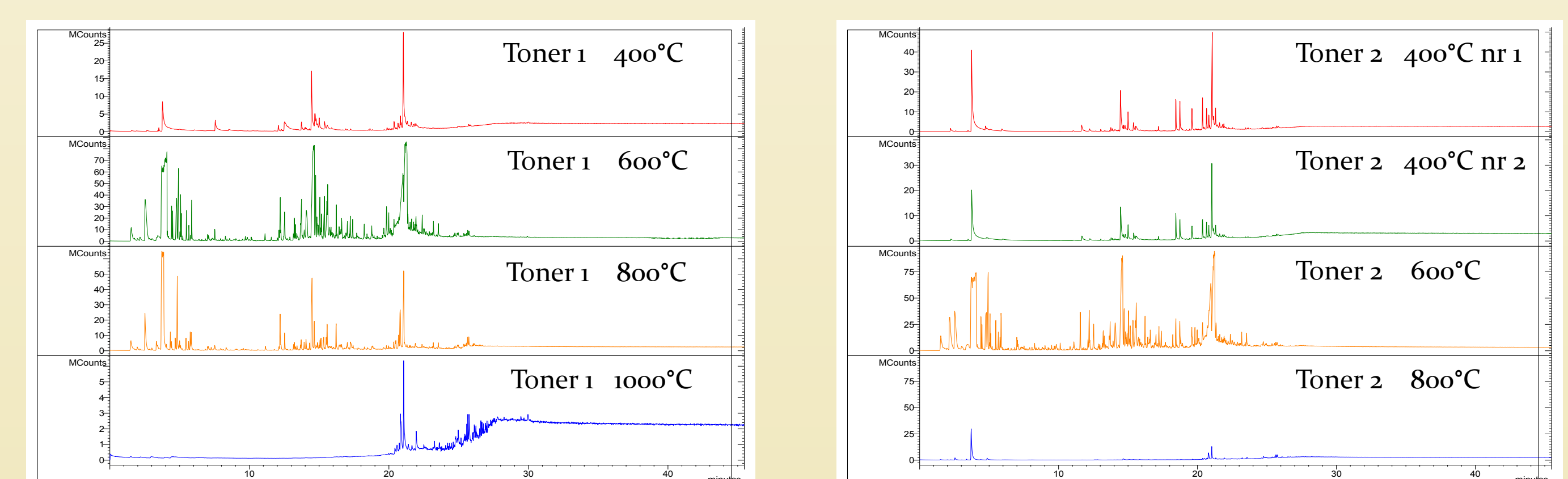


Figure 6. Fractionated pyrolysis at 400°C, 600°C, 800°C and 1000°C of two brands of toners for laser printers. From [4].

## Pyrotomy

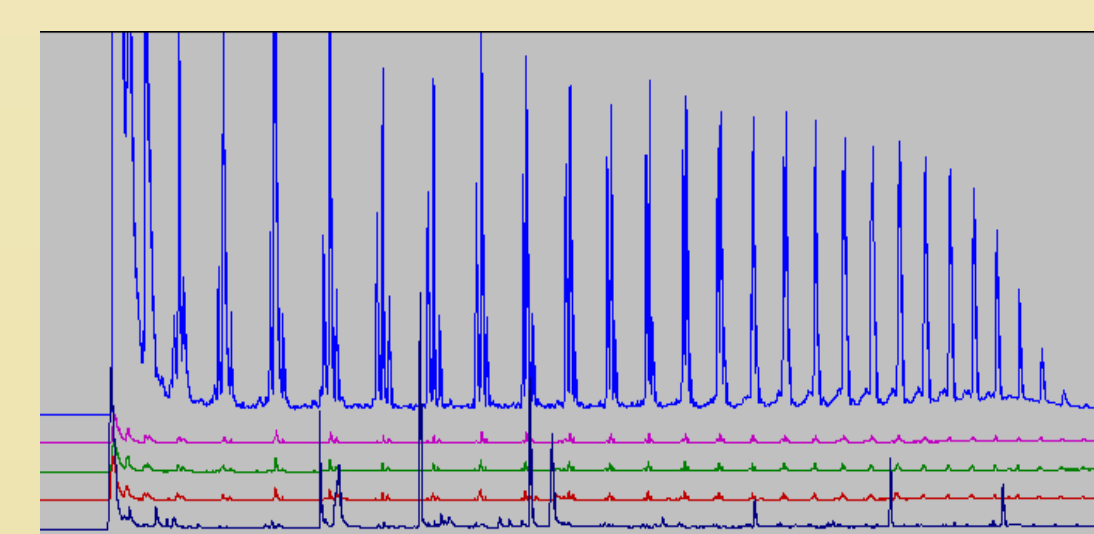


Figure 7. Pyrotomy of a PE-PET laminate. From [5].

With the same temperature profile as in figure 4, but with even shorter temperature pulses, down to 10 ms, it is possible to pyrolyse only the piece of sample that is in direct contact with the heated filament. The method is called **pyrotomy**, and makes it possible to analyse e.g. surface coatings and individual layers of a laminate. An example is shown in figure 7, where a polyethylene - polyethylene terephthalate laminate is pyrolysed 4 times for 50 ms, followed by a 2 s pyrolysis.

## Summary

By understanding the pyrolysis process, and by having a pyrolyzer capable of exploiting the possibilities, it is possible to extend the methods beyond the fingerprinting techniques of isothermal pyrolysis. Three methods developed by Pyrol AB have been presented, sequential pyrolysis, fractionated pyrolysis and pyrotomy, each giving exciting new possibilities for analysing complex samples.

## References

- [1] Inger Ericsson, Analysis of Polymers by Py-GC/MS, Pittcon 1986.
- [2] P.C. Uden, Nomenclature and Terminology for Analytical Pyrolysis, J. Anal. Appl. Pyrol., 31 (1995) 251. See also chapter 5.3 in: [http://iupac.org/publications/analytical\\_compendium/](http://iupac.org/publications/analytical_compendium/)
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- [4] Inger Ericsson, Pyrolysis Workshop, Darmstadt, Germany, 2008.
- [5] Inger Ericsson, Pyrolysis Workshop, Sprockhövel, Germany, 2005.