Analytical pyrolysis with Pyrola pyrolyzers

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Why analytical pyrolysis?

A gas chromatograph, especially in combination with a mass spectrometer, is a very powerful instrument. The obvious problem is that non-volatile samples cannot be analysed, unless they are made volatile, and this is exactly what a pyrolyzer does. By heating the sample in an inert atmosphere the large molecules are divided into smaller volatile fragments, which then can be analysed by the GC or GC/MS. The process is well-defined in the sense that an identical sample under the same conditions will give the same pyrolysis products. A substance will give a specific fingerprint that can be exploited to make detailed analyses even with very small sample sizes, making the technique ideal for applications such as product control, reclamations and forensics. The output from the GC is called a pyrogram.

The samples may be insoluble, dark or inhomogeneous, and include synthetic and natural polymers, like vulcanized rubber, resins and composites. Paper, coal, textiles and paints are all examples of materials that are successfully analysed by analytical pyrolysis.

The intention of this leaflet is to give a short summary of analytical pyrolysis, and the different innovative methods developed by Pyrol AB that can be used for straightforward routine analyses as well as dealing with complex problems.

The Pyrola pyrolyzers

Pyrol AB develops and manufactures pyrolyzers for manual and automated use, see Figure 1. Pyrol AB was established in 1984, based on the findings in Inger Ericsson's doctoral thesis from 1975, "Qualitative, Quantitative and Kinetic Studies of Salts and Polymers with a New Pyrolyzer in Combination with a Gas Chromatograph". Realizing the limitations and imperfections of other pyrolysis instruments, Inger Ericsson developed a new pyrolyzer with extremely fast temperature-rise-time, 8 milliseconds to reach temperatures up to 1400 ºC, for samples sizes in the order of micrograms. This together with a unique non-interfering temperature measurement made it possible to develop the innovative methods described in this leaflet, thermal desorption, sequential pyrolysis, fractionated pyrolysis and pyrotomy.

When comparing different instruments beware that most pyrolyzers do not have the possibilities that are presented here. The distinguishing features are the sample in direct contact with the heating element giving ultrafast heating and cooling, and the possibility to pyrolyze the same piece of sample multiple times at high temperatures.

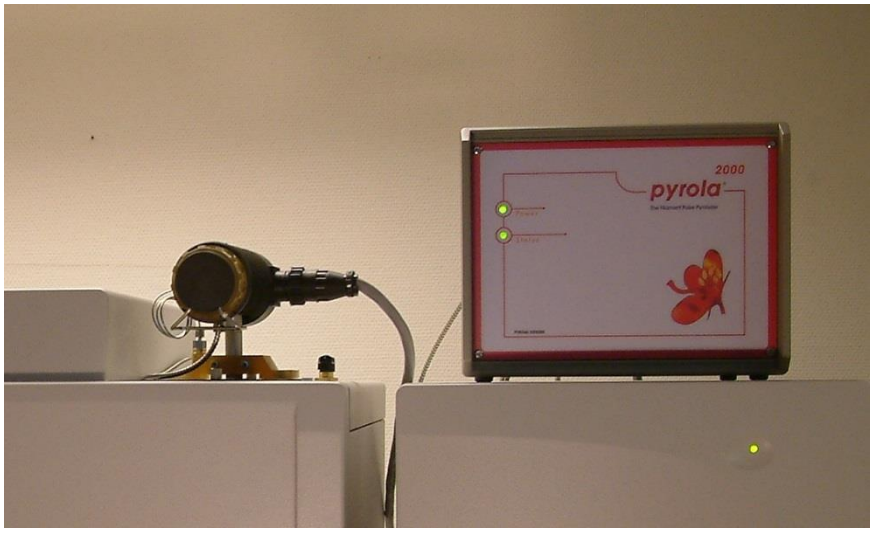

Figure 1. The Pyrola 2000 pyrolyzer.

The terminology in this leaflet follows the IUPAC recommendations (1993); P.C. Uden, Nomenclature and Terminology for Analytical Pyrolysis, J. Anal. Appl. Pyrol., 31 (1995) 251.

The basics

Thermal degradation of a sample means breaking of chemical bonds by heat. Which bonds are broken depend on the sample itself and the pyrolysis temperature. If two substances are different, then the number, kind or positions of the atoms are different, meaning in general that the pyrolysis products will be different. Then different analytical methods can be used to find the differences, by separation and identification. But the story does not end there; even more information may be obtained by varying the pyrolysis conditions. One example is to study how the formation rates of the pyrolysis products depend on temperature. This can be used for example to distinguish between a copolymer and a blend of two polymers, where the pyrolysis products are identical but the formation rates differ.

Figure 2. Platinum filament. The sample to be pyrolyzed is put on the filament.

Different pyrolyzers use different methods of heating. The pyrolyzers from Pyrol AB use a thin platinum filament where the sample is placed, see Figure 2. Liquid samples may be applied on a flat filament, whereas a small indentation can be made on the filament when analysing solid samples. The filament is heated by applying an electrical current. The heating is almost instantaneous since the sample is in direct contact with the heating source. Furthermore the mass of the filament is so small that it is rapidly cooled off by the carrier gas down to the chamber temperature, typically 175 ºC. This makes it possible pyrolyze the same sample multiple times at the same temperature, and even to make the heating pulses so short that the sample is pyrolyzed slice by slice, called pyrotomy, further described below.

Get the same results every time

The key to success is to be able to reproduce the pyrolysis conditions every time. The sample itself will influence the pyrolysis temperature, as a larger sample will require more heat to reach the same temperature. Therefore it is a good idea to keep the samples as small as possible. Pyrol AB has developed sample handlers to help making consistent sample sizes, see Figure 3.

Figure 3. Sample handlers for e.g. paper and powder.

An example of good reproducibility is shown in Figure 4, where identical samples of cotton are pyrolyzed on three different probes on the Pyrola MultiMatic. A consistent heating and a non-obstructive passage of the pyrolysis products to the GC column further enhances the repeatability.

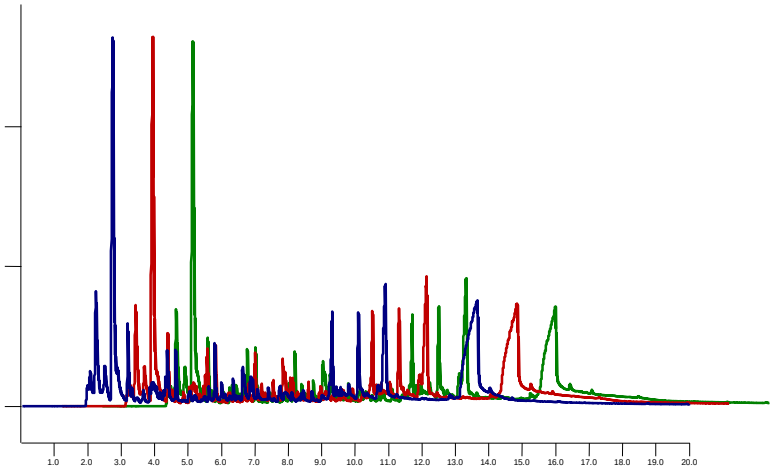

Figure 4. Pyrogram from three different probes of the Pyrola MultiMatic showing identical results.

The Pyrola pyrolyzers have the unique feature to measure the temperature-time profile (TTP) every time, see Figure 5. You can see how fast the temperature is rising (the temperature rise time, TRT), the exact pyrolysis temperature and the end temperature. Furthermore, you can also see how the sample influences the temperature and even if the pyrolysis is exothermic or endothermic. This gives you total control of the pyrolysis conditions!

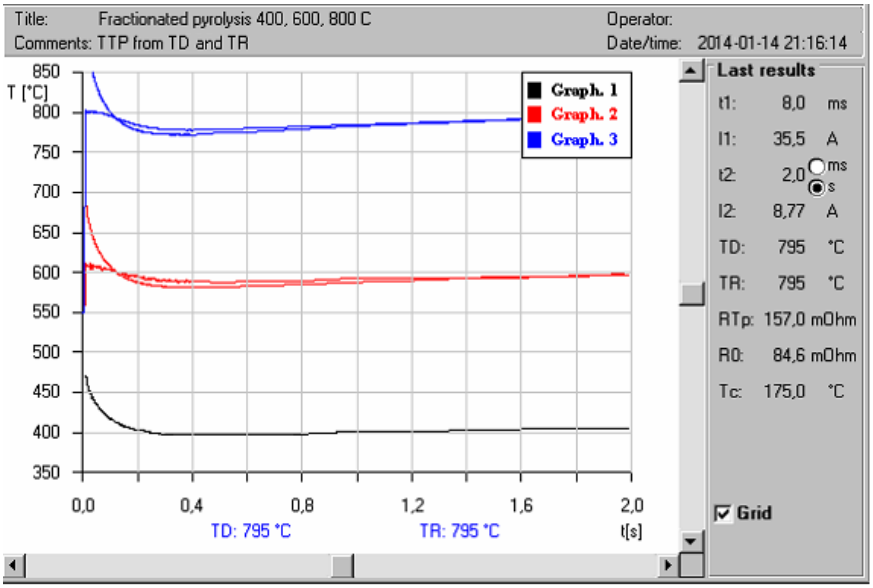

Figure 5. Output from the Pyrola 2000 program: the measured temperature-time profile (TTP) of an fractionated pyrolysis at 400, 600 and 800 °C. Two curves are shown for the higher temperatures, the temperature measured with the photodiode, and temperature measured with the photodiode, and temperature measured by the resistance of the platinum filament.

Why faster is better

The formation rates of pyrolysis products are highly dependent on temperature. Thus by increasing the pyrolysis temperature it is possible to get a total yield of a specific pyrolysis product in a shorter time, which in effect means a faster injection to the GC. This in turn means a better peak shape and peak resolution, especially for low boiling analytes, and hence no cold traps are needed for the Pyrola Pyrolyzers. For the same reason fast heating and cooling of the sample is key features of the pyrolyzer when using it as inlet device for modern capillary GC and/or GC/MS system

When the pyrolysis temperature is increased, the yield of a specific pyrolysis product might well decrease since the molecule may continue to break into smaller fragments. Thus, especially in quantitative analyses it pays off to optimize the pyrolysis temperature. An example of quantitative analysis is given in figure 6, where calibration curves of the two monomers of different co-polymers are shown.

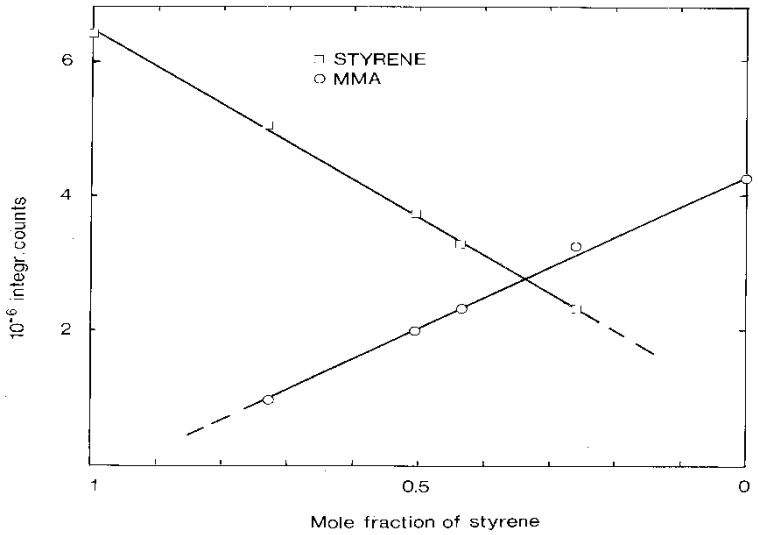

Figure 6. Example of quantitative analysis with a Pyrola pyrolyzer, showing calibration curves of the two monomers from co-polymers of PMMAS, peak area vs. mole fraction.

Straightforward analysis: Isothermal pyrolysis

The most straightforward analysis is the isothermal pyrolysis. The sample is rapidly heated to a given temperature for a given period of time, and the pyrolysis products are analysed. For many applications this is sufficient, especially if the sample is well-known for example in product control. There are however, other ways of heating the sample to get more information when dealing with more challenging problems, as will be described below.

Analyse the volatile components: Thermal desorption

Many times a sample contains both volatiles, like plasticizers, antioxidants and UV-stabilizers, and non-volatile fractions. Then it is a good idea to first heat the sample at a relatively low temperature, typically 175 °C, to evaporate the volatile fraction of the sample before pyrolysis at a higher temperature. This is called thermal desorption. The benefit is that the volatile and non-volatile constituents can be analysed separately instead of being mixed up in the same pyrogram.

Quick scan of complex samples: Fractionated pyrolysis

In fractionated pyrolysis the same piece of sample is pyrolyzed repeatedly at different temperatures, with intermediate periods at chamber temperature (typically 175 ºC). Since the formation rates of pyrolysis products are highly dependent on temperature this means that products that are formed easily at a lower temperature will dominate in the first pyrogram. These products will then have left the sample when the next pyrolysis takes place at a higher temperature, where other pyrolysis products in turn will appear in the pyrogram. The process can be repeated at several temperatures.

The benefit of fractionated pyrolysis is the same as for thermal desorption: different constituents of the sample may be analysed separately instead of being mixed up in the same pyrogram. Thus fractionated pyrolysis is especially suited for the analysis of complex unknown samples. Instead of making several isothermal pyrolyses at different temperatures in separate runs, which gives complex pyrograms, the same piece of sample is pyrolyzed repeatedly at increasing temperatures. This results in fewer pyrolysis products in each pyrogram and less secondary effects, making the result easier to interpret.

Get those formation rates: Sequential pyrolysis

Different substances in the same sample, for example in a co-polymer, may give the same pyrolysis products, and thus the same peaks in the chromatogram. Is there any way to discriminate between them, or is the situation hopeless? The answer is to look at the formation rates. Even if the resulting pyrolysis product is the same, it is likely that the formation rates are different and then the information can also be used for qualitative information.

Sequential pyrolysis is a tailor-made method to make the determination of formation rates as straight-forward and accurate as possible. The same piece of sample is pyrolyzed repeatedly to the same temperature, but for so short time that not all of the substance is degraded in one pyrolysis step. The time constant is determined by the total amount of pyrolysis products of all subsequent steps versus the total pyrolysis time. The formation rates are determined in a straight-forward way, removing the inaccuracies due to variations in sample size completely.

Slice your sample: Pyrotomy

The Pyrola pyrolyzers can heat a sample so fast and so efficiently that a sample, for example a laminate, can be pyrolyzed slice by slice; the pyrolysis equivalent of a microtome.

The method is called pyrotomy, and the sample is exposed to several extremely short thermal pulses (in order of milliseconds). Then only the part of the sample that is in direct contact with the platinum filament will be heated in each pulse, giving a separate pyrolysis for each layer of the sample. Then if the sample consists of for example a coated paper or a laminate, the pyrograms will give information of each layer separately, instead of having all of them mixed in a single pyrogram.

Dealing with polar pyrolysis products: THM

It is well known that polar substances can cause problems in GC analysis, such as tailing peaks and degradation. In many cases it requires a derivatization step prior to introducing it to the column. If polar products are formed in the pyrolysis the same applies to them.

This problem may be overcome by a method called direct alkylation: An alkylation agent is added to the sample. Polar pyrolysis products such as carboxylic acids and alcohols are then methylated by hydrolysis and heat when the sample is pyrolyzed, and thus become non-polar. The method is called thermally assisted hydrolysis and methylation (THM) and has successfully been used with Pyrola pyrolyzers in the analysis of e.g. paints.

Get in touch

To learn more about analytical pyrolysis in general, and the unique features of the Pyrola pyrolysers in particular, please get in touch:

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