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Analytical Pyrolysis:

Theory and Practice

One-day course

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Analytical Pyrolysis: Theory and Practice

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Preface

The technique, analytical pyrolysis, is not used as frequently as it ought to be. My feeling is that more knowledge is needed to start using the technique in a wider range. My intention is to teach about the theory behind analytical pyrolysis to try to explain how temperature and time will influence the result and show that pyrolysis is not difficult to use. The interpretation can also be easier if different methods, based on the heating of the samples, are used.

When I first started my research work at Lund University my project was named "Gas Chromatographic Study of the Pyrolysis of Potassium Salts of Xanthic Acids". The pyrolyzer I was offered was very simple, a Pt-coil without information of the pyrolysis temperature. I said that with this pyrolyzer I cannot make analytical pyrolysis, so I started to develop my own pyrolyzer. My intention from the start was to develop a pyrolyzer which gives reproducible results, has known conditions, fast heating and cooling times and few secondary effects. Eventually, with the new instrument I could study the influence of different pyrolysis conditions and start exploring new ways of pyrolyzing, to be able to identify unknown samples in detail. Different ways of heating have been developed like thermal desorption, sequential pyrolysis, fractionated pyrolysis and pyrotomy.

From the very beginning it was clear for me that the combination pyrolysis-gas chromatography (Py-GC) must be very useful. The differences between substances depend on the atoms in the molecule and the type of bonds between them. When breaking the bonds by heat, the type of bond must be shown by which products are formed. The problem in the 1960s was that GC was not so well developed with features like capillary columns, and small differences were difficult to observe due to bad separation. Now when GC columns, injectors and detectors are developed the ability to separate and identify products is greatly improved, most of these problems are no longer there.

Analytical pyrolysis can only be used with other techniques. Mostly gas-chromatography (GC) and mass spectrometry (MS) are used. These techniques are well known, so this course will focus on the pyrolysis.

During the last decades also the pyrolyzers have been improved and different producers are found on the market. The choice of the right pyrolyzer must depend on the kind of problems to be solved.

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Table of Contents

Chapter 1

1 Introduction

The definition of **analytical pyrolysis** in the IUPAC Recommendations of 1993[1] is: 'The characterization, in an inert atmosphere, of a material or a chemical process by a chemical degradation reaction(s) induced by thermal energy'. A more common definition is: 'Thermal degradation in an inert atmosphere'. Pyrolysis is sometimes mixed up with combustion, which means that e.g. oxygen in air is involved instead of an inert gas. Gas chromatography is used for the separation of the pyrolysis products, and mass spectrometry for the identification.

There is a rule of thumb which says that 'if the temperature is increased by ten degrees Celsius for a chemical reaction, then the reaction rate is doubled'. By experience it is found that the same is valid for thermal degradation reactions. The conclusion is that in order to get reliable and reproducible results from analytical pyrolysis the temperature time profile (TTP) of the pyrolyzer should be reproducible. By knowing the TTP also much more information can be gained about the sample that is being analyzed. The more you know about your pyrolysis conditions the easier it is to understand the pyrolysis results.

The ideal TTP, see Figure 1-1, of a sample is the combination of a short temperature rise time (TRT), a constant temperature during a known pyrolysis time, and a short cooling time. This is essential when making an isothermal pyrolysis. To get an ideal TTP of the sample, a pyrolyzer is needed which can heat the sample fast and keep the temperature constant until the sample is totally pyrolyzed or cooled quickly. The amount of sample and transfer of the heat from the pyrolyzer will determine the temperature gradient in the sample [2]. The shorter the heating time of the pyrolyzer and the smaller the sample size, the more probable the relatively volatile samples can be pyrolyzed before they are volatilized. The result from pyrolysis should only be dependant on the TTP used and the sample itself.

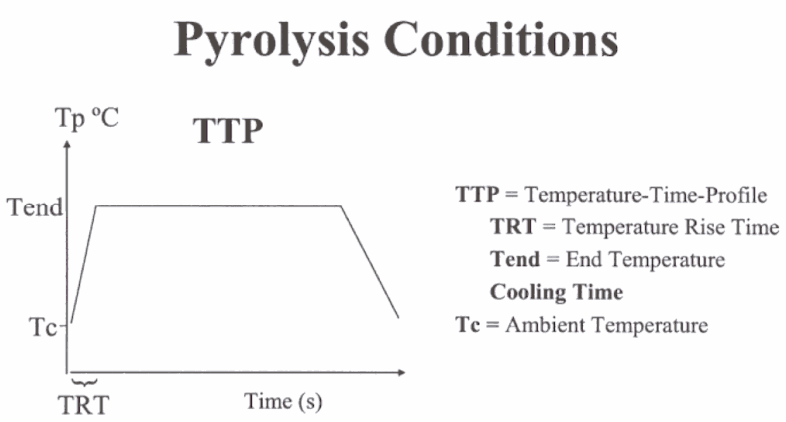

Figure 1-1. Temperature time profile

As a complement to **isothermal pyrolysis**, there are four pyrolysis methods: sequential pyrolysis, stepwise pyrolysis (fractionated pyrolysis), pyrotomy and temperature-programmed pyrolysis ("ramp"). Before each pyrolysis, **thermal desorption** can take place in the heated process unit, to take care of the volatile substances in a complex sample. In **sequential pyrolysis** the sample is heated repeatedly to the same temperature, where each pulse by itself is too short to totally pyrolyze the sample. The results can be used for determining the thermal degradation rate of the sample and the formation rates of its products. The formation rates can be used for qualitative information especially if the same product comes from different molecules in a complex sample.

In **stepwise pyrolysis** the sample is heated repeatedly, but to different temperatures and different times. The method is also called **fractionated pyrolysis**. Then it is possible to separate substances with different degradation rates. For example if a sample consists of a substance that is degraded easily at 400° C, and another substance that is degraded at 700° C. Then an initial pyrolysis at 400° C will give information of the former substance, while the subsequent pyrolysis at 700° C will give information of the latter. Thus fractionated pyrolysis is especially suited for the analysis of complex unknown samples. Fractionated pyrolysis can be preceded by thermal desorption to first evaporate volatile products at a low temperature, hereby minimizing the secondary effects at higher temperatures.

In **pyrotomy** the sample is exposed to several extremely short thermal pulses (ms), requiring a very short temperature rise time (TRT) and a fast cooling of the sample. Then only the part of the sample that is in direct contact with the heated zone will be heated in each pulse, giving a separate pyrolysis of each 'layer' of the sample. Then if the sample consists of a laminate, the pyrograms will give information of each 'layer' separately, instead of having all of them mixed in a single pyrogram. The analysis of surfaces is an area that is well suited for pyrotomy.

Temperature-programmed pyrolysis means that the sample is subjected to a controlled increasing temperature gradient. The method will not give information at what temperature the pyrolysis products are formed, and thus important information is missing. It is probably mostly used in the combination Py-MS.

In Figure 1-2 a schematic picture is shown of a Py-GC system. The result from Py-GC is called a pyrogram.

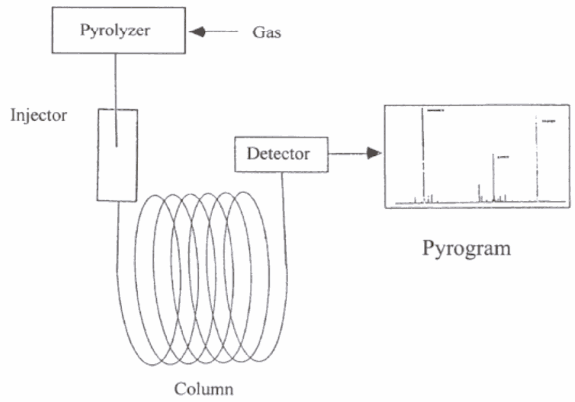

Figure 1-2. Schematic picture of a Py-GC system.

Some theory of pyrolysis is given in chapter 2, and the different ways of heating are presented in more detail in chapter 3. In chapter 4 some commercially available pyrolysis instruments are introduced, and a number of applications and techniques of analytical pyrolysis are given in chapter 5. Finally, some concluding remarks are given in chapter 6.

Chapter 2

2 Theory

An excellent motivation for studying the theory behind any method used in analytical chemistry was formulated many years ago by I.M Kolthoff and P.J. Elving in their book "Treatise on Analytical Chemistry" [13]:

> "It is important in any discussion of instrumentation and so-called instrumental methods of analysis to distinguish between instrumentation as an approach to the implementation of analytical techniques and methods, and as the manipulation of instruments. The latter is a minor result of the development of physical methods of analysis; the former is an extremely important aspect of analytical chemistry. Unfortunately, many writers on analytical chemistry, as well as many chemists in general, tend to think of instrumental analysis as being essentially the **manipulation of black boxes**.
>
> Basically, in order to be able to apply instrumentation most efficiently to his problems, **the analytical chemist must understand the fundamental relations of chemical species to their physical and chemical properties; he must know the scope, applicability, and limitations of physical property measurement in respect to qualitative and quantitative analysis**[1]. Knowing this, he can then call on the instrumentation expert to design an apparatus for the measurement-continuous or intermittent-of the desired properties with the needed precision."

The chemical process used in analytical pyrolysis is the thermal degradation of a material in an inert atmosphere. The theory behind this process is presented in this chapter.

2.1 Thermal Degradation

Thermal degradation of a sample means breaking of chemical bonds. 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 techniques can be used to find the differences, by separation and identification. However, it is important to understand that by varying the pyrolysis conditions a wealth of information may be obtained, for example by studying the formation rates of the pyrolysis products.

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[1] Emphasis added.

The thermal degradation processes of polymers are relatively straight-forward, and may serve as an example of the processes that may occur during pyrolysis.

2.1.1 Thermal Degradation of Polymers

Thermal degradation of polymers means that chain scission takes place. Three different examples of degradation types are given below.

2.1.1.1 Random Degradation

When the bonding energies are similar along the chain, random cleavage is taking place and most of the products are oligomers. In Figure 2-1 a pyrogram of polyethylene is shown as an example. Three homologues series are formed, alkadienes, alkenes and alkanes, when a high density, linear polyethylene (HDPE) is pyrolyzed. This mechanism is called random scission cleavage. When a low density, branched polyethylene (LDPE) is pyrolyzed also other products will be formed as there are different bonds along the chain, see Figure 2-2. Thus LDPE can be distinguished from HDPE.

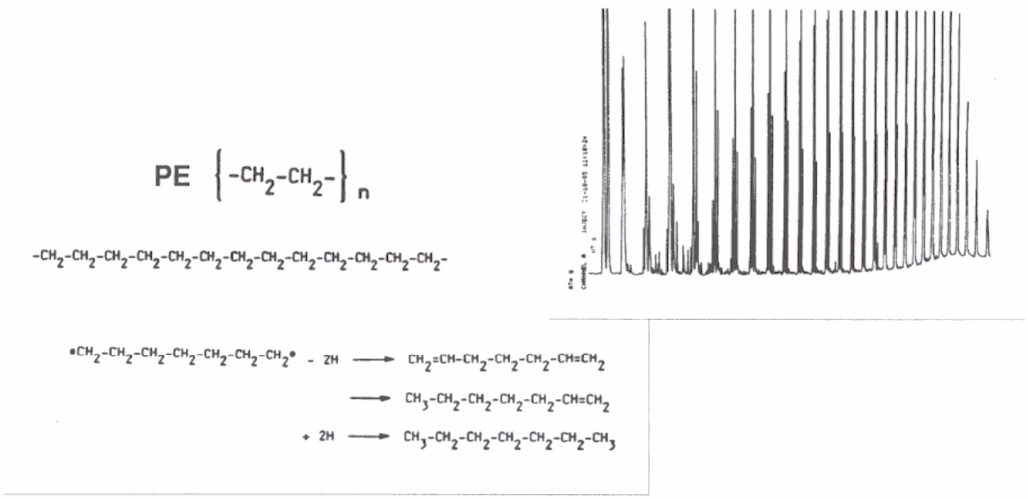


Figure 2-1. Polyethylene (HDPE) pyrolyzed at 700°C for 2s, shows an example of random degradation.

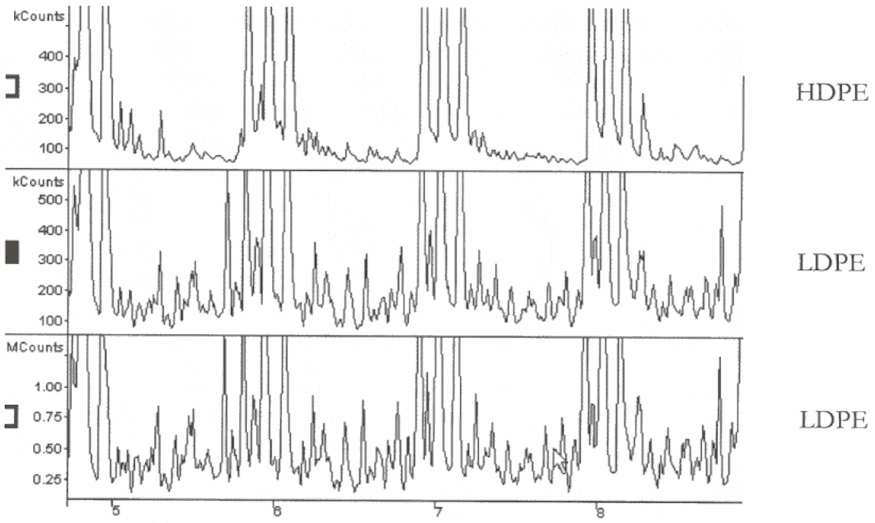


Figure 2-2. Detail from pyrograms of HDPE and a duplicate sample of LDPE. Many reproducible peaks are seen between the triplets for LDPE compared to HDPE due to the branched structure of LDPE.

2.1.1.2 Depolymerization

Another thermal degradation mechanism is depolymerization. Monomer units are released at an active chain end, see Figure 2-3. In this case butyl-lithium has been used as an initiator for polystyrene, which gives an active chain end and successive removal of the monomer, called depolymerization.

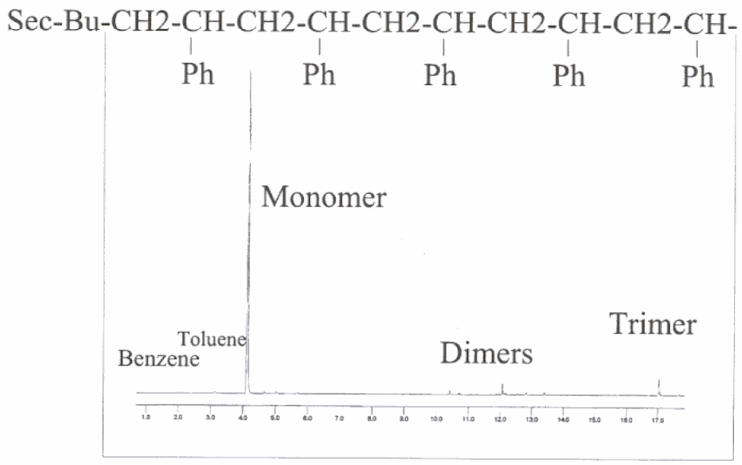


Figure 2-3. Polystyrene pyrolyzed at 700°C for 2 s, an example of depolymerization degradation.

2.1.1.3 Side Group Reactions

A typical side group reaction takes place when polyvinylchloride (PVC) is pyrolyzed. The Cl-H bond is weak and the exited Cl-atom combines with one hydrogen atom from -

CH2- and form HCl. The next step is that the residue of the chain continue with chain scission and form benzene, see Figure 2-4.

The big peak from plasticizer is not a pyrolysis product but formed from thermal desorption.

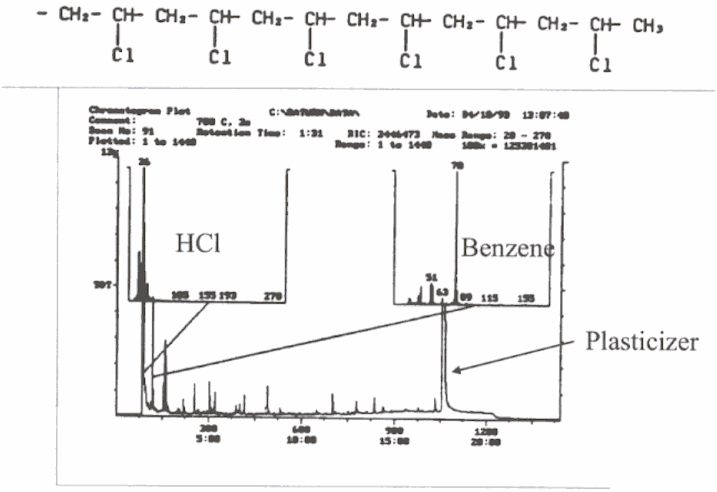


Figure 2-4. Pyrogram from PVC, an example of side group degradation.

2.2 *Influence of Temperature and Time*

The pyrolysis conditions can be described by the temperature time profile (TTP) of the pyrolyzer, shown schematically in Figure 2-5. Ideally the pyrolysis is characterized by a heating period, a period at a constant pyrolysis temperature, and a period of cooling. How the different periods will influence the pyrolysis result is discussed below.

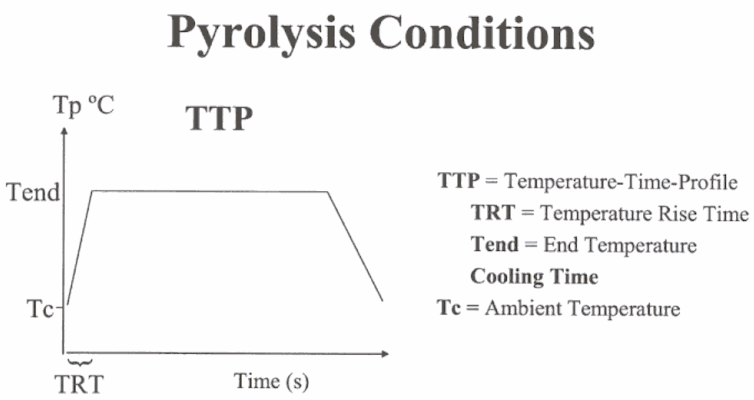


Figure 2-5. Schematic of a temperature time profile (TTP).

- **TRT**: The time to reach the final temperature is called the temperature rise time (TRT). A short temperature rise time is advantageous since relatively low boiling substances will be pyrolyzed instead of being volatized and trapped in the system.

A short TRT also means that the temperature when the pyrolysis products are formed is well defined. This is important in order to study formation rates, which will be discussed in chapter 2.3. A TRT is regarded as short if it does not influence the result in a negative way. The TRT of the pyrolyzer used can be studied by a polymer with known formation rate and constant amount of pyrolysis products depending on the maximum pyrolysis temperature [3]. There are pyrolyzers with a TRT of less than 10 ms to 1400 °C.

- Pyrolysis temperature **Tend**: The formation of pyrolysis products is very dependent of the pyrolysis temperature, yet it is not uncommon that is chosen by chance. In chapter 5.2 a more systematic way of choosing the pyrolysis temperature(s) will be discussed.
- **Cooling time**: A fast cooling time is important in order to have a well-defined pyrolysis temperature and time when the pyrolysis products are formed.
- **Tc**: The ambient temperature influence which products that will be transported to the GC. The products may be volatile substances in the sample or pyrolysis products. The lower the temperature the more non-volatile pyrolysis products will be trapped in the pyrolyzer without reaching the GC.

The temperature time profiles that can be obtained in practice are very dependent on the pyrolyzer used, since the different heating techniques will influence how fast a sample may be heated and cooled.

2.3 Calculation of Formation Rates

Thermal degradation reactions are 1st order reactions. An example is given in Figure 2-6, where sample A is degraded and forms a product B.

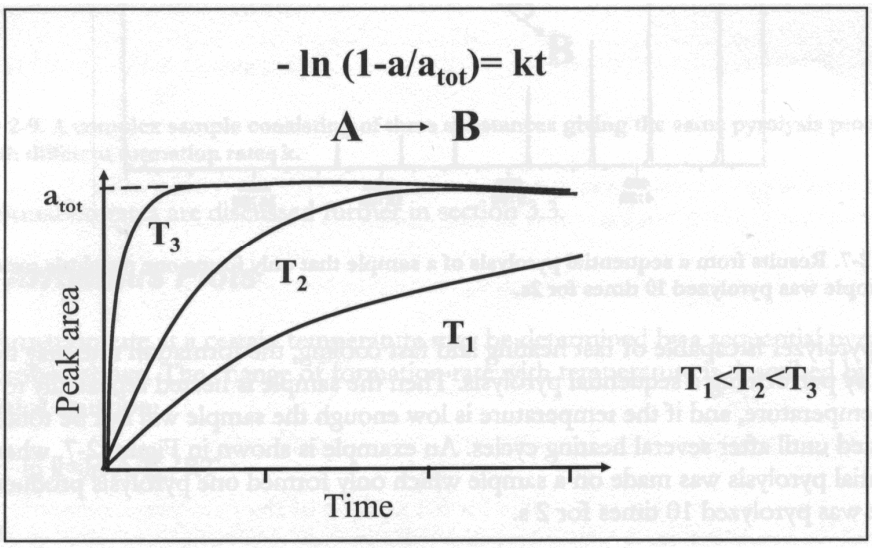


Figure 2-6. Formation of pyrolysis product B at three different temperatures.

The higher the pyrolysis temperature the faster the substance A will be totally pyrolyzed, and thus the formation rate is increased with temperature, following the Arrhenius equation, further discussed in chapter 2.4. If the degradation mechanism does not change during time, the total area (a_{tot}) of the pyrolysis product B will be constant. The pyrolysis

time, for the degradation of the total sample, can be decreased if the pyrolysis temperature increases. This can be favorable for the separation of the most volatile pyrolysis products.

A high pyrolysis temperature can cause secondary effects of the primary products. These are difficult to follow and tend to be less reproducible. If the formation rate constant, k, is known at the pyrolysis temperature, it is possible to calculate the time needed to totally degrade a substance.

Example: If you want to pyrolyze a sample to 95 % and you have a formation rate $k=1\ s^{-1}$ at the given pyrolysis temperature then

$$-\ln(1-a/atot)= kt \rightarrow -\ln(1-0.95/1)= 1t \rightarrow t= -\ln(1-0.95/1)/1 = 3\ s$$

I.e. the sample will be pyrolyzed to 95% in three seconds at the given pyrolysis temperature.

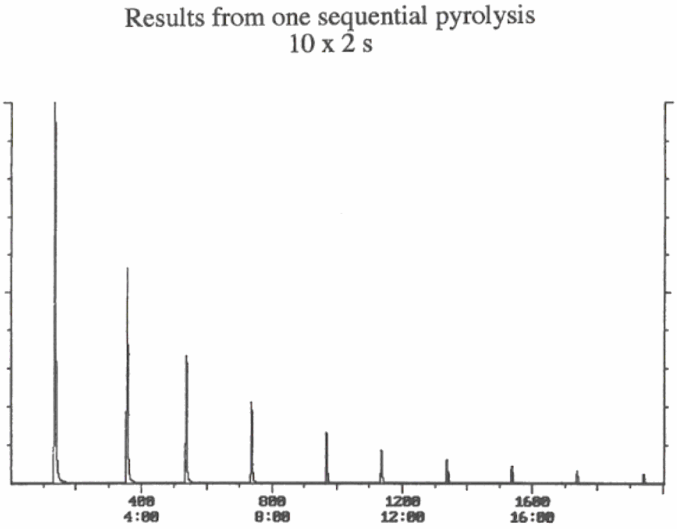


Figure 2-7. Results from a sequential pyrolysis of a sample that only forms one pyrolysis product. The sample was pyrolyzed 10 times for 2s.

If the pyrolyzer is capable of fast heating and fast cooling, the formation rate may be found by performing a sequential pyrolysis. Then the sample is heated repeatedly to the same temperature, and if the temperature is low enough the sample will not be totally pyrolyzed until after several heating cycles. An example is shown in Figure 2-7, where a sequential pyrolysis was made on a sample which only formed one pyrolysis product. The sample was pyrolyzed 10 times for 2 s.

From the result of a sequential pyrolysis a 1st order plot can be made and the formation rate of the product is determined by the slope of the plot, see Figure 2-8.

a = the cumulative sum of B at time t
a_{tot} = the total sum of B when A is totally pyrolyzed
t = cumulative pyrolysis time [s]

k = the formation rate of B at the pyrolysis temperature used [s^{-1}]

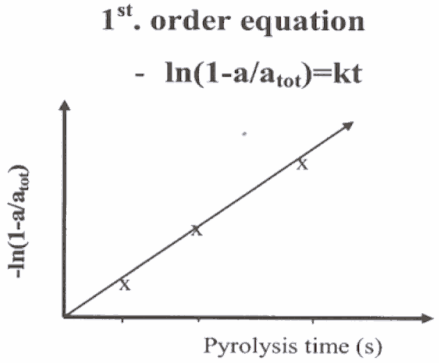


Figure 2-8. A first order plot. The formation rate can be determined from the slope of the line.

An example where the formation rate can provide additional information of a complex sample is when the same pyrolysis product B is formed from several different substances in the sample, see Figure 2-9. Then by determining the formation rate more information may be obtained of where the pyrolysis product is coming from.

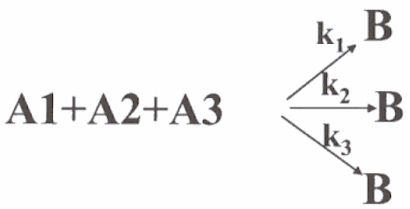


Figure 2-9. A complex sample consisting of three substances giving the same pyrolysis product, but with different formation rates k.

The formation rates are discussed further in section 3.3.

2.4 Arrhenius Plots

The formation rate at a certain temperature may be determined by a sequential pyrolysis as described above. The change of formation rate with temperature is described by the Arrhenius equation:

$$\ln k = \ln A - E_a/RT$$

where:

k = Formation rate [s^{-1}]
A = Frequency factor [s^{-1}]
E_a = Activation energy [J mol^{-1}]
R = Gas constant 8.314 J mol^{-1} K^{-1}
T = Temperature [K]

If substances are sequentially pyrolyzed at different temperatures, then the natural logarithm of the formation rates (ln k) can be plotted against 1000/T (T in Kelvin). Examples of Arrhenius plots are shown in Figure 2-10.

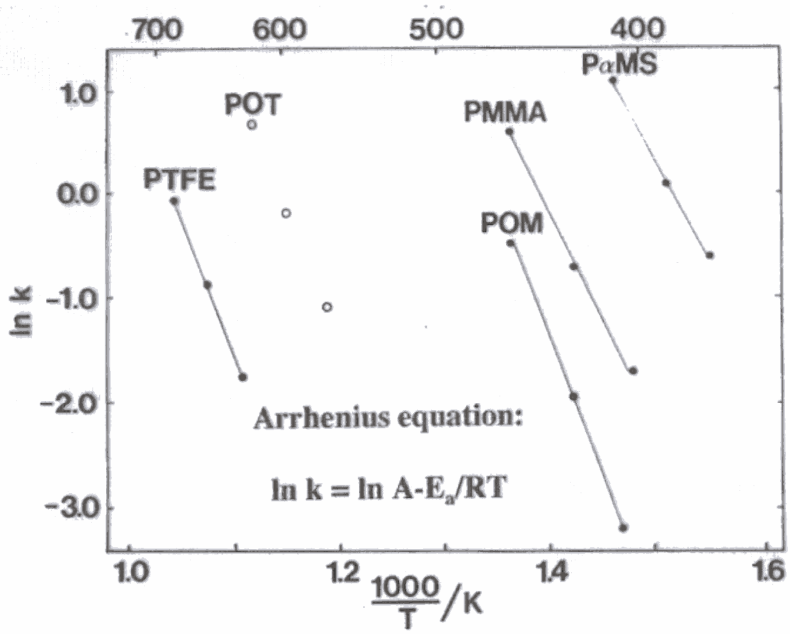


Figure 2-10. Arrhenius plot of a number of polymers.

PαMS=	Poly(α-methylstyrene)	PMMA=	Poly(methyl metacrylate)
POM=	Polyoxymetylene	POT=	Poly(3-octylthiophene)
PTFE=	Polytetrafluoroethylene	R=	Gas constant 8.314 J mol^{-1} K^{-1}
ln A=	Frequency factor [s^{-1}]	E_a=	Activation energy [J mol^{-1}]

The Arrhenius plot explains why it may be useful to perform a fractionated pyrolysis of a complex sample, where the sample is heated repeatedly to different pyrolysis temperatures. Then it is possible to separate substances with different degradation rates. The different ways of heating are discussed further in section 3.4.

Another use of the Arrhenius plot is to find which temperatures that must be used to totally pyrolyze different substances if the pyrolysis time is kept constant [4].

2.5 Determining the Temperature Time Profile

To get as much information as possible for the analysis of the pyrolysis results it is very important to know and be able to reproduce the pyrolysis conditions, i.e. the temperature-time profile (TTP) of the pyrolyzed sample. Note that the TTP of the sample may differ from the TTP of the pyrolyzer itself.

The TTP can be measured with a photo diode [5] but the TTP can also be found by sequential pyrolysis of a sample with known formation rate. In [3] cis-1.4-polybutadiene was used, and the degradation of the sample was found to be different from normal

thermal degradation. The total amount of pyrolysis products is proportional to the maximum temperature, see Figure 2-11. Normally the total amount of products are constant as long as the pyrolysis time is long enough (Figure 2-6) and no secondary effects give carbon, which can happen at high temperatures. However for this substance the ratio between the monomer and the dimer is also proportional to the temperature, see Figure 2-12. The TRT can be studied by using different times for the sequential pyrolysis, and Tend by the total amount of pyrolysis products, see Figure 2-12.

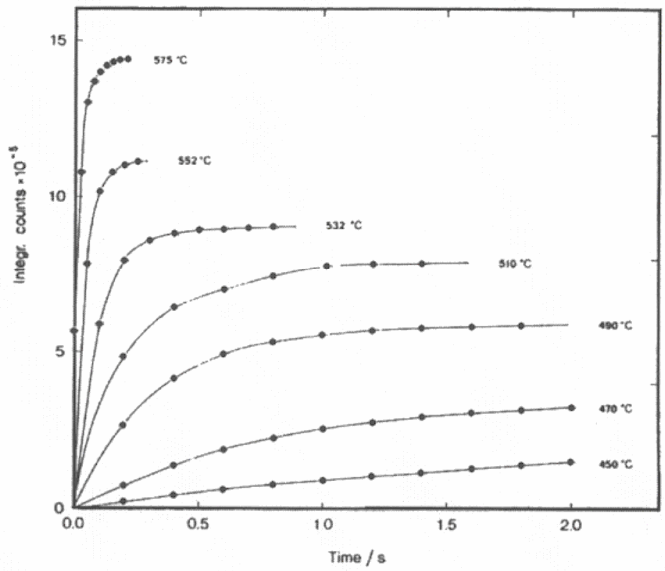


Figure 2-11. cis-1.4-polybutadiene sequentially pyrolyzed at different temperatures. The peak areas from the monomer are plotted against time

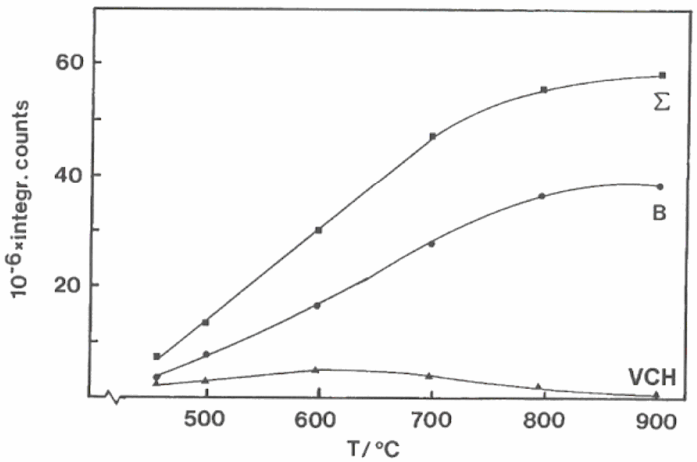


Figure 2-12. cis-1.4-Polybutadiene pyrolyzed at different temperatures. The total yield of all pyrolysis products (∑) as well as the fractional yield of butadiene (B) and of the dimer, vinylcyclohexene (VCH) are plotted against the pyrolysis temperature.

Chapter 3

3 Different ways of heating

In earlier days an isothermal pyrolysis temperature of 770 °C was often used for Curie point pyrolyzers. The reason was that a sample rod made of 100% iron gave this Curie temperature 770 °C when inductively heated. Today a normal isothermal pyrolysis temperature is 500 -700°C.

The pyrolysis result should only be dependant on the temperature-time gradient in the sample and the sample itself. The choice of TTP is dependant on the sample and what information is expected. Most temperatures can give some degradation products but do they tell you the whole story about e.g. complex samples?

Five different ways of heating a sample will be explained. The contribution from each will be discussed and exemplified.

3.1 Thermal Desorption

Thermal desorption means that heat can volatilize substances that are added to a non-volatile sample. In paper and polymers volatile additives are found like sizing agent, plasticizer, antioxidants and monomers.

An example is given when analyzing alkyl ketene dimers (AKD) as sizing agent in paper. The AKD is used to restrain ink absorption in the pores of the paper and thereby increase the printing quality. Some of the AKD is slowly hydrolyzed forming keto acids, which looses CO2 giving free ketones. It is also proposed that AKD can react with cellulose and form β-keto esters, see Figure 3-1.

It is of great interest to quantify the two forms of AKD in the prepared paper, in order to study the aging and optimize the sizing effects.

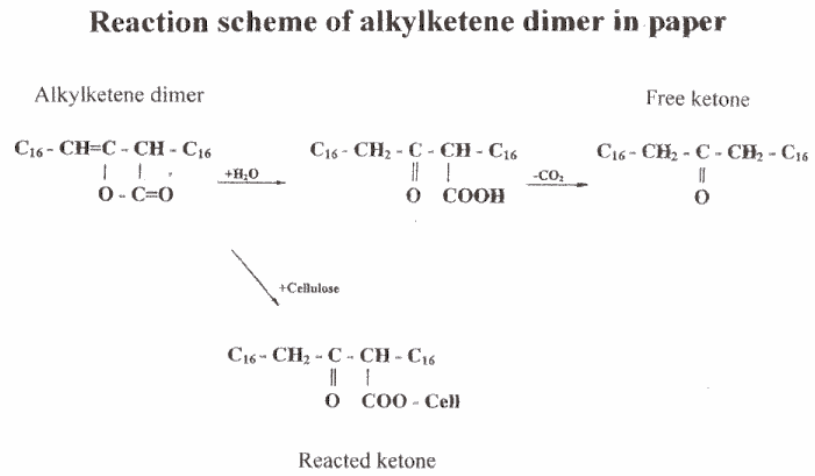


Figure 3-1. Chemical reactions of AKD in paper.

One way of trying to quantify both the free ketones and the reacted ketones was made by thermal desorption at a low temperature, 225 °C, for the free ketones and after that pyrolyzing the residue at 600 °C for quantifying the reacted AKD, which needed more energy, see Figure 3-2. It was possible to make quantitative analyses.

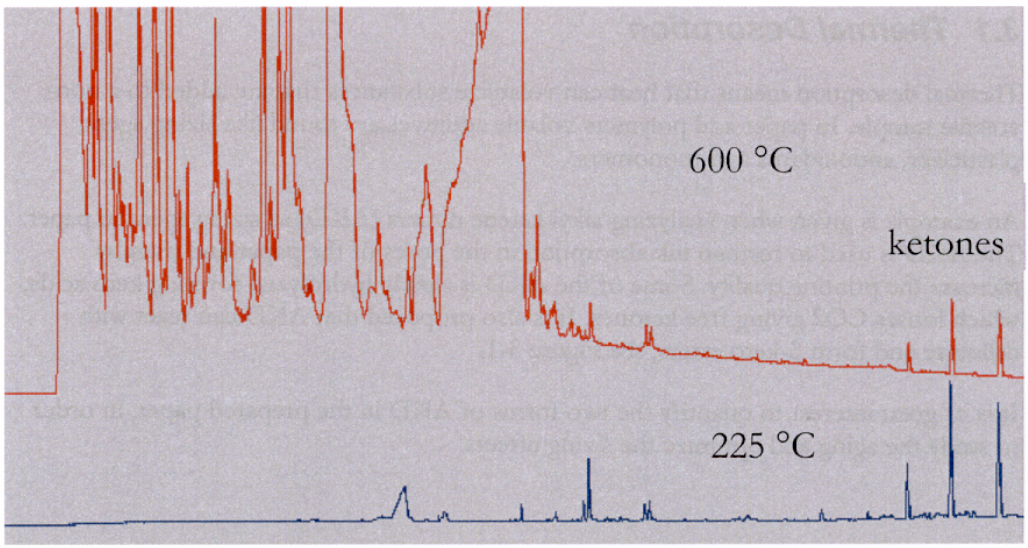


Figure 3-2. A paper sample was first heated to 225 °C (lower curve) and then the residue pyrolyzed at 600°C (upper curve).

Lately AKD oligomers were also found by extracting the paper prior to the Py-GC/MS analysis, see [6].

3.2 Isothermal Pyrolysis

Isothermal pyrolysis is defined as: "A pyrolysis during which the temperature is essentially constant". The result from an isothermal pyrolysis will only give the total amount of pyrolysis products if a high enough temperature is used. Some of the

substances in the sample with low formation rates might not be degraded at the chosen conditions, or secondary effects can be formed from those products which are exposed to higher temperatures. However, the following ways of heating will show how much more information can be obtained when heating the same sample a number of times or to different temperatures.

3.3 Sequential Pyrolysis

Sequential pyrolysis [7] is defined as: "A pyrolysis in which the same initial sample is repetitively pyrolyzed under identical conditions (final pyrolysis temperature, temperature rise time and total heating time)". An example of sequential pyrolysis is shown in Figure 3-3.

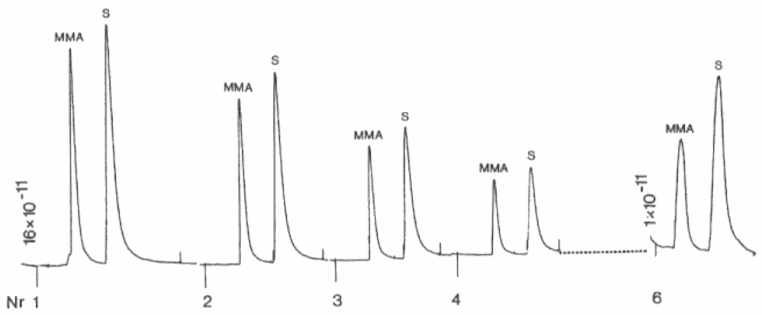


Figure 3-3. Result from a sequential pyrolysis of a co-polymer PMMAS 1:1.

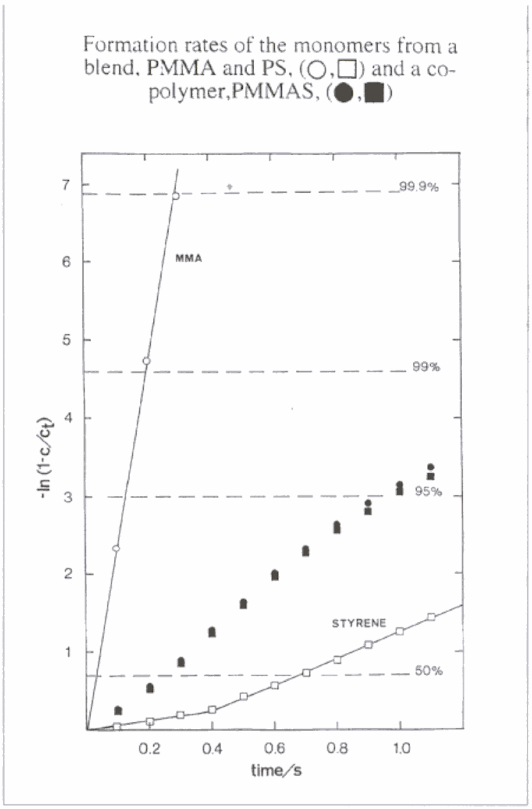
Four pyrolyses for 200 ms and at the end one pyrolysis for 2 s were used. The 2 s pyrolysis was used to be sure that the whole sample had been pyrolyzed. From a sequential pyrolysis all information needed for making a 1st order plot is there:

- a = the cumulative sum of the product at each cumulative pyrolysis time
- a_{tot} = the total sum of the product when no more of the studied product is formed,
- t = cumulative pyrolysis time (s)

to be able to calculate the formation rate k from the slope of the plot.

1st order equation:

$$-\ln(1-a/a_{tot}) = kt$$



1st order equation
$- \ln (1-a/a_{tot}) = kt$

Figure 3-4. First order plots from two homopolymers and one co-polymer.

The result from Figure 3-4 show that the homopolymer, polymethyl metacrylate (PMMA) has the fastest formation= degradation rate. The plot from polystyrene (PS) is not linear. It is not an experimental error but indicates that two different mechanisms are taking place. When the copolymer is pyrolyzed sequentially and the two monomers are plotted the result shows that the formation rates are equal and different from the two homopolymers. In a study of different mole ratios of the monomers, the formation rates were proportional to the mole ratios. Some deviations were found for the homopolymers.

It is obvious that much information can be obtained by understanding the formation rate from different samples.

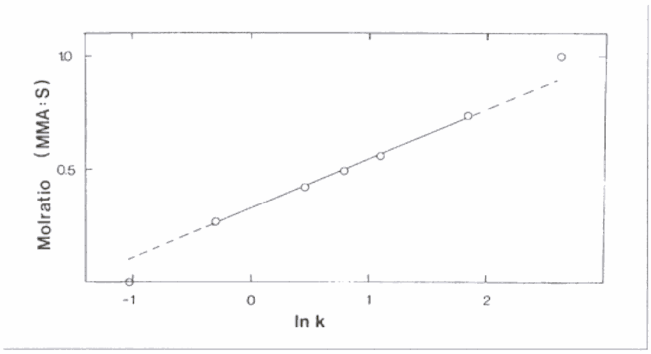


Figure 3-5. Difference of formation rates, k, depending on mole ratio of a co-polymer PMMAS.

3.4 Fractionated Pyrolysis

Fractionated pyrolysis is defined as: "A pyrolysis in which the sample is pyrolyzed at different temperatures for the same or different times in order to study special fractions of the sample" [4]. Examples are shown in Figure 3-6, Figure 3-7 and Figure 3-8.

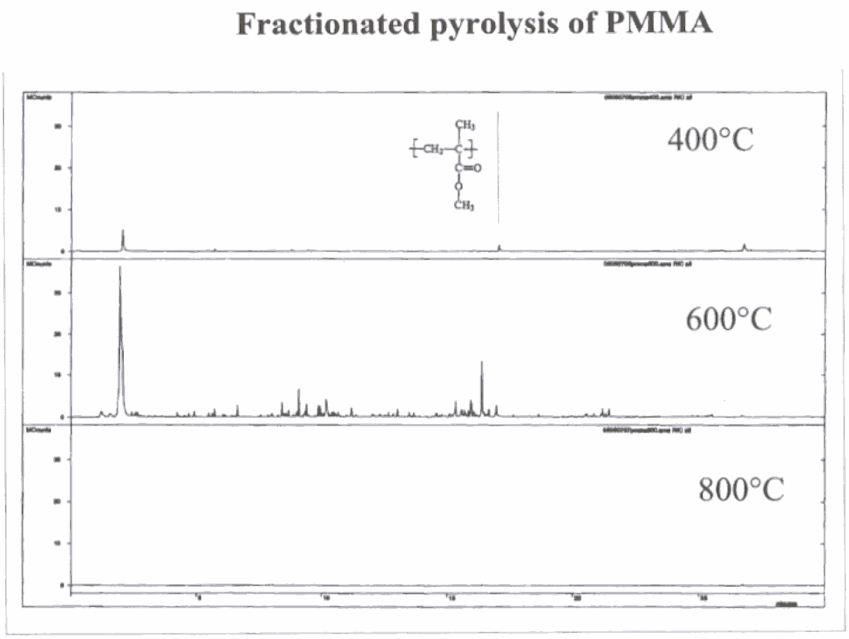


Figure 3-6. Fractionated pyrolysis of poly(methyl metacrylate).

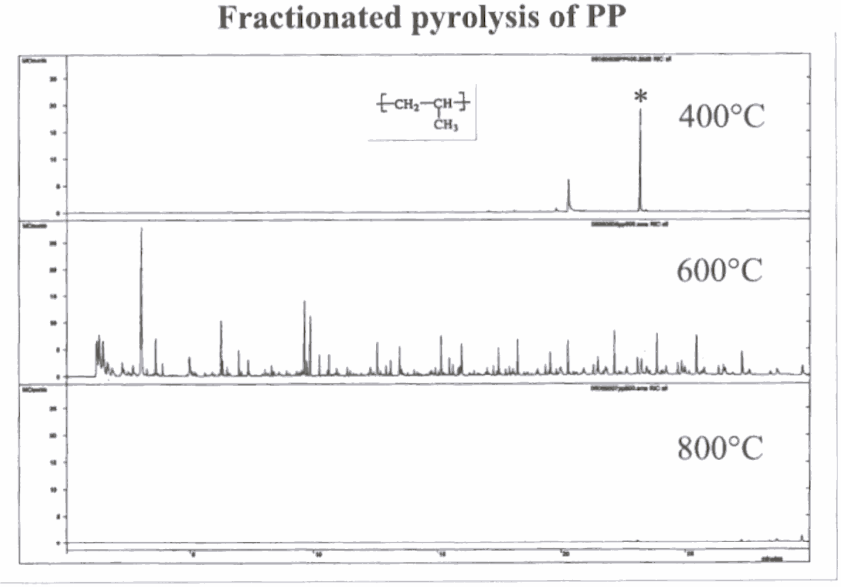


Figure 3-7. Fractionated pyrolysis of polypropylene.

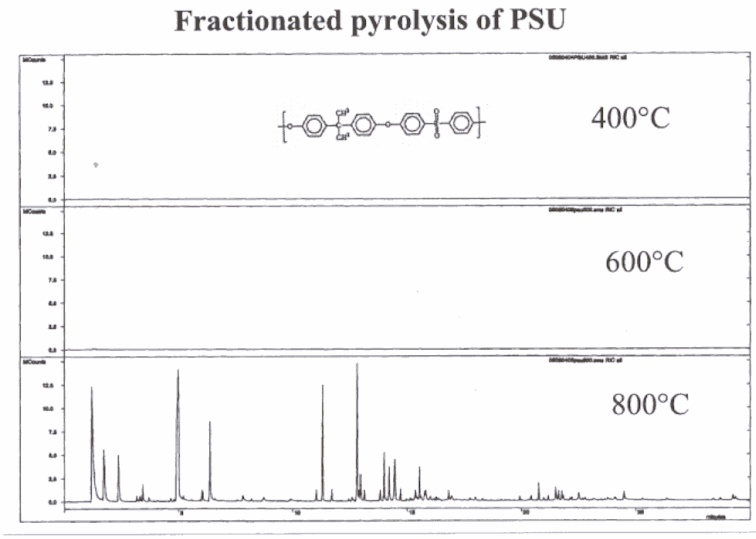


Figure 3-8. Fractionated pyrolysis of Polysulfone.

From these three fractionated synthetic polymers it is obvious that if a too low temperature is used some samples will not be degraded unless a very long time is used, but then there are problems with the injection to the GC.

It is good strategy to use a fractionated pyrolysis when an unknown sample is analyzed for the first time, starting at a low temperature to find volatile additives, and ending at a relatively high temperature.

A **vulcanized rubber** was pyrolyzed with fractional pyrolysis, see Figure 3-9. In this sample different additives were found when heating the sample to 200 °C. Afterwards the sample was pyrolyzed to 400 °C, where some hexamethylene diisocyanate (HMDI) appeared in the pyrogram. At 500 °C styrene was formed and some more HMDI and trace from bisphenol-A. Most products were formed at 600°C. The time was not long enough to totally form bisphenol-A. Some was formed at 800 °C and evidently secondary products, phenols, were formed at that high temperature. A longer pyrolysis time at 600 °C should have formed more bisphenol-A, and would have decreased secondary effects.

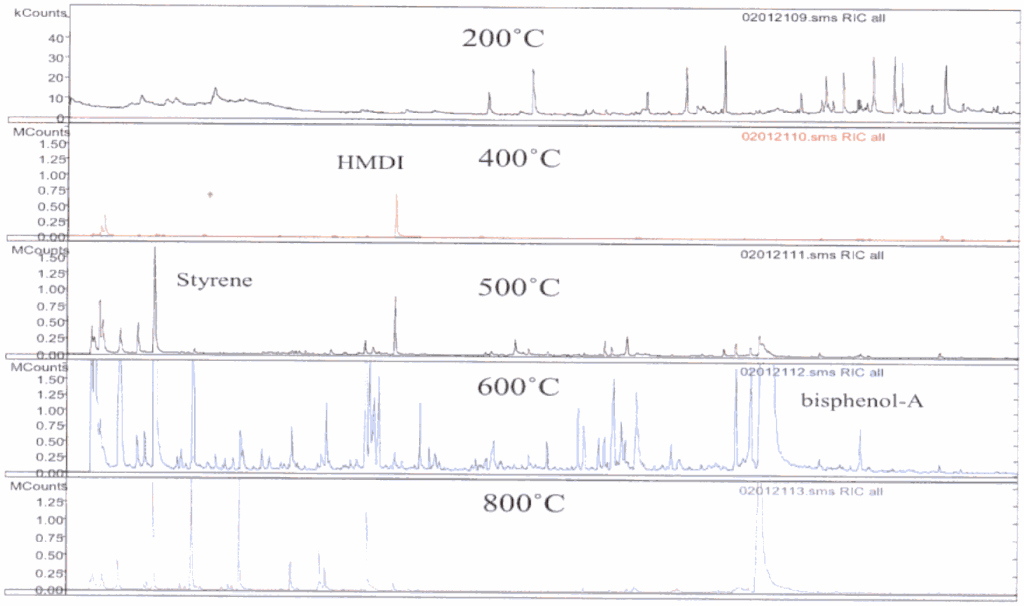


Figure 3-9. Fractionated pyrolysis is used for analyzing the substances in a vulcanized rubber.

3.5 Pyrotomy

Pyrotomy is defined as: "Heating a sample at a relatively high temperature for a short time (ms)". The layer of the sample close to the heated zone will be pyrolyzed. If the pyrolysis is repeated a number of times the next "layer" will be pyrolyzed etc [8]. Pyrotomy can be used when studying the surface of the sample as only the outer part of the sample will be pyrolyzed and not the whole sample. It is also useful when studying a laminate, see Figure 3-10.

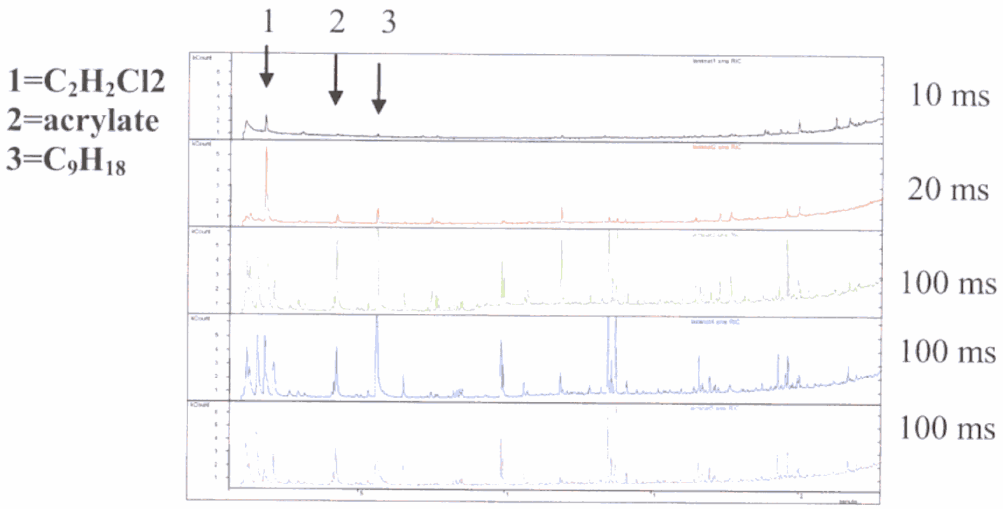


Figure 3-10. A laminate has been pyrolyzed at different pyrolysis times.

The result shows that the first layer consists of poly(vinylidene chloride) (1) characterized by the monomer. The second layer is very thick and contains polypropylene characterized by the trimer C_9H_{18} of propylene (3). The acrylate peak (2) increases and later on decrease. This product comes from the adhesive.

Another laminate was heated, see Figure 3-11. The result showed that polyethlene terephtalate PET was present. The next three pyrolyses for 50 ms of the sample showed some polyethylene (PE). The temperature and time were not high and long enough to degrade PE fully. When two seconds were used the rest of the laminate was pyrolyzed and showed a thick layer of PE.

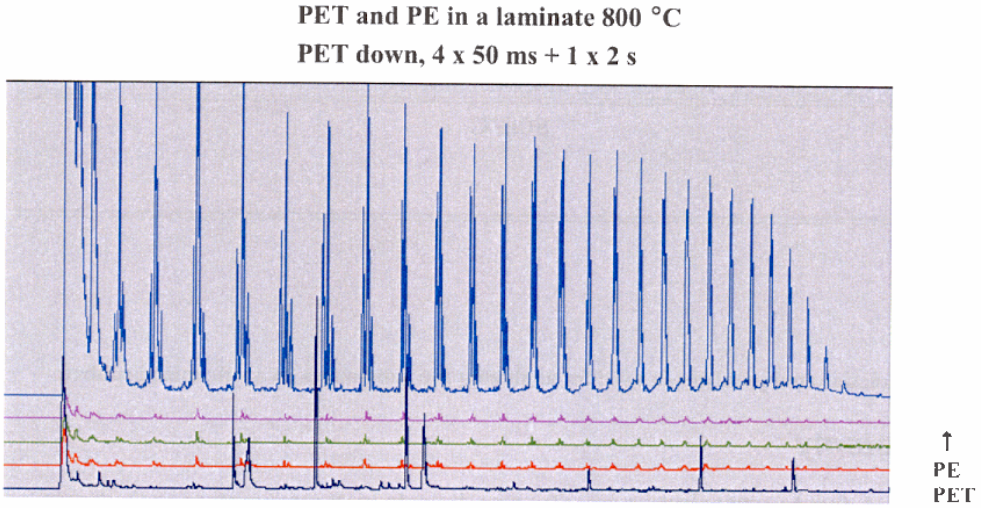


Figure 3-11. A laminate was pyrolyzed four times for 50 ms and the fifth for two seconds.

3.6 Temperature-programmed Pyrolysis (Ramp)

Temperature- programmed pyrolysis (Ramp) is defined as: "A pyrolysis during which the sample is heated at a controlled rate within a temperature range in which pyrolysis occurs".

There are problems to find practical use for this way of heating the sample. The combination of temperature and the formation of pyrolysis products are difficult unless only Py-MS is used.

Chapter 4

4 Instrumentation

There are two different types of pyrolyzers which are characterized by the way of heating the sample:

- Continuous mode pyrolyzer
  - Furnace
- Pulse mode pyrolyzer
  - Curie point pyrolyzer
  - Coil pyrolyzer (tube)
  - Filament pyrolyzer

A continuous mode pyrolyzer means that a sample is introduced into a preheated zone while the pulse mode pyrolyzer is heated after the sample has been introduced.

Four different pyrolyzers from different manufacturers are briefly presented.

4.1 Continuous Mode Pyrolyzer

4.1.1 Micro-Furnace Pyrolyzers from FRONTIER LAB, Japan

The idea of heating is that the sample in a holder is dropped into a heated micro furnace. The pyrolyzers from FRONTIER LAB are presented, see figures.

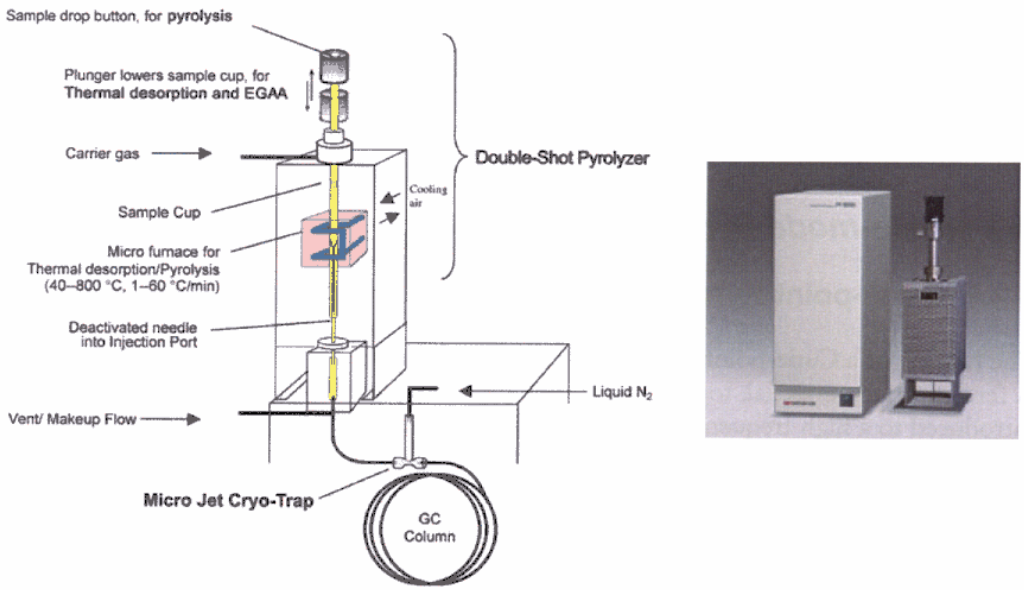


Figure 4-1. Schematic picture and photograph of double shot pyrolyzer PY 2020 iD.

The Double- Shot Pyrolyzer is found as manual pyrolyzer, Figure 4-1, and as the automated Auto-Shot pyrolyzer, Figure 4-2.

The term double-shot means that the analyzed sample can be heated at two different temperatures for thermal desorption in combination with pyrolysis.

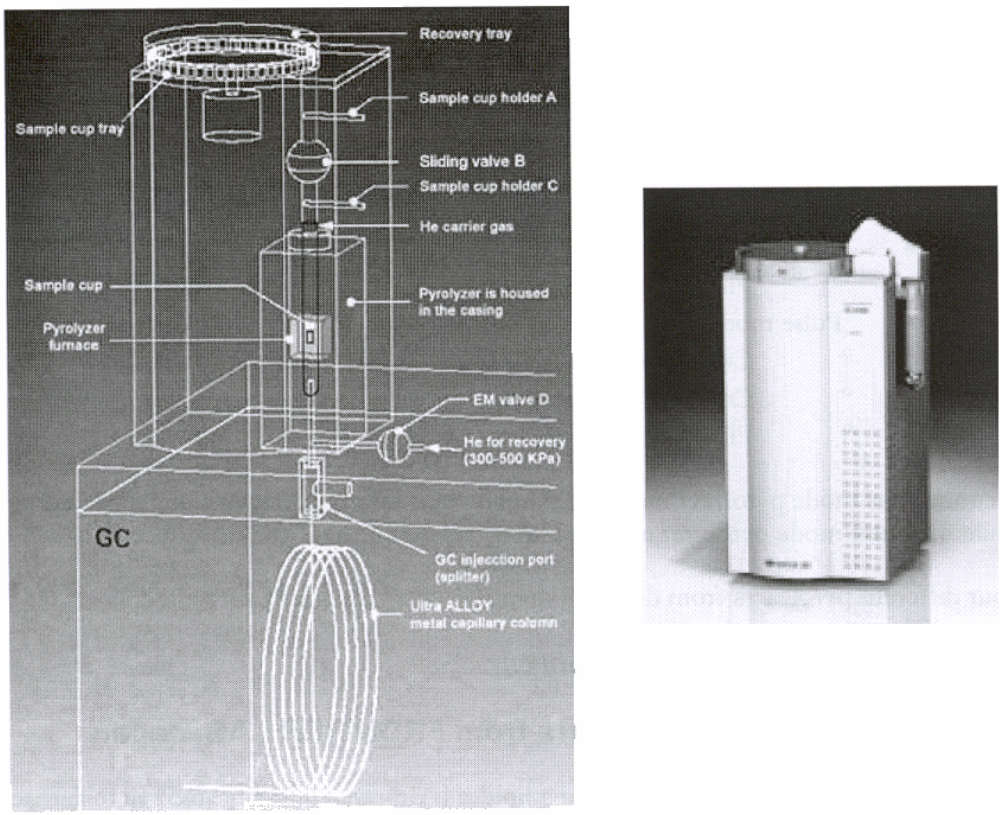


Figure 4-2. Schematic picture and photograph of the automated Auto-Shot Sampler AS-1020E pyrolyzer.

The automated pyrolyzer can handle 48 samples with pyrolysis temperatures up to 800°C. The sample is placed in a stainless steel cup and introduced by free-fall into the furnace. After the pyrolysis, the sample cup is blown up by the pressurized carrier gas and further to a receiver.

4.2 Pulse-mode Pyrolyzers

4.2.1 Curie-point Pyrolyzer from GSG, Germany

The heating of a Curie-point pyrolyzer is different from the other pulse mode pyrolyzers. A ferromagnetic material, together with the sample, is heated inductively when introduced to a high frequency electromagnetic field. The ferromagnetic material is heated until the Curie-point is reached and the material changes from being ferromagnetic to being paramagnetic, see Figure 4-3. To reach other temperatures, it is necessary to change the material of the sample holder. Different compositions of ferromagnetic alloys can give temperatures from 160 °C to 1128 °C. Examples of different compositions are shown in the table below.

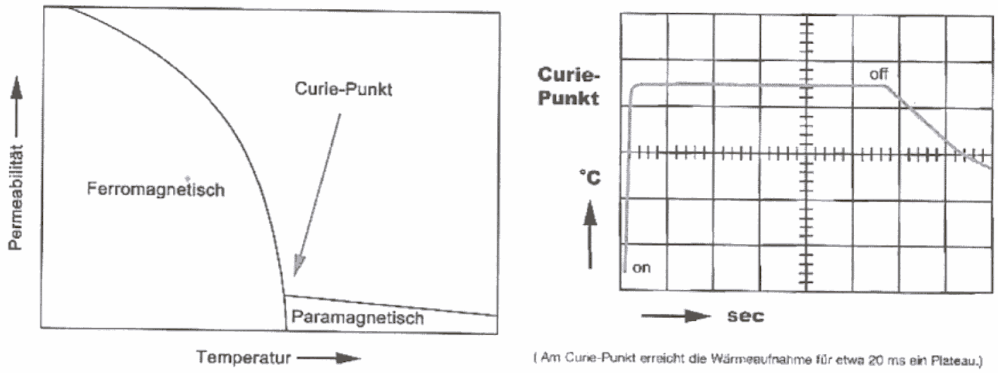


Figure 4-3. The transformation from ferromagnetic to paramagnetic at the Curie-point is shown to the left. A schematic temperature time profile is shown to the right (not recorded by the Pyrolyzer).

The TTP is dependant of the geometry of the sample holder, the high frequency field and other physical parameters of the sample holder.

Temperature	Composition [%]		
°C	Fe	Ni	Co
360	0	100	0
480	52	48	0
700	33	33	33
770	100	0	0
980	0	60	40
1130	0	0	100

Eighteen different ferromagnetic materials (160 -1040°C) are available for the Pyromat.

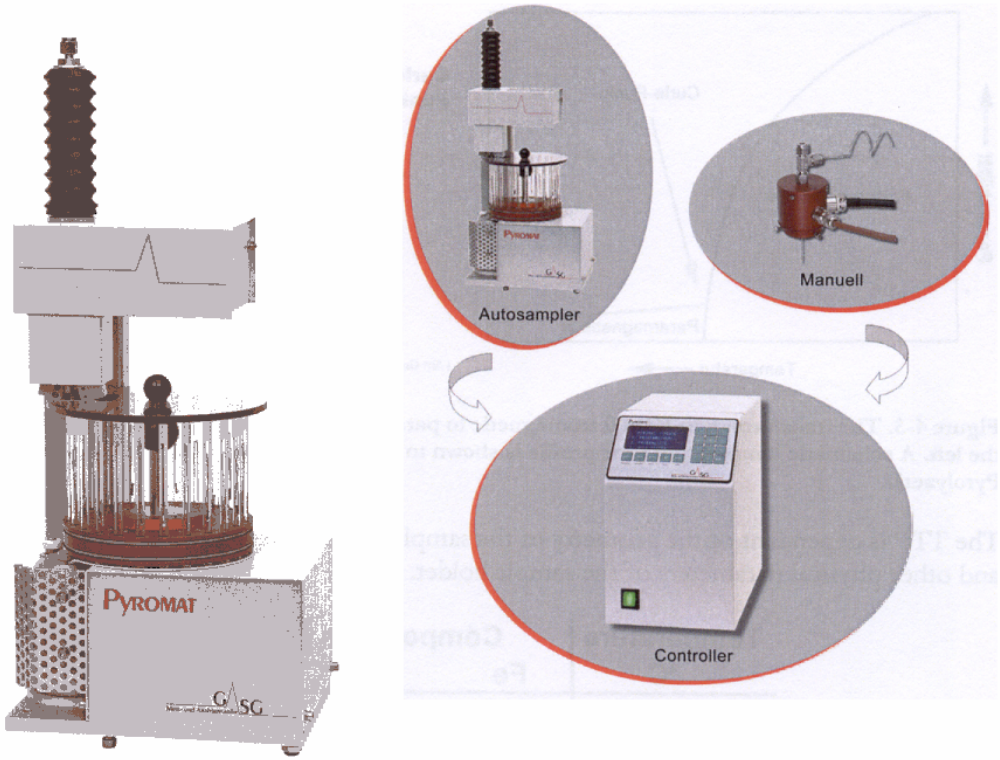


Figure 4-4. The manual and automated pyrolyzers together with the control unit.

The automated Pyromat can handle 24 samples. Each sample is placed in a ferromagnetic tube, wire or cup, which is hold in place by a metal string and placed in a glass tube. The whole glass tube is automatically placed into the magnetic field. The pyrolysis temperature is dependant on the material of the sample holder.

4.2.2 Coil and Filament Pyrolyzers from CDS Analytica, USA

A schematic picture of a CDS pyrolyzer is shown in Figure 4-5. The sample is placed either on a Pt-filament and resistively heated or placed in a quarts tube which is heated by a coil resistively heated, see Figure 4-6.

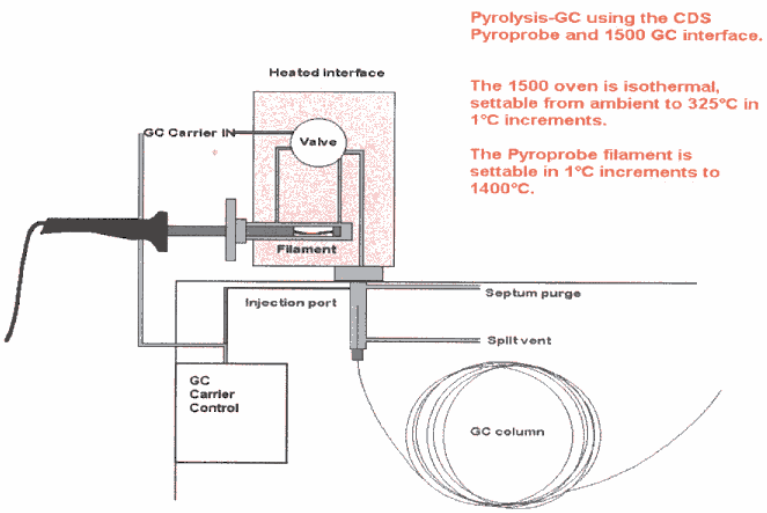


Figure 4-5. The standard manual interface with either a Pt-filament or coil.

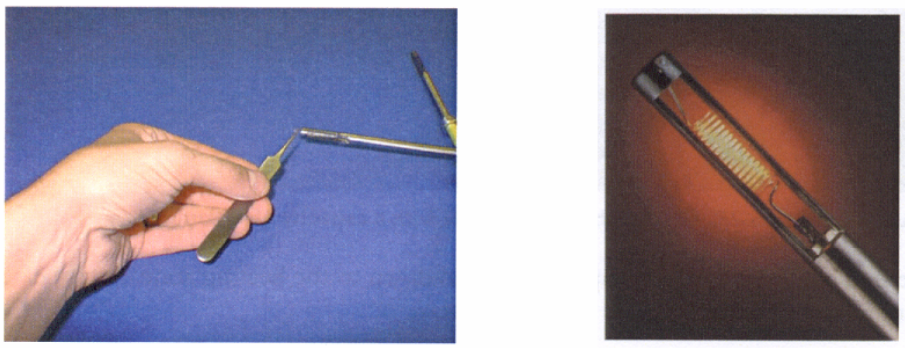


Figure 4-6. A sample is placed in a tube, which then is placed in the coil which is resistively heated.

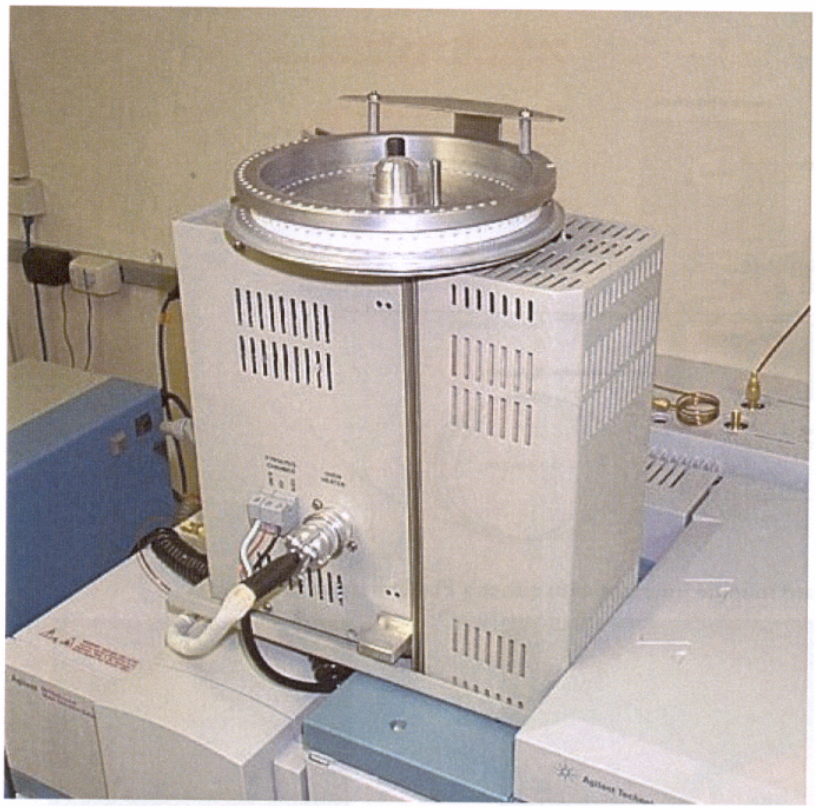


Figure 4-7. The AS-2500 Pyroprobe Autosampler with a capacity of 45 samples.

The thin quarts tube with sample is dropped down to the heating zone. After heating, the spent tube is released out into a collection tray.

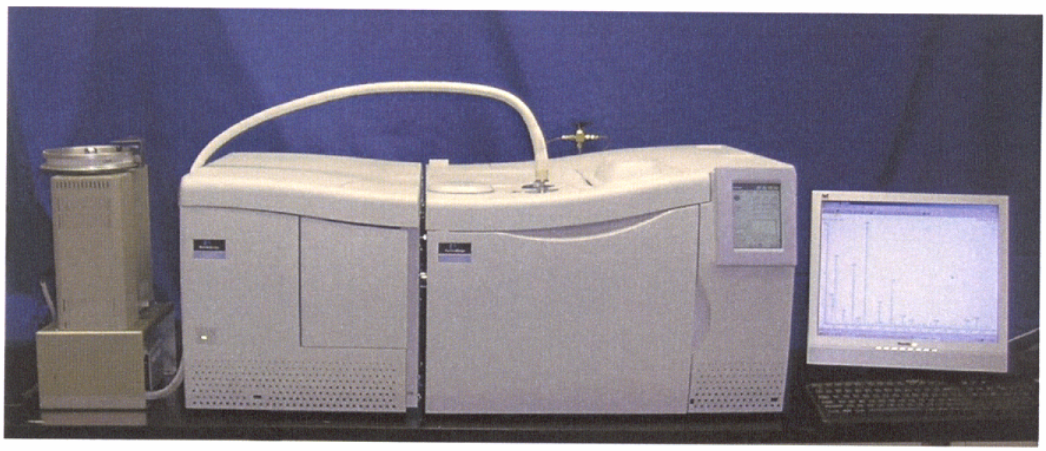


Figure 4-8. The autosampler next to a Claurus GC, using a transfer line to the GC-injector.

4.2.3 Filament Pulse Pyrolyzers from Pyrol AB, Sweden

The sample is placed on a thin Pt-filament, which is resistively heated fast (in ms) up to 1400 °C. For liquid or insoluble samples an indentation is made in the filament to keep the sample in place.

The pyrolyzer has the unique feature that the TTP is measured both by photo diode and by measuring the resistance of the filament during pyrolysis. The photo diode is used as a reference to calibrate the resistance measurement to give accurate temperatures even below the range of the photo diode, i.e. below 600 °C. A glass cell is surrounding the filament in case non-volatile products should condense. The glass cell is also necessary to allow the light pass to the optic cable connected to the photo diode.

The four different ways of heating is made automatically by the software.

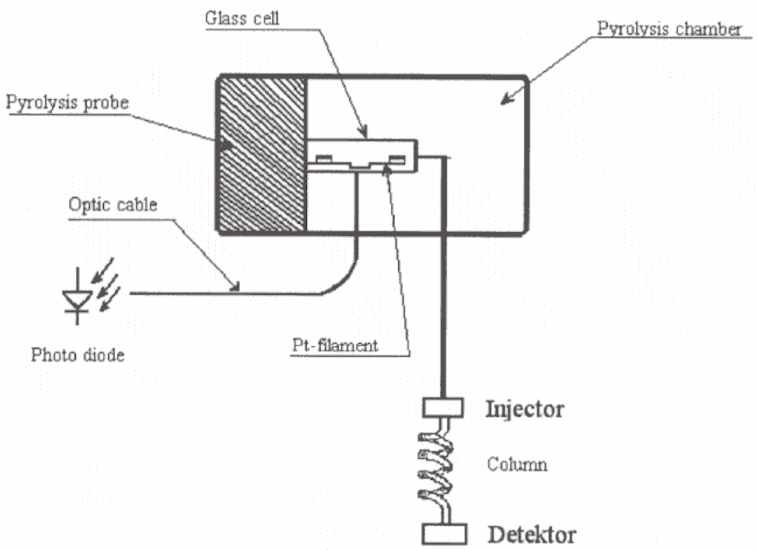


Figure 4-9. Schematic of the process unit of the Pyrola 2000.

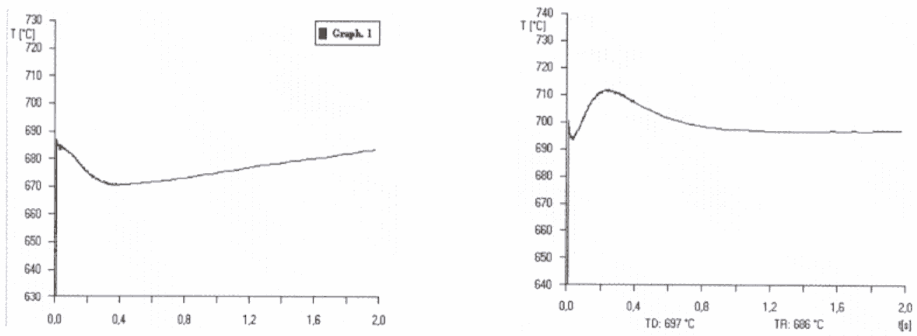


Figure 4-10. TTP in helium (left diagram) and air (right diagram).

The carrier gas will influence the TTP of the pyrolyzer, an effect that can be documented with the Pyrola pyrolyzers. Helium transport heat much more efficient than e.g. air or nitrogen, giving the differences in the TTPs shown in Figure 4-10. When pyrolysis

results, made in helium or any other gas, are compared, this should be taken into consideration.

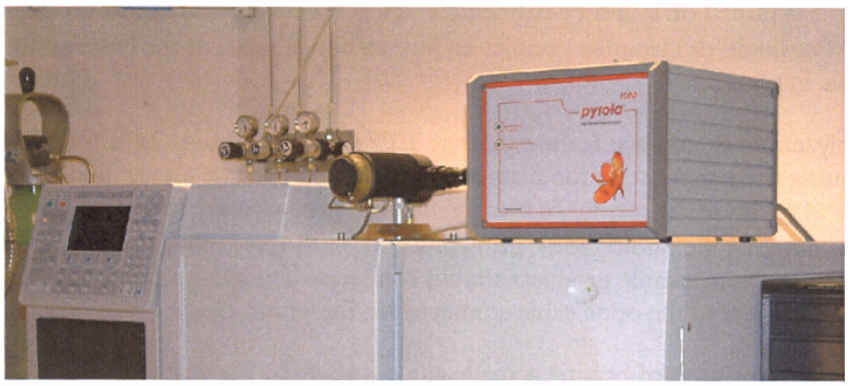


Figure 4-11. The Pyrola® 2000 mounted on a Varian GC/MS

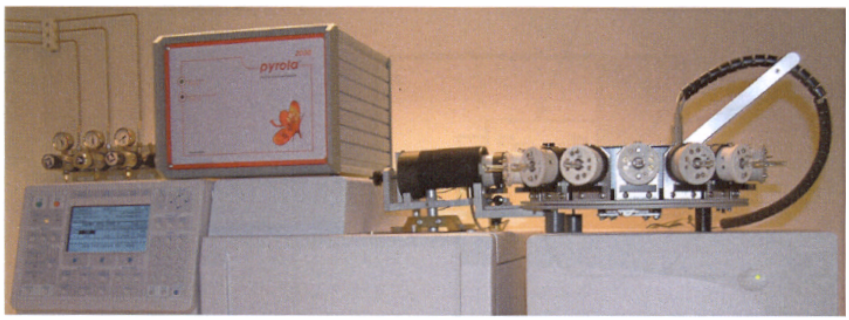


Figure 4-12. The Pyrola® 2000 MultiMatic mounted on a Varian GC/MS. The pyrolyzer has a capacity of 14 samples with individual pyrolysis programs.

Pyrola® MultiMatic is an automated pyrolyzer based on the Pyrola® 2000. A carousel with a maximum of fourteen probes is mounted together with the pyrolysis chamber. Each probe may be programmed individually with different types of pyrolysis.

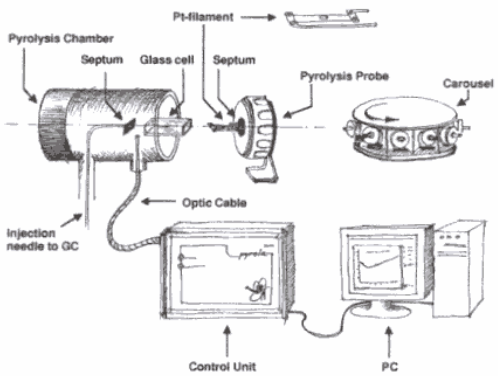


Figure 4-13. Schematic of the Pyrola®MultiMatic.

4.3 Sample Handling

Most pyrolyzers can handle both soluble and insoluble samples. All samples can be analyzed as long as they form products that are possible to detect. Inorganic salts e.g. have been analyzed when forming SO_2 [4]. Small sample sizes are favored as the temperature gradient in the sample is small. Small amounts can be difficult to handle when quantitative analyses are made. Different sample handlers are made to make it easier to handle, see Figure 4-14.

The right photo shows a sample handler for powder [9]. It consists of a micro cap, where the volume can be changed. The cap is filled with powder a number of times and the result is weighed in order to give the weight of the sample with the given volume of the sampler. A known amount of the sample can now be placed in the sample cup, filament or tube.

The left photo shows a sample handler to be able to get the same area out of e.g. a paper or laminate.

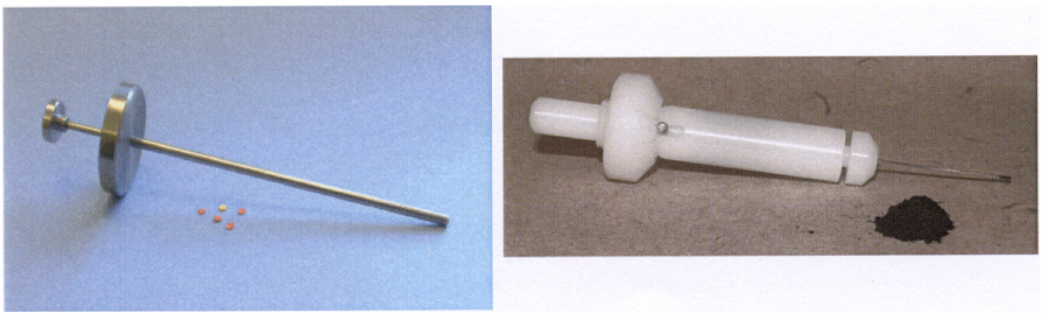


Figure 4-14. Sample handlers.

Chapter 5

5 Applications

In this chapter different applications of analytical pyrolysis are presented. All results were obtained with Pyrola® pyrolyzers from Pyrol AB, Sweden.

5.1 Qualitative Analysis

The reasons why pyrolysis-gas chromatography/mass spectrometry is so useful is because of all the possibilities the technique can offer to analyze so many different kinds of problems in so many different fields.

Quality analysis is not only used to find the different substances in the sample but more in detail what all together make the quality of the sample.

5.1.1 Example: Effect of Flame Retardants

A textile can be analyzed for the different chemicals, cotton and a fire retardant, but is it possible to find the effect of the fire retardant? The answer is yes.

In a project the effect of fire retardants on textiles has been studied. The result from pyrolysis was compared with the standard method to test the effect of fire retardants.

Pyrograms with and without fire retardant are shown in Figure 5-1. The amount of levoglucosan was related to the effect of the fire retardant.

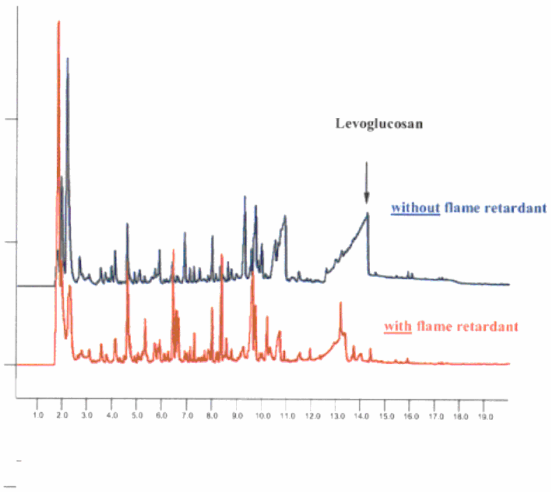


Figure 5-1. Textiles made of cotton with or without flame retardant were pyrolyzed at 600°C for 4 s.

5.1.2 Example: Qualitative Analysis of Silk

A blouse of silk, a tie and a white handkerchief were marked silk. Two different old silk threads used for pearl necklaces were used as reference material.

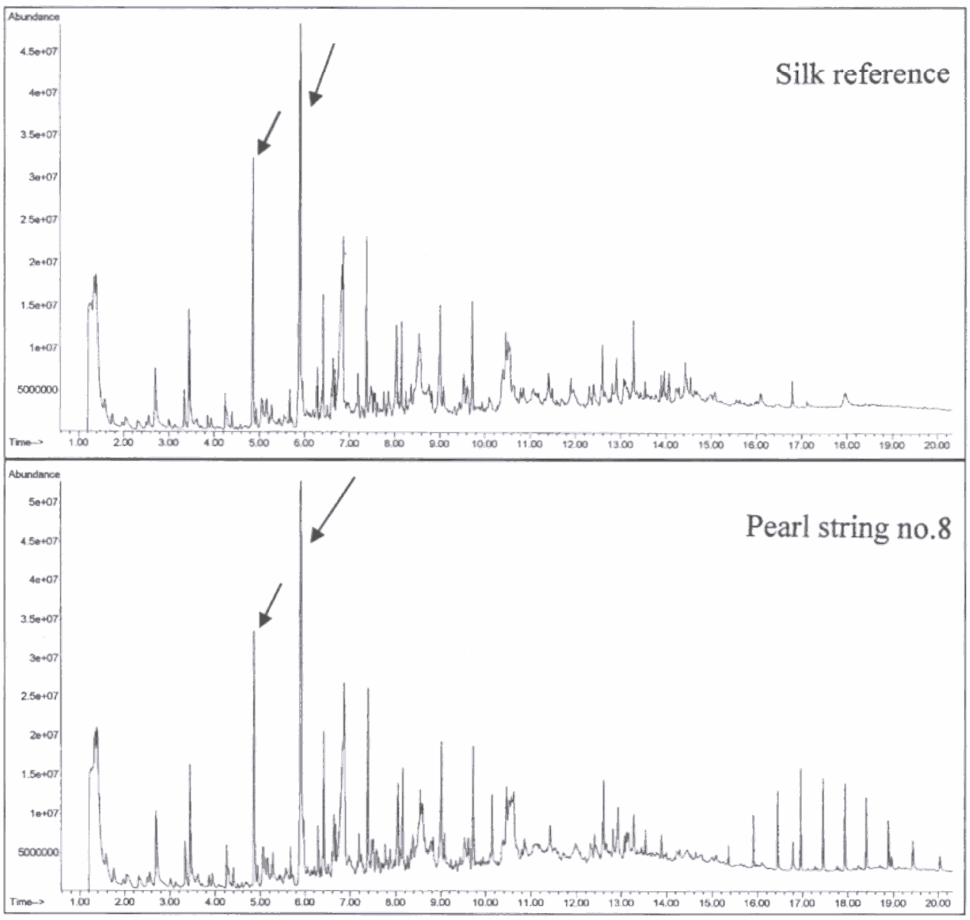


Figure 5-2. Pyrograms of two silk threads used as reference material.

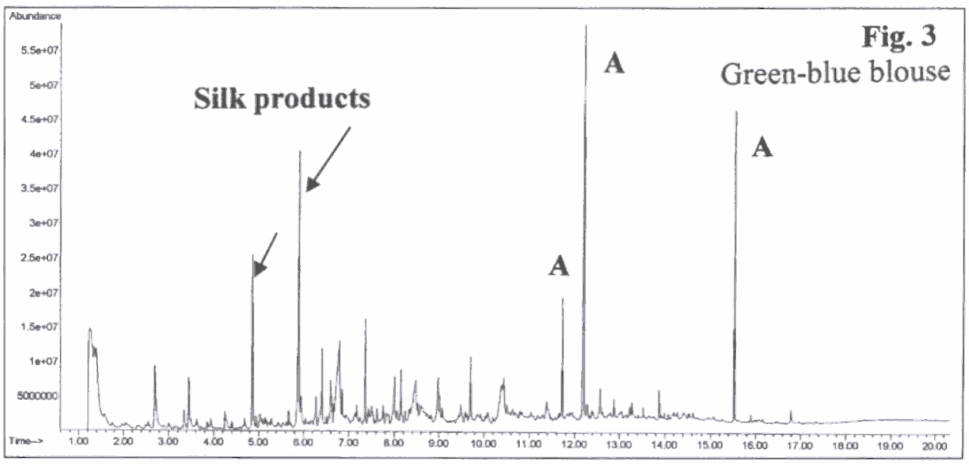


Figure 5-3. Pyrolysis of green-blue blouse, which was found to be made of silk.

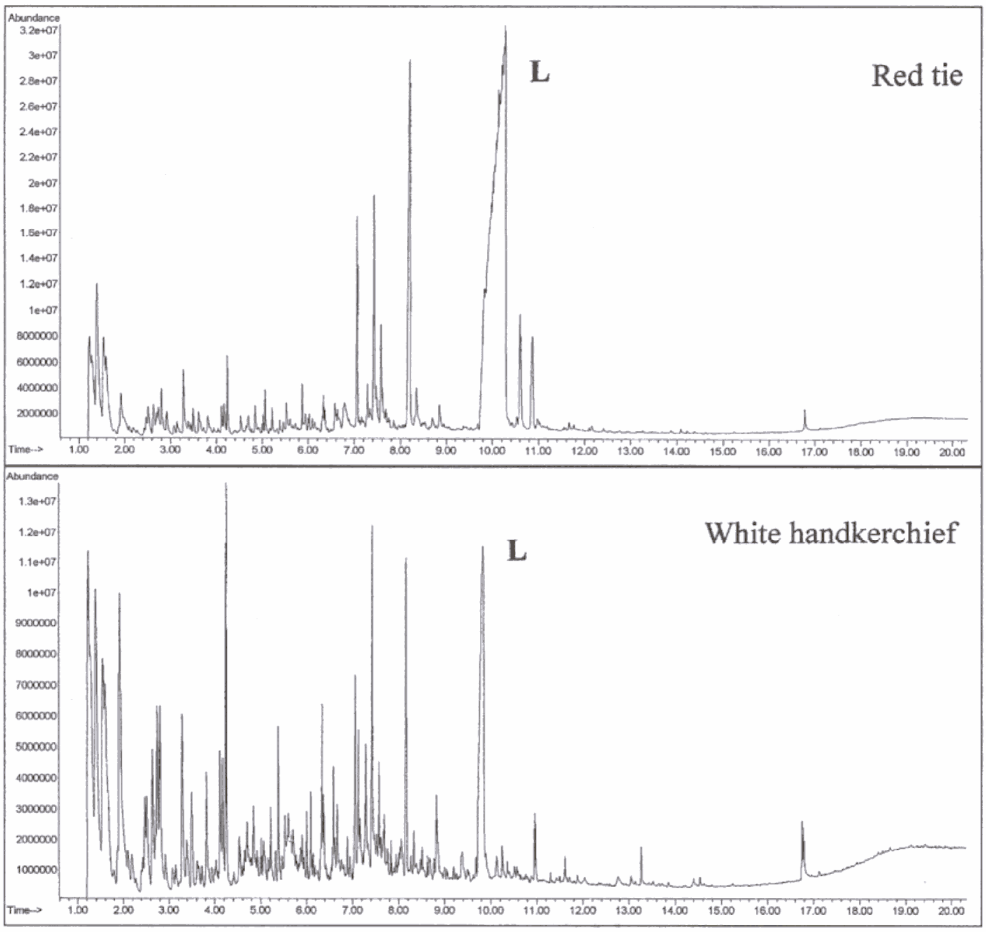


Figure 5-4. Pyrograms of the red tie and the white handkerchief. The peak marked by L is identified as laevoglucose, probably from rayon, which is regenerated cellulose.

The pyrograms of the reference materials are shown in Figure 5-2, where the arrows mark specific silk peaks. The green-blue blouse was found to made of silk, see the pyrogram in Figure 5-3, where most of the peaks also were found in the reference material. The peaks marked with an **A** came from the intensive gree-blue color.

The pyrograms of the other two samples differ from the references, see Figure 5-4 . They contain no specific peaks for silk but a large peak identified as laevoglucose, marked with an **L**. The origin of the laevoglucose is probably from rayon, which is regenerated cellulose.

5.1.3 Example: Analysis of the surface of a textile

Pyrotomy was used to study the surface of a textile. The sample was heated three times for 100 ms at 800° C[2], see Figure 5-5. Two different isocyanates, toluene-2,4-diisocyanate (TDI) and diphenylmetan-4,4-diisocyanate (MDI) were found. The two peaks decreased with each consecutive pyrolysis.

[2] A higher temperature is often used in pyrotomy as compared to "ordinary" pyrolysis.

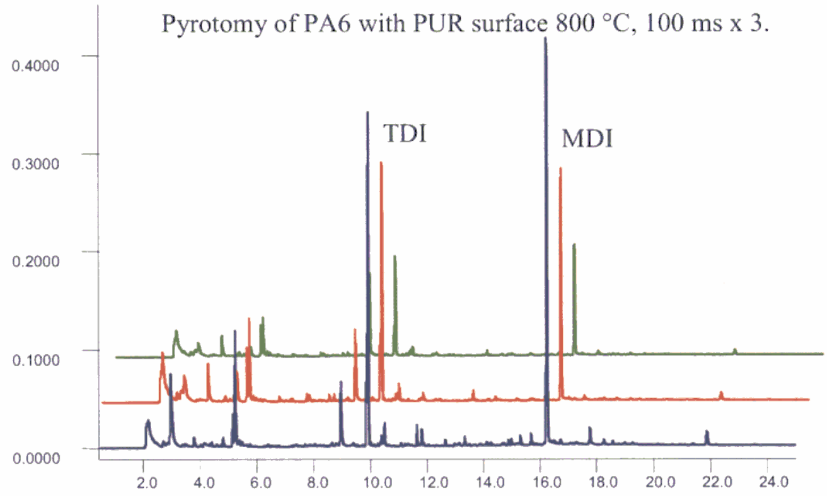


Figure 5-5. A textile material was pyrolyzed three times to 800 °C for 100 ms showing the surface of the sample.

Another two pyrolyses for 200 ms were made of the same sample. The result is shown in Figure 5-6 . It is now possible to find peaks that are increasing at the same time as the isocyanates are still decreasing.

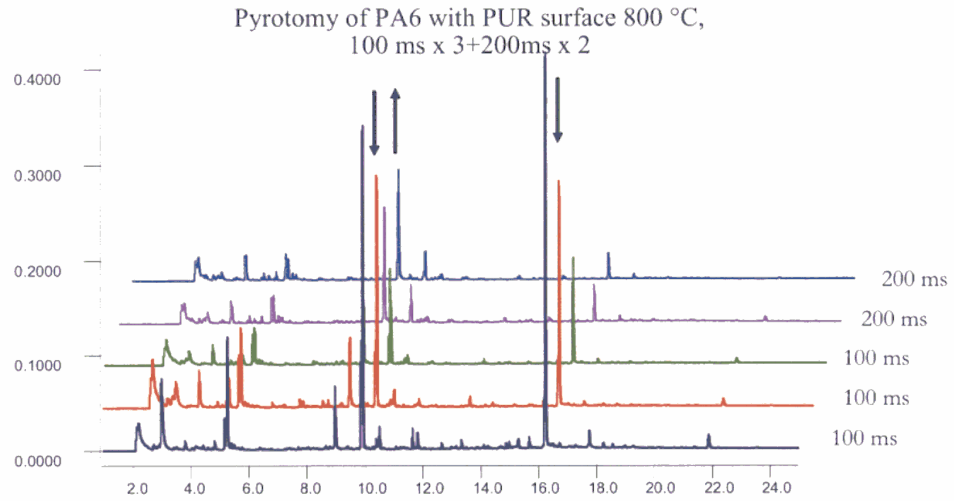


Figure 5-6. The five pyrograms from pyrolysis to 800 °C for 3x100 ms + 2x200 ms.

A final pyrolysis was made for 2 s. In Figure 5-7 all six pyrograms are presented together. A big peak, caprolactam, was formed in the last pyrolysis. This indicates that most of the sample contained nylon-6 and the sample had a surface of polyurethane.

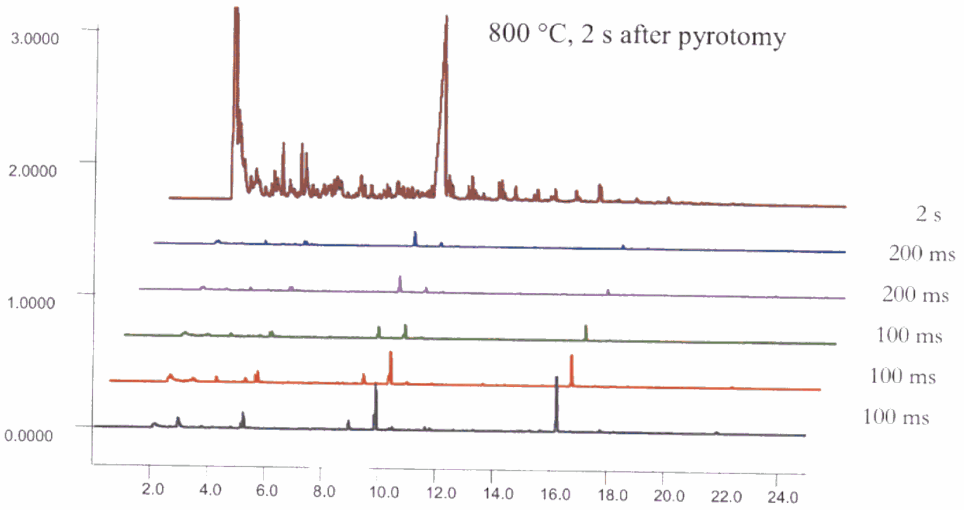


Figure 5-7. Pyrotomy of a textile material showing how the first layer is decresing and the second increasing with time.

If the sample had been pyrolyzed isothermally to 800 °C for 2 s there had been problems to find the quality of the surface layer, see Figure 5-8. The position of the monomer isocyanates are indicated by arrows.

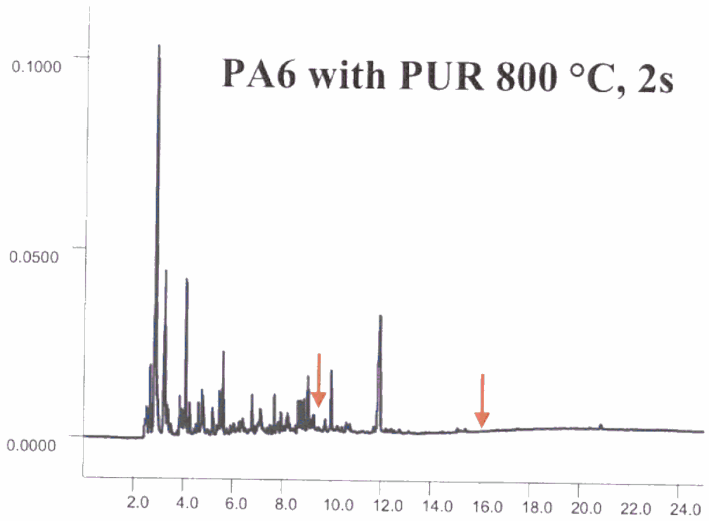


Figure 5-8. A textile pyrolyzed isothermally to 800°C for 2 s. The red arrows show where the two monomer isocyanates should be seen.

5.1.4 Example: Analysis of coal.

Coal is a very complex and heterogeneous material. Coal consists mainly of a number of organic fractions (macerals), derived from plant remains, and incorporated minerals. The aging process, when peat is transformed to anthracites, is termed coalification (the rank of coal). During the coalification the carbon content and aromaticity of coal increase and hydrogen and oxygen content decrease.

Detailed characterization of coal is important for better understanding of environmental and health effects, and for improving methods for sulfur removal. To be able to characterize coal totally, both ultimate and proximate analyses are needed. Ultimate analysis of dried coal samples are e.g. elemental analysis and analysis of ash found after combustion.

Pyrolysis-gas chromatography (Py-GC) has been used earlier to study the content of coal, which can be an example of a proximate analysis technique.

5.1.4.1 Sample handling

The solid sample dispenser shown in Figure 4-14, was used for the application of coal onto the Pt-filament. The volume of the sample could be varied. The glass micro pipette was filled up to the plunger with the coal sample. The coal sample was then pushed out of the glass micro pipette with the plunger into the cavity of the Pt-filament. To get information of the amount of coal, the volume of coal was weighed a number of times to know the RSD.

The sample size was normally 20-200μg.

Table 5-1. The composition of the samples used for the study.

COAL SBN*	TOT. S (%)	Spyr. (%)	Ssulf. (%)	Sorg. (%)	Vol.matter (%)	ASH (%)
101	1.82	0.77	0.04	1.01	7.33	5.40
126	0.93	0.54	0.22	0.17	31.64	12.16
126	2.10	0.45	0.52	1.13	20.80	12.84
134	0.60	0.01	0.01	0.58	4.50	2.05
136	5.05	1.13	0.06	3.86	44.99	18.89
141	2.54	1.85	0.58	0.11	9.67	17.51
162	0.41	0.01	0.00	0.40	42.70	1.20
171	0.83	0.03	0.07	0.73	30.12	12.64
177	1.35	0.87	0.05	0.46	32.80	17.40
501	2.46	0.76	0.93	0.77	27.11	19.96
L**					36.30	
M**					23.00	
A**					5.90	
* Stichting Steenkoolbank Nederland, SBN						
** Coals from Bergbau Research, Germany						

5.1.4.2 Volatile matter

Volatile matter is normally determined by gradually, but rapidly heating, air-dried coal up to 950 °C (±20 °C) in a closed crucible in a special oven. Volatile matter is reported as loss of weight minus the moisture determined at 105 °C [10].

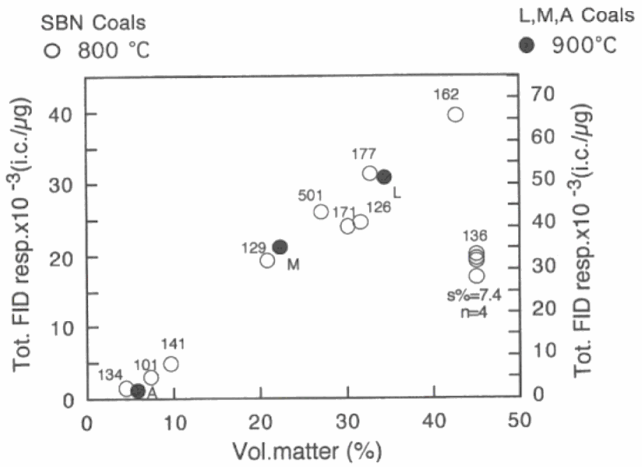


Figure 5-9. Products from a flame ionization detector (FID) at 800°C for three different coals; L, M and A.

Figure 5-9 is showing the amount of products from a flame ionization detector (FID) found at 800 °C. Coal 136 is far from the expected value. However, the RSD is relatively good. The three coals, L, M and A, were pyrolyzed at 900 °C at another occasion. However, they fall close to the line found for the other SBN coals. The difference in behavior of coal 136 might depend on wrong expected value or a characteristic form for the sample which behaved differently in the technique used for the expected value.

5.1.4.3 Coalification

The age of coal (rank) can be studied by the amount of aromaticity, hydrogen and oxygen content. Three different coal samples L, M and A were pyrolyzed at 700 °C for 2s, as well as polyethylene (PE). The pyrolysis products were detected by a FID. In Figure 5-10 the result is shown. The arrows are showing the benzene (B) and toluene (T) peaks. The alkanes are connected by a line.

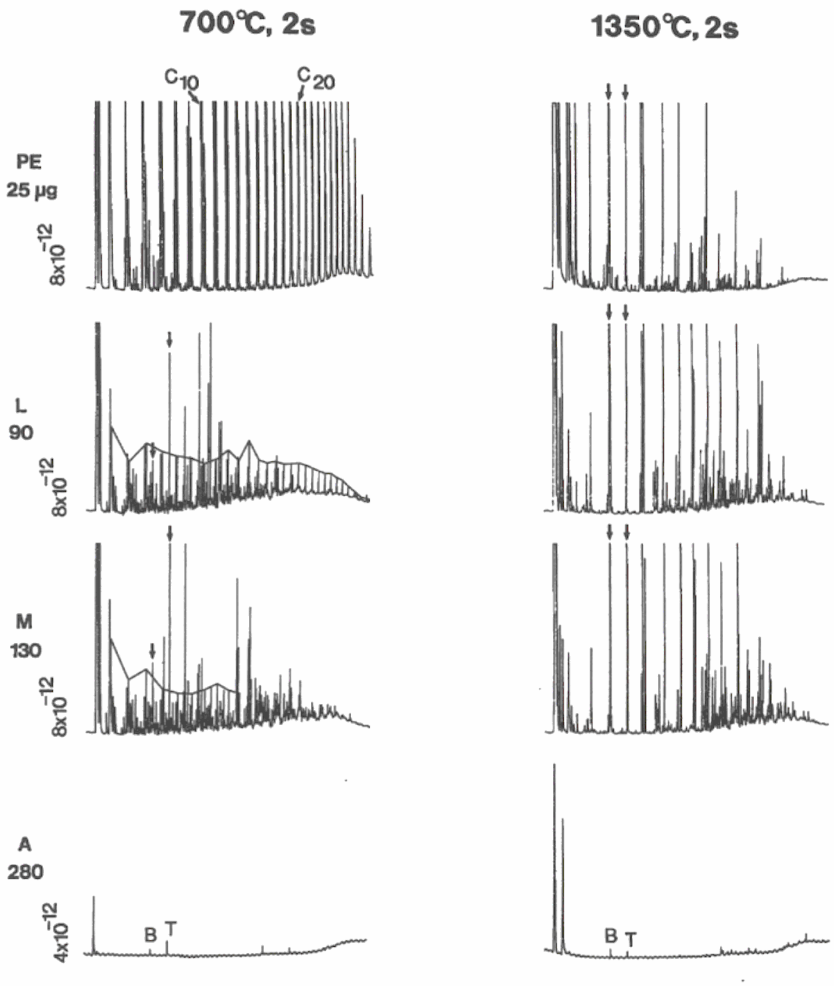


Figure 5-10. Three coal samples, L, M, A, and PE are pyrolyzed at 700°C for 2 s.

Figure 5-11. The same samples as I figure 5-9 are pyrolyzed at 1350°C for 2 s.

Coal L is the youngest coal indicated by the large number of long-chained alkanes. The older the coal, the shorter length of alkanes and more aromaticity. The result from PE shows the number of carbon atoms and retention time of the alkanes.

5.1.4.4 Influence of temperature and time

Figure 5-11, with the same samples as in Figure 5-10, shows the result when the four coal samples and PE are pyrolyzed at a higher pyrolysis temperature, 1350 °C, for 2 s. All qualitative information is missing as secondary effects are dominating and form aromates the same as for PE. There are no qualitative differences of the pyrolysis products from the coals compared to the synthetic polymer, PE, except from some peaks containing hetero atoms from coal.

Figure 5-12 shows the influence of pyrolysis time. Samples from coal L were pyrolyzed to 1350 °C during the temperature rise time, TRT, and different pyrolysis times up to 2s.

The straight line indicates the alkane peaks and the dotted, those peaks that are increasing due to secondary effects. After 200ms most of the pyrolysis products were aromates.

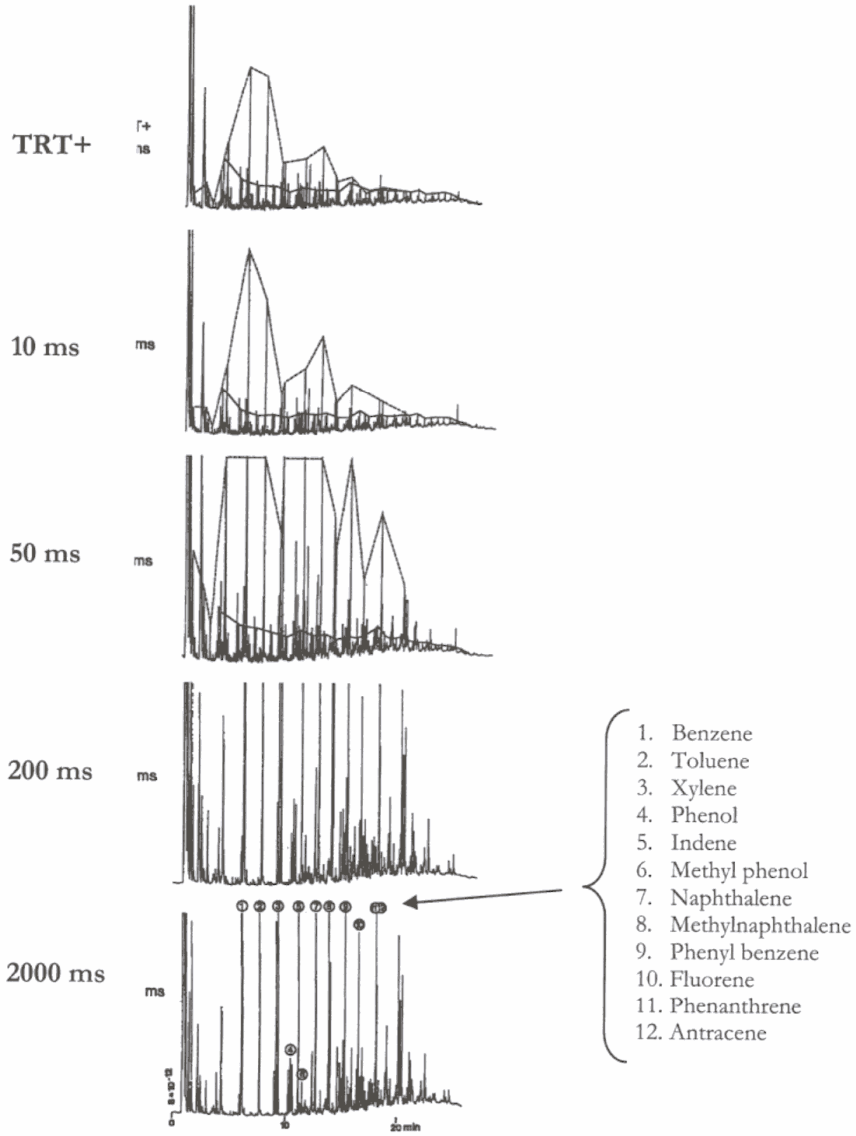


Figure 5-12. Coal L pyrolyzed at 1350 °C at different pyrolysis times. In the lowest pyrogram the aromates are indicated.

The two figures 5-10 and 5-11 show how a too high pyrolysis temperature can give secondary effects, which destroy valuable analytical information. Aliphatic hydrocarbons will be turned to aromates. The effect of time in Figure 5-12 shows the fast heating of the sample. To decrease the secondary effects fractionated pyrolysis is to a great help.

5.1.4.5 Results Py-GCxGC/TOFMS

Pyrolysis together with GCxGC and TOFMS increase the chromatographic resolution and the speed of the analyses. This makes it possible to characterize even non-volatile samples in detail. An example is shown in Figure 5-13 the total ion counts (TIC) for coal 136 pyrolyzed at 700 °C is shown. The analysis was performed on a Pegasus 4D, Leco,USA.

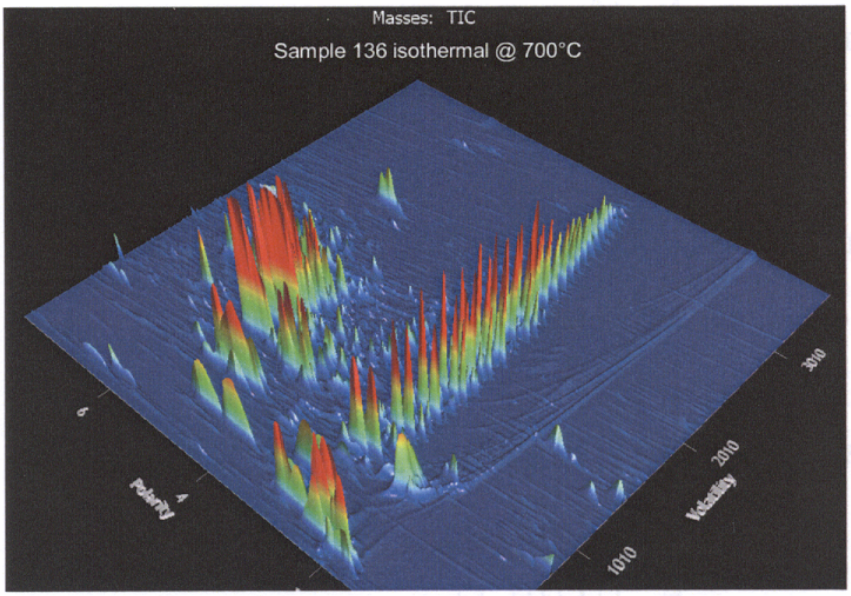


Figure 5-13. The total ion counts (TIC) for coal 136 pyrolyzed at 700 °C

Results are shown in Figure 5-14 from three different SBN coals, 136, 141, and 101. The composition of the coal samples are shown in Table 5-2.

Table 5-2. Composition of the coal samples used in the Py-GCxGC/TOFMS study.

COAL SBN*	TOT. S (%)	Spyr. (%)	Ssulf. (%)	Sorg. (%)	Vol.matter (%)	ASH (%)
101	1.82	0.77	0.04	1.01	7.33	5.40
136	5.05	1.13	0.06	3.86	44.99	18.89
141	2.54	1.85	0.58	0.11	9.67	17.51

The X-axis shows the volatility (time in seconds) of the products and the Y-axis the polarity (time in seconds). In the 3D plot the amount of products can also be found. The results are shown both in 3D and 2D plots.

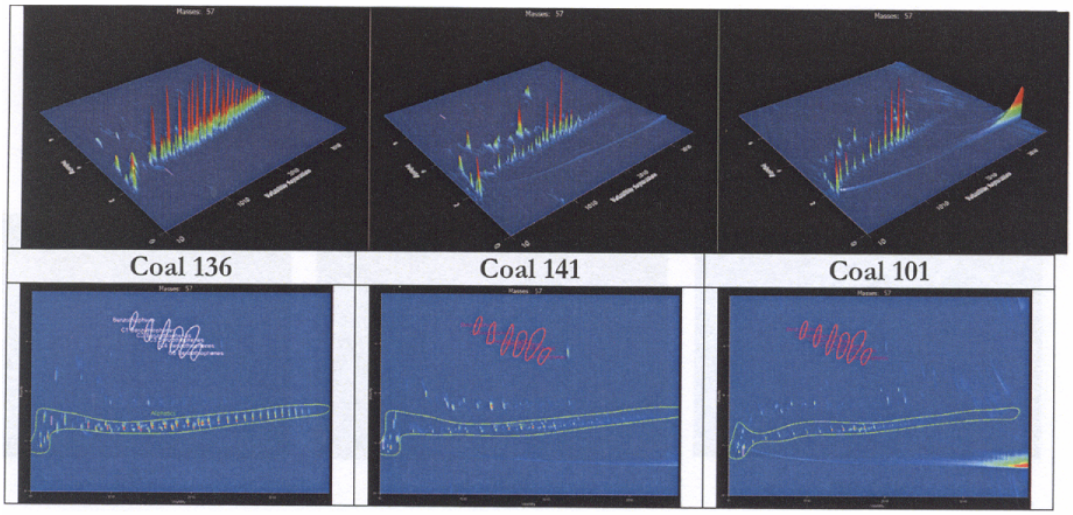


Figure 5-14. Ion 57 m/e plotted for three different coal samples in 3D resp. 2D plots.

5.1.4.6 Alkanes

From the TIC 3D plot, Figure 5-13 above, it is possible to extract different ions and their intensities for qualitative and quantitative information.

In Figure 5-14 the ion 57 m/e is chosen for 3D and 2D plots for three different coal samples. This ion is characteristic for aliphatic products. To distinguish alkanes from other aliphates the retention times and polarity helps.

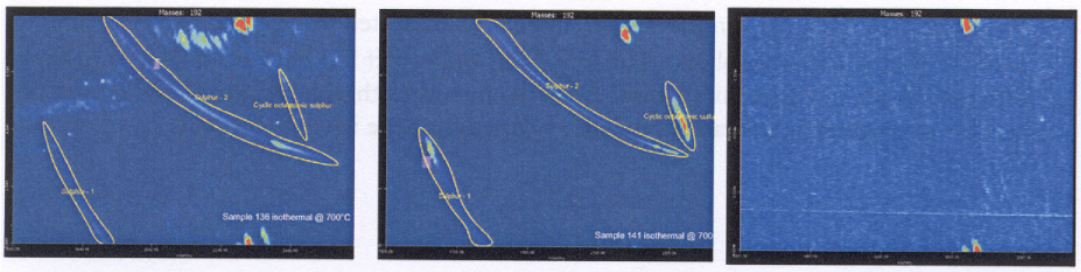


Figure 5-15. Analysis of sulfur content by using the ion 192 m/e.

In Figure 5-15 the ion 192 m/e is chosen to indicate regions where different elemental sulfur containing products can be found, S4, S6 and S8.

5.1.4.7 Fractionated pyrolysis

There are more possibilities to characterize coal samples when using Py-GC/MS. If the coal samples are pyrolyzed by fractionated pyrolysis there are possibilities to study the degradation rates and thus understand the origin of the sulfur.

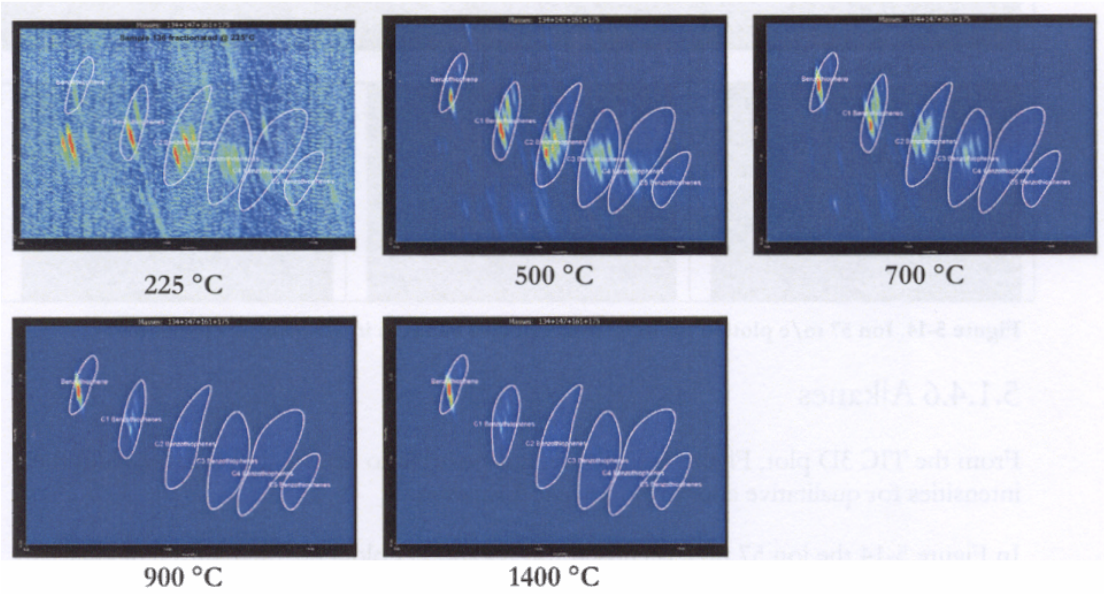


Figure 5-16. Fractionated pyrolysis of coal sample 136 at five different temperatures.

In Figure 5-16 the same sample of coal 136 has been heated to 225, 500, 700, 900 and 1400 °C (fractionated pyrolysis). The ions 134+147+161+175 have been chosen to find different forms of benzothiophenes. At all temperatures thiophenes are formed more or less. At the highest temperatures mostley benzothiophene itself is formed.

5.2 Quantitative Analysis

Quantitative analysis can be made if the system gives reproducible results. When making a calibration curve there might be problems to find reference materials. Mostly when the analysis are made in a company and the samples are similar to what the company produces there are no problems. It is important to find references as similar as the unknown sample to be quantified. Standard addition to an unknown sample can be of great help when making quantitative analysis of a specific substance, see further discussion in chapter 5.2.3.

The methodology for performing a quantitative analysis is:

1. Choose column and detector
2. Find a specific peak for quantification
3. Choose pyrolysis temperature
4. Test the reproducibility
5. Test influence of sample size
6. Make a calibration curve

Depending on how much is known about the sample there might be more or less problems to find the right conditions for separation and detection. Try to find one or more specific peaks to use for the calibration. It is important to choose the optimum temperature, where the change of pyrolysis temperature due to differences of sample size will have the least influence on the result. The process is explained in chapter 5.2.4

Before proceeding with the analysis it is necessary to test the reproducibility. A figure needs to be judged. How does the sample size influence the result? Then make a calibration curve and pyrolyze the unknown sample. The calibration curve will then give a quantitative value.

5.2.1 Example: Co-polymer PMMAS

When making co-polymers with different ratio between the two monomers methyl metacrylate (MMA) and styrene (S), the result from one sample did not correspond to the expected value obtained with NMR, see Table 5-3. Py-GC was then used to try to confirm the results from NMR analyses.

Table 5-3. Mole ratio of six different samples of copolymer between metacrylate and styren. The expected values together with the result from NMR analysis is shown. The sample where the NMR results differs from the expected value is shown in bold.

Mole % MMA							
Expected	0	26.7	**42.7**	49.6	56.6	74.0	100
NMR	0	25.0	**36.4**	49.0	56.2	75.5	100

There were no problems to find the right conditions for separation and detection. The pyrolysis products were almost the monomers, see Figure 5-17.The two monomers were used as the specific peaks.

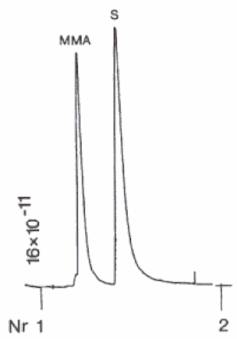


Figure 5-17. A pyrolysis of the co-polymer PMMAS. The peaks are the monomers MMA and S.

The different homopolymers were pyrolyzed at different temperatures, see Figure 5-18.

PMMA was totally pyrolyzed already at 500 °C while the PS needed a higher temperature. A temperature of 700 °C was chosen, high enough for the PS, but not too high so the MMA was further degraded.

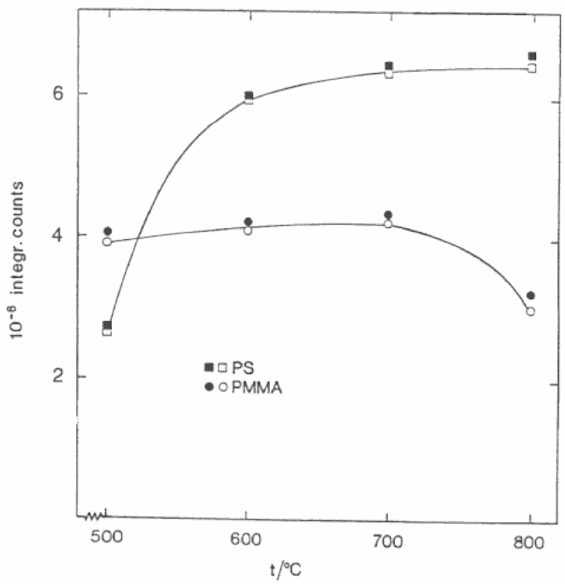


Figure 5-18. The two homopolymers pyrolyzed at different temperatures.

Calibration curves at 700 °C /2 s from the two monomers were made from the five co-polymers with different mole ratios, see Figure 5-19.

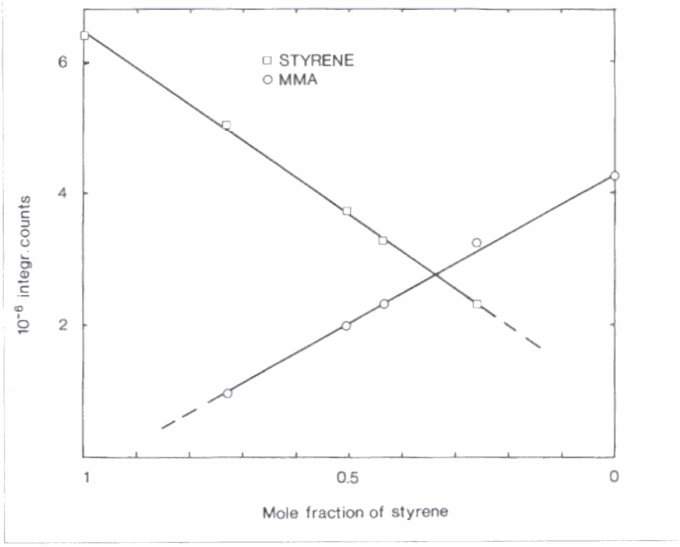


Figure 5-19. Calibration curves of the two monomers from co-polymers.

The calibration curves were used to estimate the mole ratio of the sample that gave an unexpected value in the NMR analysis. The result is shown below.

	Expected	Pyrolysis
MMA	42.7	42.3 ± 2.5
Styrene	57.3	57.6 ± 1.9

The results from both MMA and S independently, showed that the values found by pyrolysis were in accordance with the expected values.

5.2.2 Example: Quantitative Analysis of Jute in Cotton

Jute is a cheaper material than cotton and sometimes jute is mixed together with cotton in order to reduce the price. Cotton consists of pure cellulose while jute contains lignin as well. Two specific ions from lignin (m/e= 168 for 2-methoxy-4-propenyl phenol and 194 for 2.6-dimethoxy-4 propenyl phenol) were used to determine if two different samples, 1 and 2, contained jute, see Figure 5-20 and Figure 5-21.

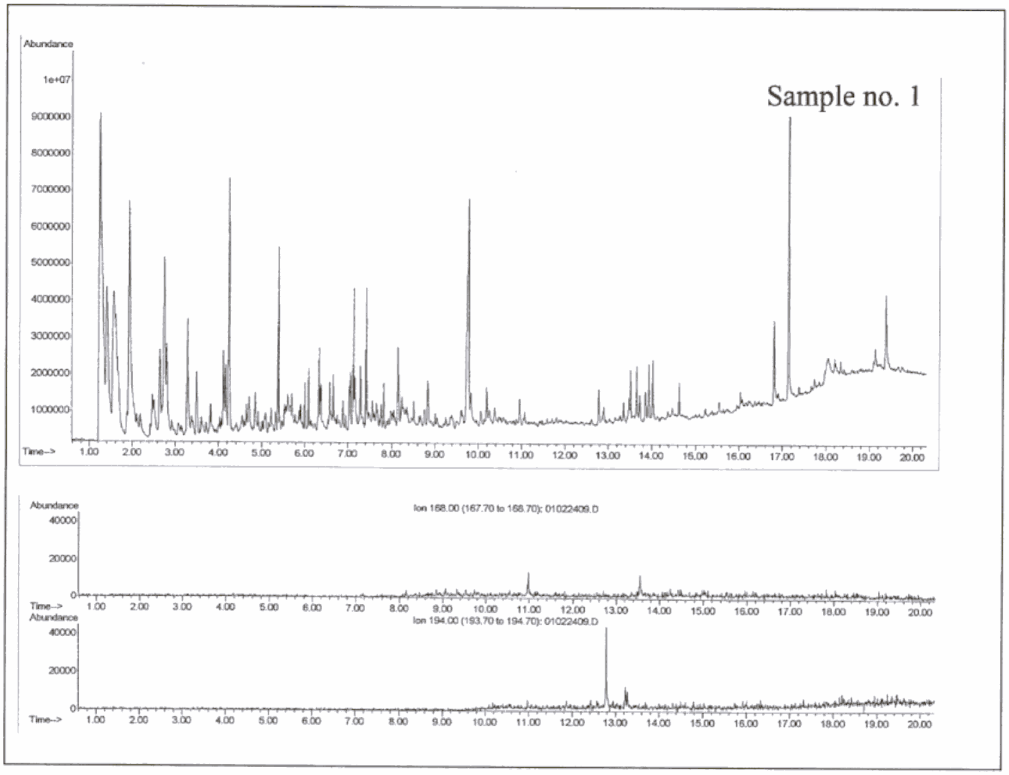


Figure 5-20. Sample no.1, cotton without lignin.

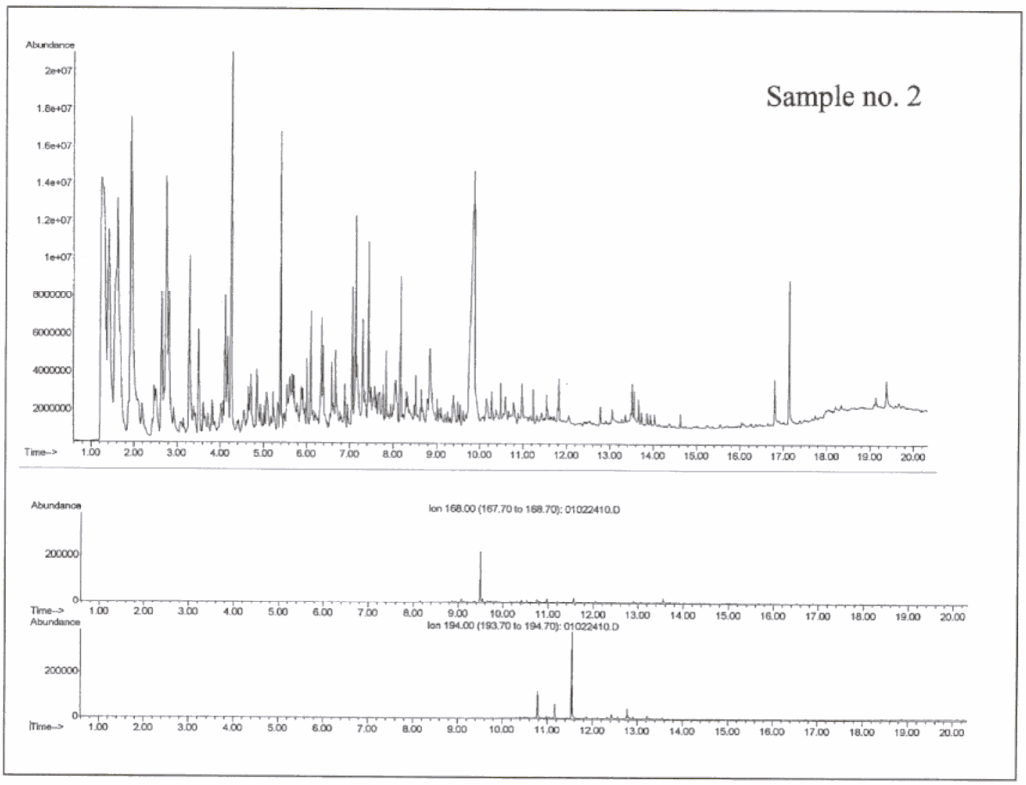


Figure 5-21. Sample 2, cotton with lignin.

The lower diagrams in Figure 5-20 and Figure 5-21 show the extracted ion mass spectra, m/e= 168 and 194, of the different samples. These ions are specific for lignin. It is evident that sample no. 2 contains jute as the ions m/e= 168 and 194 are found but not in sample no. 1.Seven reference materials were pyrolyzed.

Calibration curves were made at two different occasions, one month apart, see Figure 5-22.

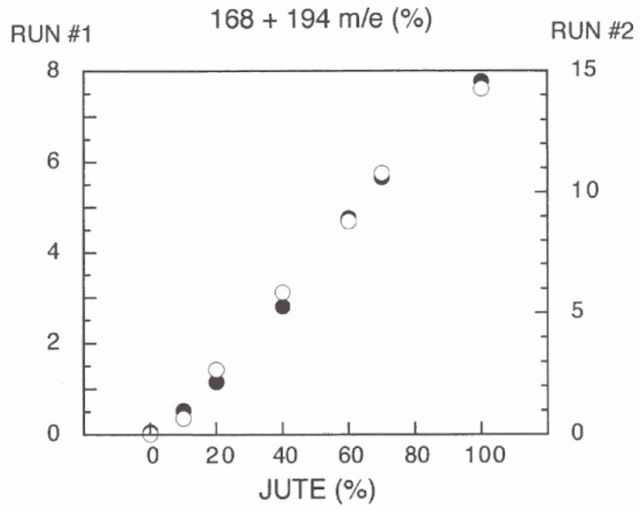


Figure 5-22. The specific ions 168 – 194 m/e (%) were plotted against the per cent of jute in cotton.

5.2.3 Standard addition method for quantitative analysis

To illustrate the standard addition method an example is presented where a polymeric plasticizer is to be found in serum, and it is of great importance to be able to quantify the concentration. The plasticizer alone is pyrolyzed and the pyrolysis temperature is optimized and the retention times of the different products were noticed. Different known amounts of the plasticizer were then added to the unknown sample. The pyrograms from the sample with the plasticizer are seen in Figure 5-23. Py-GC was used and the peak height was used as a calibration curve. A small peak was found in the sample with no added plasticizer. The separation was not good enough for quantification in those small amounts. If Py-GC/MS had been used, the quantification should have been more precise by calibration of the specific ions. In this example it was possible to find < 2 ppm.

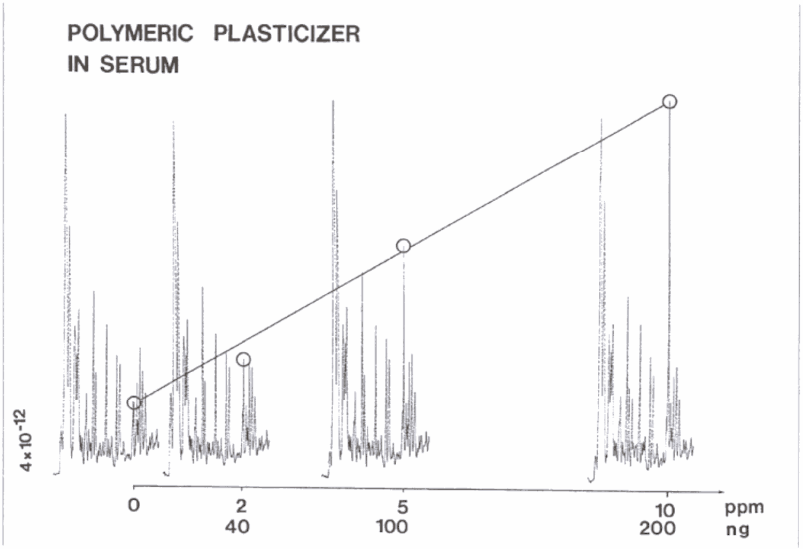


Figure 5-23. Plasticizer

5.2.4 The influence of sample size.

When making a calibration curve for quantitative analysis it is important to choose the optimum pyrolysis temperature, where the change of pyrolysis temperature due to differences of sample size will have the least influence on the result.

When the sample size is varied under otherwise identical conditions a larger sample will normally give a slightly lower pyrolysis temperature, especially if the area of the sample is constant. The decrease in temperature may lead to either a lower or a higher yield of a specific pyrolysis product, depending on the temperature chosen for the pyrolysis. To find the optimum pyrolysis temperature for a specific peak the area of the peak can be plotted against the pyrolysis temperature, keeping the sample size as constant as possible. An example is shown in the left diagram of Figure 5-24. The arrows indicate the change in peak size due to a larger sample. At low temperatures the peak will decrease, whereas a high temperature will give a higher yield since secondary effects decrease with temperature, and thus give a larger amount of the pyrolysis product.

Plotting the peak area as a function of sample size will then give the two different behaviors illustrated in the right diagram of Figure 5-24. At low temperatures the diagram will follow the blue (lower) curve, since then the yield decreases with temperature. A larger sample will then give a lower pyrolysis temperature and thus a smaller peak area.

At high temperatures the curve will follow the red (upper) curve, since then a large sample will then give a higher yield since the reduction in temperature will give less secondary effects.

It is favorable to choose the pyrolysis temperature in such a way that the yield is as constant as possible with respect to temperature. With this optimum temperature the peak area will be proportional to the sample size. The optimum temperature in the example in Figure 5-24 is 600 °C.

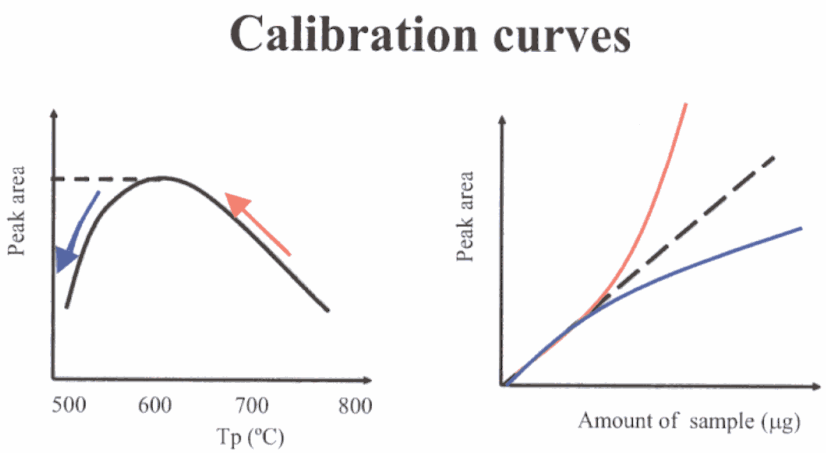


Figure 5-24. Left diagram: A sample has been pyrolyzed at different temperatures with a constant sample size, and the area of a specific peak has been plotted against temperature. The arrows indicate the effect of a larger sample. At the optimum temperature (here 600 °C) the peak area is rather constant with respect to changes in pyrolysis temperature (for example caused by variations in sample sizes).
Right diagram: The different calibration curves when different sample sizes have been used. The result depend on whether a lower or higher temperature has been used compared to the optimum temperature. The calibration curve will give a straight line at the optimum temperature.

5.2.5 Summary Quantitative Analysis

There are many possibilities to make quantitative analysis with Py-GC or Py-GC/MS. The area of specific peaks which originates from the interesting substance may be used for the quantification, or specific ions when a MS is used as detector. Normal standard addition to the unknown sample is also a useful method. Careful sample handling and an optimized pyrolysis temperature will help to get good results.

5.3 Thermally assisted Hydrolysis and Methylation (THM)

Polar pyrolysis products can be formed and thus might be adsorbed in the system, and cause difficulties for qualitative and quantitative analysis. Nowadays there are more efficient columns for polar substances and also less active parts in the systems, but it was a breakthrough when derivatization in combination with pyrolysis was introduced.

In earlier publications the technique was called SPM, Simultaneous Pyrolysis Methylation. Now the technique is called THM, Thermally assisted Hydrolysis and Methylation. It was considered that the reaction occurred in two steps: first alkaline hydrolysis followed by methylation at the pyrolysis using tetramethylammonium hydroxide (TMAH). This means that polar polymers and esters when adding the reagent, are first alkaline hydrolyzed on the filament, in cup or tube, and then derivatization takes place at the pyrolysis. Acids and salts give methyl esters and phenols and aliphatic alcohols methyl ethers at the pyrolysis.

Only polymers with alkali- hydrolysable bonds give a different pyrogram compared to conventional pyrolysis. Thus e.g. polyethylene and polypropylene give the same pyrograms with and without reagent, while lignin, containing aryl ether bonds and polyesters give different pyrograms. Even amines (–NH2) and aromatic nitrogen like in melamine, a cyclic trimer of cyan amide (NCNH2), can be methylated.

Mostly, tetramethylammonium hydroxide (TMAH) has been used for the derivatization. In Figure 5-25 other methylation reagents, phenyl trimethylammonium hydroxide (Ph-TMAH), tetraethylammonium hydroxide (TEAH), tetrabuthylammonium hydroxide (TBAH) and tetramethylammonium acetate (TMAAc) are presented. TMAH is the strongest base like NaOH and tetramethylammonium acetate TMAAc the weakest base.

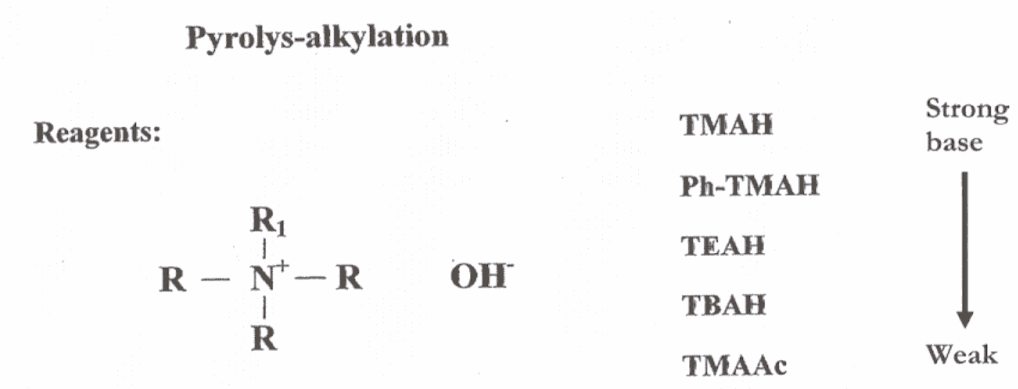


Figure 5-25. Five different methylation reagents are presented.

5.3.1 Methylation of acids and esters

If the reagents are chosen depending on basicity it is possible to quantify the amount of free acids and esterified fatty acids, see Figure 5-26. TMAAc, as the weaker base was used to methylate the free acid and TMAH as a strong base, was able to hydrolyze the ester before methylation, giving the total amount of acids [11].

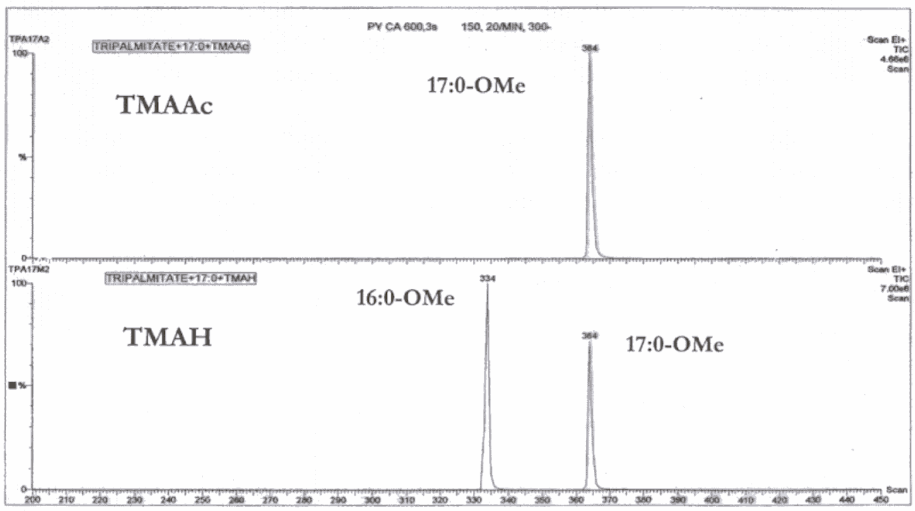


Figure 5-26. A sample of glyceryl trihexadecanoic acid and heptadecanoic acid is treated with TMAAc or TMAH.

The free acid (17:0) was found by TMAAc while the esterified acid needed to be hydrolyzed by a stronger base TMAH before methylation.

It is also possible to study the free and esterified acids in pulp , see Figure 5-27. The pyrograms show when an extract from a chemothermomechanical pulp (CTMP) sample containing both esters and free acids are pyrolyzed with the two reagents.

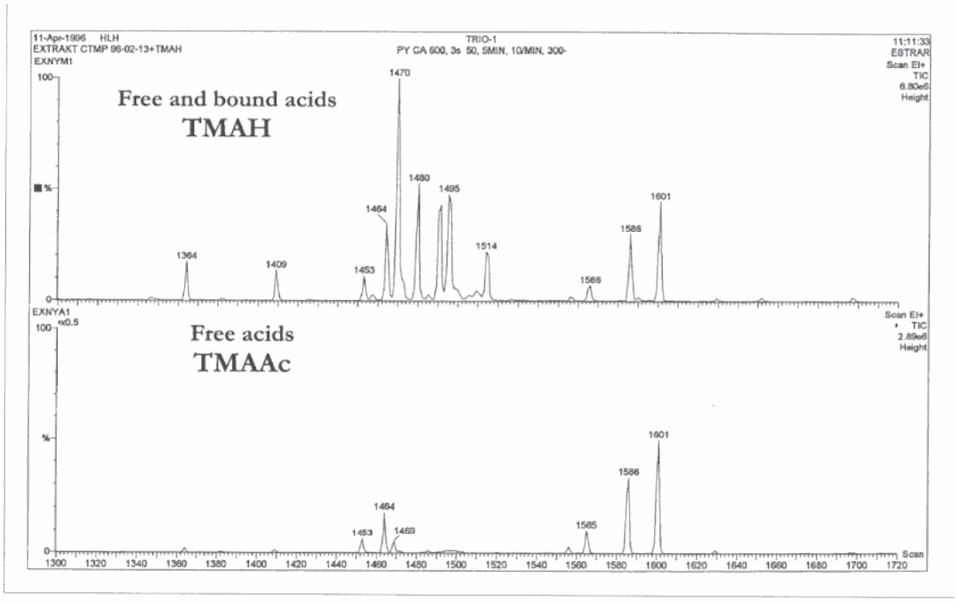


Figure 5-27. Pyrolysis of an acetone extract from CTMP.

The lower pyrogram shows the amount of free acids from TMAAc and the pyrogram above showing the sum of free and esterified acids from TMAH. (The resin acids in the area 1550-1620 are always free and can be used as internal standard.), see figure 5-25.

Free acids with low molecular weight might be difficult to separate when methylated. In Figure 5-28, dicarboxylic acids with low molecular weights were methylated with both TMAH and TBAH to show how the retention times increased when TBAH was used.

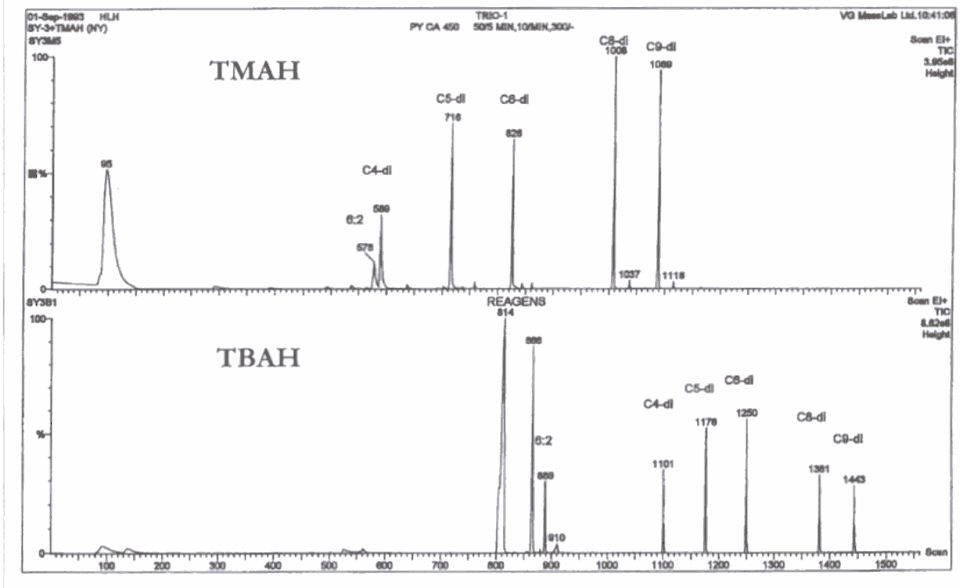


Figure 5-28. A sample containing dicarboxylic acids is treated with TMAH and TBAH.

5.3.2 Methylation of anions.

It is possible to methylate anions like carbonate, silicate, sulphite, sulphate and phosphate. Polysulphides from black liquor are pyrolyzed together with either TMAH, TEAH or TBAH, see Figure 5-29.

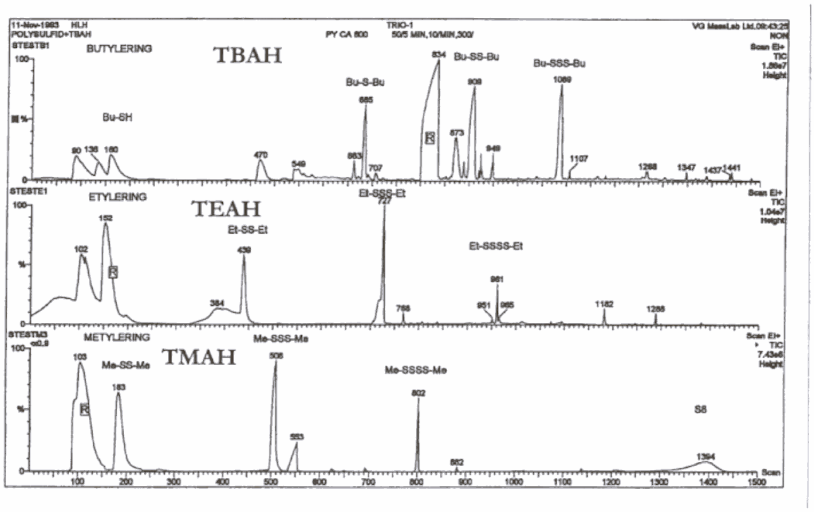


Figure 5-29. Polysulphides from black liquor pyrolyzed with different reagents showing the idea of changing the retention times.

5.3.3 Sample handling

The sample handling can be tricky to obtain reproducible results. It is necessary that the sample is totally mixed together with the reagent in order to get reproducible results for quantitative analysis. The reagents are found either in water or in methanol and different concentrations 1-25%. Water might be needed at the hydrolysis. The solvent is volatilized before heating.

No summary of the methylation method regarding sample handling, amount of reagent, concentrations or temperatures have been made or used for different type of samples. It has been found that a relatively low temperature (380 °C) for the methylation is enough for acids and esters.

Many papers, however, have been written about THM together with alkyd resins, acids, esters, lignins etc.

5.3.4 Conclusions THM

THM is a useful method for studying polar substances, but a systematic study of the THM method and other derivatization methods is yet to be made, especially for quantitative analyses. The knowledge obtained in such a study with different reagents should be very useful in order to get more information from the pyrolyzed sample. Questions to be answered could be:

- How does the methylation agent or any reagent degrade depending on temperature?
- Which different type of samples can be methylated or derivatized?
- Which different reagents for derivatization are possible together with Py-GC.
- Which different conditions, temperature and time should be used to get reliable results?

- How should the sample be treated together with the reagent?

5.4 Chemometry (Multivariate Data Analysis)

Multivariate data analysis is a tool with great potential for interpreting data acquired with analytical pyrolysis. It can be used when the samples are similar, and thus the pyrolysis gives much the same products but not the same amounts. An example is given in Figure 5-30 showing the chemical structure of amylose and amylopectin. The only difference between the two samples is that one is linear and the other branched. The resulting pyrograms from 100% amylopektin and a blend of amylopectin:amylos 80:20% is shown in Figure 5-31, where few differences can be identified with the naked eye.

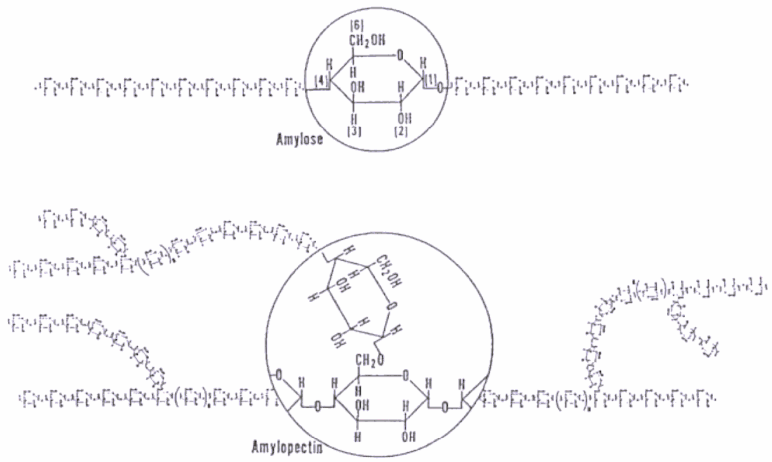


Figure 5-30. Structure of amylose and amylopectin.

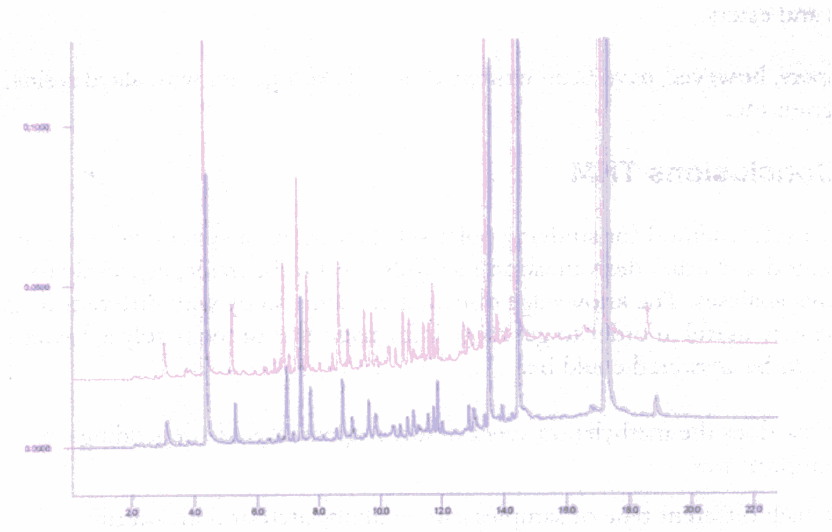


Figure 5-31. Two samples, 100% amylopectin (upper) and a blend of 80:20% amylopectin: amylose (lower), an example of two very similar chromatograms.

Examples of two different chemometry methods are given in this chapter:

1. Principal component analysis (PCA). The method is suitable for making qualitative analyses of samples by identifying differences between the pyrograms. The method will be exemplified by an analysis of lipopolysaccarides (LPS) from nine different bacteria.

2. Partial least squares (PLS). The method is suitable for making quantitative analyses, and will be exemplified by the blends of amylose and amylopektin shown in Figure 5-31 above.

5.4.1 Principal component analysis (PCA)

PCA is a qualitative analysis model and can explore for example: similarities, dissimilarities, outliers and grouping among the objects (samples). The results from PCA can be read out of score and loading plots, see Figure 5-33 and Figure 5-34 below. The closer two samples are in a score plot, the more similarities they have.

The necessary data for making a qualitative analysis with PCA is e.g. the peak area and/or the peak height for a number of peaks from each sample that you wish to characterize. An example is shown in Table 5-4, where each row represents a sample (object), and each column represents a peak retention time (X-variable).

Table 5-4. An example of a spreadsheet with retention time of the peaks as variables and the samples as objects. In this example each sample is pyrolyzed twice to give information of the reproducibility.

Variables→

Objects↓

Sample/Rt	2.47	2.6	3.12	4.09	5.13	5.8	6.12	6.17	6.24	6.31	6.35	6.64	7.17
1a	0	0	0	0	0	2.67	2.68	0	0	1.08	1.49	2.58	0
1b	0	0	0	0	0	2.52	2.4	0	0	0.95	1.28	1.98	0
2a	0	0	0	0	0	0	0	0	0	4.27	0	0	9.39
2b	0	0	0	0	0	0	0	0	0	4.03	0	0	8.29
3a	0	0	0	1.71	0.97	0	0	1.89	0	5.32	0	0	8.23
3b	0	0	0	1.72	0.87	0	0	1.95	0	5.43	0	0	6.1
4a	0	0	0	0	0	0	0	0.6	0	0	0	0	4.79
4b	0	0	0	0	0	0	0	0.98	0	0	0	0	4.36

In order for the method to work, the number of variables (peaks) must be more than the number of objects (samples).

5.4.1.1 Example: Grouping of Gram-negative Anaerobic Bacteria

Lipopolysaccarides (LPS) were prepared from nine different bacteria, four different genus and nine different strains shown in Table 5-5. The LPS were pyrolyzed twice at 600°C for 2 s, see Figure 5-32.

Table 5-5. Samples used in the LPS study.

Sample no.	Genus	Species	Strain
1a and b	Bacteroides	fragilis	NCTC 9343
2a and b	Fusobacterium	necrophorum	NCTC10575
3a and b	Fusobacterium	necrophorum	Fus-MC4
4a and b	Fusobacterium	nucleatum	NCTC 10562
5a and b	Fusobacterium	mortiferum	VPI
6a and b	Leptotrichia	buccalis	NCTC 10249
7a and b	Veillonella	parvula ss. parvula	Veill ATCC 10790
8a and b	Veillonella	alcalescens ss. alcalescens	Veill ATCC 17745
9a and b	Veillonella	alcalescens ss. dispar	Veill ATCC 17748

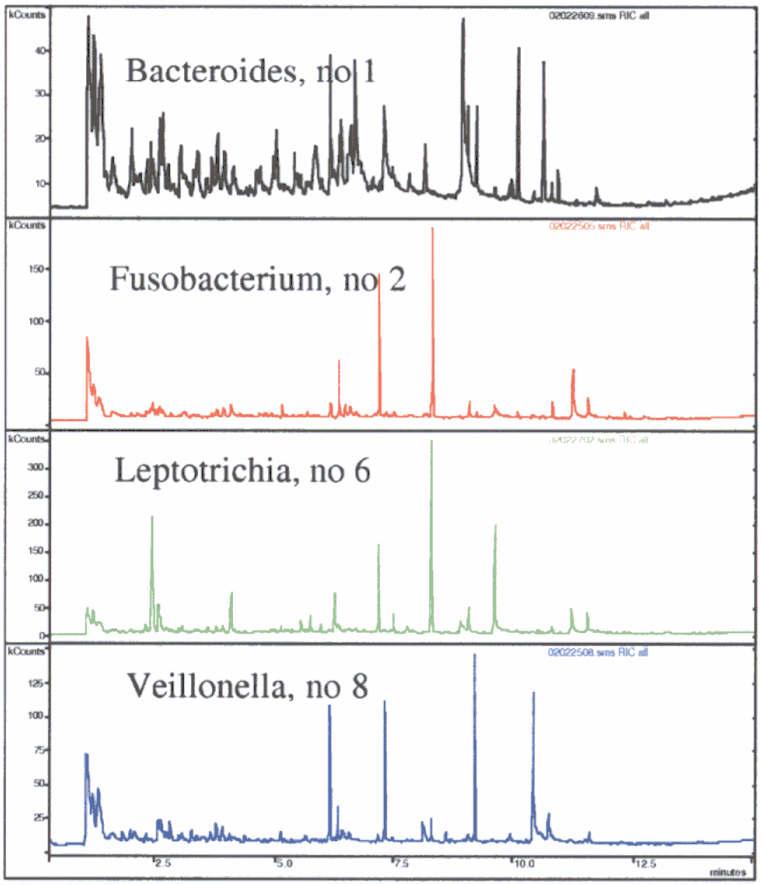


Figure 5-32. Examples of pyrograms from the four different genera.

A spreadsheet was made with peek area % and retention times of thirty-two of the different peaks in the pyrograms. Using this information a score plot was made, see Figure 5-33.

In a score plot the points are the different samples (objects), and groups and outliers can be identified. The principal axis t(1) is the linear combination of the variables showing the most difference between the objects, and the differences between objects are smaller

along the t(2) axis. For example there are more differences between Leptot. and Bact. than between Veill. and Bact.

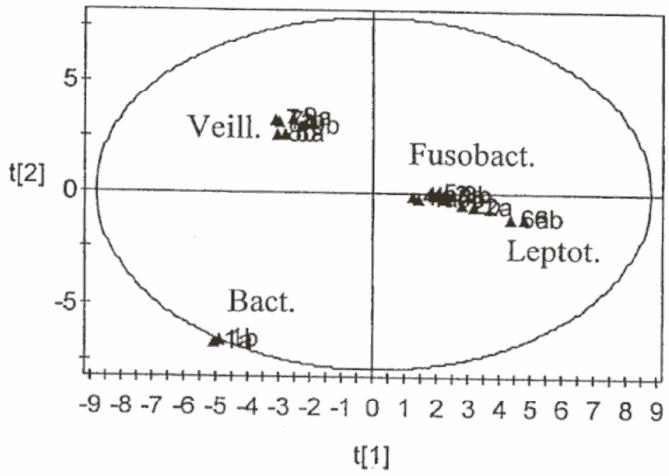


Figure 5-33. The score plot showing that the different genera are separated.

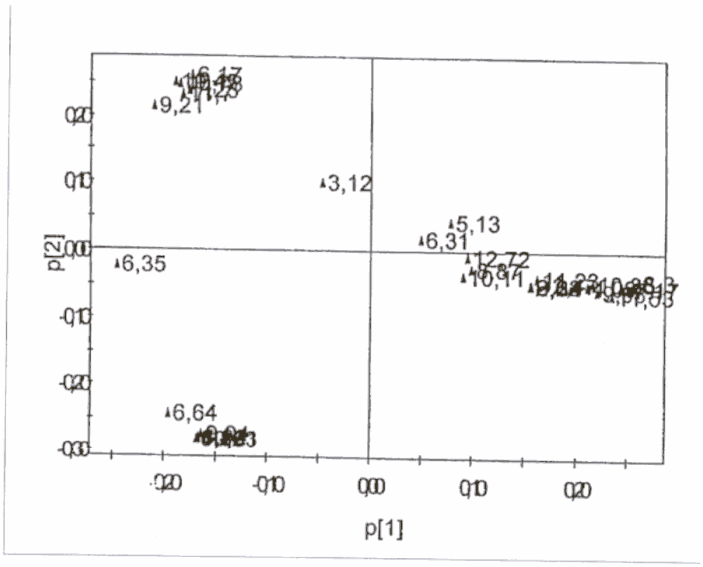


Figure 5-34. In a loading plot the dots are the different peaks (variables) named by the retention times.

In addition to the score plot a loading plot can be made, see Figure 5-34. In the loading plot the dots shows the different peaks with different retention times. If the dot in the loading plot is located in the same quadrant and in the same position as the dot in the score plot, it means that the peak in the loading plot is very much related to that specific sample. For example the dot with Rt. 12.72 is special for the Fusobact.

To achieve a better separation the results from each genus can be further examined. In Figure 5-35, Fusobacterium and Leptotrichia, located close together in Figure 5-33, have

been studied in detail. The loading plot, Figure 5-36, show which products that influence the differences.

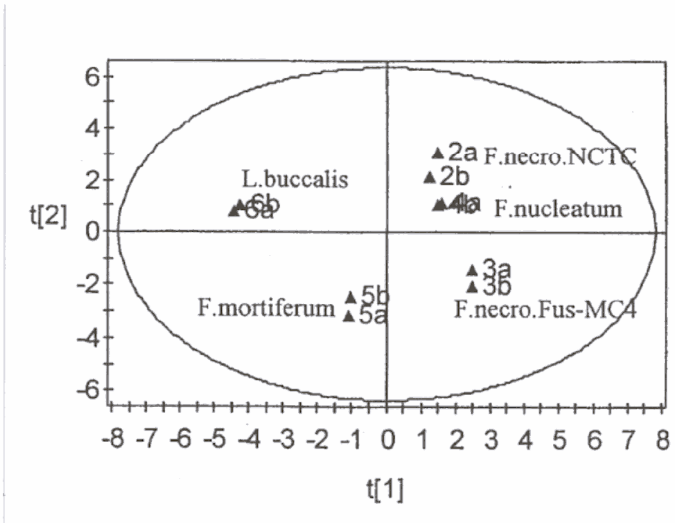


Figure 5-35. The cluster in Figure 5-34 containing four Fusobacterium and one Leptotrichia has been further differentiated.

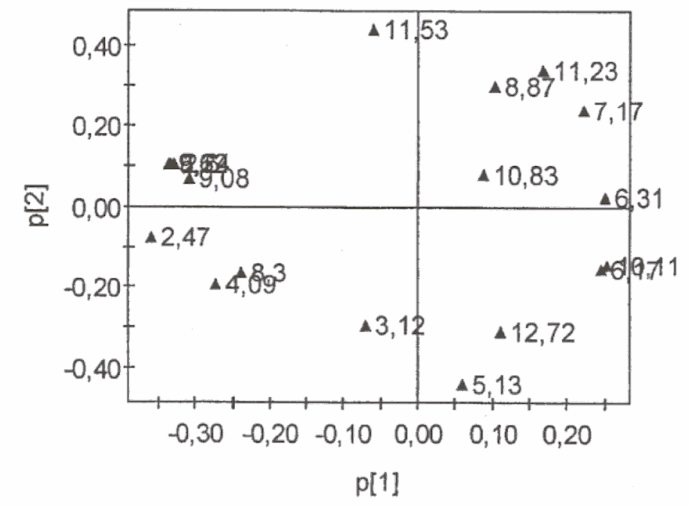


Figure 5-36. Loading plot from the results in Figure 5-35. The position of the retention times, makes it possible to judge which pyrolysis products that make the differences between the strains.

The closer the results from the same LPS the better is the reproducibility. In Figure 5-35 LPS no. 2 (Fusobacterium necrophorum NCTC) and no. 4 (Fusobacterium nucleatum) are very close, which means that they are similar. However, differences are obvious when the pyrogram are studied, see Figure 5-37.

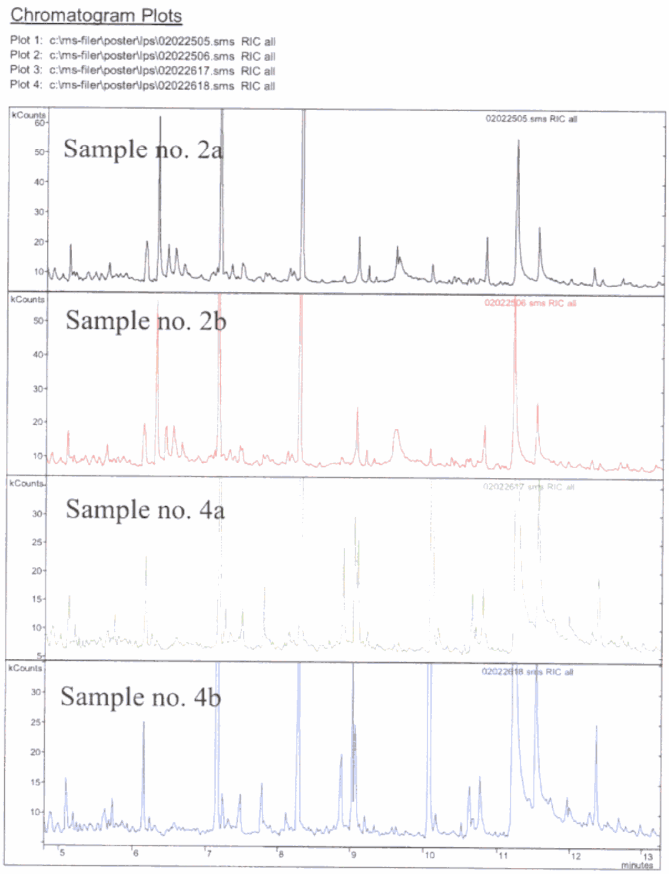


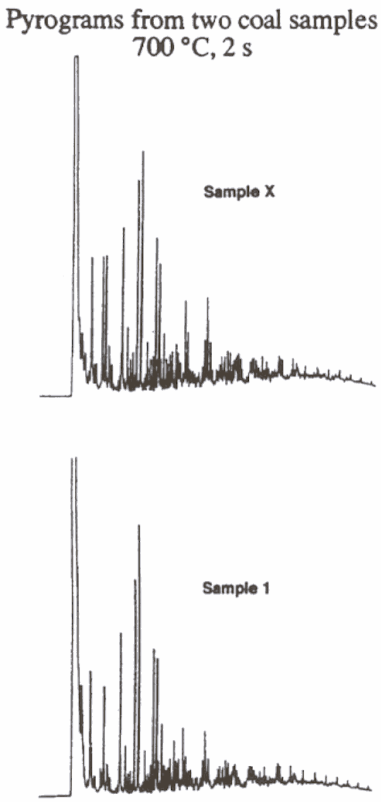
Figure 5-37. The pyrograms from the two samples no. 2 and 4 in duplicate from Figure 5-35 are presented.

5.4.1.2 Example: Are two coal samples from the same origin?

It was important to determine if two coals (1 and X) were of the same origin. They were pyrolyzed at 700 °C for 2s, see Figure 5-38. There are differences but hcan they be characterized?

To be able to evaluate the differences, two other coals (2 and 3) were pyrolyzed at the same conditions. Ten peaks with the same retention times were used from each coal and were evaluated with multivariate data analysis and gave a score plot, see Figure 5-39. In a score plot similarities and differences can be observed. In this case two groups are formed, with coal 1 and coal X in one group and coal 2 and coal 3 in another group. This result indicates that coal X is more like coal 1 than the two others.

In this example only two samples of each coal were pyrolyzed. To be able to draw more certain conclusions more samples of each coal needs to be pyrolyzed and included in the PCA analysis.



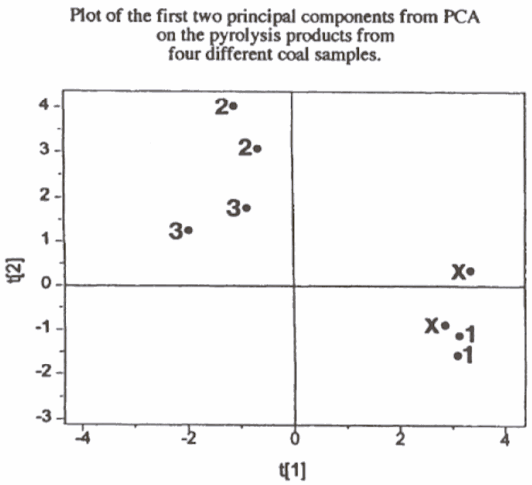


Figure 5-39. Score plot.

Figure 5-38. Pyrogram of coal samples X and 1.

5.4.2 Partial Least Squares (PLS)

In the qualitative method PCA no quantitative information is needed to perform the analysis. In a quantitative analysis with partial least square method (PLS), an additional quantitative parameter is needed for each object, such as the amount of cross-linking agent used in the example below.

The output of the PLS method is a calibration curve of the type shown in Figure 5-40.

5.4.2.1 Example: Quantitative Information of Cross-linked Starch

The PLS was used to quantify the cross linking agent in starch. Four starch samples with different amount of cross linking agent (0.021 to 0.12 %) were analyzed in duplicate. The results were used to make a method for quantification of the effect of cross linking.

The area ratio of thirty-seven peaks were used for the PLS-model. The PLS plot was made from the mean results of the four samples, see Figure 5-40.

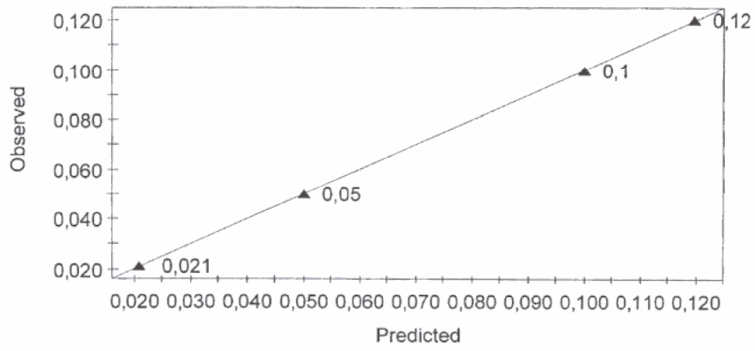


Figure 5-40. Calibration curve made by PLS from the result of four different cross linked starch samples, 0.021 to 0.12 %.

5.4.2.2 Example: Analysis of Coal with Py-GC/FID+FPD

Pyrolysis of coal yields a large amount of data. Multivariate data analysis may then be used to reduce of the large and complex data sets to a more comprehensible format.

In order to be able to quantify the different sulfur forms and volatile matter, the outlet of the GC-column was split into a FID and a sulfur selective detector (FPD). In this way the hydrocarbons and sulfur pyrolysis products could be detected simultaneously. A pyrogram from the FPD detector is shown in Figure 5-41.

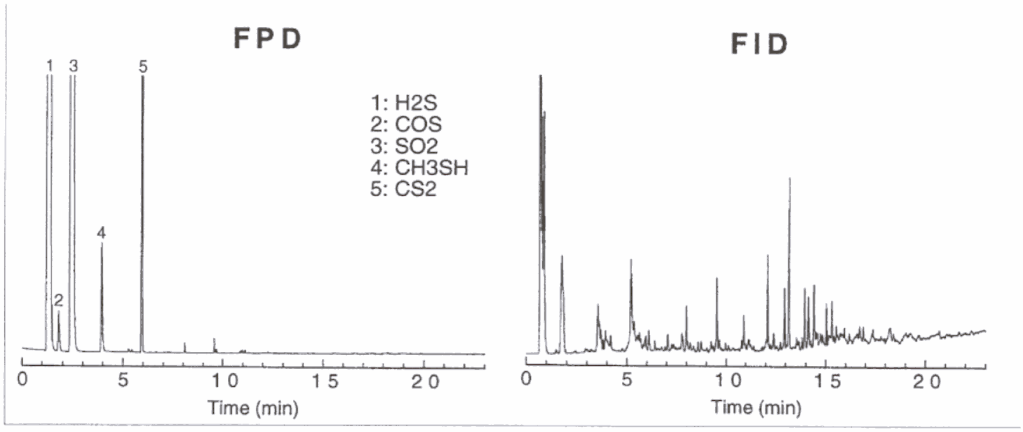


Figure 5-41. Example of pyrogram from the FDP and FID detectors.

The data were analysed with PLS plots to try to find quantitative information from different sulfur forms and volatile matter [12]. The results are shown in Figure 5-42.

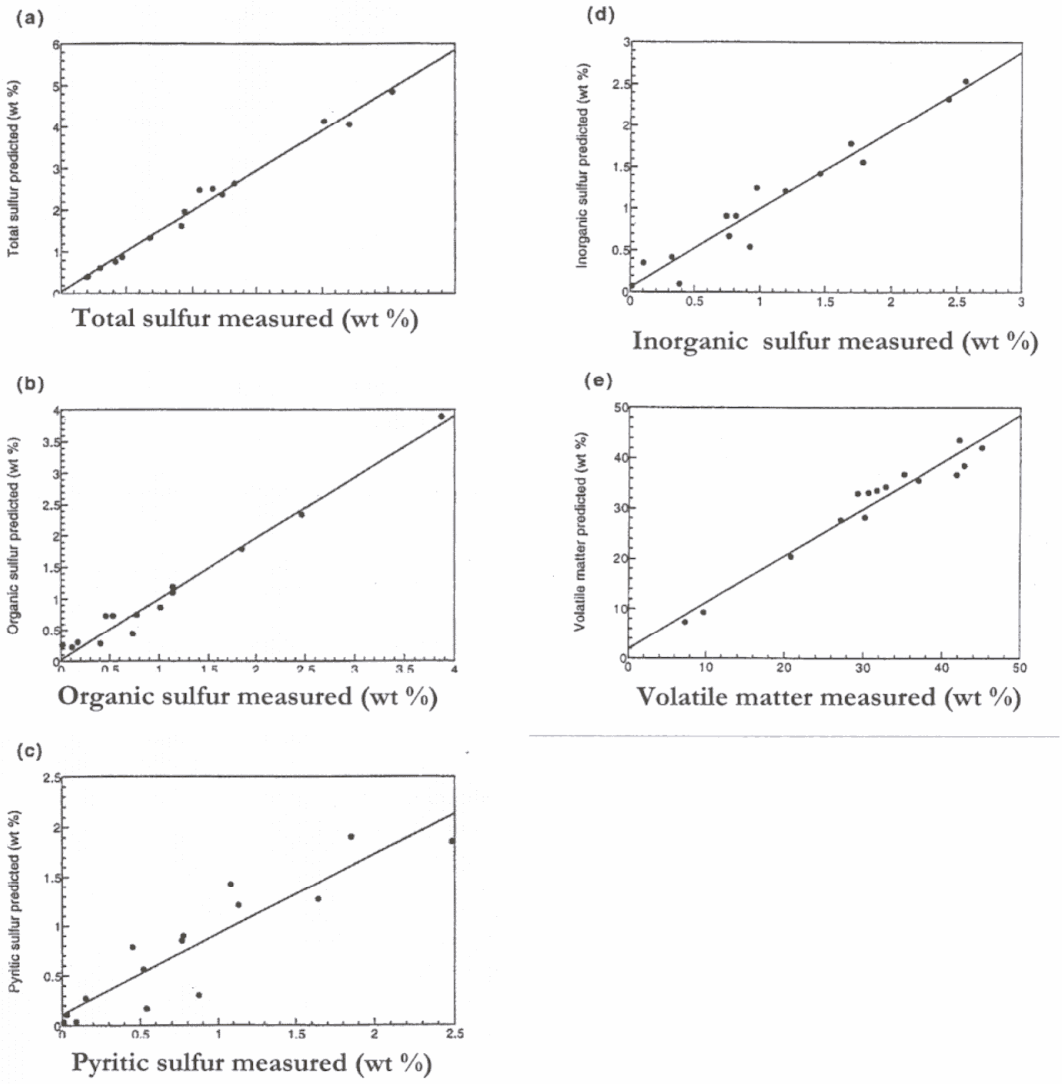


Figure 5-42. Analysis of sulfur in coal.

5.4.3 Conclusions Chemometry

It is easy to get results from chemometry programs but how reliable they are depend on the objects and variables that are used in the analysis. Treat your row data carefully and look at the result in a skeptic way.

Chapter 6

6 Concluding Remarks

Throughout the years people working in other analytical fields such as IR, NMR and HPLC have been suspicious about analytical pyrolysis. My feeling is that it is because people have not learnt the technique at Colleges or Universities, and a concentrated effort is needed to learn a new technique by oneself. So far very few places offer courses of analytical pyrolysis, and people tend to stick with the old well-known techniques.

However, life is not that simple that one technique can solve all problems. I am confident that you will eventually encounter a problem that cannot be solved by traditional methods, but where analytical pyrolysis might be an option. It will certainly produce pyrograms with a lot of peaks, but if you can get reproducible results you can use all the information for e.g. product control and complaints. The differences will be shown by extra peaks and/or different peak areas. You can go further and identify the extra peaks to understand where they came from. You have the option to use different heating methods to understand what is going on in your complex sample. Then if the pyrograms still look the same you can try multivariate data analysis to identify the differences or methylation to handle the polar pyrolysis products.

With experience interpretation of the pyrograms will be easier, and with a pyrolyzer of your own you can start making your own library of the samples in your field with your Py-GC/MS-conditions, and understand the result from unknown samples better.

I hope that this course has given an insight of all the possibilities that analytical pyrolysis can offer.

Inger Ericsson

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