Extending the molecular application range of gas chromatography by in-injector pyrolysis

Erwin Kaal, Geert Alkema and Hans-Gerd Janssen

University of Amsterdam, the Netherlands
ATAS GL, the Netherlands
Unilever Research and Development, the Netherlands

Introduction gas chromatography

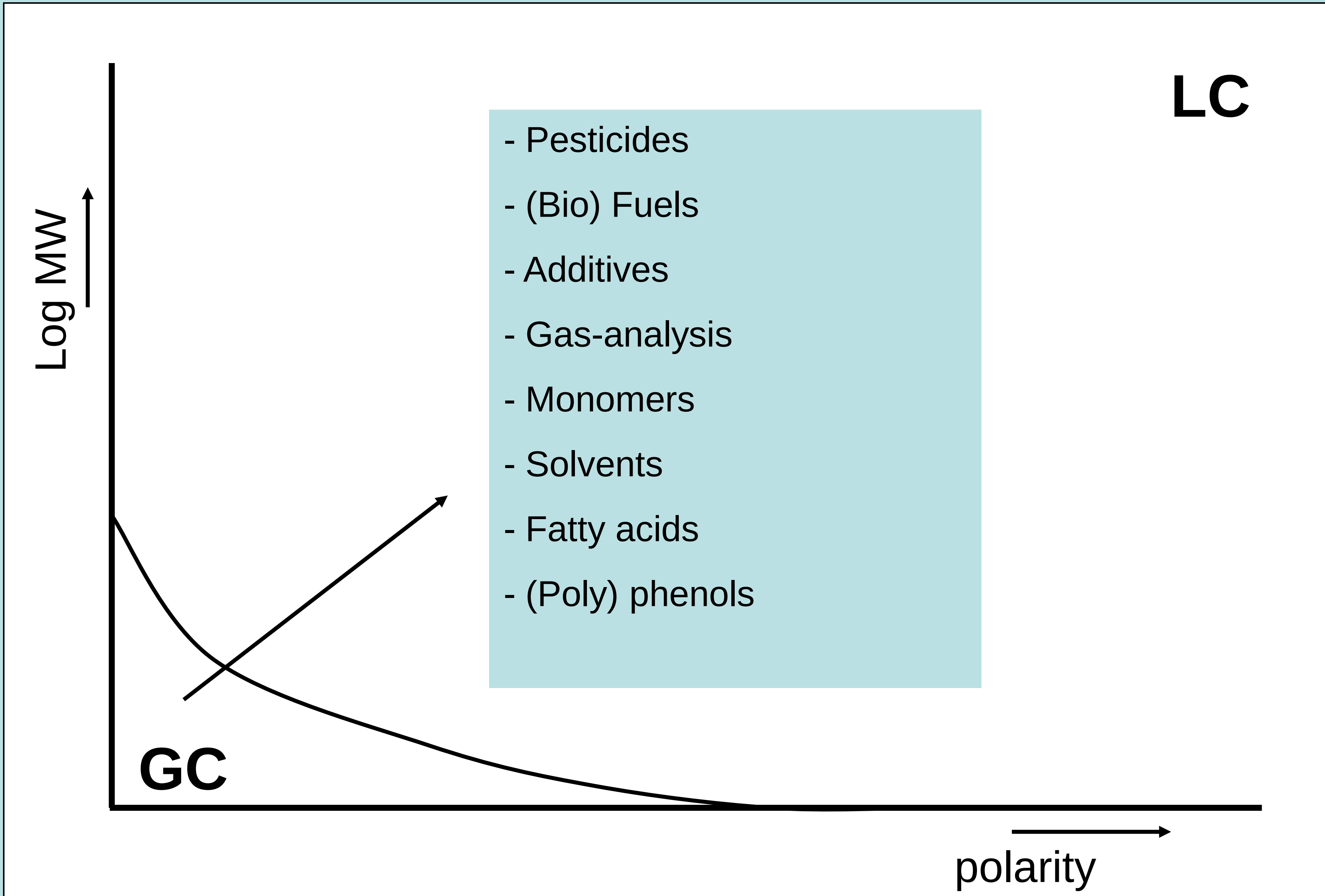
Advantages of GC

- High separation power
- Sensitivity
- Speed
- Easy identification of unknowns
- Not expensive

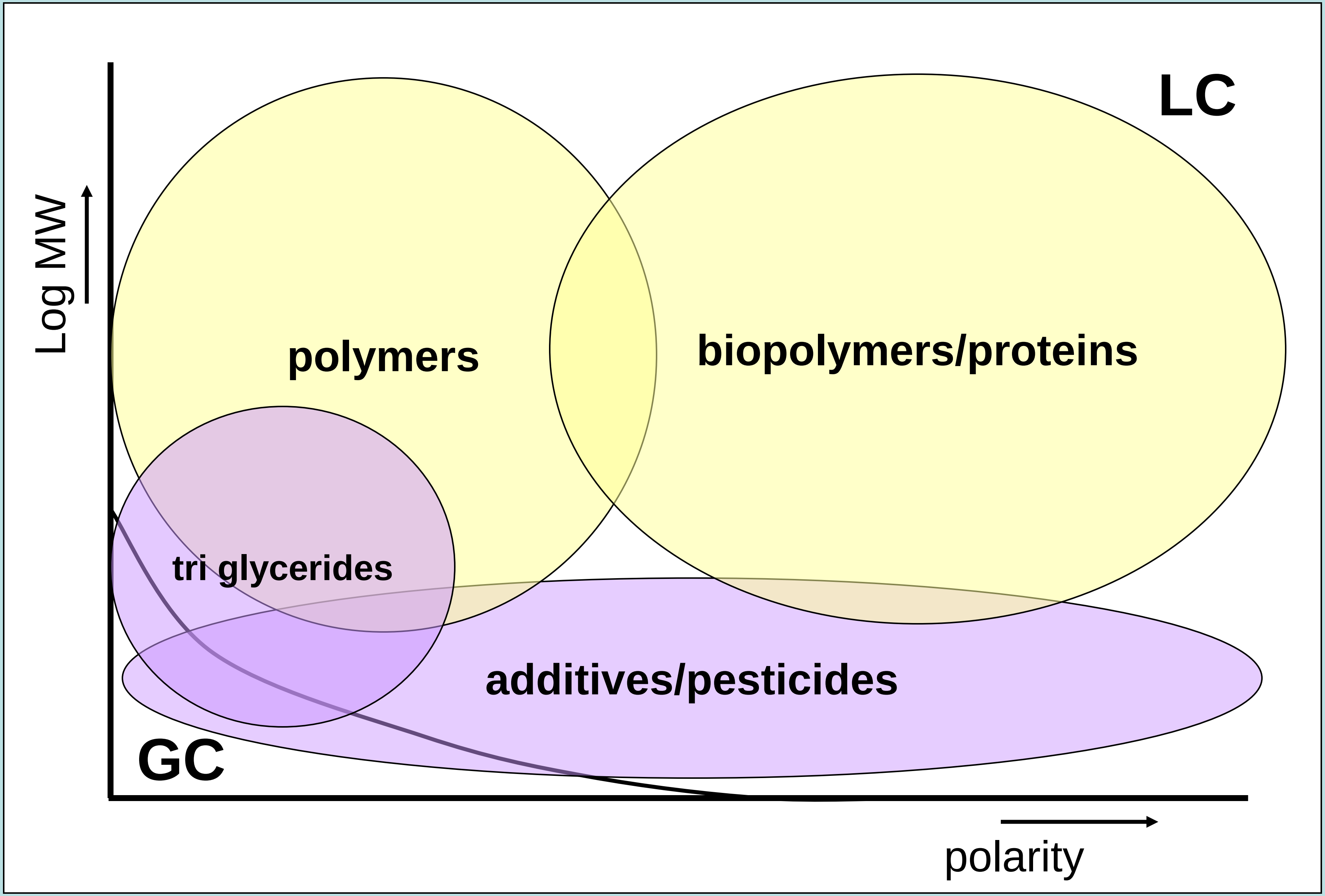
Limitations of GC

- Degradation of thermo labile compounds
- Polar compounds needs derivatization
- Mass limitations (>800-1000 Da)

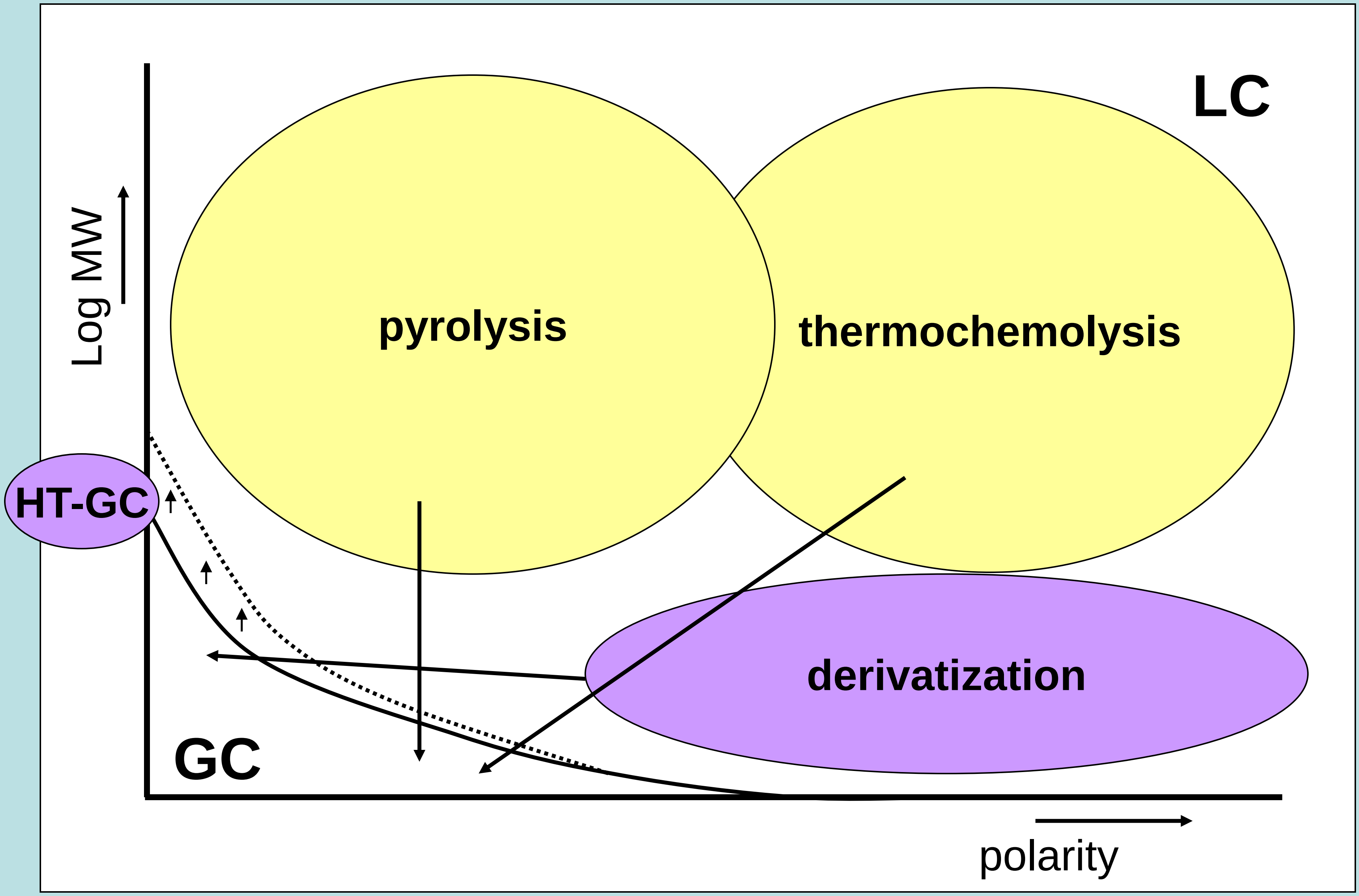
GC- versus LC-application area



Bringing more molecules into realm of GC

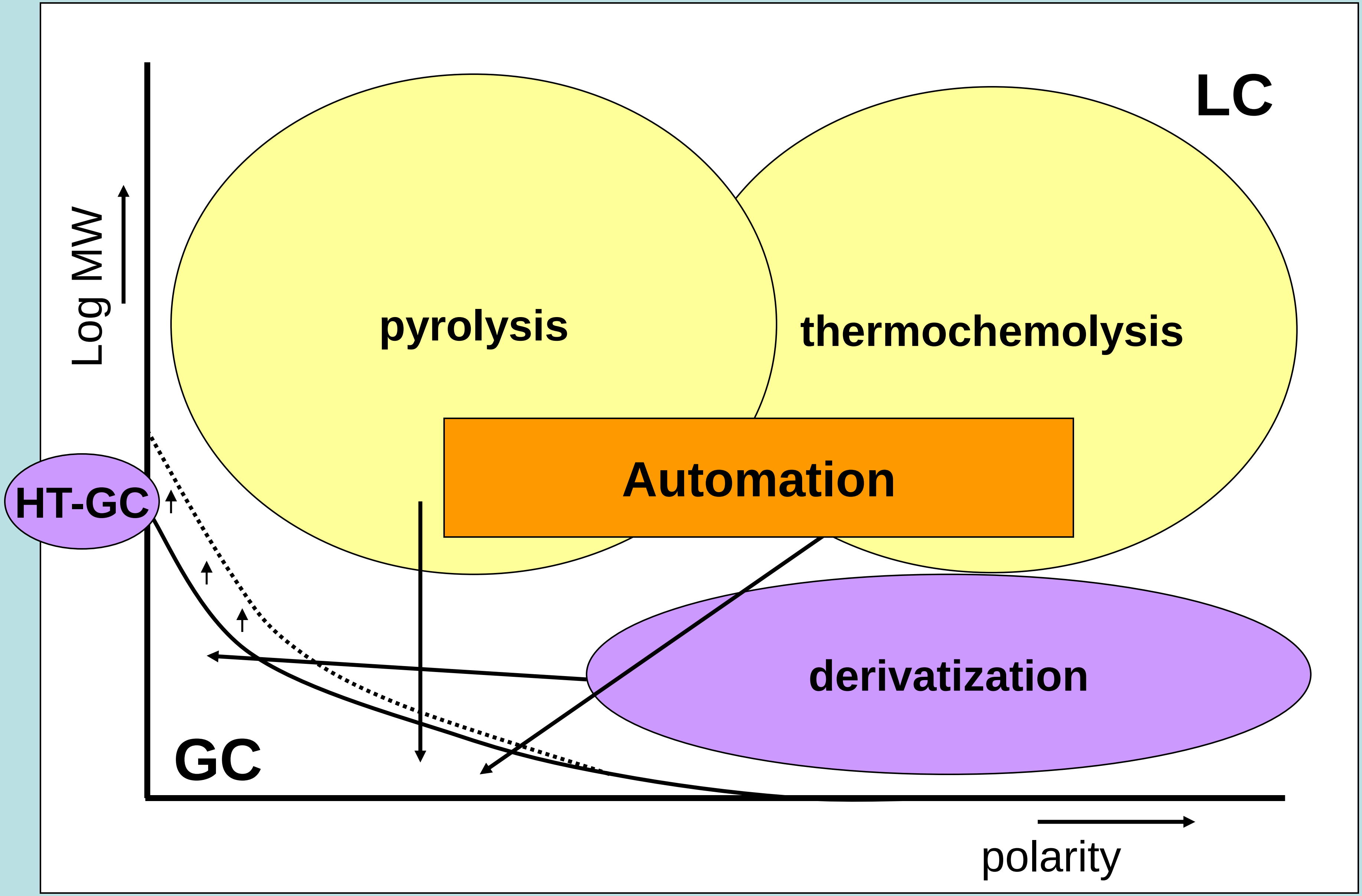


Bringing more molecules into realm of GC



Ref: H.G. Janssen, E. Kaal, J. Chrom. A 1201 (2008) 169

Bringing more molecules into realm of GC

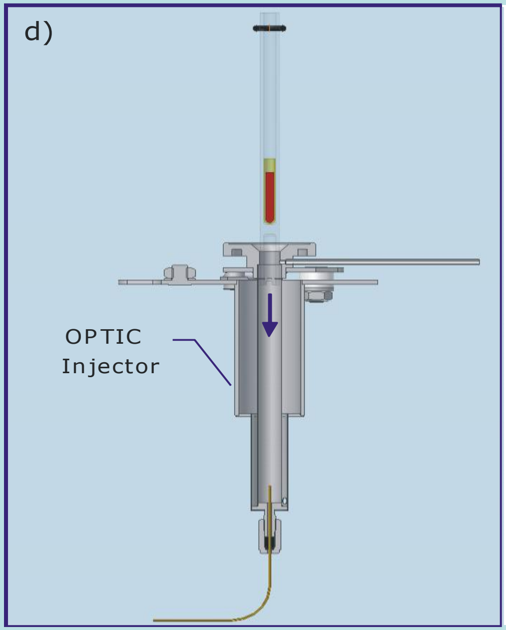


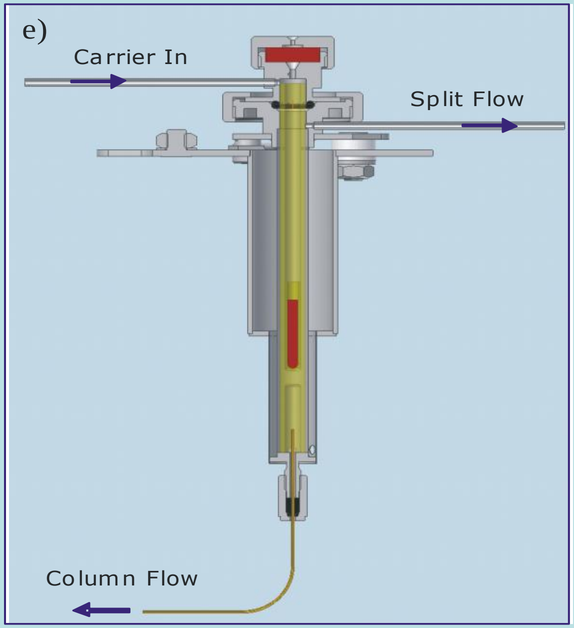
Extending the applicability

1. Automation
   - pyrolysis

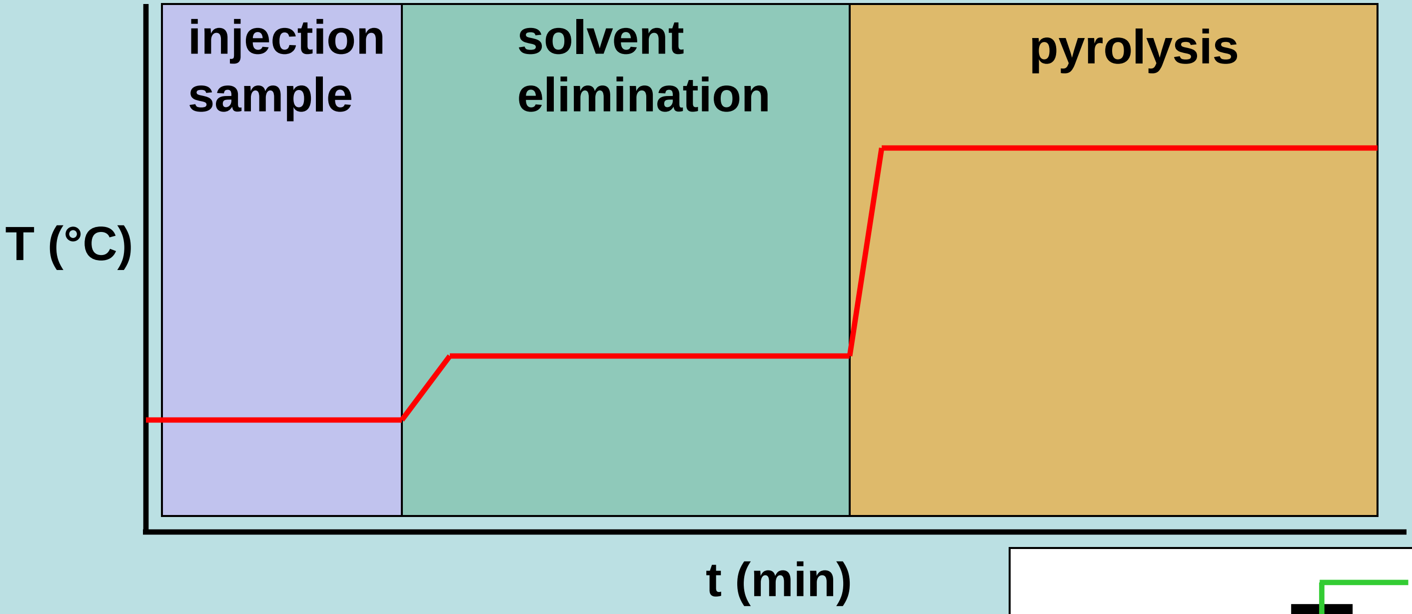
Automated pyrolysis:
in-injector pyrolysis for solid samples

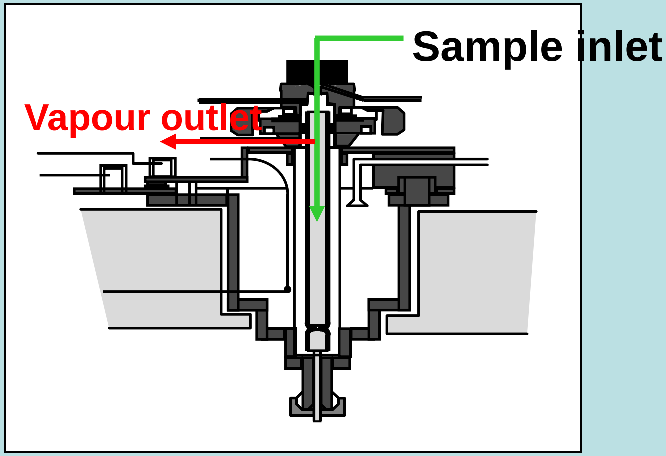
1. Put solid sample in a (micro vial of the) liner
2. Transport liner with sample into OPTIC injector with LINer EXchanger (LINEX)
3. Seal and purge the injector
4. Apply pyrolysis by heating the injector by 30 ° C/sec to 600 ° C
5. Dispose micro vial after analysis, clean and re-use liner





Automation pyrolysis:
Liquid injection of dissolved polymer





Advantages:

1. Sample is homogenious
2. Easy to inject quantitative amounts
3. Easy to inject low amounts
4. Pyrolysis direct on top of column

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Parameters to consider in Py-GC-MS using PTV-injector

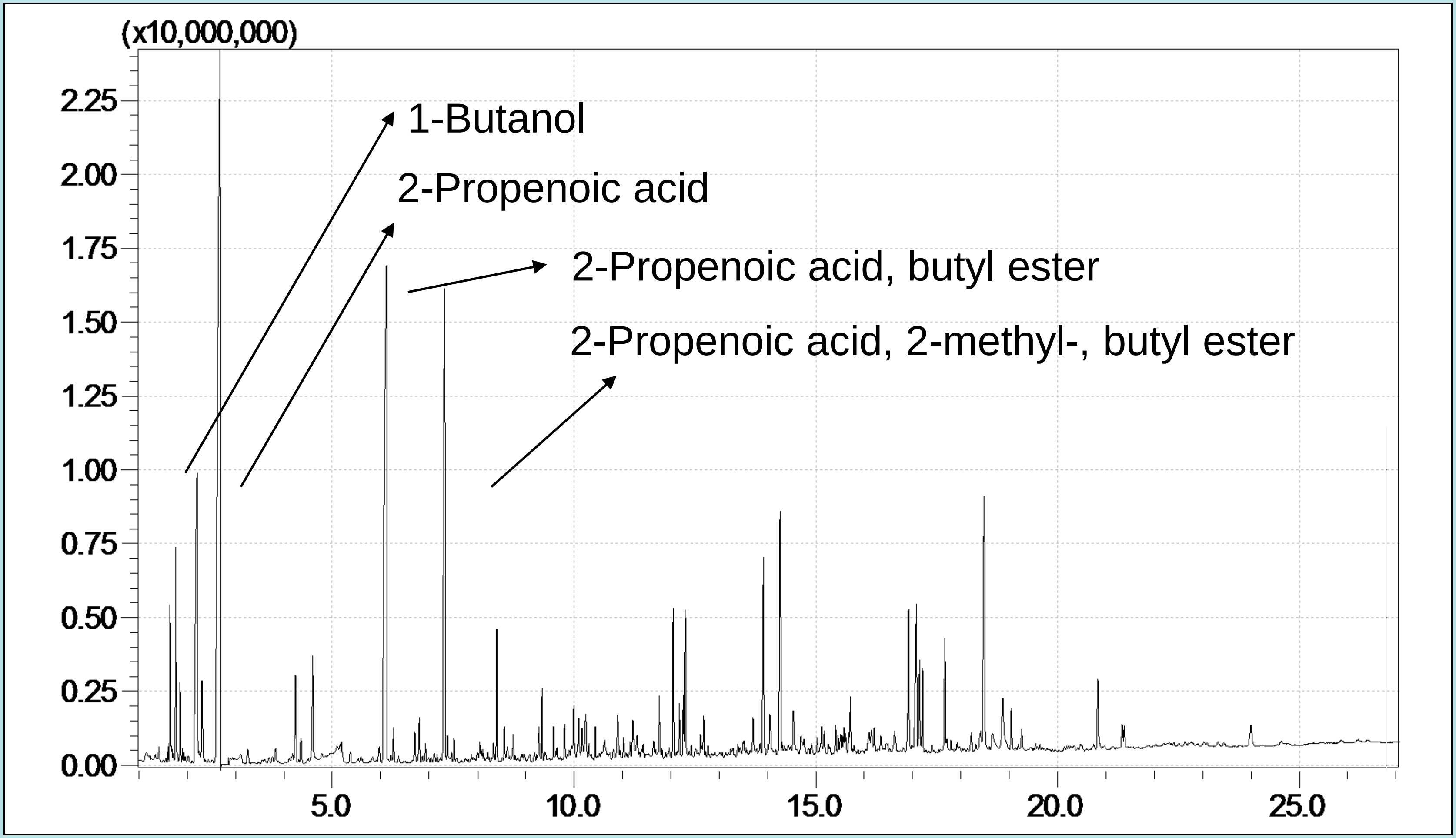
- **Repeatability pyrolysis:**
    - Large volume liquid injection
    - Approx. 100 µg/ml
    - Pyrolysis temp. 550 °C
  - For PMMA, PS, PBA, PCL: RSD < 4% (n=20)

- **Linearity pyrolysis:**
    - Large volume liquid injection
    - 0-170 µg/ml (7 standards)
  - For PMMA and PS: r^2: >0.999

- **Influence MW:**
    - Large volume liquid injection
    - 7 standards with different MW (2,000 - 1,500,000)
  - For PMMA and PS: RSD < 4%

Ref: E. Kaal et al; J. Chrom. A 1143 (2007) 182

Example of Py-GC-MS with Optic 3 injector



40 µl of 0,1 µg/ml dissolved copolymer

Extending the applicability

1. Automation:

- pyrolysis: solid samples → LINEX
  dissolved samples → ‘normal’ injection

- thermochemolysis

thermochemolysis: combined derivatization and pyrolysis

Principle: pyrolysis with *in-situ* thermally assisted derivatization

Advantages:

- Simple sample preparation
- Very fast and robust
- Pyrolysis can occur at lower temperatures (less unexpected secondary reaction products)

Difficulties:

- Quantification (also non-derivatized compounds detected)
- Repeatability of the derivatization?
- Process not well understood

Most used reagent: tetramethyl ammonium hydroxide (TMAH)

→hydrolysis followed by methylation

thermal methylation (THM)

weight solid sample	10 µg to 1 mg
add of TMAH	2 µl to 1 ml solution (25% TMAH) water or methanol
dry mixture	vacuum or oven
sealing of ampoule	Inert conditions
Incubation in oven	10 min to 27 hours (100 to 250 °C)
extraction of mixture	commonly dichloromethane
concentration	N_2 stream
GC-injection	1 or 2 µl

thermal methylation (THM)

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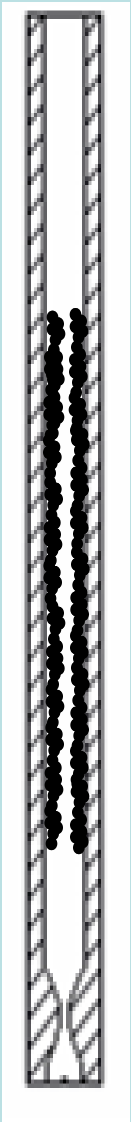
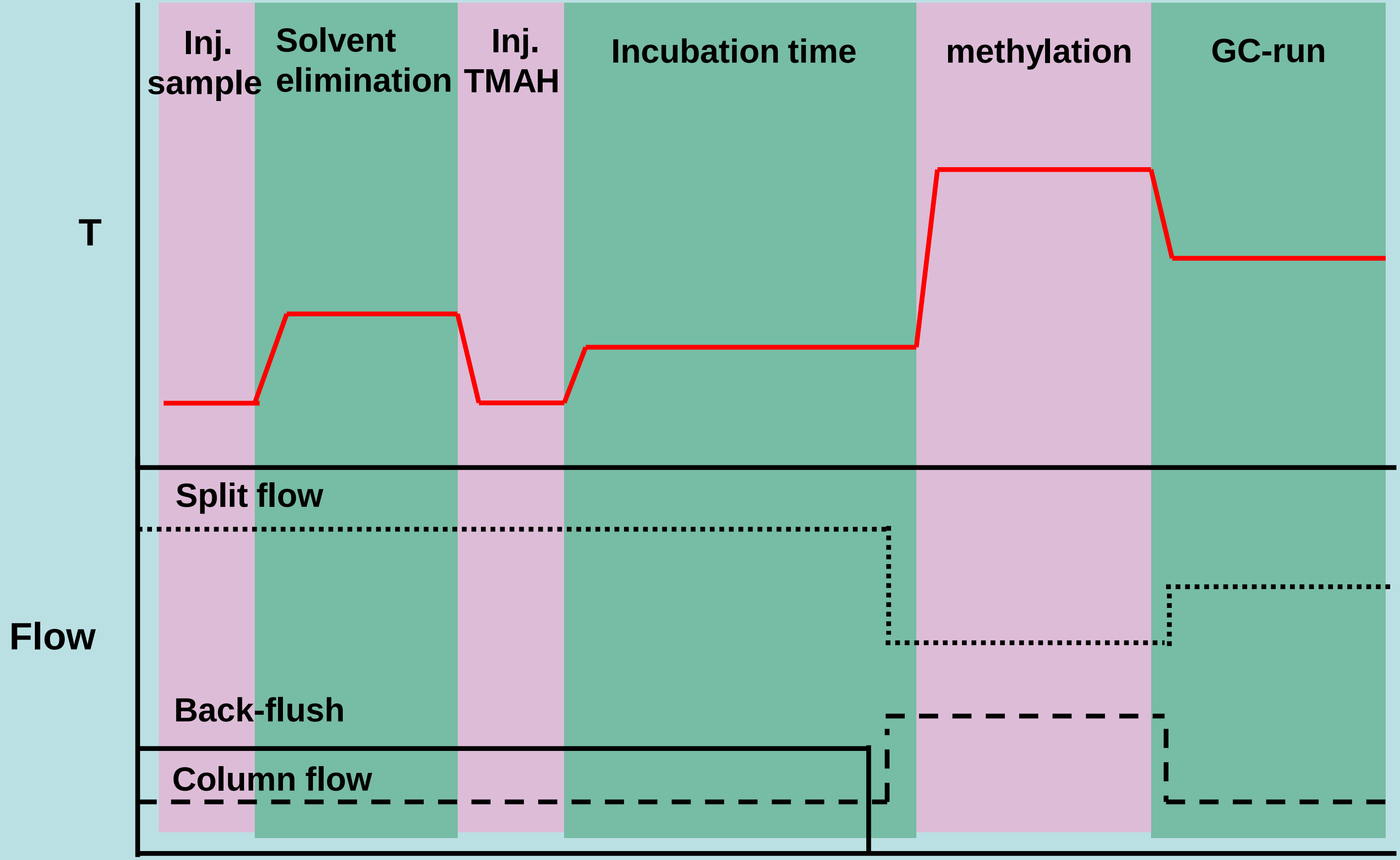
- add of TMAH →
- dry m
- inert conditions
- n in oven → 10 min to 27 hours (100 to 250 °C)
- extraction of mixture → commonly dichloromethane
- concentration → N_2 stream
- GC-injection → 1 or 2 µl

How to automate ?

Fully automated in-situ thermochemolysis





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Optimization and performance THM-procedure

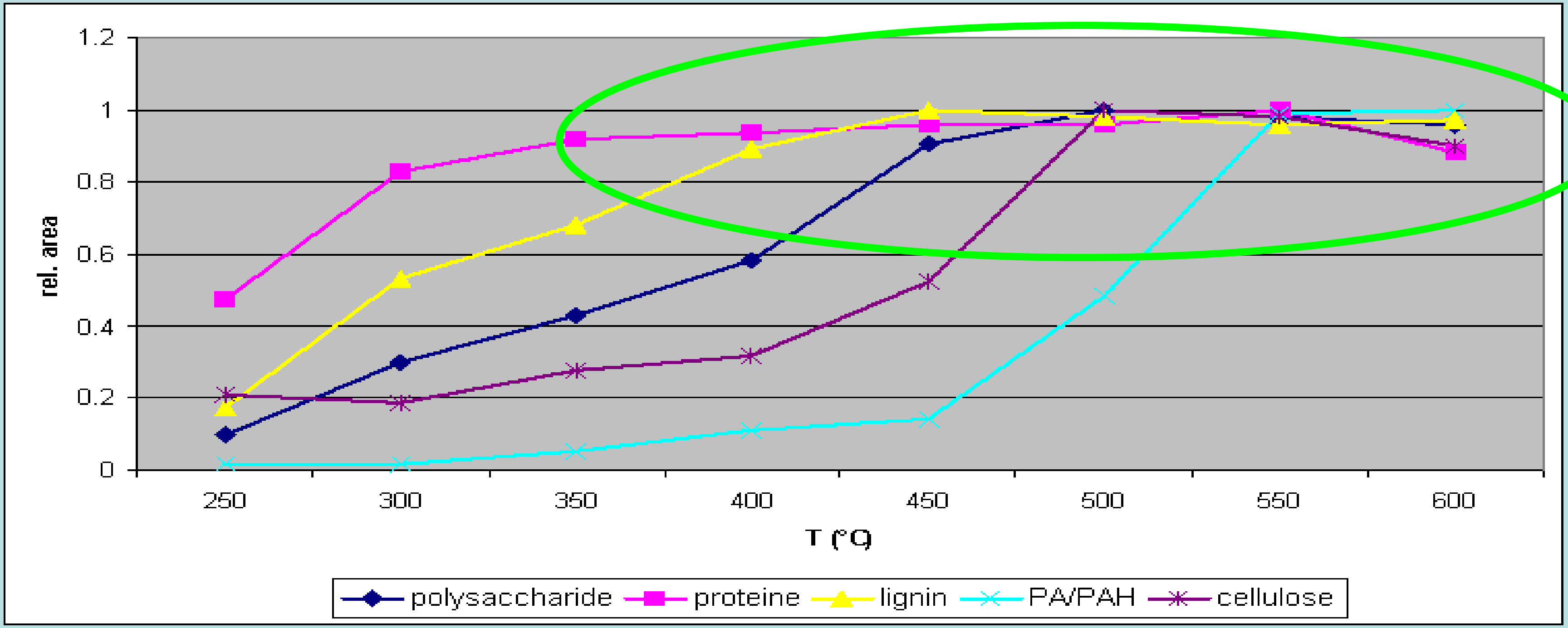
inj. sample	Solv. elimination	inj. TMAH	react. time	Pyrolysis
- temperature	- temperature	- conc. TMAH	- time	- time
- type liner	- time	- solvent	- temperature	- temperature
- concentration		- volume		
- volume		- temperature		

optimization: experimental design

parameters:

Injection temp.:	40 °C
Injection volume:	40 µl (sample)
Injection volume:	50 µl (reagens)
Conc. sample:	10-200 µg/ml
Conc. TMAH:	2% (50 µl)
Pyrolysis temp.	550 °C

Influence temperature on thermochemolysis process

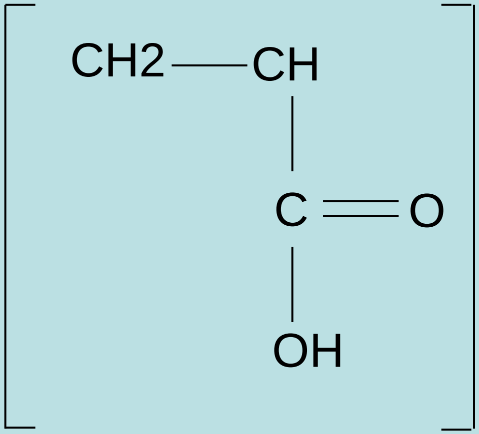


<u>Repeatability:</u>

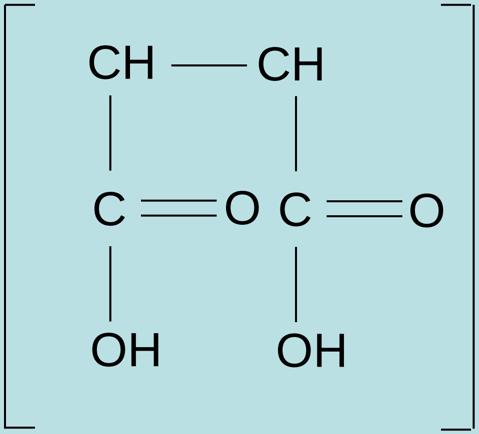
(sum of 30 peaks)

<u>Sample materials:</u>	*RSD (n=20)*
Polysaccharides	7.6%
PA/PAH copolymer	3.2%
Proteins	5.6%
Lignins	5.9%
Celluloses	7.6%

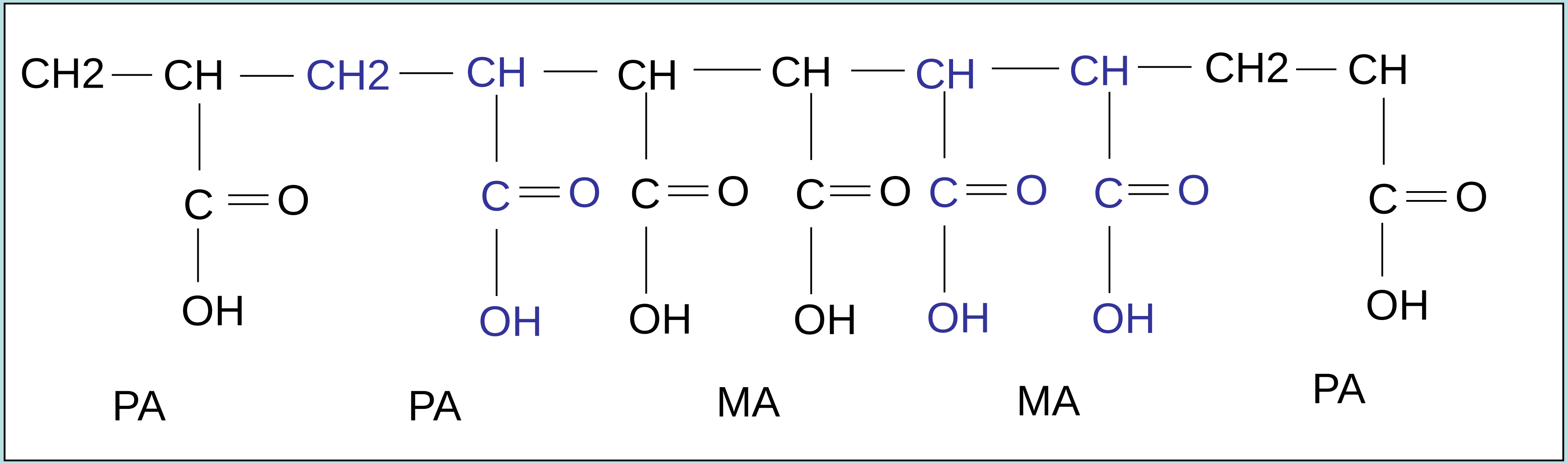
PA-PAH copolymer



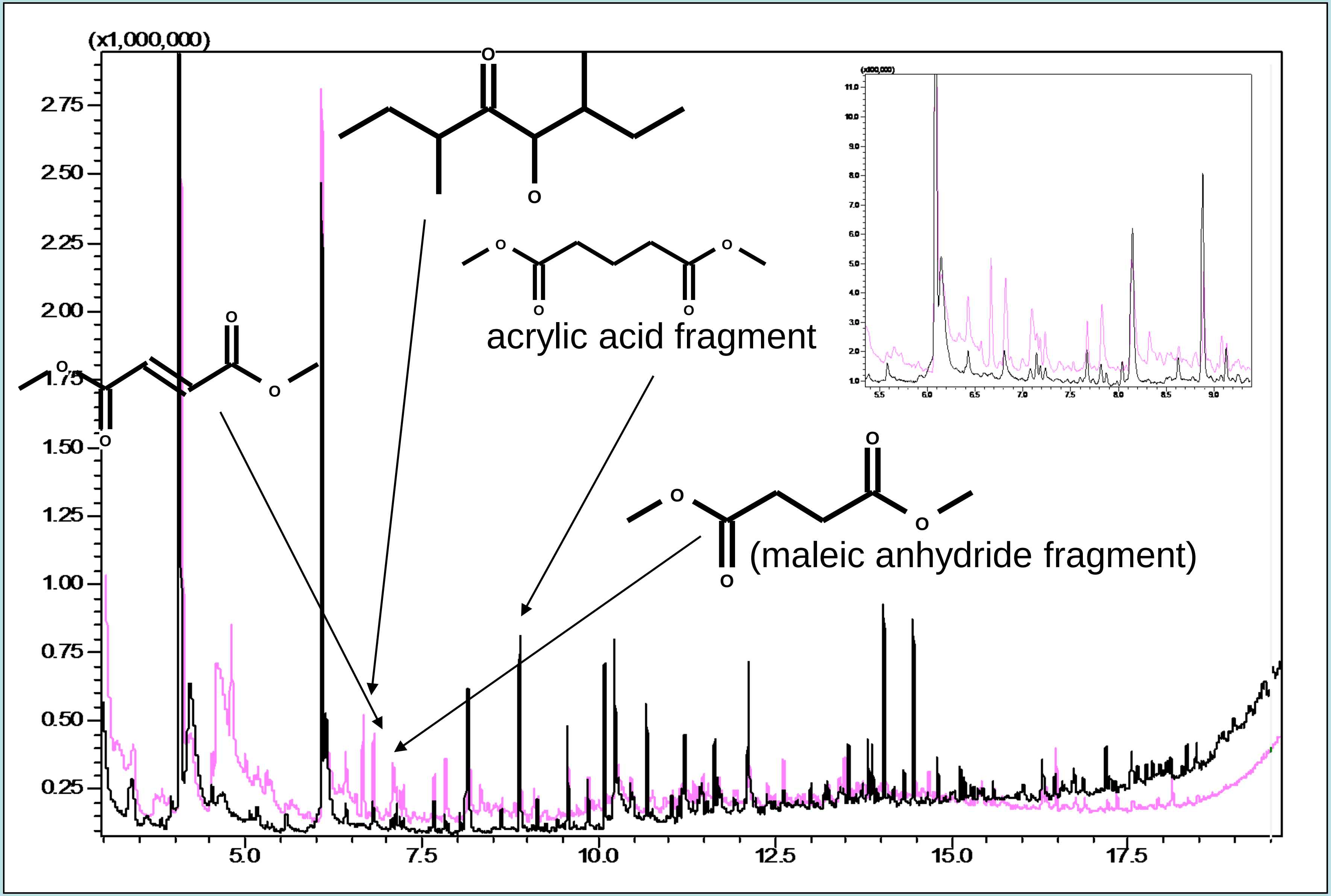
Polyacrylic acid



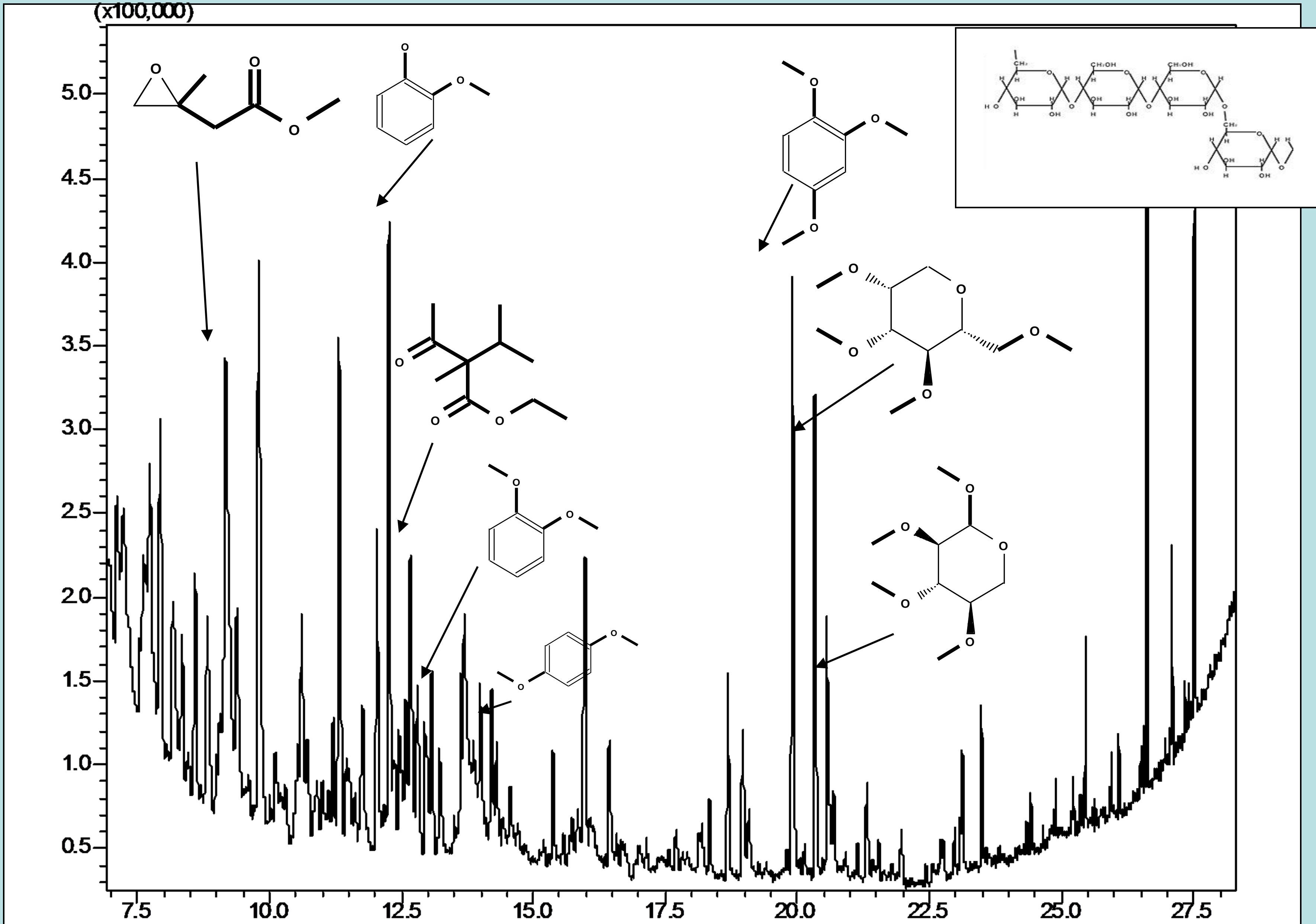
Polymaleic anhydride



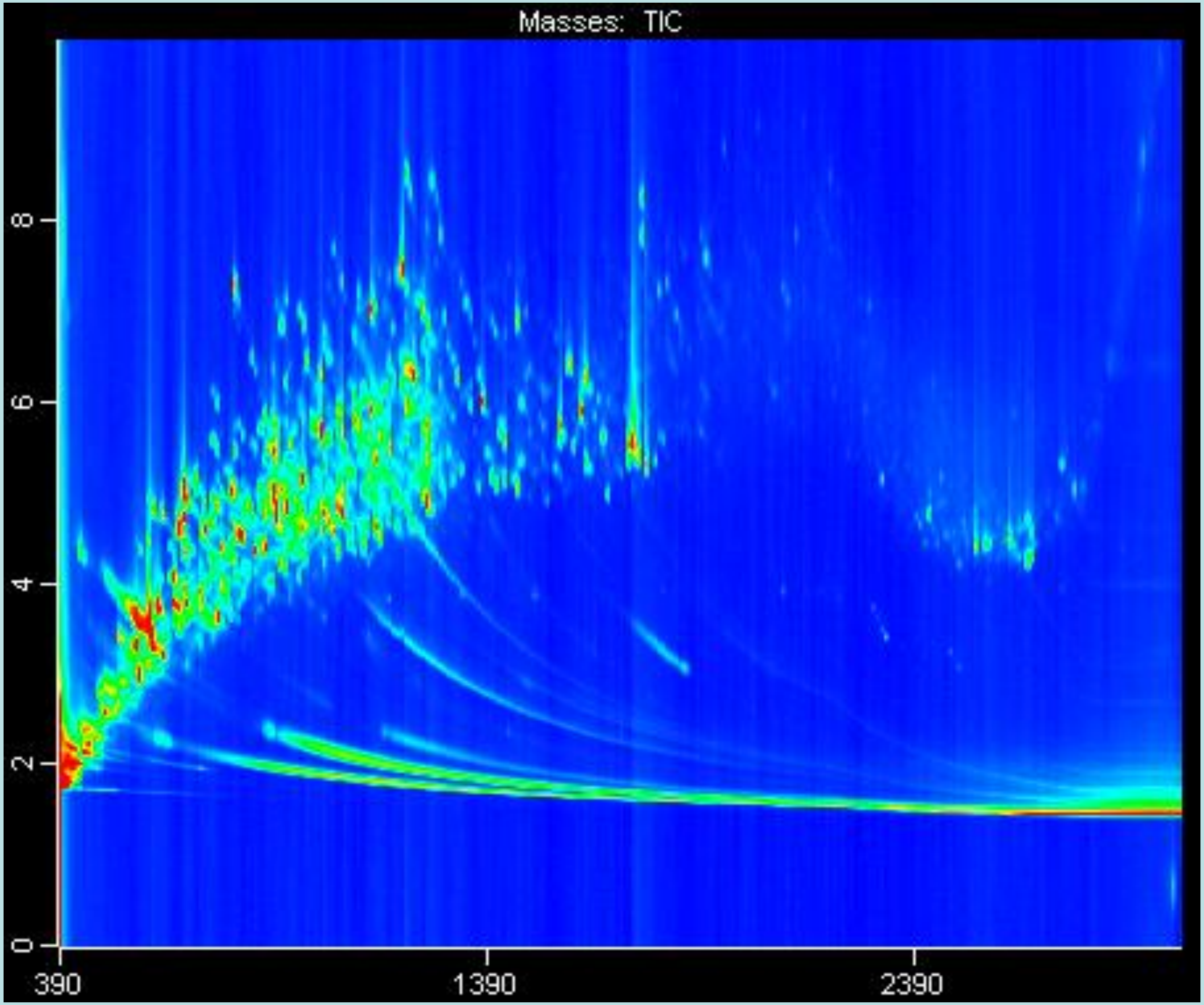
Difference PA and PA-PAH copolymer



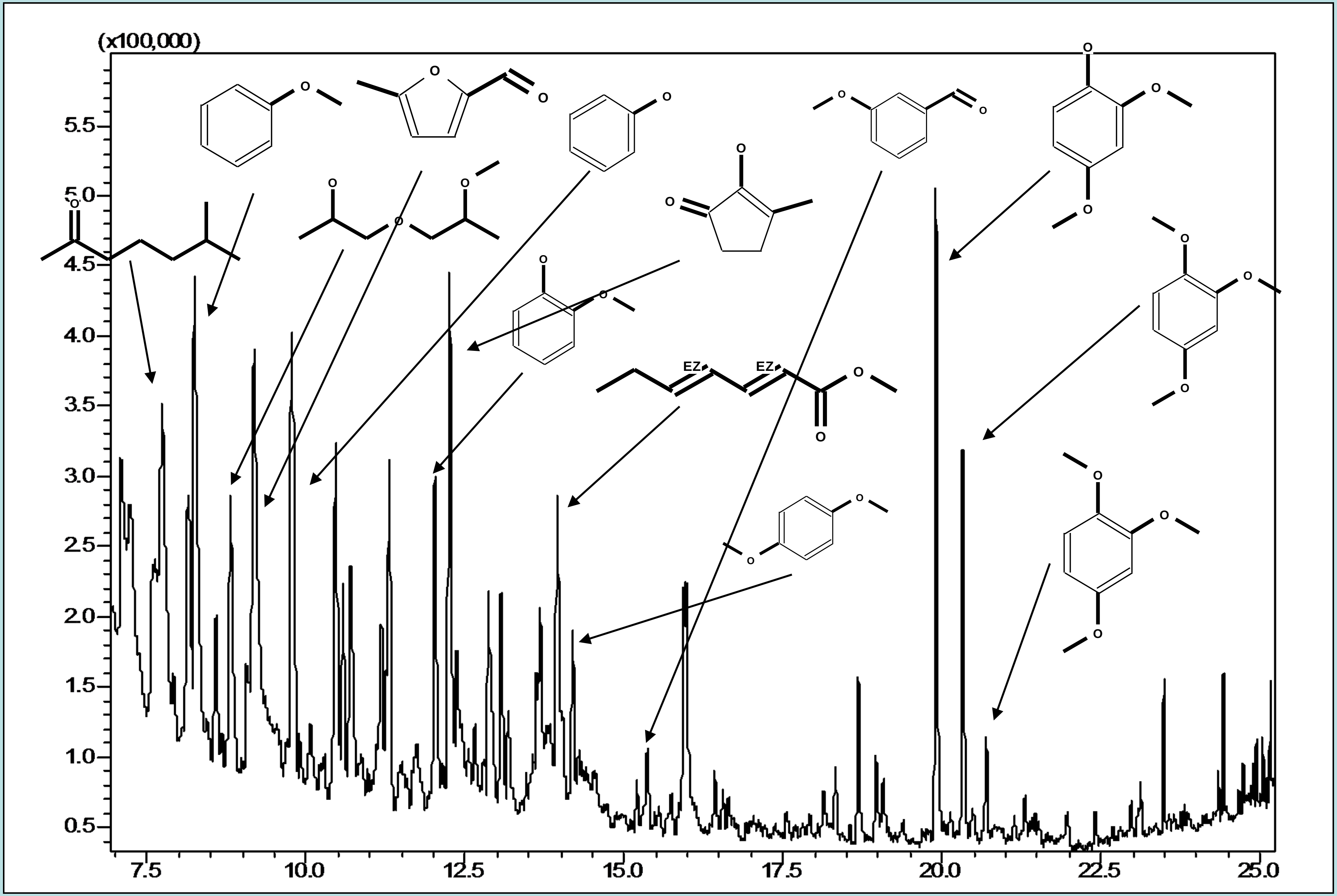
THM-GC of polysaccharide (Mw 45.000)



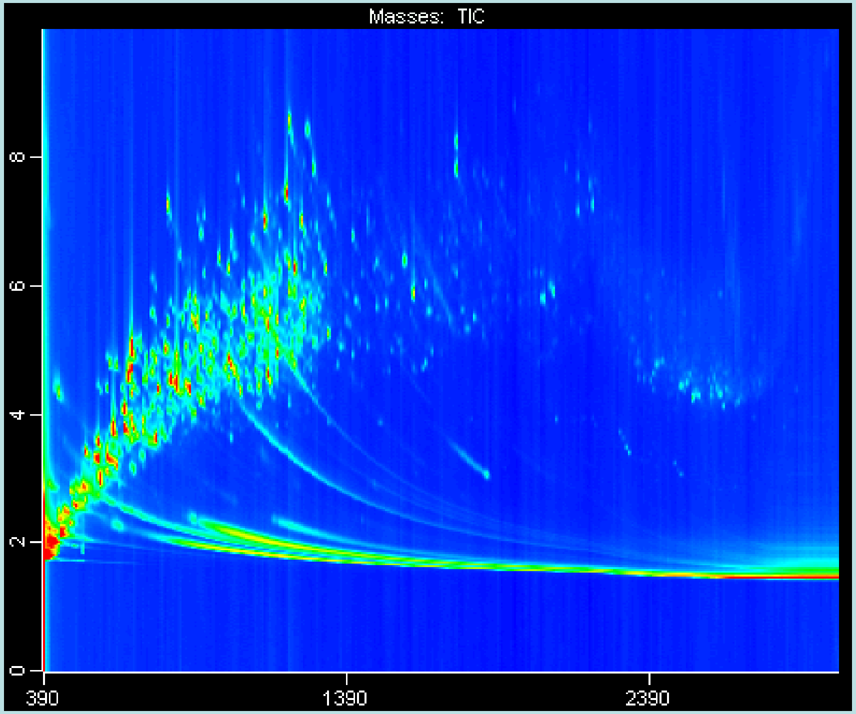
THM-GCxGC-TOF-MS of polysaccharide Pullulan 710.000Da



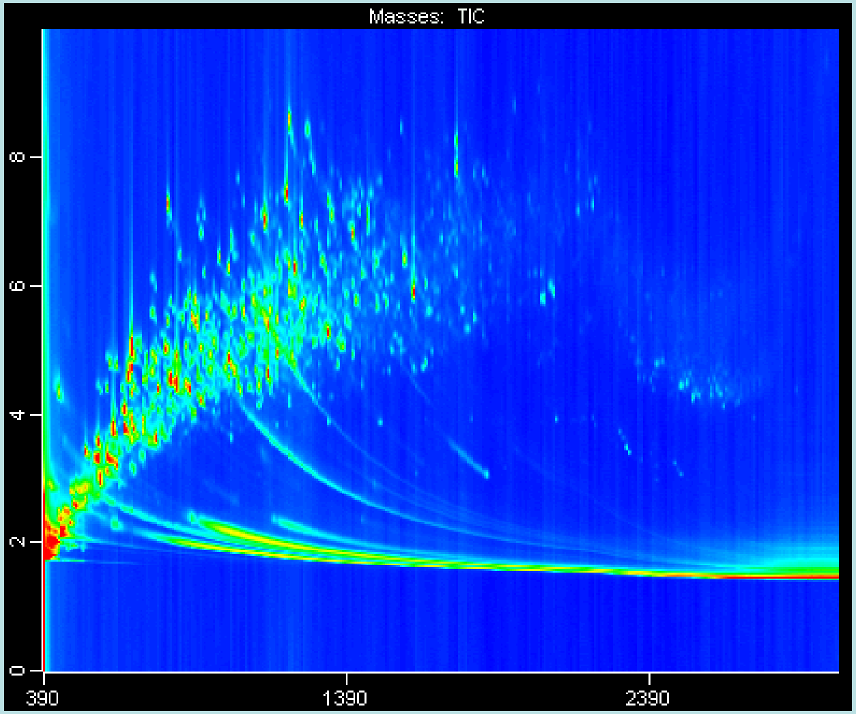
THM-GC of hydroxypropyl methyl cellulose



Comparison HPM-cellulose THM – GCxGC-TOF-MS

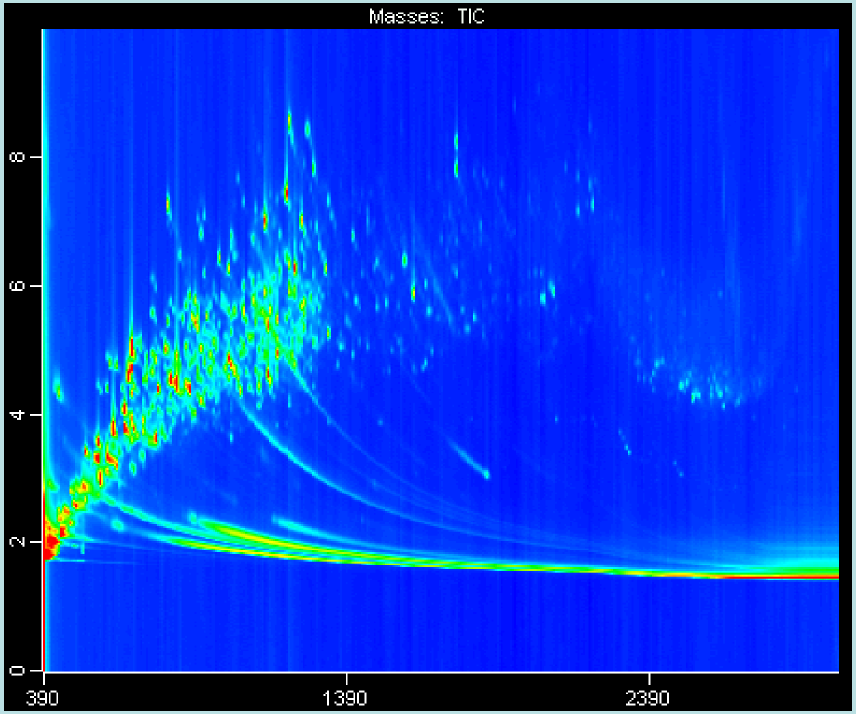


HPM-cellulose nr. 4

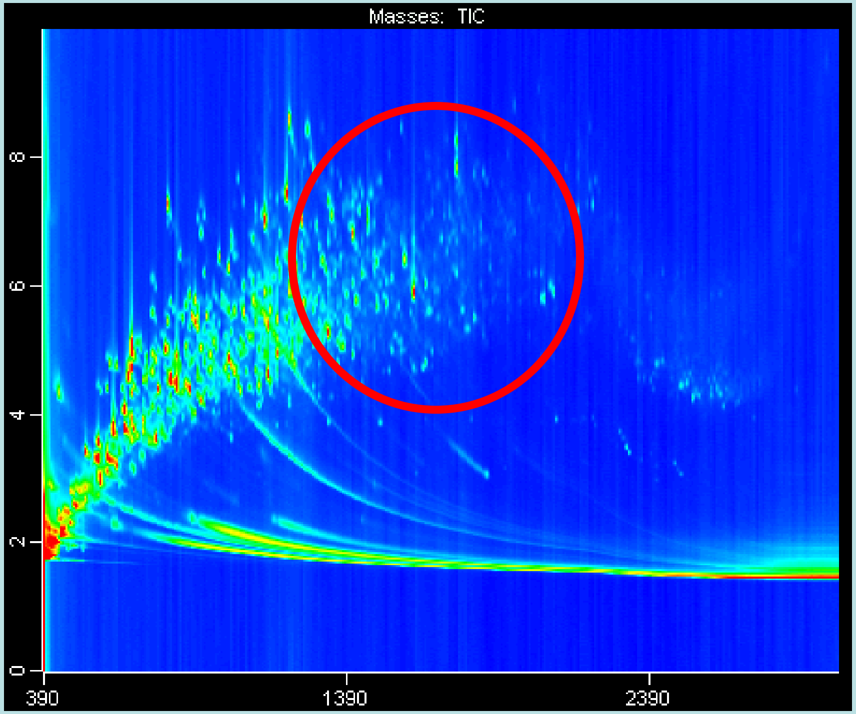


HPM-cellulose nr. 7

Comparison HPM-cellulose THM – GCxGC-TOF-MS



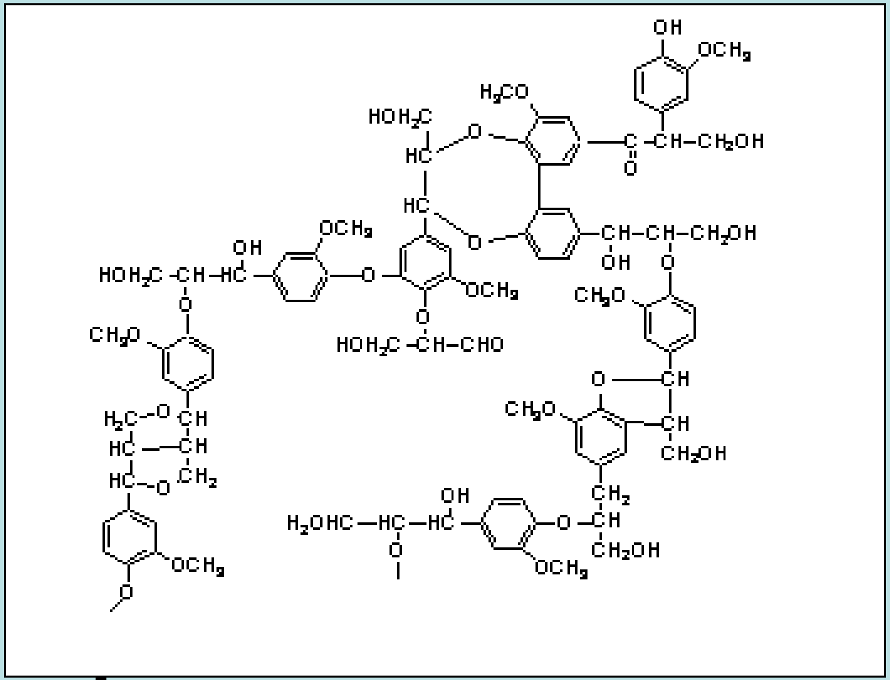
HPM-cellulose nr. 4

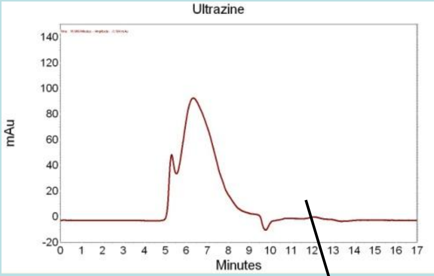


HPM-cellulose nr. 7

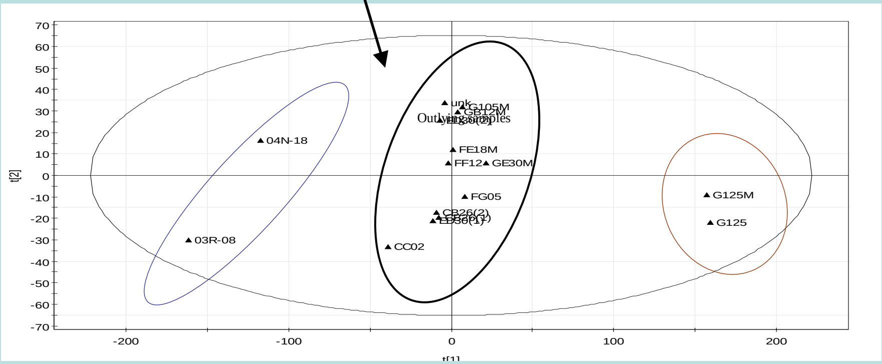
Correlating fingerprints and product properties

Characterization of Sulphonated lignins





LC-UV

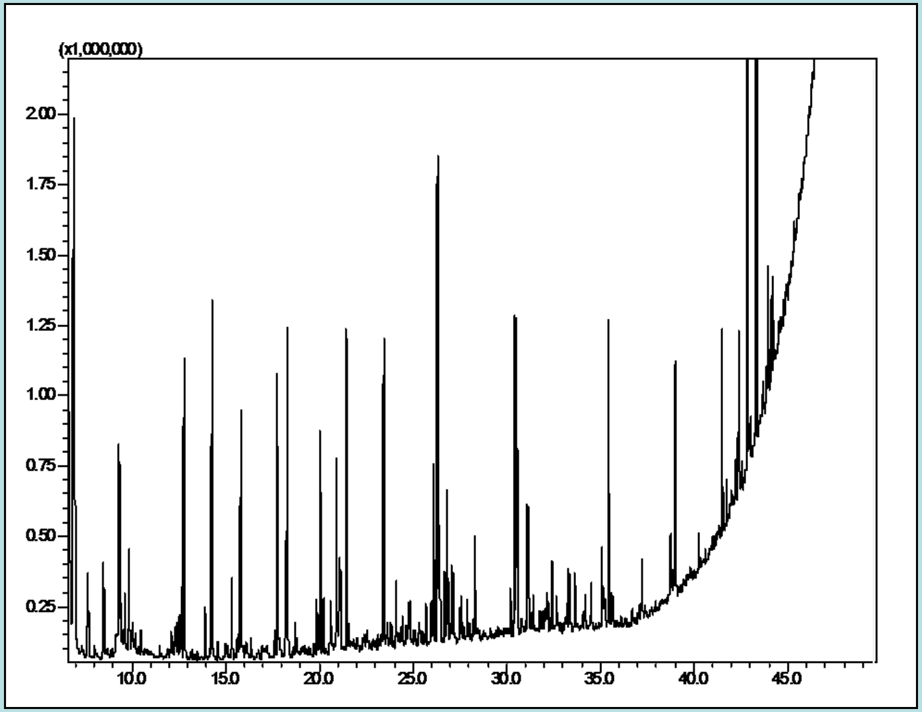


Sulfonated lignins

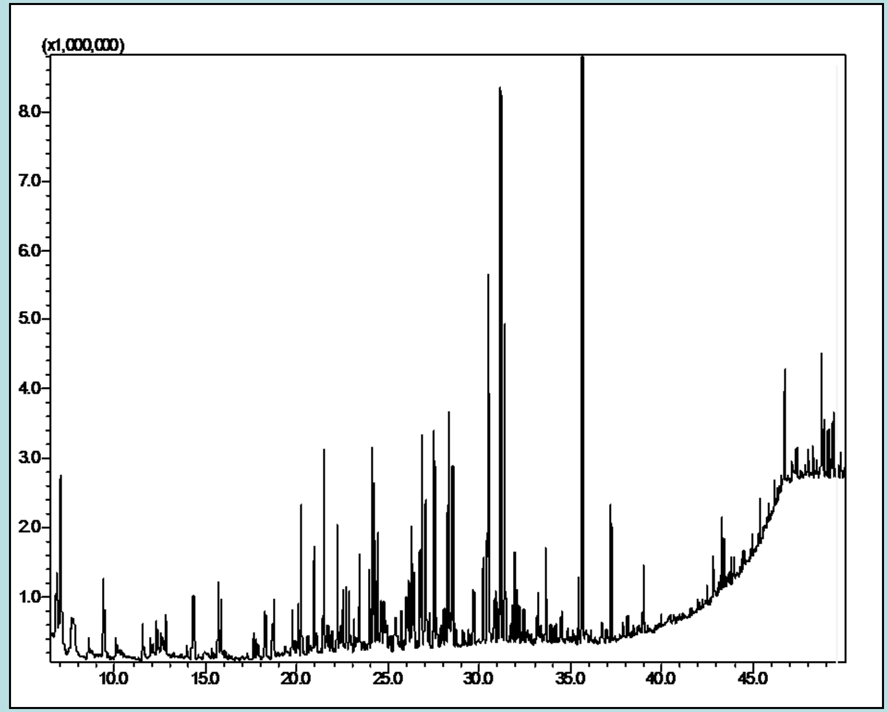
Pulping process

Improve formulation

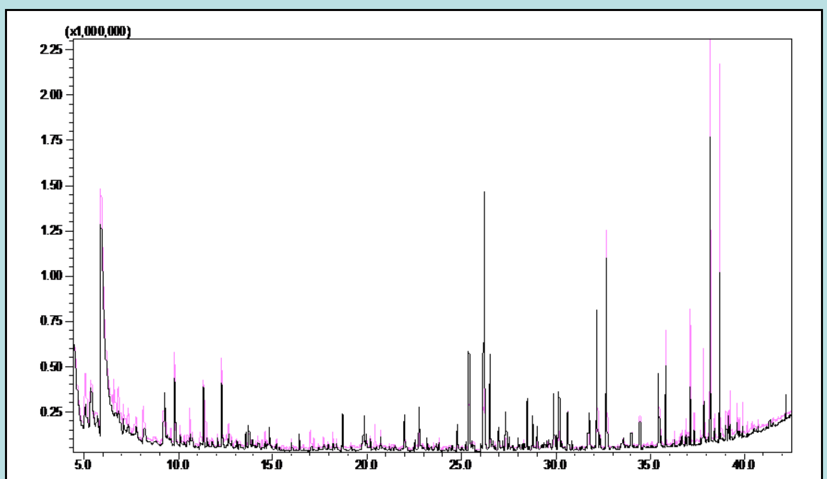
1D THM-GC of sulfonated lignins



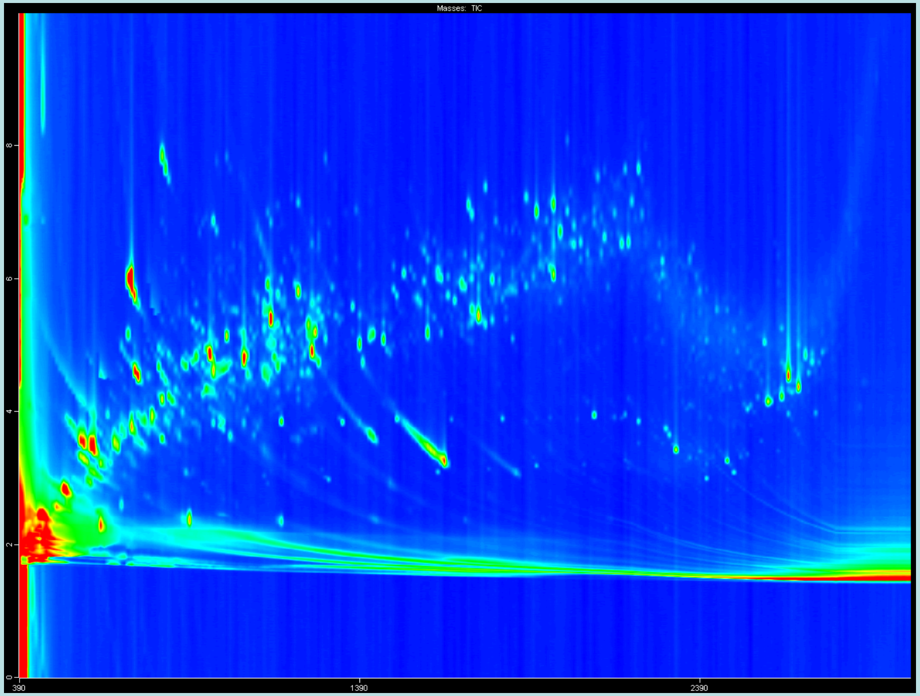
sulfonated kraft-lignin



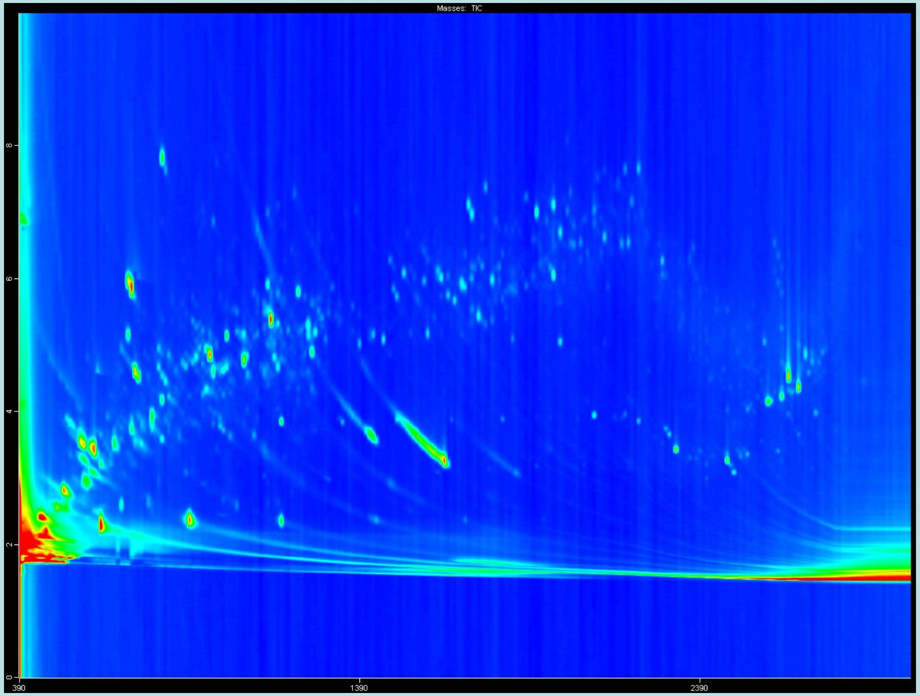
lignosulfonate



2D THM – GCxGC of lignosulfonate

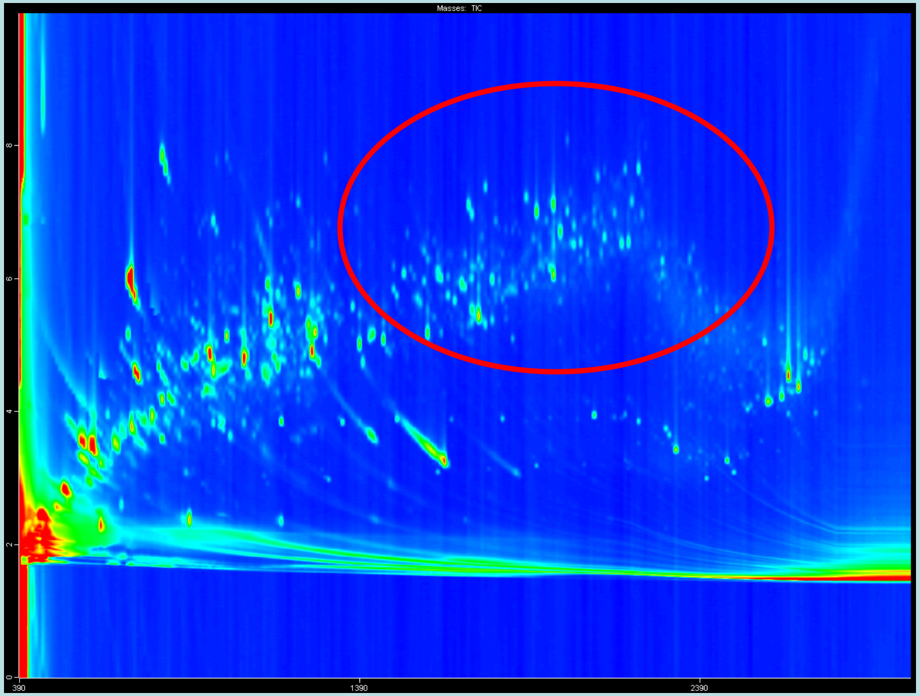


Sample A

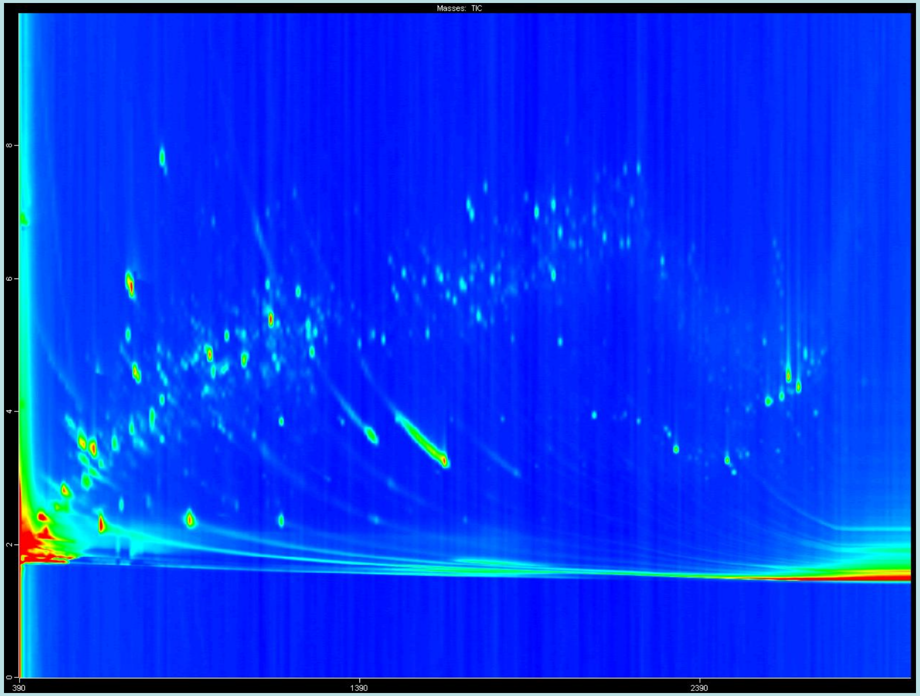


Sample B

2D THM – GCxGC of lignosulfonate



Sample A



Sample B

Summary

- The applicability of GC can be extended by the automation of THM and Pyrolysis
- Optic injector can be used as a pyrolyser, for solid and as well as for liquid samples
- THM – Py-GC-MS of relative simple biopolymers can results in complex data
- Combination pyrolysis or THM with GCxGC-TOF-MS provides very detailed sample information

Acknowledgements

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