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

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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

- Pesticides
- (Bio) Fuels
- Additives
- Gas-analysis
- Monomers
- Solvents
- Fatty acids
- (Poly) phenols
Bringing more molecules into realm of GC

- Polymers
- Biopolymers/proteins
- Tri glycerides
- Additives/pesticides

Log MW vs. polarity

GC vs. LC
Bringing more molecules into realm of GC

Bringing more molecules into realm of GC

- Log MW
- polarity

- pyrolysis
- thermochemolysis
- Automation
- derivatization

- HT-GC
- LC

- 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
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%

Example of Py-GC-MS with Optic 3 injector

1-Butanol
2-Propenoic acid
2-Propenoic acid, butyl ester
2-Propenoic acid, 2-methyl-, butyl ester

40 µl of 0.1 µg/ml dissolved copolymer
Extending the applicability

1. Automation:

- pyrolysis: solid samples $\rightarrow$ LINEX
dissolved samples $\rightarrow$ ‘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)

1. Weight solid sample
   - 10 µg to 1 mg

2. Add of TMAH
   - 2 µl to 1 ml solution (25% TMAH)
   - Water or methanol

3. Dry mixture
   - Vacuum or oven

4. Sealing of ampoule
   - Inert conditions

5. Incubation in oven
   - 10 min to 27 hours (100 to 250 °C)

6. Extraction of mixture
   - Commonly dichloromethane

7. Concentration
   - N₂ stream

8. GC-injection
   - 1 or 2 µl
thermal methylation (THM)

weight solid sample

add of TMAH

dry mix

incubation in oven

extraction of mixture

concentration

GC-injection

10 µg to 1 mg

10 min to 27 hours (100 to 250 °C)

commonly dichloromethane

N₂ stream

1 or 2 µl

How to automate
Fully automated in-situ thermochemolysis

## Optimization and performance THM-procedure

<table>
<thead>
<tr>
<th>inj. sample</th>
<th>Solv. elimination</th>
<th>inj. TMAH</th>
<th>react. time</th>
<th>Pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>- temperature</td>
<td>- temperature</td>
<td>- conc. TMAH</td>
<td>- time</td>
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<td>- type liner</td>
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<td>- volume</td>
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### 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

Repeatability:
(sum of 30 peaks)

Sample materials:
Polysaccharides
PA/PAH copolymer
Proteins
Lignins
Celluloses

RSD (n=20)
7.6%
3.2%
5.6%
5.9%
7.6%
PA-PAH copolymer

Polyacrylic acid

Polymaleic anhydride
Difference PA and PA-PAH copolymer

- Maleic anhydride fragment
- Acrylic acid fragment
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

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
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

ATAS GL International

Polymer analysis group (University of Amsterdam)

Dr. S. de Koning (Leco)