Christian Doppler Forschungsgesellschaft

CE-MS determination of degradation products of (hemi)cellulose and lignin

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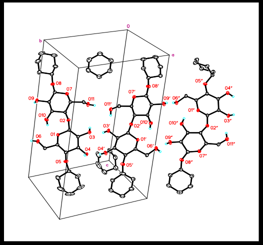
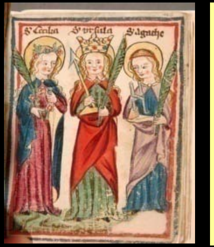
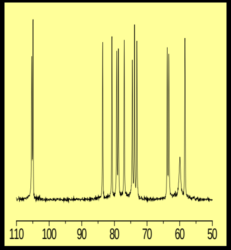
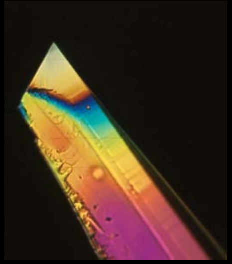
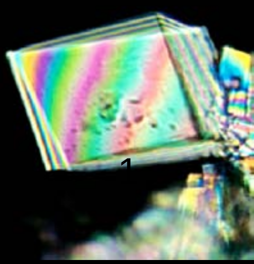






STSM

Institution: Center of research on collection preservation

Research group: Paper and cellulose

Host: Dr. Anne-Laurence Dupont

Time: 3 weeks, spring 2010

Aim:

1. Getting familiar with CE-ESI-MS
2. Applying the method to (hemi)cellulose and lignin degradation products and effluents

Outline

Separation and identification of substances contained in waste water streams

Identification of degradation products
in different bleaching effluents

Identification of „valuable“ byproducts in different effluent streams

Identification of compounds impeding the biological waste water treatment

Degradation schemes

- Fragmentation reactions
- Rearrangement / redox processes
- Condensations reactions

Complex chemical systems

- Aliphatic carboxylic acids
- Lignin-derived compounds
- Monosaccharides
- Extractives

General challenges

- ✓ very diluted solutions
- ✓ high inorganic salt concentration (~ 90% of solid content)
- ✓ different pH values (after Z, P)
- ✓ large number of different product classes to be expected
- ✓ altering prior to analysis

  (sample preparation and storage may change composition)

Sample preparation

Samples have to be concentrated without causing significant changes

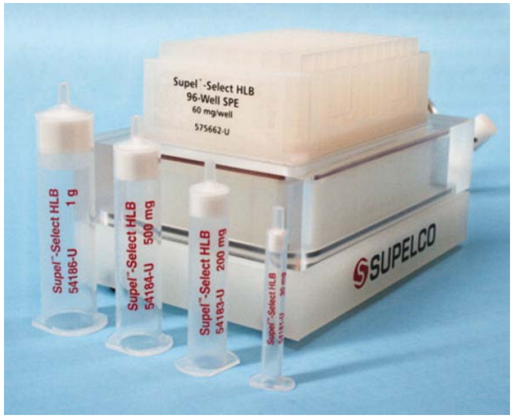
→ *Freeze dried and partly freeze dried samples*

→ *Protonation of acids prior to derivatization (P-stage)*

→ *SPE techniques*

Hydrophilic modified reversed-phase cartridges

Sample concentration



Sample desalting

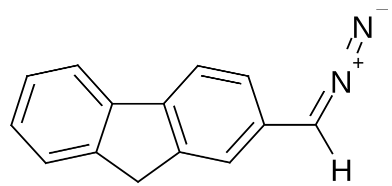
Methodology

- *HPLC-UV with and without derivatization*
- *GC-MS with various derivatization techniques*
- *Pyrolysis-GC-MS with and without derivatization*

HPLC-UV:

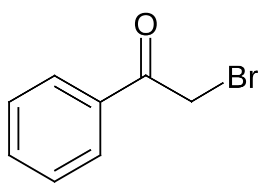
Needs UV-labeling:

- *Fluorenyl diazomethane (FDAM)*



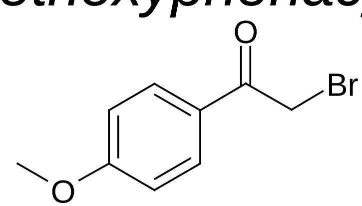
Too many side products

- *Phenacyl bromide*



Improvement (compared to FDAM)

- *p-Methoxyphenacyl bromide*



Better, but difficulties
with identification of complex mixtures

Methodology:
GC-MS and Pyr-GC-MS

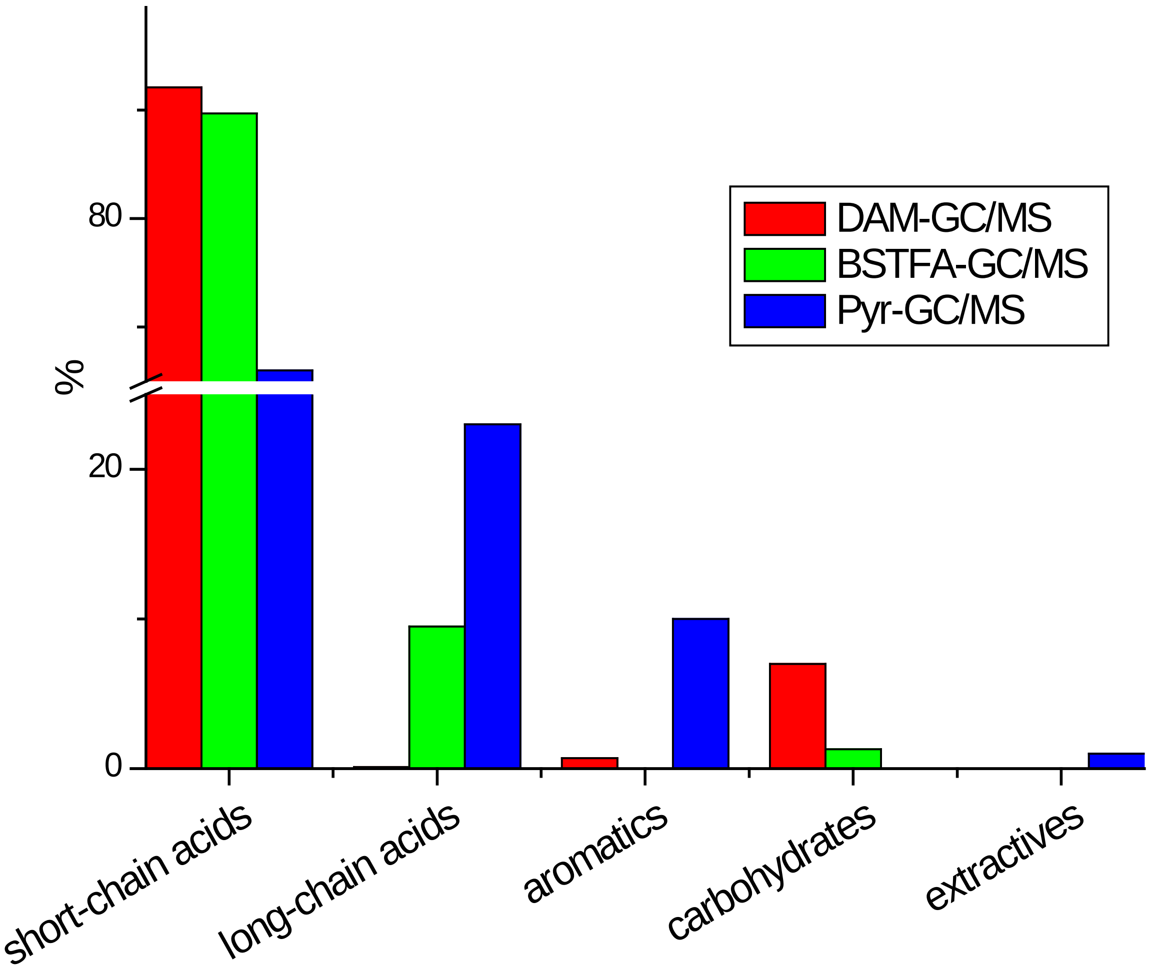
GC-MS:

- silylation with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA)
- methylation with tetramethylsilyl diazomethane (TMS-DAM)
- methylation with diazomethane (DAM)

Pyrolysis-GC/MS:

- without derivatization
- methylation with tetramethylammonium hydroxide (TMAH)

GC/MS:
Comparison of various GC-MS methods



GC/MS: Lessons

Products and profiles identified highly depend on sample preparation

→ *Silylation yields reasonable results, but fails on higher Mw samples (long chain acids) due to increased Mw*

→ *TMS-DAM is an alternative method if methylation is required*

→ *DAM works best, but has a difficulties in handling and safety constraints*

→ *Pyrolysis-GC/MS is good for lignin-derived compounds and long chain acids but needs independent confirmation*

Method without sample preparation required!

CE-MS

Why do we need a new analytical method?

- ✓ no need of sample derivatization
- ✓ robustness
- ✓ short analysis time
- ✓ low sample and chemicals amounts

CE-MS
Aliphatic carboxylic acids:
Method optimization

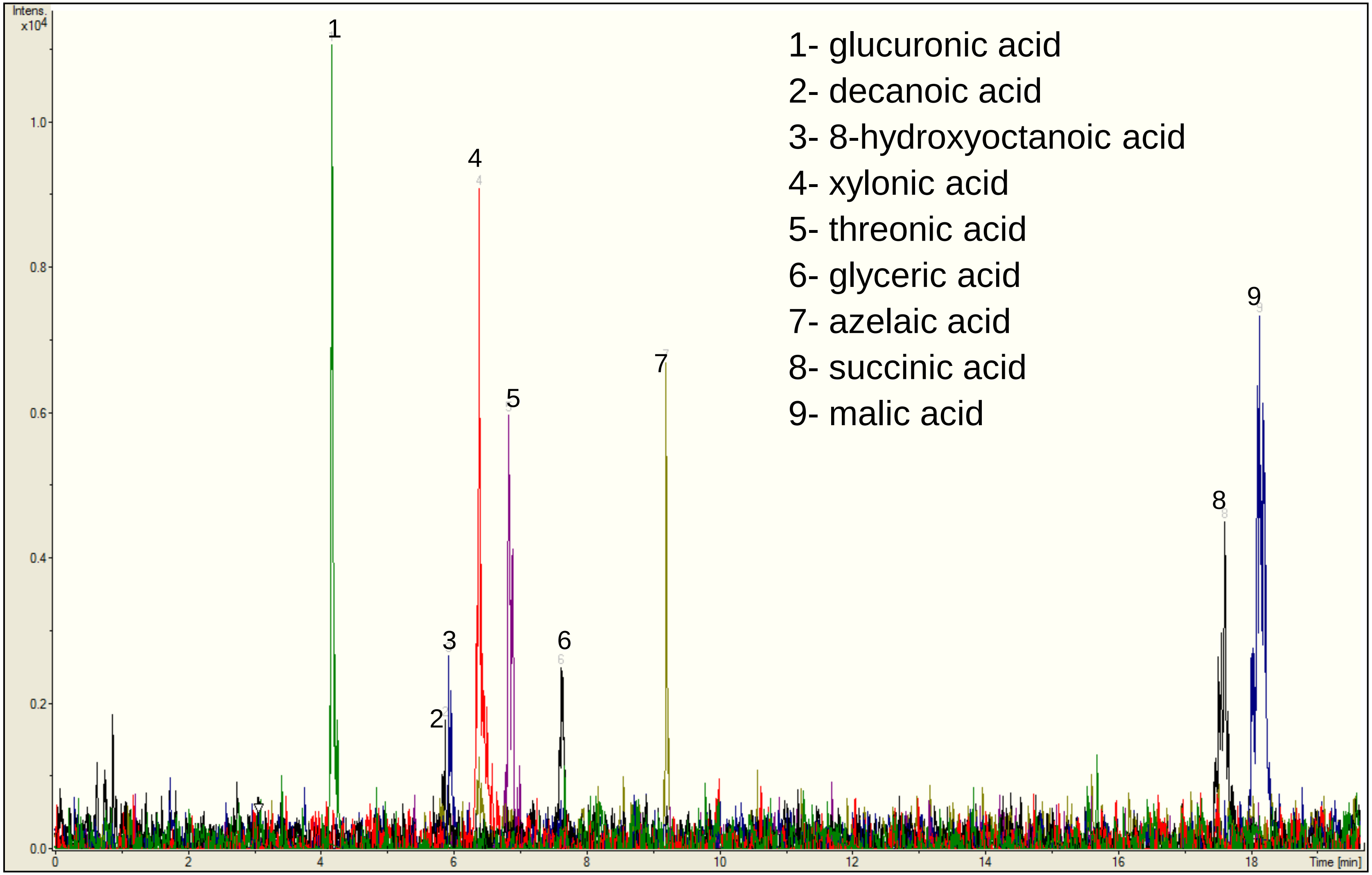
Model mixture of aliphatic carboxylic acids:
- different chain lengths
- number of carboxylic groups (mono- or diacids)
- hydroxyl groups

Method optimization

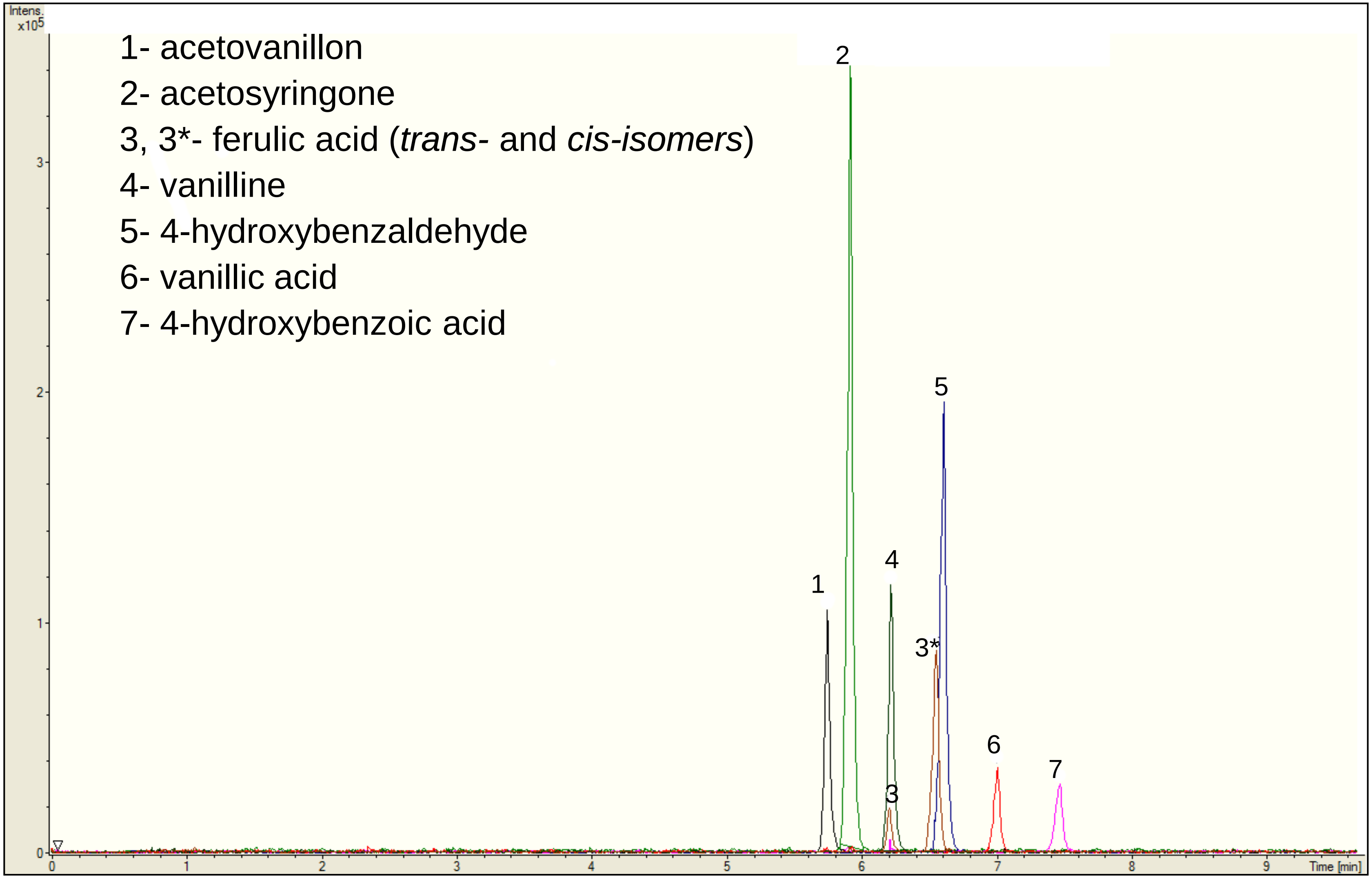
CE-parameters:	Sheath liquid:	MS-parameters:
Capillary	Composition (NH_4OH)	Neb gas pressure
Buffer	Organic solvent	Dry gas flow
Buffer concentration	Flow	Dry gas temperature
Buffer pH		

CE-MS: Method optimization

Aliphatic carboxylic acids (model mixture)



CE-MS: Method optimization
Lignin-derived compounds (model mixture)

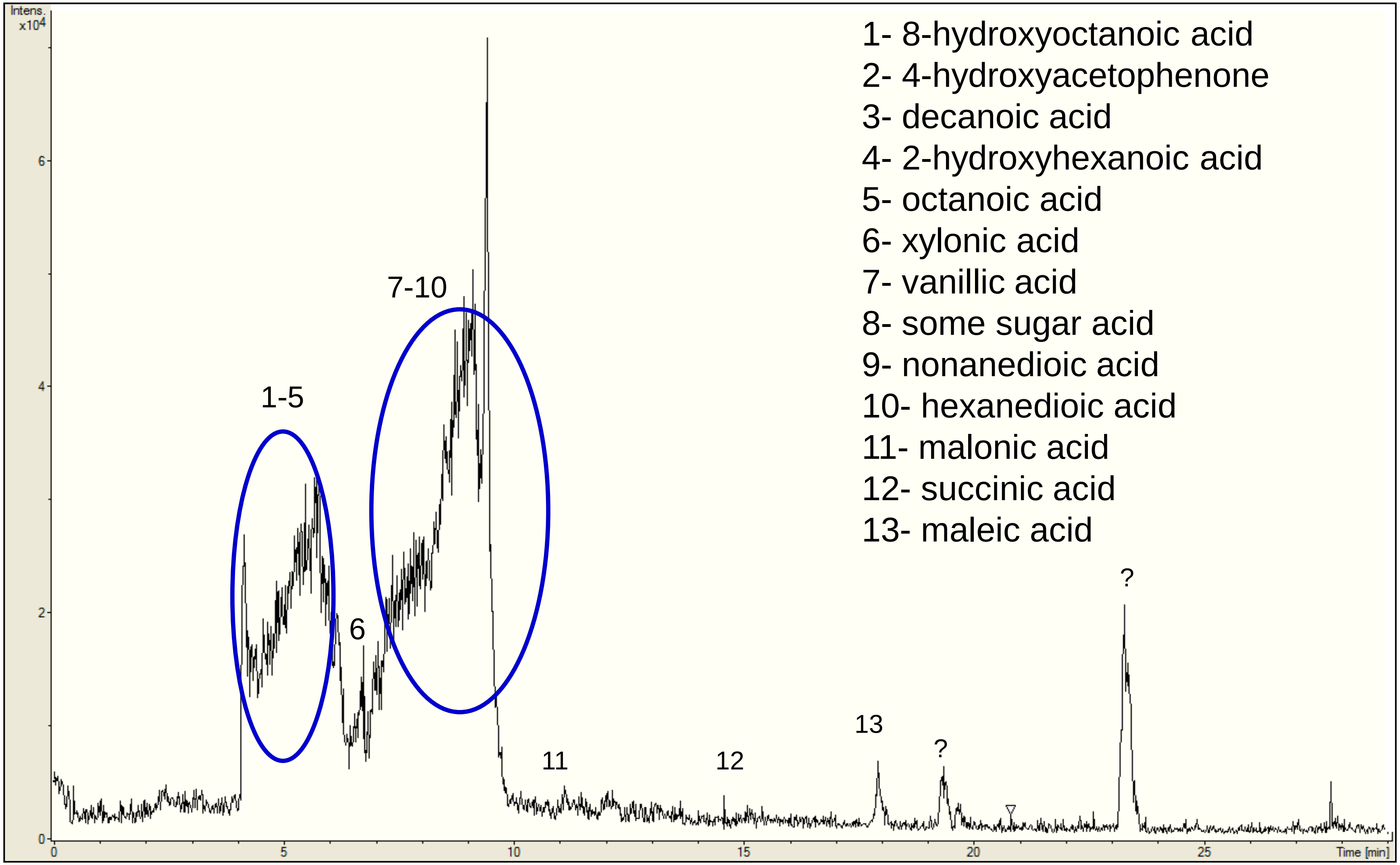


CE-MS:
Degradation products of carbohydrates and lignin

Lessons after method optimization on model mixtures:

- ✓ Simultaneous determination of aliphatic acids and aromatics is possible
- ✓ Up to chain length $C_{10\text{-}12}$
- ✓ Short di-acids are not visible
- ✓ Aromatics show very high intensities

CE-MS application:
Pulp bleaching effluents



CE-MS application:
Pulp bleaching effluents

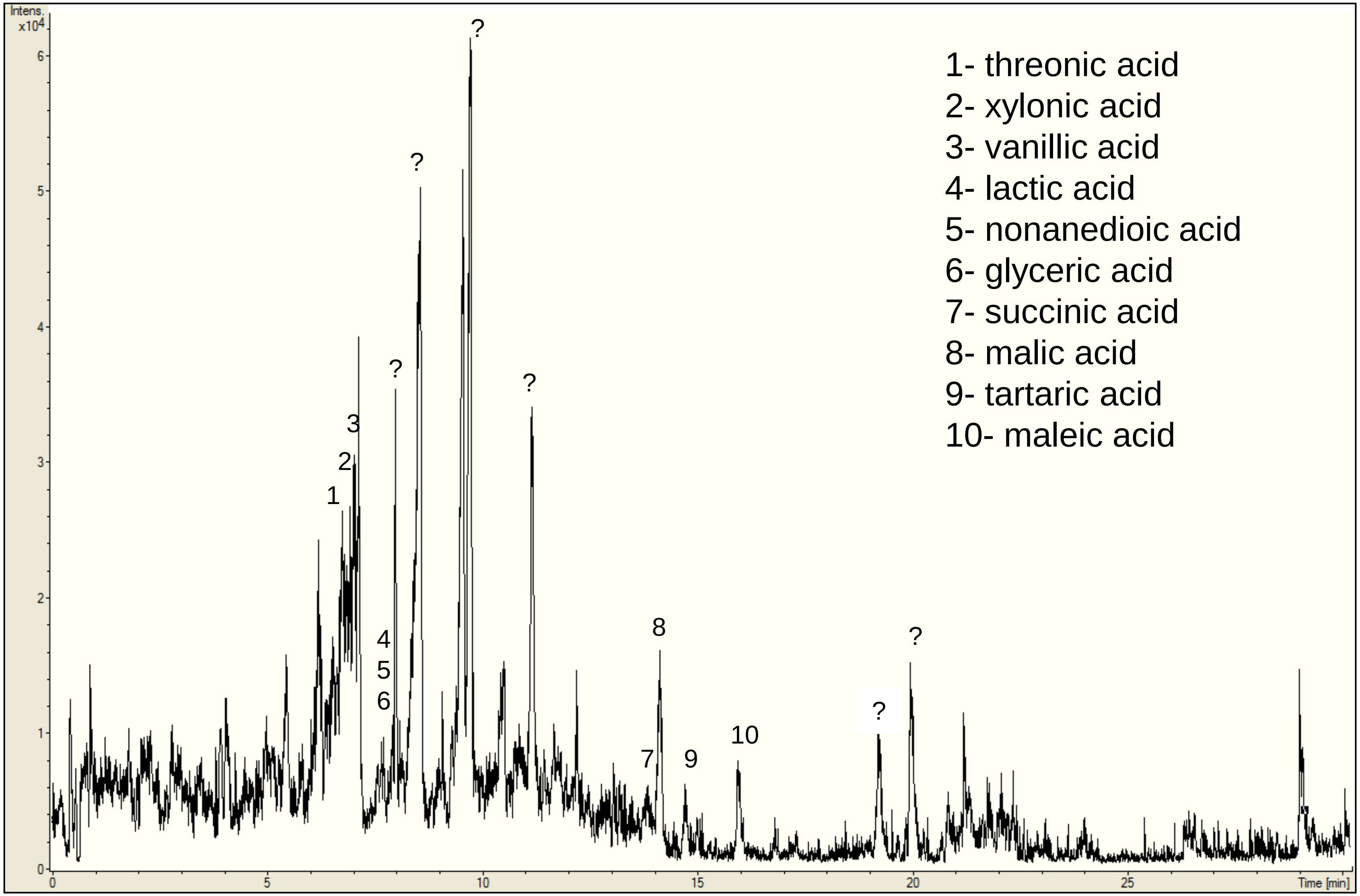
Information achieved:

- The main component detected by GC-MS and pyrolysis-GC-MS
- Analysis time ~ 20 min
- Identification mainly according standards (Mw and migration time)

Difficulties:

- matrix influence
- “stacking effect” at run times after EOF
- peak identification (standards limited, ESI mass not always conclusive)

CE-MS application:
Naturally aged paper extracts



CE-MS application:
Outlook

Problems and their solution:

✓ Combining CE-MS with GC-MS and/or pyrolysis-GC-MS

✓ Principal information on sample composition:
class of compound,
length of C-chain,
number of COOH-, OH- groups,
etc.

Conclusions

CE-MS:

- fast
- aqueous
- simultaneous determination of (hemi)cellulose and lignin degradation products
- need to be combined with other analytical methods (GC-MS, pyrolysis-GC-MS, etc.)
- …