PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

# Hot water extraction of inner and outer bark of Norway Spruce (*Picea abies*)

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COST FP0901 meeting

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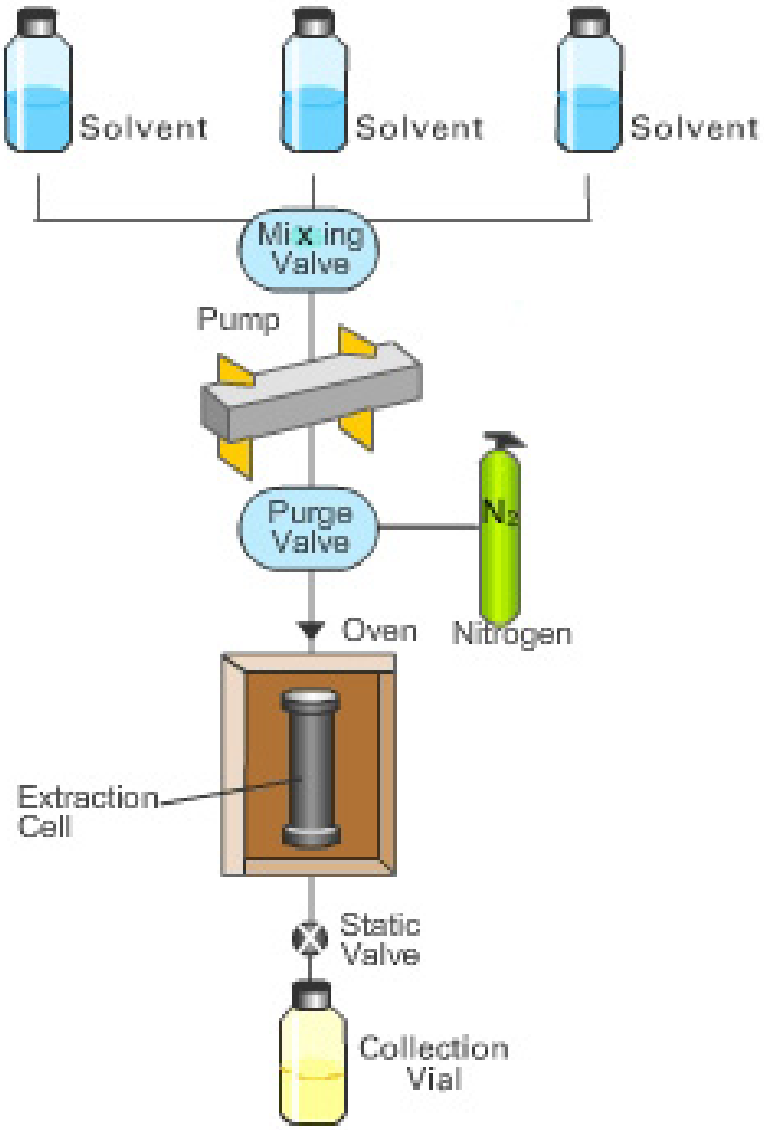
# Spruce bark

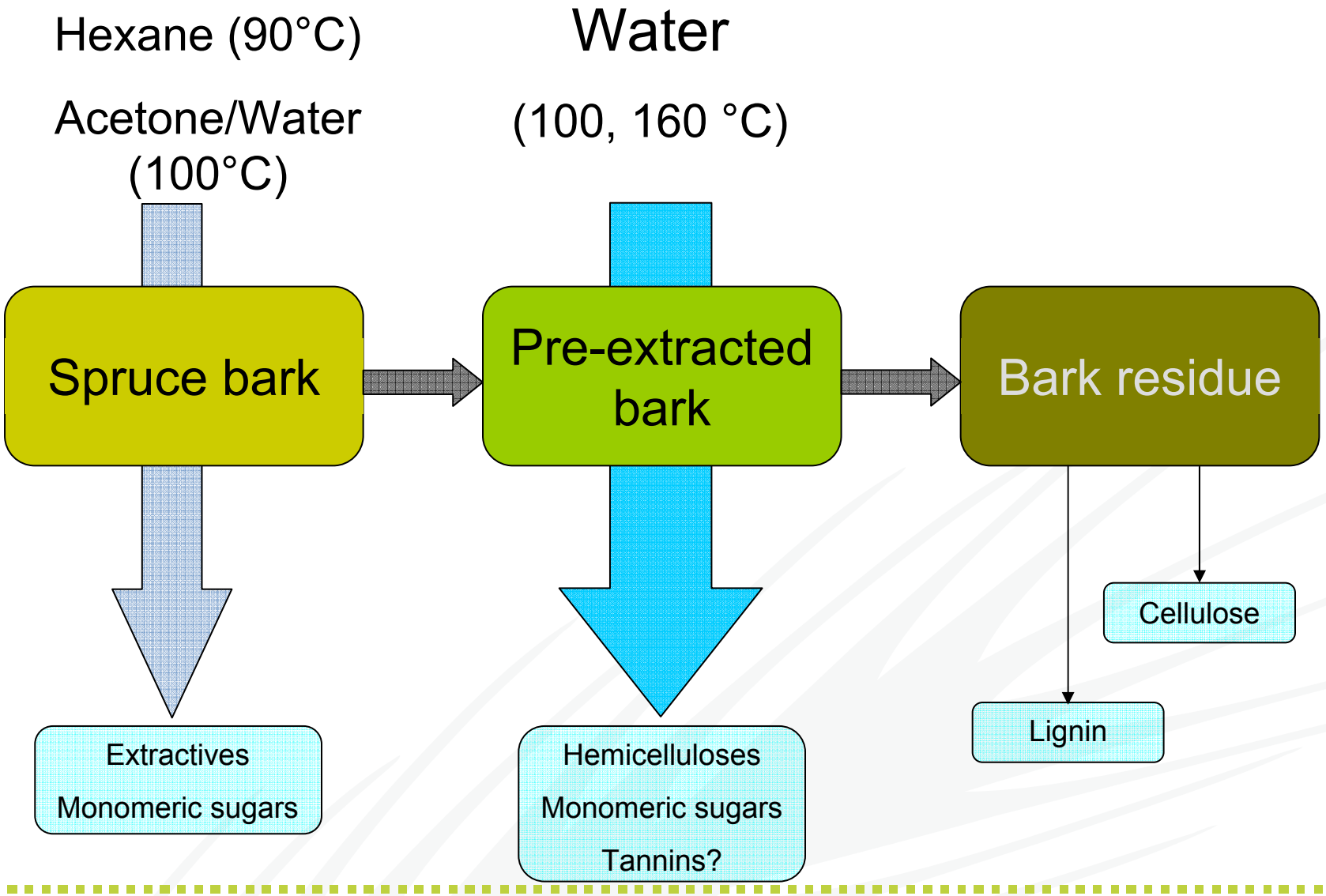
- Inner bark (~90 vol-%) and outer bark (~10 vol-%)
- Huge valuable side stream in wood industry
- Chemical composition not completely known, differs from wood
- Known composition of bark → better utilisation

# Accelerated Solvent Extraction (ASE)

- Automated extraction with different times and pressures
- Sequential extractions with different solvents possible

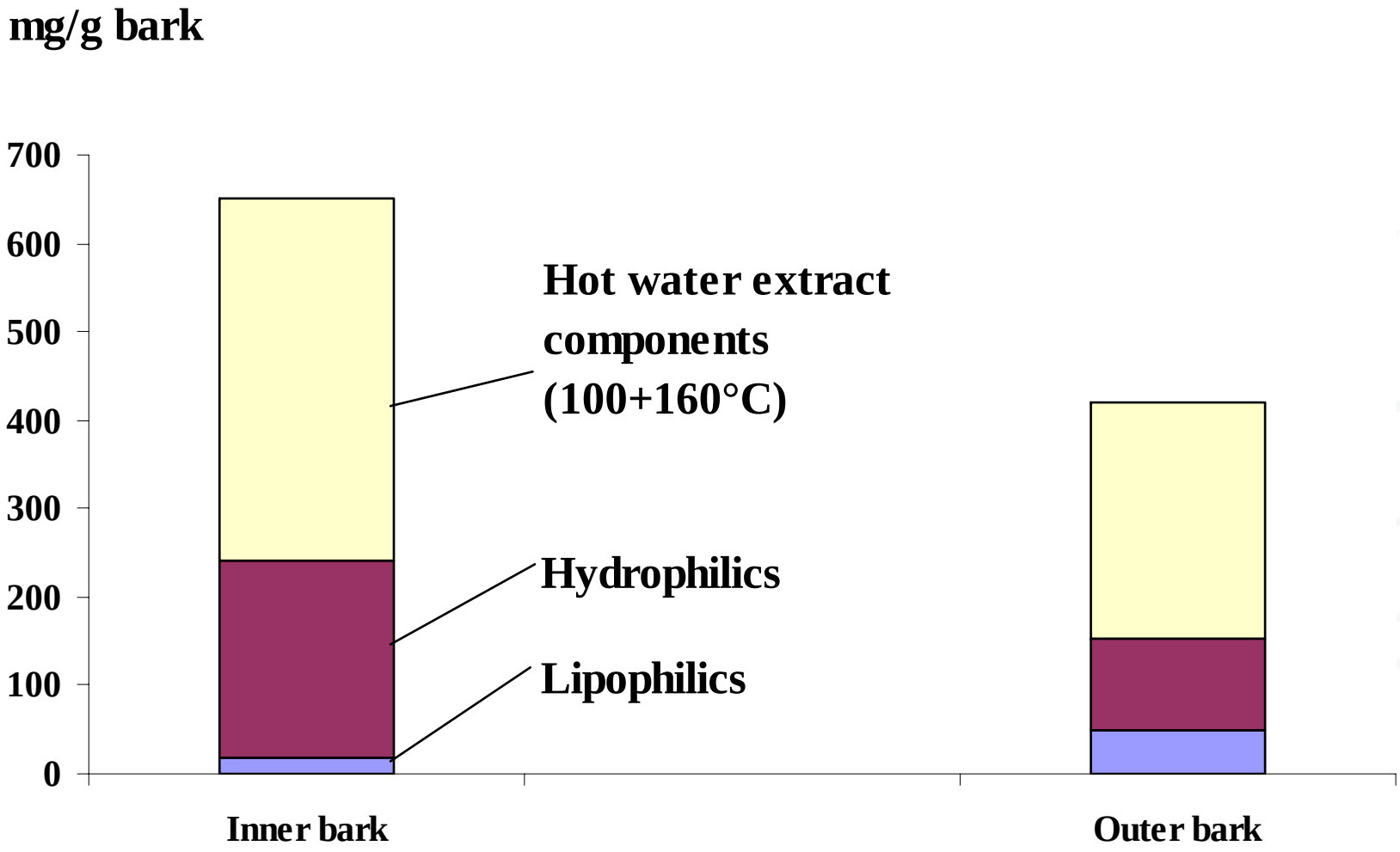


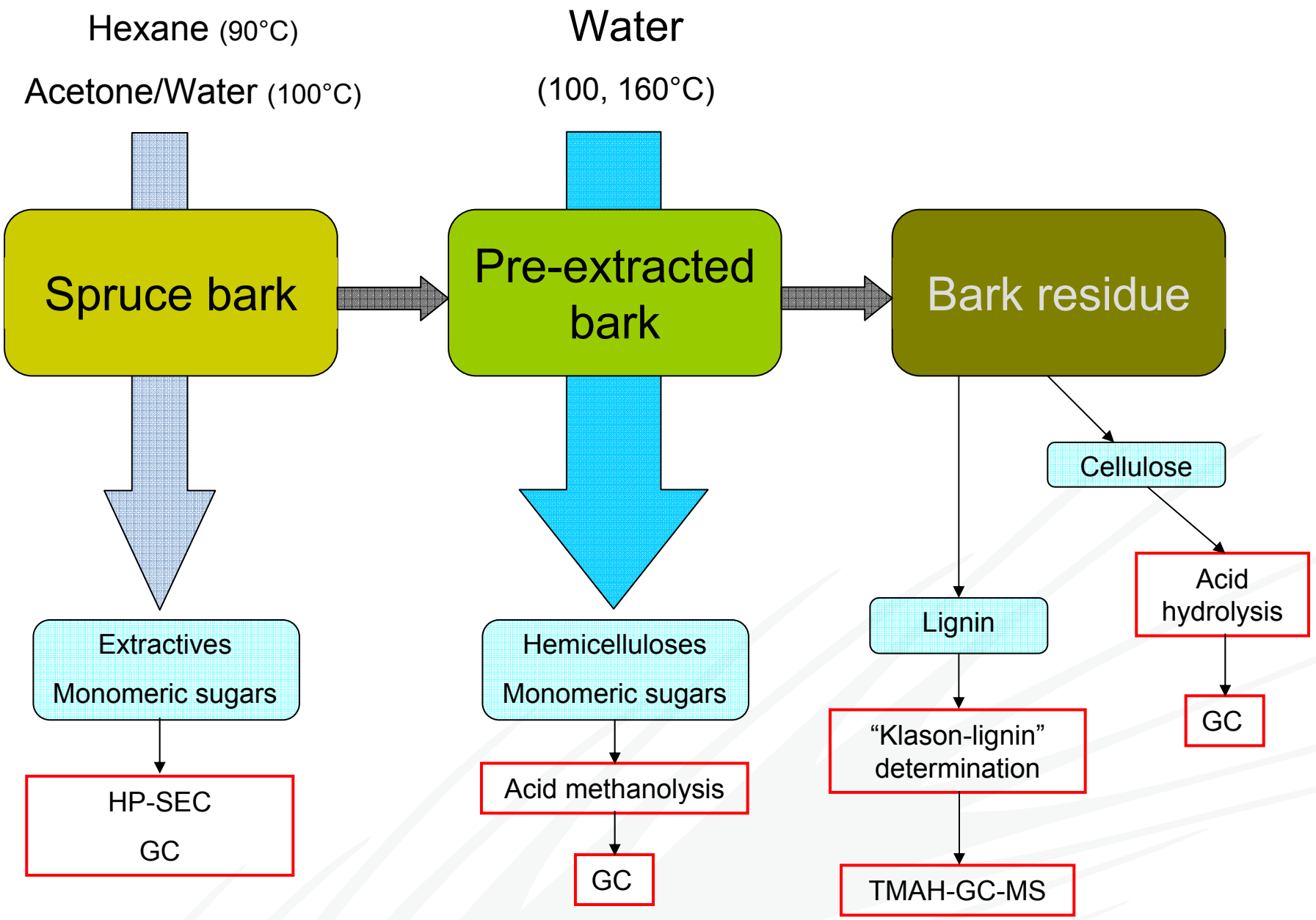
# Extraction scheme



# Totally dissolved solids (TDS)

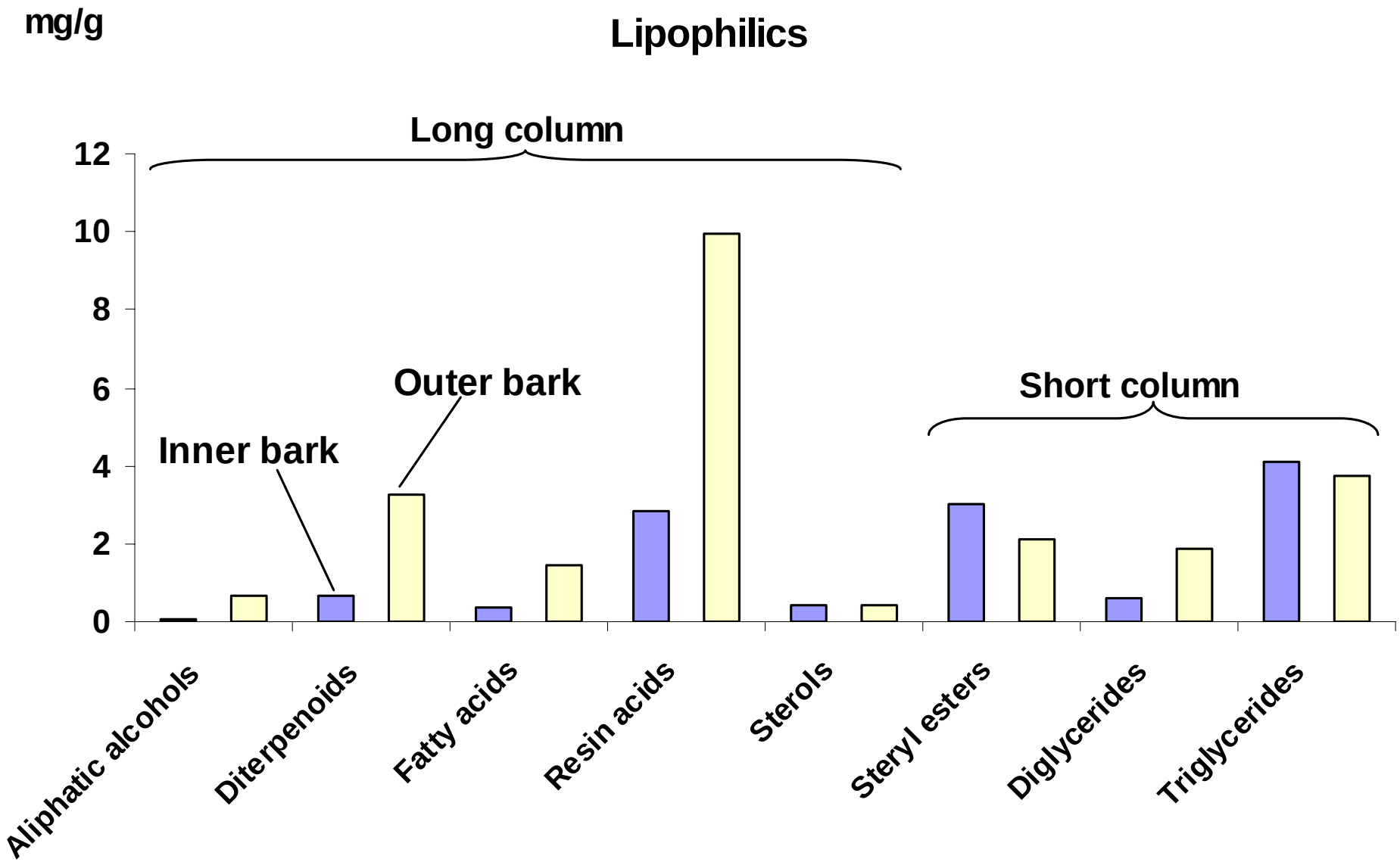
## Gravimetrically determined

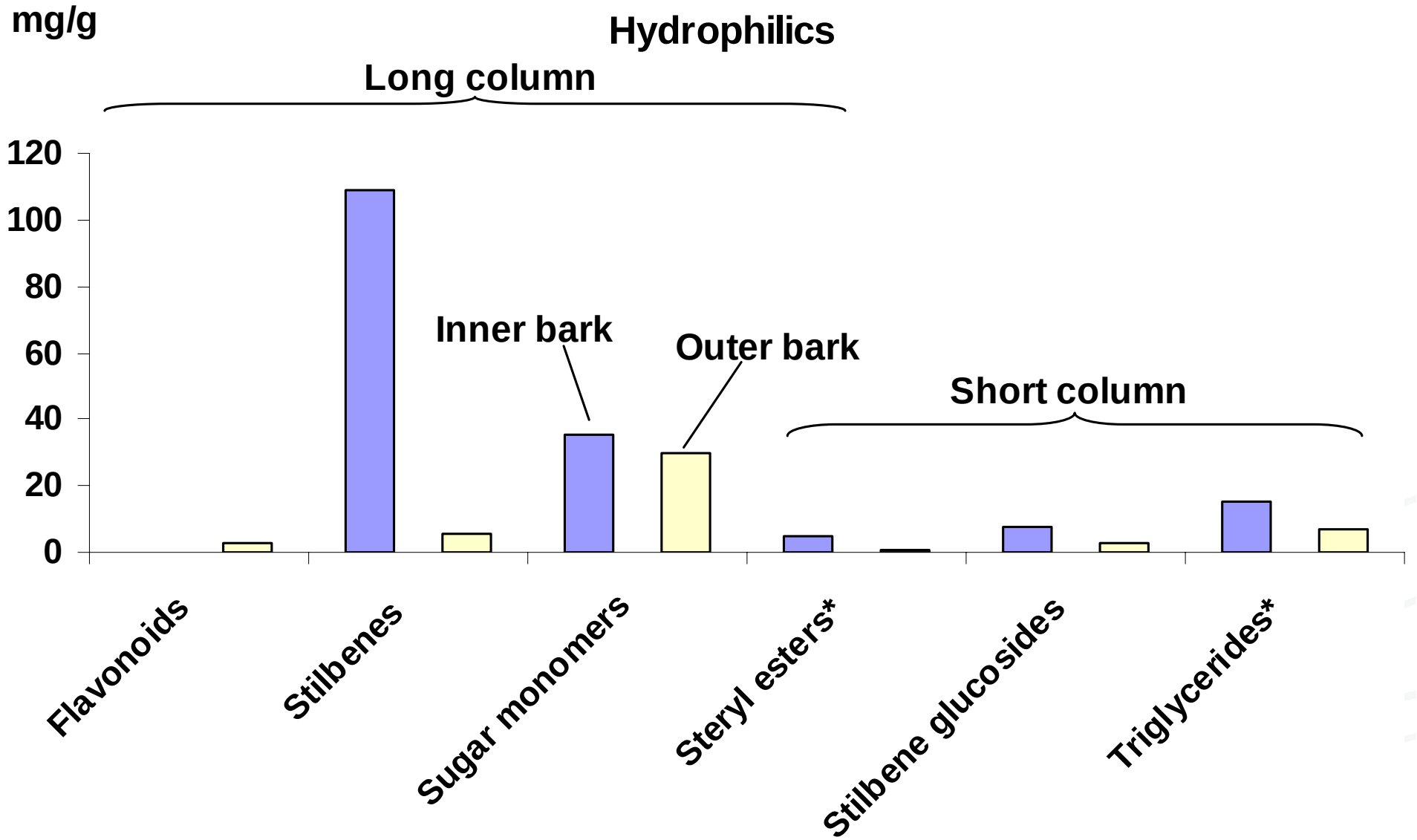



Hexane (90°C)
Acetone/Water (100°C)
Water
(100, 160°C)
Spruce bark
Pre-extracted bark
Bark residue
Extractives
Monomeric sugars
HP-SEC
GC
Hemicelluloses
Monomeric sugars
Acid methanolysis
GC
Lignin
"Klason-lignin" determination
TMAH-GC-MS
Cellulose
Acid hydrolysis
GC

# Extractives

- Lipophilic and hydrophilic compounds extracted with hexane and acetone/water
- GC results gives both quantitative and qualitative results
- Long or short column GC


mg/g
Lipophilics
Long column
Short column
Outer bark
Inner bark
12
10
8
6
4
2
0
Aliphatic alcohols
Diterpenoids
Fatty acids
Resin acids
Sterols
Steryl esters
Diglycerides
Triglycerides




* Components that eluates at the same time as steryl esters and triglycerides

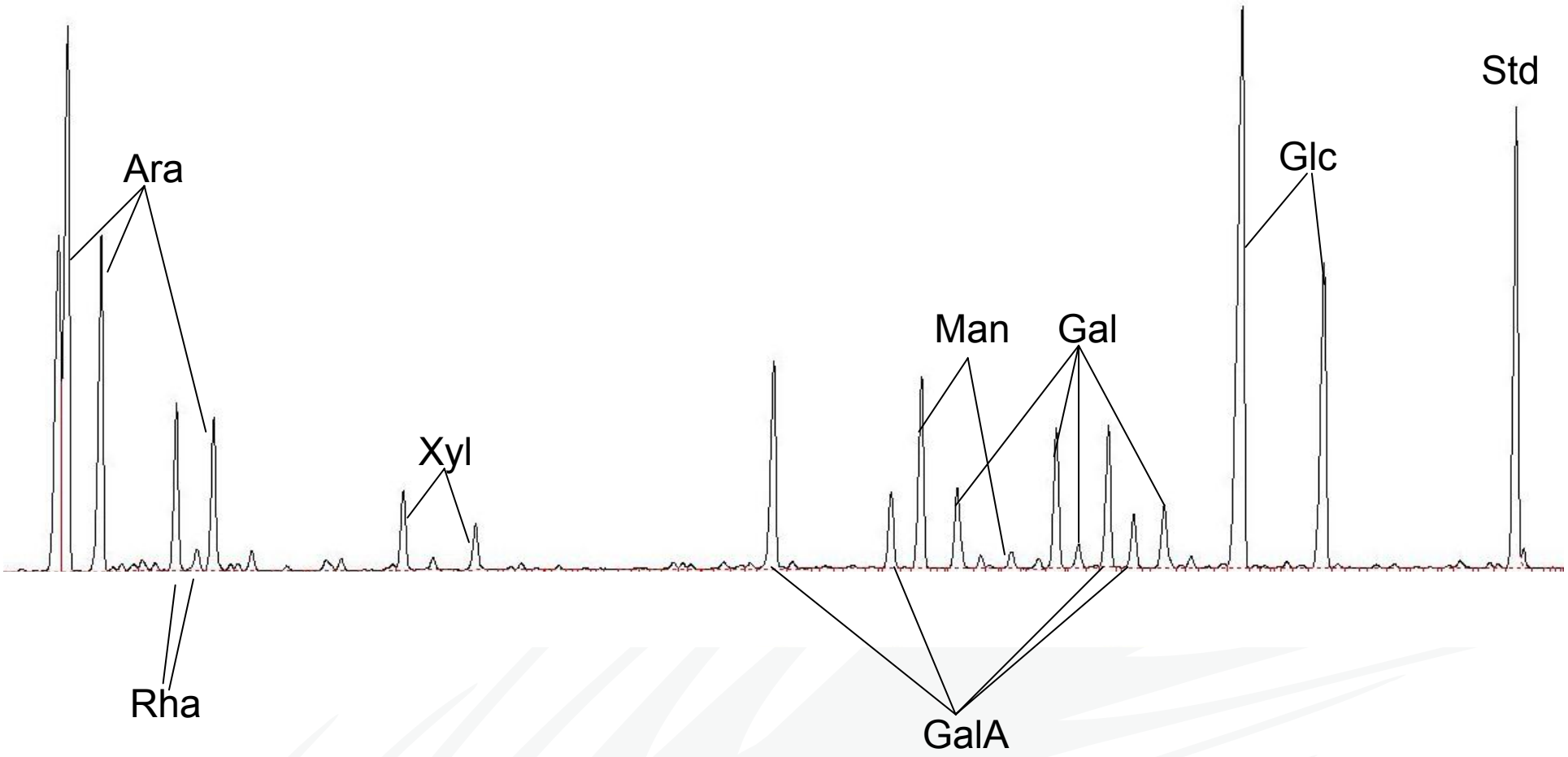
# Hemicelluloses and monomers

- Mild depolymerization  of hemicelluloses
  - Adding 2 M HCl in methanol to freeze-dried sample and in 105 °C for 3 hours cleaves hemicelluloses but not cellulose
  - Samples are further silylated with HMDS and TMCS
- Good method for uronic acids determination (mild conditions)

- Gives hemicellulose content in monomeric form
- Methanolysis can be done on both solid and liquid samples
- Monomers determined after direct silylation

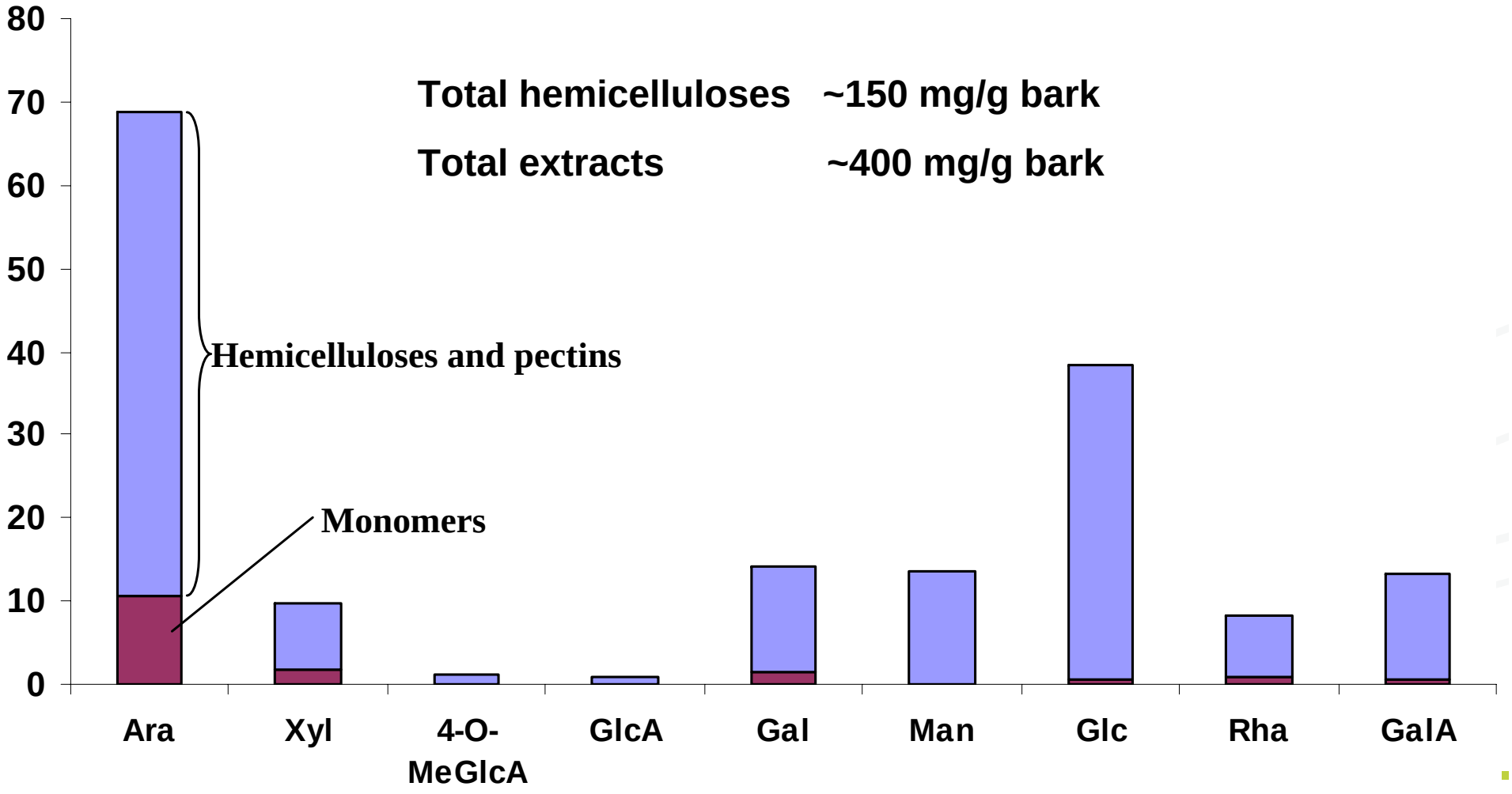
# Chromatogram of sugar units in bark extract

Inner bark, 160°C

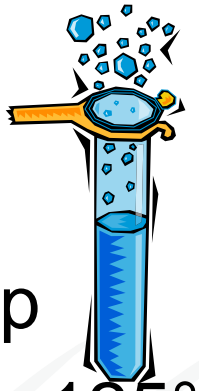


# Bark water extract

## Inner bark 160 °C, 60 min



# Cellulose



- Two step acid hydrolysis
  - 72 % sulfuric acid,  2 hours, room temp
  - Dilute with water, over night, autoclave 125°C 90 min

- Cleaves cellulose to glucose → cellulose content in sample

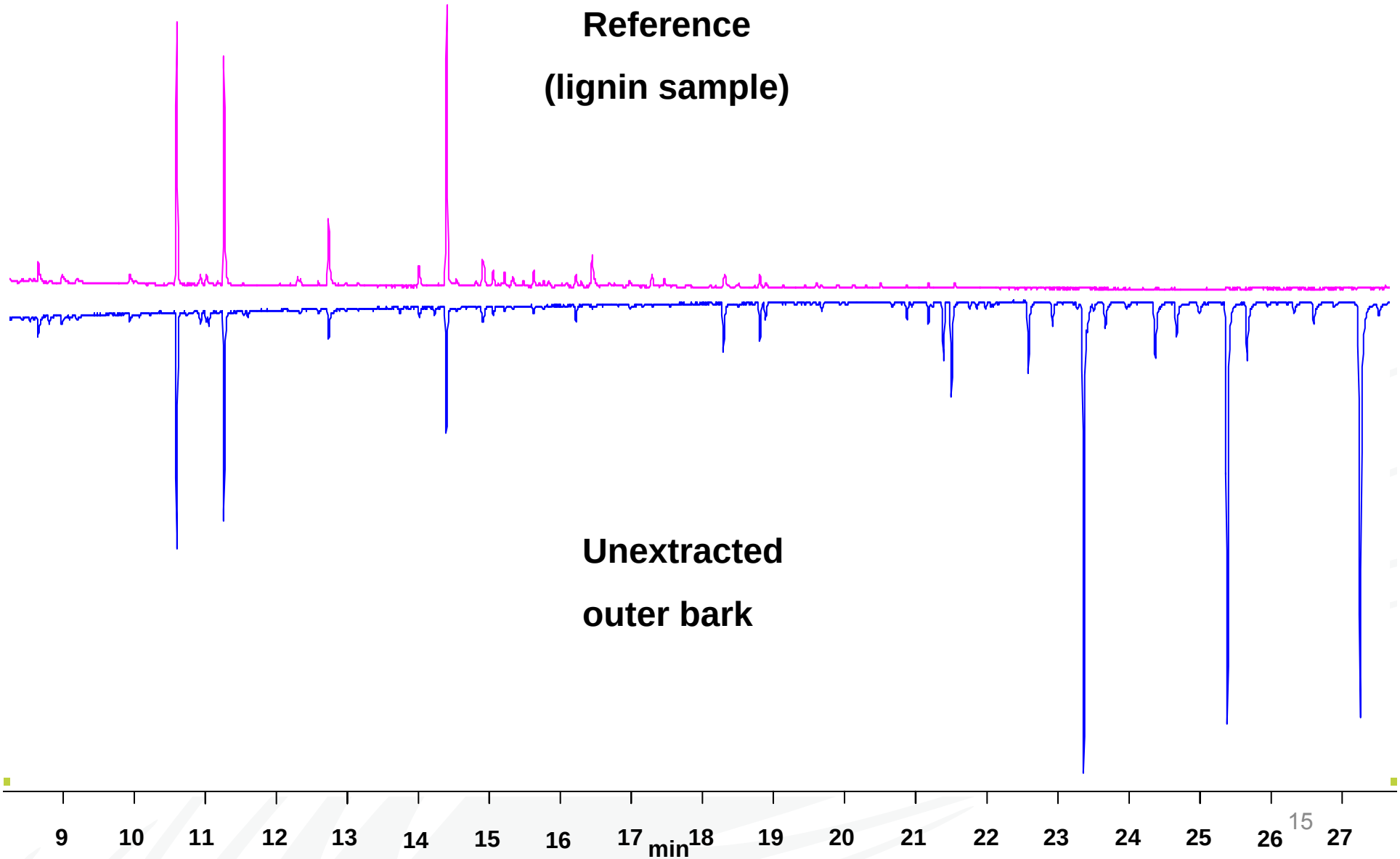
# “Klason-lignin”

- Improved Klason-lignin method (gravimetrically) + TMAH*-GC-MS
  - Py-TMAH-GC-MS milder conditions than py-GC-MS
- Not all “Klason-lignin” is lignin, lot of long chained fatty acids probably originated from suberin
- 32% in inner bark, 45% in outer bark

* tetramethylammonium hydroxide

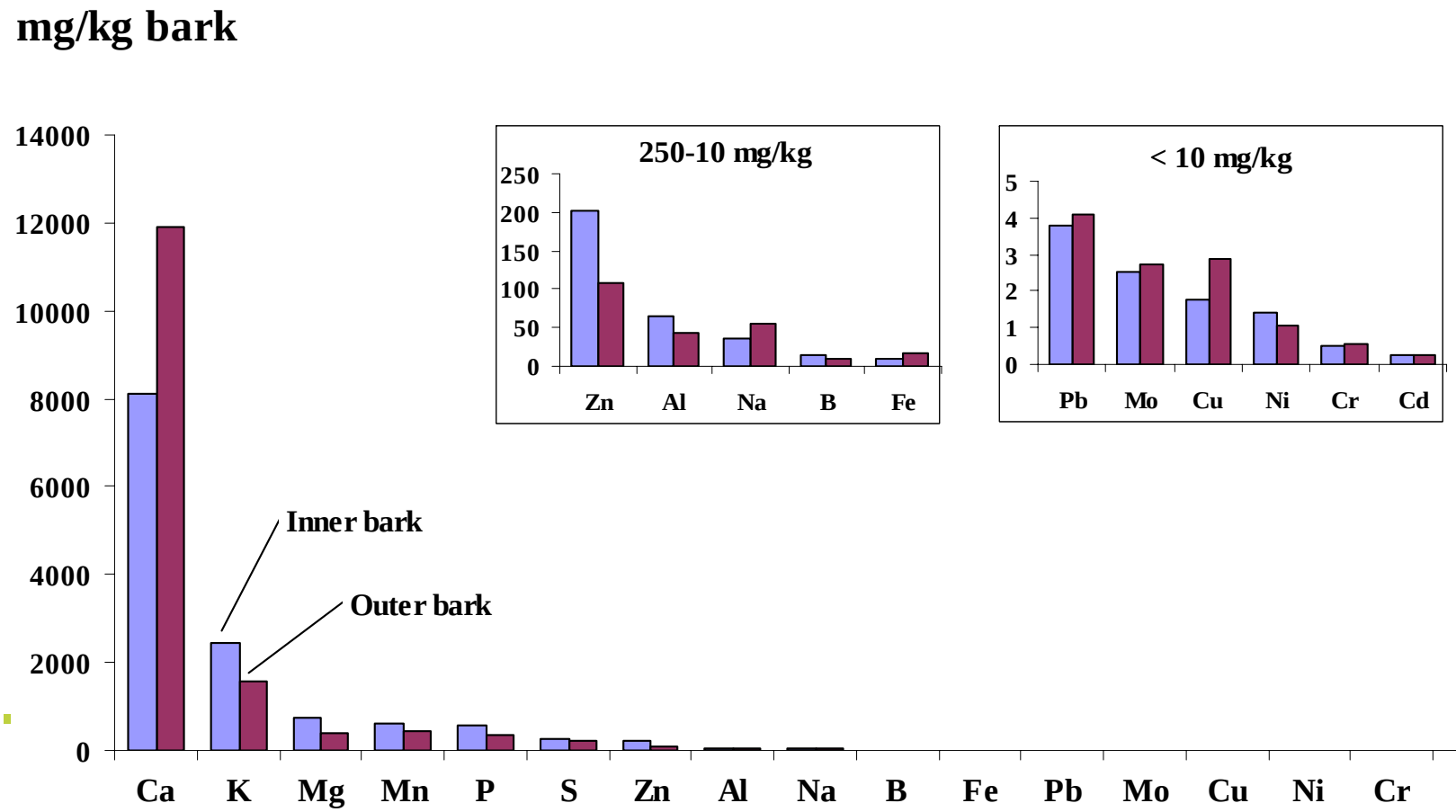
Ref: Scwanninger, M., Hinterstoisser, B., 2002, *Klason Lignin: Modifications to Improve the Precision of the Standardized Determination*, Holzforshung 56 161-166

# TMAH-GC-MS chromatogram

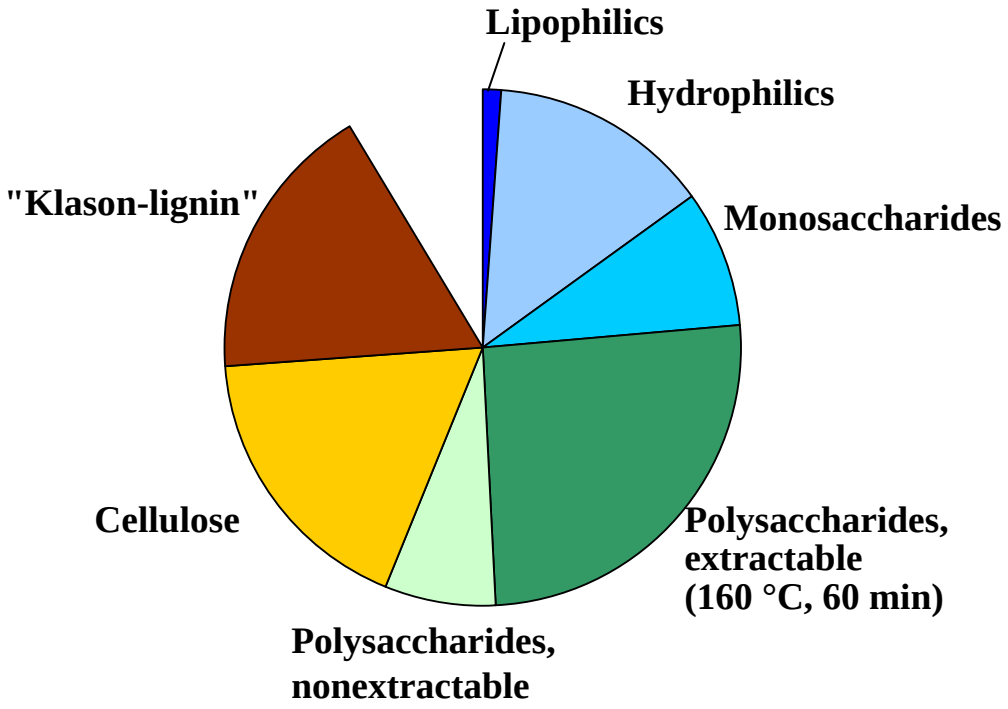


# Metals by ICP-MS

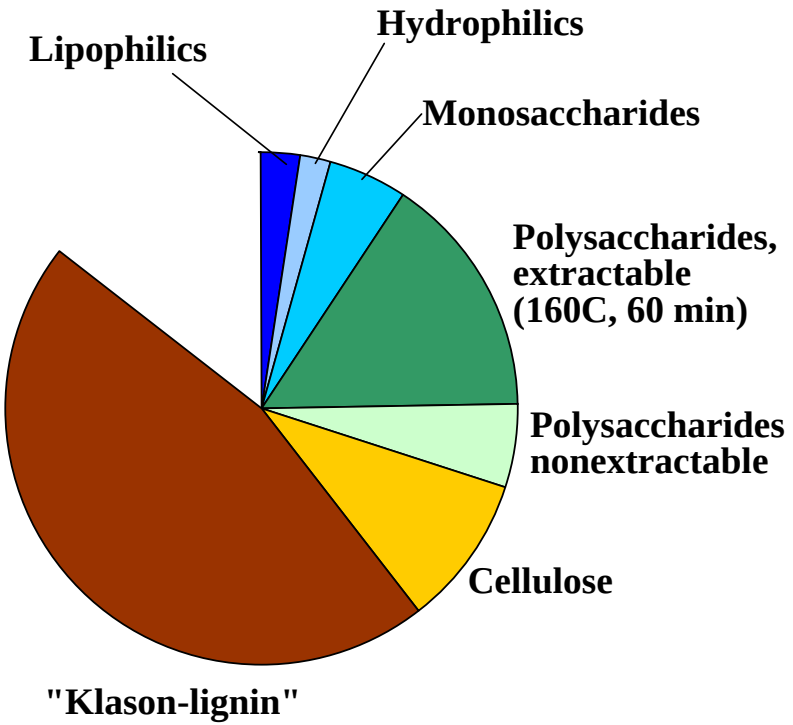
- Gives a detailed picture of the amount of inorganic elements in the bark



## Inner bark




## Outer bark




- Silylation + GC
- Methanolysis + silylation + GC
- Hydrolysis + silylation + GC
- Klason method + TMAH-GC-MS

# Conclusions

- 15% of total weight of bark is extractable hemicelluloses and pectins
- 91 % of dried inner bark characterized
- 86 % of dried outer bark characterized

- Important to get as much knowledge as possible of bark (valuable side chain)
  - ➔We need good extraction and analytical methods

# The future…

- Purify the bark hemicelluloses (arabinans?)
- Improve the extraction
- More work needed on industrial bark
- Develop existing and new analytical methods

# Applications

- Platform chemicals
- Animal feed
- Specialty sugars
- Bioethanol?