Ionic liquid mediated biomass deconstruction: from analysis challenges to fermentable sugars

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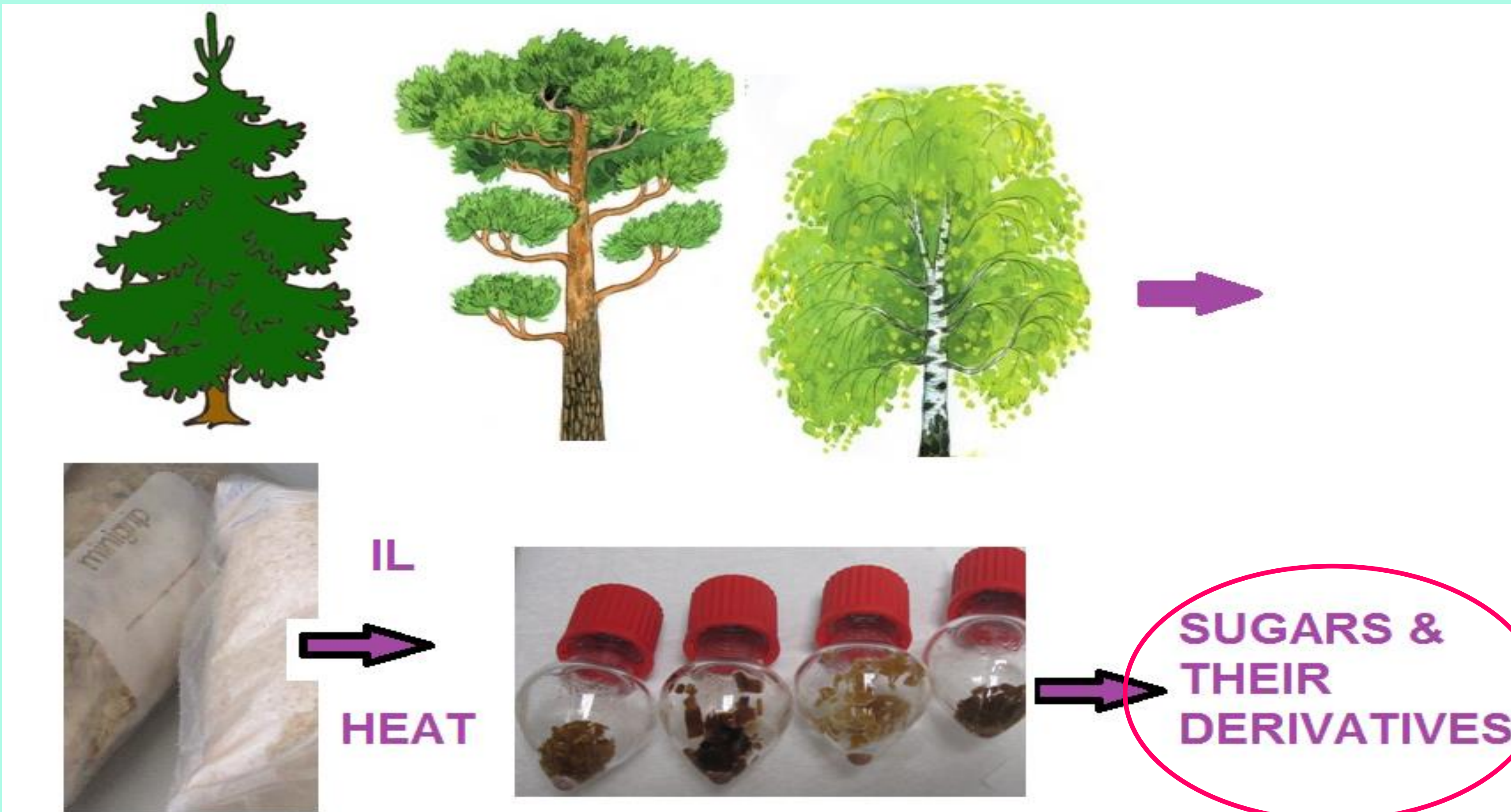
The focus/aim of the research



Saccharides & their derivatives – why?

- Furfural
- 5-HMF
- Cellobiose
- Gal
- Glc
- Man
- Fru
- Ara
- Xyl

Valuable platform chemicals

monosaccharides

Background & reasons for this research work

- **Climate change**

  →EU legislation to promote the biofuels & renewable energy sources

- **Increased demand for oil, especially in Asia**

  → We should not be too dependent on oil

How about possibilities to compensate or substitute petrochemical based industry?

- Replacing of some **oil** based industrial products with the **ethanol** based ones:
  - E.g. Örnsköldsvik, Sweden in wartime

    Paper mill cellulose → Glc → fermentation to EtOH → used as fuel etc.
  - USA and Brazil are interested in ethanol as a chemical feedstock →

    (e.g. ethylene from ethanol instead of olefins from petrochemical steam cracking)

SAMPLES

The studied LIGNOCELLULOSICS

Softwood from Central Finland:

•**Scots pine** (*Pinus sylvestris*)

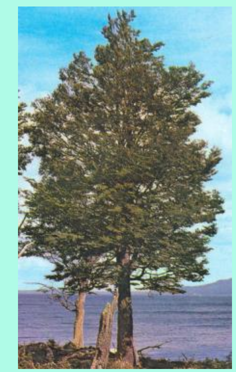
•**Norway spruce** (*Picea abies*)

•**Silver Birch** (*Betula pendula*)

…and in Chile

Forest residues:

- **Eucalyptus**
- **Lenga** *Nothofagus pumilio*



Crops residues:

- **Corn**
- **Wheat straw**

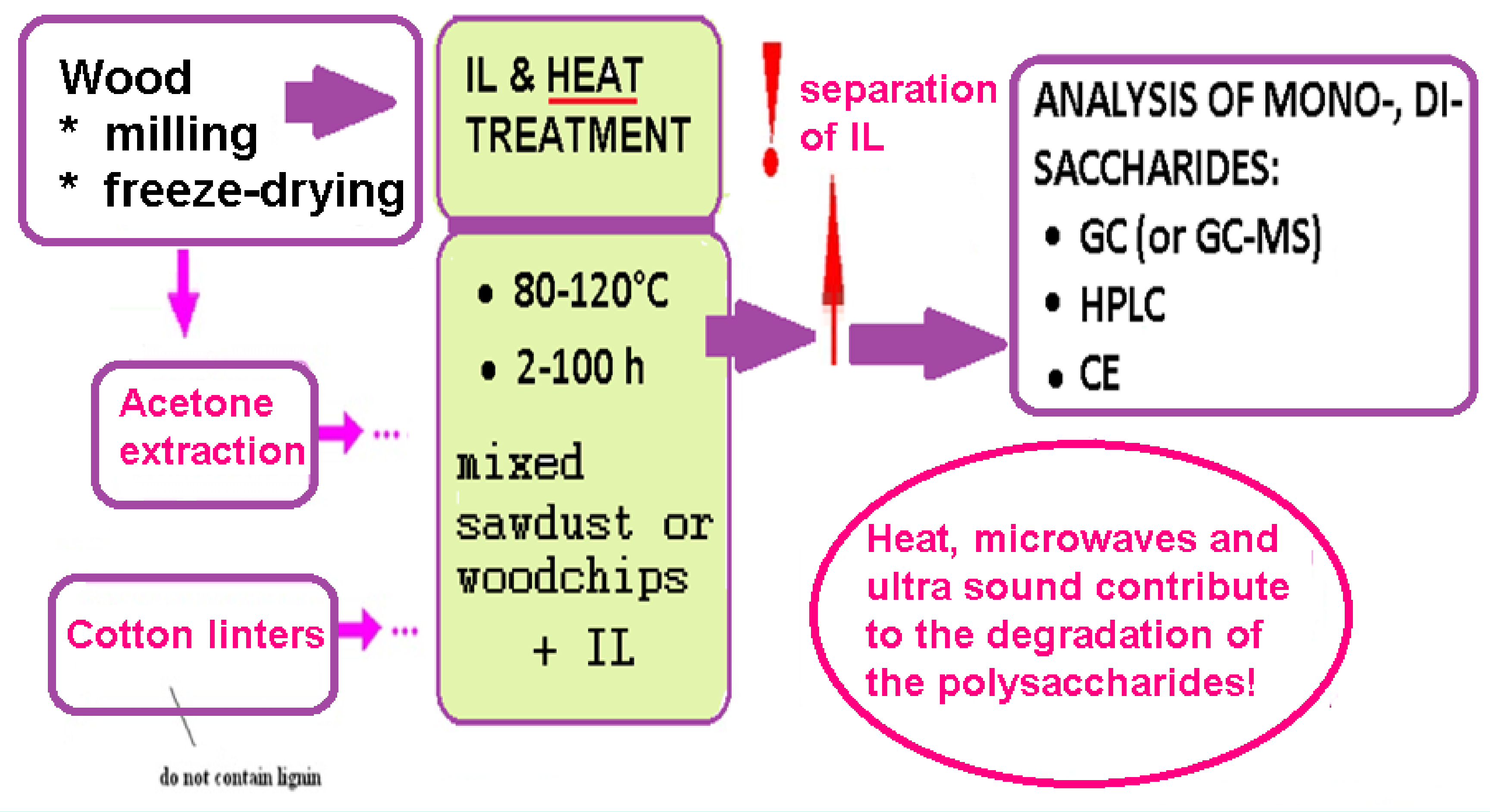
Sample collecting and sampling

To be considered before collecting sample - Things that might affect the results

- heart wood vs. sapwood
- growing place (e.g. heavy metals in soil?)
- age of wood
- condition/healthy of wood (fungi etc.)
- height where sample is taken from (1.2 - 1.50 m)
- Usually samples should be free from reaction wood & compression wood, branches and knots

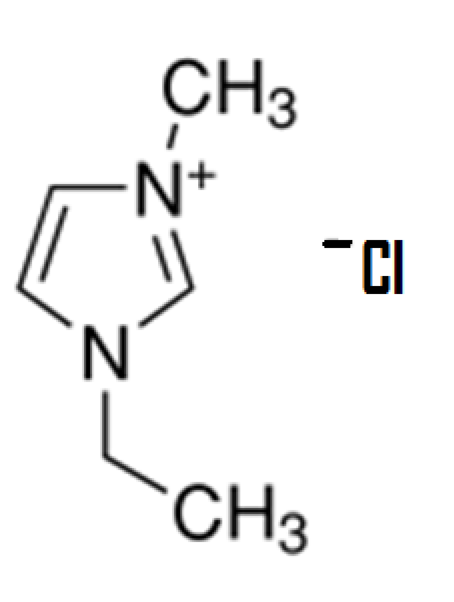
EXPERIMENTAL PROCEDURES

Experimental conditions & procedures:



IONIC LIQUIDS (ILs)

1-Ethyl-3-methylimidazolium chloride
EmimCl or $[emim]^+ [Cl]^-$



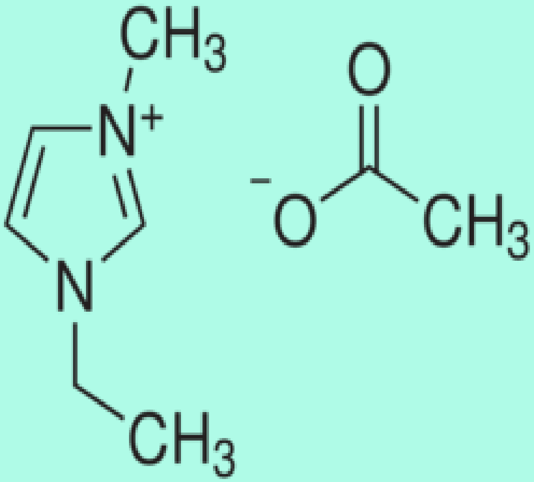
Molar mass:	146,62 g/mol
Density	1,1120 g/cm^3 (at 80 °C)
Melting point	77-80 °C ← impurities effect
Flash point:	186 °C
Viscosity	47.4 mPas (at 80 °C)
Flame point	515 °C
Solubility in water	∞

Very hygroscopic

Information concerning melting point varies in literature

1-Ethyl-3-methylimidazolium acetate

EmimOAc or $[emim]^+ [CH_3COO]^-$



- Molar mass: 170,21 g/mol
- Density 1.027 g/cm^3 at 25 °C
- Melting point > 30 °C
- Flash point: 164 °C
- Viscosity 10 mPas (at 80 °C)
- Solubility in water ∞

THE ANALYSIS METHODS (CE, GC & HPLC) AND COMPARISON OF THEM IN THIS PARTICULAR CASE

(FOR ANALYSIS OF CARBOHYDRATES & THEIR DEGRADATION PRODUCTS IN LIGNOCELLULOSIC SAMPLES IN THE PRESENCE OF IONIC LIQUIDS)

GC, HPLC & CE

GC analysis

Analysis of carbohydrates on extract

Without acid methanolysis

- calibration samples: STD sugars with xylitol in MeOH
- ISTD: xylitol instead of sorbitol

→Evaporation (N_2) + vacuum oven →

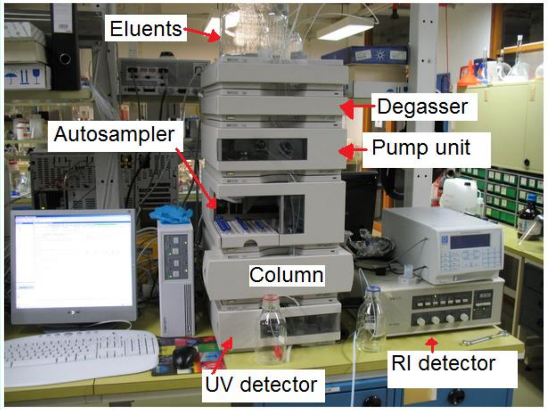
- silylation:

  pyridine, HMDS and TMCS

→ shaking (and ultrasonic bath)

HPLC analysis

- calibration samples in eluent solution
- no derivatization/silylation needed

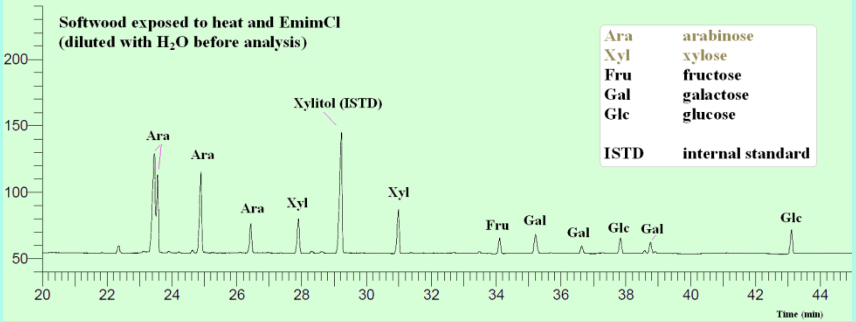


CE analysis

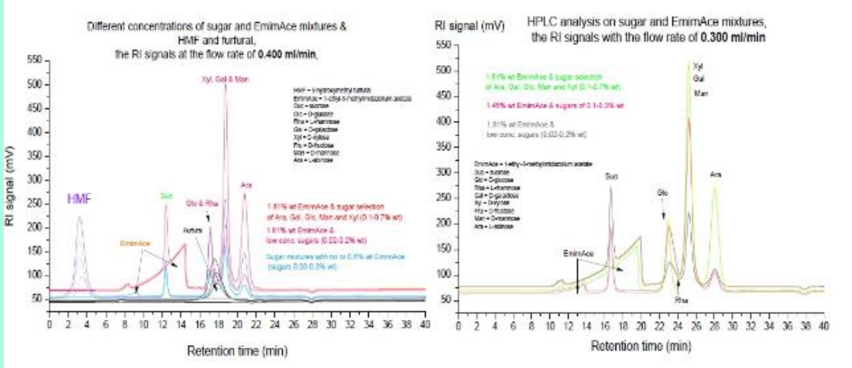
- calibration: STD sugars + ISTD (e.g. sucrose)
- no derivatization/silylation needed
- liquid phase can be analyzed after centrifuging and filtering

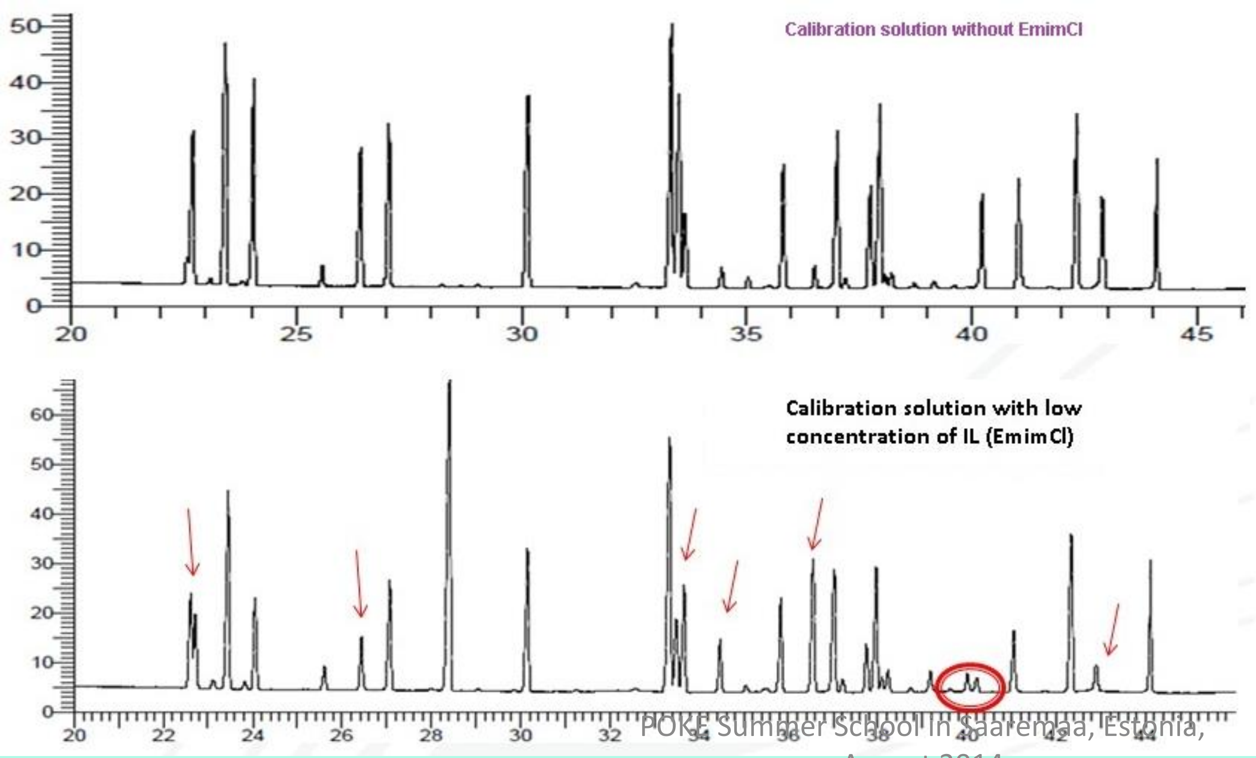
Differences in analysis methods

Sample results: GC analysis



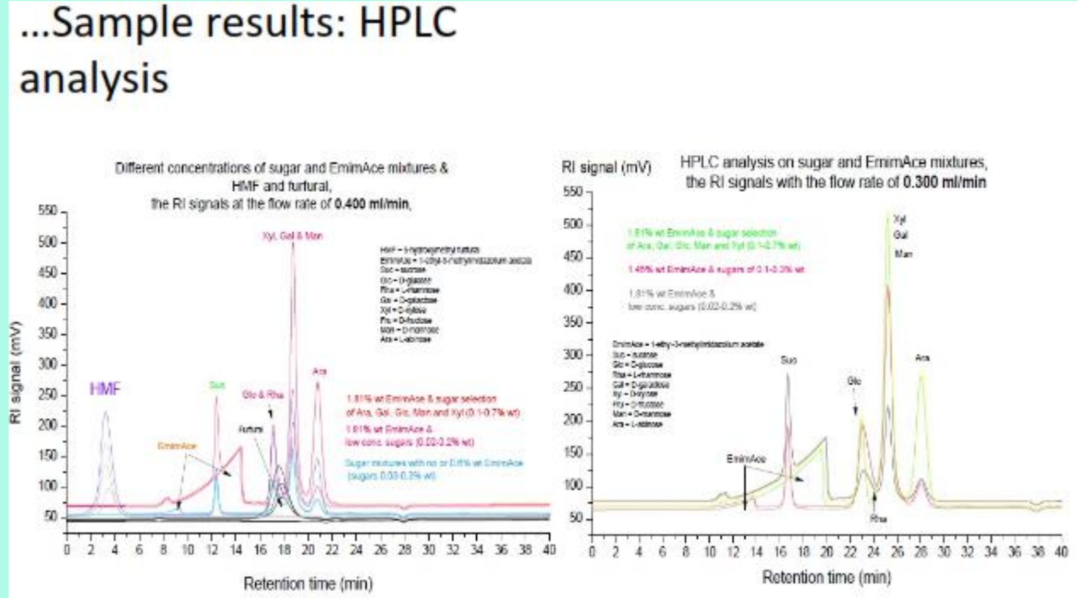
...Sample results: HPLC analysis

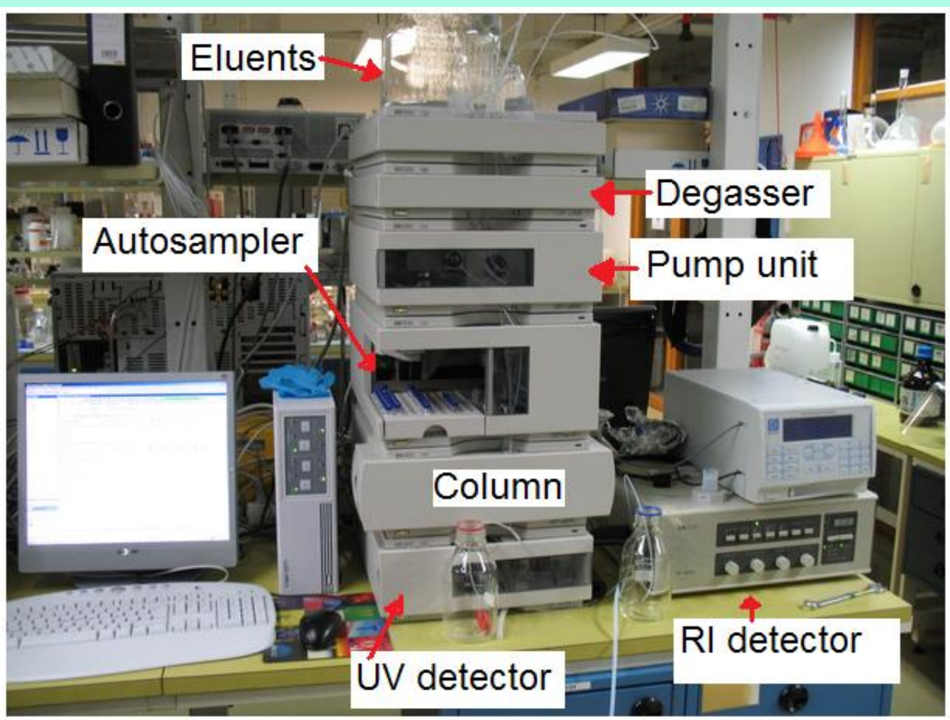




Reliability problem with GC monosaccharide calibration

HPLC analysis

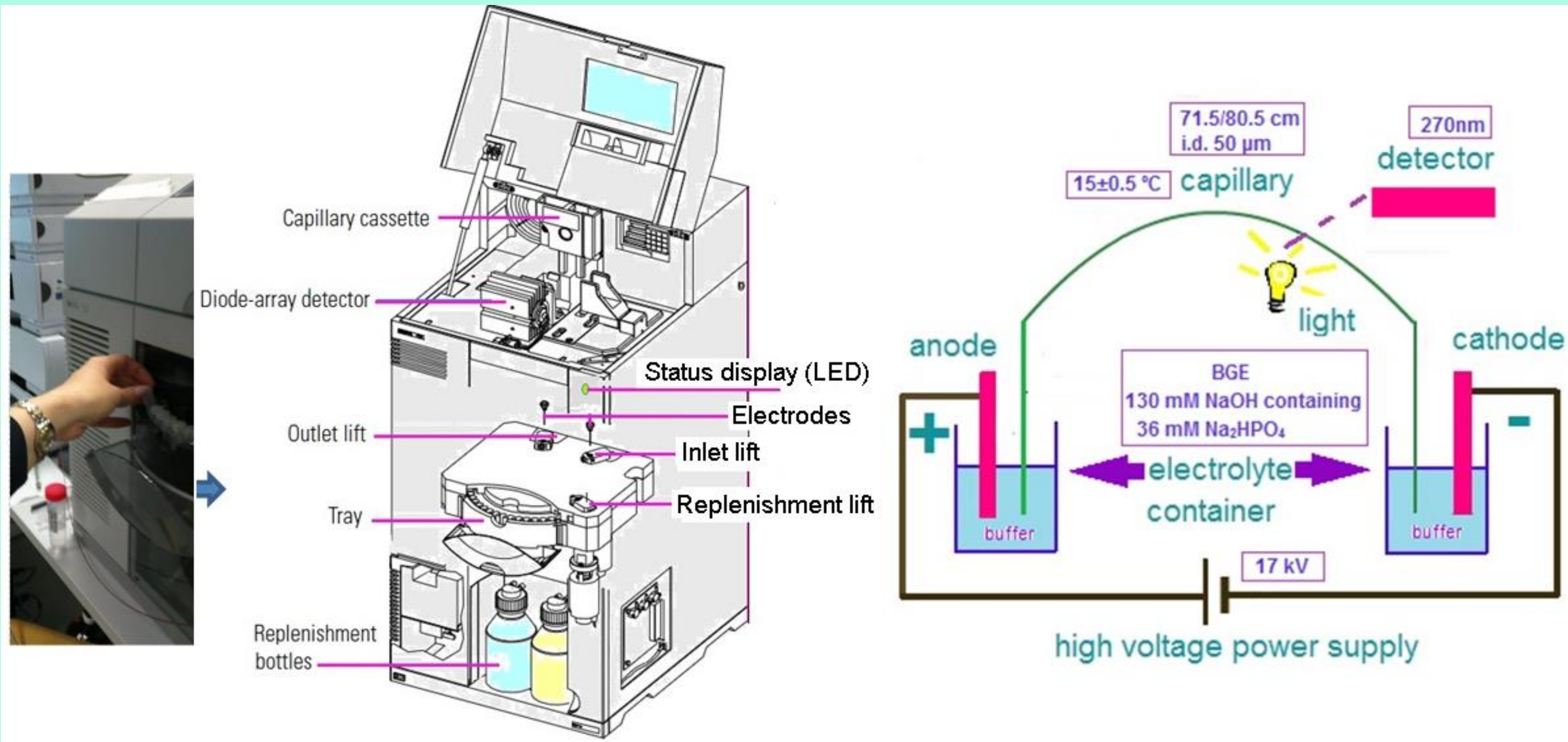




Chromatography involves a mass transfer process involving adsorption

CE (Capillary electrophoresis)

- Separates ions based on their electrophoretic mobility
- Electrophoretic mobility depends on the charge of the molecule, the viscosity, and the atom's radius.



CE (Capillary electrophoresis)

- Detector: diode array UV/Vis
- Background electrolyte/buffer solution:

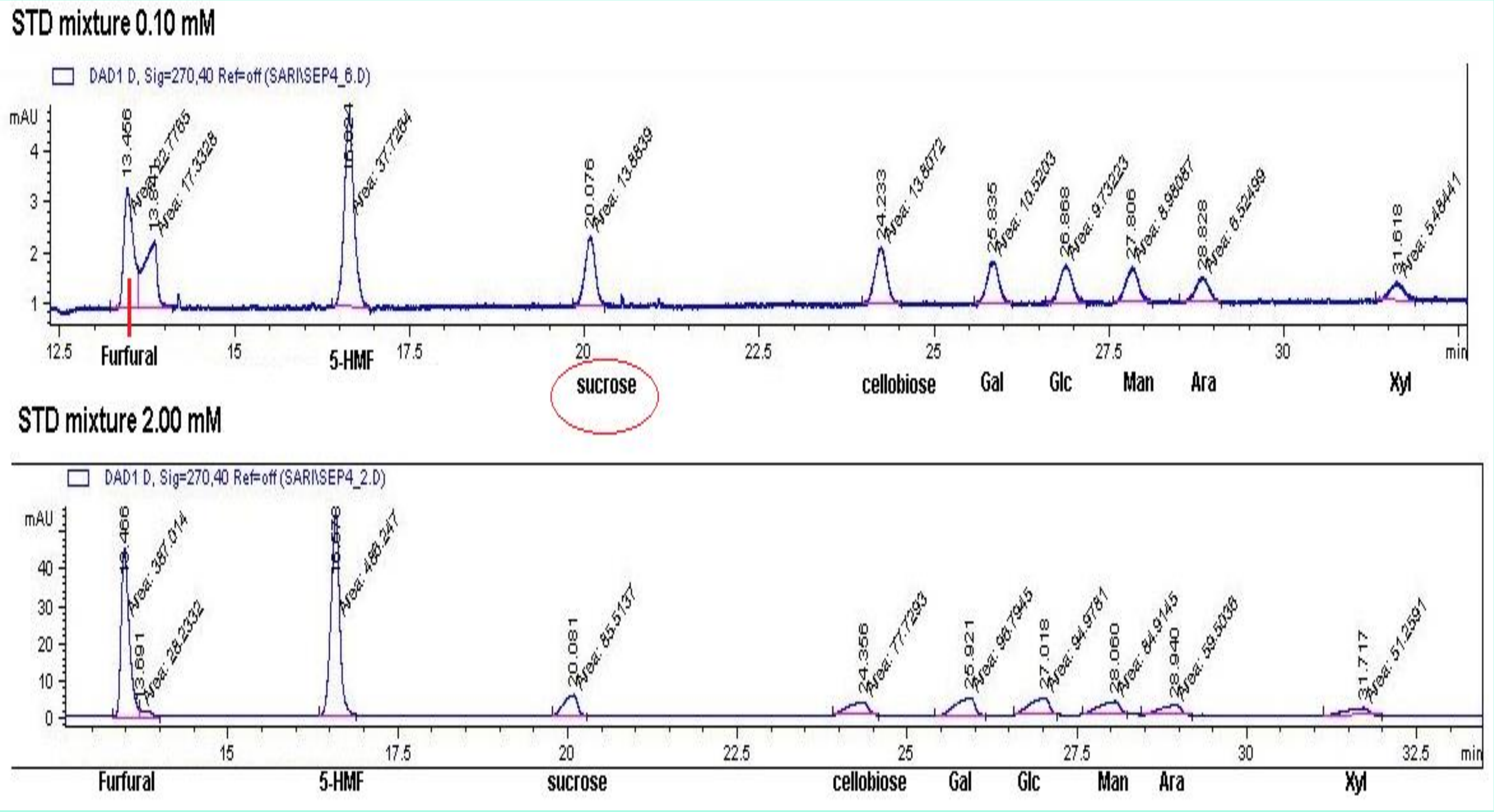
  130 mM NaOH containing 36 mM Na_2HPO_4

  - ❖ must always be fresh

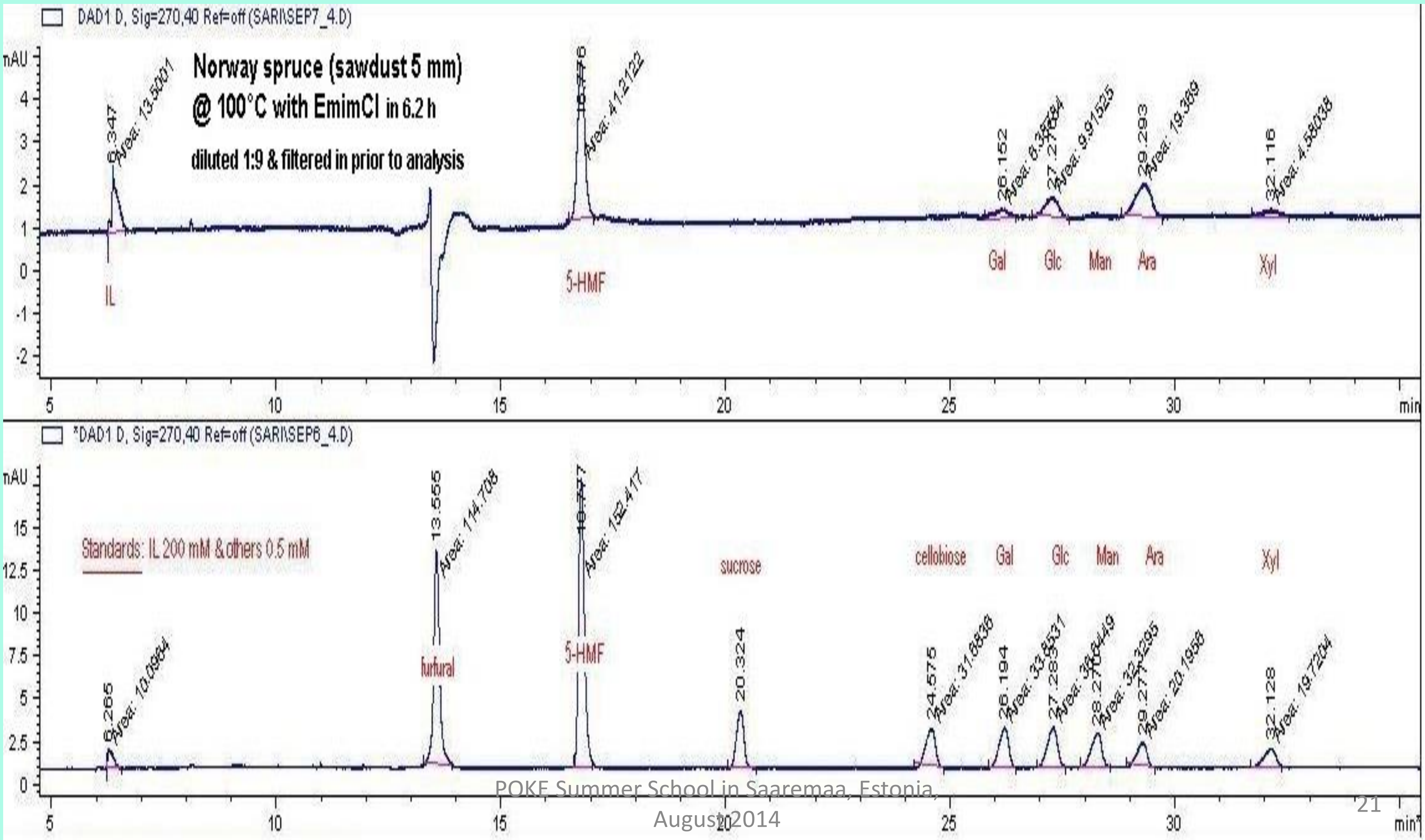
❖ **Sample derivatization is not needed**

→ instead: dilution, centrifugation & filtration

CE calibration standards

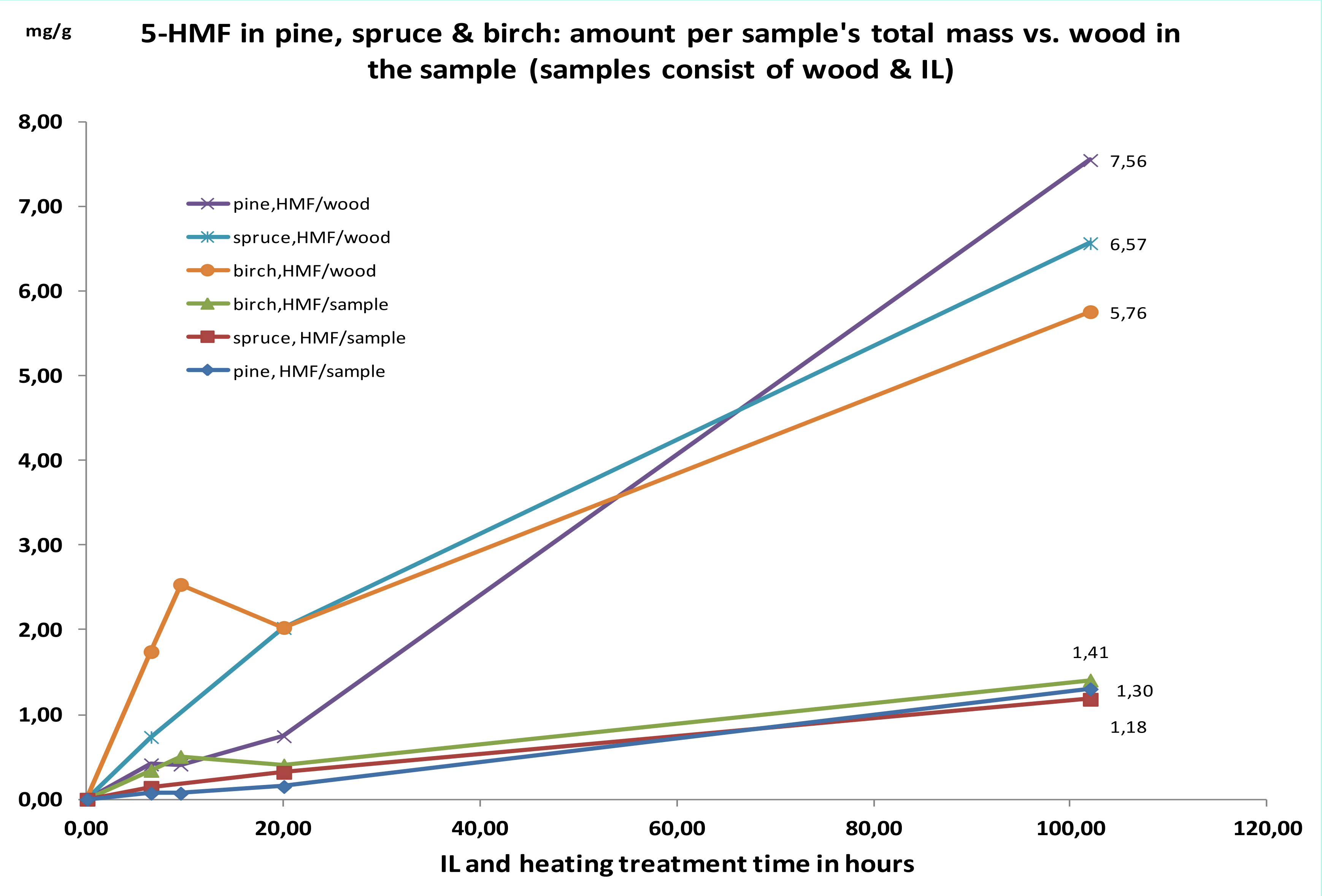


A typical example of CE results



HMF

in pine, spruce and birch samples


mg/g
5-HMF in pine, spruce & birch: amount per sample's total mass vs. wood in the sample (samples consist of wood & IL)
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
pine,HMF/wood
spruce,HMF/wood
birch,HMF/wood
birch,HMF/sample
spruce, HMF/sample
pine, HMF/sample
7,56
6,57
5,76
1,41
1,30
1,18
0,00
20,00
40,00
60,00
80,00
100,00
120,00
IL and heating treatment time in hours

Comparison summary (CE, HPLC, GC)

- CE analysis is the method of choice
- GC (+ STD sugar column) is unreliable when ILs are present: concentration of IL is critical
- HPLC suffers from peak overlapping

Conclusions

IL pretreatment leads to significant formation of HMF and in some cases furfural

(like all depolymerization/ degradation processes) – good indicator to follow up (e.g. fermentation inhibitors, degree of depolymerization, colorization …)

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ACADEMY OF FINLAND

RAISIO

COST ACTION CM0903

DoRa

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ARCHIMEDES

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