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Metals in Biorefineries

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Why are metals of importance ?

It is important to understand the natural existence and distribution of metal ions in tree material and the reactions of the metal ions with wood fibres and other chemicals in different stages of the paper making process and in the energy conversion processes.

The reasons to study

- Chemical forms of metals in wood, pulp and process liquors varies from metal to metal
- Study on metals gives important information to predict their behavior in different parts of paper making and energy conversion processes as well as their environmental impact.

Objectives

- Effects of metals on:
  - Flows, Balances, Processes and products
- Metals in wood= metals in fuels
- Important to understand because of:
  - Fouling of equipment (K, Ca, Si)
  - Corrosion of hot heat transfer surfaces (K, Zn, Pb)
  - Emission (EU directive for heavy metals: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Tl, Sb, V)

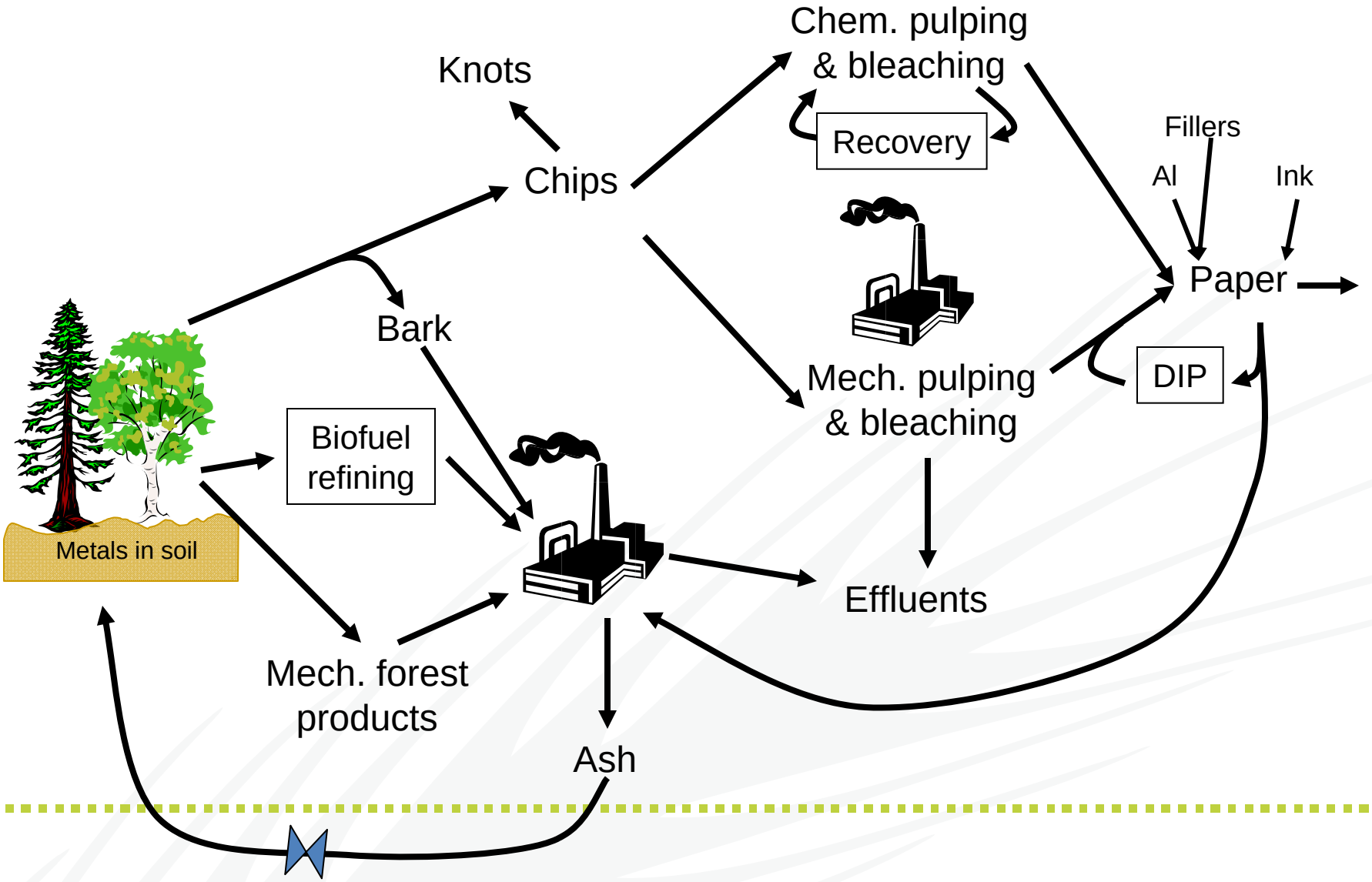
Metals are important for the growth of the tree and excist as natural components in tree material

Elemental distribution of different concentration ranges for stem wood of Scots pine (*Pinus sylvestris*) tree

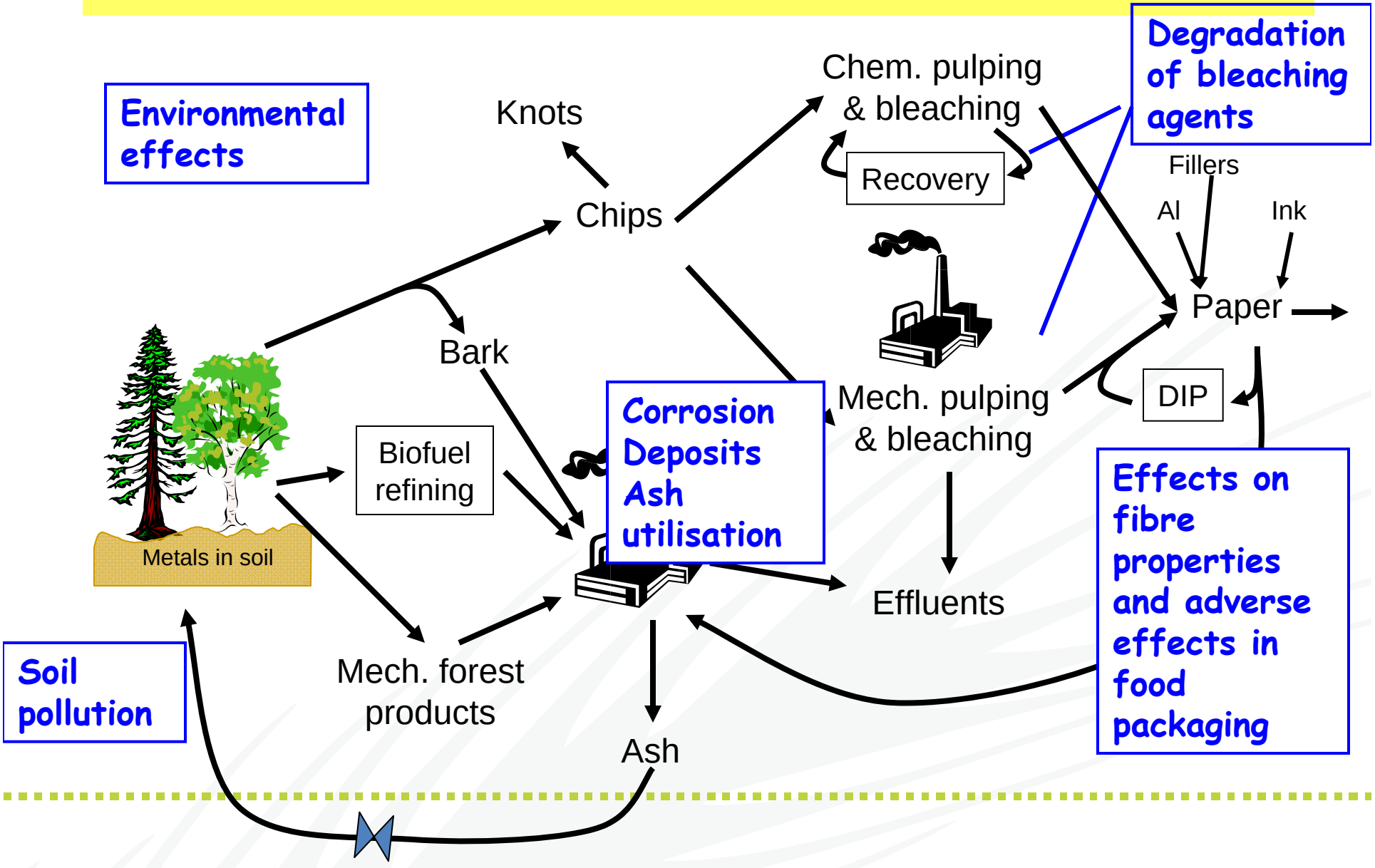
Concentration range, ppm (*mg/kg*)	**Elements**
1000 – 100	Ca, K, Mg
100 – 10	F, Fe, Mn, Na, P, S
10 – 1	Al, B, Si, Sr, Zn, Ti
1 – 0.1	Ag, Ba, Cd, Cr, Cu, Ni, Rb, Sn
0.1 – 0.01	Bi, Br, Ce, Co, I, La, Li, Pb, Se, W
0.01 – 0.001	As, Eu, Gd, Hf, Hg, Mo, Nd, Pr, Sc, Sb

Elements in red are from the EU list of ”dirty dozen”.

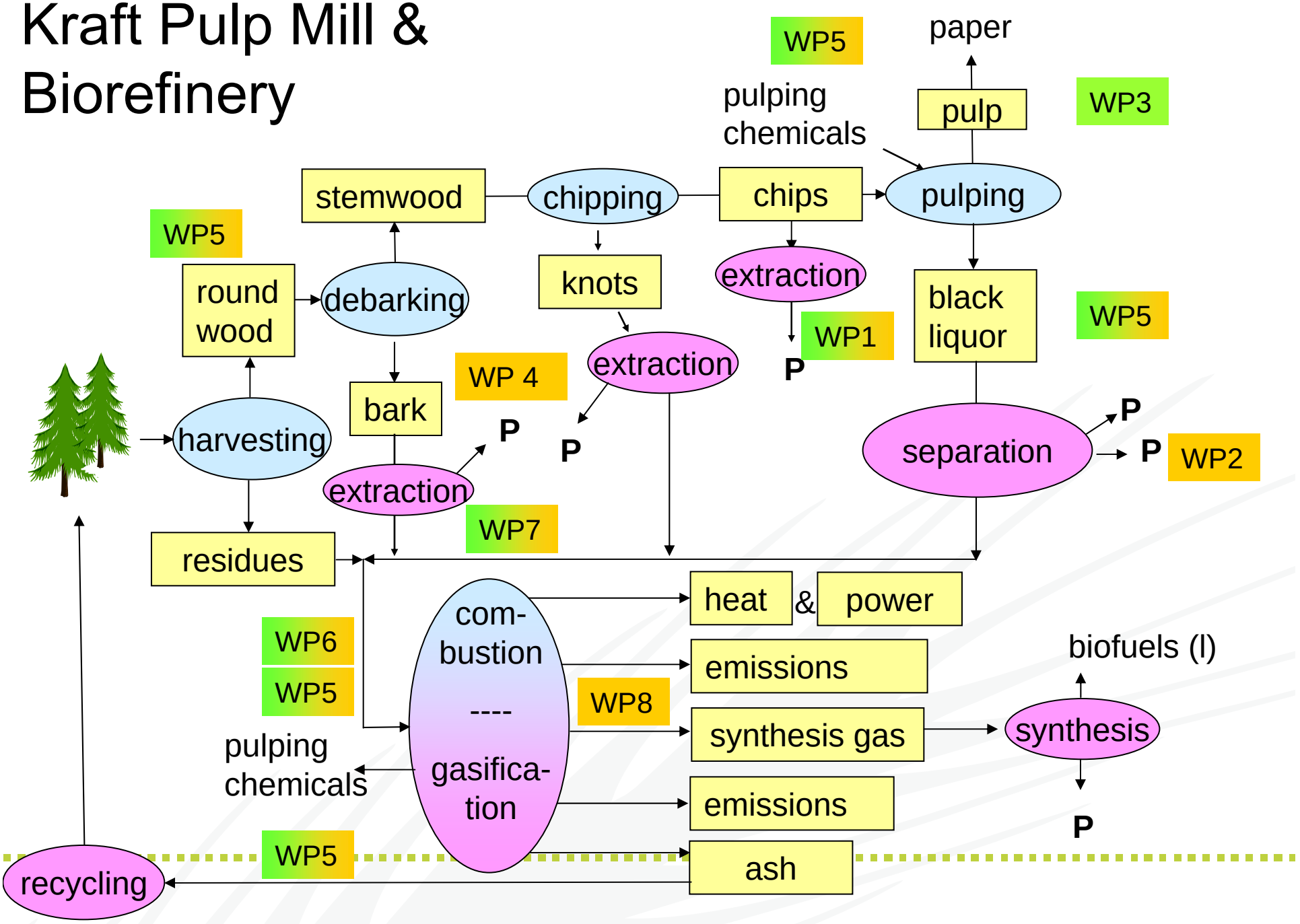
Metals in wood are significant!



Metal management is important

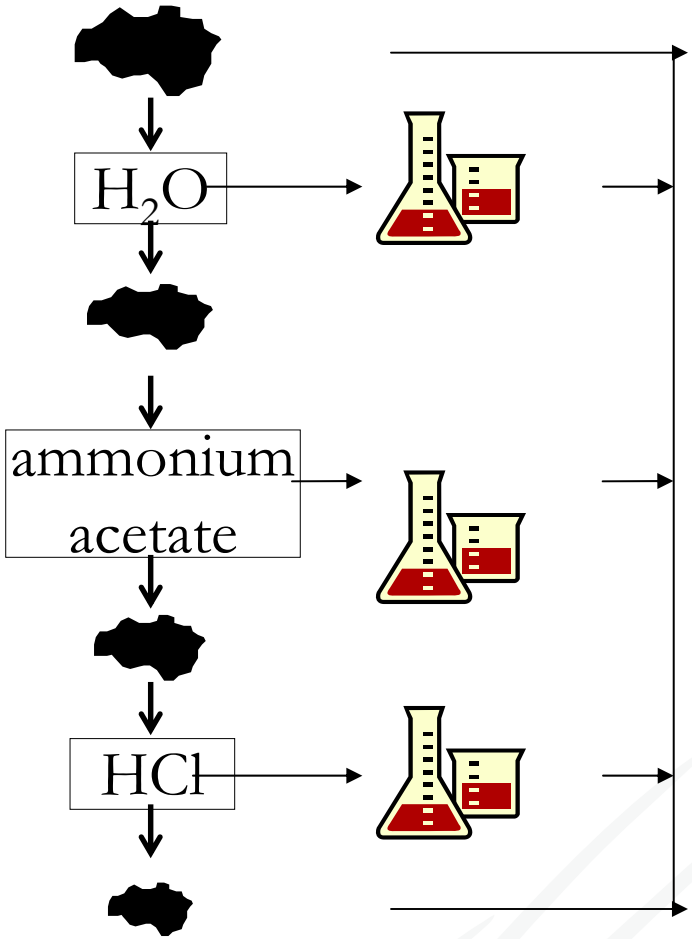


Kraft Pulp Mill & Biorefinery



Characterization of biofuel

Chemical fractionation



Analysis

all major ash elements

alkali sulfates/ carbonates, chlorides

exchangeable some $CaCO_3$

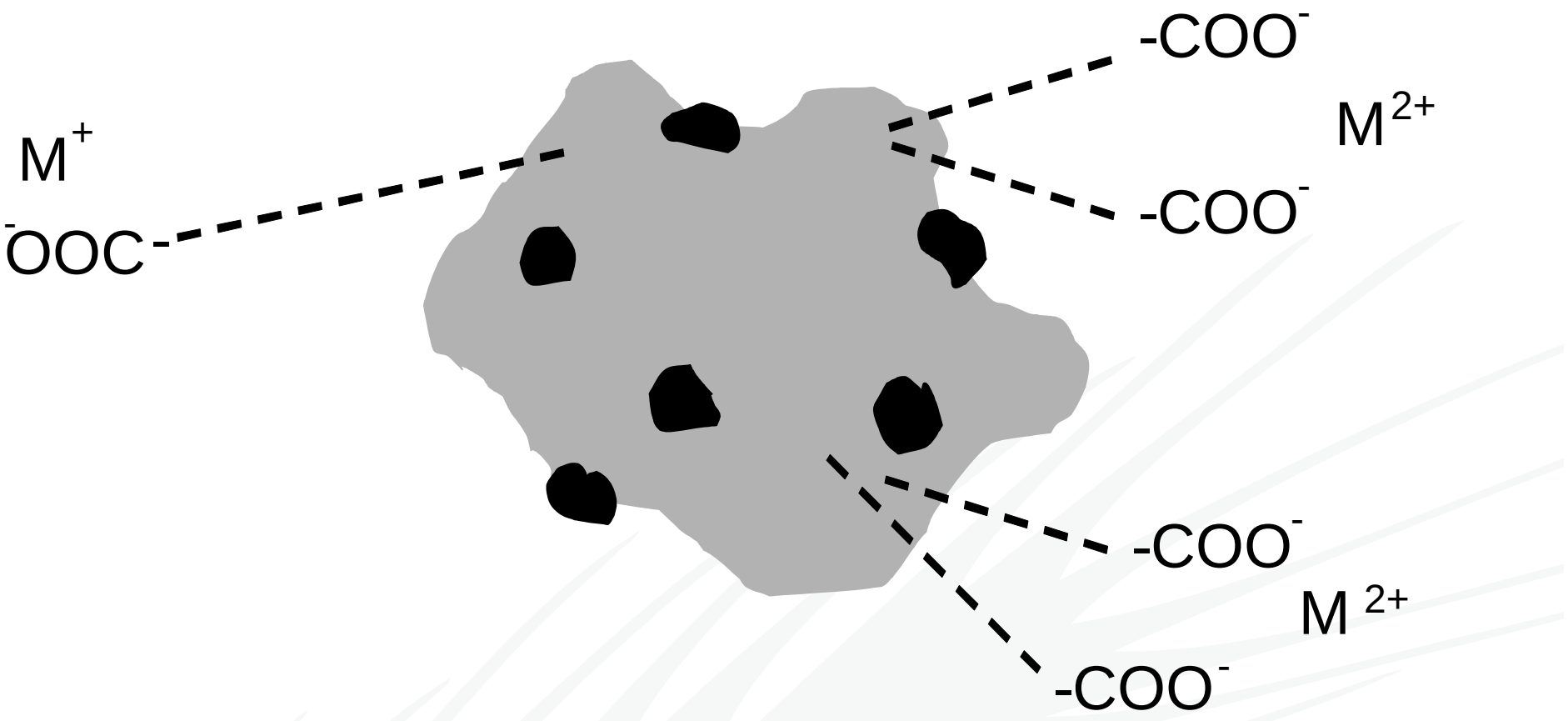
carbonates, sulfates

silicates, insoluble rest

Objective

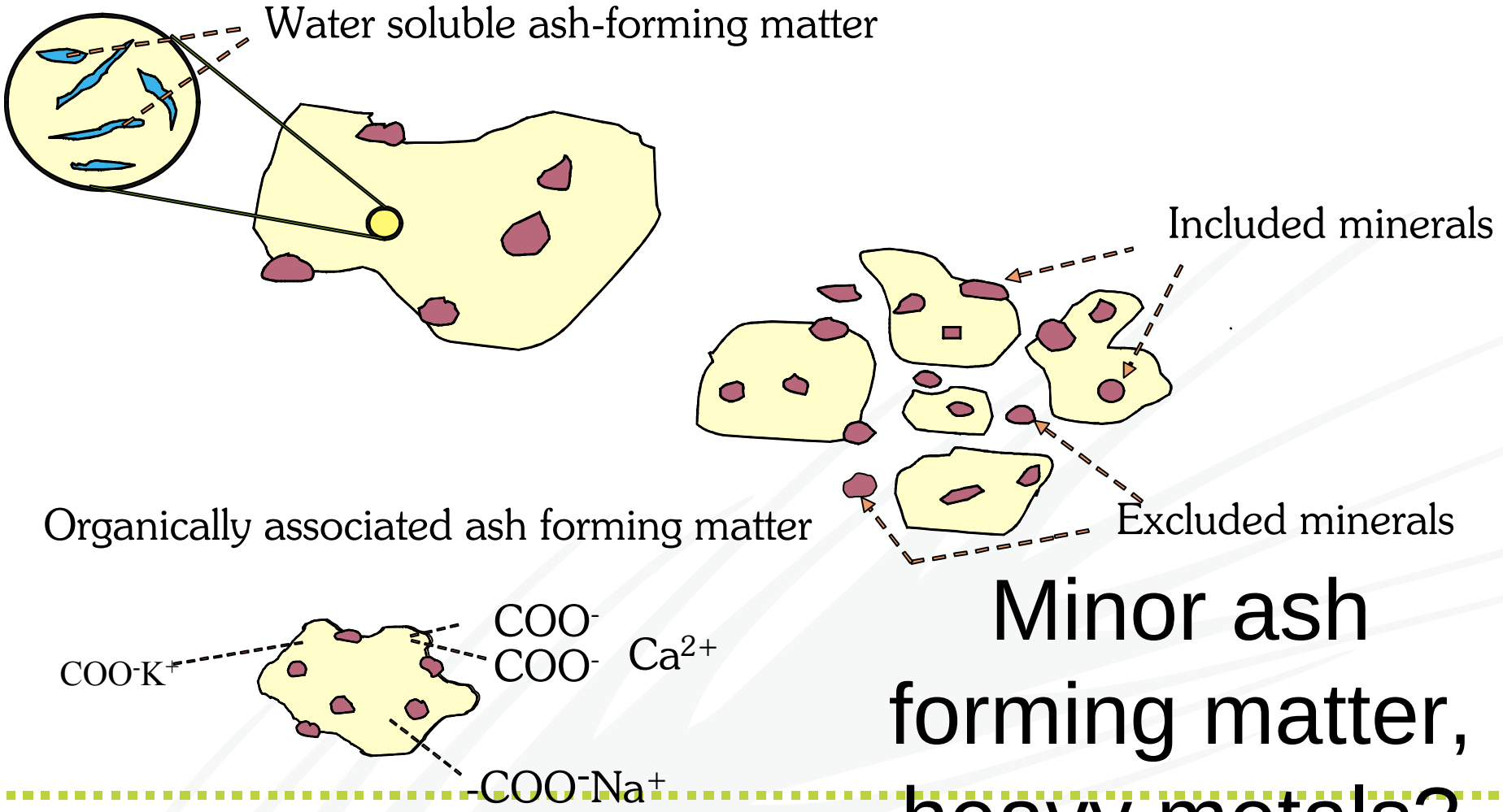
- to investigate the forms of metal binding in Scandinavian wood-fuels by
  - sorption of a color dye
  - step-wise leaching in H_2O, NH_4Ac and HCl
    - element analyzes of the leachates
    - ion-chromatography of the leachates
  - potentiometric titration
- of the pure biomass from tree samples

Metals associated with fuel matrix



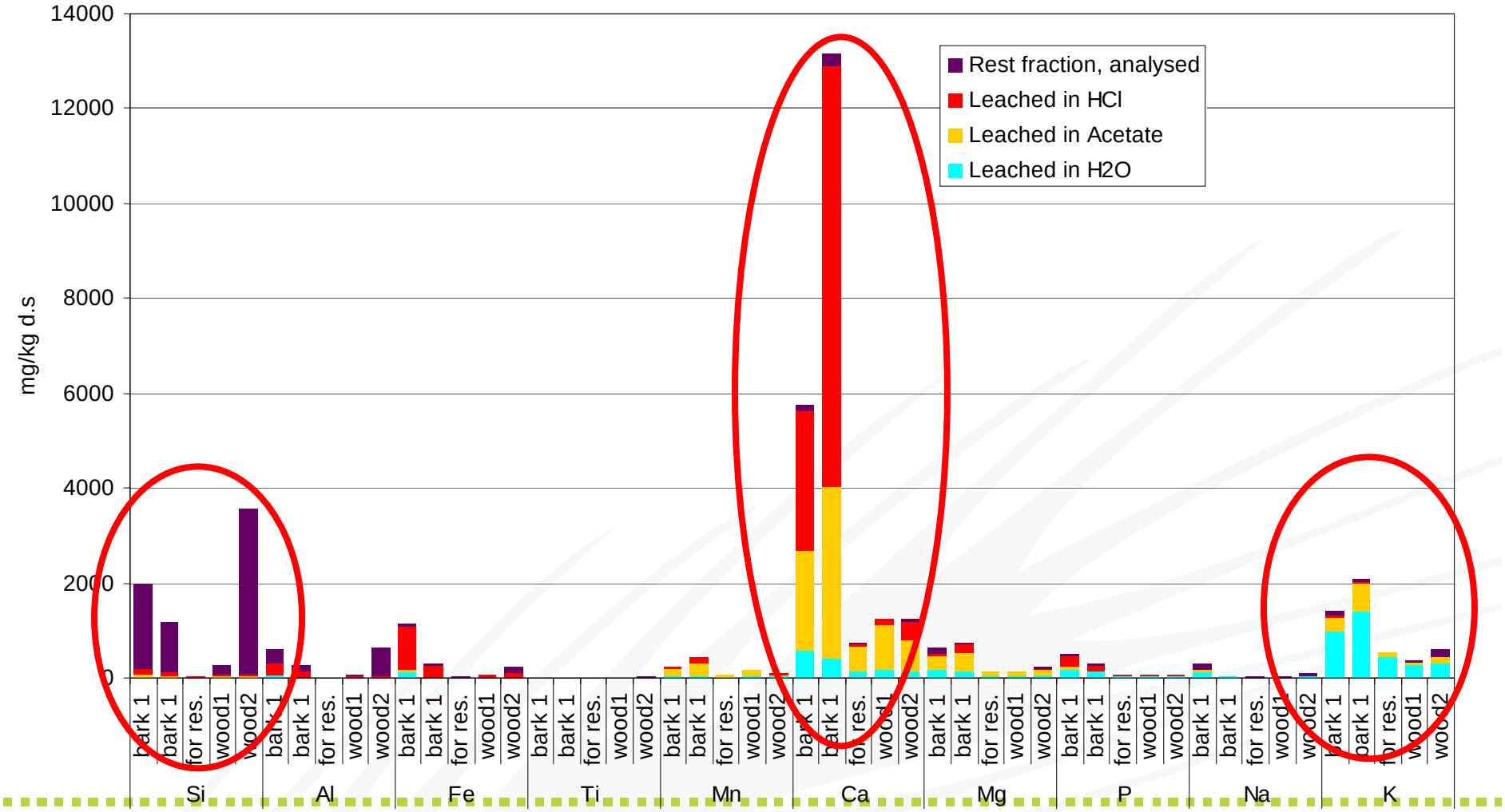
Johan Werkelin, Maria Zevenhoven

Major Ash Forming Matter in Fuels

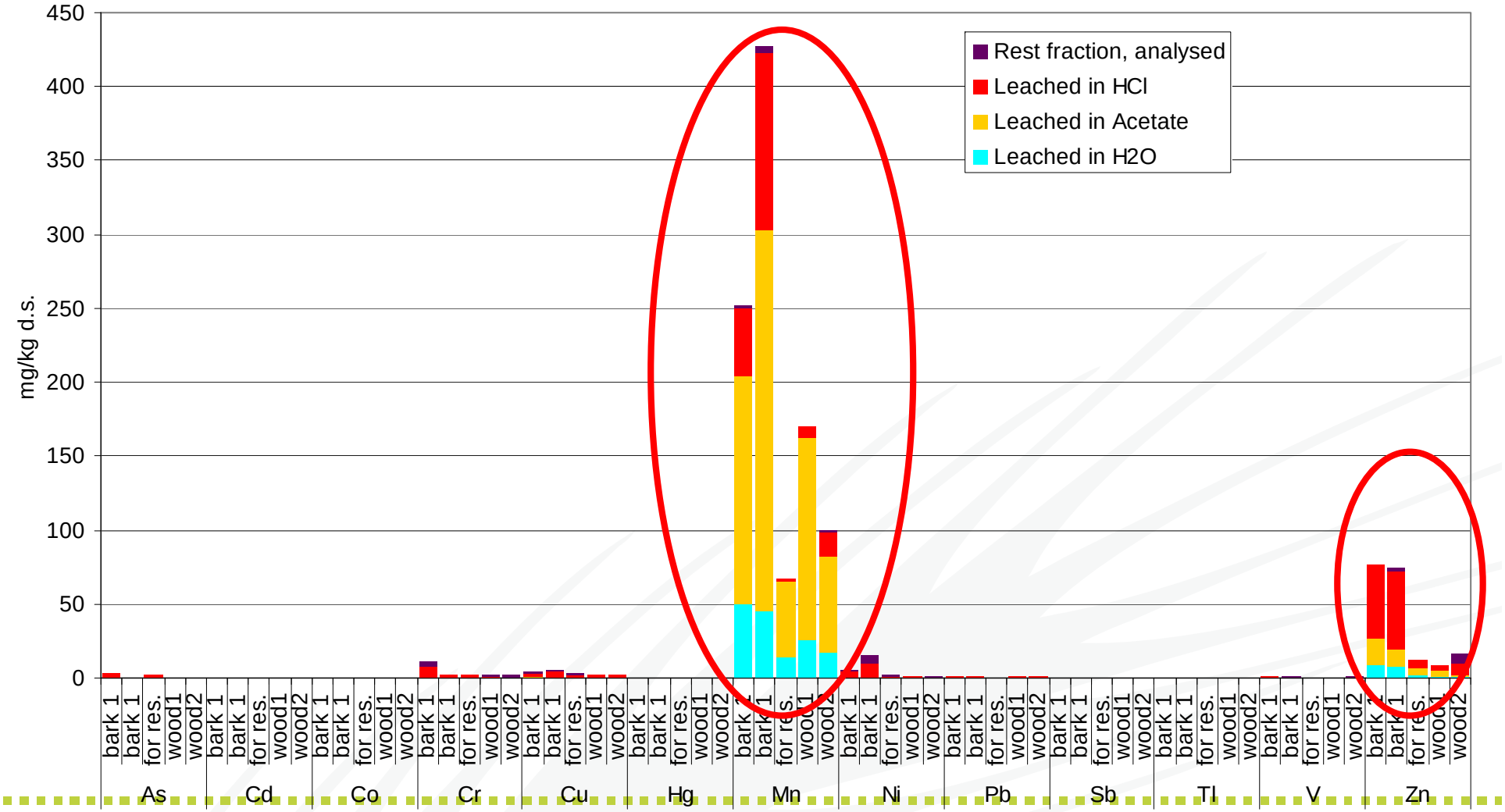


Minor ash forming matter, heavy metals?

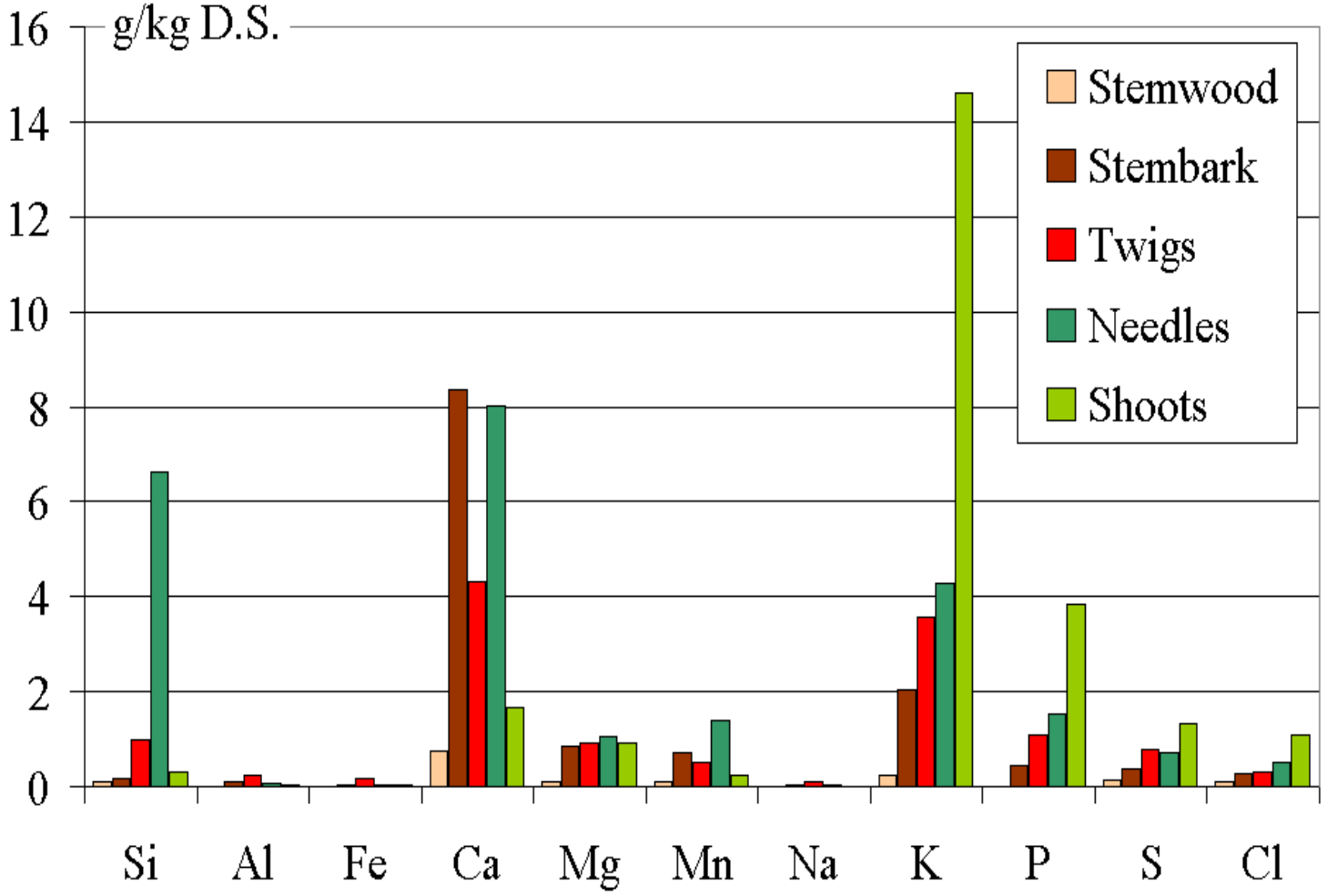
Main Ash-forming Matter



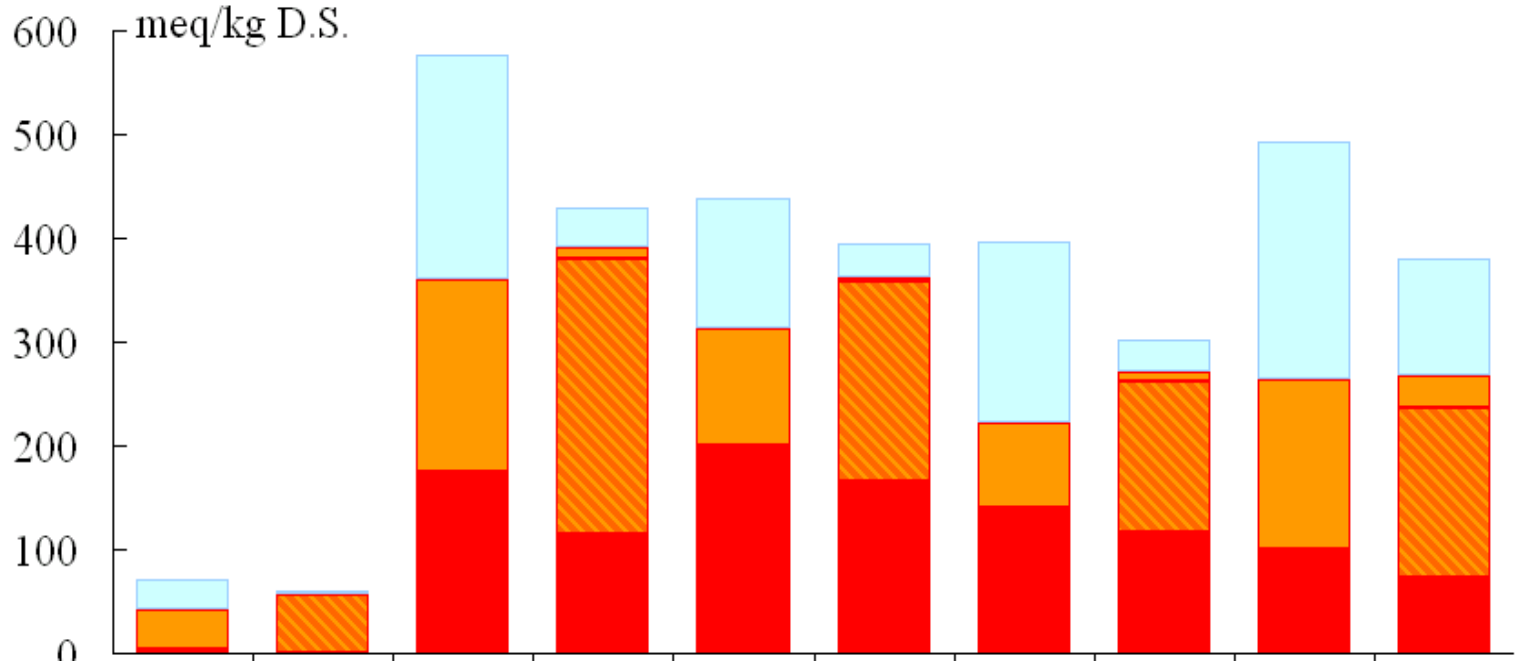
Heavy Metals (EDD12+Zn)



Ash Elements in Spruce



Balance for Pine wood, bark & foliage



	Pine Wood		Pine Bark		Pine Twigs		Pine Needles		Pine Shoots	
	cations	anions	cations	anions	cations	anions	cations	anions	cations	anions
Leached in H2O	28	4	217	39	126	32	175	32	229	112
Leached in A.A.	38	1	185	11	112	4	82	9	165	29
Anionic groups		56		264		193		145		165
Leached in HCl	4	0	175	115	201	166	140	116	99	73

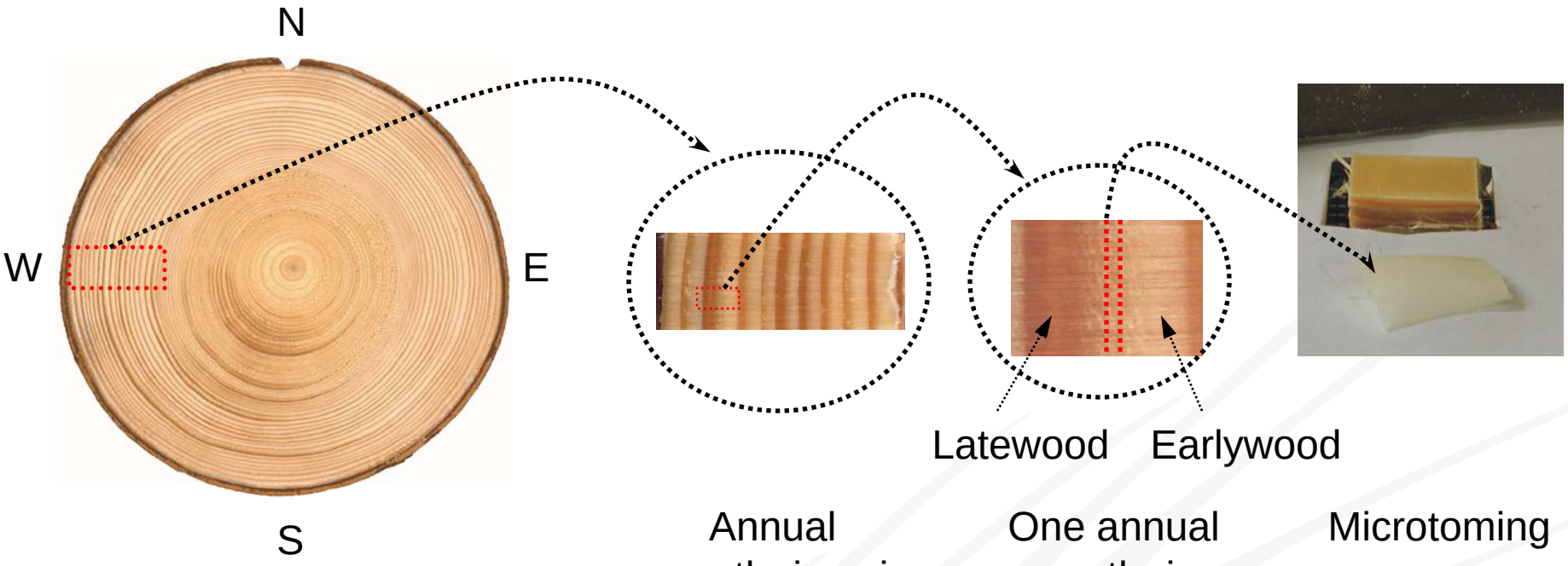
Johan Werkelin

Conclusion

- Metal binding in trees was determined
- Metals: in wood: in bark: in foliage:
  - as salts 5 – 10% 5 – 10% 10 – 30%
  - anionic gr 80 – 90% 20 – 50% 20 – 50%
  - as oxalate 0 – 10% 20 – 50% 10 – 40%
- Chemical mode of ash-forming elements
  - influence ash chemistry and deposit formation

Metals in wood

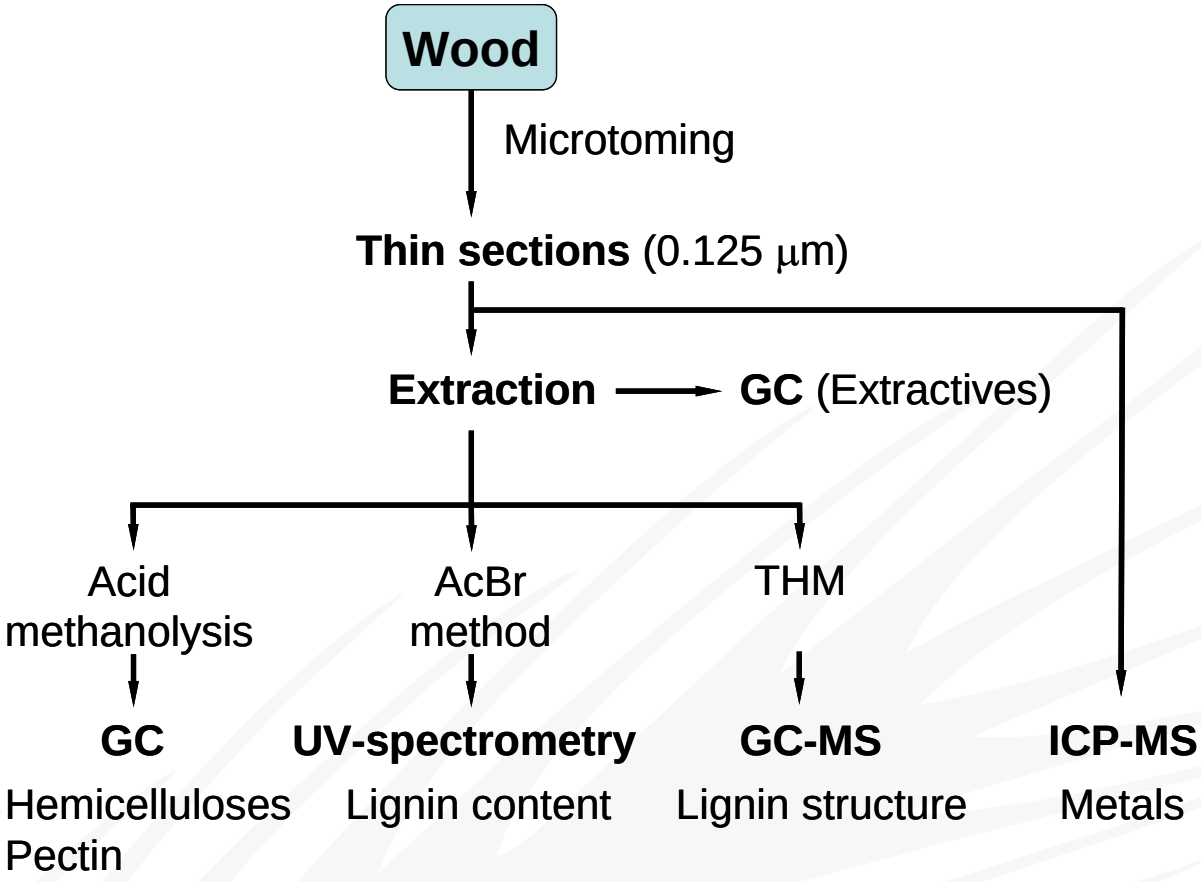
Sampling for microanalysis

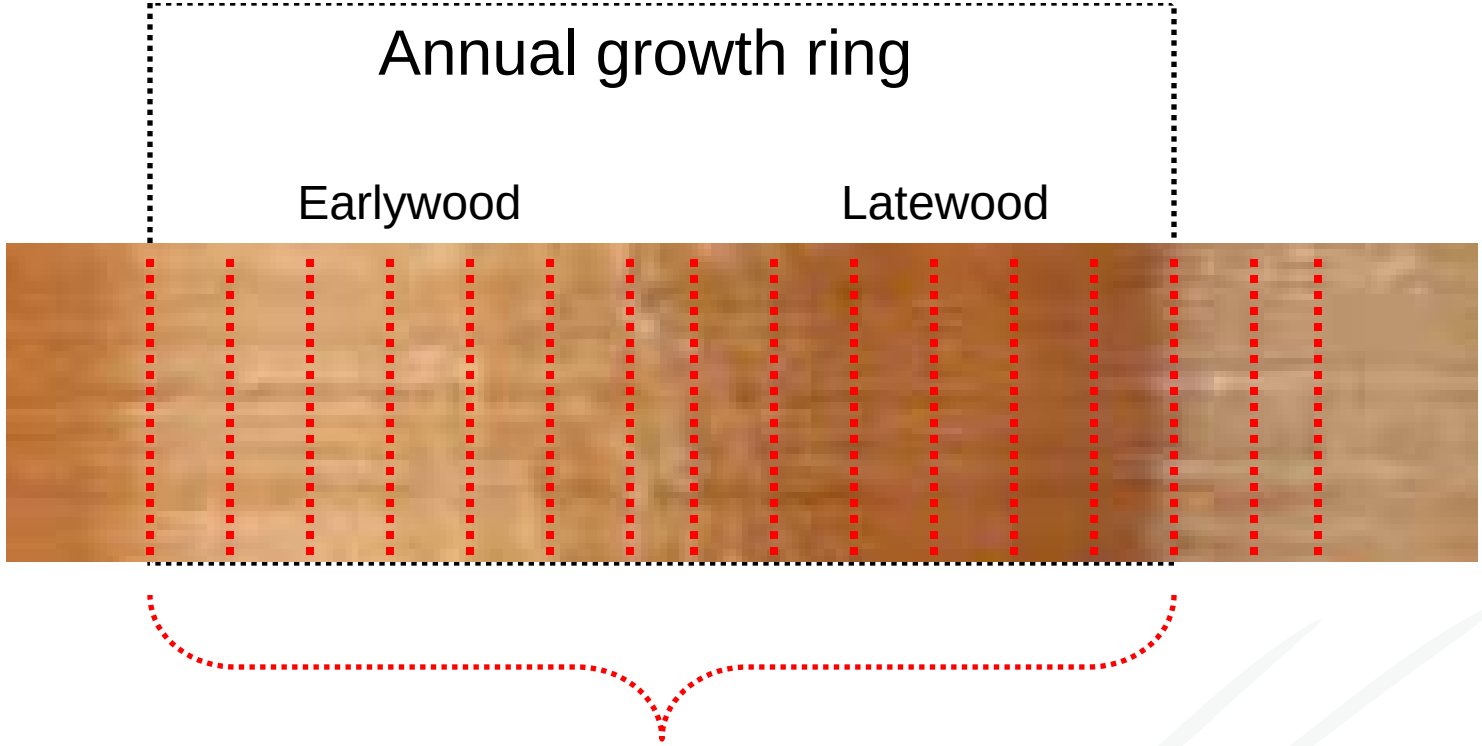


Wood discs from 2 meters height of a ~40-year-old Norway spruce tree were used.

Andrey Pranovich

Scheme used for chemical microanalysis of wood samples



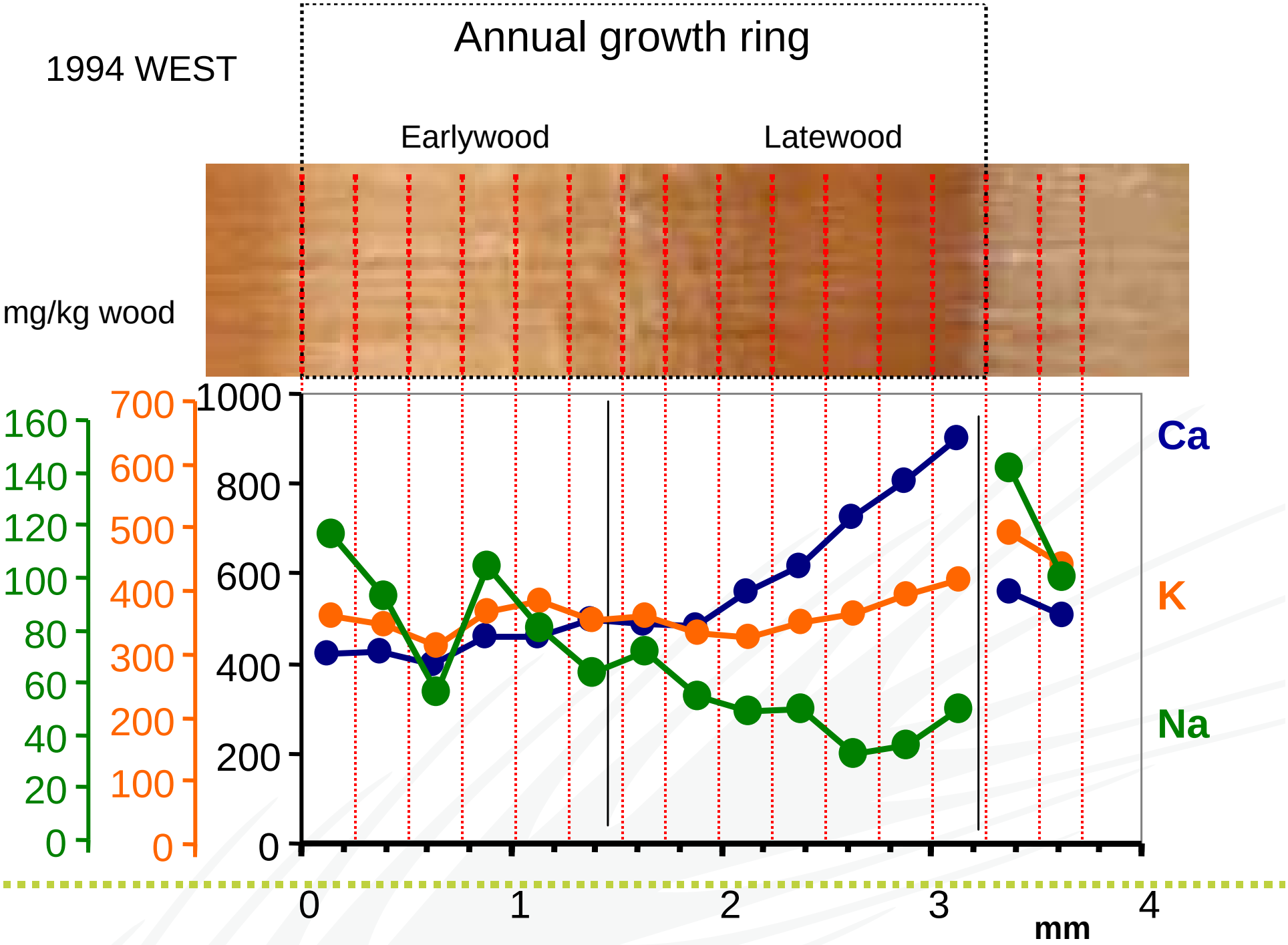


Distribution of analytes within annual growth ring

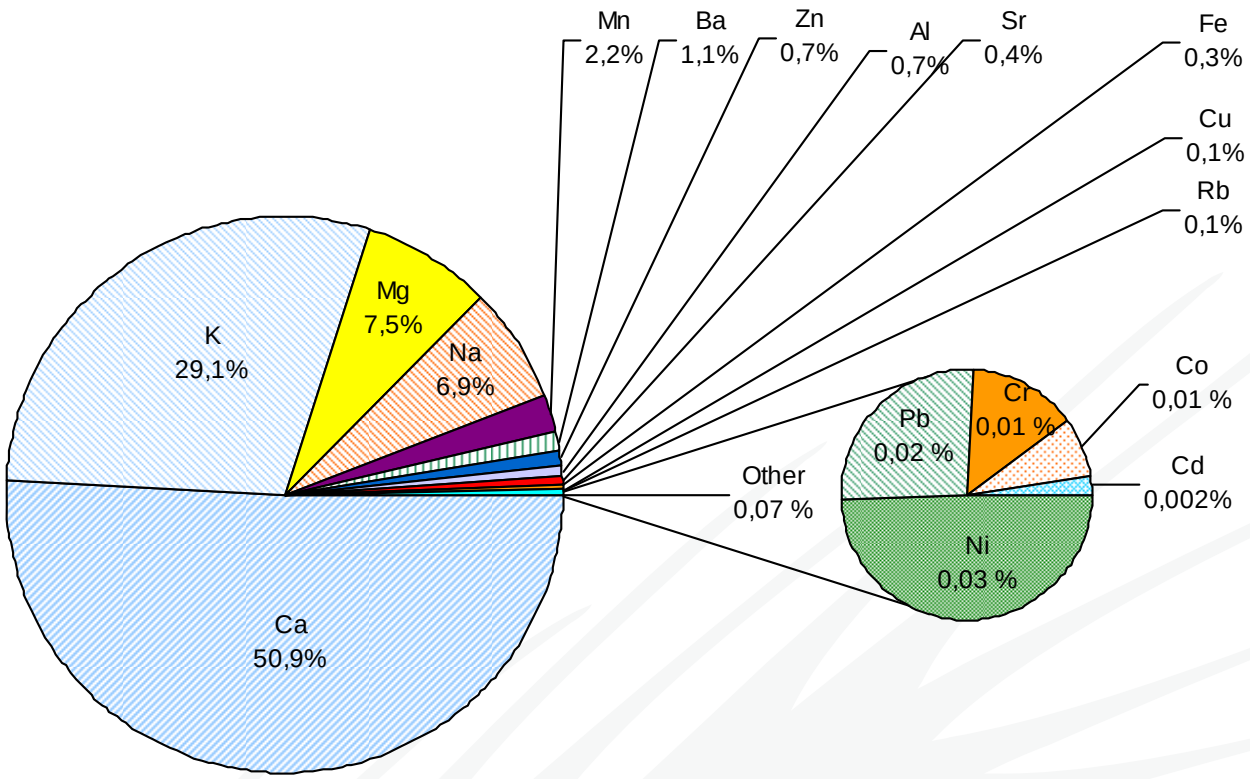
sugars from hemicelluloses, uronic acids

lignin

metals

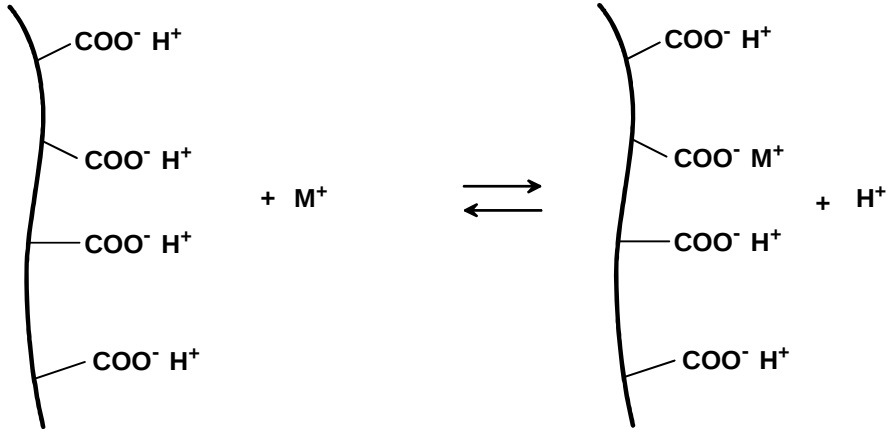

1994 WEST
Annual growth ring
Earlywood
Latewood
mg/kg wood
160
140
120
100
80
60
40
20
0
700
600
500
400
300
200
100
0
1000
800
600
400
200
0
Ca
K
Na
0
1
2
3
4
mm

Metal content in spruce stemwood (average from 1989 and 1994 annual growth rings across the stem)



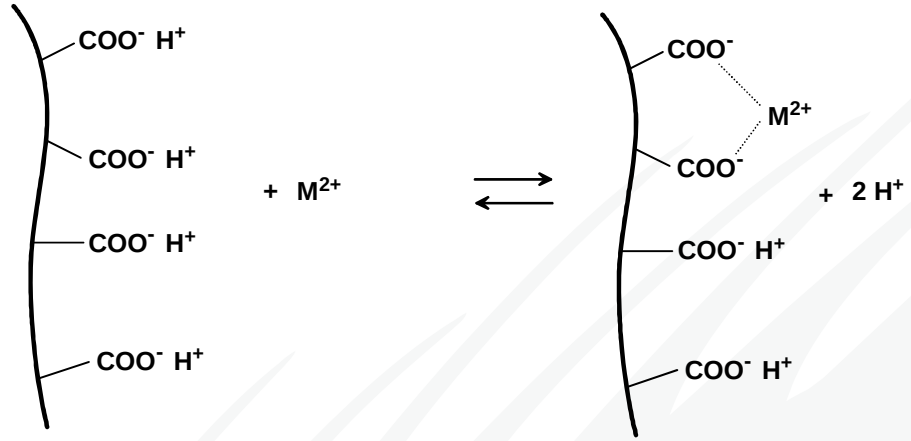
Binding of metal ions to wood fibres

Ion-exchange equilibria in wood fibres



$$M^+ + \overline{HR} \rightleftharpoons \overline{MR} + H^+$$

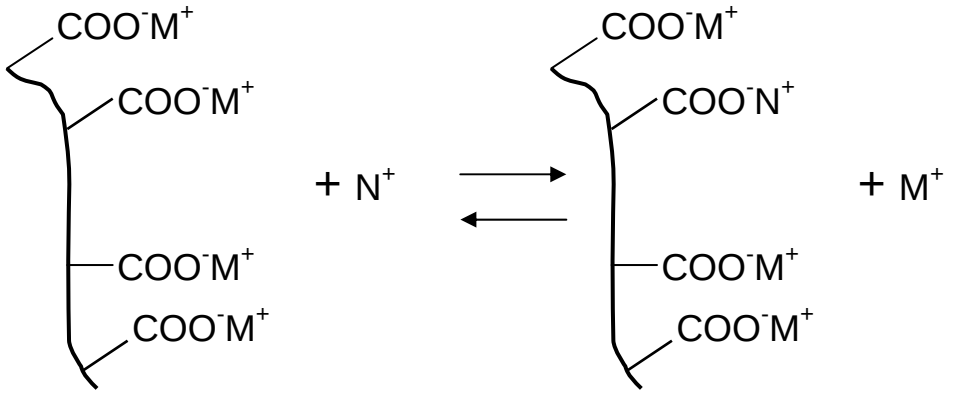
$$K_H^M = \frac{\left[\overline{MR}\right]\left[H^+\right]}{\left[M^+\right]\left[\overline{HR}\right]}$$



$$M^{2+} + 2\overline{HR} \rightleftharpoons \overline{MR_2} + 2H^+$$

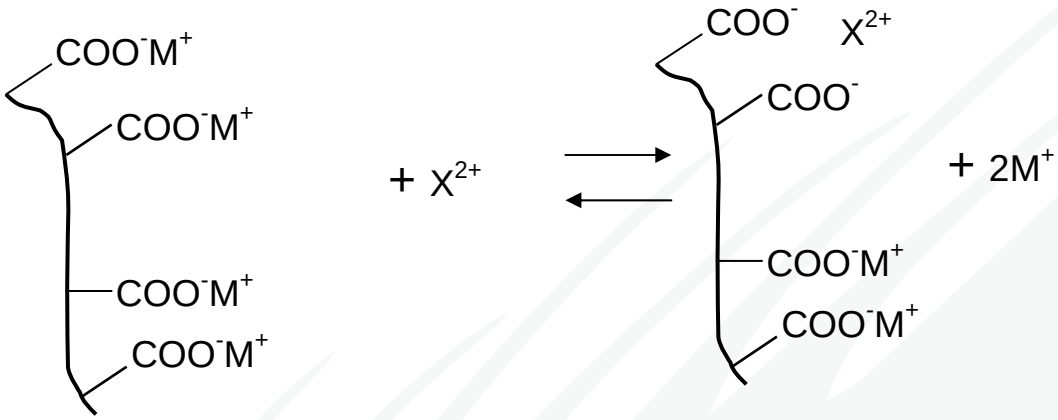
$$K_{2H}^M = \frac{\left[\overline{MR_2}\right]\left[H^+\right]^2}{\left[M^{2+}\right]\left[\overline{HR}\right]^2}$$

Ion-exchange equilibria in wood fibres



$$N^+ + \overline{MR} \rightleftharpoons \overline{NR} + M^+$$

$$K_N^M = \frac{\left[\overline{NR}\right]\left[M^+\right]}{\left[N^+\right]\left[\overline{MR}\right]}$$



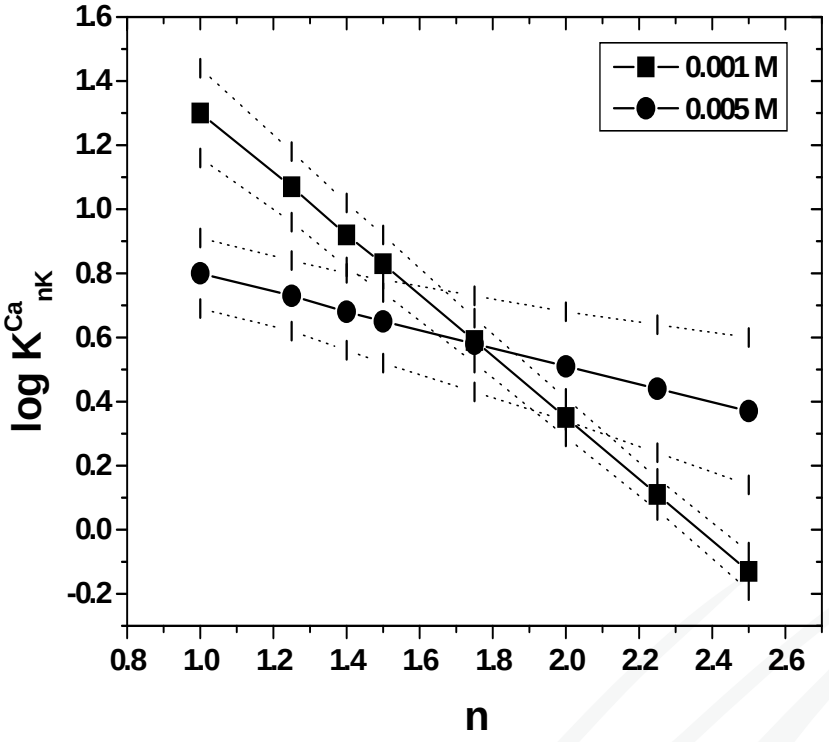
$$X^{2+} + 2\overline{MR} \rightleftharpoons \overline{XR_2} + 2M^+$$

$$K_{2M}^X = \frac{\left[\overline{XR_2}\right]\left[M^+\right]^2}{\left[X^{2+}\right]\left[\overline{MR}\right]^2}$$

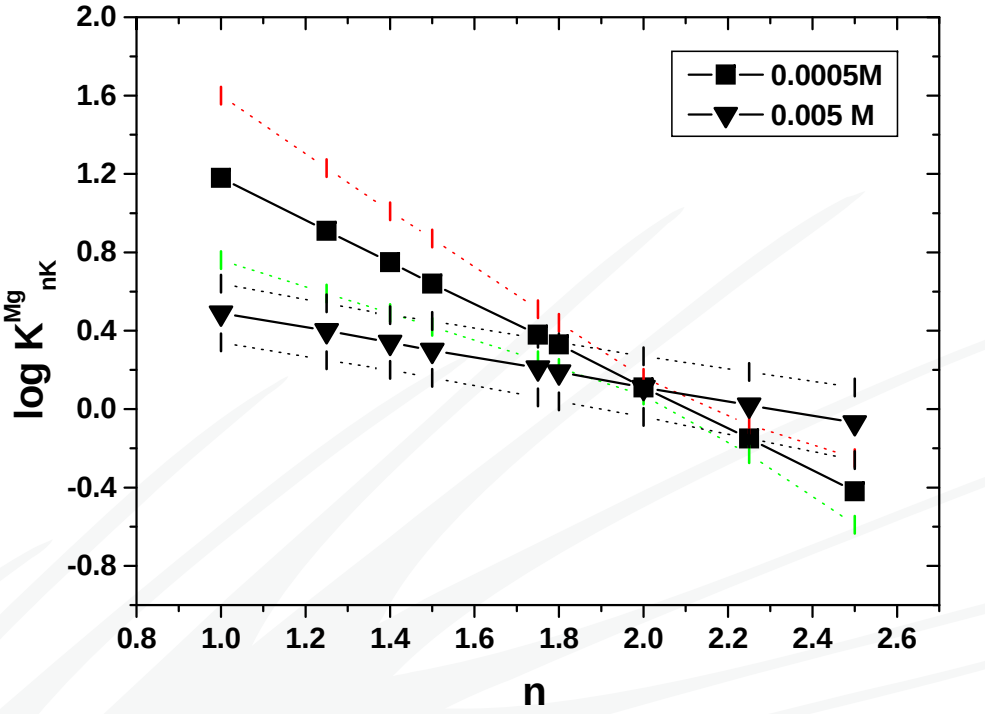
Determination of stoichiometry of the ion exchange reaction

pH:4-10

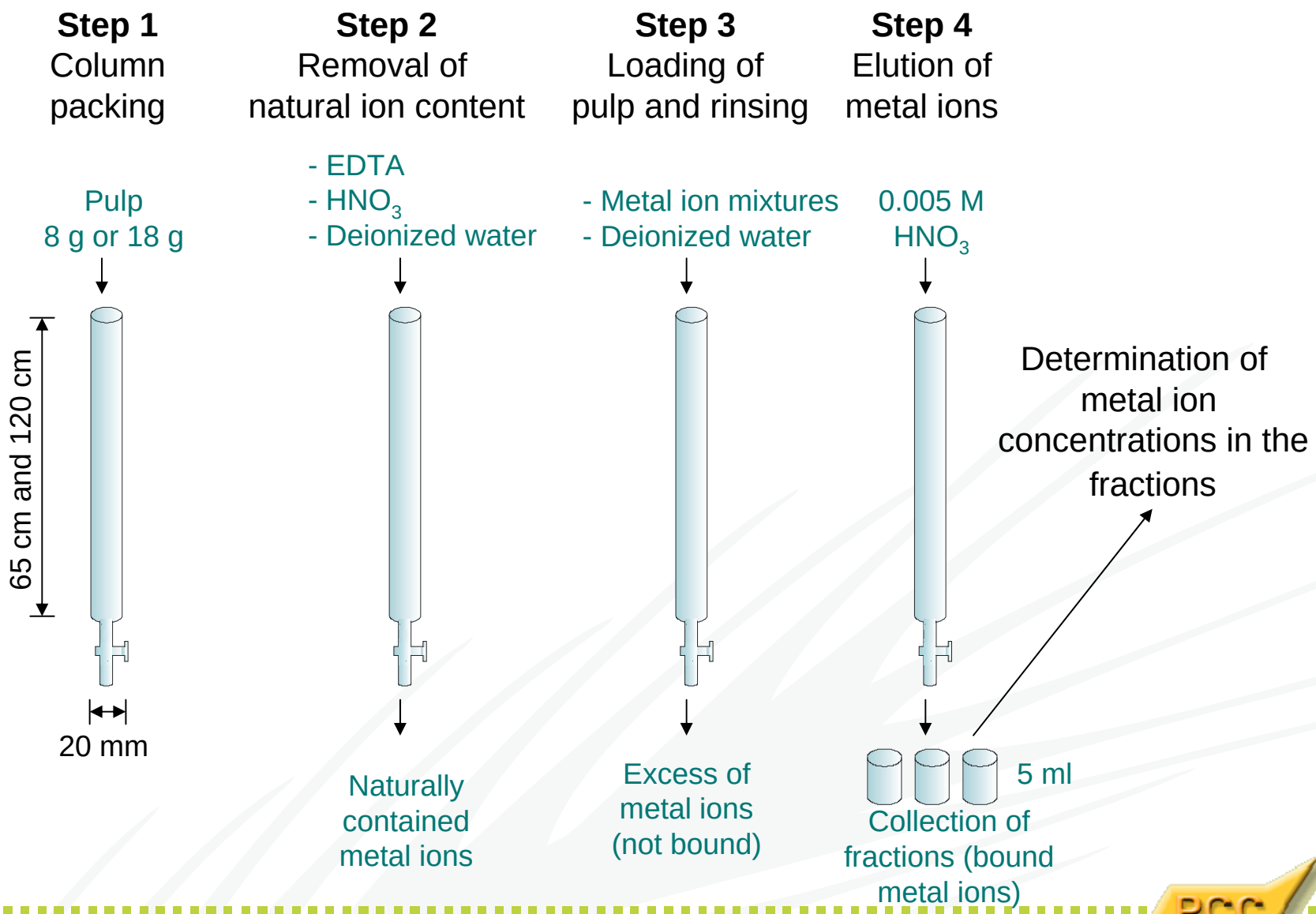
Ca - nK



Mg - nK



The column chromatographic method



Study on metal ion affinities to oxygen delignified hardwood kraft pulp by a column chromatographic method

Procedure:

- A column (65·2 cm and 120·2 cm) packed with pulp
- Natural ion content removal (EDTA, HNO_3) and a rinsing with deionized water
- Addition of mixtures of metal ions (loading) and washing away the excess (unbound) of metal ions with deionized water
- Elution of metal ions with 0.005 M HNO_3
- Collection of fractions (5 or 10 ml) during elution
- Determination of metal-ion concentrrations in the fractions

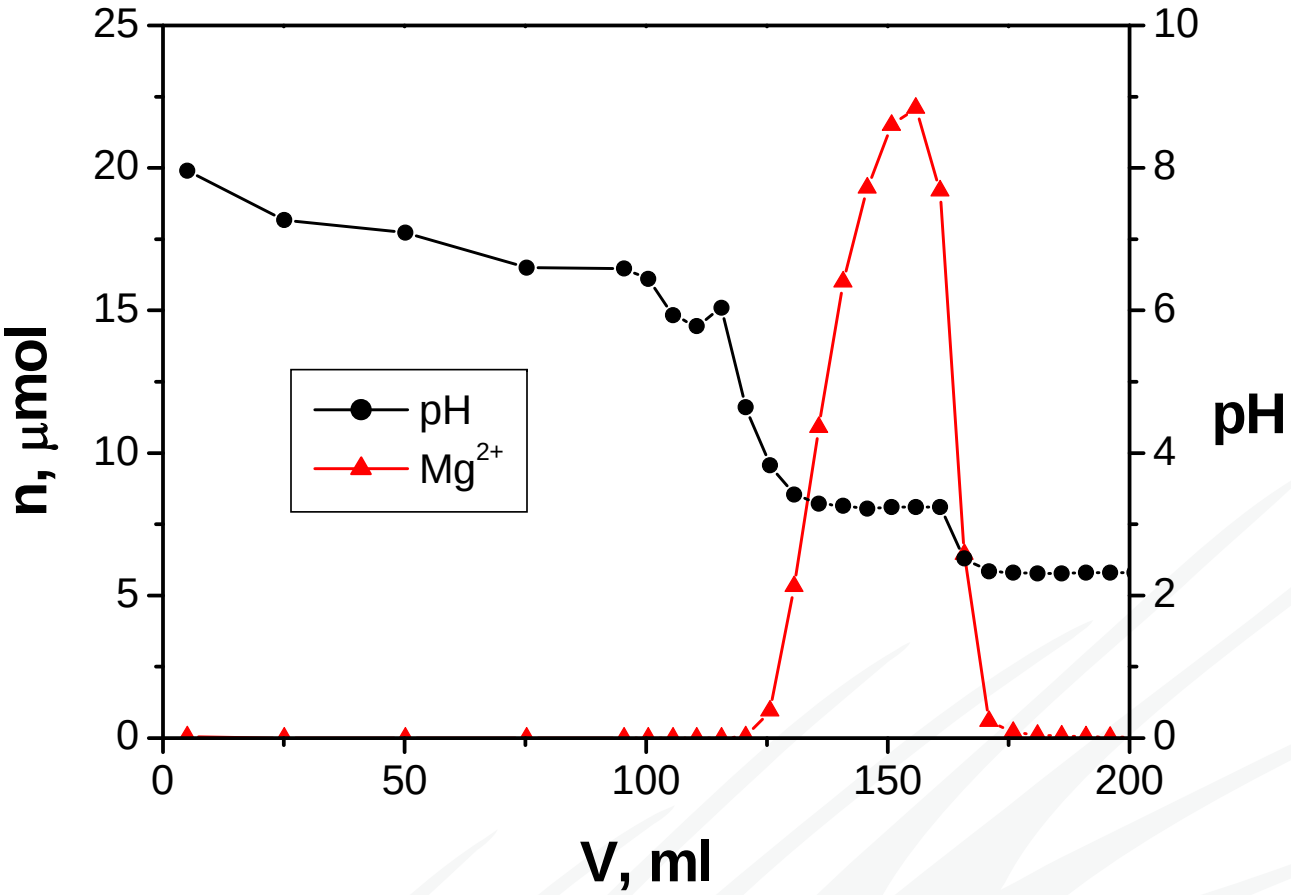


Fig. 1. pH and the number of mikromoles (n) of magnesium ions as function of the volume (V) of eluate in the collected fractions.

$$MR_2 + nH^+ \leftrightarrow 2HR + M^{2+} (n-2)H^+ \qquad K_{2H}^{M} = \frac{[HR]^2[M^{2+}]}{[MR_2][H^+]^2}$$

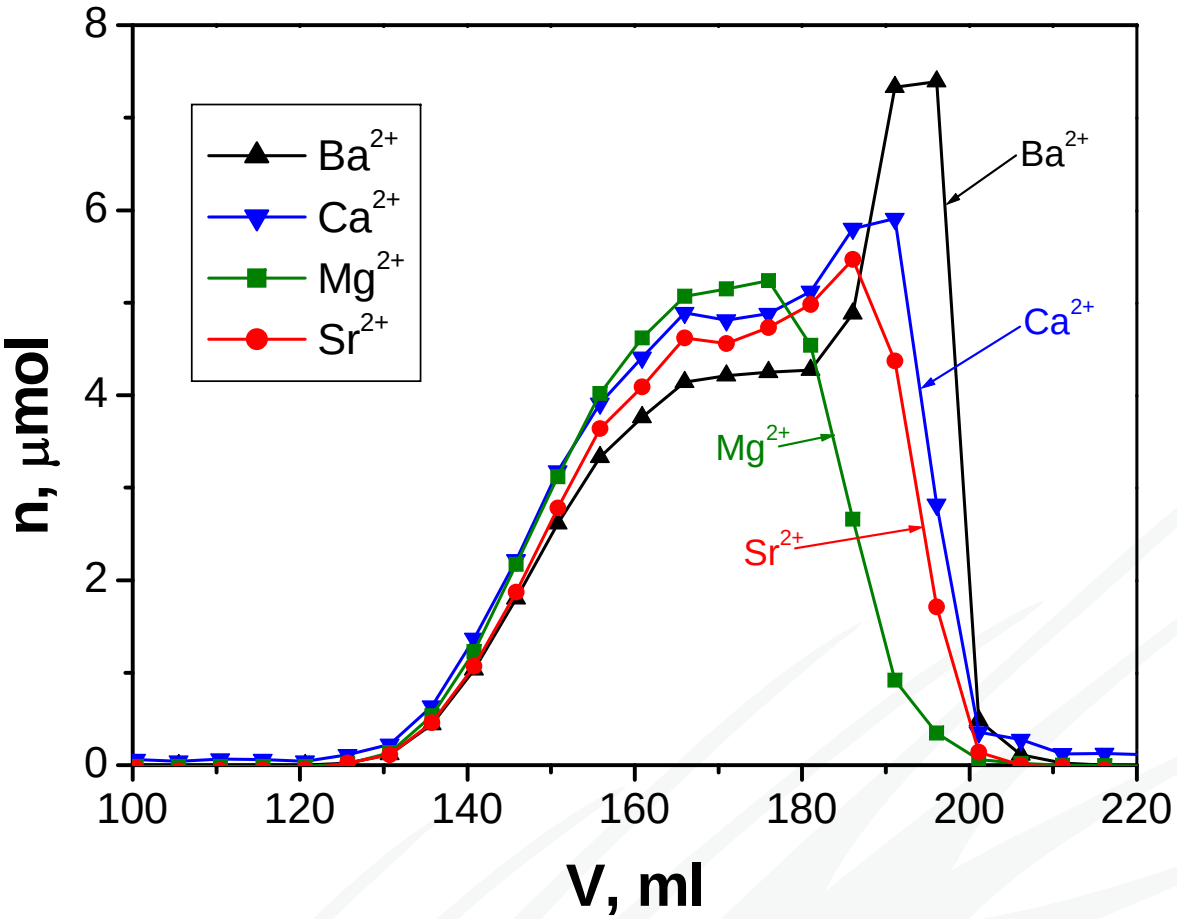


Fig. 2. The number of mikromoles (n) of Ba^{2+} , Ca^{2+}, Mg^{2+} and Sr^{2+} as function of the volume (V) of eluate in the collected fractions.

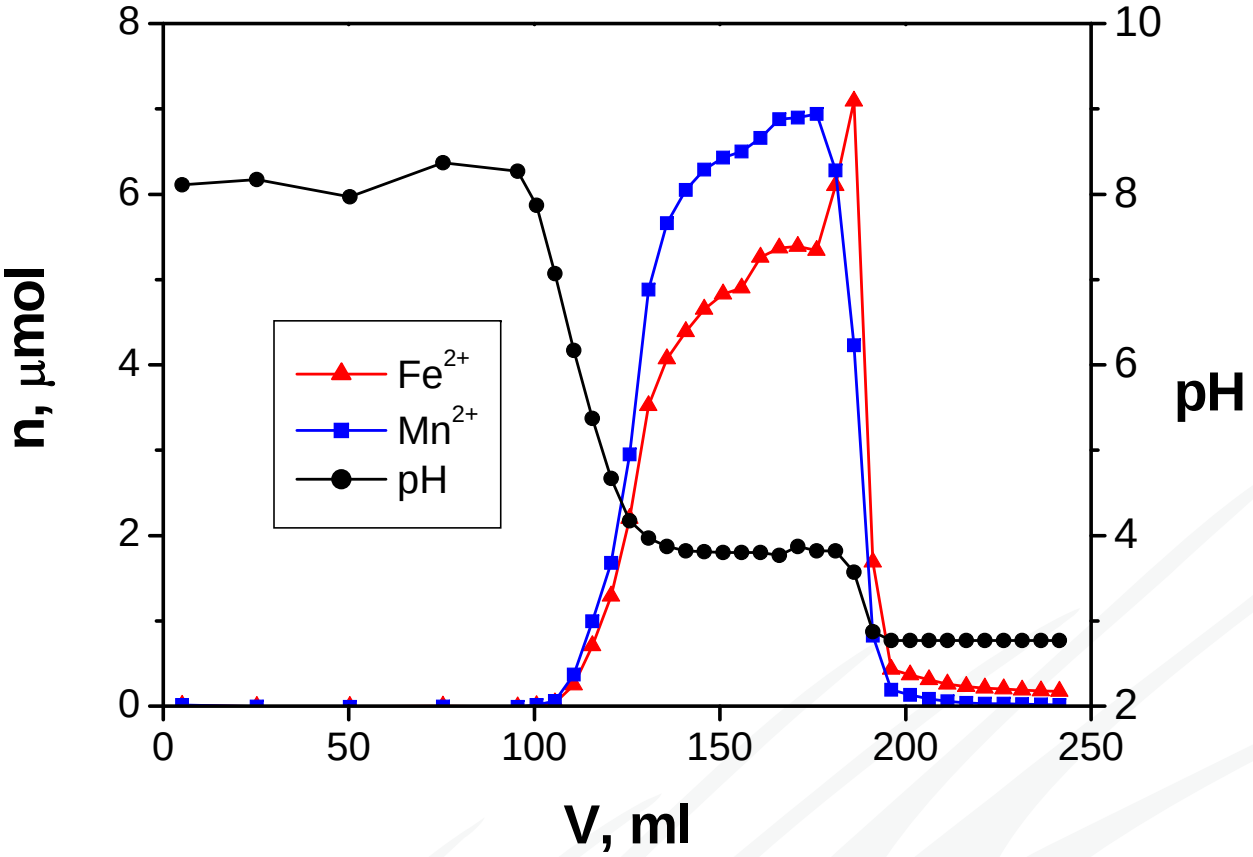


Fig. 3. pH and the number of mikromoles (n) of Fe^{2+} and Mn^{2+} as function of the volume (V) of eluate in the collected fractions.

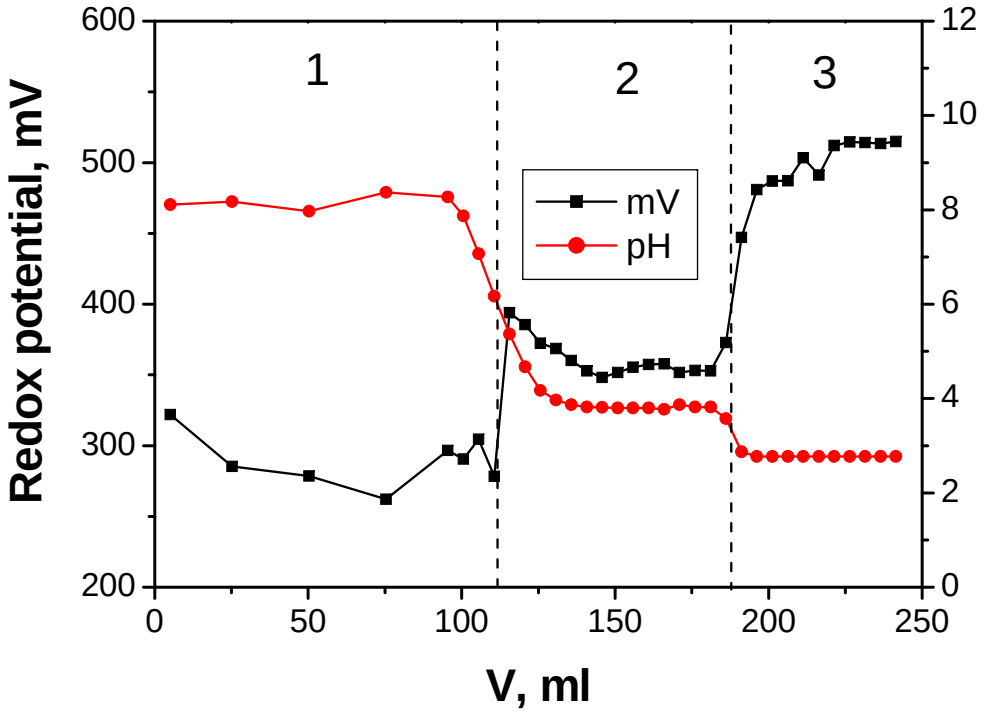


Fig.4. The redox potential and pH plotted as function of the volume (V) of eluate for the sorption of Fe^{2+} and Mn^{2+}.

$$E_{Cell}=E^{o}_{Cell}+59.2mV\cdot\log\frac{[Fe(III)]}{[Fe(II)]}$$

$$[M]=\frac{[M']}{\alpha_{M(OH)}}$$

$$\alpha_{M(OH)}=1+[OH^-]K^{MOH}_{M,OH}+\ldots+[OH^-]^n K^{M(OH)n}_{M,nOH}$$

$$\frac{[Fe(III)']}{[Fe(II)']}=\frac{\alpha_{Fe(III)}[Fe^{3+}]}{\alpha_{Fe(II)}[Fe^{2+}]}$$

Table 1. Calculation of the Fe^{3+} /Fe^{2+} ratios from the mean values of the redox potentials and pH from the data presented in fig. 4.

Level	Redox Potential (mV)	pH	$\log\frac{[Fe(III)]}{[Fe(II)]}$	Fe(III) (%)	Fe(II) (%)	$\alpha_{Fe(III)(OH)}$	$\alpha_{Fe(II)(OH)}$	$\log\frac{[Fe(III)']}{[Fe(II)']}$	Fe(III) (%)	Fe(II) (%)
1	290	8.2	-4.0	0.01	99.9	$10^{9.7}$	1	5.7	~100	0
2	354	3.8	-2.9	0.1	99	$10^{1.2}$	1	-1.7	2	98
3	514	2.7	-0.25	36	64	$10^{0.2}$	1	-0.05	47	53

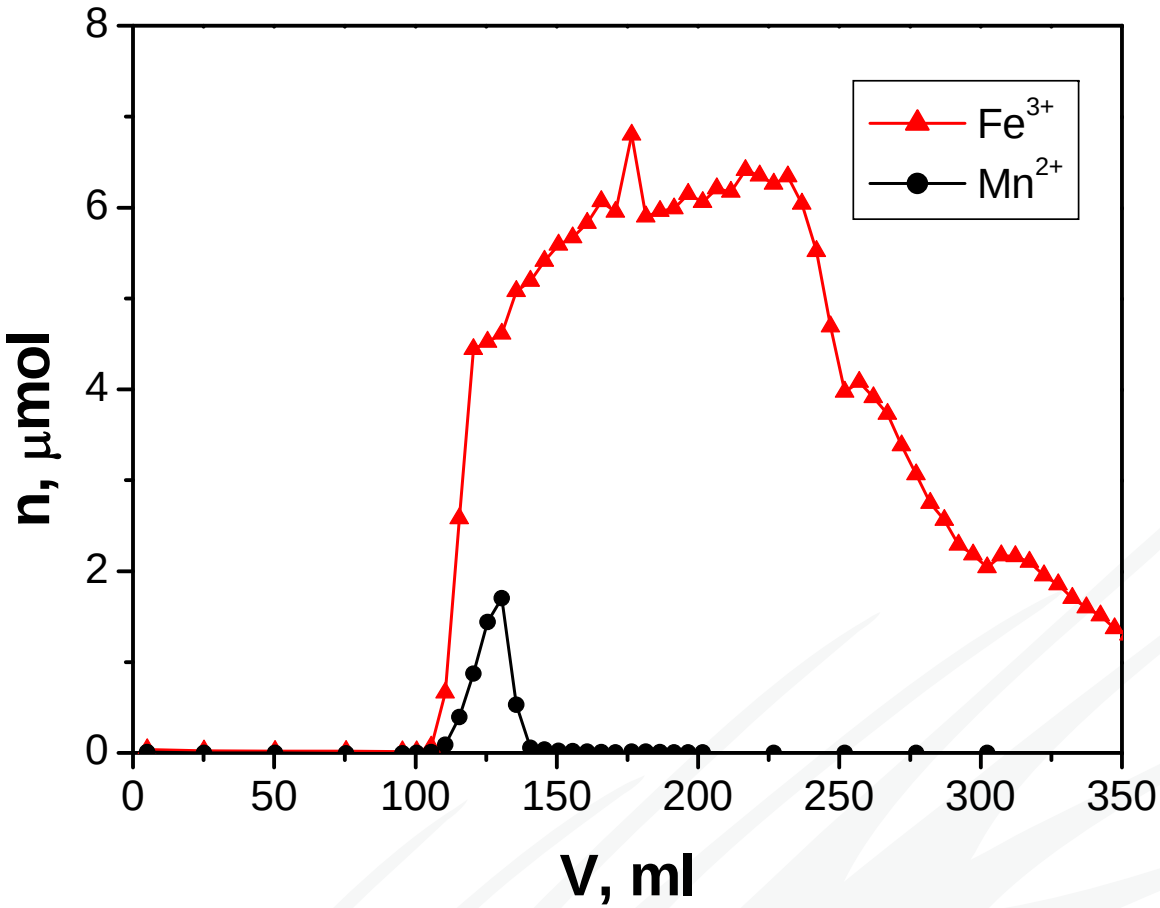


Fig. 5. The number of mikromoles (n) of Fe^{3+} and Mn^{2+} as function of the volume (V) of eluate in the collected fractions.

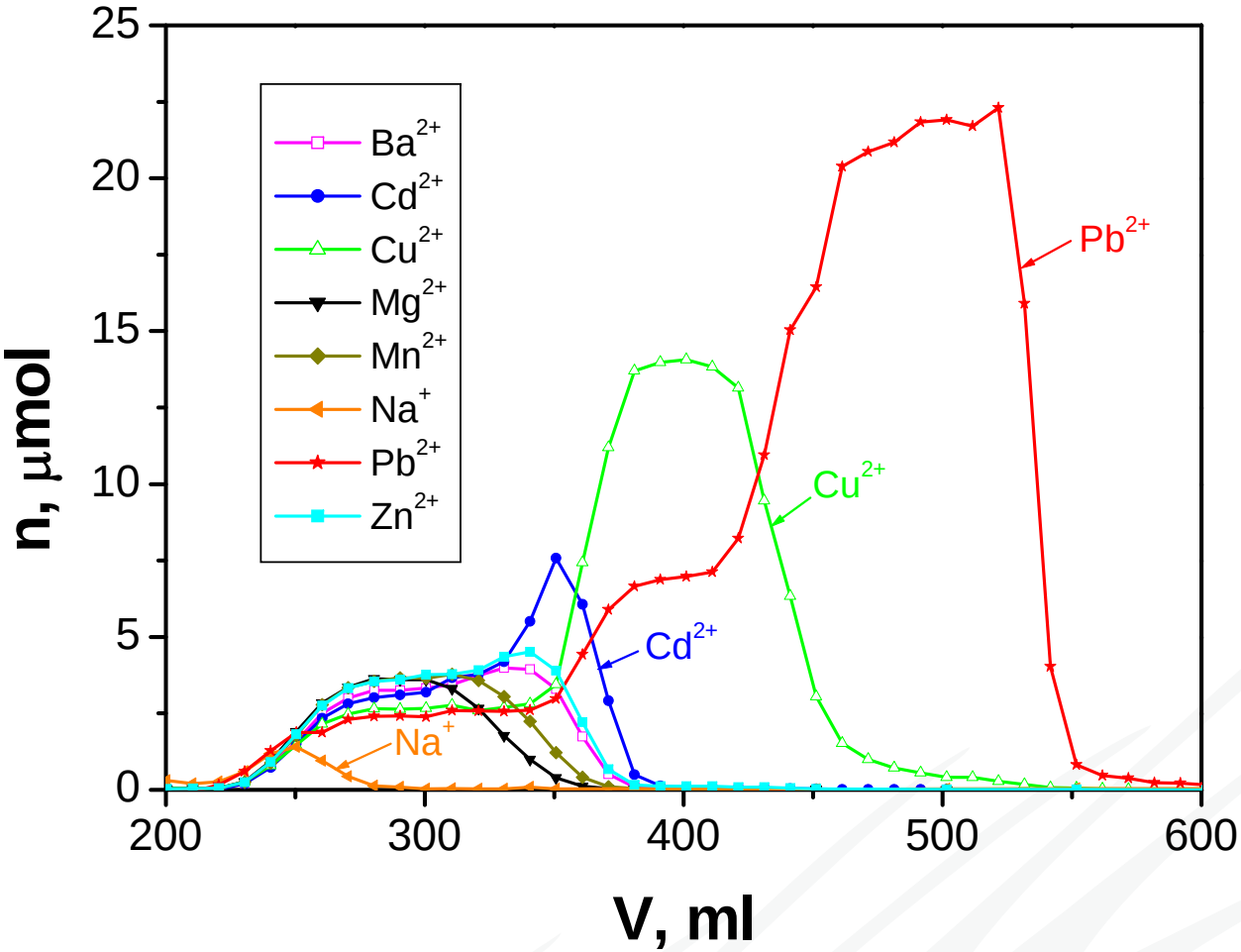
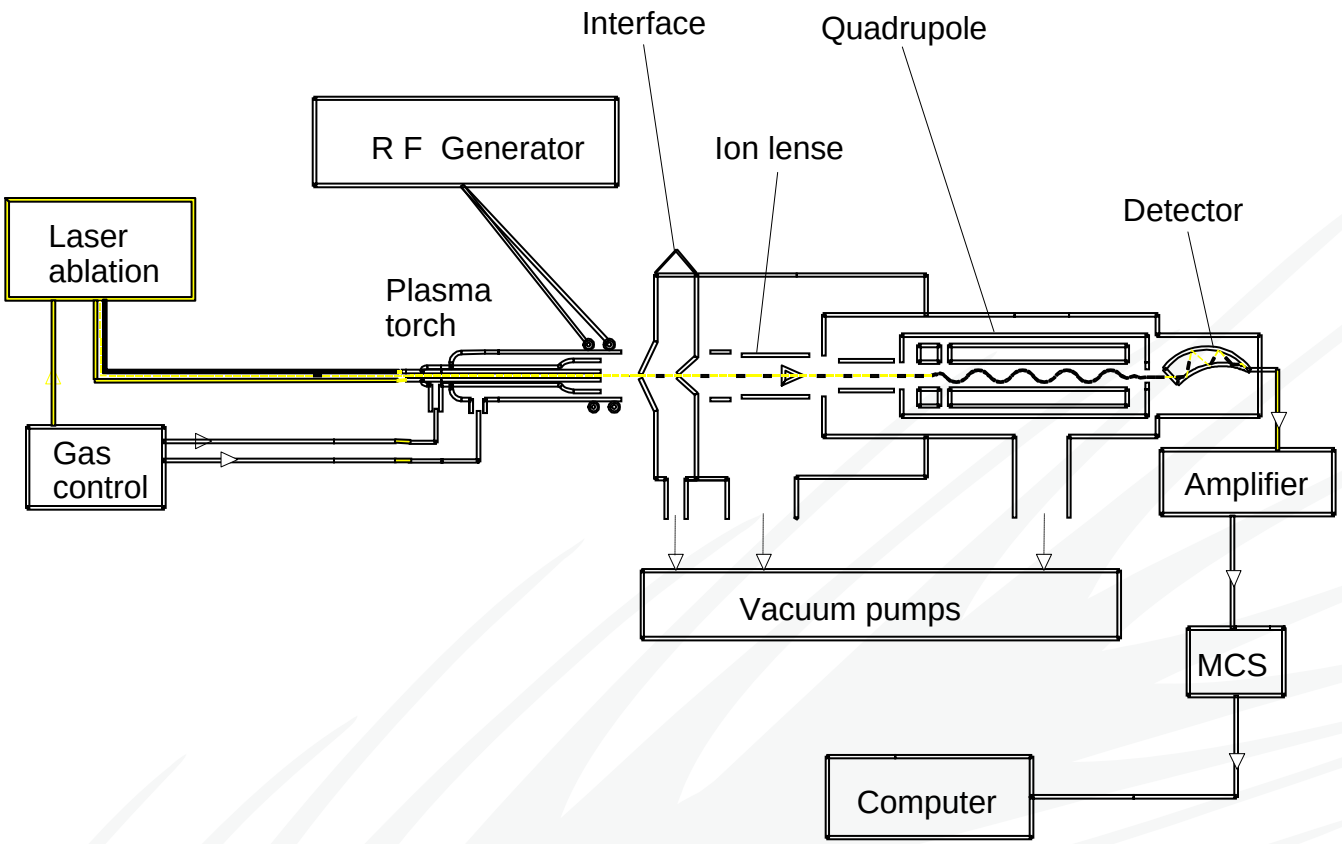


Fig. 6. The number of mikromoles (n) of Ba^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Pb^{2+} and Zn^{2+} as functionof the volume (V) of eluate in the collected fractions.

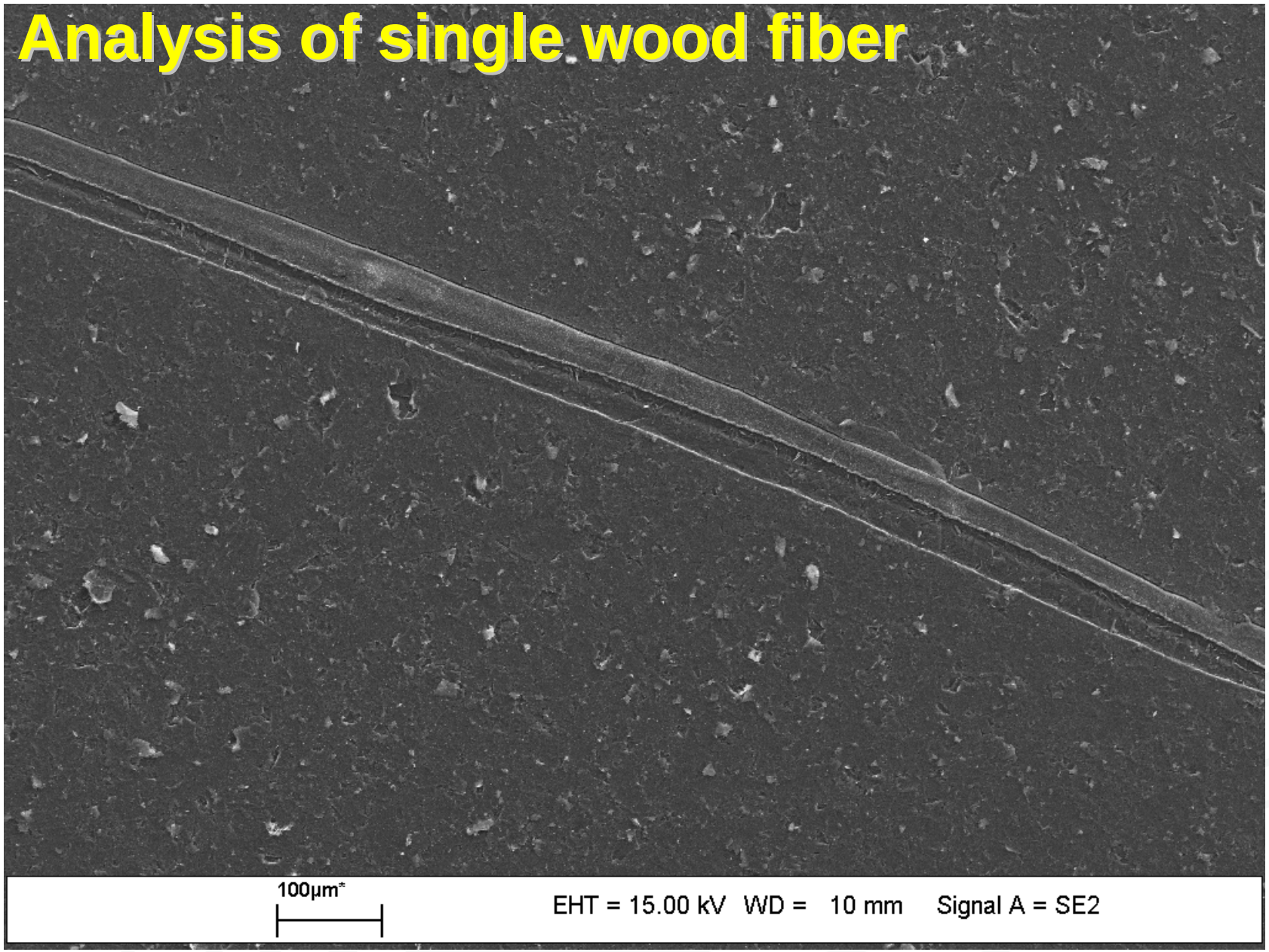
Order of affinities to the pulp:

$Fe^{3+}>>Pb^{2+}>>Cu^{2+}>>Cd^{2+}>Zn^{2+}>Ba^{2+}>Ca^{2+}>Mn^{2+}>Fe^{2+}>Sr^{2+}>Mg^{2+}>K^{+}>Rb^{+}>Na^{+}$

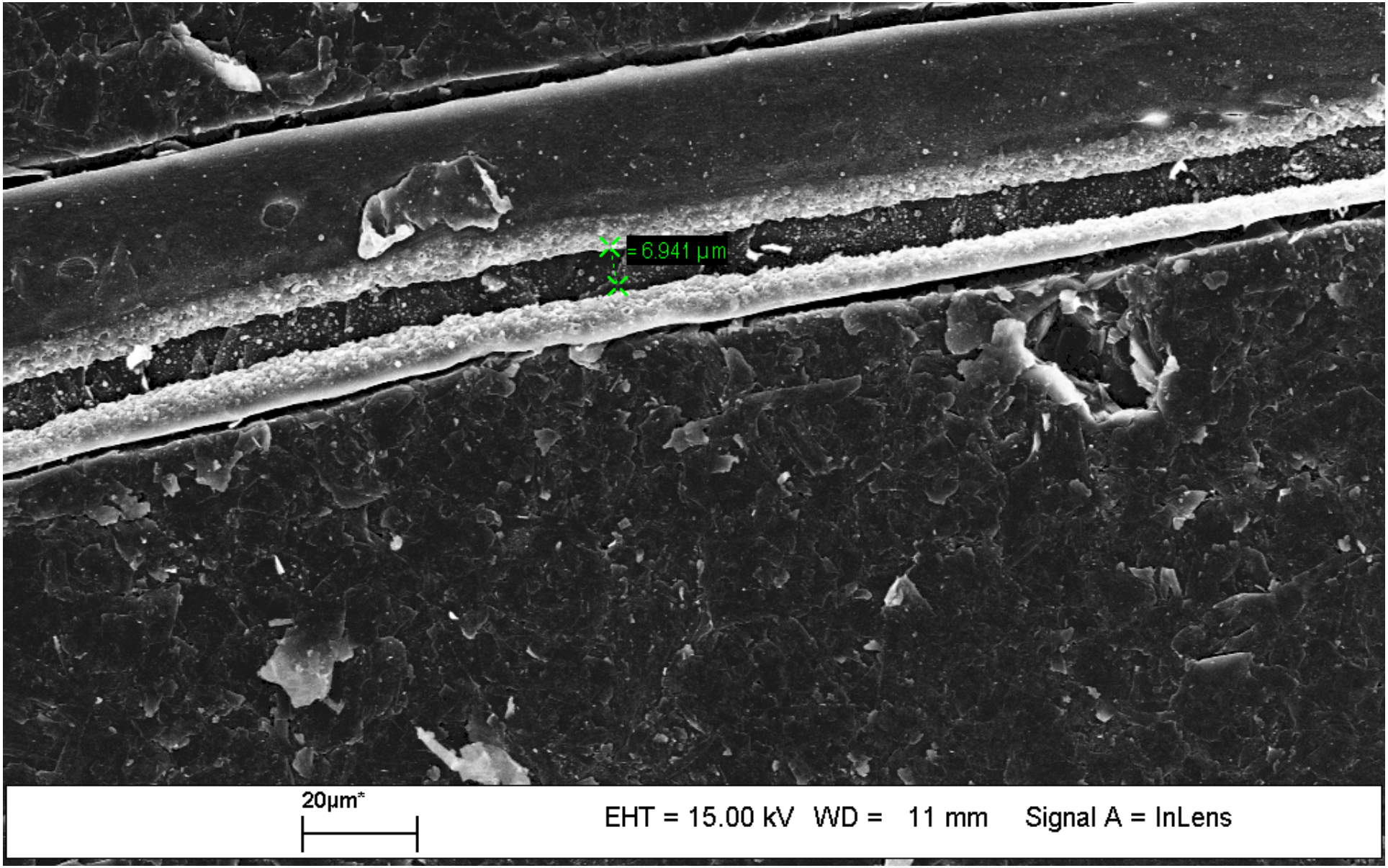
LA-ICP-MS for element analysis



Analysis of single wood fiber



Pingping Su, Paul Ek



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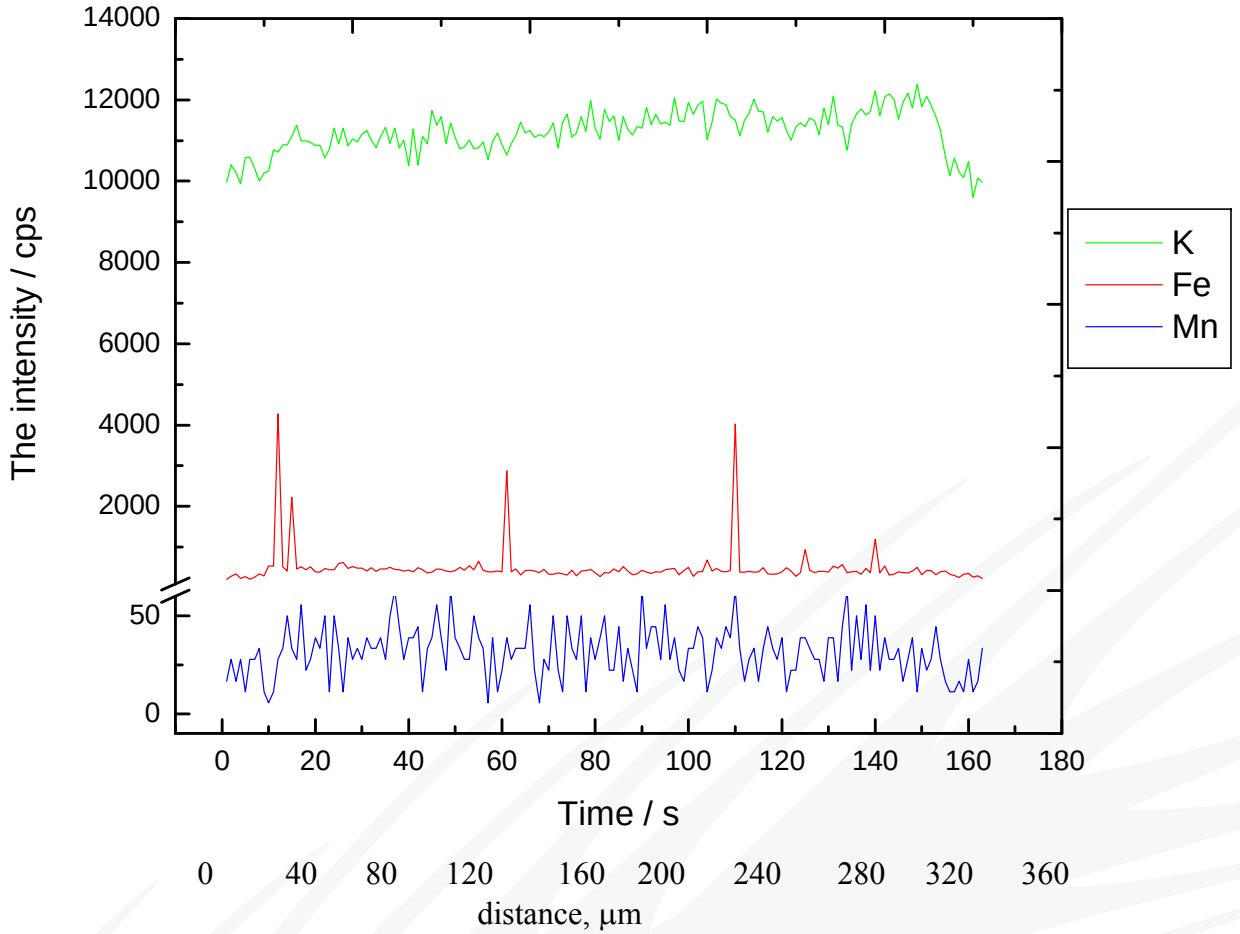
LA-ICP-MS scan along a single wood fiber

The distribution of the metals in the single fibre of the unbleached kraft softwood

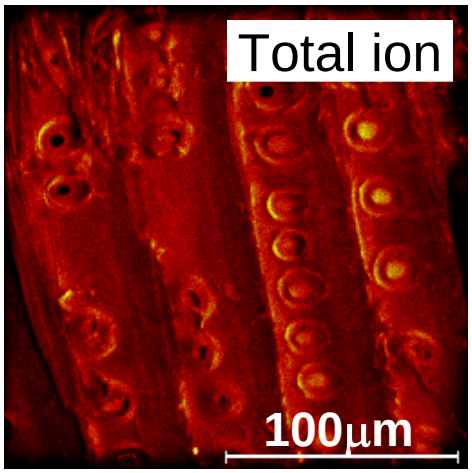


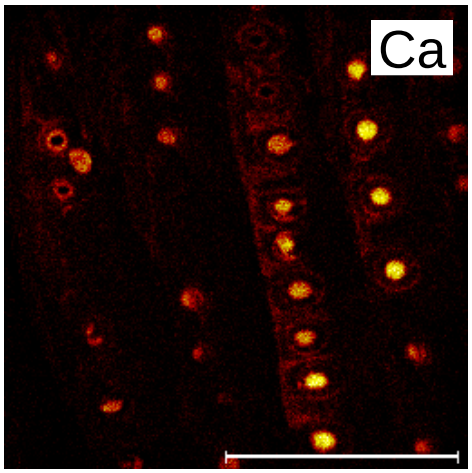
Distribution of metal ions in tree

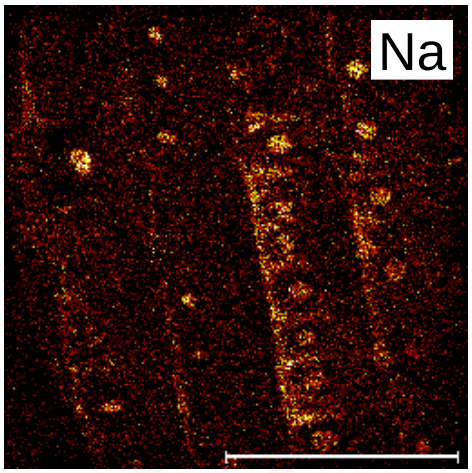
Objectives

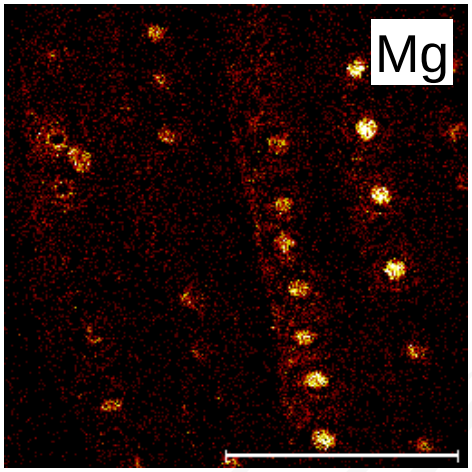
- Detailed localisation of metals in different wood species (spruce, aspen, birch, larch) and tissues (sapwood, heartwood, EW, LW) by chemical microscopy

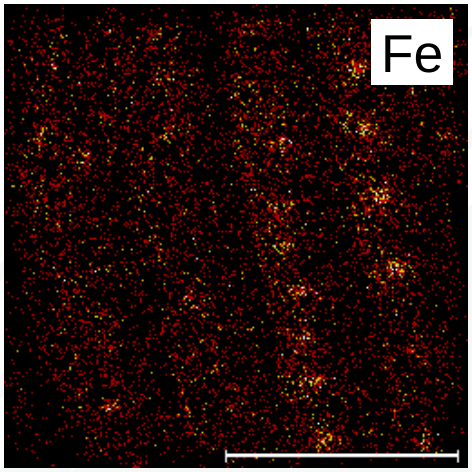
ToF-SIMS imaging of radial section from spruce sapwood.

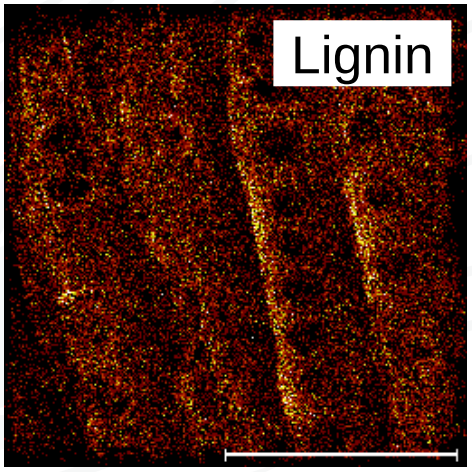








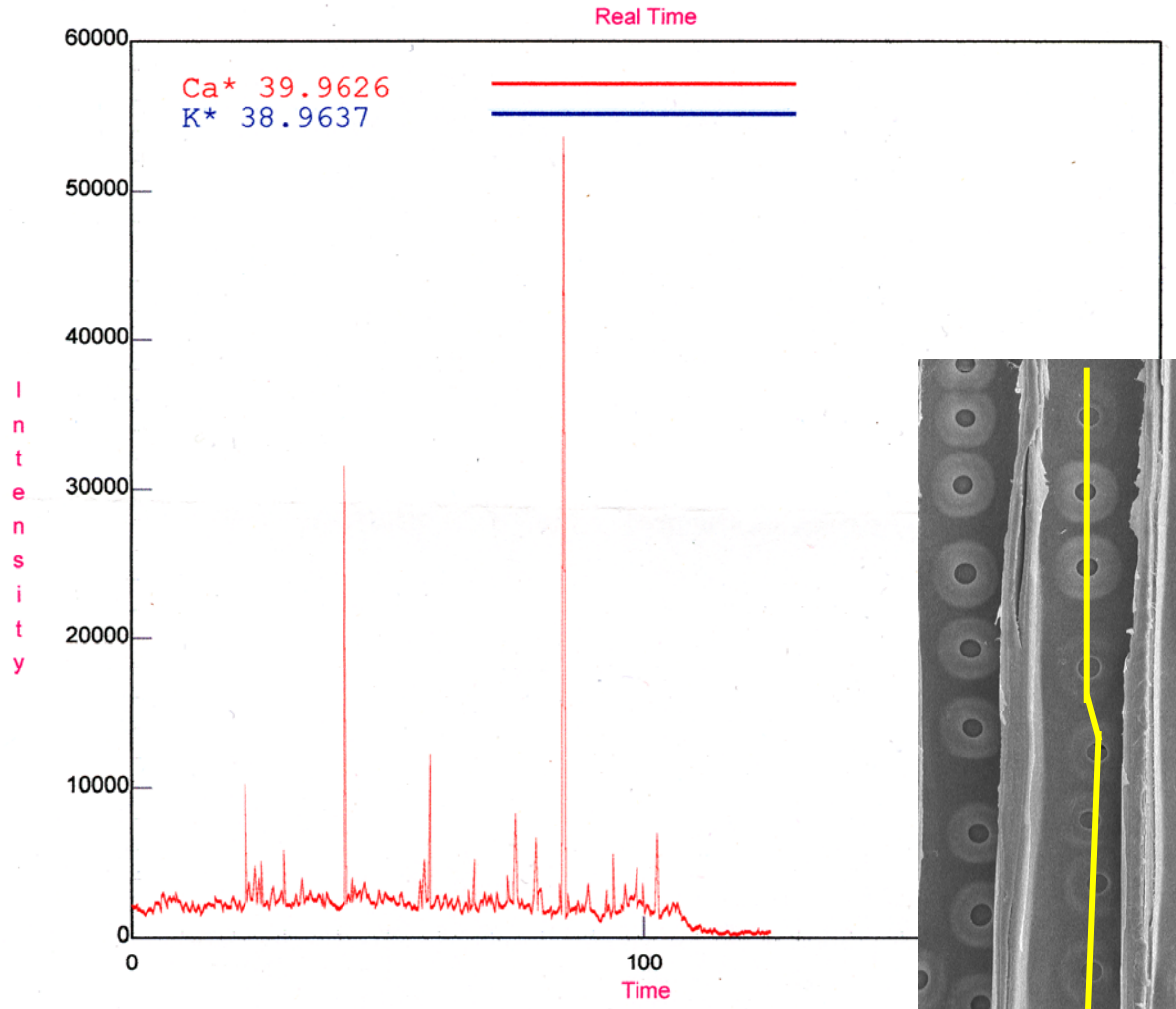


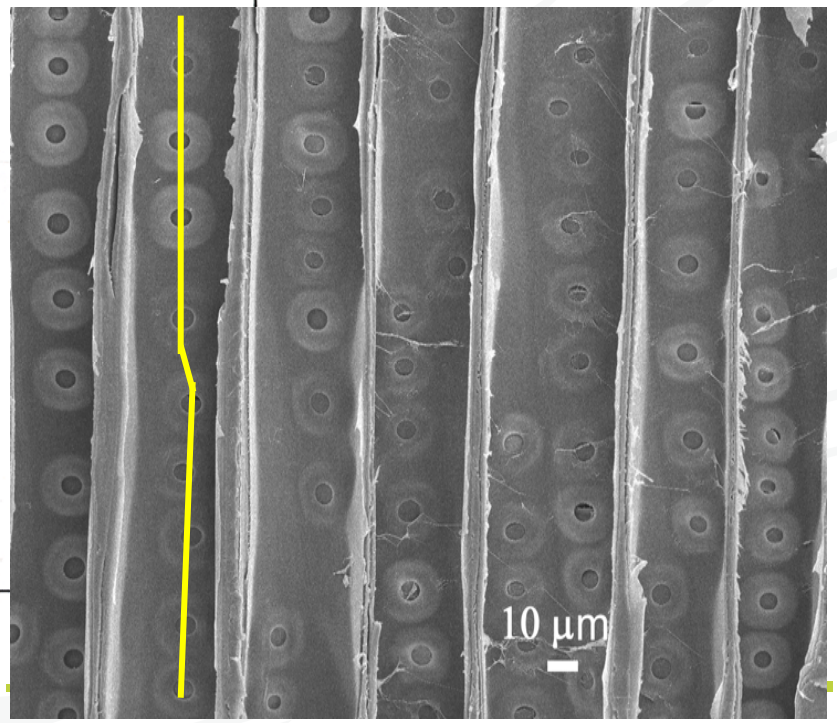


Ca, Na, Mg, K, Fe dominate in bordered pit tori.
Only little lignin was observed in the same regions.

Elena Tokareva

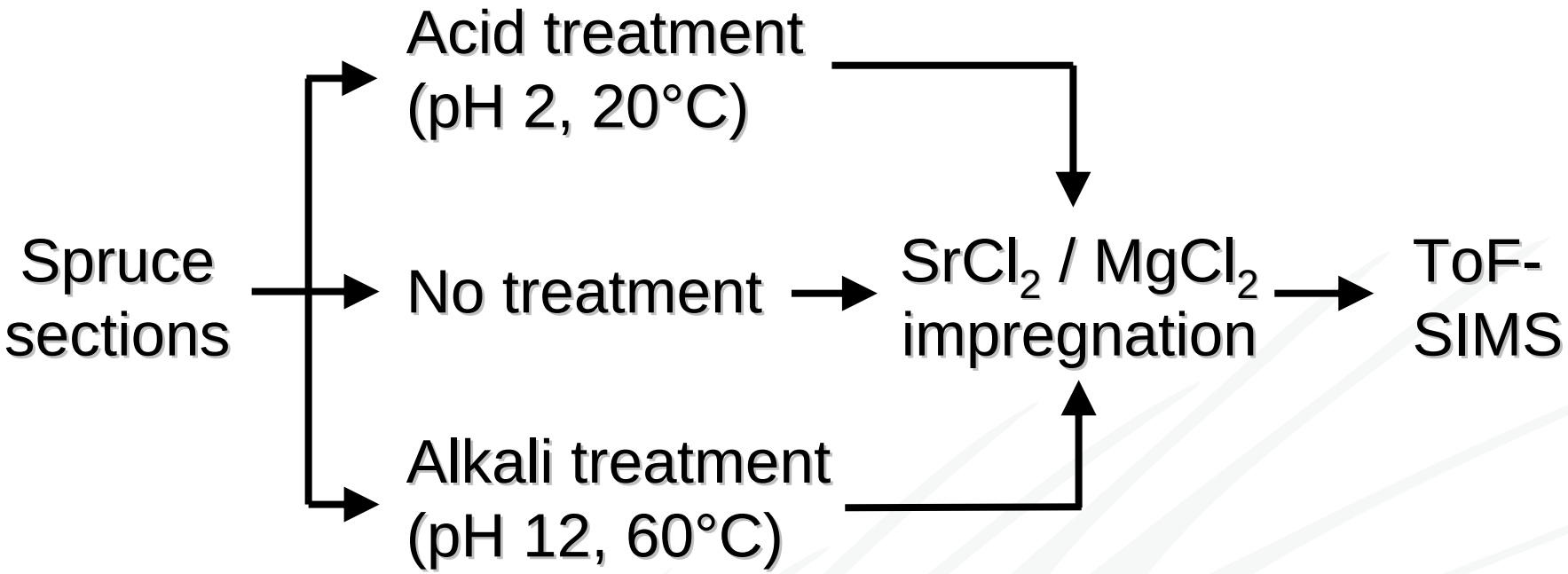
LA-ICP-MS of radial section from spruce sapwood

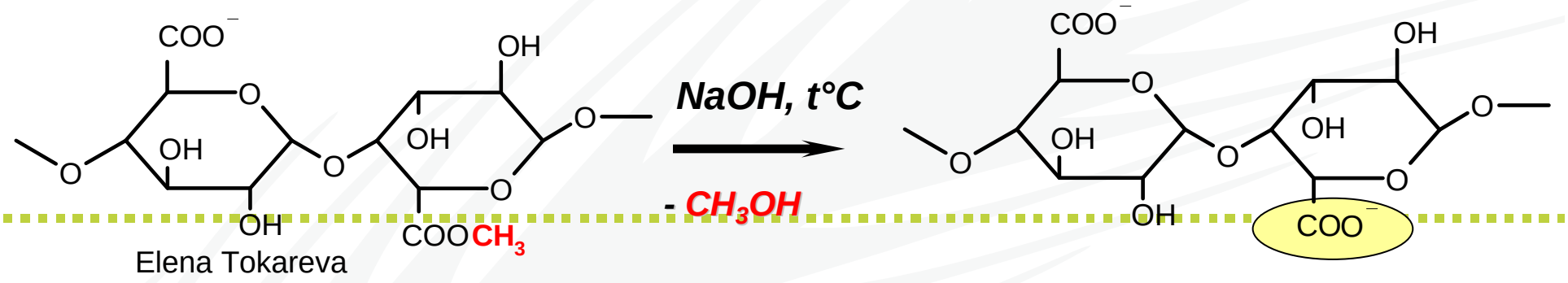




Elena Tokareva, Paul Ek

Labelling of anionic groups

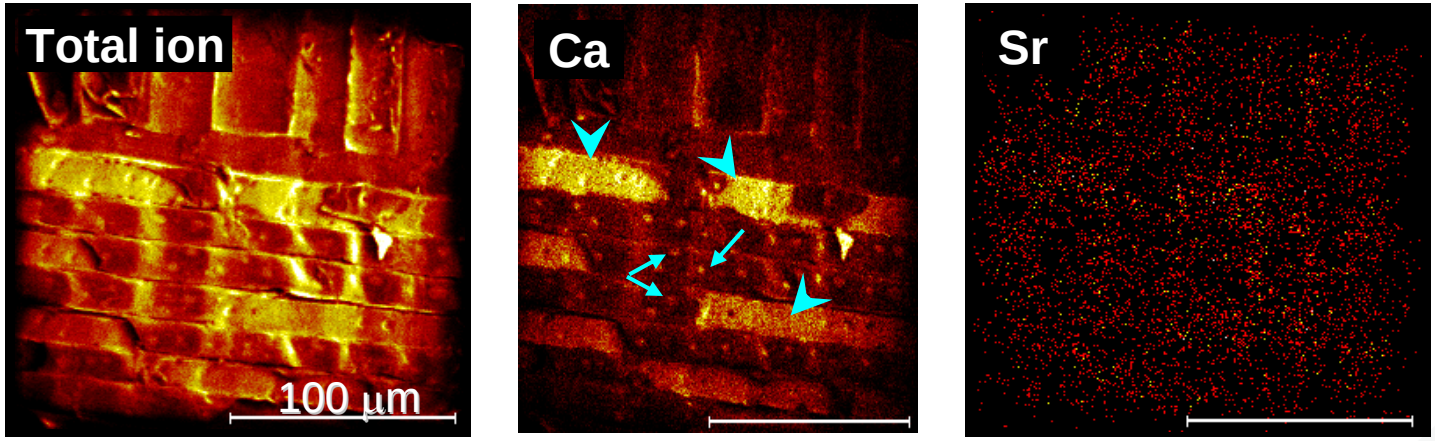




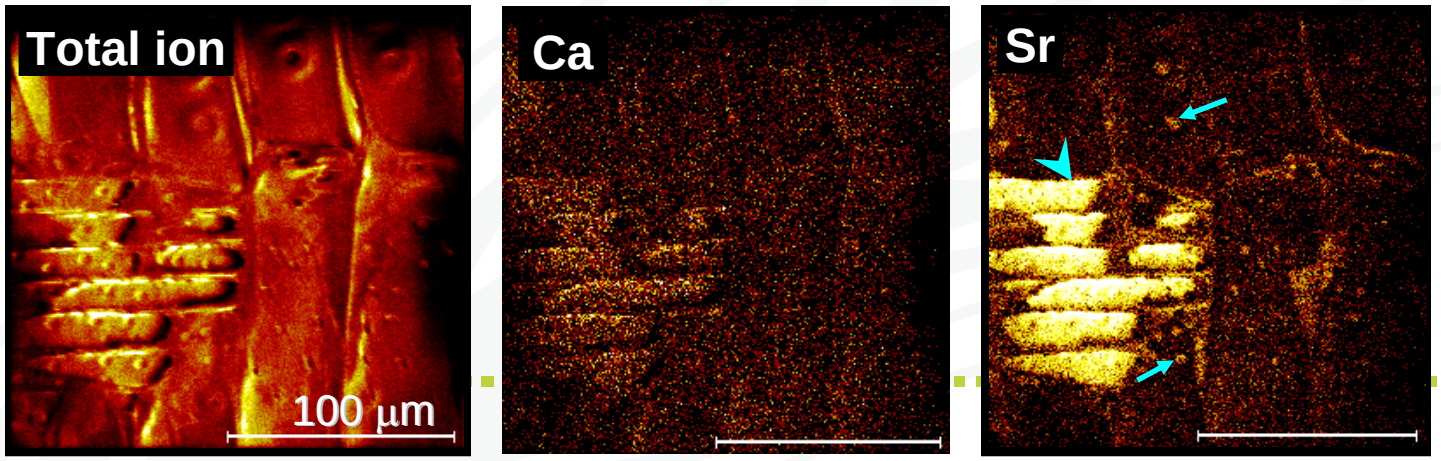
Elena Tokareva

ToF-SIMS images

Original spruce section



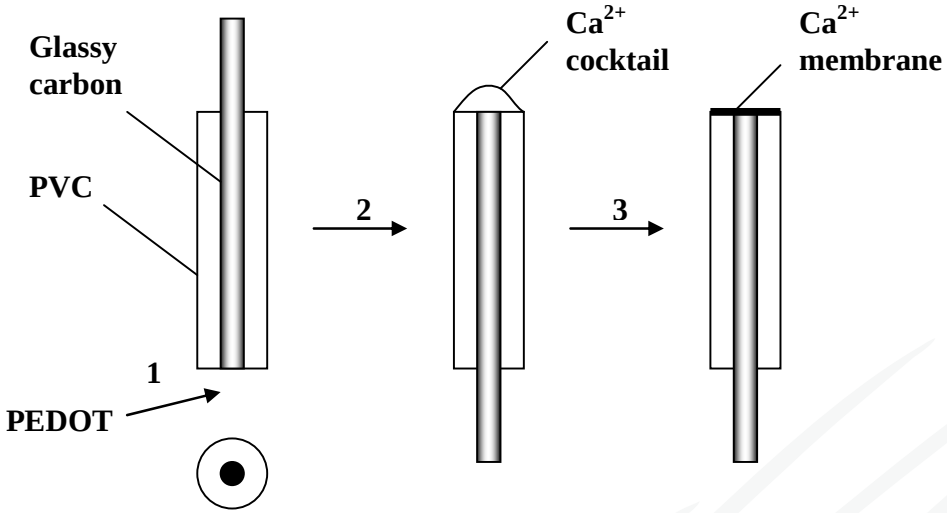
Sr^{2+} impregnated section



Speciation of calcium in black liquor

Construction of all-solid-state Ca^{2+} ISE

(= ion-selective electrode)



Galvanostatic Electropolymerization:
- 0.01 EDOT+ 0.1 M NaPSS
- +0.0014 mA (0.2mA/cm2), 714 s
- Condition in 0.1 M $CaCl_2$, 24 h

Drop-casting:
- 4.65 mg ETH 1001,1.62 mg KTpClPB, 3.73 mg ETH 500, 161 mg PVC, 325 mg o-NPOE, 3ml THF
- Condition in 0.01 M $CaCl_2$, 24 h

1. Electrosynthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) = electically conducting polymer

2. Drop-casting of Ca^{2+} selective cocktail

3. All-solid-state Ca^{2+} ISE

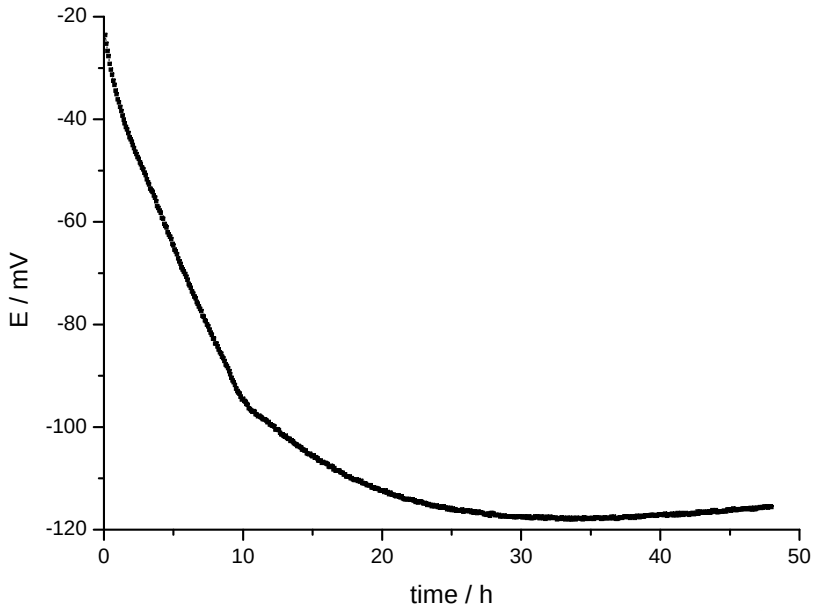
Original, evaporated sample, 78% dry matter

3 % dry matter, **diluted with water**

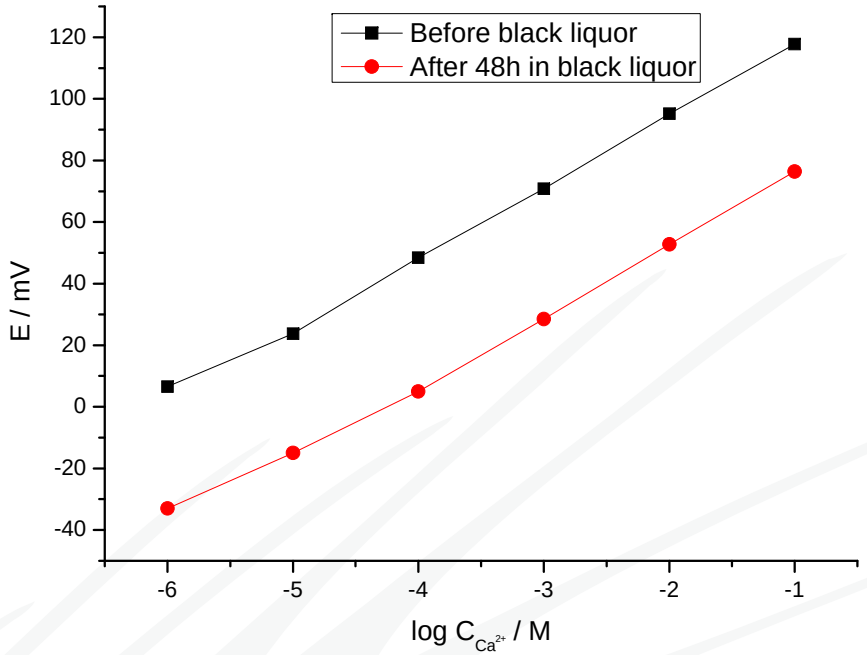
Kim Granholm

Durability test of Ca^{2+}-ISE in black liquor

48h in black liquor (3.3%)



Calibration curves



Selectivity coefficients

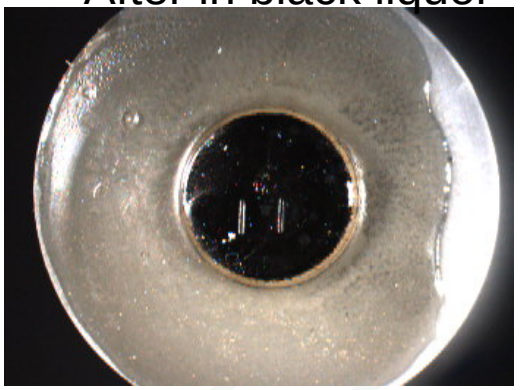
	lg $K_{Ca,Na}$	lg $K_{Ca,K}$	lg $K_{Ca,Mg}$	lg $K_{Ca,Al}$
Before	**-1.8**	**-2.2**	**-3.8**	**-4.3**
After 48 h	**-1.8**	**-1.7**	**-3.6**	**-4.0**

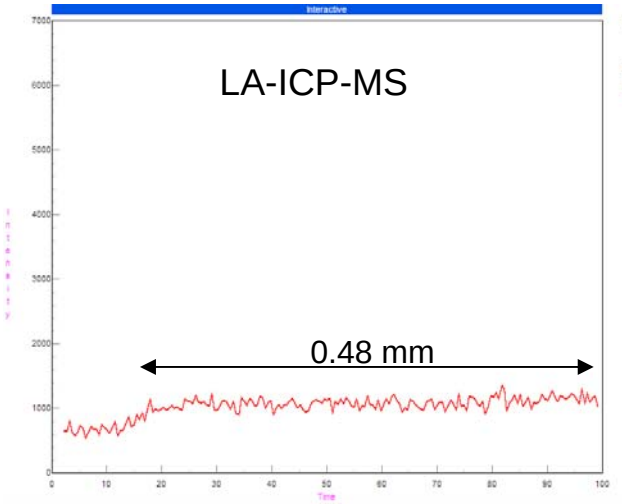
Calcium distrubution at the membrane surface

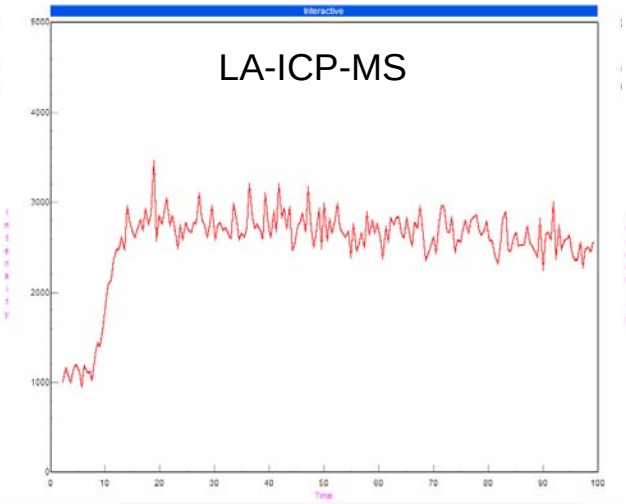
No conditioning

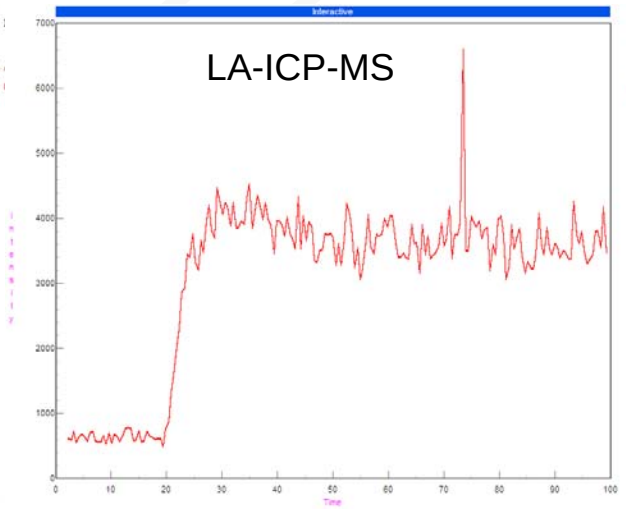
After Ca^{2+}-conditioning

After in black liquor









Scan rate: 6 µm/s

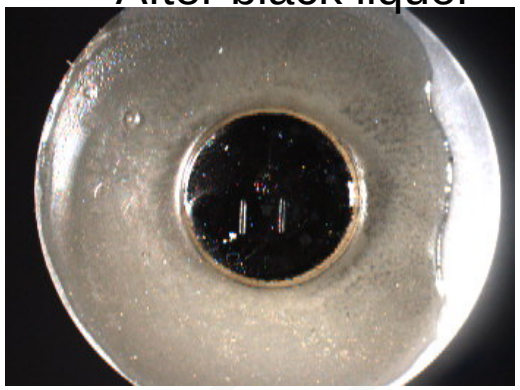
Laser: spot size = 15 µm, effect = 45 %, 5 Hz

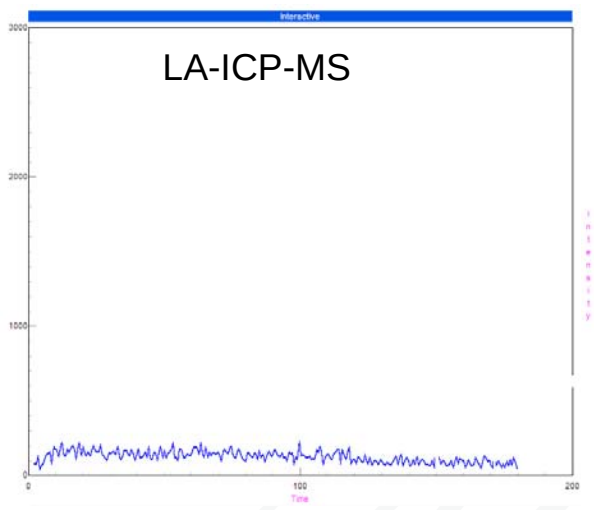
Sodium distrubution at the membrane surface

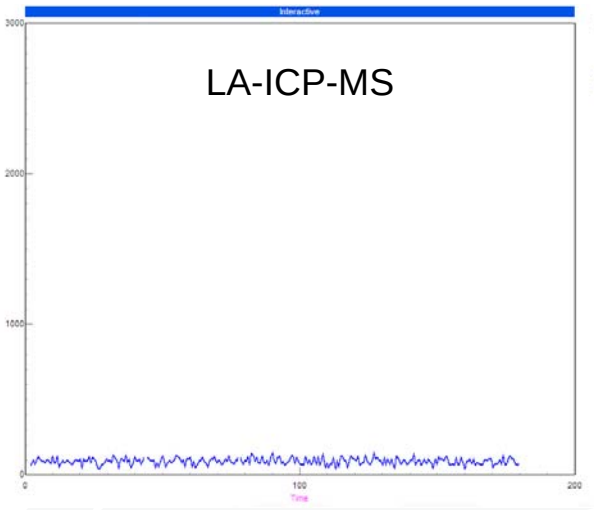
No conditioning

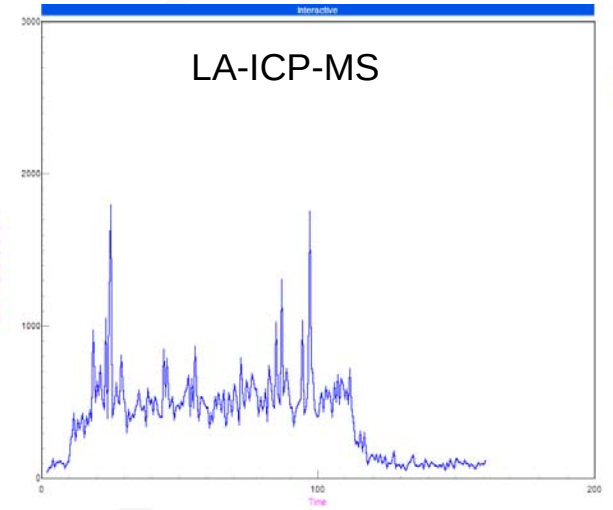
After Ca^{2+}-conditioning

After black liquor







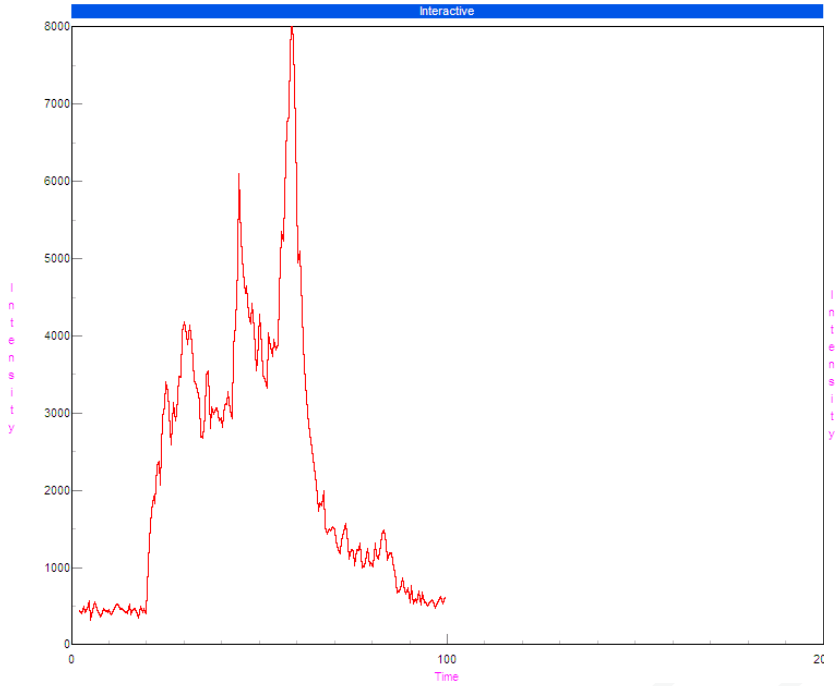


Scan rate: 6 µm/s Laser: spot size = 15 µm, effect = 45 %, 5 Hz

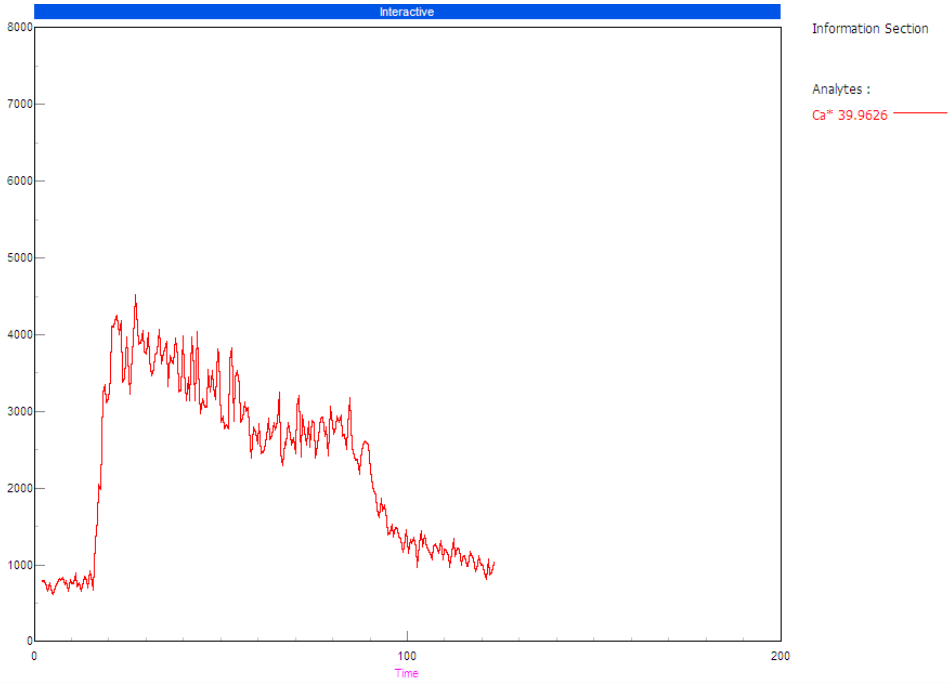
LA-ICP-MS

Depth profile of Calcium in the membrane

After Ca^{2+}-conditioning



After black liquor

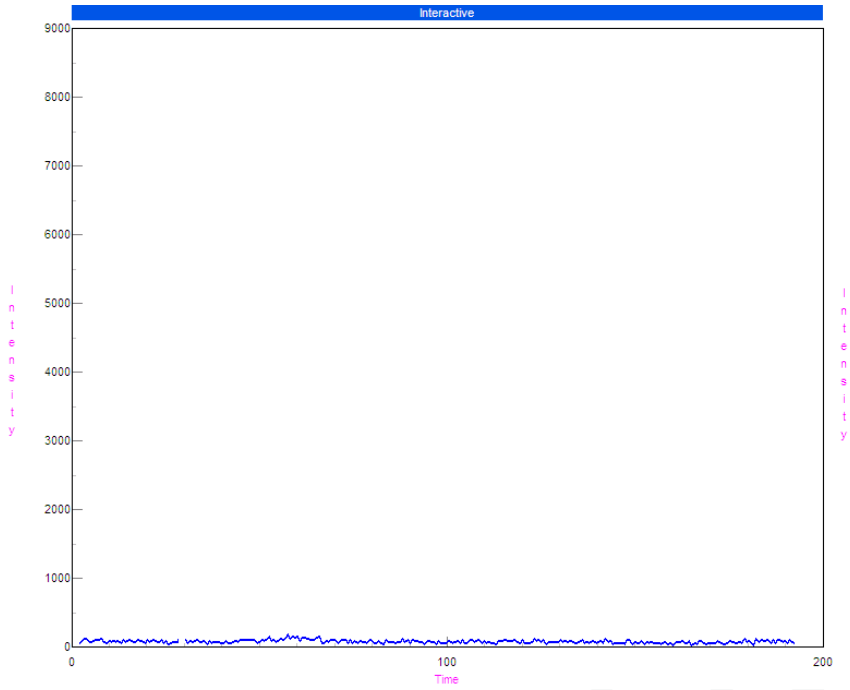


Membrane thickness: ~200 µm

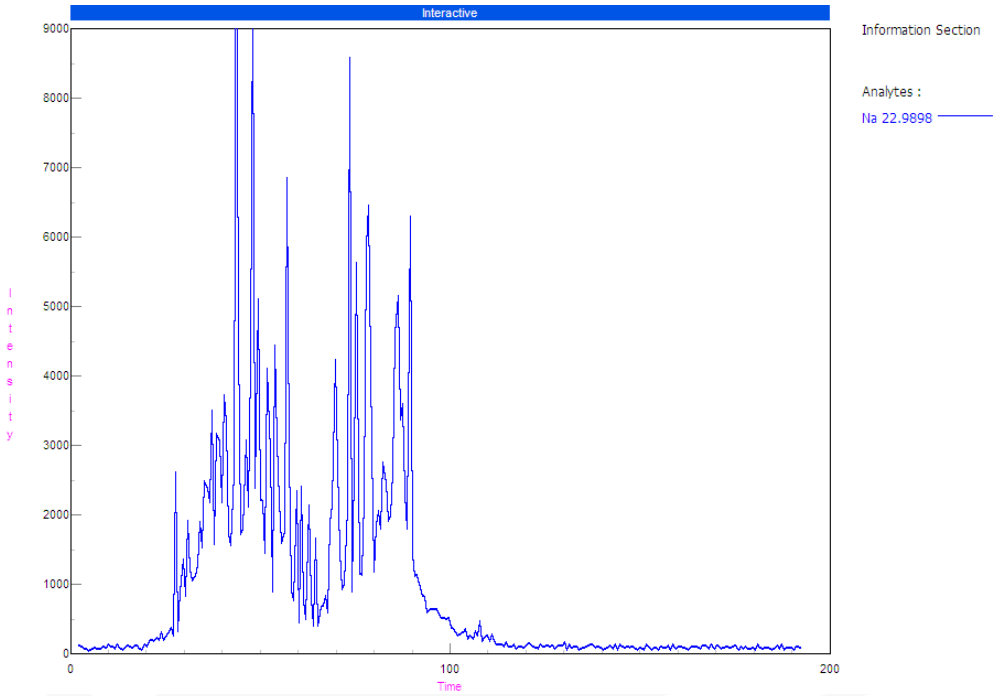
Laser: spot size = 40 µm, effect = 35 %, 5 Hz

Depth profile of Sodium in the membrane

After Ca^{2+}-conditioning



After black liquor



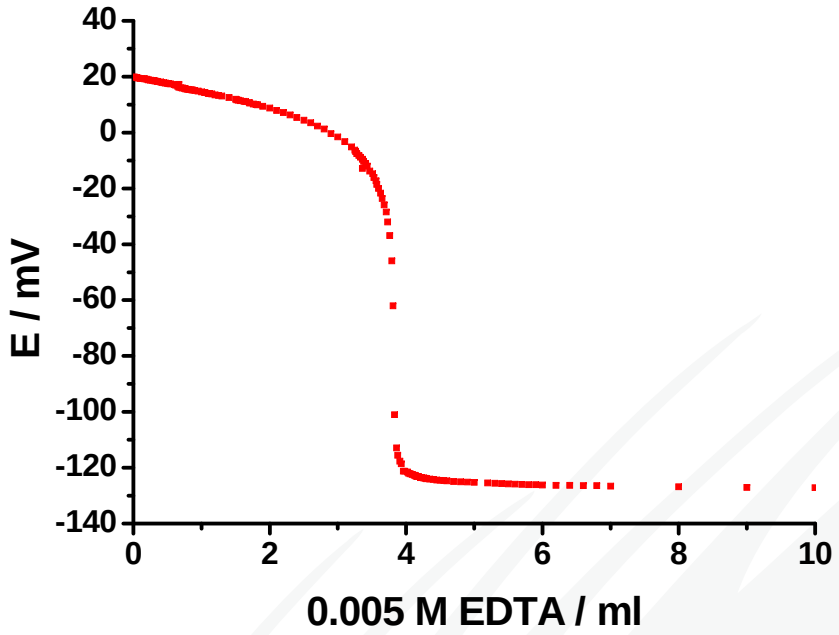
Membrane thickness: ~200 µm

Laser: spot size = 40 µm, effect = 35 %, 5 hz

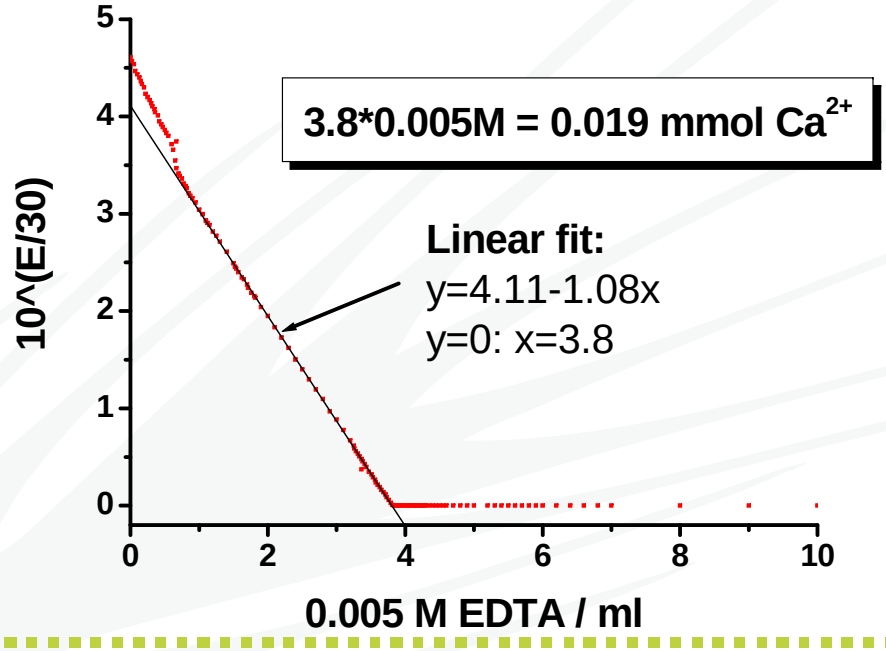
Titration of Ca^{2+}-solution with EDTA using Ca^{2+} ISE

(100 ml of $2*10^{-4}$ M $CaCl_2$ ⟶ 0.02 mmol Ca^{2+})

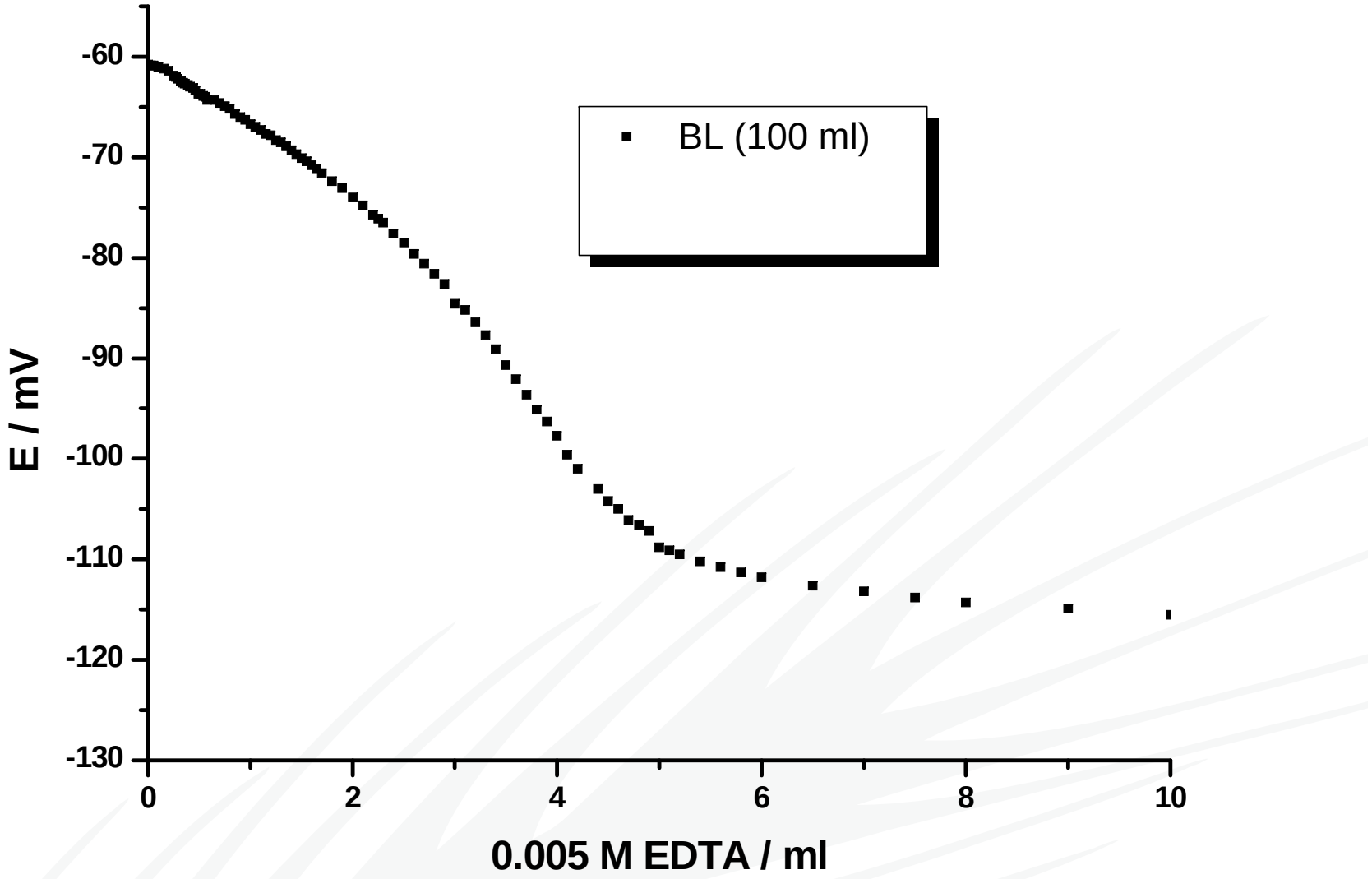
Titration curve:



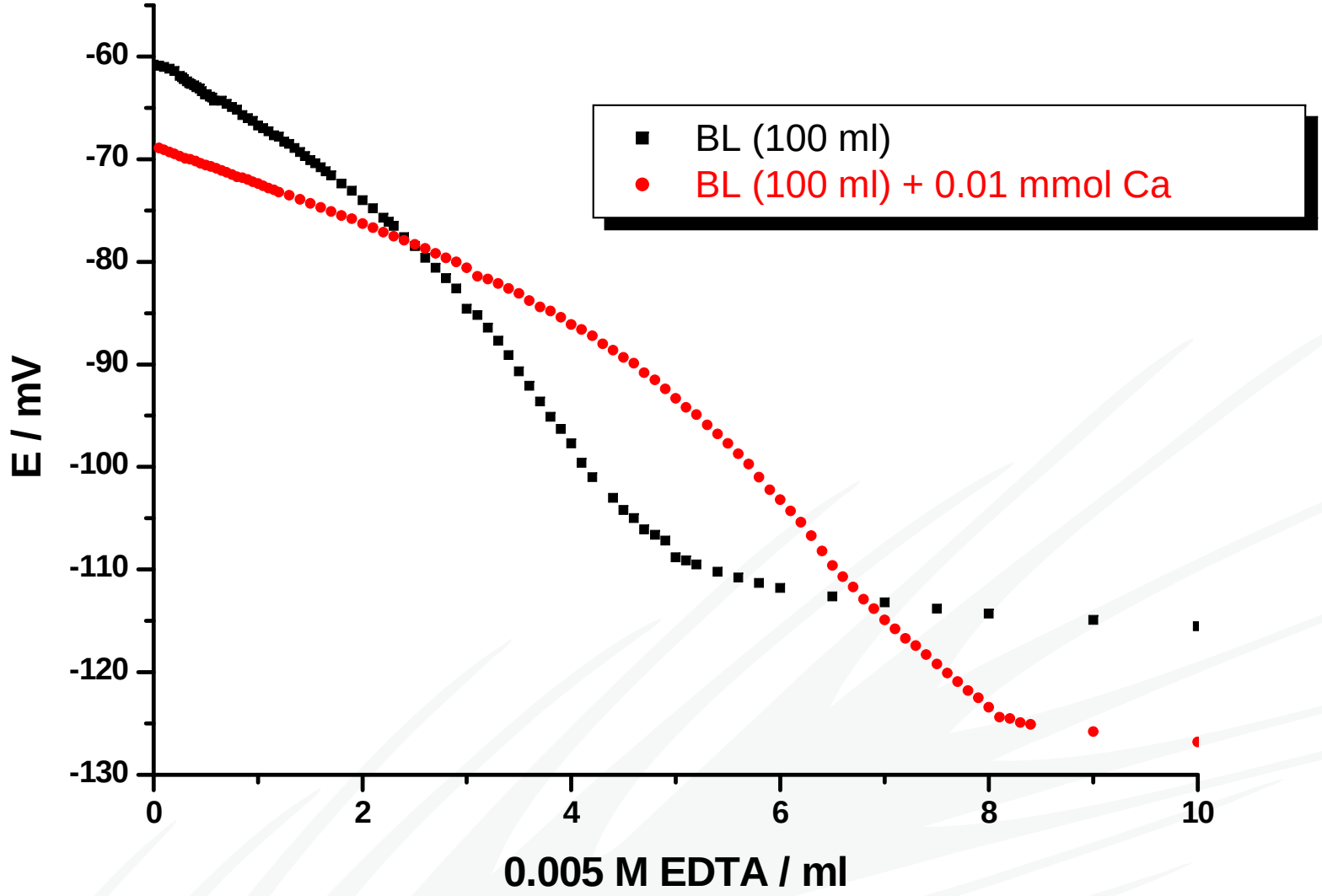
Gran's Plot:



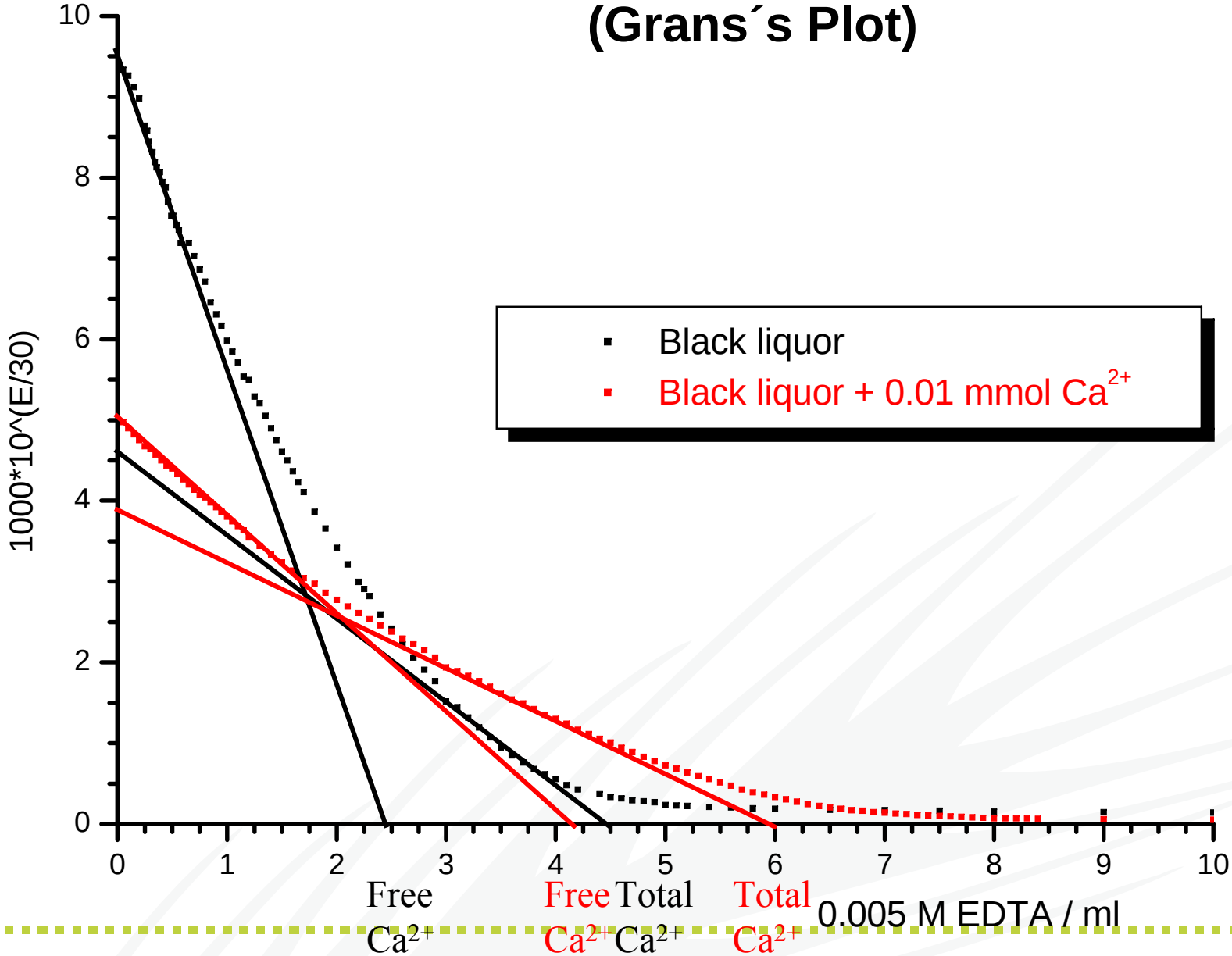
Potentiometric titrations with EDTA using Ca^{2+}-ISE

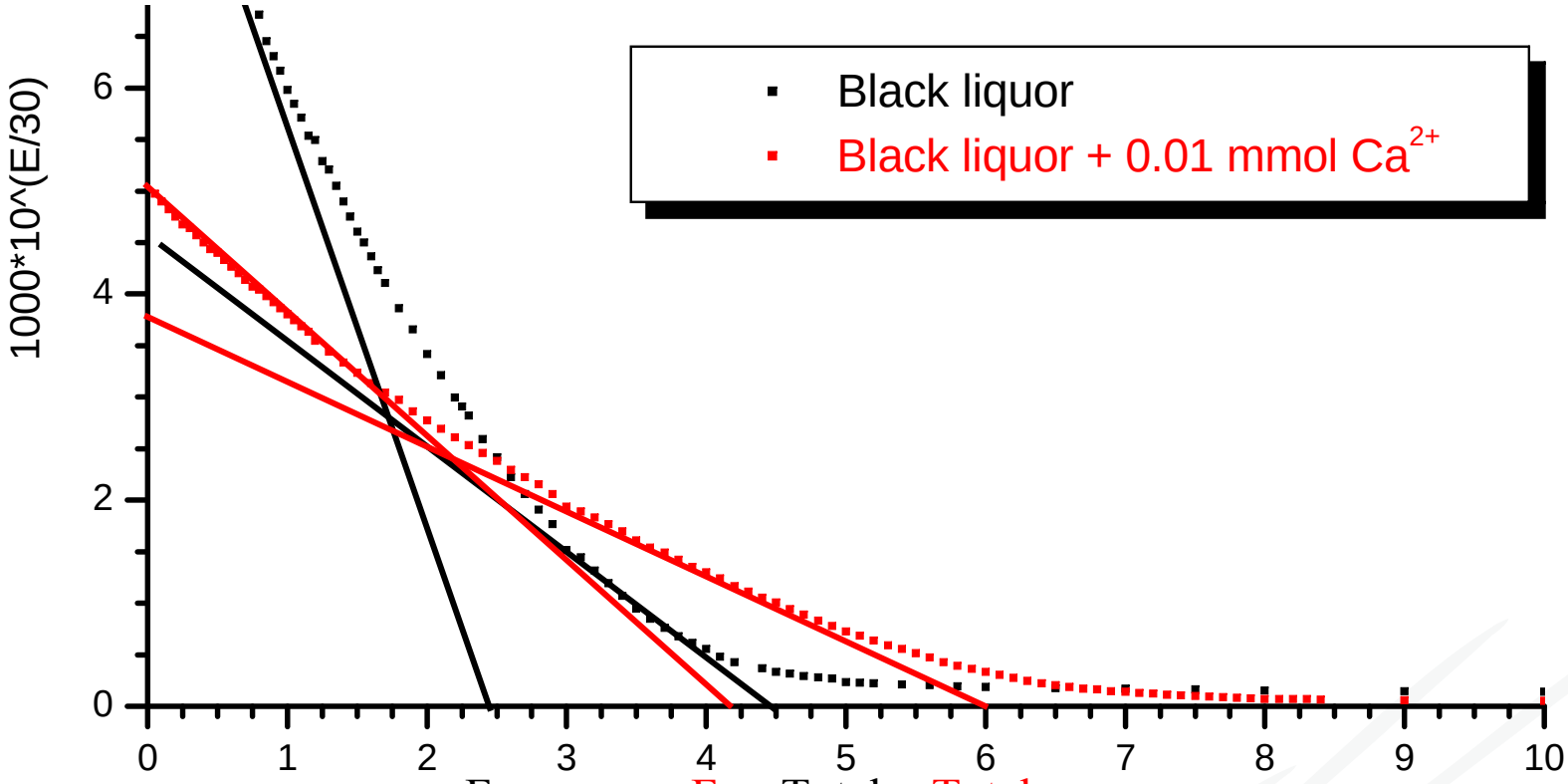


Potentiometric titrations with EDTA using Ca^{2+}-ISE



Potentiometric titrations with EDTA using Ca^{2+}-ISE (Grans´s Plot)





0.01 mmol

0.02 mmol

Free Ca^{2+} = 0.01 mmol

Bound Ca^{2+} = 0.01 mmol

0.02 mmol

0.03 mmol

Free Ca^{2+} = 0.02 mmol

Bound Ca^{2+} = 0.01 mmol

Conclusions

- The Ca^{2+}-ISE can be ”conditioned” in black liquor to eliminate the potential drift
- It is possible to measure Ca^{2+} ions in diluted black liquors
- The selectivity coefficients for the Ca^{2+}-ISE remains high after black liquor measurments
- A speciation of complexed Ca^{2+} ions and uncomplexed Ca^{2+} ions seems to be possible