The use of FTIR-spectroscopy and chemometrics for analysis of kraft pulps

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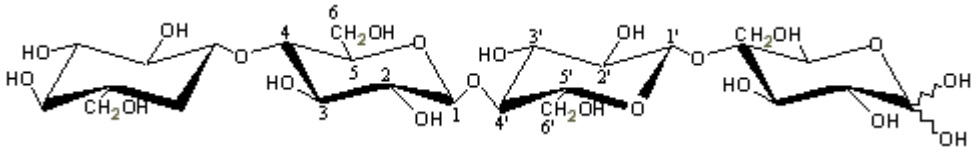
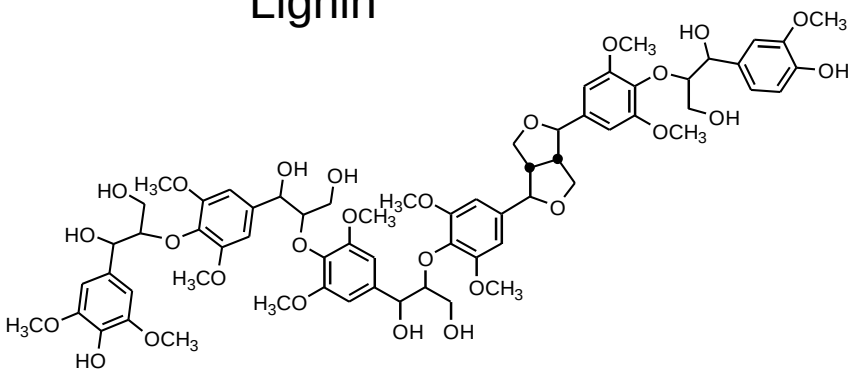
Wood and pulp structure

Cellulose



Hemicelluloses

Lignin

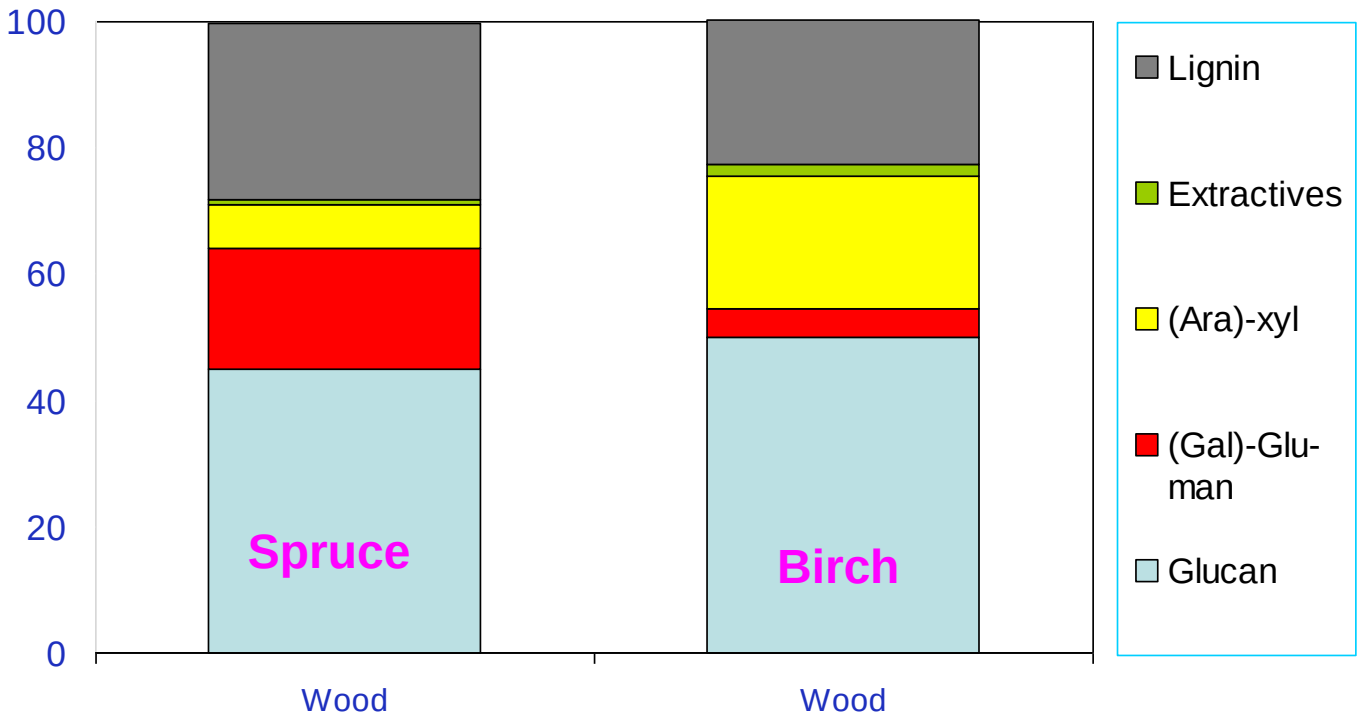


Cellulose consists of glucose forming linear chain

Hemicellulose contains many different sugar monomers such as glucose, xylose, mannose, galactose, rhamnose, and arabinose. Hemicellulose consists of chains of 500-3000 sugar units.
(Galacto)glucomannans are principal hemicelluloses of softwood.
The main hemicellulose of hardwood is *xylan* or arabinoglucuronoxylan.

The softwood lignins are built from the guaiacyl propane units (92–95%) with small amount of the syringyl propane and 4-hydroxylphenyl propane units (3–8%).
The hardwood lignins are built from the guaiacyl propane units and the syringyl propane units.

Chemical composition of spruce and birch wood species



Wood treatments:

- cooking
- explosion
- refining
- bleaching
- **Acid hydrolysis**
- the others

different fibers products

This work: studying kraft pulping

Objects of investigation:

four wood species -

spruce, pine, aspen and birch

Pulping conditions:

a heating-up time from 80C to 170C.: 100 min,

alkali charge: 17% active alkali (as Na2O),

sulfidity 25%.

Kinetic of spruce and pine wood species kraft pulping:

Changing two main parameters at pulping - pulp yield and lignin content values - in dependence on cook time

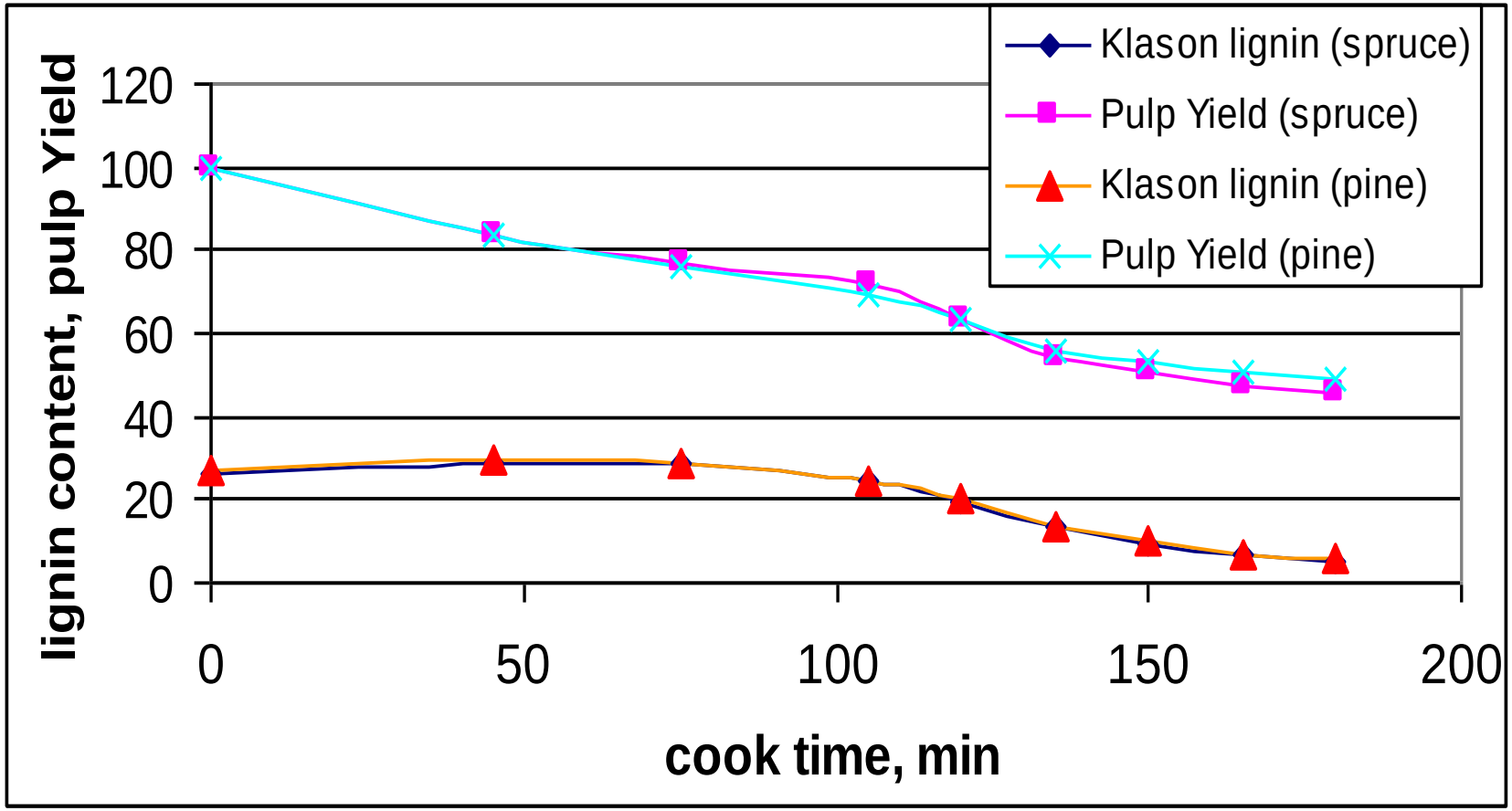


Table. Ranges of changes of lignin content and pulp yield of the four type of wood and kraft pulp samples (9 points for each wood species)

Species	Klason lignin in wood, %	Klason lignin in kraft pulp, %	Yield value, %
Aspen	**20,95**	**21,27 - 1,35**	**83,7 - 32,6**
Birch	**23,16**	**24,9 - 2,26**	**81,3 - 40,4**
Spruce	**27,16**	**29,79 - 5,56**	**83,9 - 49,3**
Pine	**26,22**	**28,32 - 6,42**	**83,7 - 47,6**

Kraft delignification kinetic depends on

- wood species
- cook time
- temperature profile
- content of chemicals
- pretreatment
- other factors

the material with different composition and properties will be produced

Characterizing plant cell wall composition and structure

Nondestructive spectroscopic methods:
(poor resolution and overlapping signals)

- solid-state NMR – spectroscopy
- IR-spectroscopy
- NIR –spectroscopy

Destructive chemical and physical methods:
(Modification of components, degradation, isolation of part of component)

- acydolys
- oxidation by permanganate
- Pyrolysis
- oxidation by nitrobenzene
- HRLC

FTIR-spectroscopy (range 400 – 4000 см-1) for investigation wood and pulps

Advantages

- Non-destructive method – there is no chemical modification and breaking bonds
- It allows to investigate all lignocellulosics samples
- It is possible to study main wood polymers *in situ*
- Different mathematical treatments can be applied

Difficulties

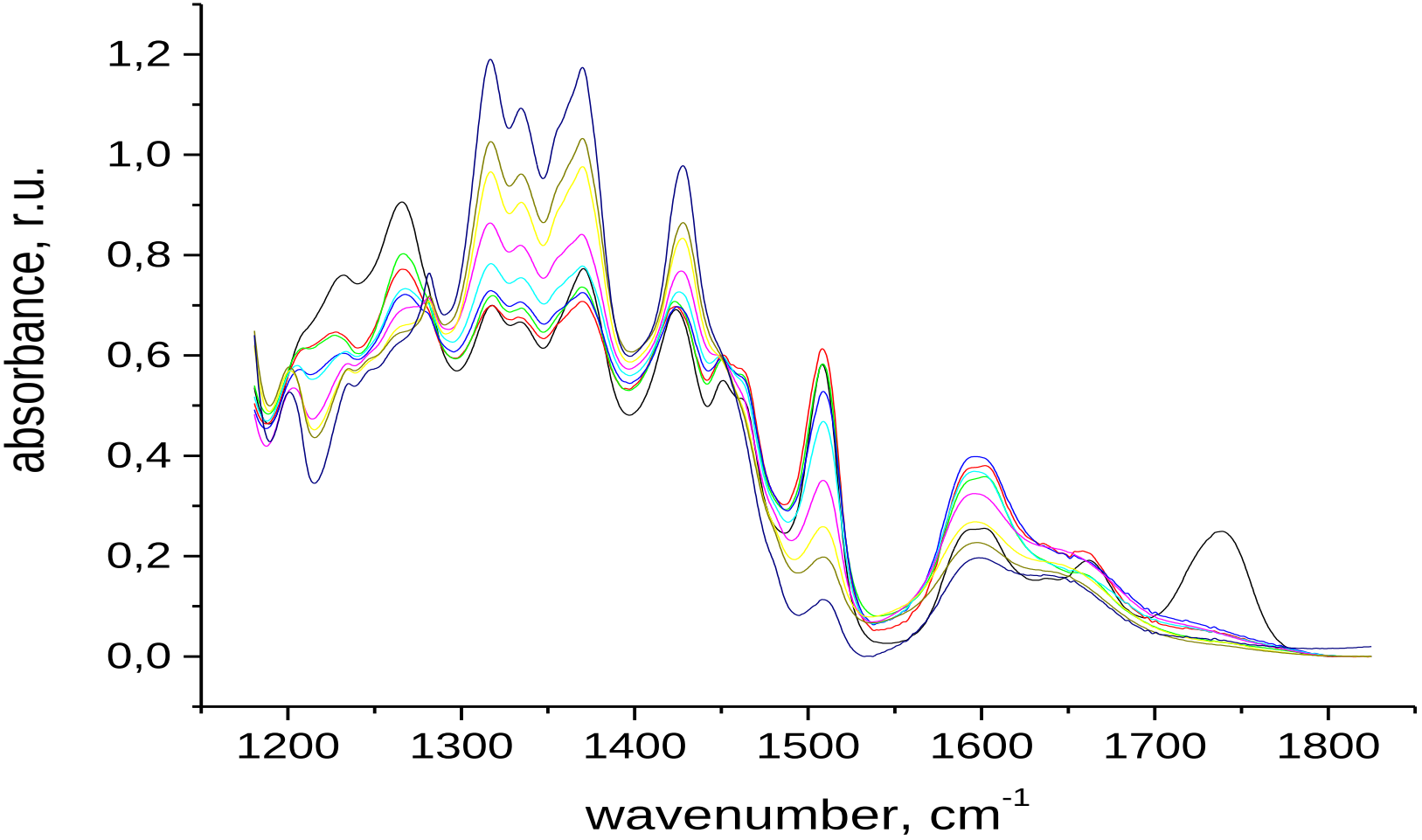
- Correct selection of information about one of compound composing wood/pulp
- Band interpretation

In the work we investigated

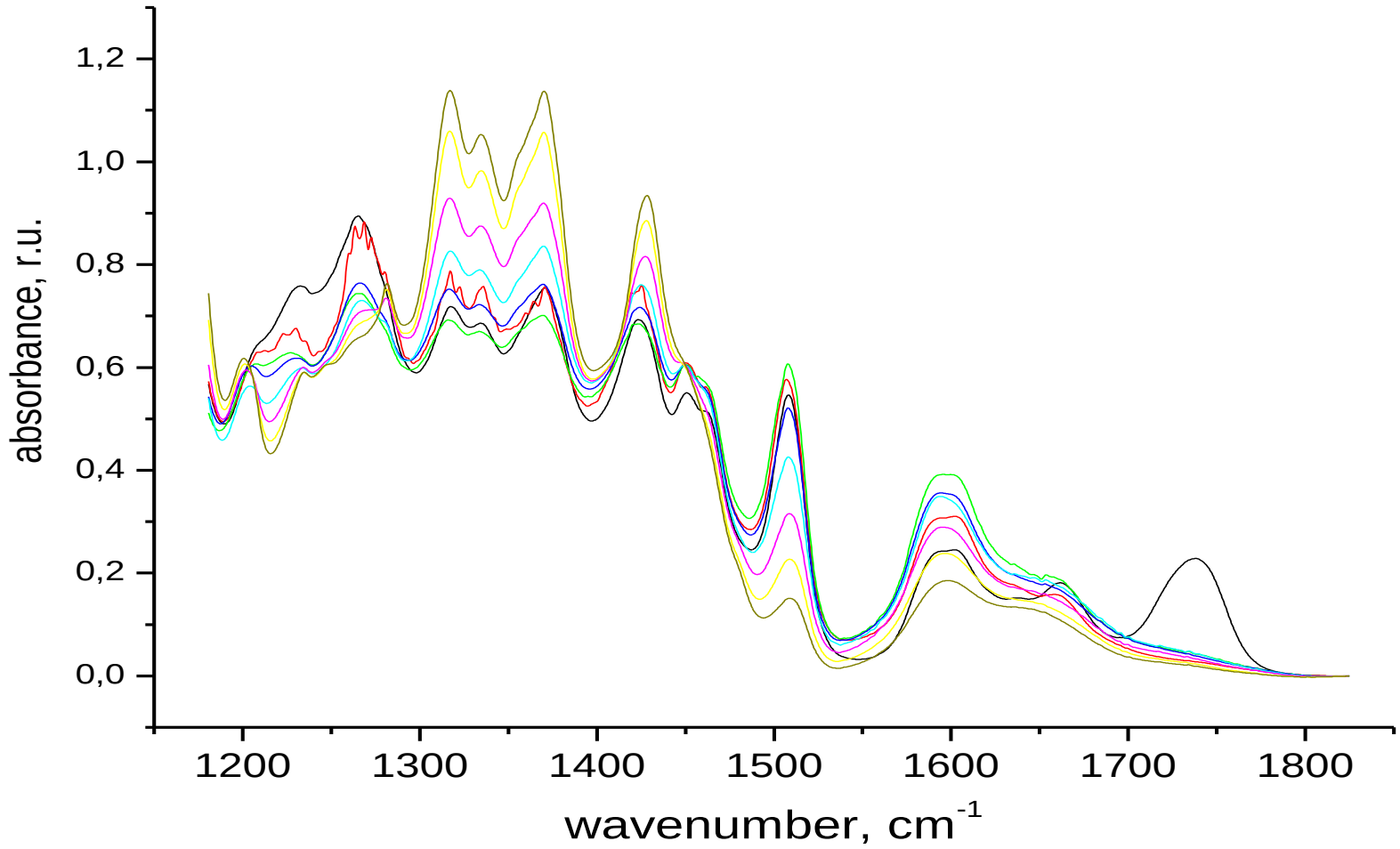
FTIR - spectra of kraft pulp samples for four series (pine, spruce, aspen, birch)

Each series - 9 samples (origin wood and kraft pulps) of different delignification level

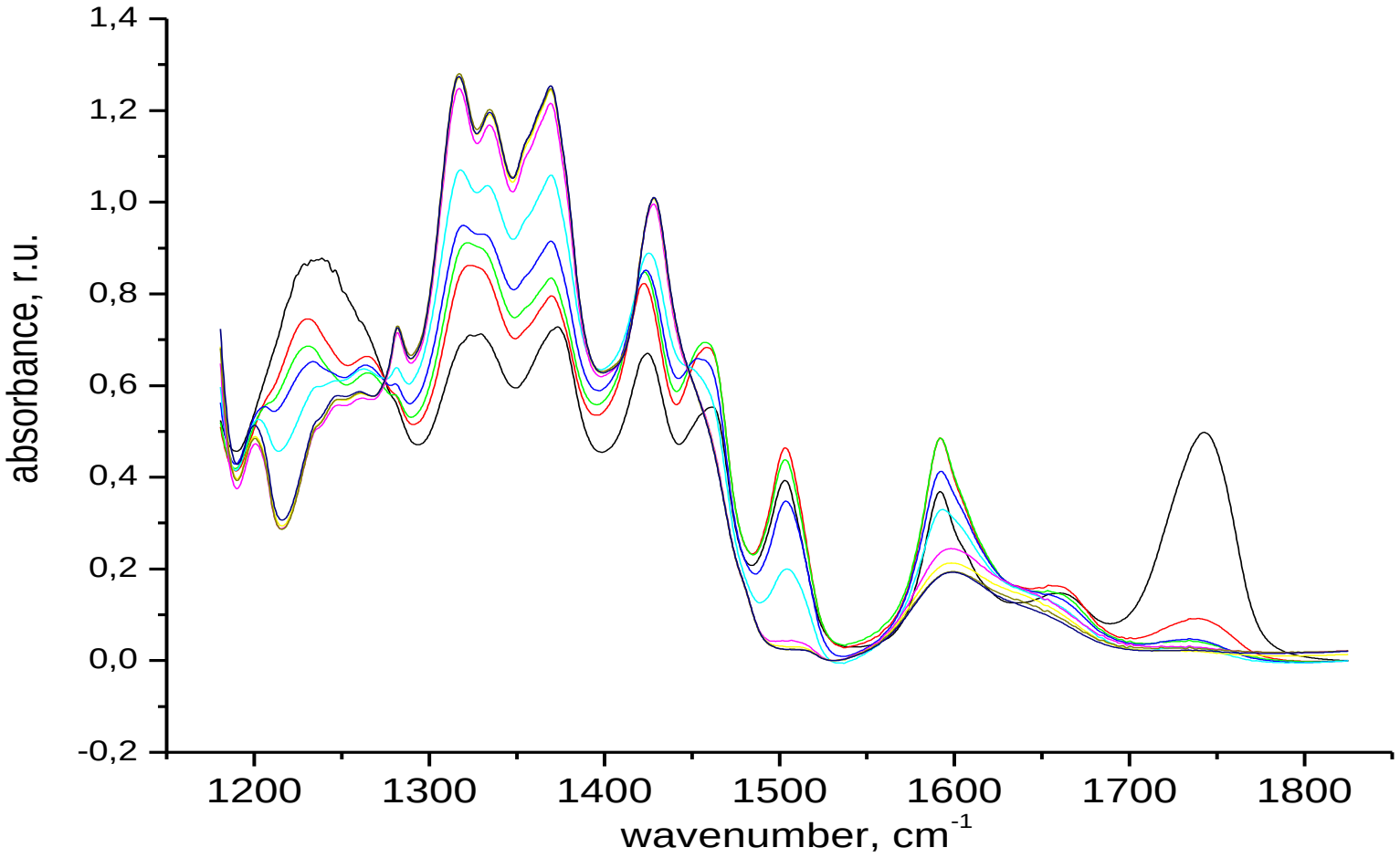
IR-Spectra of kraft pulping spruce wood samples (normalized and base line corrected)



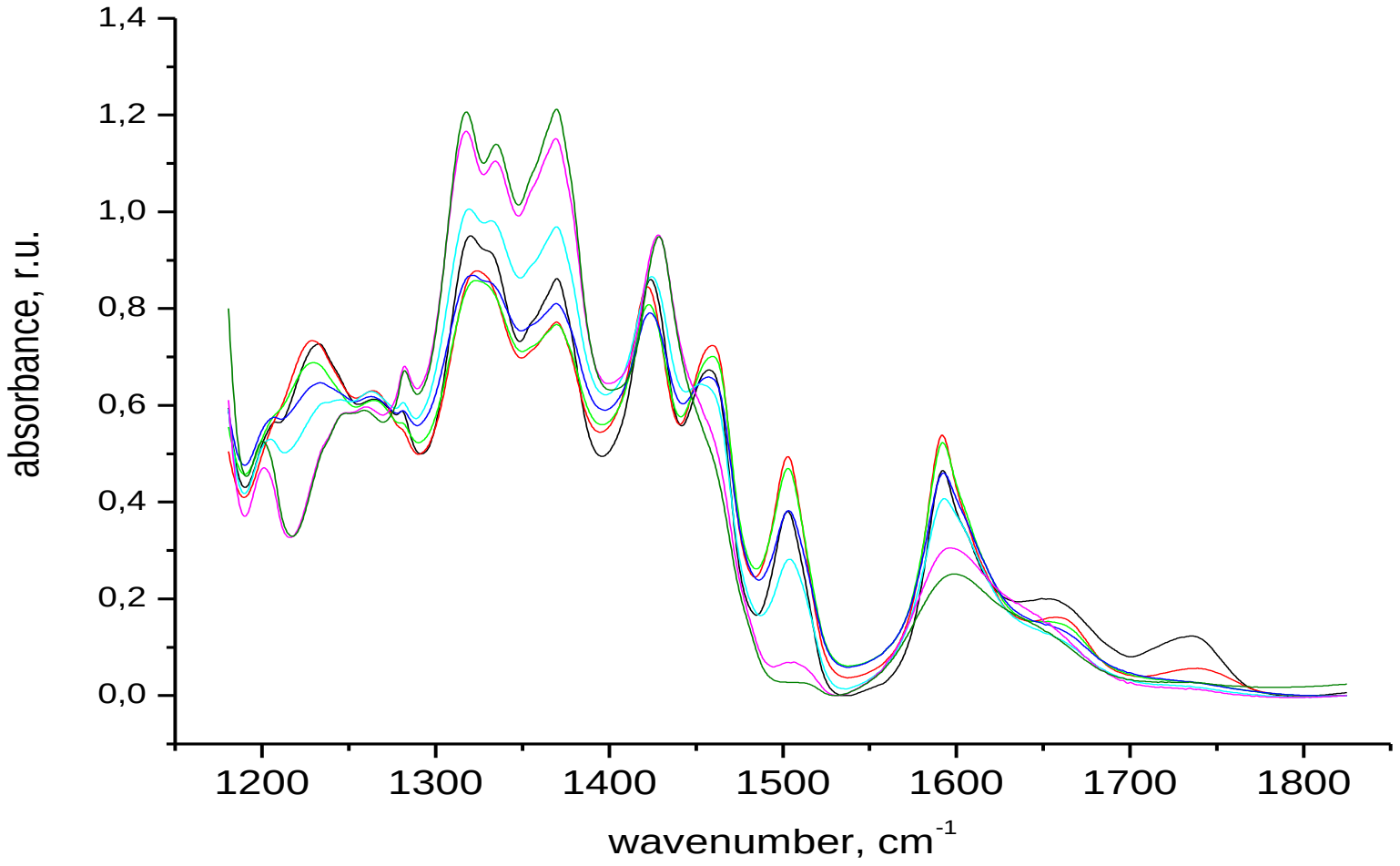
IR-Spectra of kraft pulping pine wood samples



IR-Spectra of samples after kraft pulping aspen wood



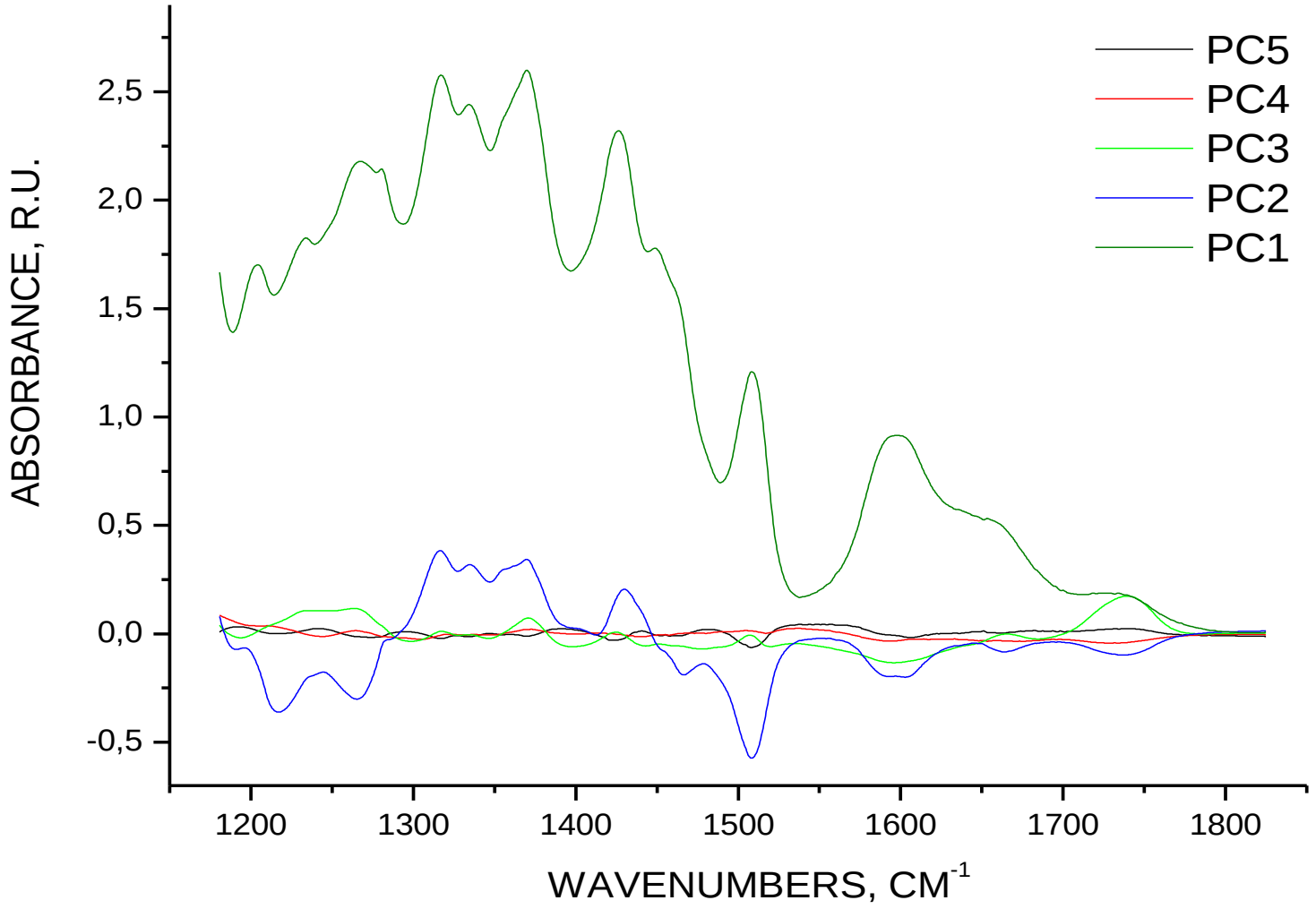
IR-Spectra of samples after kraft pulping birch wood



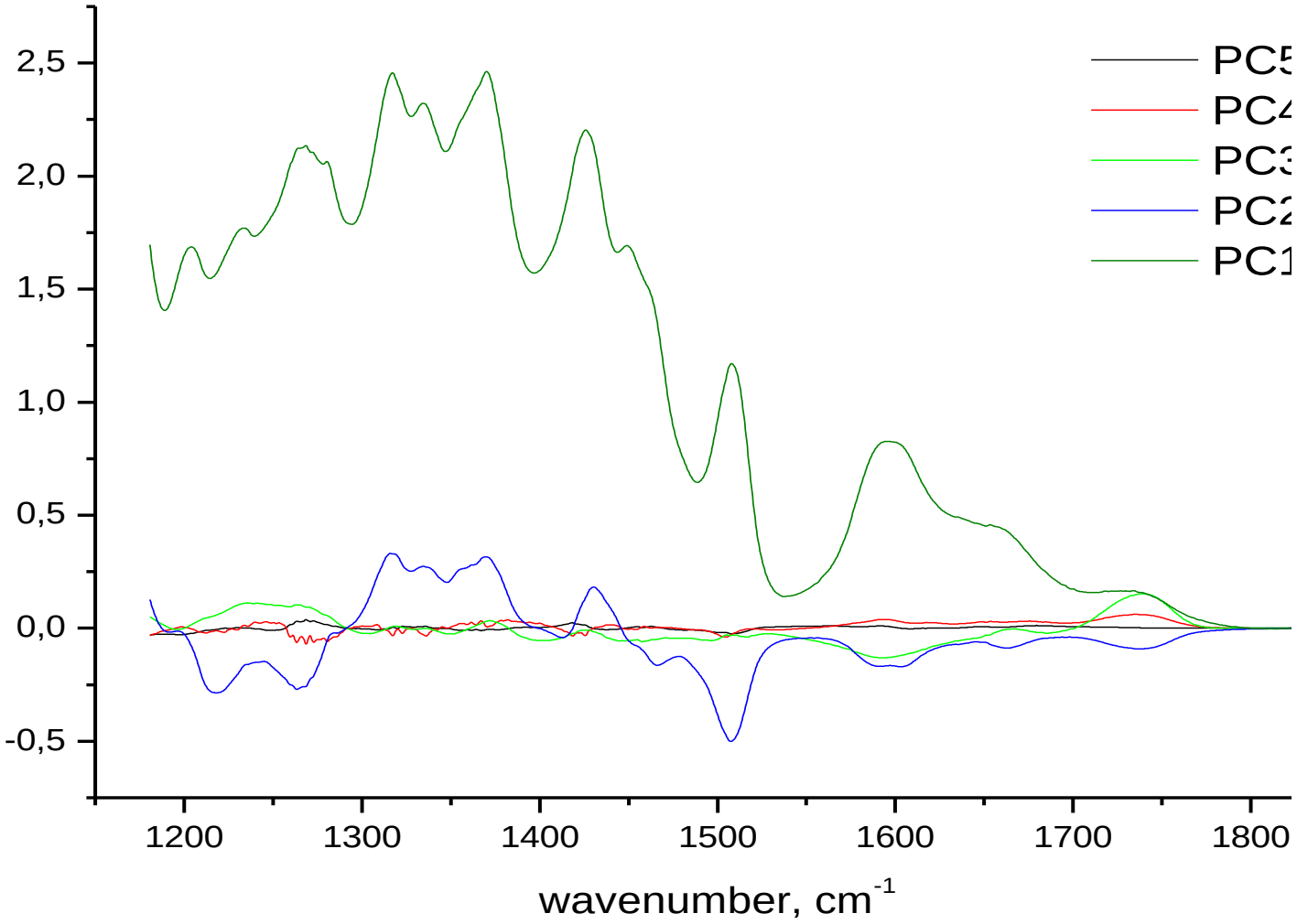
The aim of this study was for four pulp kraft pulp sets:

- to evaluate a number of principal components
- to produce pure spectra
- to compare pure spectra with spectra of isolated pure lignin and spectra of models
- to interpret bands
- to have calibration models for two parameter - lignin content and pulp yield

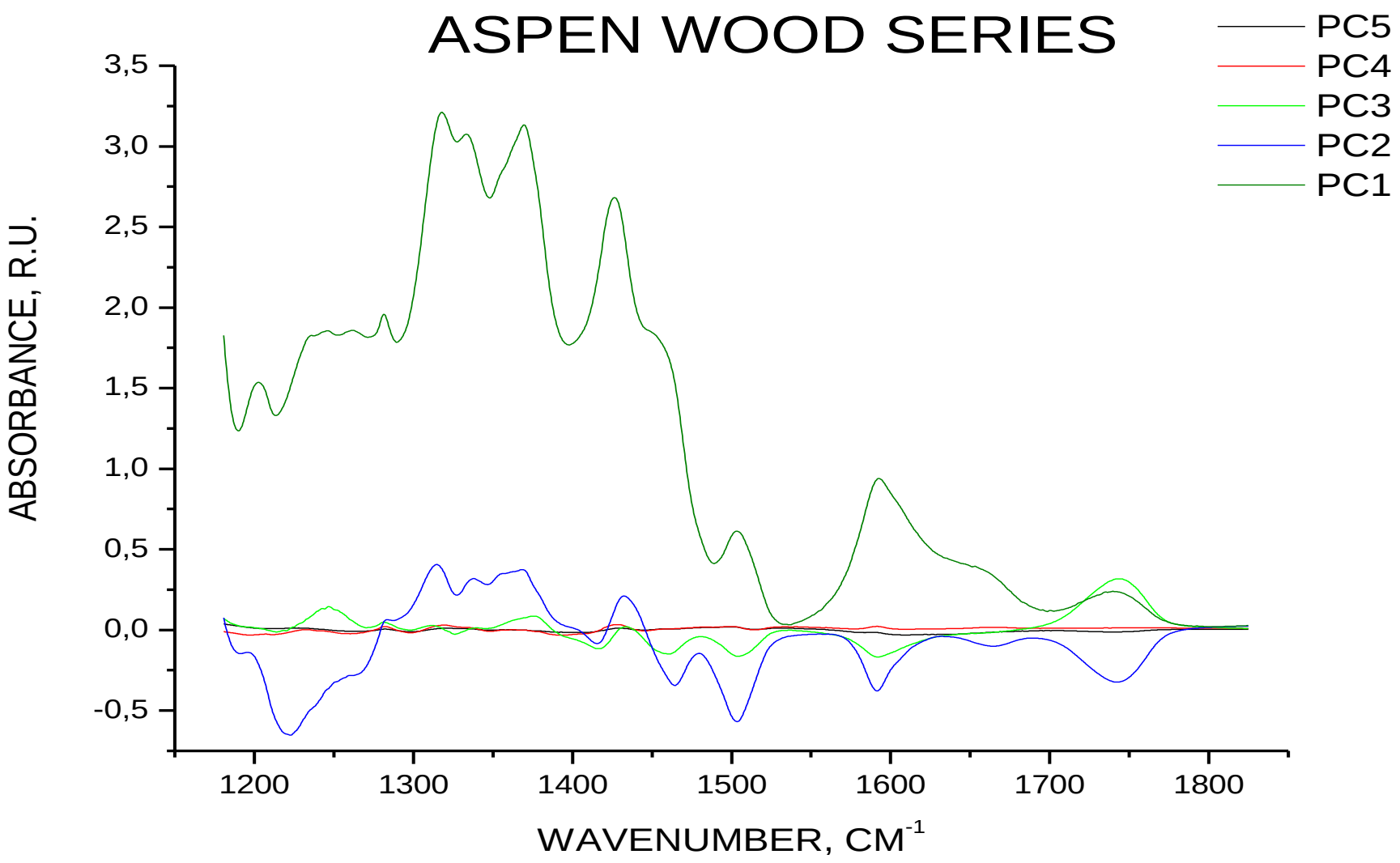
Principal component analysis of spruce species spectra



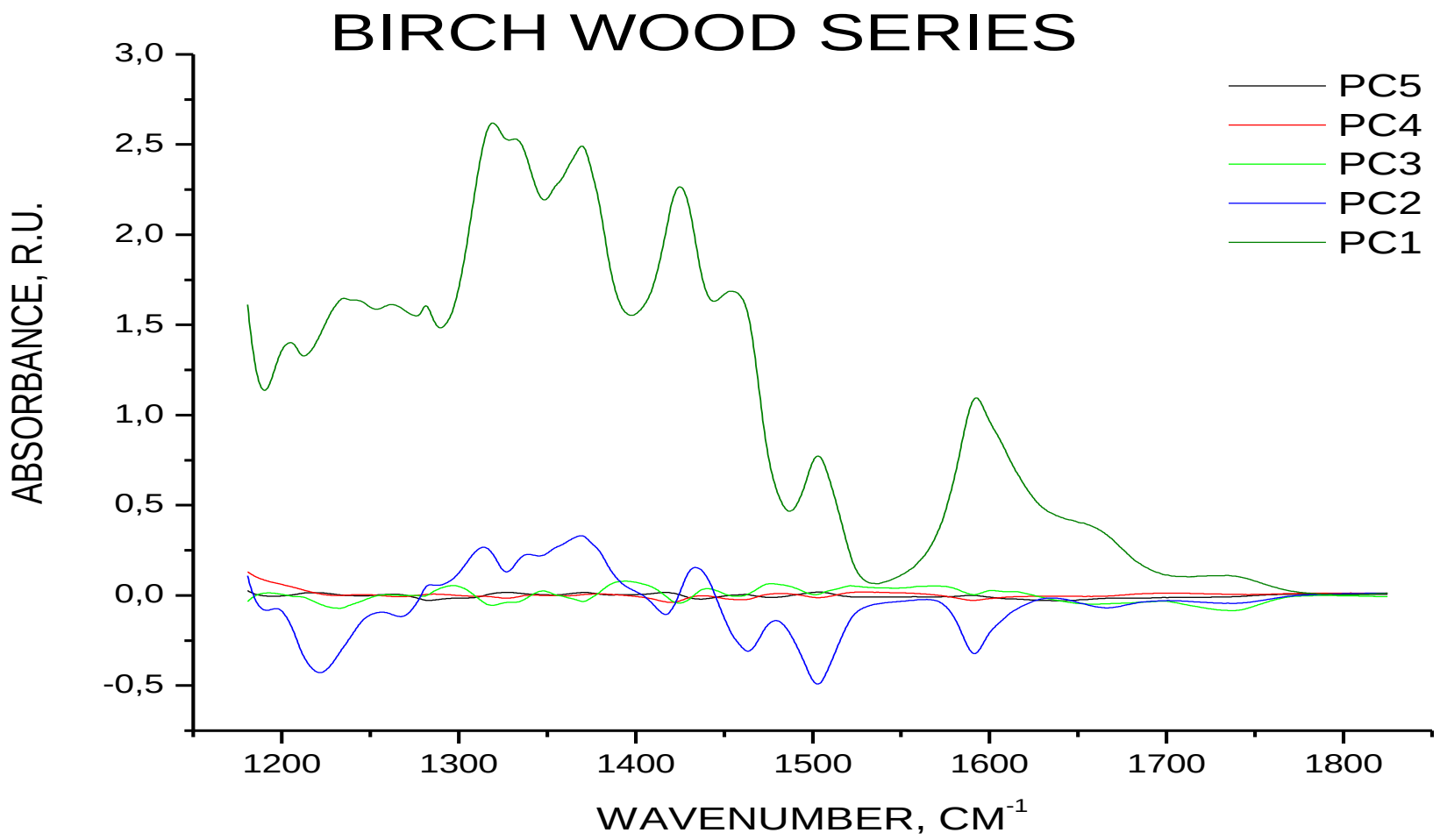
Principal component analysis of pine species spectra



Principal component analysis of aspen species spectra

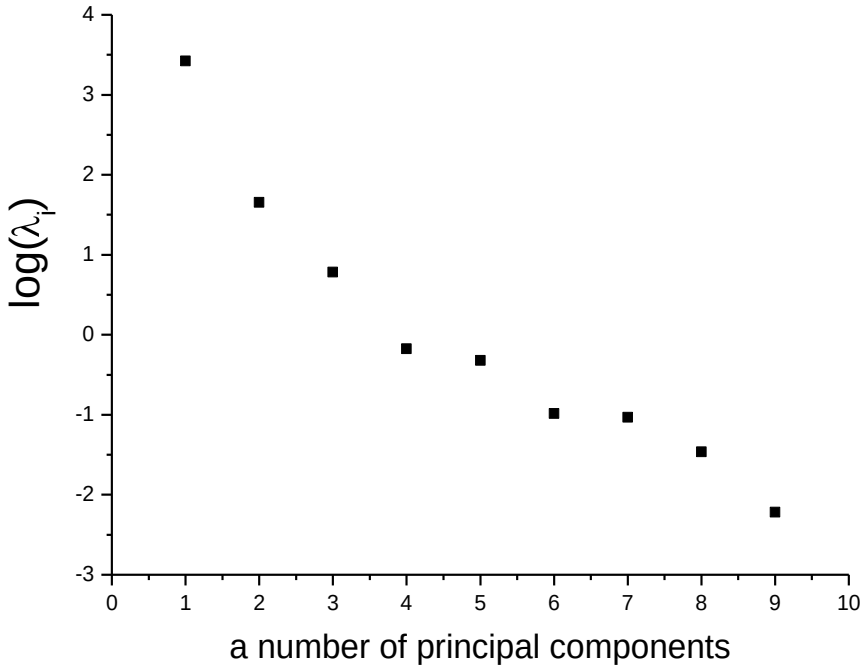


Principal component analysis of birch species spectra

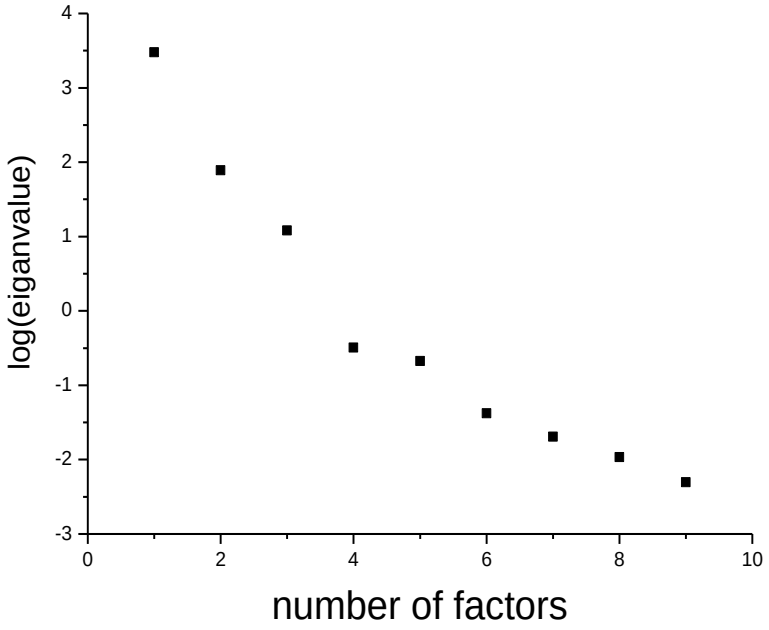


Dependence log(eigenvalue) on a number of Principal components

spruce



aspen



A number of principal components for four spectral sets. Criteria- dependence of parameter ERV and Eigen value on a number of Principal components

type species	series	PC's number
SW	spruce	5
SW	pine	4 - 5
HW	aspen	4 - 5
HW	birch	3 - 4

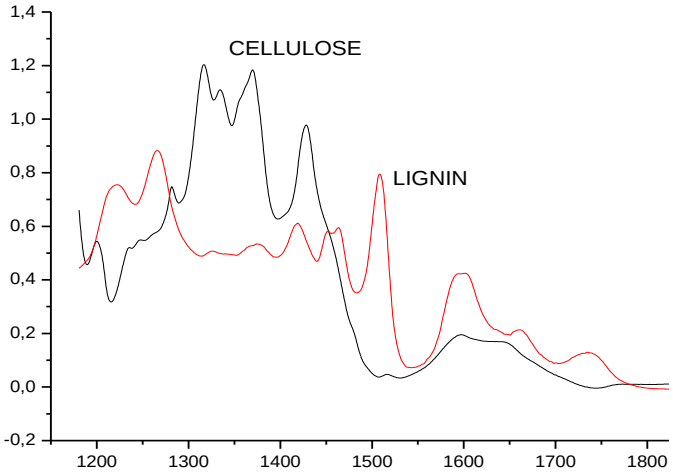
PCA models showed:

- PC1 and PC2 explain approximately 99% of variances - describe changes in content carbohydrate and lignin polymers
- PC3, PC4, PC5 probably describe structural changes of carbohydrate and lignin, acetyl groups removing, forming hexenuronic acids
- Five first components describe 99.9% of all variances

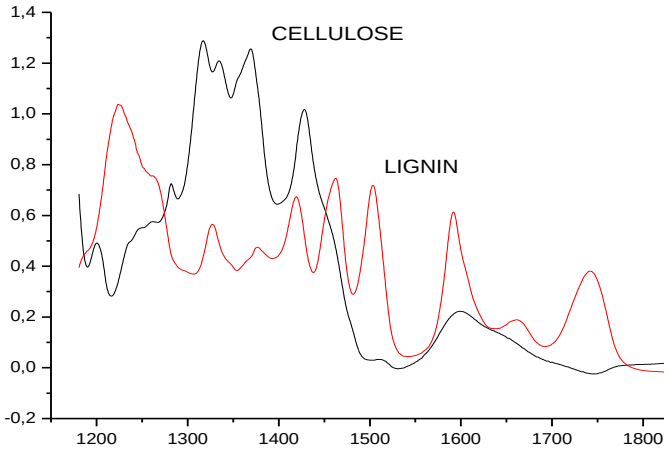
Pure spectra

-

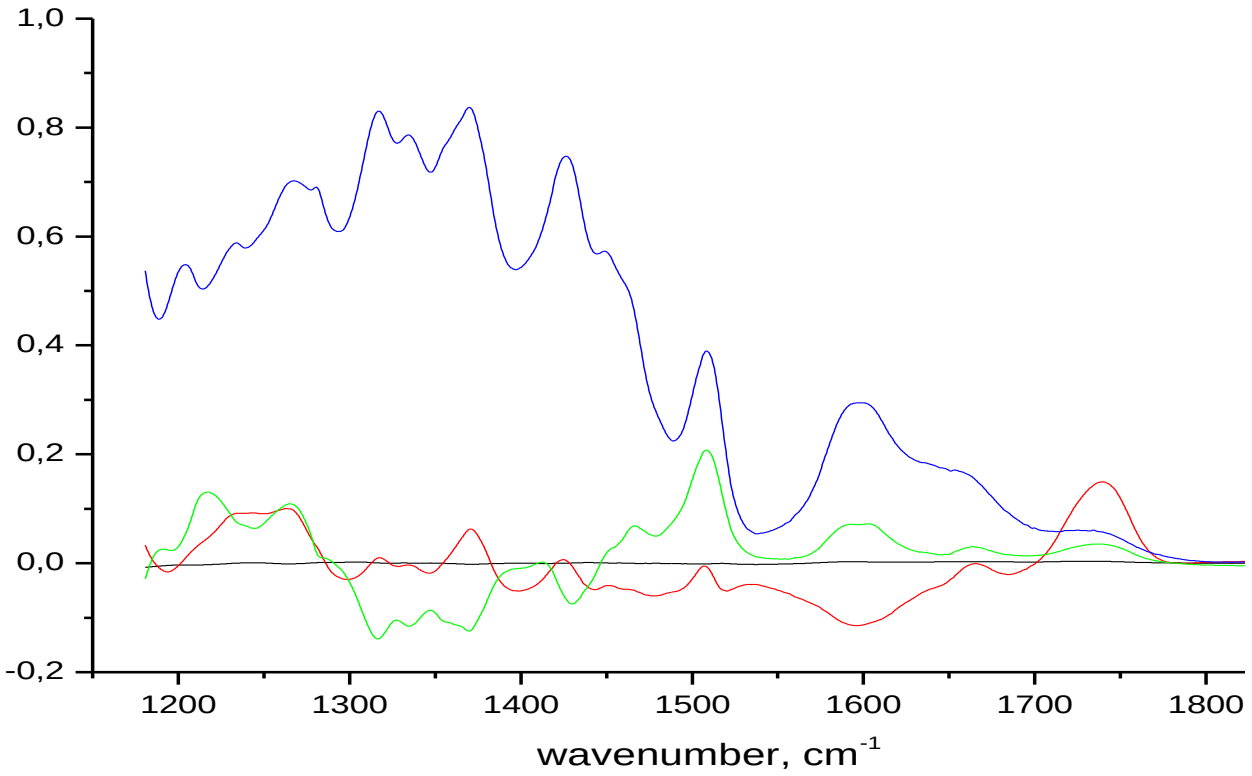
spruce



aspen



Second help which we wait from PCA is interpretation some bands



PCR models

Four wood species:

- Pine kraft pulps and wood
- Spruce kraft pulps and wood
- Aspen kraft pulps and wood
- Birch kraft pulps and wood

Two parameter:

- Pulp yield
- Lignin content

Calculated vs. measured pulp yield for softwood pulps

Calculated vs. measured lignin content for hardwood pulps

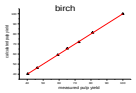


Table. Parameters of calibration models for determination of Klason lignin and pulp Yield : Correlation coefficient, SEP and rank

	pulp Yield			**Klason lignin**		
	R 2	Rank	SEP	*R*2	Rank	SEP
spruce	0.97	6	0,6	0.99	5	0,2
pine	0.99	6	0,2	0.99	4	0,2
aspen	0,99	5	0,4	0.99	4	0,1
birch	0,99	5	0,2	0.99	5	0,2

CONCLUSIONS

The multiple data analysis allowed:

- to reveal the number of principal components – dimension of four investigated systems
- to reveal correlations of bands
- to resolve bands and do some interpretations
- to model “pure” spectra of cellulose and lignin
- to create good calibration models for a fast estimation of the important chemical and economical parameters of different origin kraft pulps.

Acknowledgement

Professor Evstigneev E.I. is gratefully acknowledged for his fine characterized samples and for numerous discussions.

Thank you for your attention

All computations were carried out on a personal computer using a Bruker’s software package OPUS and Maple software package.