STUDY OF DIFFERENTLY TREATED (COOKED ONLY AND BLEACHED THEREAFTER) INDUSTRIAL GRASS FIBRES BY RAMAN, FTIR-ATR AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY

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In cooperation with the Szarvas Research Group, the Hungarian Paper Research Institute Sopron and the Research Group at the Department of Organic Chemistry and Technology of the Budapest University of Technology and Economics have started research activities for utilising this grasses in biorefinery.

I have already reported about the Industrial Grass generated and cultivated in Hungary as potential raw material for bio-fuel and biorefinery at the former COST FP0901 Meetings at 25th January 2011 in Paris and 7th September 2011 in Viterbo. First of all about the cultivation and characteristic properties of Industrial Grass and physical-mechanical characteristics of pulps made at laboratory-, pilot plant- and industrial level from it has been discussed there.

„New annual Hungarian plants (industrial grasses) adaptable as biofuels and as raw materials in biorefinery"

Zsolt Janowszky, János Janowszky, István Lele, Mariann Lele and András Víg

Oral Presentation FP0901 25.01.2011, Paris

Place: FCBA – 10 Av Saint Mandé – 75012 – Paris – France
***Session 1, chair Callum Hill* 9:30**

"New annual plant (industrial grass) as raw material for pulp and paper industry 2; Physical-mechanical characteristics of pulps made at laboratory-, pilot plant- and industrial level of production"

András Víg, Mariann Lele, István Lele, Zsolt Janowszky and János Janowszky

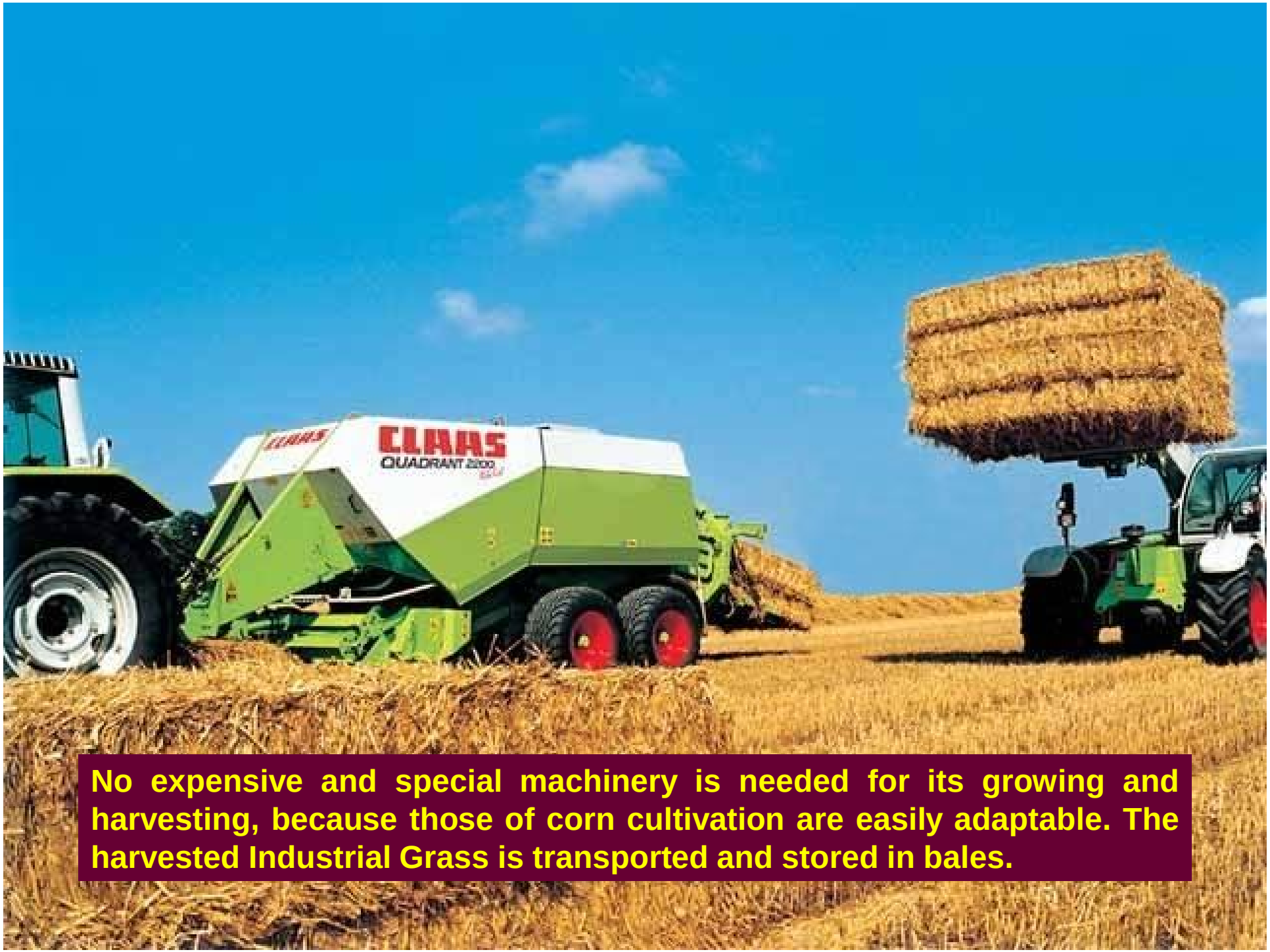
Oral Presentation FP0901 07.09.2011, Viterbo

Place: Viterbo – Italy

Produced biomass by one hectare

Raw material	Biomass suitable for industrial utilisation, t/year/hectare
Coniferous	1.5 – 2.0
Broad-leaved trees	2.5 – 3.0
Grain straw	3.5 – 4.0
Flax	2.5 – 3.0
Hemp	6.0 – 8.0
Industrial grass	**10.0 – 15.0**

The yearly production of biomass/hectare of industrial grass compared with that of different plants are shown in the table. The relative yearly production of biomass by industrial grass is twice up to ten times of that by other plants.



No expensive and special machinery is needed for its growing and harvesting, because those of corn cultivation are easily adaptable. The harvested Industrial Grass is transported and stored in bales.

Summarising: the industrial grass proved to be a hopeful yearly renewable raw material for energetic as well as for industrial application. Consequently detailed analytical study of its chemical composition and physical properties has to be considered important in point of you of biorefinery.

Before elaboration proper cooking and bleaching technologies the following essential requirements and questions should be taken into consideration.:

Two important aspects have to be taken into consideration in the course of elaboration of the cooking and bleaching technologies:

1.) Exact analytical data about the chemical composition of the raw material.

2.) How could the highest yield in pulp gained by applying environmental friendly pulping technologies.

The first question has already been partly answered in our presentations in Paris at the foregoing COST FP0901 meeting.

The second question has already been partly answered in our presentations in Viterbo at the foregoing COST FP0901 meeting.

Based upon cooking and bleaching treatments the following conclusions might be formulated

The best cooking parameters are the following:

Hydromodulus: 1:4
Temperature: 165-170 °C
Time of treatment: 25 minutes
Chemicals: 16% NaOH + 0.1% anthraquinone

Based upon the laboratory bleaching experiments the following sets of steps have been suggested for the pilot scale experiments:

- **TCF bleaching: Q + EOP + P + P + P**
- **ECF bleaching: P + D + P + P**

The characteristics of industrial grass cellulose are close to that of Broad-leaved trees.
The rather low freeness of Industrial Grass cellulose is promising as far as favourable running on the paper machine is concerned.

EDS, RAMAN and FTIR spectroscopic studies of industrial grass samples

At present I would like to inform you about the possibilities of application of modern analytical techniques, in the development of pulp and paper production.

Goal was the ENERGY-DISPERSIVE X-RAY, RAMAN and FTIR-ATR SPECTROSCOPY studies of industrial grass cellulose samples scoured bleached and ground at pilot scale under different conditions.

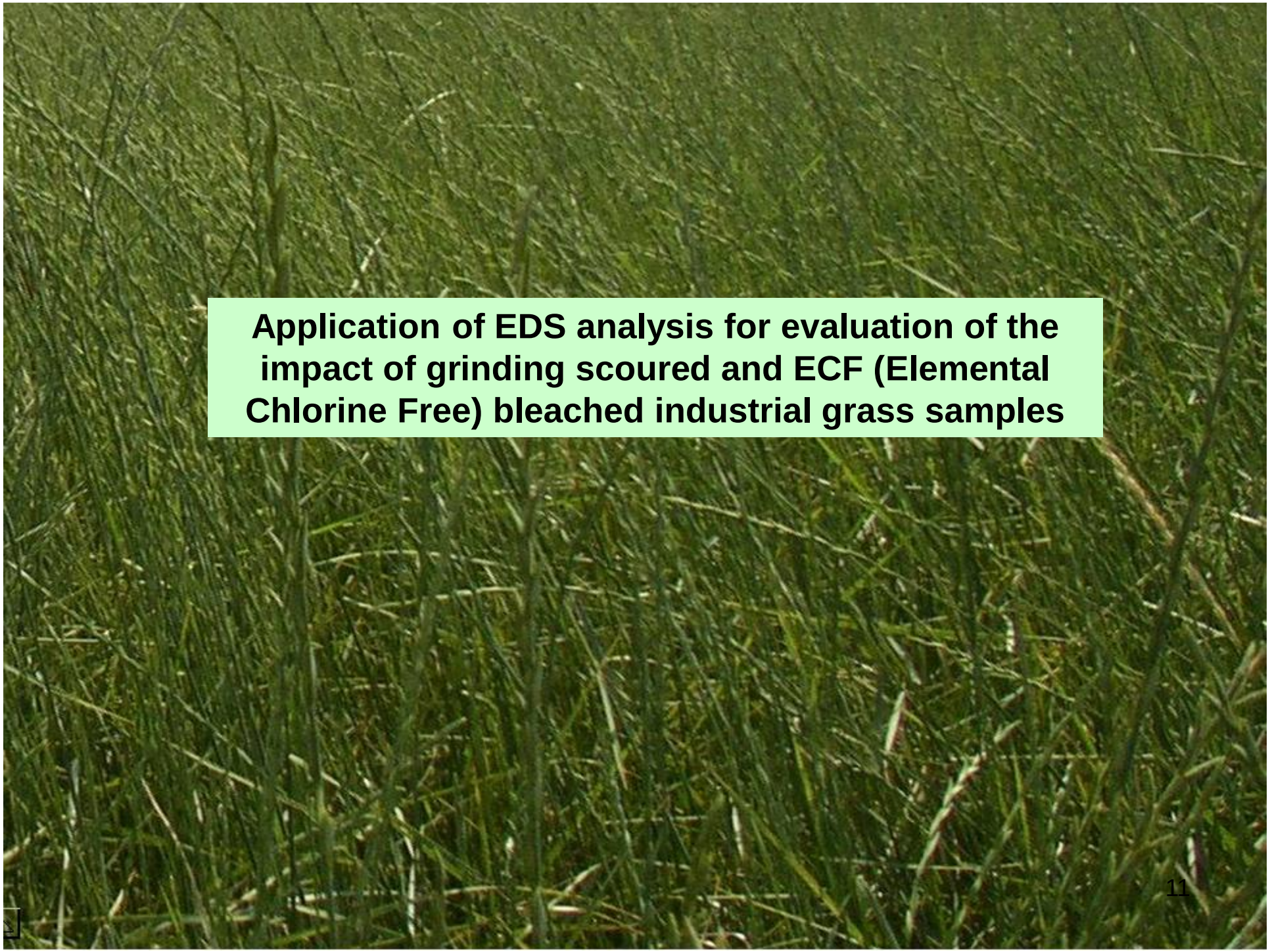
Principal basis of Energy Disperse Spectroscopy (EDS)

Energy disperse spectroscopy is a method used to determine the energy spectrum of x-ray radiation in an electron microprobe. Electron microprobe is an analytical tool used to non-destructively determine the chemical composition of small volumes of solid materials. It uses a high-energy focused beam of electron to generate X-rays characteristic of the elements present within a sample 1-to 3 micrometers across and quantitatively analyze elements from boron to plutonium at routine levels as low as 100 parts par million (ppm).

Energy-Dispersive X-ray Spectroscopy (EDS)

JEOL JSM-6380LA scanning electron microscope type

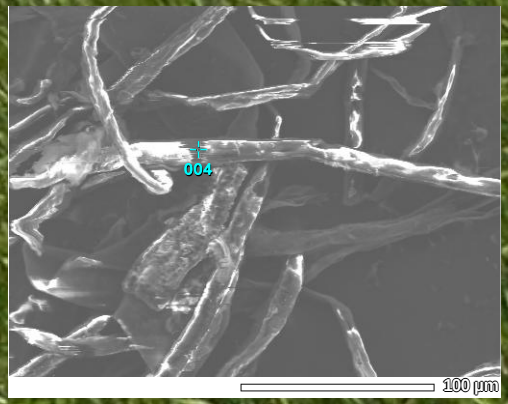
Scanning parameters:
• accelerating voltage: 15 kV
• spot size: 65–75
• working distance: 10 mm
• Signal: SEI (secondary electron beam)
EDS measurements of the carbon atom and the higher atomic number elements to obtain chemical information.


Application of EDS analysis for evaluation of the impact of grinding scoured and ECF (Elemental Chlorine Free) bleached industrial grass samples

SEM and EDS Studie of Unbleached Industrial Grass Cellulose Fibres, Cooked in Pilot Device Unbleached and Grinded 5 min. in PFI Mill

K5 (a)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	29748.44	90.03	92.66
O	0.525	7627.44	8.92	6.90
Mg	1.253	345.13	0.30	0.15
Si	1.739	463.19	0.44	0.19
Ca	3.690	188.87	0.30	0.09
			100.00	100.00



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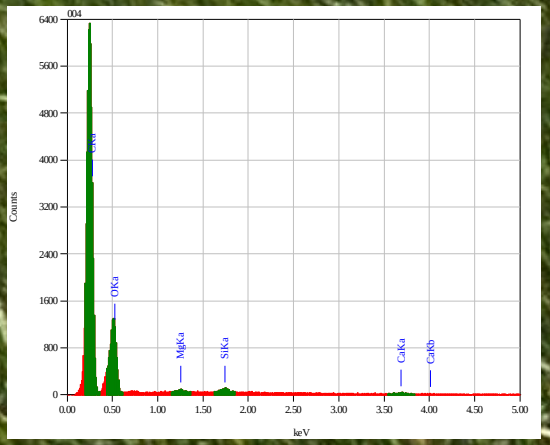
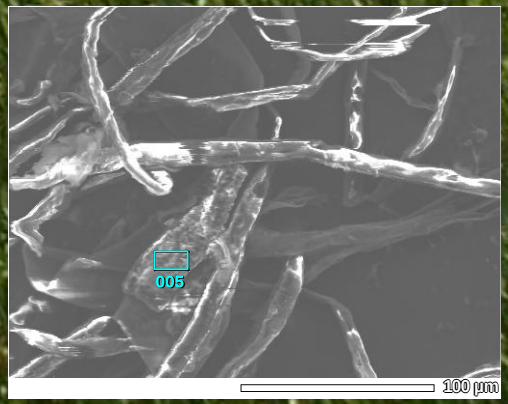


K5 (b)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	26456.09	89.87	92.69
O	0.525	6638.43	8.72	6.75
Mg	1.253	234.00	0.23	0.12
Si	1.739	527.33	0.56	0.25
Ca	3.690	345.95	0.62	0.19
			100.00	100.00



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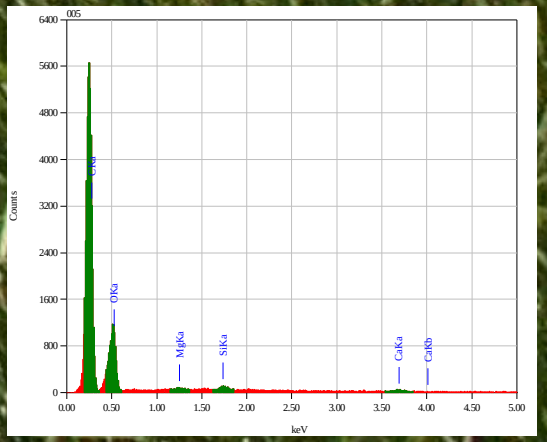
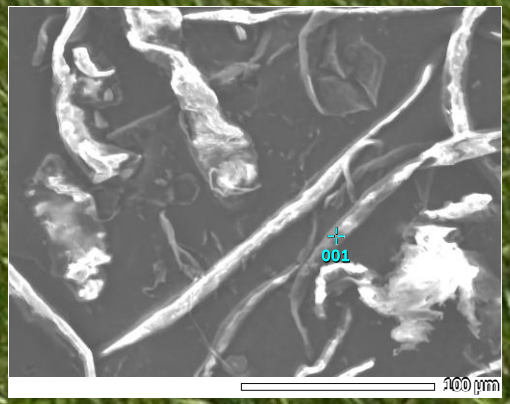


SEM and EDS Studies of Unbleached Industrial Grass Cellulose Fibres, Cooked in Pilot Device TCF Bleached and Grinded 5 min. in PFI Mill

TCF5 (a)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	7767.49	91.81	93.72
O	0.525	1793.20	8.19	6.28
			100.00	100.00



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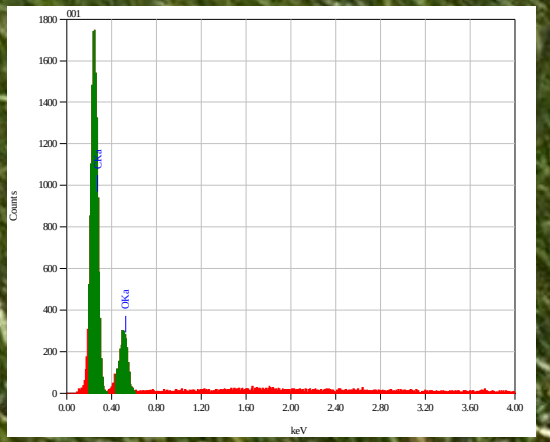
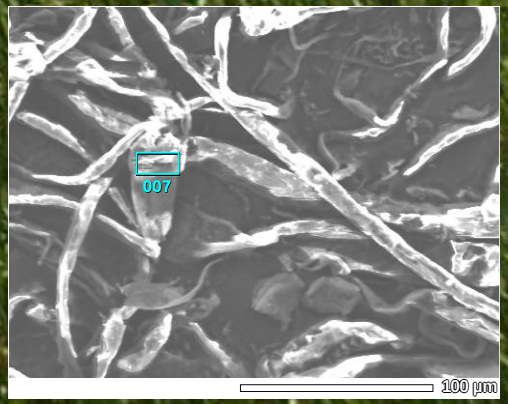


TCF5 (b)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	15195.43	90.14	92.41
O	0.525	4299.66	9.86	7.59
			100.00	100.00



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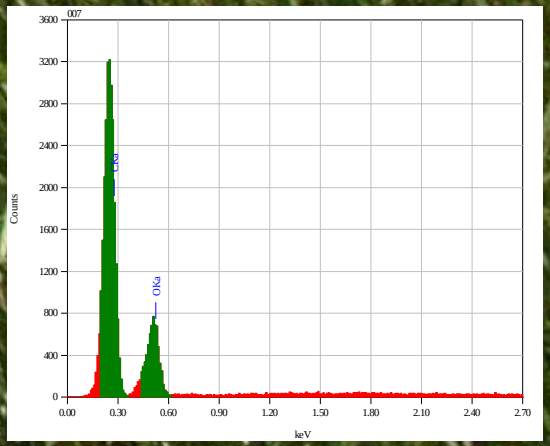
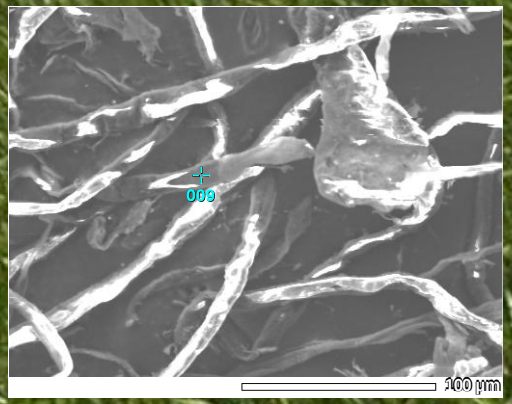


SEM and EDS Studie of Unbleached Industrial Grass Cellulose Fibres, Cooked in Pilot Device ECF Bleached and Grinded 5 min. in PFI Mill

ECF (a)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	6258.61	87.47	90.87
O	0.525	2048.85	11.07	8.63
Si	1.739	70.25	0.31	0.14
Ca	3.690	155.79	1.15	0.36
			100.00	100.00



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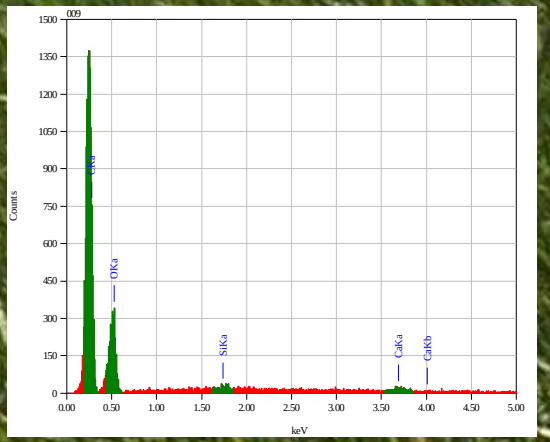
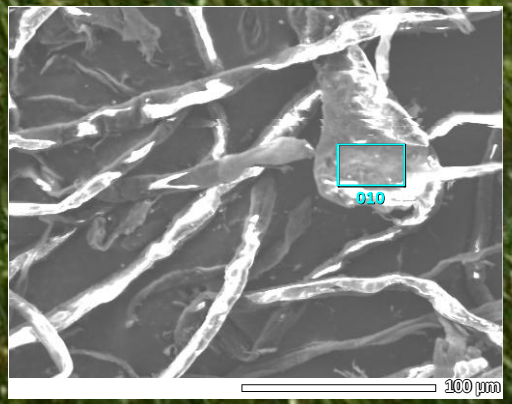


ECF (b)

Chemical Elements	Sing keV	Number of impulses	Ratio	
			mass%	atom%
C	0.277	15060.92	81.41	85.98
O	0.525	8134.10	17.00	13.48
Si	1.739	152.68	0.26	0.12
Ca	3.690	468.26	1.34	0.42
			100.00	100.00



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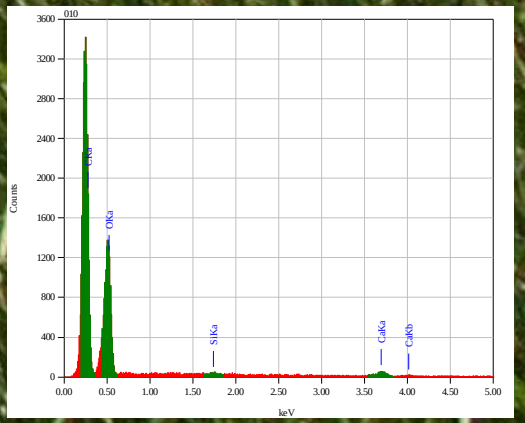


Summerising results of EDS studies (Gd. for 0, 5, 10, minutes)

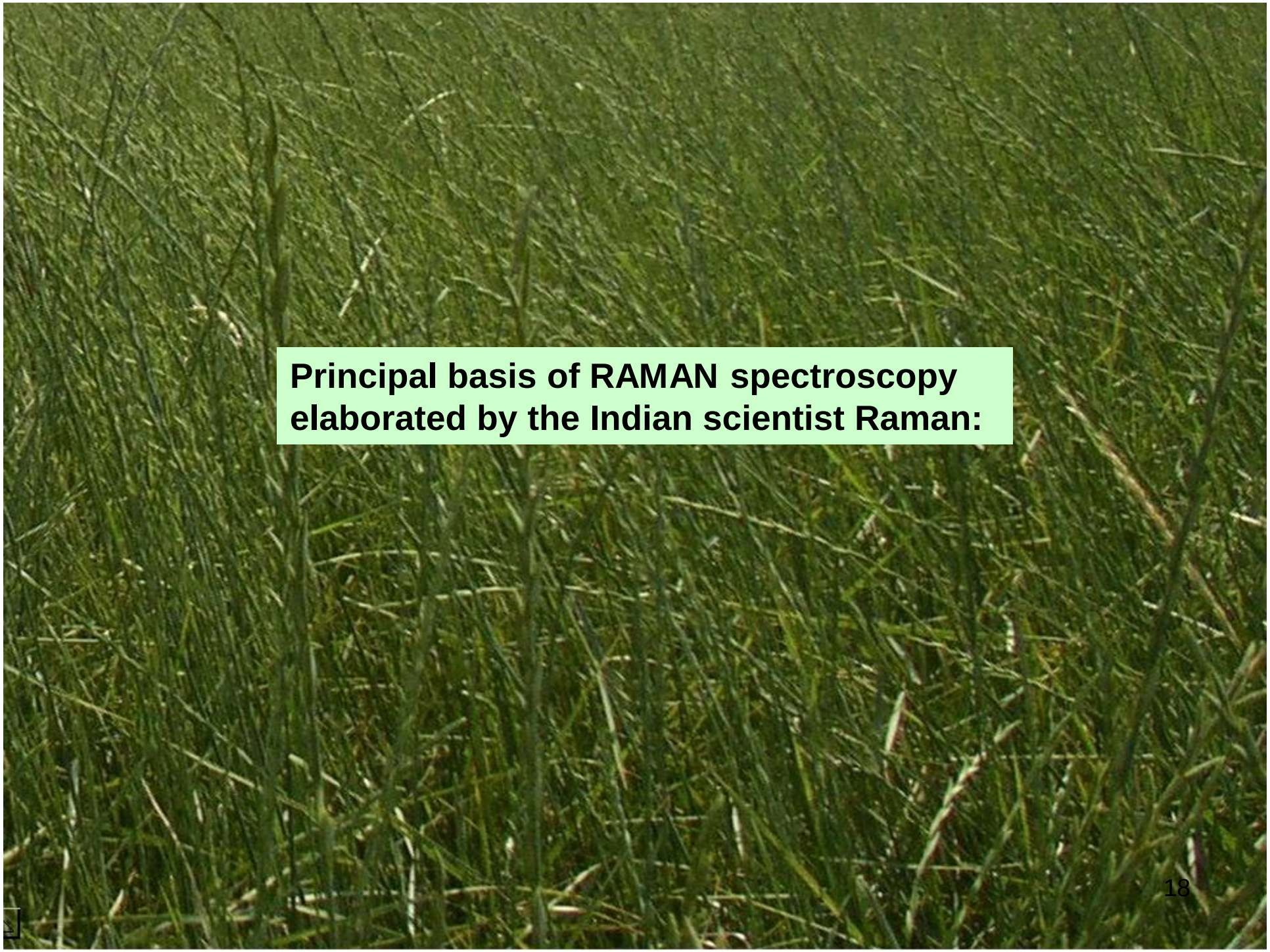
Sample code	Space of sampling	Characteristics				
		Chemical elements	Sign (keV)	Number of impulses	Ratio	
					Mass g%	atom%
K0	a	C	0.277	45435.98	97.53	98.13
		O	0.525	2979.95	2.47	1.87
					100.00	100.00
	b	C	0.277	38080.23	92.72	95.73
		O	0.525	4594.76	4.33	3.35
		Ca	3.690	2295.43	2.95	0.91
					100.00	100.00
K5	a	C	0.277	29748.44	90.03	92.66
		O	0.525	7627.44	8.92	6.90
		Mg	1.253	345.13	0.30	0.15
		Si	1.739	463.19	0.44	0.19
		Ca	3.690	188.87	0.30	0.09
					100.00	100.00
	b	C	0.277	26456.09	89.87	92.69
		O	0.525	6638.43	8.72	6.75
		Mg	1.253	234.00	0.23	0.12
		Si	1.739	527.33	0.56	0.25
		Ca	3.690	345.95	0.62	0.19
					100.00	100.00
K10	a	C	0.277	17571.52	89.61	93.36
		O	0.525	3169.28	6.25	4.89
		Mg	1.253	594.45	0.88	0.45
		Si	1.739	1313.11	2.10	0.93
		Ca	3.690	430.76	1.16	0.36
					100.00	100.00
	b	C	0.277	16118.69	86.81	90.35
		O	0.525	5569.28	11.60	9.06
		Mg	1.253	93.61	0.15	0.08
		Si	1.739	298.22	0.50	0.22
		Ca	3.690	333.36	0.95	0.30
					100.00	100.00

Summerising results of EDS studies (TCF, Gd. for 0, 5, 10, minutes)

Sample code	Space of sampling	Characteristics				
		Chemical elements	Sign (keV)	Number of impulses	Ratio	
					Mass g%	atom%
TCF0	a	C	0.277	26558.06	96.10	97.04
		O	0.525	2789.46	3.90	2.96
					100.00	100.00
	b	C	0.277	22615.06	85.13	88.41
		O	0.525	10218.97	14.87	11.59
					100.00	100.00
TCF5	a	C	0.277	7767.49	91.81	93.72
		O	0.525	1793.20	8.19	6.28
					100.00	100.00
	b	C	0.277	15195.43	90.14	92.41
		O	0.525	4299.66	9.86	7.59
					100.00	100.00
TCF10	a	C	0.277	13833.54	94.69	95.96
		O	0.525	2004.78	5.31	4.04
					100.00	100.00
	b	C	0.277	14015.18	84.95	88.26
		O	0.525	6422.31	15.05	11.74
					100.00	100.00

Summerising results of EDS studies (ECF, Gd. for 0, 5, 10, minutes)

Sample code	Space of sampling	Characteristics				
		Chemical elements	Sign (keV)	Number of impulses	Ratio	
					Mass g%	atom%
ECF0	a	C	0.277	16451.36	89.39	92.33
		O	0.525	4364.21	9.17	7.11
		Mg	1.253	153.50	0.24	0.12
		Si	1.739	288.31	0.49	0.22
		Ca	3.690	249.23	0.72	0.22
					100.00	100.00
	b	C	0.277	4677.02	81.85	86.45
		O	0.525	2392.82	16.19	12.84
		Si	1.739	116.86	0.64	0.29
		Ca	3.690	143.01	1.32	0.42
					100.00	100.00
ECF5	a	C	0.277	6258.61	87.47	90.87
		O	0.525	2048.85	11.07	8.63
		Si	1.739	70.25	0.31	0.14
		Ca	3.690	155.79	1.15	0.36
					100.00	100.00
	b	C	0.277	15060.92	81.41	85.98
		O	0.525	8134.10	17.00	13.48
		Si	1.739	152.68	0.26	0.12
		Ca	3.690	468.26	1.34	0.42
					100.00	100.00
ECF10	a	C	0.277	13357.54	90.53	93.21
		O	0.525	3050.65	7.99	6.18
		Mg	1.253	169.37	0.33	0.17
		Si	1.739	317.16	0.67	0.30
		Ca	3.690	132.39	0.47	0.15
					100.00	100.00
	b	C	0.277	4174.71	81.22	86.13
		O	0.525	2123.93	15.97	12.72
		Mg	1.253	61.87	0.35	0.18
		Si	1.739	223.71	1.36	0.62
		Ca	3.690	106.82	1.10	0.35
					100.00	100.00



Principal basis of RAMAN spectroscopy elaborated by the Indian scientist Raman:

IR and Raman spectroscopy

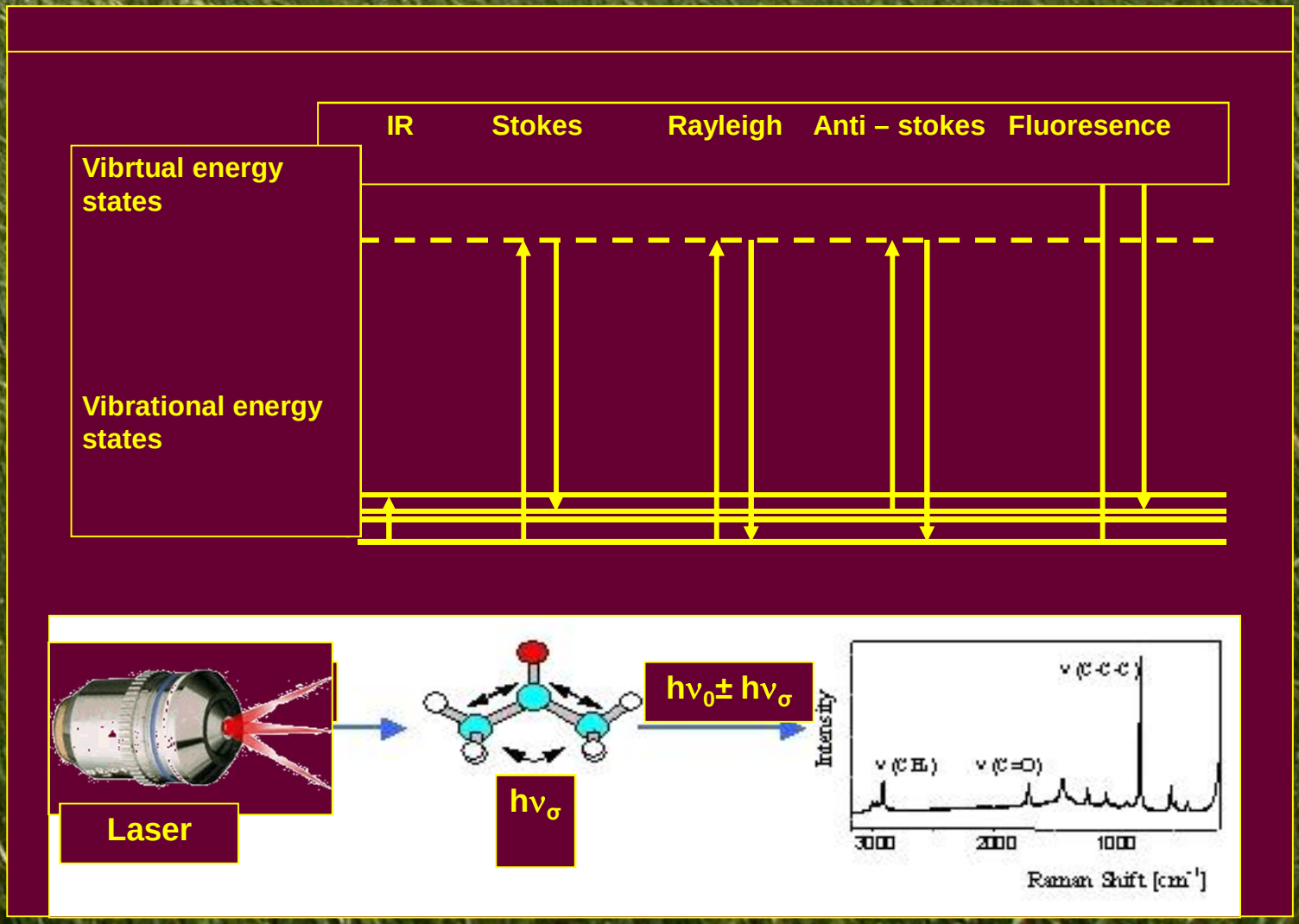
Vibration based methods of spectroscopy

Raman	IR

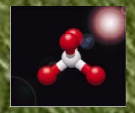
Energy transit of vibrations states of molecules
Information about the Chemical structure

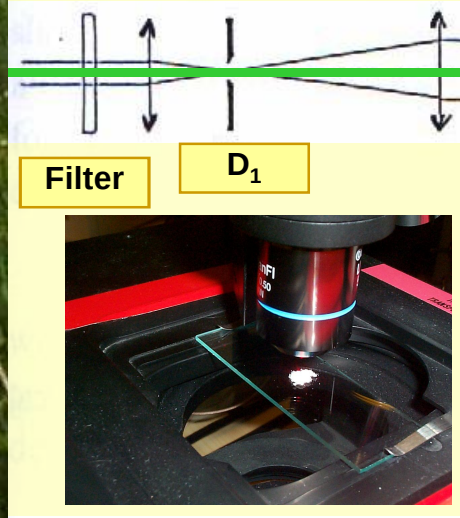
Polarisability **Monochromatic light** **Scattering**	**Dipolmoment** **Polichrometic light** **Absorbance**

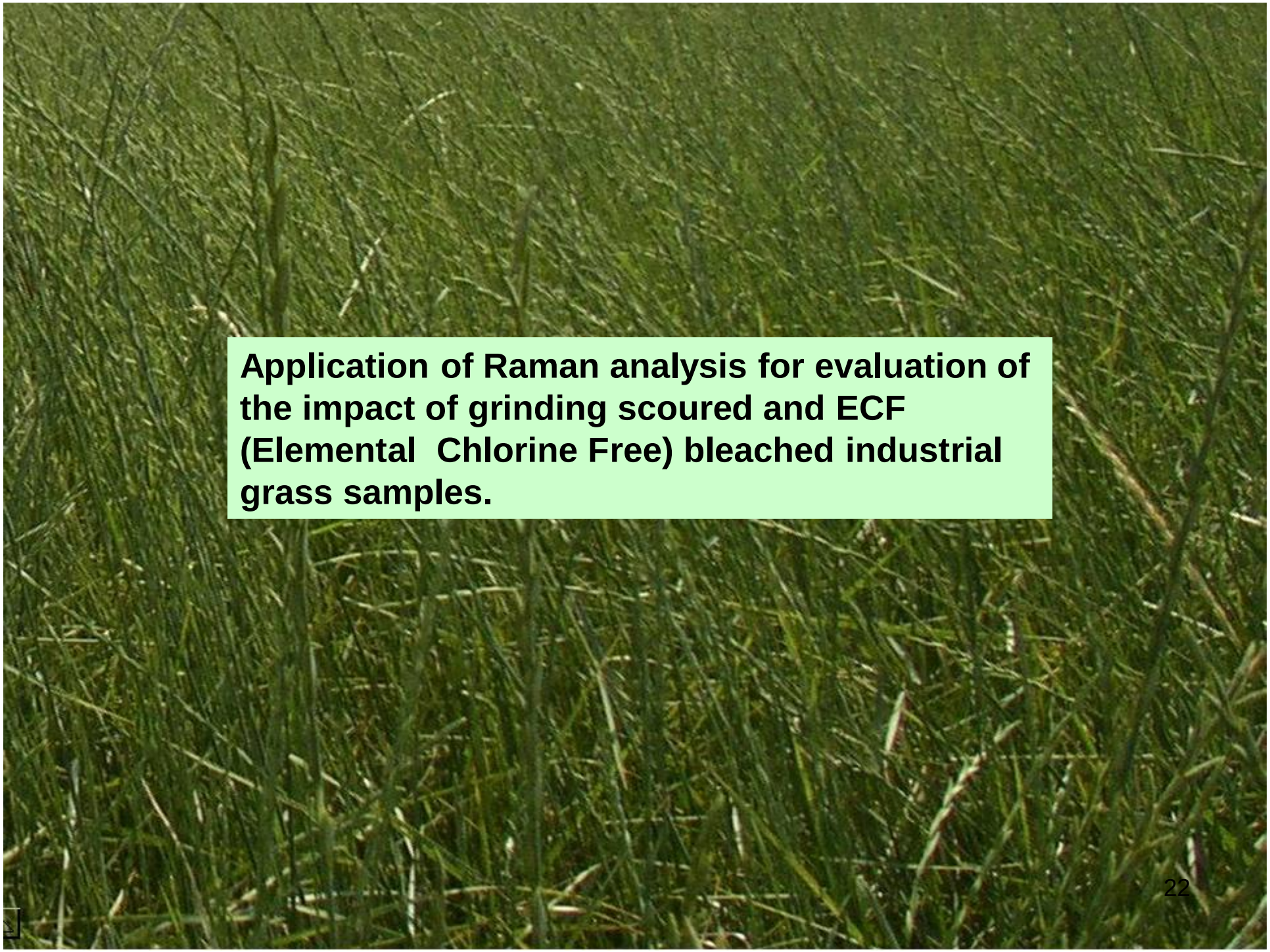
Raman spectroscopy



Raman equipment

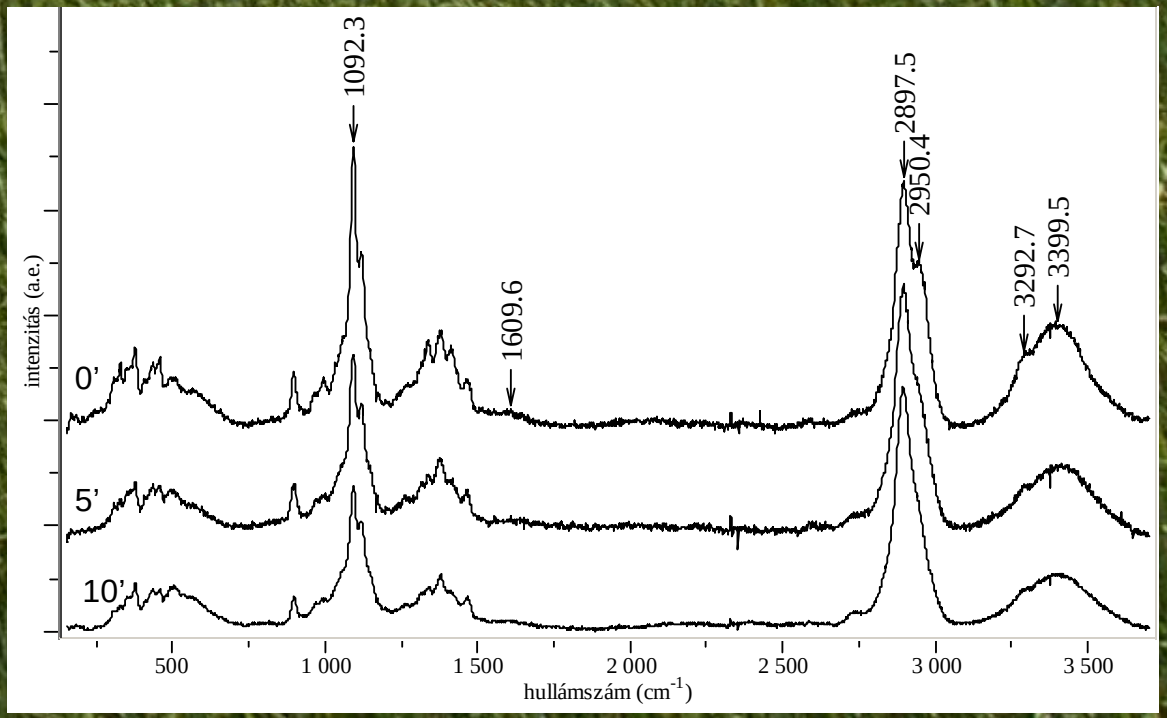






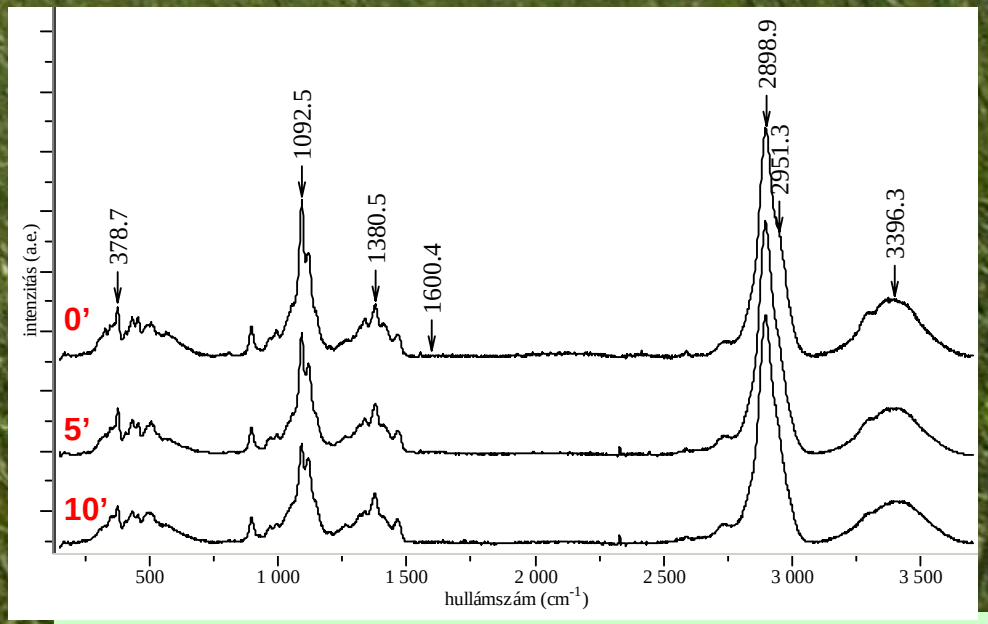
Application of Raman analysis for evaluation of the impact of grinding scoured and ECF (Elemental Chlorine Free) bleached industrial grass samples.

Lignin content was represented by the band at 1610 cm^{-1}. The lignin content of the system drastically decreased during bleaching but the remaining small amount has not been influenced by the duration of the grinding.

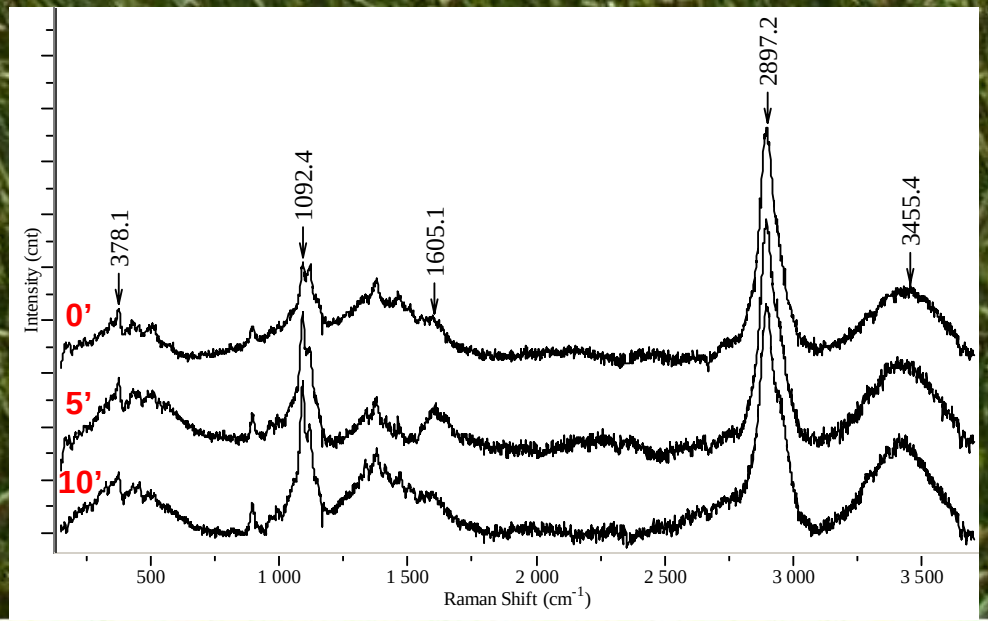


Impact of grinding, scoured and ECF (Elemental Chlorine Free) bleached industrial grass samples.

The degree of polymerisation of cellulose generally decreased after bleaching. Grinding generated further decrease in the DP the longer was the grinding the intensive was the loss in DP.
The bleaching generally increased the proportion of the crystalline regions against the amorfous ones where us the grinding had an opposite impact

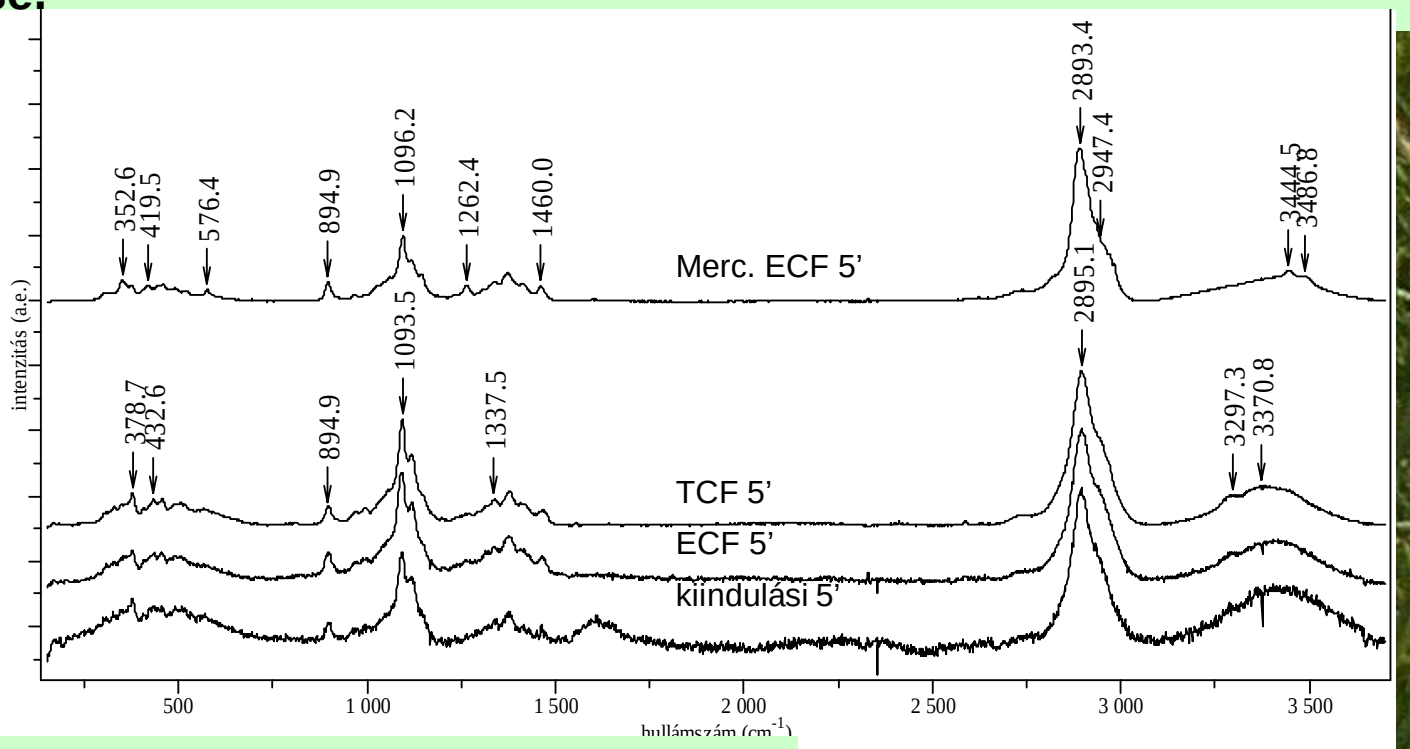


Impact of grinding, TCF bleached industrial grass samples.



Impact of grinding, unbleached industrial grass samples.

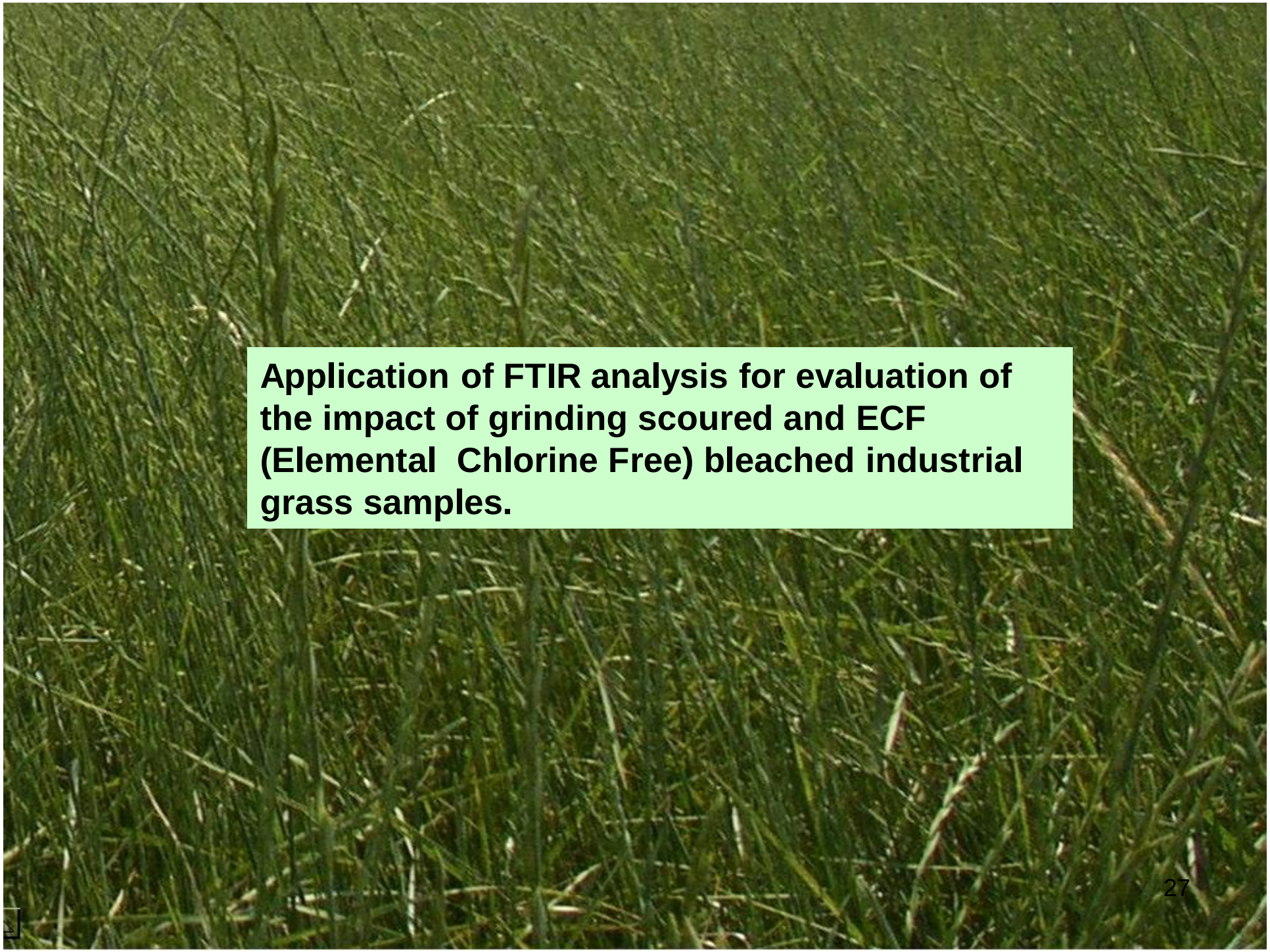
It is well known that scouring and bleaching of native cellulose did not change the crystalline structure (cellulose I) of the native cellulose. We have observed by Raman method that cooking, bleaching and grinding of industrial grass did not generate any changes in its cellulose I crystalline structures. After treating the mentioned fibres with mercerising strong sodium hydroxide solution (25%) the change of cellulose I to cellulose II structure proved to be dominant.
It is possible to declare that the RAMAN Spectroscopy can also be applied to distinguish between I and II crystalline structures of cellulose.



Comparing the differently treated samples (5 min ground) with the strong NaOH (25%) treated one

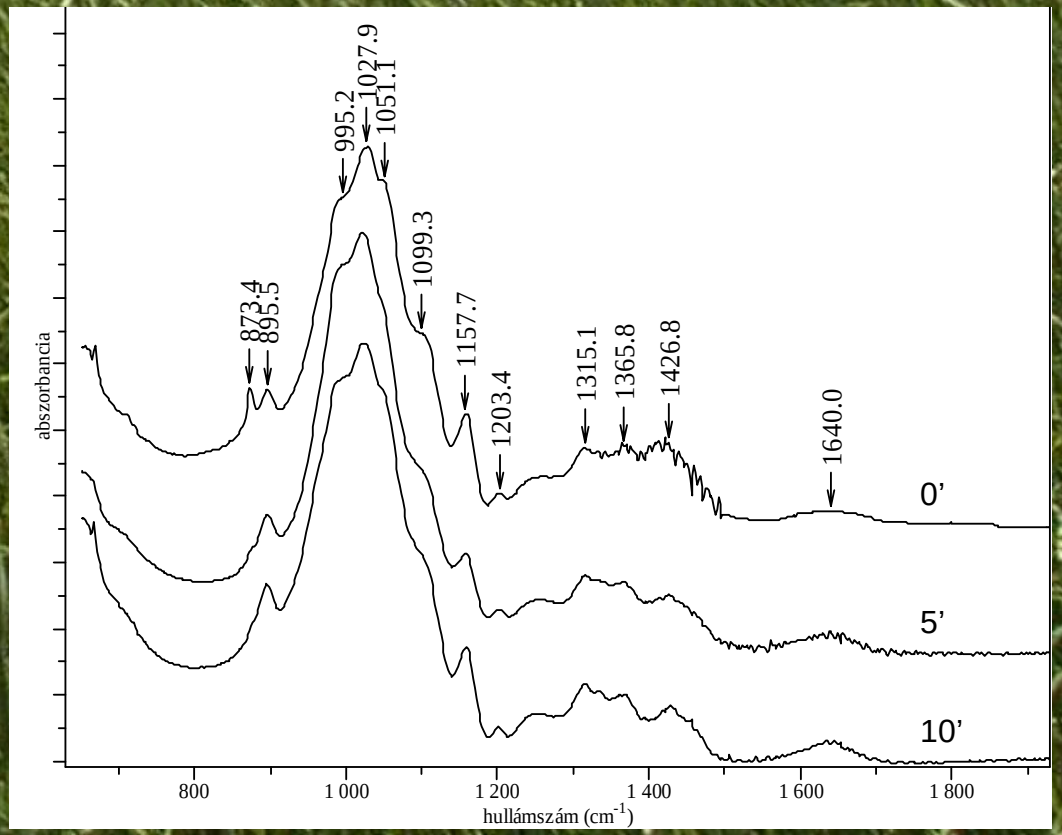
Fourier Transformed Infra Red (FTIR) Attanued Total Reflection (ATR) spectroscopy

Attenuated total reflectance (ATR) is a sampling technique used in conjunction with *infrared spectroscopy* samples to be examined directly in the *solid*, *liquid* or *gas* state without further preparation. After irradiation the samples with light undergoes multiple internal reflections in the crystal (e.g. diamond) of high refractive index. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres. Circular surface of a diameter of 100 micro metre can be analysed and the studied depth was that of the wave length of the IR light (1000–2000 nm). The investigation has been performed with an IlluminatIR type FTIR spectroscope equipped with a Smiths ATR 36×IR objective and with a MCT (mercury–tellur) - detector cooled by liquid nitrogen with a spectral resolution of 4 cm–1. 5 shots have been taken from the samples in the region of 650-4000 cm^{-1}. Each shot took 10 minutes.



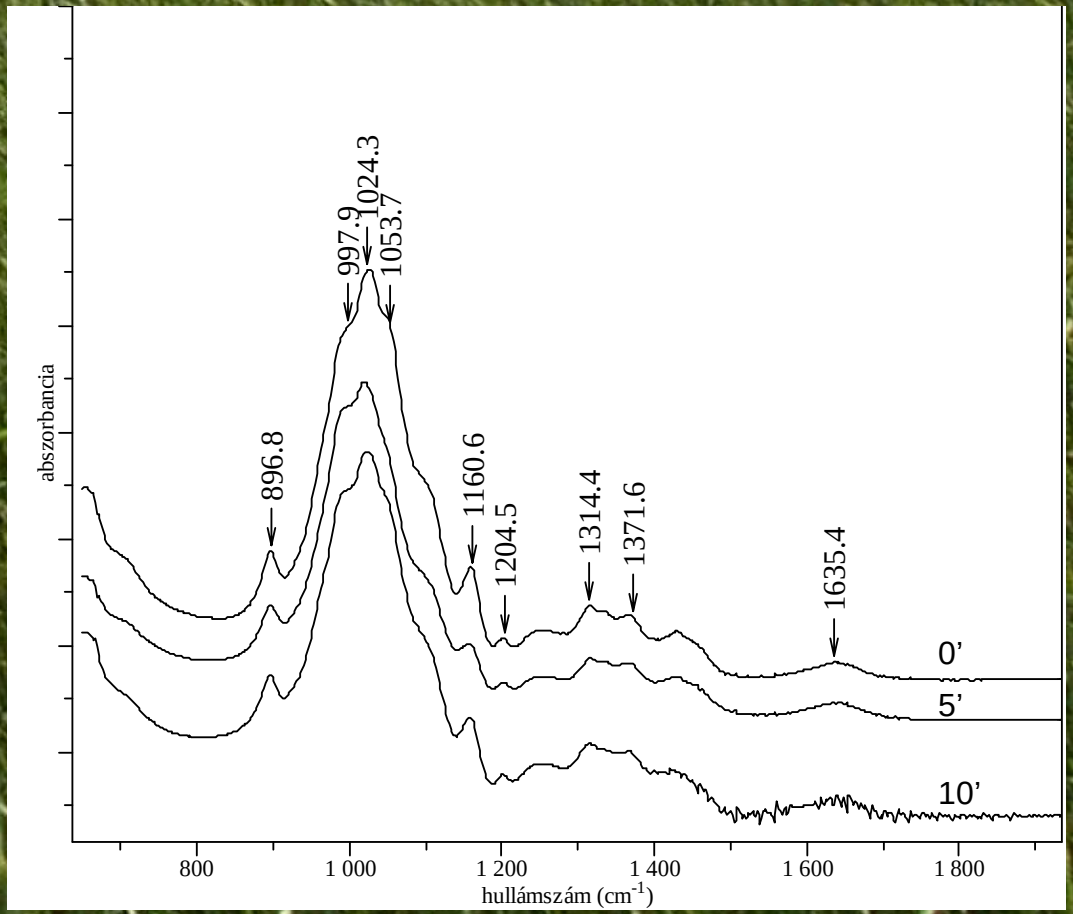
Application of FTIR analysis for evaluation of the impact of grinding scoured and ECF (Elemental Chlorine Free) bleached industrial grass samples.

Not systematic relatively small changes cloud be observed on the studied samples in the region from 1000 through 1050 cm^{-1}. At samples bleached Elemental Chlorine Free the peak increased at 1315 cm^{-1} with the increase in duration of grinding time whereas it decreased at 1427 cm^{-1} with it.



Impact of grinding, ECF bleached industrial grass samples.

The explication of the contradictory changes is at the moment impossible. The IR spectroscopy is more sensitive than the Raman one for this study consequently the band characteristic for lignin is more significant.



Impact of grinding, TCF bleached industrial grass samples.

To distinguish between the cellulose I and cellulose II, respectively between native and sodium hydroxide treated cellulose, the applied IR is not sufficiently reliable.

The lignin content of the studied samples could how ever been sensitively distinguished by IR spectroscopy based upon the integrated values observed between 1525–1745 cm^{-1}.

On the base of the integrated values can be conclude that the least lignin content was in the sample not grinded and totally chlorine free bleached sample.

Sample	Lignin content
Unbleached (K0)	10.00
Unbleached (K5)	13.89
Unbleached (K10)	10.50
TCF0	7.08
TCF5	7.70
TCF10	8.36
ECF0	7.55
ECF5	8.19
ECF10	7.57
25% NaOH treated ECF5	8.39

Conclusions:

Valuable information could be obtained about the structure and contaminants of cellulosic fibres used in the paper industry by up to date, destruction free, analytical procedures requiring tiny amount of materials. However, the sampling has to be made very carefully. To arrive reliable result necessary number of samples has to be taken from different arias of the fibres.


Thank you for your kind attention