

REFLECTANCE UV-VIS AND UV RESONANCE RAMAN SPECTROSCOPY IN CHARACTERIZATION OF KRAFT PULPS

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Reflectance UV-Vis spectroscopy and UV resonance Raman (UVR) spectroscopy are both nondestructive techniques that are applicable to study trace concentrations of lignin *in-situ*. In this study, unbleached and bleached softwood kraft pulps were analyzed by reflectance UV-Vis (k/s) and UVR spectroscopy to follow lignin and hexenuronic acid (HexA) contents and structural changes in residual lignin. The height of the lignin band in the UV-Vis spectra (280 nm) correlated well with the lignin band in the UVR spectra (1605 cm⁻¹) for semi- or fully-bleached pulps. However, the correlation was much weaker for unbleached pulps. Also the results for hexenuronic acid content by UV-Vis (240 nm) and UVR (1658 cm⁻¹) methods correlated well for most of the pulps, but for unbleached or peroxide-bleached samples the interference from other structures affecting these bands was obvious.

Keywords: Bleaching; Kraft pulps; UV resonance Raman (UVR) spectroscopy; UV-Vis spectroscopy

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INTRODUCTION

In chemical pulping and bleaching, the target is to remove all the lignin in wood fibers. Despite the extensive research carried out on pulp bleaching for many years, the chemistry of bleaching is still far from being fully understood. The analysis of lignin chemistry in bleaching is challenging, because the lignin content in the bleached pulps is often less than 2% on weight. For such a low lignin content, the accuracy of the most commonly applied residual lignin determination methods (such as Klason lignin content) is relatively poor (Jääskeläinen et al. 2005). In addition, most of the analytical and spectroscopic techniques used to characterize lignocellulosic materials also require separation and isolation of components in ways that disrupt the studied structures, and the isolation yields are often low and impure (Tamminen et al. 2004).

There are only few wet-chemical and spectroscopic techniques available to study the structure of lignin directly in bleached pulps. Reflectance UV-Vis spectroscopy and UV resonance Raman (UVR) spectroscopy are both nondestructive techniques that are applicable to study lignin *in situ*, even if the lignin content is very low.

In pulp research, UV-Vis reflectance spectroscopy has traditionally been used to investigate the formation of pulp chromophores during ageing, as has been described in the review by Schmidt and Heitner (1999). The method has also been shown to have great potential for monitoring other pulp components in pulp bleaching. Changes induced by bleaching in the structures of lignin, hexenuronic acid (HexA), and carbonyl contents

of pulps can be studied using UV-Vis reflectance spectroscopy (Ragnar 2001; Liitiä et al. 2004). By converting reflectance spectra to absorbance (k/s) spectra using the Kubelka-Munk equation, it is possible to follow changes in the content of these UV-active pulp components (Liitiä et al. 2004).

Resonance Raman spectroscopy has long been used for studying organic materials (Brahma et al. 1983). In recent years, the technique has been used in lignin studies, as it gives relatively strong responses to aromatic structures (Halttunen 2001). The problem of the laser-induced fluorescence that has made the analysis of visible Raman spectroscopy very difficult (Atalla et al. 1992) does not interfere in UV resonance Raman spectroscopy. In addition, the UV light used in excitation enhances the signals arising from aromatic and unsaturated structures by several orders of magnitude. Thus UVRR spectroscopy reveals information even on small amounts of aromatic structures, and indications on structures like ethylenic units can be obtained (Halttunen 2001; Saariaho 2004).

UV-Vis, UVRR, and FTIR spectroscopies have been applied to investigate the changes in birch wood during peroxide bleaching (Mononen et al. 2005). Based on these spectroscopic analyses, oxidation of lignin, possibly via aromatic ring cleavage, was observed in wood samples *in-situ*. However, the sensitivity of FTIR spectroscopy is limited, and hence it is not applicable to investigate lignin reactions in pulp bleaching *in-situ*. On the other hand, UV-Vis and UVRR spectroscopy can be utilized to study lignin even in trace concentrations, and both spectroscopic techniques could also with certain limitations be used to determine free phenolic hydroxyl groups directly in pulps and without any need of lignin isolation (Liitiä and Tamminen 2007; Lähdetie 2007).

In this study, softwood kraft pulps were cooked to different kappa levels under various conditions. One of the pulps was also bleached with varying chemical charges of chlorine dioxide, ozone and peroxide, and with different elemental chlorine-free (ECF) and totally chlorine-free (TCF) sequences. The pulps were analyzed by both reflectance UV-Vis and UVRR spectroscopic methods to get a detailed understanding of bleaching chemistry and applicability of the spectroscopic methods for bleachability studies, instead of the traditional more laborious wet chemical methods. In addition, these techniques were compared in order to figure out more detailed information on the sample structure. Combining these spectroscopic methods provided a unique starting point to identify the reactions taking place in pulp bleaching.

EXPERIMENTAL

Pulps

Four unbleached softwood (SW) kraft pulps were cooked in the laboratory to different kappa numbers (51.7, 33.2, 27.9, and 22.2) as explained in detail by Enqvist (2006). Two profiled alkali-cooked (PA) pine kraft pulps (kappa numbers 34.6 and 17.3) and one low sulfidity (LS) pulp (kappa number 27.4) were produced as explained in detail elsewhere (Liitiä et al. 2005).

The profiled alkalinity kraft pulp (PA) was oxygen-delignified (O) to the kappa level 18, and then bleached using three different bleaching stages chlorine dioxide (D) and ozone (Z) followed by alkaline extraction (E) or alkaline peroxide (P) after a

chelation stage (Q). Three different chemical charges were utilized for chlorine dioxide, ozone, and peroxide bleaching (Liitiä et al. 2004, 2005). Three chlorine-dioxide bleached pulps were also produced without preceding oxygen delignification (PA-DE).

Fully-bleached pulps were prepared from the profiled alkalinity pulps using ODEDD, ODEDP, OQPPaaP, and OQPZP sequences (Liitiä et al. 2005). The target brightness of ODEDD and ODEDP-bleached pulps was 88-89% ISO, and 83-84% ISO for the OQPPaaP and OQPZP pulps.

Laboratory handsheets (60 g/m² for SW kraft pulps and 20 g/m² for all other pulps) were prepared from each pulp sample using the method described in the international standard ISO 5269-1.

Chemical Analyses

Kappa number determination was done using the method described in the SCAN 1:00 standard. Hexenuronic acid content determination was done using mild, selective acid hydrolysis followed by UV detection (HUT method, Tenkanen 1999) or by extensive enzymatic hydrolysis followed by HPAEC/PAD detection (VTT method, Tenkanen 1999). HexA corrected lignin kappa was calculated according to Li and Gellerstedt (1997). Pulp carbonyl content was determined using hydroxyl amine method (Neimo and Sihtola 1963).

UV-Vis Reflectance Spectroscopy

The UV-Vis reflectance spectra of the pulp handsheets were recorded on a Perkin Elmer Lambda 900 spectrometer (Perkin Elmer, Boston) equipped with an integrating sphere. The measurements took place at 50% relative humidity. The wavelength range was 200-800 nm. The spectral data was processed with UV WinLab software. The reflectance values were recorded against black (R_0) and white (R_{wb}) backings, and the infinite reflectance (R_∞) was calculated from these spectra according to equation [1] (Schmidt and Heitner 1999; Liitiä et al. 2004), where R_w is the reflectance of the white backing.

$$R_\infty + \frac{1}{R_\infty} = \frac{R_0 - R_{wb} + R_w}{R_w R_0} + R_{wb} \quad [1]$$

The infinite reflectance spectra were converted into k/s curves using the Kubelka-Munk equation [2] (Schmidt and Heitner 1999; Liitiä et al. 2004).

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad [2]$$

UV Resonance Raman (UVR) Spectroscopy

The UVR spectra were collected with a Renishaw 1000 UV Raman spectrometer equipped with a Leica DMLM microscope and an Innova 90C FreD frequency-doubled Ar⁺ ion laser (Coherent Inc., California). The excitation wavelength applied was 244 nm. The output power of the laser was adjusted to 10 mW, and the laser

beam was attenuated with a neutral density filter with 50% transmittance. After that, the beam was reflected by mirrors to a dielectric edge filter. The beam was further directed to the microscope equipped with a deep UV LMU-40X objective. Due to losses in the light path, the final power at the sample level was ca. 2 mW. The backscattered Raman light was passed through the microscope to the edge filters and was further focused on a 30 μm slit by an additional lens. The transmitted Raman beam was reflected by prism mirrors to a diffraction grating of 3600 grooves/mm, and finally to the UV-coated, deep-depletion charge-coupled device (CCD) camera. The spectral data from the CCD camera was processed with GRAMS/32 AI software (Galactic Industries Corporation, New Hampshire). The spectral range was 500-2000 cm^{-1} , and the resolution was ca. 6 cm^{-1} .

The surfaces of the pulp handsheets were smoothed by pressing the sheets between two metal plates (100 kN, 15s) prior to their analyses. Each sample was measured from three different positions for 30 s and spinning the sample simultaneously. That way no changes due to UV light irradiation were observed, while it was taken into account that a longer UV irradiation could cause significant changes in the sample (Pandey and Vuorinen 2008).

All spectra were baseline-corrected, and the band heights were normalized to the cellulose band at 1098 cm^{-1} (= 1 a.u.). The baseline correction was performed by calculating the average intensity at 800-900 cm^{-1} and 1800-2000 cm^{-1} . These regions were free from Raman bands and hence represented only the background. A linear function was fitted between the calculated average values, and thus this background was set to zero. In each sample, the slope of the baseline function was close to zero, and hence no distortion of the bands occurred. Due to overlapping of the aromatic and unsaturated bands in the UVRR spectra, the band height determination of the UVRR bands was performed from deconvoluted spectra. Deconvolution was performed for the spectral range of 1500-1800 cm^{-1} by using two Lorentzian functions, as illustrated in Fig. 1. The best curve-fittings (R^2 values 0.988-0.998) were obtained by least-squares method, and the band maxima of the fitted lines were at $1605 \pm 2 \text{ cm}^{-1}$ and $1658 \pm 2 \text{ cm}^{-1}$.

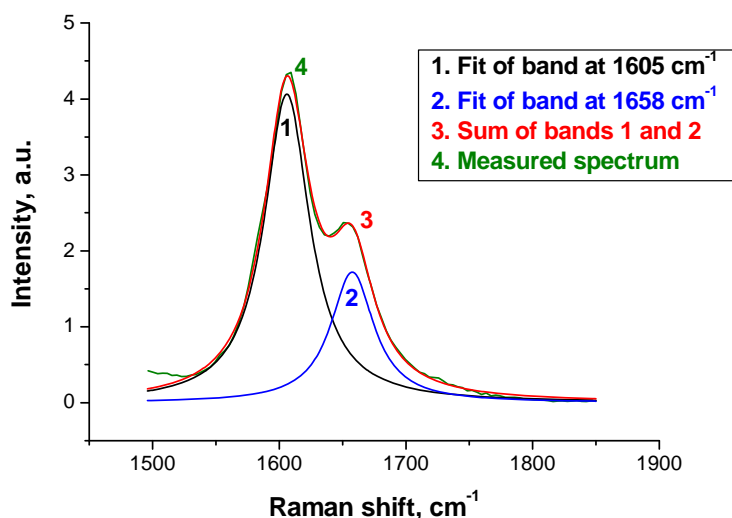


Fig. 1. Least-square fit of Lorentzian curves in the spectral range of 1500-1700 cm^{-1} for the PA-OEDP sample.

RESULTS AND DISCUSSION

Kraft Pulps

The residual lignin structures of eight different softwood (SW) kraft pulps were studied by UV resonance Raman (UVR) and UV-Vis spectroscopic methods, which both can be applied to pulps without the need to isolate the lignin. Four kraft pulps were cooked by the conventional kraft pulping method to kappa numbers 22.2-51.7. In addition, two profiled alkali-cooked pulps (kappa numbers 34.6 and 17.3), one low-sulfidity pulp (kappa number 27.4) and one profiled alkali-cooked pulp after oxygen delignification (kappa number 18.0), were studied to observe the changes that altering pulping conditions and the extent of delignification induce in residual lignin structure and HexA content. The lignin and HexA contents determined by traditional methods are given in Table 1.

Table 1. Kappa Numbers, Hexenuronic Acid Group and Lignin Contents of Unbleached Softwood Kraft Pulps (Enqvist 2006; Liitiä et al. 2004; Liitiä et al. 2005)

Sample code	Kappa number	Hexenuronic acid (mmol/kg)	Lignin Kappa
SW-22	22.2	28.2	19.8
SW-28	27.9	31.3	25.2
SW-33	33.2	32.9	30.4
SW-52	51.7	35.2	48.7
LS-30	27.4	15	26.1
PA-30	34.6	42	31
PA-18	17.3	24	15.3
PA-O	18.0	40	14.6

The UVR spectra of the softwood kraft pulps with different delignification degree are shown in Fig. 2. Because the absolute intensity of the spectra depended on the excitation light focus on the sample and the roughness of the sample, the spectra could not be compared without spectral processing. In this case, the carbohydrate (cellulose) content of these samples was presumed to remain nearly constant, and therefore the UVR spectra were normalized to the glycosidic COC stretching band at 1098 cm^{-1} . In this way the comparison of the UVR spectra of different samples was straightforward, as the height of the bands was directly proportional to the concentration of corresponding structures in the samples. In these unbleached samples, the band at 1098 cm^{-1} was ca. 3-5 times as high as the spectral noise, and hence this normalization was justified.

The UVR spectra of unbleached softwood kraft pulps show clearly the aromatic stretching band at ca. 1605 cm^{-1} . The height of this band correlated directly with the lignin kappa number of these pulps (Fig. 2 and Table 1); the higher the kappa number, the higher the aromatic stretching band. Similar correlation has also been observed earlier (Saariho et al. 2003a; Jääskeläinen et al. 2005).

The shoulder at ca. 1658 cm^{-1} arises from the unsaturated and carbonyl structures in the samples (Halttunen et al. 2001). The intensity of this band was clearly lowest for the pulp cooked to kappa 22.2, while it was nearly constant for other conventionally cooked kraft pulps. For these pulps, the main origin of this band is hexenuronic acid,

although other structures, such as ethylenic and carbonyl structures in lignin or extractives, may influence in this band. Based on chemical analyses, the hexenuronic acid group content of these pulps decreased by ca. 25% during further cooking to kappa 22.2 (Table 1), which explains most of the decrease in the C=C stretching band.

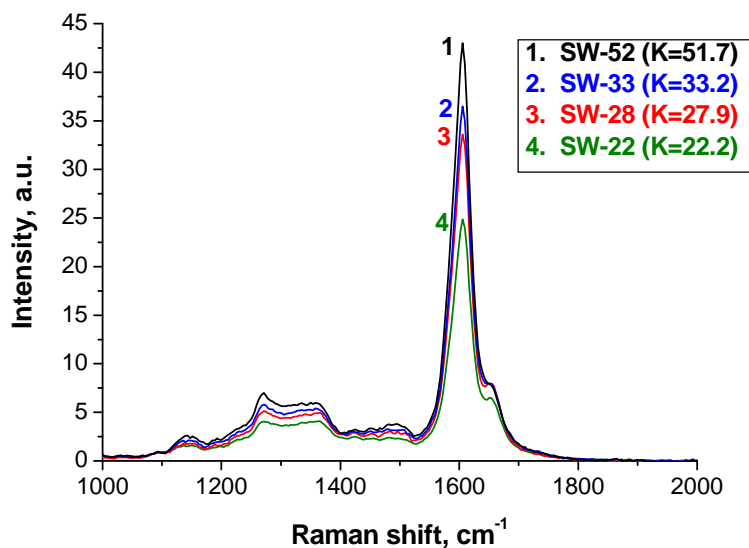


Fig. 2. UVRR spectra of unbleached softwood (SW) kraft pulps with kappa numbers 22-52. The heights of the spectra were normalized to the COC stretching band at 1098 cm^{-1} .

The numerous bands within the range 1500-1100 cm^{-1} are overlapping, and many lignin-originating bands in this range have been identified in model compound experiments (Saariaho et al. 2003b). Even if the exact assignment of each band is not possible, it can be observed that the intensity of these bands did not decrease uniformly. For example, the bands at ca. 1605 and 1270 cm^{-1} decreased more than 40%, while those at 1370 and 1429 cm^{-1} decreased by only ca. 30%. It is therefore obvious that the residual lignin at the end of cooking contained more structures that give rise to the bands at 1370 and 1429 cm^{-1} than the residual lignin after only a moderate cooking time. Based on model compound spectra (Saariaho et al. 2005) bands at these positions can be observed in C=C conjugated aromatic structures such as stilbenes and C5 condensed structures, respectively. Formation of conjugated structures affecting lignin color has been reported to increase with prolonged cooking time (Litiä et al. 2005). The direct correlation of the band assignment of model compounds to lignin spectra is not entirely justified and would need further evidence. However, these results suggest that in addition to the decrease on lignin content there were also structural changes in residual lignin.

The UV-Vis reflectance spectra were converted to absorption spectra to improve the assignment of light absorbing species in the sample. The light scattering properties were assumed to remain constant in all the samples, and hence the ratio of light absorption coefficient (k) to scattering coefficient (s) could be used without resolving k and s separately.

The UV-Vis spectra (k/s) of unbleached softwood kraft pulps in Fig. 3 show distinct changes during pulping. The height of the aromatic absorption band at ca. 280-290 nm decreased with the decreasing lignin content of the pulps. This was expected, since the band at 280 nm has been assigned to originate from residual lignin in the pulp (Schmidt and Heitner 1999). In addition to the decrease in the band intensity, there was a small shift in the band maximum to lower wavenumbers.

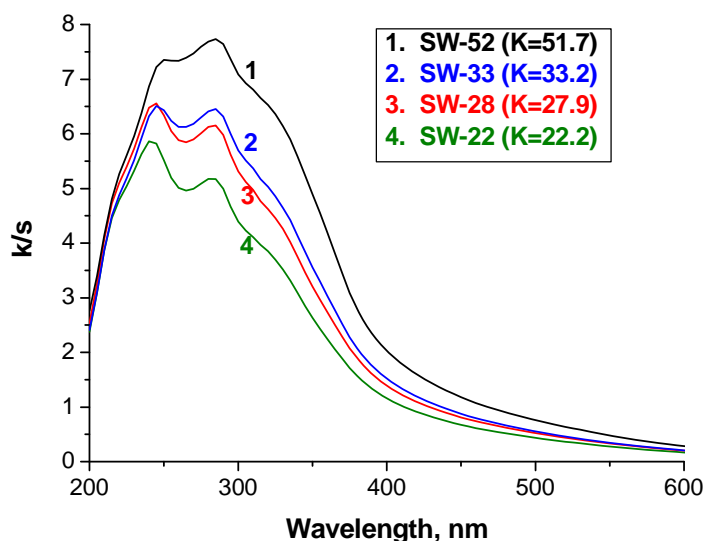


Fig. 3. UV-Vis spectra of unbleached softwood (SW) kraft pulps with kappa numbers 22-52. The reflectance spectra were converted into k/s spectra.

The height of the band at ca. 240 nm, which has been assigned to hexenuronic acid groups (Ragnar 2001; Liitiä et al. 2004) correlates with the hexenuronic acid group content in the samples (Fig. 3 and Table 1). However, the overlapping lignin signals also influence the intensity of the signal assigned to HexA, and various methods to exclude the effect of delignification on HexA removal in UV-Vis spectra has been suggested (Ragnar 2001; Liitiä et al. 2004).

In addition to changes in the spectral range of ca. 240 and 280 nm, also some decrease in the shoulder at ca. 320 nm can be observed as pulping proceeds (Fig. 3). This band has previously been assigned to the α -carbonyl structures (Liitiä et al. 2004), but also some conjugated structures, e.g. stilbenes are known to affect this range. Unpublished model compound studies of ours also support the assertion that various alkali-induced unidentified structures affecting lignin color can absorb in this spectral range.

The effect of delignification conditions were also studied by UVRR and UV-Vis spectroscopy. For this purpose, two pulps with kappa level 30 were produced either by pulping with low sulphidity (LS) or by using profiled alkali (PA) cooking. In addition, extended delignification to kappa level 18 was studied by extending the profiled alkali cook to 18 or by finishing pulping at kappa level 30 and continuing the delignification with oxygen to kappa level 18. Differences the UVRR and UV-Vis spectra of these pulps are shown in Figs. 4 and 5.

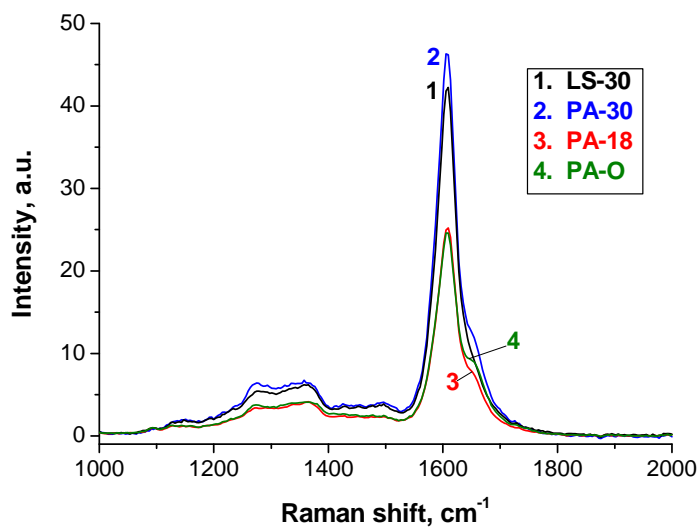


Fig. 4. UVRR spectra of low sulphidity pulp at kappa level 30 (LS-30), profiled alkali-cooked pulps at kappa levels 30 and 18 (PA-30 and PA-18, respectively), and profiled alkali-cooked pulp after oxygen delignification at kappa level 18 (PA-O).

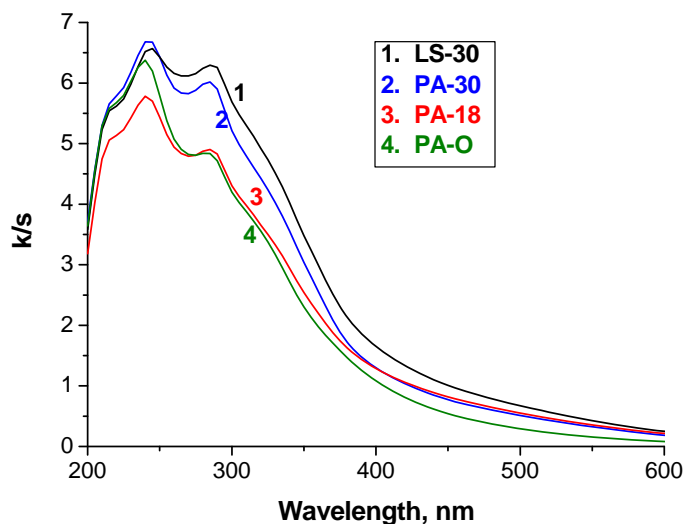


Fig. 5. UV-Vis (k/s) spectra of low sulphidity pulp at kappa level 30 (LS-30), profiled alkali-cooked pulps at kappa levels 30 and 18 (PA-30 and PA-18, respectively), and profiled alkali-cooked pulp after oxygen delignification at kappa level 18 (PA-O).

In Fig. 4 the UVRR spectra the aromatic stretching band at 1605 cm^{-1} was higher for the PA pulp than for the LS pulp, which agrees with the results from the wet chemical analyses (Table 1). Also the unsaturated band at ca. 1658 cm^{-1} was higher for the PA pulp, which also correlates with the hexenuronic acid content of the pulp (Table 1). On the other hand, the results from the UV-Vis spectroscopy were not as straightforward. The band intensity at 280 nm in UV-Vis spectra was higher for LS, which had lower

lignin content as measured by kappa number (Table 1). The higher intensity at 280 nm despite the lower lignin content of the LS pulp was probably affected by different structure and higher absorptivity of LS lignin, which could be seen also as a darker color of LS residual lignin, as reported previously (Liitiä et al. 2005). The difference between LS and PA pulps at wavelength of 240 nm at kappa level 30 was minor, although HexA content of LS pulp was significantly lower (Table 1). The higher absorptivity of LS lignin probably also reduced the differences observed at 240 nm.

Oxygen delignification did not remove hexenuronic acid groups, which can be seen as a higher band intensity at 1658 cm^{-1} in the UVRR spectra and at 240 nm in the UV-Vis spectra when compared to PA-18 cooked to the same kappa level (Table 1 and Figs. 4 and 5). On the other hand, when the same kappa level was reached by extending the cook to kappa level 18, remarkable degradation of hexenuronic acid groups occurred.

Both UVRR and UV-Vis spectra suggested changes in residual lignin structure during kraft pulping. Based on the UVRR spectra, accumulation or formation of some structures containing C=C aromatics exist, while UV-Vis revealed reduction in C=O structures. Based on literature (Froass et al. 1996; Gellerstedt and Lindfors 1984) the residual lignin after a prolonged cooking contains more COOH, more phenolic OH, and more condensed structures than after a short cooking. On the other hand, aliphatic OH and β -O-4 structures are lower in concentration. The increase in the phenolic OH group content of residual lignin in the unbleached kraft pulps with decreasing kappa number was indeed observed earlier (Lähdetie et al. 2007).

Semi-bleached Pulps

Both UVRR and UV-Vis spectroscopy were utilized to characterize semi-bleached softwood kraft pulps. As an example, only the spectra from the chlorine dioxide (DE)-bleached profiled alkalinity (PA) pulp samples are shown in Figs. 6 and 7, and oxygen delignified hydrogen peroxide bleached PA-OQP pulps are shown in Figs. 8 and 9. The ODE and OZE series were, however, also measured, and the results are included in the later discussions and correlations.

For the semi-bleached PA pulps the UV resonance Raman and UV-Vis spectroscopic results correlated very well when the lignin and hexenuronic acid contents were observed. In all cases (PA-DE, PA-ODE, PA-OZE and PA-OQP) the lignin content decreased as the chemical dosage increased, as shown by UV-Vis and UVRR spectra and the wet chemical methods (Table 2). However, PA-OQP pulps differed from the others, as the hexenuronic acid content was not decreasing when the hydrogen peroxide charge was increased. This is in accordance with the known stability of hexenuronic acid with alkaline hydrogen peroxide. The decrease of signal intensity of 240 nm in the UV-Vis spectra was mainly due to the removal of overlapping lignin signals, as discussed previously. Consumed OXE/BDt, kappa numbers, hexenuronic acid group and lignin contents of semi-bleached pulps are presented in Table 2.

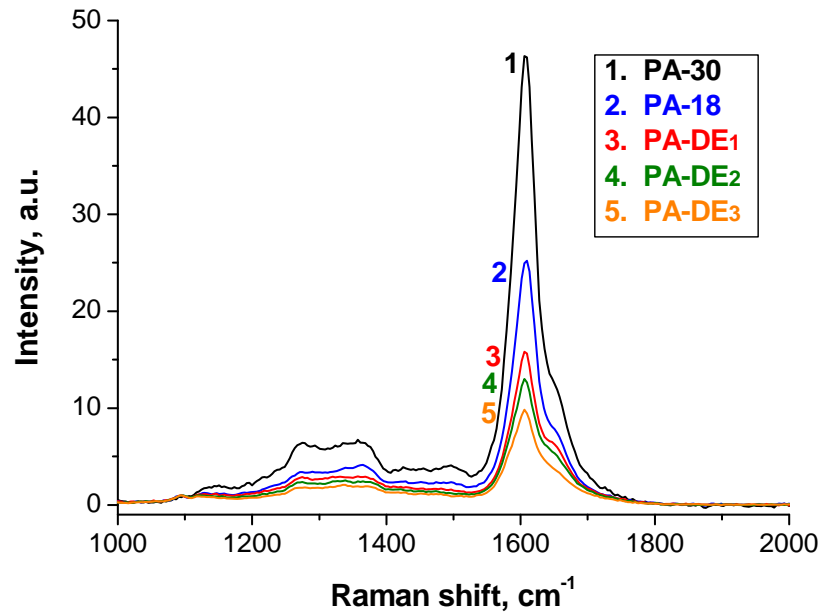


Fig. 6. UVRR spectra of profiled alkaline-cooked (PA) pulps at two different kappa levels (kappa 30 and 18) before and after chlorine dioxide bleaching. Chlorine dioxide charge increased in order $PA-DE_1 < PA-DE_2 < PA-DE_3$.

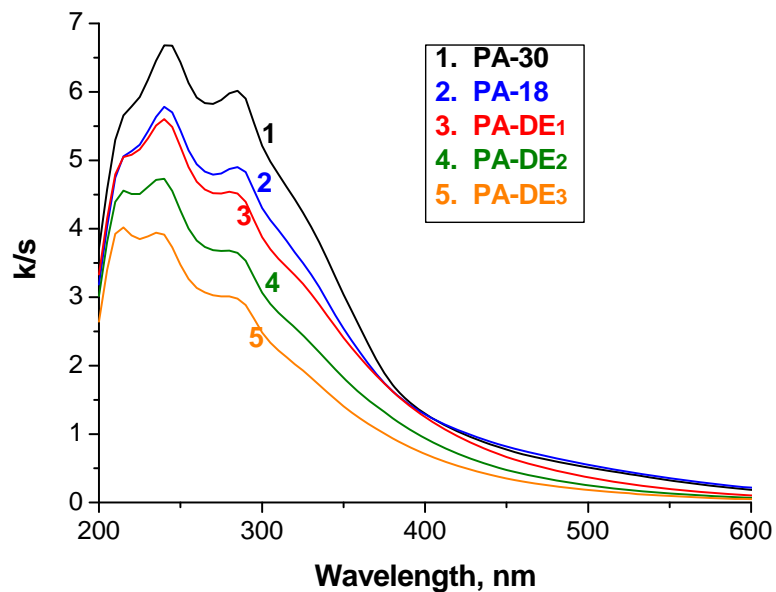


Fig. 7. UV-Vis spectra of profiled alkaline-cooked (PA) pulps bleached with chlorine dioxide, converted into k/s curves. Chlorine dioxide charge increased in order $PA-DE_1 < PA-DE_2 < PA-DE_3$.

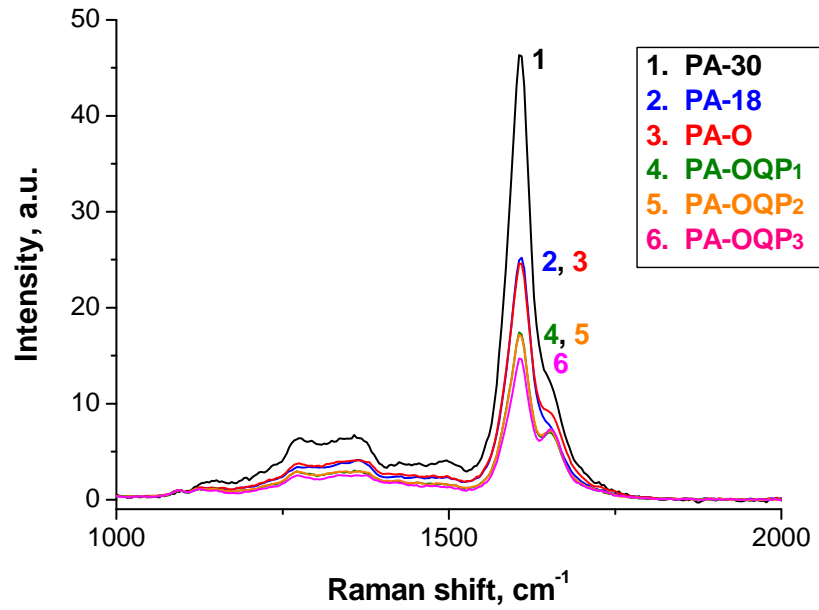


Fig. 8. UVR spectra of profiled alkaline-cooked (PA) pulps bleached with hydrogen peroxide. Peroxide charge increased in order PA-OQP₁<PA-OQP₂<PA-OQP₃.

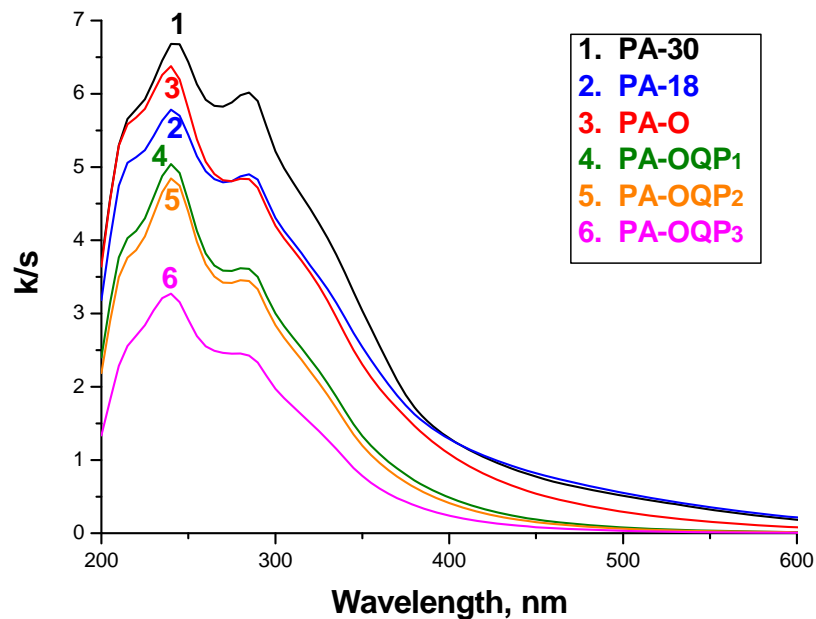


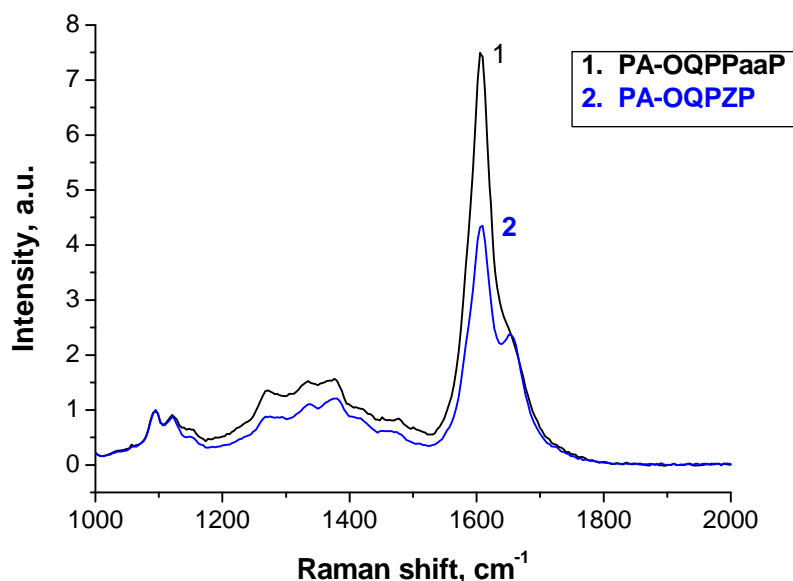
Fig. 9. UV-Vis spectra of profiled alkaline-cooked (PA) pulps bleached with hydrogen peroxide, converted into *k/s* curves. Peroxide charge increased in order PA-OQP₁<PA-OQP₂<PA-OQP₃.

Table 2. Consumed OXE/BDt, Kappa Numbers, Hexenuronic Acid Group and Lignin Contents of Semi-bleached Pulps

Sample code	Consumed OXE/BDt	Kappa number	HexA (mmol/kg)	Lignin kappa
PA-DE ₁	987	16.0	23	14.0
PA-DE ₂	1489	9.8	11	8.9
PA-DE ₃	1974	6.5	4.2	6.2
PA-O-DE ₁	254	12.2	35	9.2
PA-O-DE ₂	508	8.6	29	6.1
PA-O-DE ₃	761	6.3	20	4.6
PA-O-ZE ₁	363	12.5	29	10.0
PA-O-ZE ₂	550	11.7	26	9.5
PA-O-ZE ₃	883	10.3	20	8.6
PA-O-QP ₁	300	12.0	34	9.1
PA-O-QP ₂	379	11.0	34	8.1
PA-O-QP ₃	835	8.8	33	6.0

Fully-bleached Pulps

The spectra of fully-bleached PA-OQPPaaP and PA-OQPZP pulps are shown in Figs. 10 and 11. In the UVRR spectra, the band at 1658 cm^{-1} from hexenuronic acid groups was equally high in both samples, while peracetic acid bleached pulp contained much more lignin than the ozone-treated pulp. However, the hexenuronic acid content of peracetic acid bleached pulp was much lower than that of ozone-bleached pulp (Table 3). This contradictory result could be due to seriously overlapping bands and hence high lignin content increased also the intensity at 1658 cm^{-1} . The UV-Vis spectra also revealed the higher lignin content for peracetic acid bleached pulp, but it also seemed to contain slightly more hexenuronic acid groups than the ozone-bleached pulp. This is again due to the effect of higher lignin content and overlapping lignin signals at 240 nm.

**Fig. 10.** UVRR spectra of PA-OQPPaaP and PA-OQPZP pulps.

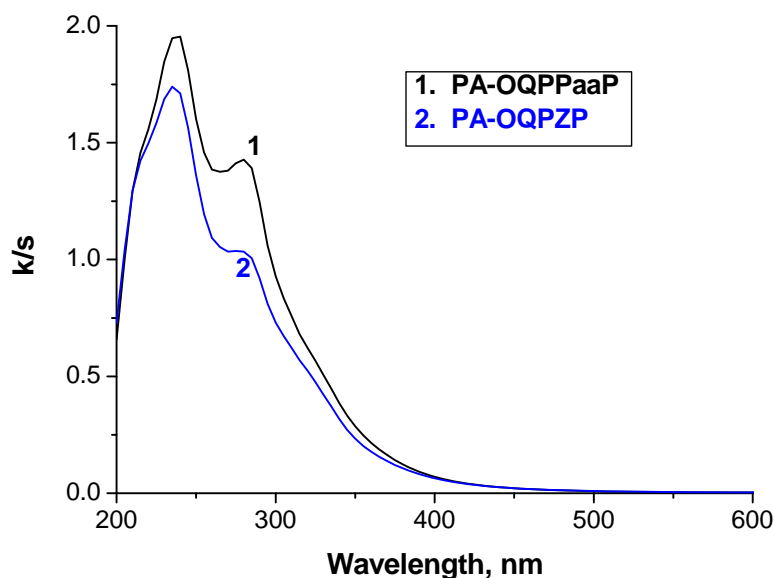


Fig. 11. UV-Vis spectra of PA-OQPPaaP and PA-OQPZP pulps, converted into k/s curves.

The UVRR and UV-Vis spectra of PA-OQPPaaP and PA-OQPZP pulps show that peracetic acid (Paa) removed hexenuronic acid relative to lignin much more efficiently than ozone (Z). On the other hand, ozone removed more lignin structures than hexenuronic acid from the pulp, as shown also by the chemical analyses given in Table 3 and as stated in the literature (Vuorinen et al. 2007).

The spectra of the fully-bleached PA-OEDDD and PA-OEDDP pulps are shown in Figs. 12 and 13. The UVRR spectra of these pulps were very similar, and only slightly higher intensity was observed for PA-OEDDD pulp at 1658 cm^{-1} . On the other hand, the UV-Vis spectrum of PA-OEDDP-bleached pulp was lower in the range of 200-450 nm. According to chemical analyses, these pulps contained practically the same amount of lignin and they did not contain any hexenuronic acids. Despite these spectral differences, the wet chemical analyses indicated that the samples were very similar.

It is probable that the difference in the UVRR and UV-Vis spectra (Figs. 13 and 14) was caused by carbonyl or unsaturated structures of higher absorptivity in the PA-OEDDD pulp than in PA-OEDDP pulp. Higher carbonyl content was detected by the hydroxyl amine method for PA-OEDDD (Table 3), which could explain the increased absorbance. Difference in carbonyl group content could partly explain the deviation between the UVRR and UV-Vis spectra, since these structures give a strong absorption bands in the UV region, while they are relatively weak Raman scatterers. These structures could be some types of quinones, which are known to form during chlorine dioxide bleaching (Gierer 1986), but they would be oxidized to muconic acids and other degradation products during the following alkaline peroxide treatment. Although UV-Vis spectroscopy did not show this difference very clearly, the UV-Vis absorption band at ca. 210 nm relative to absorption band at ca. 280 nm was slightly higher in the PA-OEDDD

spectrum than in the PA-OEDDP spectrum. The absorption band at 210 nm has been assigned to carbonyl groups (Liitiä et al. 2004), which are expected to be prominent after the ODEDD sequence similarly to quinone structures. Accordingly, the intensity at ca. 400 nm assigned to quinones was higher in PA-OEDDD.

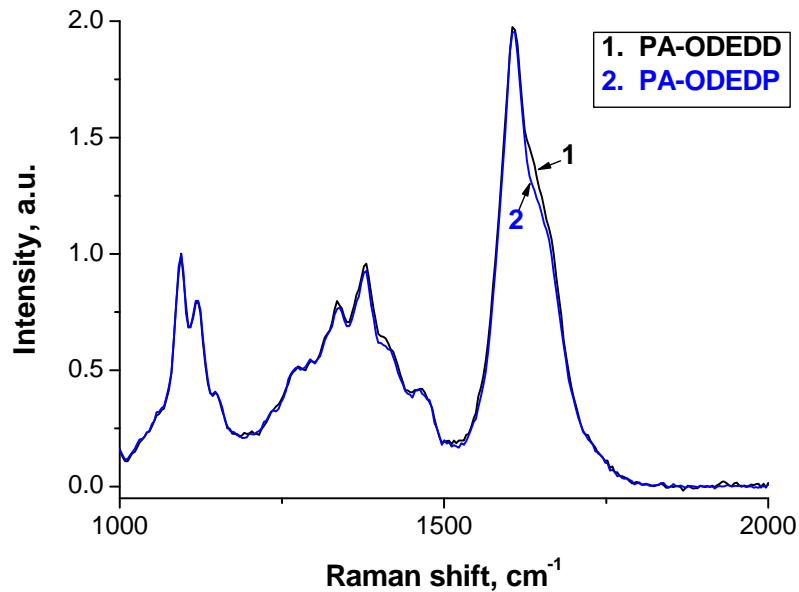


Fig. 12. UVRR spectra of PA-OEDDD and PA-OEDDP pulps.

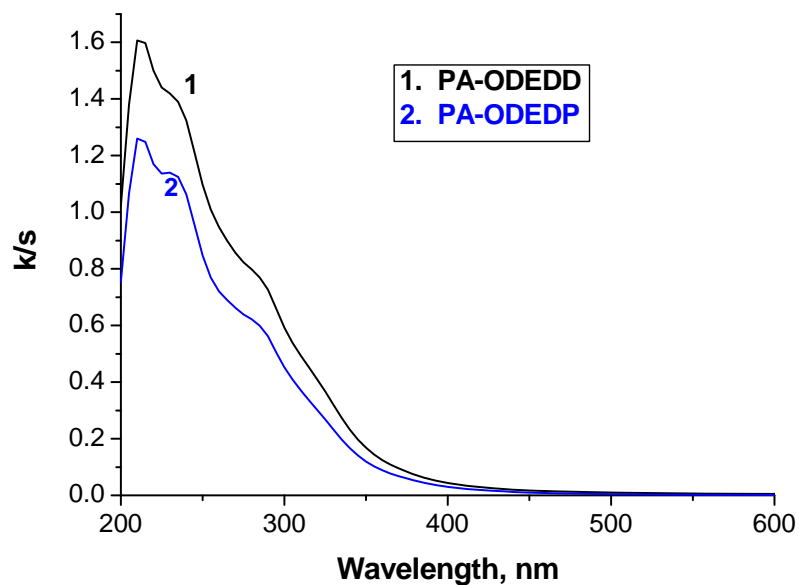


Fig. 13. UV-Vis spectra of PA-OEDDD and PA-OEDDP pulps, converted into k/s curves.

Table 3. Kappa Number, Hexenuronic Acid Group, Lignin and Carbonyl Group Content of Fully-bleached Pulps

Sample code	Kappa number	HexA (mmol/kg)	Lignin kappa	C=O (mmol/kg)
PA-OQPPaaP	3.7	4.1	3.3	6
PA-OQPZP	3.3	11	2.3	7
PA-OEDDD	0.7	-	0.6	10
PA-OEDDP	0.6	-	0.5	6

Comparison of UVRR and UV-Vis Spectroscopy

As was illustrated above, both UVRR and UV-Vis spectroscopy revealed changes both in residual lignin and hexenuronic acid content in pulps. It has been well documented that lignin content of a sample is directly proportional to the intensity of the aromatic stretching band of the UVRR spectrum (Jääskeläinen et al. 2005) and the absorbance of the UV-Vis spectrum (Schmidt and Heitner 1999). Hence, the results obtained by these two methods were compared.

In order to determine the height of the UVRR bands, the spectra were deconvoluted to minimize the influence of partly overlapping bands. This way the heights of the bands at 1605 cm^{-1} and 1658 cm^{-1} could be defined without remarkable interference from the neighboring bands (Fig. 1). On the other hand, the UV-Vis spectra were not deconvoluted, because the number of components in the spectra and their band height maxima could not be defined with good repeatability. Hence, the absorbances at the band maxima of the UV-Vis spectra were defined directly from the spectra.

The comparison of the absorbance of the UV-Vis band at 280 nm and intensity of the UVRR band at 1605 cm^{-1} showed an adequate correlation, as illustrated in Fig. 14. Only at high lignin content, the deviation between UV-Vis and Raman spectroscopy increased remarkably.

The increased deviation may be partly due to the saturation of UV-Vis spectra of the unbleached pulps, and hence a linear correlation of the absorbance with lignin content no longer exists (Liitiä et al. 2004). This was the case especially when standard pulp handsheets of 60 g/m^2 (SW kraft pulps) were used instead of thin 20 g/m^2 sheets (other pulps). Also some deviation in the UVRR band height determination could be expected because the cellulose band in the UVRR spectra of unbleached kraft pulps was only a few times as high as the spectral noise, and hence spectral normalization to this band may induce a large deviation in the band height at 1605 cm^{-1} . Despite of these limitations, both of these techniques gave similar results and hence are well applicable for samples with low lignin content.

Hexenuronic acid groups are partly responsible for the UVRR band at 1655 cm^{-1} (Halttunen et al. 1999; Jääskeläinen et al. 2005) and the UV-Vis band at 240 nm (Ragnar 2001; Liitiä et al. 2004), indicating that both of these techniques could be applied in quantification of hexenuronic acid groups in the pulps. However, the correlation of the unsaturated stretching band at 1658 cm^{-1} in the UVRR and the absorbance at 240 nm in the UV-Vis spectra was found to be only indicative (Fig. 15). The correlation was moderate for the fully- and semi-bleached pulps, excluding the peroxide-bleached (PA-OQP) pulps, whereas the unbleached pulps showed practically no correlation.

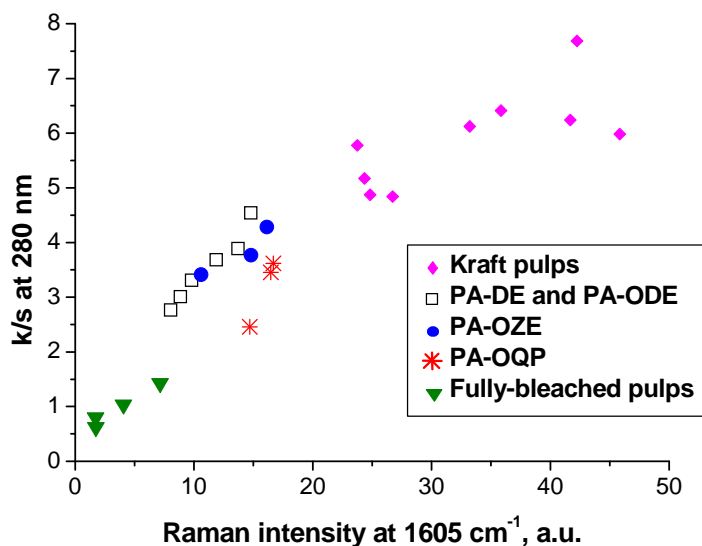


Fig. 14. Correlation of UV-Vis absorption band at 280 nm to Raman band at 1605 cm⁻¹.

The poor correlation between these bands can be explained by the contribution of other pulp structures at these spectral regions. In the UV-Vis spectra the signal intensity at 240 nm is influenced by the pulp lignin content, because lignin has absorbance also in this range (Ragnar 2001; Liitiä et al. 2004). This was clearly seen for the peroxide-bleached pulps (Fig. 15). For these pulps, increasing peroxide charge did not affect the hexenuronic acid group content of the pulp (Table 2), while it remarkably decreased the UV-Vis band at 240 nm. Therefore, the effect of delignification should be taken into account when analyzing the UV-Vis spectra. This could be performed e.g. by using the ratio of signal intensities of 240 nm and 280 nm, as described earlier (Liitiä et al. 2004).

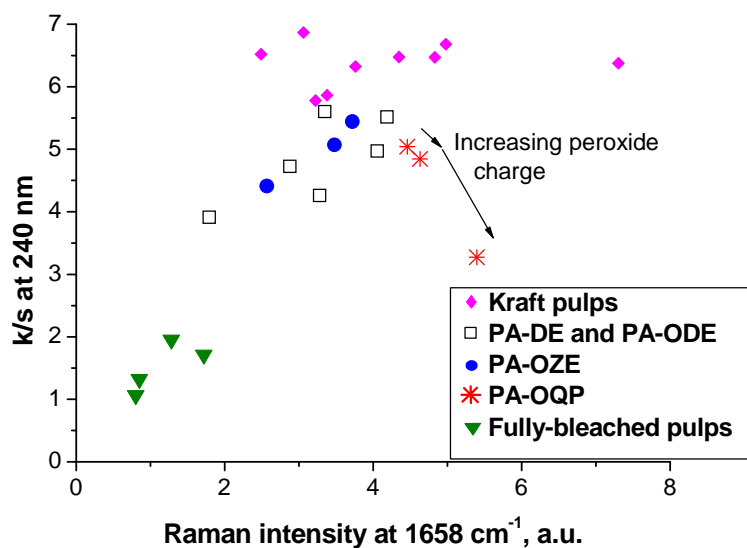


Fig. 15. Correlation of UV-Vis absorption band at 240 nm to Raman band at 1658 cm⁻¹.

The UVRR band at 1658 cm^{-1} was also influenced by other structures in addition to hexenuronic acid. It has been observed that hexenuronic acid groups give rise to a band at 1655 cm^{-1} , as has been defined with hexenuronic acid model compound (Adorjan et al. 2006) and pulps with high amount of hexenuronic acid groups (Jääskeläinen et al. 2005). However, in this study the deconvoluted UVRR spectra revealed the band maximum at 1658 cm^{-1} , which is at higher wavenumbers than that of hexenuronic acid. In addition, a notable band was present also in pulps with practically no hexenuronic acid groups (Fig. 1).

The presence of other structures affecting this band is also shown in Fig. 16, where the deconvoluted Raman band intensity at 1658 cm^{-1} was plotted against the hexenuronic acid content of the pulps as measured by wet chemical methods. Since the 1658 cm^{-1} band intensity was ca. 0.8 a.u. for the pulps with no detectable amount of hexenuronic acid groups, it is obvious that also other substances contribute to this band. The result thus agrees with the earlier experiments, where no deconvolution of the bands was performed (Jääskeläinen et al. 2005). However, the slope of the regression line was much steeper in the previous work, probably due to overestimation of the band height.

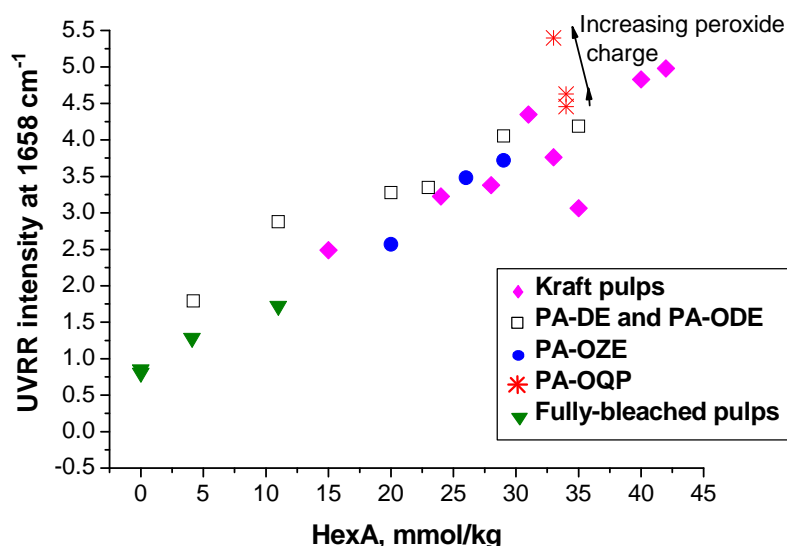


Fig. 16. Correlation of the intensity of the deconvoluted UVRR band at 1658 cm^{-1} nm with hexenuronic acid group content of the pulps.

The peroxide-bleached samples showed remarkably different trends than other samples in Fig. 16. Even if increasing peroxide charge did not have an impact on the hexenuronic acid content of the sample, the intensity of the band at 1658 cm^{-1} increased. This became evident only after the deconvolution, since the original UVRR spectra of these samples (Fig. 8) showed that the aromatic band intensity decreased remarkably, together with lowered lignin content (Table 2), whereas the intensity of 1658 cm^{-1} remained nearly at the same level regardless of the bleaching. However, since the bands were partly overlapping, deconvolution of these bands revealed an apparent increase in the band at 1658 cm^{-1} together with a decrease in the band at 1605 cm^{-1} . It has been observed earlier (Mononen et al. 2005) that peroxide treatment of birch wood samples

increased the intensity of the UVRR bands at this range. However, based on these data only, it is not possible to unambiguously confirm the formation of new structures that would have a band at 1658 cm^{-1} .

CONCLUSIONS

The data presented in this paper illustrated that both UV resonance Raman spectroscopy and UV-Vis reflectance spectroscopy are valuable techniques in lignin analysis *in-situ* for samples with low lignin content. The lignin content determination is fast with both of these techniques, and only small amounts of sample and little sample preparation are required. In addition, these techniques correlated well for semi- or fully-bleached pulps. On the other hand, samples with higher lignin content (unbleached pulps) showed much more variance. This was possibly due to saturation of UV-Vis spectra and low intensity of the internal standard band in the UVRR spectra.

Hexenuronic acid group determination by these techniques showed much more variance. For certain semi- and fully-bleached pulps a relatively good correlation was observed, while unbleached and peroxide-bleached pulps showed clearly scattered data. Basically, the height of the deconvoluted UVRR band at 1658 cm^{-1} correlated well with the measured hexenuronic acid group content of the samples, even if it is probable that also other structures in pulps affected this band.

ACKNOWLEDGMENTS

Anni Lähdetie and Anna-Stiina Jääskeläinen acknowledge the Academy of Finland for financial support. This study has been performed as a part of KCL College. D.Sc. Eric Enqvist is thanked for providing conventionally cooked unbleached softwood kraft pulp samples.

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Article submitted: May 27, 2009; Peer review completed: July 6, 2009; Revised version received: Oct. 14, 2009; Article accepted and published: Oct. 19, 2009.