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UV-absorbance of oxidized xylan and monocarboxyl cellulose in alkaline solutions

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Abstract

The absorbance in the 190–500 nm range of oxidized lignin-free xylan isolated from unbleached and ozone-bleached hardwood kraft pulps as well as monocarboxyl cellulose in NaOH solution was examined by UV/VIS-spectroscopy and SEC employing multi-wave UV-detection. The first derivative of UV-spectra has been shown to be more useful to investigate the chromophore composition. The chromophore composition of oxypolysaccharides was as follows: carboxyl and carbonyl groups absorbing at 200–220 and 270–290 nm, respectively, heteroaromatics of furan- and pyron-type absorbing additionally at 230–250 and 290–320 nm as well as conjugated heteroaromatics absorbing above 300 nm with maximums at 350–370 and 430–450 nm due to the charge-transfer complexes. Problems regarding the attribution of absorbance to lignin- and heteroaromatics-derived chromophores are discussed. Conjugated heteroaromatic compounds, non-uniformly distributed over MWD, are supposed to be the source for the gel-fraction and contributors to the colour of oxidized polysaccharides.

Keywords: Xylan; Monocarboxyl cellulose; Alkaline solution; UV/VIS-spectroscopy; SEC; Multi-wave UV-detection; Chromophore composition

1. Introduction

The thermo-oxidative destruction of polysaccharides during pulping and bleaching leads to accumulation of carboxyl, aldo- and keto-groups (Dudkin, Gromov, Vedernikov, Katkevich, & Cherno, 1991; Ermolenko, 1959; Röhrling, Potthast, Rosenau, Sixta, & Kosma, 2002). These chromophore groups in cellulose and hemicelluloses absorb in the 210–320 nm UV range (Eremeeva & Bikova, 1998; Ermolenko, 1959; Rydlund & Dahlman, 1997; Sixta, Schelosky, Milacher, Baldinger, & Röder, 2001).

Apart from the mono- and di-substituted by carboxyl and/or carbonyl groups pentoses and hexoses, the unsaturated pyron rings such as hexenuronic acids (HexA) are also formed (Dudkin et al., 1991; Ermolenko, 1959). The contribution of these chromophore structures to the colour of pulp fibres is an open question up to now. The indirect studies on the brightness gain of the fibres during bleaching could not be taken as an irrefutable evidence of the fact that the unsaturated HexA are really colourless (Pettersson, Ragnar, & Lindström, 2002; Ragnar, 2001a,b; Torngren & Ragnar, 2002).

In fact, the UV/VIS spectral properties of oxidized cellulose and hemicelluloses are poorly investigated, in spite of the well-established role of polysaccharide-derived carboxyls and carbonyls in the formation of coloured structures (Beyer, Lind, Koch, & Fisher, 1999; Chirat & De la Chapell, 1999; Forsskåhl, Tylli, & Olkkonen, 2000; Granström, Ericsson, Gellerstedt, Rööst, & Larsson, 2001; Granström, Rööst, Eriksson, Larsson, & Gellerstedt, 2000). The significant role of HexA in the pulp brightness reversion has been shown by several authors (Forsskåhl et al., 2000; Granström et al., 2000, 2001). The dark coloured oligodihydrofurans as well as the 'unknown' unsaturated structures originated from polysaccharides were also found in bleached pulp samples (Beyer et al., 1999; Domingues & Evtuguin, 2001). The formation of adducts with hydroxymethyl furaldehyde derived intermediates, as well as the cross-linking in the cellulose matrices with heteroaromatics of furan-type have been assumed (Forsskåhl et al., 2000; Beyer et al., 1999).

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The impact of the hemicelluloses and cellulose derived chromophores absorbing in a visible range seems to be more and more important under total chlorine-free (TCF) bleaching sequences, since peroxide and ozone are strong and non-selective oxidizing agents for lignin, hemicelluloses and cellulose. Moreover, the degree of their oxidation during processing is an important point affecting the physical properties and derivatisation of polysaccharides. The chromophore composition of oxidized polysaccharides is an essential subject of investigation. In the present work, the UV/VIS absorbance of xylan isolated from kraft pulps and monocarboxyl cellulose (CMC) in comparison with lignin are described.

2. Experimental

2.1. Xylan samples

Xylan was extracted by 5% KOH from hardwood kraft pulp fibres after oxygen delignification and ozone stage of the TCF bleaching sequence (marked KO_2- and Z-xylan, respectively). For the KO_2- and Z-xylan, the contents of HexA and 4-*O*-methyl glucuronic acids were 4:1.2 and 1.8:1.2 (in molar ratio), respectively. In detail, the isolation procedure and characterization of xylan were described elsewhere (Jacobs & Dahlman, 2001). Commercial monocarboxyl cellulose (CMC) from cotton (6.2% COOH), xylan from alder wood and holocellulose characterized elsewhere (Bikova & Treimanis, 2002) as well as birch kraft lignin were utilized for comparison.

2.2. Dissolution of xylan

The xylans from pulps, in comparison with those from wood and holocellulose, were hard-to-dissolve in 5–10% KOH and 10–18% NaOH at ambient temperature. To reach full dissolution, KO_2- and Z-xylan samples (10 mg) were incubated at 5 °C in 18% NaOH (2 ml), then the solution was diluted with water four times. As a result, clear solutions were obtained. The dissolution time was 5 and 10 h for KO_2- and Z-xylan, respectively. The dissolution time of CMC as well as other xylan samples in 1 and 10% NaOH, respectively, was equal to 5–10 min at ambient temperature. The clear solutions diluted with water by 1:2 and filtered through a 0.45 μm nylon filter (Millipore) were subjected to SEC and UV/VIS spectroscopy analyses.

2.3. SEC

SEC analyses were carried out using a Gilson liquid chromatograph equipped with RI- and two UV/VIS detectors connected in line. UV-chromatograms were obtained at 205, 210, 215, 225, 232, 246 (AUFS: 0.2×10^{-4}), 252, 266, 275, 282, 295, 312, 322 (0.1×10^{-4}), 346, 370, 415 and 457 (0.05×10^{-4}) nm. A cartridge glass column Separon HEMA BIO 2000 CGC (TESSEK Ltd Prague, Czech Republic) was applied. Aq. 10 mM NaOH was used as an eluent. Analyses were carried out at ambient temperature. Injection volume was 5 μl of 0.125% solution of xylan and CMC dissolved in 4.5 and 0.5% NaOH, respectively.

2.4. UV- and IR-spectroscopy

The UV/VIS-spectra and their first derivative were recorded from alkaline solutions using a Spectra 2000 spectrophotometer (Carl Zeiss, JENA, Germany). The IR-spectra of the samples in KBr pellets were recorded with a Perkin Elmer spectrometer.

3. Results and discussion

3.1. UV-spectroscopy

In Fig. 1, the UV/VIS-spectra of xylans, CMC and lignin are compared. In the 190–270 nm range, for xylans, in comparison to CMC, that has a shoulder around 215 nm, a maximum at 210 and a shoulder around 230 nm were observed. Above 260 nm, maxima at 270–290 and 350–380 nm were found for all samples. The maxima at 210–220 and 270–280 nm were attributed to the absorbance of carboxyl and carbonyl groups, respectively (Ermolenko, 1959). The spectra were obtained in alkaline media, so the dissociation of carboxyl groups as well as the ionization followed by the izomerization of keto- and aldo-groups took place. Their absorbance is supposed to be shifted towards a longer wavelength range. For CMC, a direct correlation between the carbonyl content and absorbance at 290–320 nm has been estimated (Eremeeva & Bykova, 1998).

The first derivative revealed a very complex and distinctive chromophore composition for KO_2-, Z-xylan and CMC in the 200–260 nm range (Fig. 1), which reflects the interference from furanoid structures. HexA in xylan and products of their destruction, such as furanic acids and aldehydes, absorb at 235–245 and 280 nm, respectively (Kazitsyna & Kupletskaja, 1971; Rydlund & Dahlman, 1997; Vuorinen, Fagerström, Buchert, Tenkanen, & Teleman, 1999). Apart from carboxyl- and carbonyl-related bonds, the so-called charge-transfer band around 252 nm (Nakanasy, 1962), which indicates the ionized aromatic structures and causes the absorbance above 280 nm, was also observed. Structures containing dicarbonyl fragments conjugated with double bond absorb at 305–330 nm (Kazitsyna & Kupletskaja, 1971). For cellulose, the expanding absorbance at 320–410 nm observed during NO_2 oxidation has been previously attributed to the nitrates (Ermolenko, 1959). However, in our opinion, carbonyl- and carboxyl-conjugated heteroaromatic compounds of pyron- and furan-type, which form charge-transfer complexes,

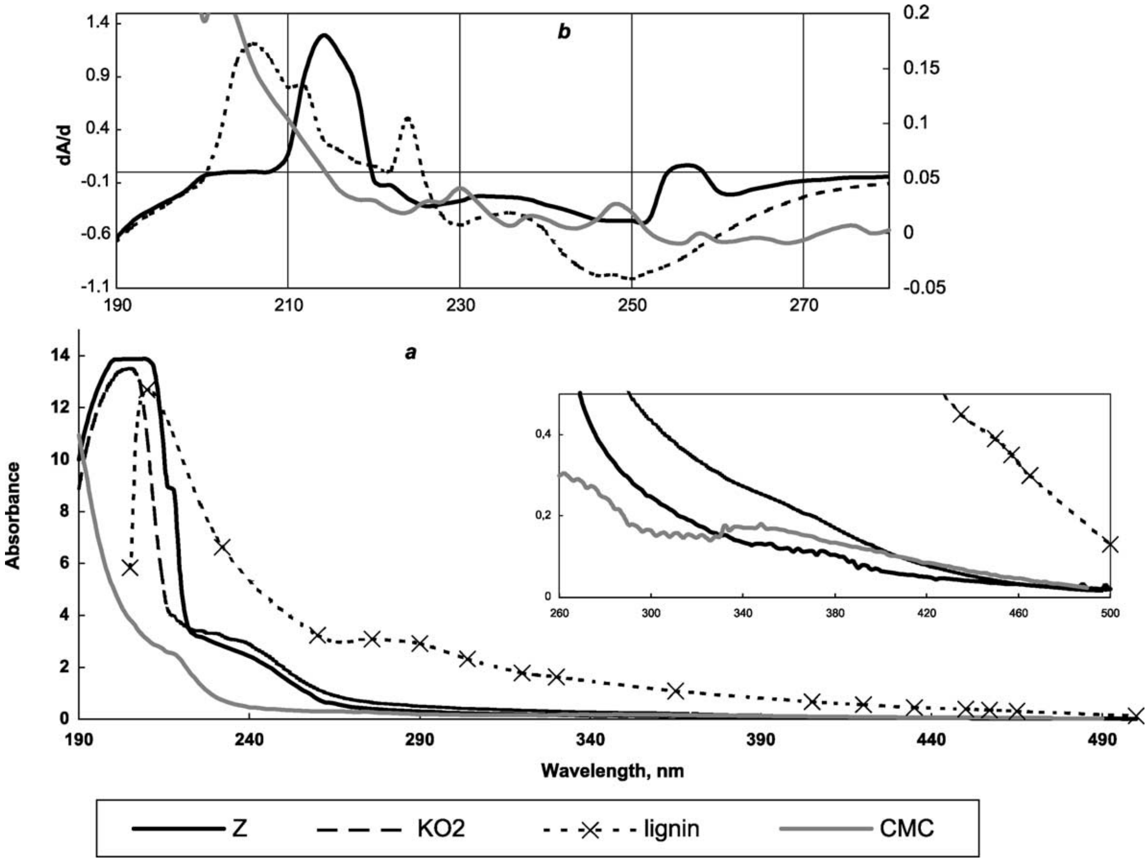

Fig. 1. UV/VIS-spectra of xylan isolated from unbleached (KO_2) and bleached (Z) hardwood kraft pulp, and of CMC and kraft lignin.

cause the absorbance observed for xylan and CMC above 280 nm with maximum at 350 nm and diminishing in the visible range. These findings are in line with the assumption that the UV-absorbance cannot be attributed solely to lignin or carbohydrates. Obviously an alternative method is required to confirm that the UV-absorbing material is derived veritably from certain compound (Forsskåhl et al., 2000; Wong & Yokota, 1995).

In Fig. 2, the IR-spectra of KO_2- and Z-xylan are compared with those of lignin and xylan from wood and holocellulose containing 1.8 and 0.2% of lignin, respectively. No absorbance at 1500–1515 and 870 cm^{-1}, which corresponds to stretch bonds for the benzene ring in lignin, was observed for KO_2- and Z-xylan. It was assumed as indication that these samples are lignin-free. The IR-spectra of xylan from wood and holocellulose have revealed lignin-related bonds at 870, 1515 and 1610 cm^{-1}. Hence, we may conclude that the UV/VIS absorbance in the case of KO_2- and Z-xylan was originated from the oxidized structures.

To avoid the destruction of HexA under desalting, the samples were analysed in the original form. Therefore, the wide strong band with a maximum at 1620 cm^{-1}, which overlaps the double bond- and carbonyl-related region, together with 1440 and 3250 cm^{-1} bands, signified the salt form of carboxyl groups in the KO_2- and Z-xylan samples (Ermolenko, 1959; Kazitsyna & Kupletskaja, 1971; Zhbankov, 1964). The oxidation of xylan under pulping and bleaching causes changes in the IR-spectra. Strong bands at 600, 700, 950 (δ_{CH}), 1005, 1165, 1280 (ν_{COC}), 1360 and 1440(ν_{CH}) cm^{-1} appear. This set signifies the existence of heteroaromatics of the pyron- and furan-type in the oxixylan structure (Kazitsyna & Kupletskaja, 1971; Nakanasy, 1962; Zhbankov, 1964). HexA, which are a pyron derivative, were identified in KO_2- and Z-xylans by chemical analysis. Full interpretation of the IR-spectra of oxidized polysaccharides requires a special description and it was not the aim of the present work. Here, furan and pyron nuclei containing double bond and conjugated carbonyl/carboxyl groups absorb at 1470–1620 and 1660–1750 cm^{-1} similarly to lignin (Kazitsyna & Kupletskaja, 1971; Nakanasy, 1962). Therefore, the stretch of heteronuclei and C–O–C in the 500–1200 cm^{-1} range seems to be more suited to identify HexA residues and other heteroaromatics in the case of oxixylan.

Thus, the heteroaromatic compunds originated from pentoses and hexoses during the pulp fibres processing represent conjugated derivatives of pyron and furan. Similarly to lignin-derived quinones (Furman & Lonsky, 1988; Pasco & Suckling, 1998), they cause the absorbance above 320 nm up to the visible range due to charge-transfer complexes. Therefore, the UV/VIS-spectra of oxidized

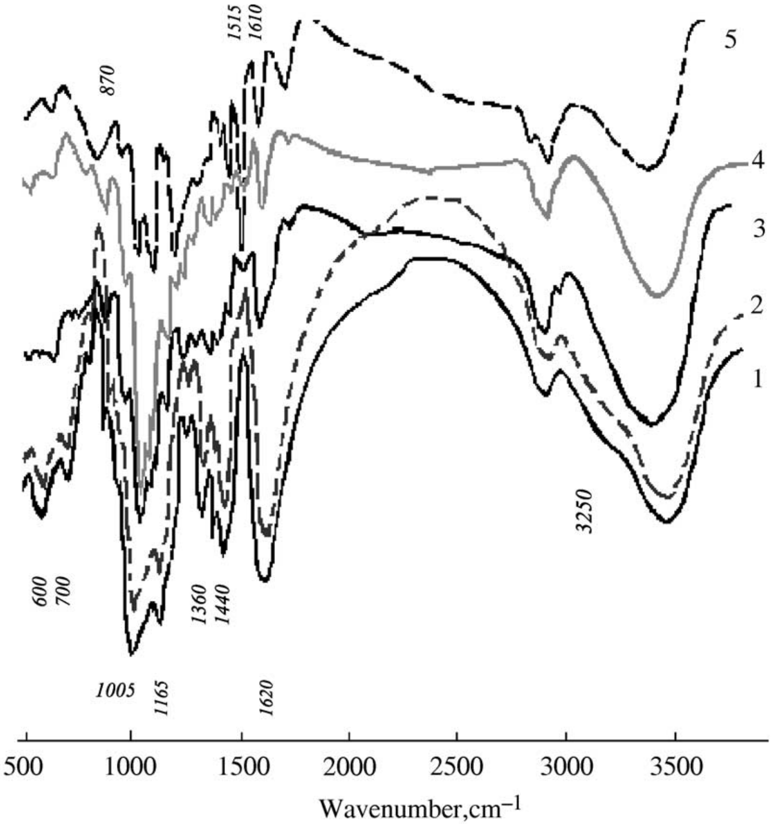

Fig. 2. IR-spectra of xylan isolated from alder wood (4), holocellulose (3), unbleached and bleached kraft pulps: KO_2- and Z-xylan (1 and 2, respectively), and kraft lignin (5).

xylan and CMC in alkaline solution above 270 nm are similar to that of lignin.

For polysaccharides, the low-molecular weight (MW) products of destruction, such as furfural and its derivatives, are considered to cause absorbance in the visible range (Ziobro, 1990). From this standpoint, classical UV/VIS spectroscopy is not able to indicate the originator of absorbance. Therefore, the xylans and CMC were analyzed by SEC utilizing the multi-wave UV detection in the 200–470 nm range, aiming at investigating the chromophore distribution over the MWD.

3.2. SEC with multi-wave UV detection

In Fig. 3, the RI- and UV-chromatograms obtained at 215, 224, 232, 266, 280, 370 and 457 nm for KO_2- and Z-xylan are combined. Xylan samples showed a multi-modal distribution pattern, and the chromophores were adequately distributed over the RI-response. Taking into account the well-known phenomenon of the formation of gel-particles by hemicelluloses in different solvents (Bikova, 1991; Jacobs & Dahlman, 2001; Saake, Kruze, & Puls, 2001; Sixta et al., 2001; Sjöholm, Gustafsson, Eriksson, Brown, & Colmsjö, 2000), the first peak eluted at the void volume of the column could be attributed to the gel-particles in the solution. For KO_2-xylan, this fraction took about 25% of the polymer content and 17–19% of absorbance in the 205–250 and over 400 nm ranges, as well as 21–22% of absorbance in the 260–380 nm range. For Z-xylan, it made about 40% of the sample, which occupied 25, 35 and 40% of the polymer absorbance at 210–240, 250–330 and 340–460 nm, respectively. When compared, Z-xylan showed a poorer solubility and formed a significant gel fraction enriched with conjugated heteroaromatics. In our opinion, xylan macromolecules that were crosslinked by furfural-derived intermediates during pulping and bleaching created the gel-fraction, which is rather stable under alkaline conditions.

Although the SEC method is not effective to analyze the low-MW substances, different products derived in the case of KO_2- and Z-xylan under alkaline conditions were evident from Fig. 3. Table 1 drastically reflects the contribution of low-MW substances in alkaline solution, especially from Z-xylan, into the total absorbance of oxidized xylan at wavelengths, which are usually attributed to lignin.

The ratio between UV- and RI-chromatogram heights is equal to the absorbance per mass unit, i.e. it is the absorptivity value at the given wavelength. Therefore, from UV-chromatograms obtained in the range 200–460 nm (reduced to the equal sensitivity) and RI-chromatograms, the UV-spectra for I–III peaks were evaluated (Fig. 4). They clearly revealed the quantitative

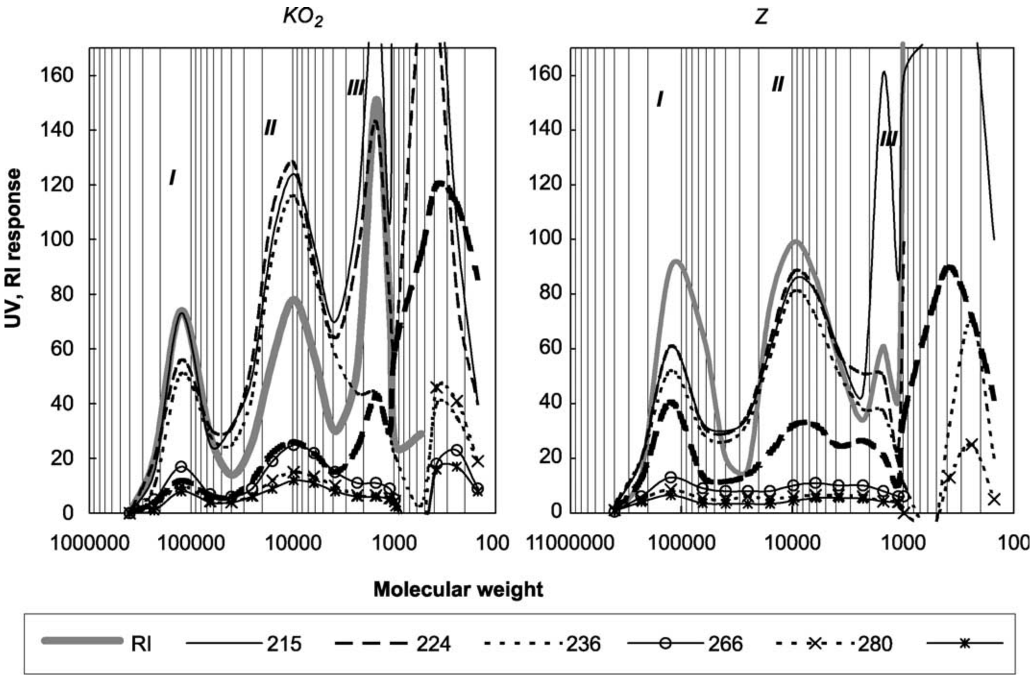

Fig. 3. Set of experimental chromatograms for xylan isolated from unbleached (KO_2) and bleached (Z) hardwood kraft pulps.

and qualitative differences in the chromophore composition of xylans. For KO_2-xylan, in comparison to Z-xylan, the absorptivity of first and second polymer peaks was doubled due to the two-times higher contents of HexA. While during the pulp bleaching process, a part of extended chromophores structures absorbing at 370–410 nm was eliminated from KO_2-xylan; heteroaromatics absorbing at 240–260 nm remained in Z-xylan. The latter form charge-transfer complexes due to conjugation with aldo- and keto-groups absorbing at 280–320 nm and, similarly to lignin-derived quinones, are responsible for the absorbance in the visible range with maxima at 370 and 430 nm.

More likely, the III peak (Fig. 3) combines the heteroaromatics olygomers (Beyer et al., 1999; Domingues & Evtuguin, 2001) that require further elucidation.

Fig. 5 shows the chromophore groups and structures absorbing in the 220–460 nm range distributed over the MWD of CMC. The set of chromatograms (Fig. 5a) clearly reveals that not only the low-MW products of CMC destruction under alkaline conditions, but also the polymer itself absorb above 330 nm. While the former took about 90% of absorbance at 210–350 nm, the latter introduced up to 35–50% in the absorbance at 390–420 nm and about 25% in the visible range at 440–460 nm (Table 1). In Fig. 5b, the UV/VIS-spectra, which were calculated from UV/SEC data, show that the polymer was enriched with the extended chromophores structures absorbing in the 400–480 nm range with a maximum at 435 nm.

For cellulosic materials, the absorbance in this range is usually attributed to lignin-derived quinones (Furman & Lonsky, 1988; Pasco & Suckling, 1998). However, there was no real resource of quinones in the samples under study. In our opinion, apart from pyrons, the intermediates of carbohydrate destruction under processing, such as furfural and its derivatives, which, due to a high reactivity, can graft within the reactive sites of the oxidized polymer, create charge-transfer complexes in cellulosics.

So, xylan as well as oxicellulose oxidized under kraft pulping and TCF bleaching contain heteroaromatic groups in the polymer backbone, which form coloured complexes. Quinones are considered to be one of the last preserved chromophores in fully bleached pulp (Mateo, Ait-Ouaret, Chirat, Jeunet, & Lachenal, 2001). It has been found that, apart from lignin and HexA, so-called unknown structures originated from polysaccharides, which contain double bonds and carbonyls, are significant contributors to the Kappa number value (Axelsson & Teder 2002; Pettersson

Table 1
Contribution of low-MW fraction into the total absorbance of xylan samples and CMC

Wavelength (nm)	Kraft O_2 xylan (%)	Z-xylan (%)	CMC (%)
210	46	46	87
232	10	25	90
280	38	63	89
350	52	54	93
390	22	30	52
420	46	32	65
457	75	82	76

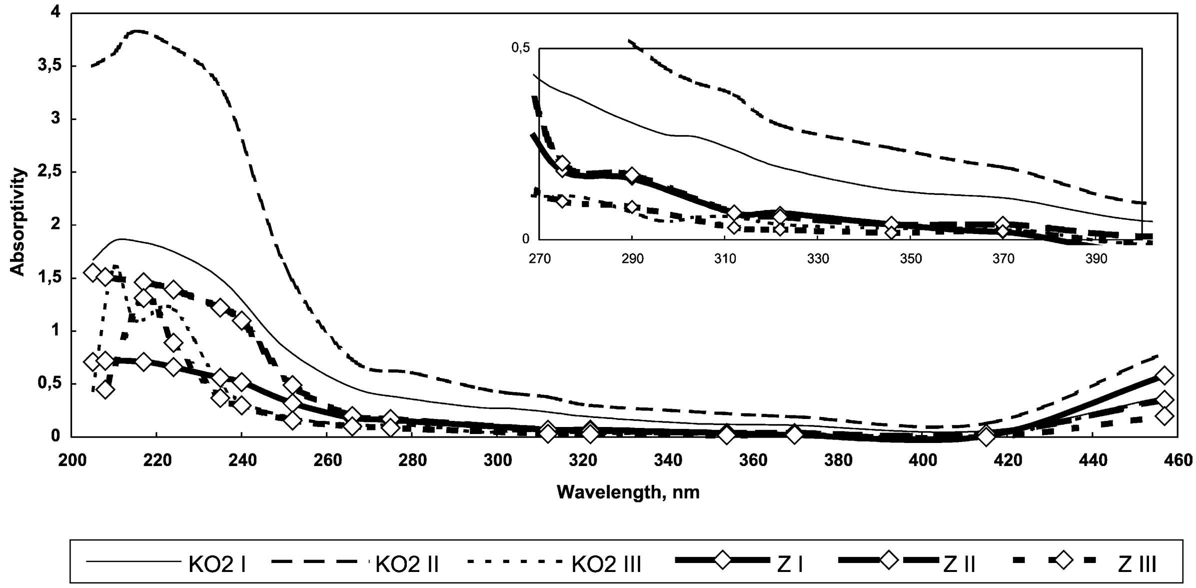

Fig. 4. UV/VIS-spectra evaluated as UV/RI from SEC chromatograms for peaks I–III.

et al., 2002; Li, Sevastyanova, & Gellerstedt, 2002; Sevastyanova, Li, & Gellerstedt, 2001; Sjöholm, Ludquist, Liljenberg, & Backa, 2001). Heteroaromatics, i.e. conjugated unsaturated furanoids and pyranoids, could be easily attributed to quinones from UV/VIS and Kappa numbers monitoring. Therefore, the question arises whether lignin is the sole and actual bearer of 'quinones' and colour in the oxygen delignified kraft pulp and in bleached pulp. In the case of unbleached pulp fibres, the lignin's absorbance significantly overlaps the absorbance from chromophore structures in oxidized polysaccharides, as is reflected in Fig. 1. At the same time, the role of chromophores originated from heteroaromatics in hemicelluloses and cellulose due to the oxidation during bleaching has been increased. It is obvious that heteroaromatic compounds and lignin require distinctive conditions for elimination.

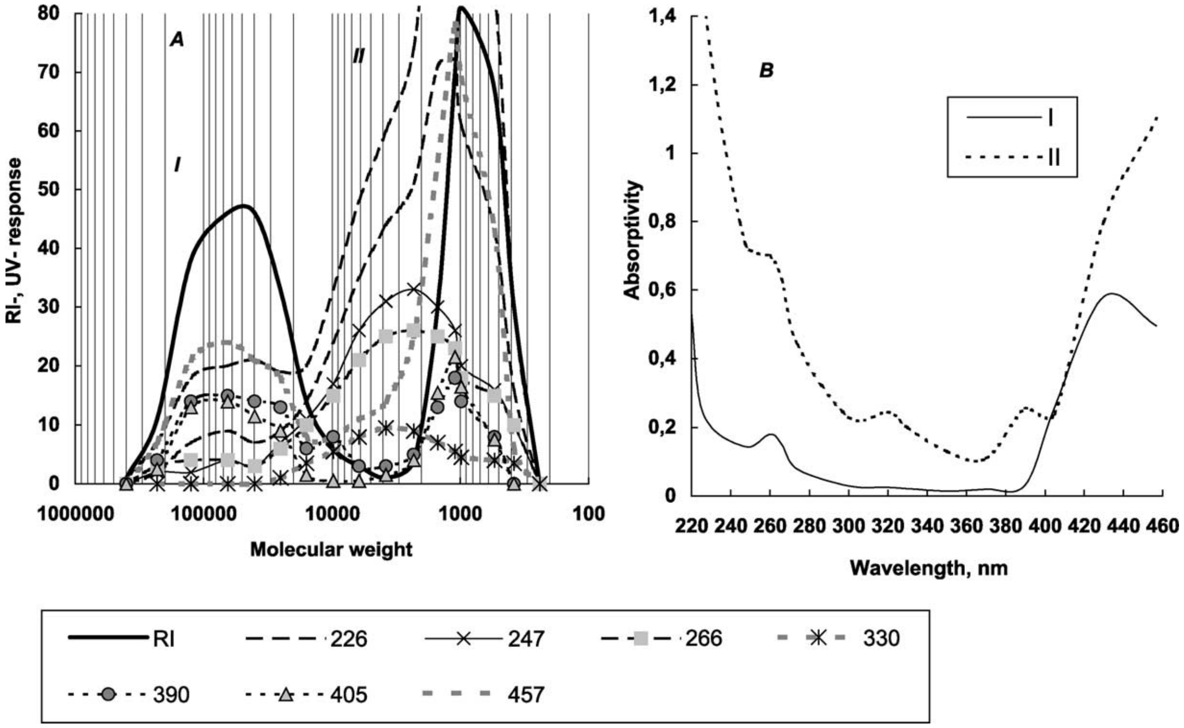

Fig. 5. Set of experimental chromatograms (a) and calculated UV/VIS-spectra (b) in peaks I and II for CMC.

4. Conclusions

The data of multi-wave UV detection during SEC analysis clearly reveal that the polymer backbone of oxidized xylan and cellulose contains both UV and VIS range absorbing chromophore groups and structures. Unsaturated heteroaromatic residues conjugated with carbonyl and/or carboxyl groups, which form charge-transfer complexes, are the source of the colour of the oxidized xylan and cellulose. The transformations of furanoids, which produce reactive intermediates during pulping and bleaching processes, require systematic studies regarding the ability of condensation on cellulose fibres. Taking into account the fact that hemicelluloses and CMC are used in the pharmaceutical and food industry, the differentiation of heteroaromatic- and lignin-derived impurities is rather important.

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