

Artificial Ageing of Wood Monitored by DRIFT Spectroscopy and CIE L*a*b* Color Measurements

1. Effect of UV Light*

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Summary

The effect of UV irradiation up to 200hrs was monitored on five wood species (*Picea abies*, *Pinus sylvestris*, *Larix decidua*, *Populus euramericana*, *Robinia pseudoacacia*) by spectro colorimetry and diffuse reflectance infrared Fourier transform (DRIFT) spectrometry. The CIE L*a*b* color calculations exemplified the rapid change of total color difference (ΔE^*) in the first 25 to 50hrs of irradiation. All samples exhibited yellowing, i.e. a pronounced steep shift to positive Δa^* values in the Δa^* , Δb^* coordinate system. *Robinia p.* showed an additional shift to redness, i.e. towards positive Δb^* values. The colored compounds developed could be removed by water extraction only to a moderate extent. Thus it was concluded that the yellow color was mainly due to oligomeric chromophores, arisen probably from leuco chromophores of the lignin moiety of wood. In agreement with the literature, DRIFT measurements revealed the preferred degradation of aromatic structures and the formation of nonconjugated carbonyl and carboxyl groups. The DRIFT spectra indicate dehydration, oxidation to carboxyl groups and the formation of lactones or other esters. It was demonstrated by spectral subtraction that the increasing carbonyl bands consisted in the case of softwoods of two sub-bands with equal intensity at 1763 and 1710 cm^{-1} . The formation carbonyl bands of the hardwoods obeyed different rules. The formation of conjugated carbonyl groups below 1700 cm^{-1} was observed only to a limited extent. The carboxyl group containing photodegradation products could easily be removed by water extraction. This was interpreted that the oxidized compounds did not necessarily contribute to the formation of colored compounds. The plots of DRIFT band intensities, derived from baseline corrected and normalized spectra, vs. the irradiation time revealed pronounced intensity changes in the first 50 hrs of irradiation. The coherent intensity profiles were beveling above 100 hrs of irradiation.

Introduction

Although wood is a traditional construction material, its outdoor application is afflicted with some difficulties, such as color changes in various degrees and surface roughening. This process, called weathering, is in the first instance a surface phenomenon, but it reduces not only the aesthetic value of wood. The micro pores developing during weathering are the entrance of fungi which are then responsible for the bulk destruction of wood. The complex process of weathering is mostly paraphrased as photochemically initiated oxidation triggered by UV light. For monitoring of these processes surface specific instruments are desirable.

With the advent of FTIR spectroscopy as a routine, DRIFT (diffuse reflectance infrared Fourier trans-

form) spectroscopy was soon recognized as a convenient technique for the investigation of wood, wood components, and pulps (Schultz and Glasser 1986; Faix *et al.* 1987; Michell 1988), which requires a simple sample preparation, and, which is specific for the surface. On the other hand, Michell (1991) called attention to anomalous effects in the range of 950–1200 cm^{-1} of DRIFT spectra of pulps due to the interference of directly and specularly reflected radiation. Several authors have demonstrated that the particle size or surface roughness influences the quality of DRIFT spectra to a considerable degree (Zavarin *et al.* 1990; Bouchard and Douek 1992; Faix and Böttcher 1992). The “anomalous” effects can be diminished to a certain extent by increasing the surface roughness or by dilution of small particles with KBr, respectively.

Notwithstanding, it was also demonstrated that DRIFT is suitable for quantitative lignin analysis

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* Dedicated to Prof. Dr. H.H. Nimz on the occasion of his 65th birthday and his retirement

(Schultz and Glasser 1986) and for determination of the lignin content of pulps (Faix *et al.* 1987; Berben *et al.* 1987). In combination with partial least squares (PLS) calibration even the polysaccharide composition of pulps can be determined (Backa and Brodin 1991). Using DRIFT spectroscopy, it can conveniently be differentiated between "hardwoods" and "softwoods" (Owen and Thomas 1989). Feist and Hon (1984) demonstrated the usefulness of traditional IR spectroscopy for monitoring wood weathering. It is therefore not surprising that DRIFT spectroscopy was also used by several authors for the same purpose (Faix and Németh 1988; Anderson *et al.* 1991a, b; Németh and Faix 1994; Horn *et al.* 1994) as soon as commercial DRIFT accessories were available. Although the quantitative evaluation of DRIFT spectra of solid wood surfaces is not an easy routine, it was demonstrated by Horn *et al.* (1994) by quantitative DRIFT spectroscopy that the chemical changes due to artificial weathering are confined to the upper 200 μm .

Also in this paper, DRIFT spectroscopy will be applied for objective monitoring the chemical changes on the wood surface, which follow the color change with some retardation. Thus both the color and DRIFT behavior of the samples were monitored in dependence of irradiation time. We selected experimental conditions in which all relevant IR bands can be observed upon UV irradiation. (Until now mainly the spectral regions at 1510, 1600 cm^{-1} , and 1750 cm^{-1} have been observed in the context of weathering.) Both softwoods and hardwoods were included into the evaluation program. Since DRIFT is known to be sensitive to surface quality, the sampling was done carefully to avoid deviations due to differences in density, surface roughness or inhomogeneity. Uniformly, the tangential cuts taken from the earlywood of sapwood were investigated. For DRIFT measurements the wood slices were positioned into the accessory in a way that the grains were parallel to the IR beam. To improve the quantitative evaluation, the 1373 cm^{-1} band was selected as reference due its central position within the wavenumber range to be investigated. Moreover, we used the relative band intensities instead of relative integrals, to be able to observe the relative intensity changes of non-resolved bands, too. The first publication deals with UV ageing while the second with thermal ageing and the effects of steaming.

Experimental

Sampling

Wood samples were collected from trees grown in Hungary. Deciduous trees ("hardwoods"): Locust (*Robinia pseudoacacia*), which is rather stable against UV degradation but sensitive to color change; a fast growing poplar (*Populus euramericana*

I-214). Coniferous trees ("softwoods"): spruce (*Picea abies*); scots pine (*Pinus sylvestris*); larch (*Larix decidua*). Homogeneous uniform wafers were carefully prepared from the sapwood by tangential cuts of the earlywood using a fine saw. Two mm thin disks with 12 mm diameter, which fit into the accessory, were prepared. The surface of the samples was smoothed by a fine grade polish paper (grit 800). Grains from the polish paper were eliminated from wood surface under a stereomicroscope. The samples were stored before and between the treatments in a desiccator in total darkness over P_2O_5 at room temperature. The same samples were used for infrared study and color determination.

Artificial weathering

The UV irradiation was carried out with a wide range mercury vapor light source without filter (Hanau, F.R.G.; 300W). The samples were situated in a distance of 20 cm from the lamp. The samples had a temperature of 45 °C under these conditions. The relative air humidity was 50%. The irradiation was interrupted after 5, 10, 17, 25, 35, 50, 70, 100, 200 hours of treatment, respectively. After 200 hours UV treatment the samples were submerged into distilled water for a day and then vacuum dried.

Instruments

The IR measurements were performed with a Bio-Rad Digilab FTIR spectrophotometer FTS-40 equipped with a Spectratech diffuse reflectance unit of the type "Collector". Detector: DTGS; apodization: triangle; resolution: 4 cm^{-1} ; 64 scans. The background spectra were obtained against the metal plate supplied by Spectratech. The spectral intensities were calculated in Kubelka-Munk (K-M) units. After a three point baseline correction at 3800, 1900, and 850 cm^{-1} the spectra were normalized to the band between 1352 cm^{-1} and 1406 cm^{-1} . For difference spectroscopy the spectrum of the untreated sample was subtracted from the spectrum of the irradiated one. As DRIFT is sensitive to surface peculiarities, care was taken that the grain of the samples was parallel to the irradiating IR-beam. The color measurements were carried out with an Elrepho-2000 computer supported spectro colorimeter. A BaSO_4 plate was used as standard. The reflection spectrum was measured in the 400–700 nm region. From these data, the L^* , a^* , b^* color coordinates were calculated based on a D65 light source as established by the Commission Internationale de Enluminure (CIE) in 1976.

Results and Discussion

Color measurements

The effect of chemical changes induced by UV light can readily be observed by the human eye after 1 or 2 hrs of treatment: The wood samples become darker and their color tone turns to yellow. Locust also shows an additional reddish tone.

These subjective observations can be rationalized by applying reflection spectrometry in the visible range and presentation of the results in the CIE $L^*a^*b^*$ color coordinate system. Figure 1, displaying the remission spectrum of spruce, is representative for all other species investigated in this work: The wood spectra exhibit a pronounced intensity increase towards the longer wavelengths, which means that wood reflects a higher portion of the red components of the light than of the blue one. After UV treatment the reflection has decreased in the whole visible region (Fig. 1). For this reason the samples seem to be

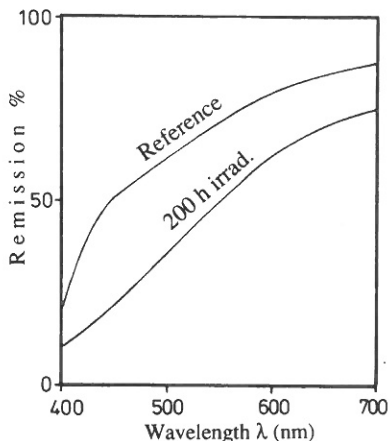


Fig. 1. Change in the visible reflection of spruce wood after 200 hours of UV irradiation.

darker after irradiation. However, the intensity decrease is greater in the blue region ($\lambda < 500\text{nm}$) than in the orange region.

Figure 2, in which the color differences ΔE^* are plotted vs. the irradiation time, reveals that in the first 50 hrs of irradiation the color change is very rapid. (ΔE^* is the distance between the color points in the three dimensional L^*, a^*, b^* coordinate system.) This rapid period accounts for ca. 70% of the total color change. Even faster is the color change of locust wood, where the essential color changes are finished after 25 hrs of irradiation. The E^* changes in these experiments were generated mainly by the change of lightness (ΔL^*). (The development of ΔL^* is not presented here, since the curves of ΔE^* and ΔL^* were very similar.)

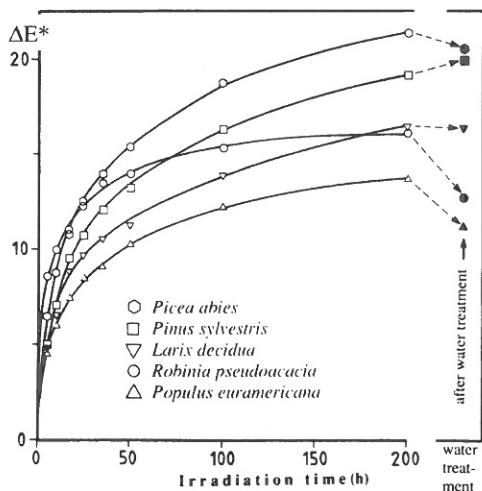


Fig. 2. Change of total color difference ΔE^* as a function of UV irradiation time. (Water treatment was conducted after 200 hours of UV irradiation.)

Also informative is the presentation of the results in a coordinate system, in which the Δb^* values (shift to yellowness) are plotted vs. Δa^* values (shift to redness) (Fig. 3). An intense yellow-shift is always discernible with the exception of locust, which shows an additional shift to red. These results are an instrumental confirmation of the visual impression about the wood color. However, the experience that intensity and route of the color change vary according to wood species (Yoshimoto 1989) is confirmed only in parts. The ΔE^* curves are indeed different for the wood samples investigated, but the plots in the a^*, b^* coordinate system show a nearly identical course of yellowing for the three softwoods. The poplar wood also behaves analogously to the softwoods in this regard. Only locust wood shows a deviating color development with the shift to a reddish color tone.

The question about the reason of color changes of woods upon UV irradiation cannot be answered in a definite way. Since locust contains a lot of extractives – its robinetin contents, for example, amounts to 2% according to Freudenberg and Hartmann (1954) – it is reasonable to argue that its yellow-reddish color is closely related to the chemistry of its extractives. Yoshimoto (1989) refers to specific extractives in woods which display distinct color change on irradiation, such as leucorobinetidin, various tetra-hydroxystilbenes, rengasin, sequirin, flavan $4\beta\text{-ol}$, etc. Yazaki *et al.* (1994) also called attention to the fact that there is a direct correlation between the

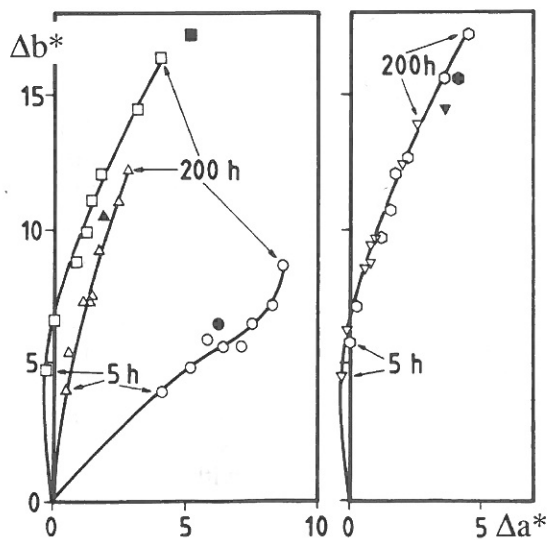


Fig. 3. Plots of Δb^* (yellowness) versus the Δa^* (shift to red) values after 5, 10, 17, 25, 35, 50, 100, 200 hours of UV irradiation. (The filled marks represent the results obtained after water treatment of 200h irradiated samples.) \circ locust; \triangle poplar; \square scots pine; \diamond spruce; ∇ larch.

redness values (a^*) and the extractive contents of blackbutt (*Eucalyptus pilularis*) veneers. The yellowing of the other wood species, which are poorer in extractives, is certainly primarily governed by the photochemistry of the essential wood components, and particularly of lignin. Nimz (1973) referred to leuco chromophoric systems within the structure of a hardwood lignin and their potential contribution to colored substances under alkaline or acidic conditions or oxidative photocyclization. The β -1 units, for example, can turn into colored derivatives of the methylenquinone or phenanthrene type. Phenylcoumaran and pinosresinol dimers within the lignin macromolecule can also give rise to numerous conjugated double bond systems with intense colors.

It is well established that the yellowing of TMP or pulp – even with low lignin content – is due the residual lignin (Heitner and Schmidt 1991). In this context is appropriate to recall the experimental conditions of this work: The samples were submitted to irradiation at 40 °C under semi-dry conditions (50 % rel. humidity). Under these conditions the transport of extractives, low molecular weight degradation products of the essential wood components, or inorganic compounds – which can participate in catalytic reactions – through capillary water is limited. (Note, however, that the photochemical dehydration can continuously supply water.) Therefore, the probability is high that the yellow color is formed literally in situ reactions, in which the natural structures are slightly modified without being moved to longer

distances or involved in complicated “wet chemistry”. In the next publication it will be demonstrated that very different color reactions occur in the presence of humidity.

To simulate the leaching of chromophores by rain in outdoor weathering, the samples were submerged for one day in distilled water after 200 hrs of irradiation. Then the samples were dried in a vacuum desiccator and the color measurement was repeated. The visible impression of faded colors after watering – particularly obvious in the case of locust, poplar and spruce – was also readily apparent from the ΔE^* values in Figure 2. In the a^* , b^* coordinate system (Fig. 3), the color points moved towards the origin after the water treatment of locust, poplar and spruce, which means that the color tone of these samples was partly reversed toward the original color. The opposite shift direction was observed for larch and pine, i.e. these woods are prone to additional yellowing after water treatment. Altogether, the color changes after water extraction were weak, which imply that the main part of the chromophores are oligomers fixed in the cell wall matrix.

DRIFT spectroscopy

Band assignment

As pointed out in the introduction, the DRIFT spectra of solid woods are suitable to reveal typical group characteristics which permit to differentiate between softwoods or hardwoods. Individual spectral features

Table 1. Position of the bands of DRIFT spectra of five wood species as detected by the automatic “peak peaker” of the spectrometer at 4 cm⁻¹ resolution and band assignments

#	<i>Beech</i>					Assignment
	Pine cm ⁻¹	Spruce cm ⁻¹	Larch cm ⁻¹	Locust cm ⁻¹	Poplar cm ⁻¹	
1	3468	3464	3476	3499	3462	3520 OH stretching
2	2929		2932	2937		2957 CH and CH ₂ stretching (asymm.)
3	2905	2904	2904	2908	2904	2915 CH and CH ₂ stretching (symm.)
4	1740	1741	1740	1749	1741	1750 CO stretch. in unconjugated ketone, acetyl, carboxyl groups, (e.g. in xylans)
5	1662	1662	1655	1665	1655	1655 H ₂ O; CO stretching in conjugated systems
6	1598	1598	1599	1599	1597	1603 aromatic skeletal breathing with CO stretch
7	1510	1509	1510	1507	1506	1510 aromatic skeletal
8	1457	1457	1457	1465	1461	1465 C-H deformation (asymm.)
9	1427	1426	1427	1428	1426	1436 C-H deformation (asymm.)
10	1373	1373	1372	1380	1372	1387 C-H deform. (symm.); here used as IS
11			1333	1337	1334	1392 C-H deform., C-OH stretch., syringyl ring
12	1319	1319				CH ₂ wagging, C-H deformation
13	1275	1274	1278	1273	1274	1277 C _{aryl} -O, guaiacyl ring breathing with CO stretching
14	1237	1238	1238		1244	— C _{aryl} -O stretching, OH i.p. bending, acetyl in xylans
15	1170	1167	1174	1172	1171	1174 C-O-C stretching (asymm.) <i>in cell and hemicell</i>
16	1132	1132	1134	1137	1136	1138 C-O-C stretch. (symm.); arom. C-H i.p. deformation; glucose ring vibration
17	1047	1046	1046			1036 C _{alkyl} -O
18	1003	1003	998	994	1002	1006 C _{alkyl} -O
19	898	898	898	900	898	906 C ₁ -H deformation of cellulose; frequently used as IS
20	< 800	< 800	< 800	< 800	< 800	pyran ring vibration

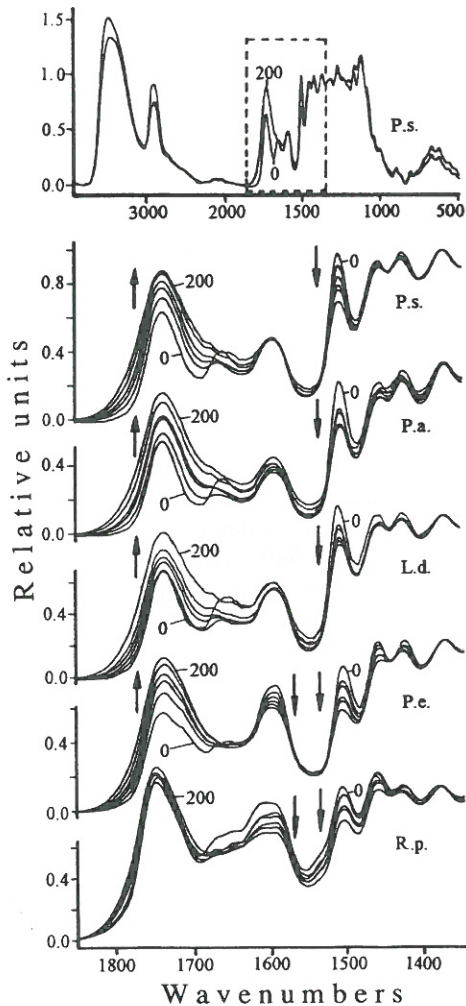


Fig. 4. Top: DRIFT spectrum of *Pinus sylvestris* before (0) and after 200 hrs of UV irradiation (200) in the range of 4000 to 500 cm^{-1} . Below: DRIFT spectra of various wood species after 10, 25, 50, 100 and 200 hours of UV irradiation in the range of 1900 to 1300 cm^{-1} . P.s.: *Pinus sylvestris* (scots pine); P.a.: *Picea abies* (spruce); L.d.: *Larix decidua* (larch); P.e.: *Populus euramericana* (poplar); R.p.: *Robinia pseudoacacia* (locust).

of wood species having different OMe or hemicellulose content can also be perceived to a certain extent. To demonstrate the complexity of wood spectra, the entire spectrum of *Pinus sylvestris* is presented in the top of Figure 4 before and after UV irradiation. Around twenty major bands are roughly discernible in DRIFT spectra without using mathematical resolution enhancement. The position of the IR bands are listed in Table 1 together with their assignments. The latter can be given only in general terms since wood spectra are the result of heavily overlapping bands of lignin, hemicelluloses, and cellulose. The bands typical for lignins are assigned according to Hergert (1971) with modification of Collier *et al.* (1992) in the range of aryl-alkyl ether C-O stretch-

ing. Fengel and Ludwig (1991) recently summarized the cellulose band assignments of the literature. A comparison of the band positions of IR spectra of wood recorded by the transmission (KBr) technique and various diffuse reflectance techniques is presented by Faix and Böttcher (1992). According to Németh and Faix (1994), the bands of DRIFT spectra of hardwoods show an average shift of 12cm^{-1} to higher wavenumbers in the range of 1164–961 cm^{-1} which is a manifestation of the anomalous effects of DRIFT spectroscopy.

Qualitative changes

Figure 4 demonstrates how the spectral range between 1900 and 1300 cm^{-1} is influenced by UV irradiation. (The rapid disappearance of the band at 1650 cm^{-1} in the reference spectrum is interpreted as loss of water, and will not be discussed.) Arrows indicate the direction of the relevant changes: The composed carbonyl band between 1900 and 1690 cm^{-1} is increasing and broadening, the aromatic skeletal vibration around 1510–1515 is decreasing. The same is true for the 1600 cm^{-1} band (aromatic skeletal vibration together with CO stretching) in the case of hardwoods. These phenomena are well documented in the literature (Feist and Hon 1984; Faix *et al.* 1992; Németh *et al.* 1992; Németh and Faix 1994; Kimura *et al.* 1994). In this work, however, we were

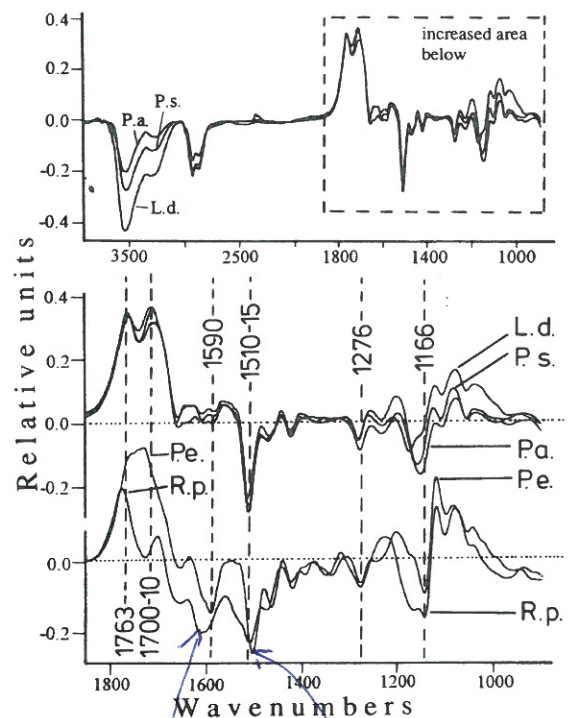


Fig. 5. DRIFT difference spectra of the type "irradiated wood minus blank" of various wood species after 200 hours of UV irradiation (for abbreviations see Fig. 4).

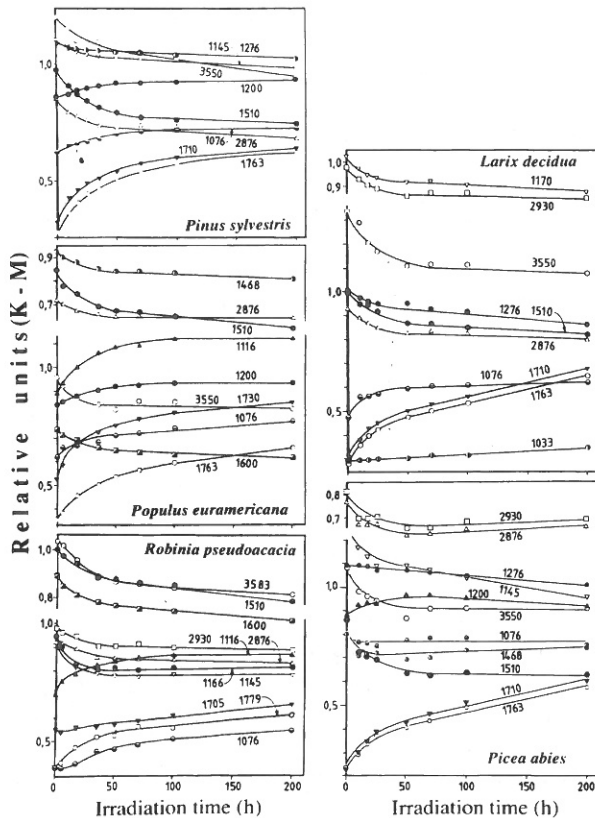


Fig. 6. Changes in DRIFT band intensities as a function of UV irradiation time.

looking for additional information retrievable from DRIFT spectra of solid wood surfaces in the following way: Firstly, the difference spectra "spectra after 200 hrs of irradiation minus spectra of original wood" were recorded in order to detect the wavenumbers at which the maximal spectral changes occur (Fig. 5). Secondly, the relevant intensity changes – measured at wavenumbers shown in Figure 5 – were plotted vs. the irradiation time (Fig. 6).

Several spectral changes can be observed from the difference spectra in Figure 5. The OH bands are decreased at 3500cm^{-1} and, to a less extent, at 3200cm^{-1} . This is partly an effect of drying, i.e. the elimination of water from the wood's capillary systems. However, the results should preferably be interpreted as manifestations of the loss of OH groups followed by dehydration upon UV irradiation. Dehydration belongs to the plausible reactions, in the course of which double bonds – responsible for colored compounds – are formed. The formation of esters and lactone rings, also common features of photodegradation, occur via water loss and OH group

consumption. The OH band region in the IR spectra of woods is dominated by the OH group of cellulose and hemicelluloses. Intramolecular [O(2)H...O(6) and O(3)H...O(5), above 3350cm^{-1}] and intermolecular [O(6)H...O(3), below 3350cm^{-1}] vibrations of cellulose can be differentiated (Fengel and Ludwig 1991). The intensity loss at 3500cm^{-1} can be attributed to the rupture of intramolecular OH bonds of cellulose, i.e. it can be an expression of the change of the secondary structure of cellulose.⁴

The CH_n valence vibrations at 2930 and 2905cm^{-1} are supposed to be stable upon photoirradiation (Forsskähl and Janson 1992). The intensity loss in this range can be an artifact, which is related to the low resolution in this range, because the CH_n band is not well separated of the (decreasing) OH band. But it could be partly due to demethylation, elimination of CH_2OH groups both from lignin and polysaccharides, and formation of new $\text{C}=\text{C}$ bonds in photocyclized ring systems.

The enlarged segments of the difference spectra in Figure 5 reveal an intensity increment in the carbonyl region in two distinct wavenumber ranges: at 1763m^{-1} (CO stretching in unconjugated ketones, carboxyl groups, and lactones) and at $1700\text{--}1710\text{cm}^{-1}$ (CO stretching of various functional groups). The latter probably originates from unconjugated structures as well because conjugated CO stretching vibrations and quinone carbonyl groups can mainly be expected between $1600\text{--}1690\text{cm}^{-1}$. In this region, however, only minimal changes are perceptible for softwoods and even intensity decrease can be observed for hardwoods. At this point one should bear in mind that color change (yellowing) is the result of the formation of conjugated double bonds. The rise of new CO bonds, perceptible in the DRIFT region between 1650 and 1770cm^{-1} does not necessarily mean the formation of colored compounds with conjugated double bonds. One should also remember that IR (and DRIFT) spectroscopy does not lend itself for trace analysis. Thus the lack of pronounced bands between 1690 and 1600cm^{-1} does not cogently imply the absence of quinones or conjugated CO bonds. Quinones can cause an intense color by very low concentrations which are below the detection limit of DRIFT. On the other hand, it is possible that the decrease of aromatic skeletal vibrations in the 1600cm^{-1} region is more pronounced than the increment of conjugated CO bonds, i.e. the decrease of the former may have superimposed the increase of the latter.

The lowering of the aromatic skeletal vibrations at 1510 to 1515cm^{-1} must be accompanied by diminishing guaiacyl vibrations at 1276cm^{-1} which indeed can be observed. While considering the 1276cm^{-1} region, however, one should bear in mind that here the CO

⁴ Hydroperoxidation, as claimed by Hon and Feist (1992), could not be observed in the OH region. The "hydroperoxide" bands observed by these authors are probably artifacts.

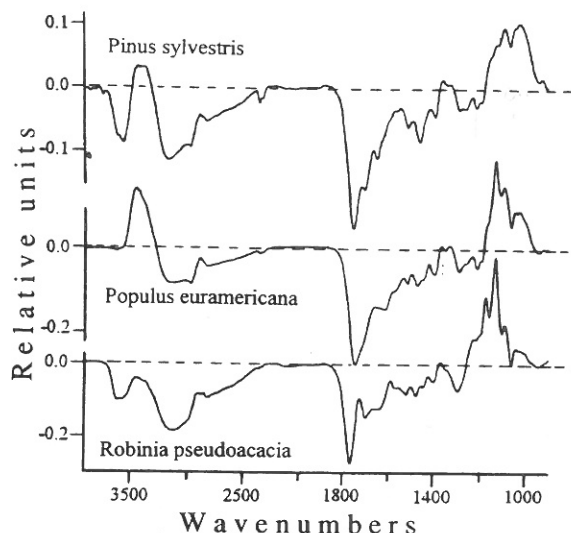


Fig. 7. DRIFT difference spectra of 200h UV irradiated woods "water treated wood minus wood before water treatment" illustrating the effect of water extraction to photooxidized compounds.

stretching and the guaiacyl ring vibration superimpose each other. The intensity decrease in the range of 1100 to 1200cm^{-1} (C–O–C and C–O–H) is probably the expression of ether splitting and OH group consumption followed by dehydration during UV irradiation, as discussed already for the 3500cm^{-1} spectral range. Finally, the absorption increment below 1100cm^{-1} (various C–O–C stretching of polysaccharides) can indicate a preferential destruction of aromatic structures by UV light causing a relative concentration increase of non-aromatic compounds on the wood surface.

The DRIFT difference spectra "water treated sample minus sample after UV irradiation" in Figure 7 inform about the chemical nature of the hydrophilic compounds formed during photodegradation. The broad negative bands between 1600 and 1800cm^{-1} with a maximum at 1780cm^{-1} exemplify the elimination of carbonyl and carboxyl groups for all wood species. The broad negative band in the OH stretching region between 3400 and 2100cm^{-1} is also indicative of OH stretching of carboxylic acids. Obviously, the photodegradation leads to hydrophilic substances with low molecular weights, which contain carboxylic acids and which can easily be removed by water extraction.

Quantitative evaluation

As indicated in Table 1, the band no. 10 (a C–H band around 1373cm^{-1}) was used as "an internal standard", i. e. its intensity was adjusted after baseline correction to 1.0. The small band no. 19 (C₁–H deformation of cellulose) is frequently used for standardization

(Horn *et al.* 1994). However, the band no. 10, which was also used by Forsskåhl and Janson (1992), is advantageous due to its high intensity and its central position in the spectrum. The advantage of this evaluation mode based on "heights" over the integral method is that the data generation is not confined to spectral ranges with distinct minima which are necessary as integration limits.

The most meaningful intensity changes were plotted vs. the irradiation time in Figure 6. (Note that the intensities were taken at wavenumbers, which were indicated by the difference spectra as relevant, irrespective of whether the spectra have a maximum at these points or not.) All diagrams represent coherent, continuous dependencies in which most curves flatten after 50 hrs irradiation time. Then nearly linear correlations are visible. The various intensities of different wood samples show individual characteristics. Accordingly, the band "heights" of normalized spectra have diagnostic value for monitoring ageing. The beveling curve profiles indicate that the photooxidation leads to stable chemical structures which are less susceptible to further reactions. The photooxidized layer formed on the upper $200\mu\text{m}$ surface protects the deeper layers.

As familiar from previous publications, the intensities of the carbonyl bands at 1710 and 1763cm^{-1} and the aromatic skeletal vibrations at 1510cm^{-1} show very typical profiles when plotted against the irradiation time (Faix *et al.* 1992; Németh *et al.* 1992; Németh and Faix 1994; Kimura *et al.* 1994). The two curves behave like mirror images, i. e. the CO bands are increasing to a similar extent as the aromatic band is decreasing, which suggests a strong correlation between the underlying photochemical events. These observations are associated with opening of aromatic rings via the muconic acid splitting mechanism, in the course of which carboxylic acids and/or their lactones are formed which give rise to the CO vibration in the range above 1700cm^{-1} (Forsskåhl and Janson 1992; Németh and Faix 1994). On the other hand, carbonyl and carboxyl group containing compounds can also arise from polysaccharides upon irradiation, as demonstrated IR spectroscopically by Tylli *et al.* (1993). Judged by the CO band profiles, the pace of oxidation is slowing down around 200 hrs irradiation time, but the oxidation potential is not yet exhausted. A closer look at the CO band development of the hardwoods demonstrates the advantages of the separate consideration of the higher (1763 – 1780cm^{-1}) and lower wavenumber range (1710 – 1730cm^{-1}). The intensity profiles of the sub-bands are always close together for softwoods, but in the case of hardwoods the deviating courses of the sub-bands are manifestations of various types of CO group formation which obey different kinetic rules.

Besides the region between 1900 and 1400 cm⁻¹, the OH stretching mode around 3550 cm⁻¹ shows distinct curves. The rapid initial decrease and a slow lowering after 50 hrs is typical for this band. The nearly linear decrease of the 1276 cm⁻¹ band (guaiacyl ring and CO) is also worth to mention in this context. In view of the ambiguous band assignments of woods in the fingerprint region due to overlapping, the quantitative changes of the other bands are too small to provide a basis for far reaching conclusions. However, it can be concluded that a DRIFT spectrum in the middle IR range is a useful supplementary method to other techniques (e.g. diffuse reflectance in the near IR, or in the UV-VIS region) for monitoring of weathering.

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