Isolation and Identification of Residual Chromophores in Cellulosic Materials

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Summary: A general procedure was developed for the isolation of residual chromophores in or on cellulosic material, which were hitherto inaccessible to structure elucidation due to their extremely low content in the ppb concentration scale. It is applicable to cellulosic pulp, cellulosic fibers (viscose, Lyocell) and cellulose derivatives (acetate, carbonyl-labeled cellulose) as well. The chromophore identification comprises treatment of the cellulosic material with boron trifluoride – acetic acid complex (BF_3*2HOAc) containing sulfite, chromatographic separation of the resulting chromophore-containing mixture, and structure determination of the main constituents by NMR / MS and comparison to authentic samples. Both adsorbed and covalently bound aromatic and quinoid compounds are selectively released by the treatment. Covalent ester, ether and secondary alkyl links between chromophore and cellulose are broken.
Two cellulosic example substrates have been analyzed for their chromophore content: Lyocell fibers and non-bleached viscose fibers, and up to eleven chromophores per sample have been identified.

Keywords: cellulose; chromophores; fibers; pulp; quinines; trace analysis

Introduction

The cellulose material in cellulosic fibers (viscose, Modal, Lyocell) or cellulose derivatives (esters, ethers, nitrates) has undergone a large number of process steps. The general process stages of pulping and bleaching, which are required to provide the starting cellulose free from non-cellulosic wood components, are followed by the process-specific manufacturing steps. Apart from chemically pure cellulose – as for instance present in bacterial cellulose – cellulosic pulps, fibers and derivatives contain minute amounts of chromophoric compounds. These chromophores either originate from the starting pulp, or they are newly formed during the subsequent processing stages of fiber formation or derivatization. The concentration of these chromophores is generally extremely low, mostly in the ppm to ppb range. However, due to their high extinction coefficient, the chromophores are nevertheless easily noticed as an off-white discoloration or yellowing

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effect, especially as the human eye is very sensitive in the yellow spectral range. The chromophore content has been traditionally quantified as "brightness", which – as a parameter inversely related to yellowing – was measured as UV absorbance at 457 nm.[1]

The chemical nature of the chromophores in cellulosic fibers and derivatives has remained largely unclear to date. The chemical identification of the trace compounds is rendered difficult by their low concentrations and by the large number of different compounds contributing to the overall discoloration effect. In addition, the chromophores might be bound to the cellulose matrix in different ways, either covalently or just simply by adsorption, and they might be present in different locations, either on the surface or in the interior. Isolation and chemical identification of individual chromophores in cellulosic fibers has not been described so far.

In this study, we wish to communicate a novel chemo-analytical approach, by which it now became possible to selectively release aromatic and quinoid chromophores from cellulosic materials, which were subsequently separated and analyzed.

Experimental

General. All chemicals were available from commercial suppliers and of the highest purity available. Sodium sulfite was finely powdered shortly before use.

A bleached beech sulfite pulp (kappa number 0.36, ISO brightness 87.8, carbonyl content 23.8 μmol* g^{-1}, cuen viscosity 565, Mn 41.27, Mw 289.8)[2] was used as the starting material for the production of Lyocell fibers and viscose fibers.

Chromophore extraction with BF_3*2 HOAc. In a round-bottom flask, the cellulosic material (50 – 100 g) and sodium sulfite (0.50 g) were suspended in BF_3-acetic acid complex (150 mL) and dichloromethane (350 mL). The vessel was closed and shaken at room temperature for 48 h. The solids were separated on a filter, pressed out and washed with small amounts of glacial acetic acid. The organic phases were combined, and the pressing – washing cycles were repeated until the solids appeared bright white. After addition of methylene chloride (100 mL) containing α-tocopherol (vitamin E, 1.00 g), water (1.00 L) was added, and the mixture was vigorously shaken. After phase separation, the extraction of the aqueous phase by CH_2Cl_2 (100 mL) was repeated four times. The combined organic extracts were washed carefully with water and dilute aqueous $NaHCO_3$ solution until acid-free, and were dried over Na_2SO_4. The organic phase was concentrated *in vacuo* at r.t. to a volume of about 5 mL. Higher temperatures must be avoided as they

promote condensation reactions. MeOH (50 mL) and 2 mL of 2 M ethereal HCl were added. The mixture was refluxed for 5 min, cooled to r.t., and evaporated. The dark oily residue was chromatographed on basic aluminum oxide (Brockmann grade I). Elution was performed with n-hexane to remove the stabilizer and polymeric, highly condensed chromophores, followed by ethyl acetate / toluene (v/v = 1 : 9), ethyl acetate and ethyl acetate / methanol (v/v = 1 : 1). The fractions were analyzed by MS and NMR, the latter only in the case of sufficient material available. Unambiguous identification of the compounds was accomplished by comparison with authentic compound samples, which were either commercially available, or synthesized according to standard techniques.

Results and Discussion

Chromophore isolation by BF_3 * 2 HOAc – general aspects. Chromophores in/on cellulosic fibers generally proved to be completely resistant towards extraction with various organic solvents, regardless of being polar, non-polar, protic or non-protic. This indicated either a covalent link of the chromophores to the fibers, or at least strong adsorptive binding. In preliminary experiments, we had established that the UV spectrum of a methanolic chromophore extract reversibly changed upon reduction and exposure to air, accompanied also by a clearly visible color change between brown and faint yellow. This was indicative of the presence of phenolic compounds, which underwent phenol-to-quinone conversions and oxidative coupling reactions. We therefore searched for a method that was able to specifically release aromatics from complex matrices, largely independent of how the aromatic was attached. For that purpose, we elaborated a procedure according to which the cellulosic material was treated with boron trifluoride – acetic acid complex, BF_3*2HOAc, containing small amounts of sodium sulfite. This reagent cleaves ester and ether and carbon-carbon bonds extending from aromatic systems. The selectivity of the method is due to the high complexation tendency of the BF_3 complex with electron-rich aromatic systems. In addition, quinoid systems are reductively converted by sulfite into the corresponding aromatics, and then similarly released. The approach has some parallels to an analytical technique in lignin chemistry known as nucleus exchange, which comprises treatment of the lignin material with BF_3 – phenol complex to replace non-condensed lignin aromatics by phenol moieties in Friedel-Crafts type transalkylations. The present approach has the advantage to use the better-to-handle acetic acid complex instead of the ill-defined phenol adduct with its largely unknown chemistry.[3] For separation of the

isolated chromophores a technique from the analysis of stabilizer reaction products in polymeric plastics was adapted, the so-called "staircase adsortion", which is optimized for the separation of phenolic and quinoid compounds.

It should be noted that in some cases, such as hydroxyl-*p*-benzoquinones or β-hydroxy-[1,4]naphthoquinones, the reducing power of the medium was insufficient, so that the quinones were directly released – but not the corresponding aromatics. This behavior is due to the high stability of these quinones which originates either from strong hydrogen bridges in acidic solutions or from pronounced mesomeric stabilization in basic media, which make these compounds rather redox-inert. The sulfite present generates a reducing medium both in the extract and in the contacting gaseous phase due to the slow release of SO_2. Thus, oxygen is barred from entering the extraction solvent and phenol oxidation or coupling is prevented so that the nature of the released chromophores is preserved and a nearly colorless extract resulted.

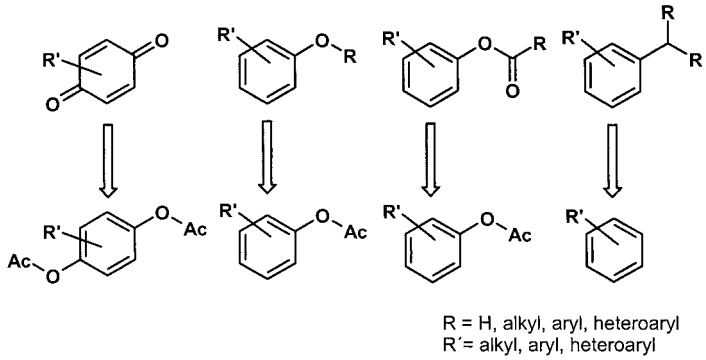

Figure 1. Schematic overview of the chromophore release with BF_3*2HOAc.

An additional benefit with regard to oxidative stability during extraction is the fact that phenolic and aliphatic hydroxyls are acetylated, giving acetates. These acetates are much more stable towards oxidation than the corresponding free phenols, which greatly facilitates the handling during the separation procedure. Moreover, the antioxidant added during the separation procedure acts as a radical scavenger and sacrificial substrate, its oxidation being preferred over oxidation of other phenols present. As antioxidant α-tocopherol, the main component of vitamin E, was used, which is distinguished by its high antioxidative efficiency and its superb separability, which is due to its strongly lipophilic isoprenoid side chain. Thus, the antioxidant and its reaction products did not interfere with

the chromatographic separation of the much less lipophilic isolated chromophores. After separation of the released chromophores from the extraction mixture, a hydrolytic step can be used to improve further chromatographic separation: treatment with gaseous HCl in MeOH regenerated the free hydroxyls by cleaving the acetates. The reactions brought about by BF_3*2HOAc treatment are schematically summarized in Figure 1.

To demonstrate that the chromophores are not artifacts produced during the release / extraction procedure due to the action of the Lewis-acidic reagent, a cotton linters sample was used as a blank: no chromophores were isolated in this case. In addition, also the extract from a second, extensively prolonged BF_3*2HOAc–treatment of cellulosic materials[4] provided no second charge of chromophores in isolable amounts. This confirmed on one hand that no "new" chromophores were generated during this subsequent treatment, and demonstrated on the other hand that the release after the first treatment was quite complete. For Lyocell fibers, it was shown that the chromophoric compounds isolated were independent of the pulp source. Lyocell materials from either a bleached beech sulfite pulp (see experimental section) or a bleached Eucalyptus prehydrolysis kraft pulp afforded the same chromophores, confirming that the chromophores isolated were formed in later processing stages, but were not contained in the pulps from the beginning. This result cannot be generalized, since especially for pulps containing residual lignins or large amount of hemicelluloses the structure and number of chromophores generated could well be different.

Chromophores in Lyocell fibers. Lyocell fibers are the product of the modern, environmentally benign Lyocell technology, according to which cellulose is directly dissolved in a melt of *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) at about 100°C, giving a tractable spinning dope that is spun into air and water. The amine *N*-oxide is able to dissolve cellulose without the need of any chemical derivatization, and acts thus as a physical, recyclable and environmentally fully compatible cellulose solvent. Due to side reactions in the spinning dope between the strongly oxidizing solvent NMMO and the solute cellulose,[5] Lyocell material contains trace amounts of chromophores, which might impair the brightness properties of the resulting fibers.

Using the above chromophore isolation procedure, six compounds as shown in Figure 2 (upper row) were determined in the extract from standard Lyocell fibers. From Lyocell material which had suffered prolonged NMMO treatment (2 h in NMMO at 130°C or 24 h

in NMMO at 100°C) and thus exhibited an increased chromophore content, five additional chromophores were isolated (Figure 2, lower row). Each of the eleven compounds in Figure 2 and all those reported in the following were unambiguously identified based on the MS and NMR (^{1}H and ^{13}C) spectra, and on comparison with authentic samples, which were either commercially available or synthesized according to standard techniques.

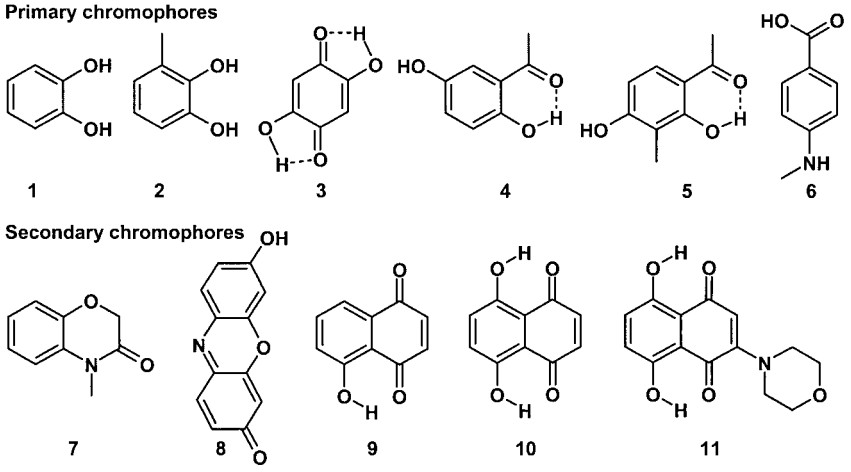

Figure 2. Chromophores isolated from Lyocell fibers.

Compounds **1** – **5** are typical condensation products which can generally be obtained mainly from monosaccharidic carbohydrates upon either thermal, acidic or basic treatment, so-called "Theander-products".[6] In the special case of Lyocell material, they have been formed by cellulose degradation during the thermal conditions of Lyocell processing.[7] Compounds **1** – **5** can be considered as primary chromophores, as their formation is caused just by the thermal treatment and is thus largely independent of the reaction medium present. In the material having undergone prolonged thermal treatment in NMMO, these chromophores formed higher condensed chromophoric structures (**7** – **11**) under the prevailing more drastic and oxidative conditions. Formation of these secondary chromophores is no longer independent of the reaction medium. Compounds **6** – **8** and **11** proved the participation of NMMO or NMMO degradation products, respectively, in chromophore generation since these compounds contained nitrogen, of which NMMO was the only possible source.

It has long been known that alkaline, acidic, or thermal treatment of monosaccharides and also of cellulose in the presence of oxygen or other oxidants gives rise to EPR-active species after only a few minutes reaction time. The most prominent of the radicals produced is 2,5-dihydroxysemiquinone[8], which upon further oxidation readily affords **3**. This compound, which was found in all cellulosic materials investigated so far, can be seen as an elementary "chromophore precursor structure", which can on the one hand readily be degraded to smaller, reactive fragments, but on the other hand can also easily condense to larger structures, so that in any case other chromophores and highly condensed structures are formed from **3** by a complex interplay of fragmentation / condensation sequences.

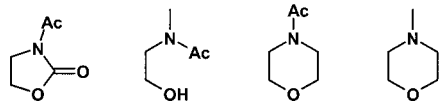

Figure 3. Non-chromophoric degradation products of NMMO isolated from Lyocell fibers.

In addition to the aromatic and quinoid compound in Figure 2, four non-chromophoric degradation products of NMMO (**12** – **15**) were found. The *N*-acetyl groups in these compounds are not genuine, but originate from reaction with the BF_3*2HOAc reagent. Morpholine and *N*-methylmorpholine have been known for long as the major degradation products of NMMO.

Preliminary model experiments on chromophore removal used a mixture of the secondary chromophores **6** – **11** being 1 mM of each component. This chromophore mix showed a dark violet color in acidic medium (pH 1), but was deep black in basic solution (pH 10). This color intensification was expected as most of the compounds were phenolics which experience a bathochromic shift of their UV/VIS spectrum upon phenol – phenolate transition. The chromophore mix was subjected to several simulated bleaching stages using peracetic acid, performic acid, a P stage (H_2O_2, pH 10, 70°C, 10 min), an H stage (HOCl, pH 11, 50°C, 10 min) and sodium borohydride reduction (pH 11, 70°C, 15 min). Only peroxide and hypochlorite caused permanent chromophore destruction, the solutions became nearly colorless after the treatment. In the case of percarboxylic acids, the bleaching was insufficient. Reduction with $NaBH_4$ gave an interesting effect: treatment of the chromophore mix with $NaBH_4$ gave a noticeable decolorization of the solution. When this reduced sample was shaken with air, the original color returned as the oxygen present

caused re-oxidation. Upon standing, this color disappeared again, since reduction by excess $NaBH_4$ proceeded once more. This oxidation – reduction cycle could be repeated several times as long as oxygen and $NaBH_4$ were present. The gist of the model experiments was that oxidative chromophore destruction was by far more effective than reductive one, with hydrogen peroxide or hypochlorite being more efficient than percarboxylic acids. It should be noted that the results of these model bleaching trials are not necessarily representative of fiber material or pulp. In our model case, an equimolar, rather concentrated mixture of six selected model chromophores in homogeneous solution was used, which is completely different from the situation in fibers or pulp.

Chromophores in non-bleached viscose fibers. During production of viscose or Modal fibers (rayon), cellulose is exposed to several rather "drastic" conditions. The starting dissolving pulp is treated with strong alkali, the resulting alkali cellulose undergoes a ripening step, where mainly homolytic degradation reactions are used to adjust the molecular weight distribution. This is followed by a heterogeneous reaction with CS_2, followed by dissolution to give the viscose dope, and finally coagulation in an acidic spinning bath (H_2SO_4) containing metal salts. These treatments leave their traces in the form of chromophores which are usually removed by a final bleaching and washing treatment of the fiber. For the present study of the generated chromophores, standard viscose fibers were produced from a beech sulfite pulp, but the bleaching stage was omitted and just a thorough washing was performed. According to the novel procedure, eleven chromophores were isolated and identified (Figure 4).

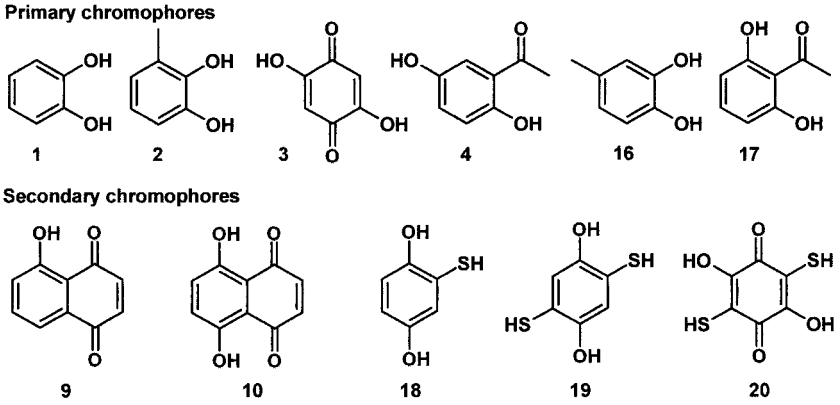

Figure 4. Chromophores isolated from non-bleached viscose fibers.

A comparison of Figures 2 and 4 showed that six of the chromophores found in Lyocell material (see above) were also detected in viscose (compounds **1** – **4** and **9** – **10**). Furthermore, two additional primary chromophores (**16**, **17**) and three additional, sulphur-containing secondary chromophores (**18** – **20**) were isolated. As in the case of Lyocell chromophores, the primary chromophores are formed by condensation reactions of (monosaccharidic) carbohydrates, although the primary viscose chromophores were supposed to be caused by alkali-promoted reactions, unlike primary Lyocell chromophores that result from thermal condensations. The three sulphur-containing secondary chromophores proved that also in the viscose case, process chemicals are involved in chromophore formation. Here was CS_2 the sole source of sulfur.

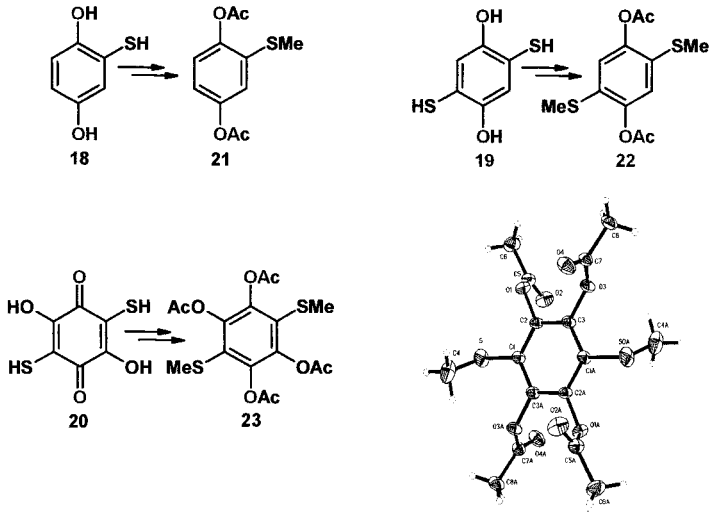

Figure 5. Structure determination of sulphur-containing chromophores from non-bleached viscose fibers: reactions and example crystal structure (20% thermal ellipsoid plot) of hexasubstituted benzene **23**.

Identification of compounds **18** – **20** was rather intricate, as they were quite sensitive towards oxidation, readily forming disulfides and condensation products of higher molecular weight. Quinone **20** was not reduced by sulfite during chromophore isolation, but remained as quinone, a behaviour analogous to 2,5-dihydroxybenzoquinone (**3**). Compounds **18** and **19** were present in the reduced aromatic form as *O*-acetates, the mercapto groups were not affected by acetylation. Also the acetates were rather labile and

prone to oxidation, as the SH groups remained unprotected. For final identification, **20** was reduced, *O*-acetylated and subsequently *S*-methylated; **18** and **19** were only *S*-methylated. The resulting products (**21** – **23**) were white, crystalline substances, from which crystal structures were obtained as an unambiguous proof of their chemical constitution. The crystal structure of **23** is shown in Figure 5 as an example.

The formation of the sulphur-containing quinones in the viscose process is likely to proceed by addition of H_2S to the parent benzoquinones followed by re-oxidation, a sequence known to proceed rather easily. Monoaddition of H_2S to *p*-benzoquinone with subsequent oxidation would afford 2-mercapto-*p*-benzoquinone, while bisaddition yielded 2,5-dimercapto-*p*-benzoquinone, which upon chromophore isolation produced **18** and **19**, respectively. Bisaddition of H_2S to 2,5-dihydroxybenzoquinone (**3**) yielded 2,5-dihydroxy-3,6-dimercapto-*para*-benzoquinone (**20**), which is an illustrative example of how secondary chromophores are formed from primary ones.

Yet another chromophoric byproduct from non-bleached viscose fibers was identified by crystal structure analysis: after chromatographic purification it formed orange-colored prisms: [1,3]dithiole-2-thione (vinylene trithiocarbonate, **24**). It is likely that trithiocarbonate – a major transformation product of the process chemical CS_2 – was involved in its formation, although at the moment the exact formation pathway and the origin of the C_2-unit can only be speculatively described. For this reason, 24 can be assigned neither to primary nor to secondary chromophores.

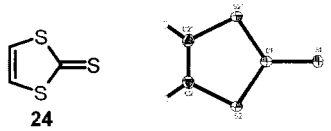

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Figure 6. Vinylene trithiocarbonate, a chromophoric reaction product of CS_2, isolated from non-bleached viscose fibers.

Comparison: Non-bleached viscose fibers *vs.* Lyocell fibers. A comparison of the chromophores isolated from Lyocell and from non-bleached viscose fibers is shown in Table 1. It is evident that the structures of primary chromophores are equal or largely similar for both cellulosic sources. This appears reasonable as these compounds were formed by "Theander-type" condensations of carbohydrates, which are known to afford similar products under either thermal, acidic or basic conditions.[6] Secondary chromophores were formed by further condensations of the primary chromophore

precursors. In this category, there was a minor fraction of hydroxyl-[1,4]naphthoquinones which was found in both Lyocell and viscose. The major fraction was formed under involvement of process-specific chemicals, *i.e.* NMMO and nitrogen-containing degradation products for Lyocell or CS_2 and sulfur-containing degradation products for viscose. Additionally found were non-chromophoric, *N*-containing saturated compounds (Lyocell) and a chromophoric, S-containing heterocycle (viscose).

Table 1. Summary of isolated chromophoric compounds from different cellulosics.

	In both viscose and Lyocell	**Only in Lyocell**	**Only in viscose**
Primary chromophores	Catechol (**1**), 3-methylcatechol (**2**), 2,5-dihydroxybenzoquinone (**3**) 2,5-dihydroxyacetophenone (**4**)	2,4-Dihydroxy-3-methylacetophenone (**5**)	4-Methylcatechol (**16**), 2,6-dihydroxyacetophenone (**17**)
Secondary chromophores	5-Hydroxy-[1,4]naphthoquinone (**9**) 5,8-Dihydroxy-[1,4]naphthoquinone (**10**)	4-Methylaminobenzoic acid (**6**), 4-methyl-4*H*-benzo-[1,4]oxazin-3-one (**7**), 7-hydroxyphenoxazin-3-one (**8**) 5,8-dihydroxy-2-morpholin-4-yl-[1,4]naphthoquinone (**11**)	2-Mercaptohydroquinone (**18**), 2,5-dimercaptohydroquinone (**19**), 2,5-dihydroxy-3,6-dimercaptobenzoquinone (**20**)
Other cpds. isolated	none	3-Acetyl-oxazolidin-2-one (**12**), *N*-(2-hydroxyethyl)-*N*-methylacetamide (**13**), acetmorpholide (**14**), *N*-methylmorpholine (**15**)	[1,3]Dithiole-2-thione (**24**)

Conclusions

Formation mechanism of Lyocell chromophores. As to the mechanism of Lyocell chromophore formation, the initial stages comprise the formation of primary, thermal condensation products of (mono)saccharides, mainly 2,5-dihydroxybenzoquinone, polyphenols, and hydroxyacetophenones (**1** – **5**). Upon longer reaction times and progressing NMMO decay, these primary chromophores undergo further condensation processes, which also involve degradation products of the solvent NMMO, to secondary products. Mainly polycyclic compounds of aromatic and quinoid nature (benzoxazines, naphthoquinones) are formed this way (**6** – **11**). Not only "small" NMMO degradation fragments, such as C_2 units, were built into the condensed structures, but also largely unchanged primary degradation products, such as an intact morpholine ring in **11**. Each of

the secondary chromophores (**6** – **11**) can be formed from more than one of the primary condensation products (**1** – **5**), and can also be generated from furfural and hydroxymethylfurfural, as shown in model condensation experiments.[7b] The presence of NMMO was required for the formation of the secondary chromophores. That compounds with different carbon number and different general structure react to the same products underlines the complexity of the underlying chemistry. This is furthermore supported by the fact that the same chromophores were found in Lyocell materials produced from two different starting pulps. Chromophore formation under Lyocell conditions must be described as a complex set of reactions between three components: NMMO degradation products, carbohydrate condensation products, and the oxidant NMMO itself. Chromophore isolation from Lyocell material has been described in detail previously,[7b] also the mechanism of chromophore formation has been studied by means of kinetics and model experiments.[7a] The overall concentration of Lyocell chromophores found was below 10 ppm.

Formation mechanism of viscose chromophores. The mechanism of viscose chromophore formation finds many parallels to the Lyocell case. Primary chromophores, once more 2,5-dihydroxybenzoquinone, polyphenols, and hydroxyacetophenones (**1** – **4**, **16**, **17**), were formed as alkaline condensation products of (mono)saccharides. Further reaction of these compounds with the xanthation medium or degradation products of the xanthation reagents – mainly H_2S – produced secondary chromophores. Beside naphthoquinones which were also found in Lyocell material (**9** – **10**), mainly mercaptobenzenes and mercaptoquinones were formed this way (**18** – **20**). The overall chromophore concentration in the non-bleached viscose material was about 25 ppm and thus rather high. However, by bleaching the nature of the chromophores is changed and their overall concentration is drastically lowered (< 5 ppm).

Chromophore isolation and identification – weighing the pros and cons of the analytical method. No analytical approaches existed to date for the isolation and identification of chromophores on cellulosic fibers and other cellulosic materials. A novel isolation method has been developed, which applies boron trifluoride – acetic acid complex in combination with sodium sulfite for that purpose. The isolation procedure cleaves possible covalent links between aromatic chromophores and the fiber matrix, and converts most quinoid compounds into the corresponding aromatics beforehand.

Due to the nature of the BF_3*2HOAc reagent the chromophore release works only for aromatic (quinoid) chromophores. No information on the binding of the chromophore to the cellulose matrix is gained. At present, it cannot be decided whether the released compound was simply adsorbed, or covalently bound as ester or ether, before being released into the extraction medium. It remains moreover unclear whether the chromophore was genuinely present as an aromatic, or if it was reduced from the quinoid into its aromatic form upon the isolation. The high complexity and tediousness of the isolation and identification procedure is a clear limitation to routine applicability. As a combination of several analytical techniques (NMR, MS, TLC, column chromatography), and synthesis of authentic samples is required, the method will probably remain a special technique restricted to selected samples, rather than becoming a quick standard technique.

Despite these drawbacks, the presented approach allowed for the first time isolating and identifying well-defined, chromophoric trace compounds from cellulosics. It is applicable to different cellulosic (polymeric) substrates. The application to cellulose acetates and cellulose carrying selective fluorescence labels as "chromophores" has been reported recently.[9]

Knowledge of the structure of the chromophoric compounds contained in/on cellulosic fibers will now allow to devise suitable means for their temporary or permanent removal, and can even reveal a new facet of bleaching chemistry. The approach may also open new ways in the analysis of residual lignins, in monitoring bleaching efficiencies or in textile / dye chemistry.

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[1] Brightness was measured as UV absorbance at 457 nm according to ISO 3688/2470.
[2] Kappa number was determined according to Tappi T 236 cm-85 and cuen viscosity according to SCAN-CM 15:88.
[3] a) M. Funaoka, I. Abe, *Mokuzai Gakkaishi* **1978**, *24*, 892-897. The reactions of lignin under the presence of phenol and boron trifluoride. II. The effect of methoxyl group and ethylenic double bond on the formation of catechol. b) M. Funaoka, I. Abe, *Mokuzai Gakkaishi* **1985**, *31*, 671-676. Degradation of protolignin by the nucleus-exchange method.
[4] Lyocell fibers and pulp heated in DMAc were used as cellulosic materials.
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