

THE EFFECT OF PAPER DEGRADATION ON UNCERTAINTY OF DETERMINATION OF INITIAL LIGNIN CONTENT

SHORT COMMUNICATION

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Abstract

The non-invasive method of determination of lignin content based on measurements of reflectance at 280 nm was evaluated. The application of this method for estimation of the initial content of lignin in degraded samples is problematic due to uncertainty introduced by the degradation processes. The use of the spectroscopic method for non-destructive determination of lignin content is inappropriate, especially for materials with a low content of lignin.

1. Introduction

Lignins are complex phenolic polymers occurring in higher plant tissues and are the second most abundant terrestrial polymer after cellulose.¹ Lignin plays an important role in wood chemistry, pulp and paper industry and as a paper component also in paper conservation.

For quantitative determination of lignin, we have invasive (gravimetric determination i. e. ASTM, TAPPI, SCAN) and non-invasive methods on our disposal.²⁻⁴ Invasive methods are not suitable for historical documents. On the other hand, several spectroscopic techniques are in use, based on IR⁵⁻⁸ and UV^{6,9-18} spectroscopy. The absorption of light of $\lambda > 300 - 310$ nm by pure cellulose is minimal¹⁹ and most UV-spectroscopic methods are based on the fact that lignin absorbs light in this interval much more strongly than carbohydrates.^{2,11}

Knowledge on lignin content is important, as paper properties such as tear resistance, bursting and tensile strength are closely related to fibre morphology and chemical composition.²⁰ Therefore, non-destructive methods for lignin determination in archival and library documents would be of great use.

The aim of this study is to quantify the effect of sample degradation on the reliability of UV-spectroscopic determinations of the *initial lignin content* in the original lignocellulosic material at the time of its production. Namely, results could be influenced by oxidation or other degradation processes in lignin, polysaccharides or other components of lignocellulosic materials.

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2. Experimental

2.1 Paper samples

Paper sheets with different content of lignin were prepared using sulphite bleached spruce wood pulp (Biocel Paskov) and stone-groundwood. Suspension of the sulphite bleached spruce wood pulp and chip groundwood was prepared using a laboratory blender. It was subsequently used for the preparation of laboratory paper sheets containing 0, 40, 60, 80 and 100% of groundwood. The paper sheets were prepared using UNGER laboratory sheet-former with a screen of 200 mesh according to ISO 5269-1 standard.

2.2. Determination of lignin

The determination of lignin content according to Klason (Klason lignin) was performed using 2.0 ± 0.1 g of paper samples according to the T 222 om-88 standard. Relative uncertainty in the determination of lignin content is $<2.5\%$.

2.3 Accelerated degradation

Accelerated degradation of paper samples at 105 ± 2 °C was realized according to ISO 5630-1 standard. Samples were monitored at 0, 3, 6, 9, 12 day of the experiment. The samples were conditioned according to ISO 187 ($T = 23 \pm 1$ °C, $RH = 50 \pm 2$ %).

2.4 Diffuse reflectance spectroscopy

The in-situ spectroscopic measurements of reflectance at 280 nm were carried out on a double beam spectrometer (SPECORD M-40 instrument, Carl Zeiss, Jena) in the reflection mode with in an integrating sphere assembly. Relative uncertainty is estimated to be $<1.8\%$. $BaSO_4$ powder served as the reference.

3. Results and discussion

The principal question to be solved is calibration, i.e. the choice of a model set of well-defined cali-

bration samples. The representative calibration set should be as similar to real samples as possible. Had we chosen the documents in archives and libraries themselves, then the calibration model would be quite complex and would include variability in both the lignin content and in the spectral signal (reflectance). It was our aim to quantify only the effect of the most important source of variability – the duration of ageing.

The model set was prepared with the initial lignin content ($L_{K,0}$) 0.80%, 10.02%, 15.03%, 20.04% and 25.06%. This model set was subjected to accelerated degradation for 0, 3, 6, 9 and 12 days at 105 °C. The variability of reflectance has been expressed in terms of correlation coefficients. Standard r^2 values for both linear and polynomial regressions have been calculated.

Heterogeneity $H<0-t>$ of the model set was expressed in terms of duration of accelerated degradation (in days). E.g., at heterogeneity $H<0-6>$ the sample set includes the original sample and those degraded for 3 and 6 days, all with different initial lignin contents. Thus, the set of samples with heterogeneities 0-0; 0-3; 0-6; 0-9; 0-12 was studied.

In Table 1, we summarize the determinations of the initial lignin content (Klason lignin) ($L_{K,0}$) and reflectance at 280 nm (R_{280}) for the set of samples with heterogeneity $H<0-t>$. Within each set the reflectance at 280 nm decreases with increasing initial lignin content. This confirms the work by Boutelje and Jonsson.⁹ It can be observed that for samples with identical initial lignin content, the reflectance at 280 nm decreases with duration of accelerated degradation. E.g., for $L_{K,0} = 0.8\%$, the initial reflectance is 30.5%, and after 12 days it is 18.5%.

As it can be seen from Figure 1, the reflectance variability R_{280} increases with duration of accelerated degradation. The r^2 values increase with increasing heterogeneity and express the influence of the studied factor: the heterogeneity of the measured set of samples on the measured property, i.e. reflectance. Its influence on estimation of the initial lignin content of a sample set $H<0-t>$ is summarized in Table 2 and Figure 2, where r^2 values are depicted for both linear regression models.

The degradation processes increase the uncertainty of spectroscopically determined lignin content and impair the reliability of the non-destructive method. The determina-

LK,0 (%)	R ₂₈₀ (%)				
	t = 0 days	t = 3 days	t = 6 days	t = 9 days	t = 12 days
0.80 ± 0.02	30.50 ± 0.03	25.33 ± 0.04	22.42 ± 0.04	20.67 ± 0.05	18.50 ± 0.09
10.02 ± 0.05	13.42 ± 0.04	12.33 ± 0.03	11.33 ± 0.07	10.33 ± 0.06	9.83 ± 0.06
15.03 ± 0.08	11.00 ± 0.05	10.25 ± 0.06	9.58 ± 0.05	8.33 ± 0.08	8.00 ± 0.03
20.04 ± 0.11	7.25 ± 0.08	7.00 ± 0.04	6.33 ± 0.06	5.58 ± 0.04	5.25 ± 0.08
25.06 ± 0.07	5.00 ± 0.03	4.75 ± 0.05	4.50 ± 0.08	4.00 ± 0.03	3.75 ± 0.04
Heterogeneity					
	H<0-12>				
	H<0-9>				
	H<0-6>				
	H<0-3>				
	H<0-0>				

Figure 1: The effect of degradation of the model sample set on the variability of reflectance (R_{280}) at maximum of heterogeneity $H<0-12>$. a) Linear regression model ($Y = A+B*X$); b) linearised square root regression model ($Y = A+B*\sqrt{X}$).

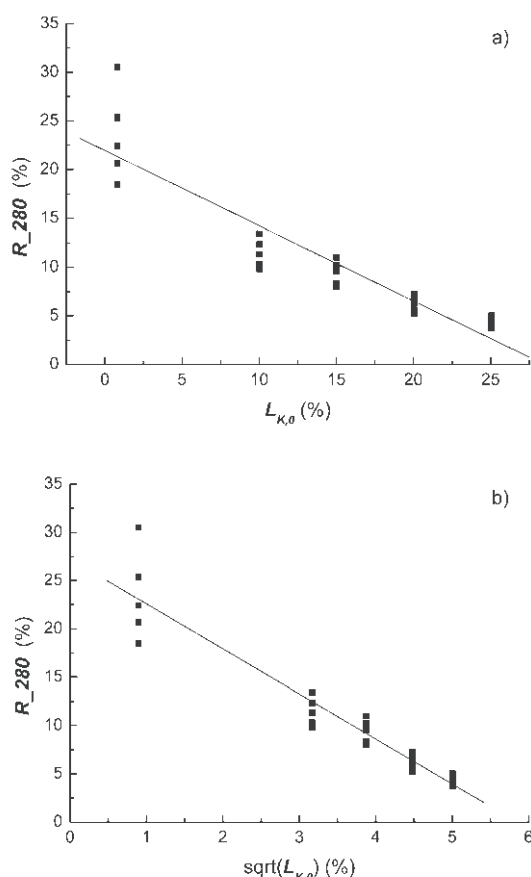


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tions using the destructive wet chemical methods (acid-soluble lignin) can also be influenced by changes in the quality and structure of the lignin, so that these data are also prone to systematic error, which need to be evaluated.

4. Conclusions

The aim of the work was to evaluate the uncertainty of initial lignin content in degraded samples using the UV spectrophotometric method. The results have shown that the UV spectrophotometric method of lignin estimation is not suitable for degraded paper with low lignin content. Even in the case of higher contents of lignin, the uncer-

	Y = A+B*X			Y = A+B*sqrt(X)		
	N	SD	r2	N	SD	r2
H <0-0>	5	3.62	0.903	5	1.41	0.985
H <0-3>	10	2.97	0.895	10	1.64	0.968
H <0-6>	15	2.83	0.882	15	1.86	0.949
H <0-9>	20	2.83	0.865	20	2.04	0.930
H <0-12>	25	2.85	0.846	25	2.22	0.907

Table 2: Statistical parameters for both linear regression models of dependencies of R_{280} on lignin content for heterogeneity $H<0-t>$. (t - duration of accelerated degradation, N - number of samples; SD - standard deviation; r - correlation coefficient).

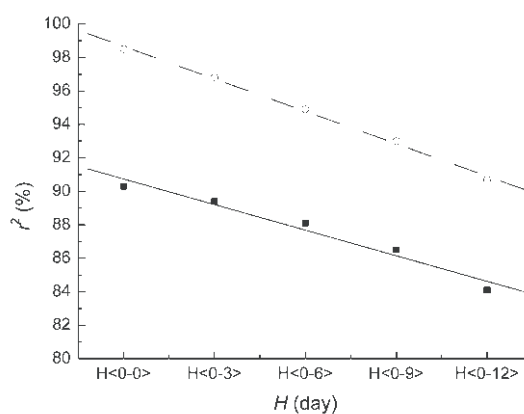


Figure 2: The influence of heterogeneity $H<0-t>$ on r^2 values for both linear (*) and linearised square root (™) regression models.

tainty is not satisfactory low. On the other hand, it is questionable, whether determination of lignin content according to Klason is suitable for degraded samples, in which the initial quality and structure of lignin may have changed.

Further research with a larger sample set is required to assess if the accuracy of determination of initial lignin content can be increased.

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