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THE EFFECT OF AGEING ON VARIABILITY OF THE UV-VIS SPECTROSCOPIC LIGNIN ESTIMATION IN PAPER

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ABSTRACT

The conventional non-destructive method of lignin content estimation based on reflectance at 280 nm (R_{280}) measurements is used world-wide for characterization of lignocellulosic materials. The application of this method brings some problems with its reliability due to variability of composition of lignocelulosics induced by oxidation and other heat and light induced reversion processes, fibres and paper composition, age of the tested material etc. In present work, UV-VIS spectroscopic method is re-evaluated in an order to analyze and quantify the effect of ageing on its reliability in the estimation of the initial lignin content of original lignocellulosic materials (LCM). Statistical analysis of multiple linear regression model indicates that the use of UV-VIS method for nondestructive evaluation (NDE) of initial lignin content is, especially in materials with low content of lignin (e.g. historical documents), inappropriate. Lignocelulosics with higher concentration of lignin shows the lower rate of uncertainty using reflectance method, than that of pulp or paper with low content of lignin, but the uncertainty of determination and so the reliability of this method is still dissatisfactory. The multiple linear regression model was used to describe the relationship between initial lignin content ($L_{k,0}$) and independent variables such as yellowness (Ys), lightness (L), color difference (ΔE), R_280 (remission at λ = 280 nm), R_280/Ys and Ys/b* coordinate. The equation of the fitted model is $L_{k,0}$ = 161.713+1.003*Ys–1.470*L–2.571*ΔE+1.043*R_280 -13.145*R_280/Ys – 16.108*Ys/b*. The R-Squared statistic indicates that the model as fitted explains 98.85% of the variability in initial lignin content.

KEY WORDS*:* lignin, lignocellulosic, cellulosic biomaterials, paper, historical documents, NDE, nondestructive methods, UV spectroscopy, archives, libraries

INTRODUCTION

Lignins are complex phenolic polymers occurring in woody plant tissues and are the second most abundant terrestrial polymer after cellulose. Due to their very complex structure, lignins are amorphous polymers with rather limited industrial use. They are usually seen as waste products of pulp and paper industry and often used as fuel for the energy balance of the pulping process (Pouteau et al. 2003, McCarthy et al. 2000). Despite the fact, information on lignin content is basic characteristic parameter for recognition of qualitative classes (RQC) of lignocellulosics, as well as for sorting of

lignocellulosics such as paper and documents, including historical books, newspaper and archive documents for historical, cultural and technological purposes. Nondestructive methods of estimation of the lignin content in fibers or paper used for the production are very useful e.g. for sorting large quantities of valuable materials or documents without any destructive interventions.

In the field of cultural heritage, reflectance spectroscopy is extensively used for the optical characterization of paint pigments in the visible and infrared wavelength range, as well as for the lignin content determination and other (Missori et al. 2004, Clarke 2001, Davidson 1996).

The factors of variability, reliability and the information value of the traditional UV method of lignin estimation are oxidation and other heat and light induced reversion processes, fibre and paper composition, age of the tested material etc.

The aim of present study is to analyze and quantify the effect of ageing on the reliability of the UV and VIS spectral method of the estimation of the *initial lignin content* in the original lignocellulosic material which had been used for the production of the paper or document at the time of its production.

The results could have been impaired through the oxidation or ageing processes in lignin, polysaccharides and other components in lignocellulosics. It is useful to improve the knowledge on effect of ageing on the reliability of the spectral methods and quantify their variability. The oxidation processes at the room temperature as well as the oxidation or thermally induced ageing at the increased temperatures used for accelerated ageing tests by oxidants present in air can cause changes in spectra of wood or lignocellulosics (LC) components (Davidson 1996, Katuščák et al. 1971, 1973).

It is the initial lignin content that could be used as the basic parameter, usable for characterization of the sort of paper used for the document production. It is not any other value estimated in any changed or aged material. There exists a theoretical continuum of the changed materials after the time of its production corresponding to the endless number of the data on lignin content but there is only one data for the one type of the paper used for its production.

MATERIAL AND METHODS

Paper samples preparation

Paper sheets with different content of lignin were prepared using sulphite bleached spruce wood pulp (Biocel Paskov) and chemi-thermo-mechanical-pulp (CTMP), respectively. The sulphite bleached spruce wood pulp and CTMP were both repulping into water suspension using laboratory blender. The suspension was subsequently used for the preparation of laboratory paper sheets with weight of 2.4 g (75 g/sq. m) containing 0, 11, 22, 48, 67 and 100 % of CTMP. The paper sheets were prepared using UNGER laboratory sheetformer with wire of 200 meshes according to STN ISO 5269-1 standard.

The determination of Klasson lignin

The determination of Klasson lignin content was realized using 2.0 ± 0.1 g of paper samples according to the T 222 om-88 standard.

Accelerated ageing at 105 °C

The thermally accelerated ageing of paper samples at 105 ± 2 °C was realized according to STN ISO 5630-1 standard. The kinetic parameters of thermally forced samples were monitored exactly at 0, 3, 6, 12, 24 day of accelerated ageing. The samples were conditioned according to ISO 187(T = 23 ± 1 °C, RH = 50 ± 2 %).

Accelerated ageing at 100 °C

Paper were conditioned for 24 hours at T = 23 ± 1 °C, RH = 50 ± 2 %. The six papers was formed from the previously air conditioned papers and subsequently was put into the PET/A1/PE bag. The bag was closed and put into the thermostat for 2, 5, 8 days at temperature 100 ± 2 °C. The optical properties were measured after the 24 hours of air conditioning at T = 23 ± 1°C, RH = 50 ± 2 %.

Diffuse reflectance spectroscopy

The in situ spectroscopic measurements of remission at wavelength of 280 nm were carried out on a double beam spectrometer (SPECORD M-40 instrument (Carl Zeiss, Jena)) working in the reflection mode with in an integrating sphere assembly. $BaSO_4$ powder served as reference surface.

Optical properties

The optical properties such as brightness (B, %), yellowness (Y_S, %), CIELab coordinates (lightness (L), a* and b* coordinate) were measured on an ELREPHO 2000 colorimeter.

Statistical analysis

The data was evaluated using Statgraphics software.

RESULTS AND DISCUSSION

The principal question to be solved for the non-destructive spectral measurement is to choose the model set of defined calibration samples. The representative multiple linear regression model should be as consistent with the real measured samples as possible. If the measured samples would come from documents from archives and libraries, the multiple linear regression model would be quite complex, including the most meaningful factors (dimensions) of variability of both the lignin content and spectral signal.

The aim of this work is to quantify the effect of the most important factor of the variability – the time of ageing on the reflectance and calculated lignin content variability. The model set of the lignocellulosic samples with lignin content 0.048 %, 3.4 %, 5.7 %, 9 %, 14.52 % and 22.26 % respectively have been prepared from sulphite pulp and CTMP. Then this model set has been aged for 0, 3, 6, 12 and 24 days at 105°C and 2, 5 and 8 days at 100°C.

Nondestructive evaluation of the lignin content in praxis e.g. in archives and libraries should have been performed in real heterogeneous set of aged lignocellulosic materials.

For our multiple regression models, we have used the model set containing samples aged in the time interval from 0 – 24 days at 105°C and 0 – 8 days at 100°C.

The influence of lignin contents on the optical properties are shown in Tab. 1. The output shows the results of fitting a multiple linear regression model to describe the relationship between initial lignin content and 22 independent variables. The equation of the fitted model is $L_{k,0}$ = 6.245 - 2.689.B - 2.182. Ys + 0.408.L + 1.421.a* +1.957.b* - 2.449.ΔE + 15.830.R_280 + 106.266.R_280/B -77.995.R_280/Ys - 1368.43.R_280/L + 0.065.R_280/a* + 14.861.R_280/b* + 4.451.B/Ys + 203.647.B/L -0.130.B/a* + 6.059.B/b* + 135.604.Ys/L - 0.081.Ys/a +4.992.Ys/b* + 0.116.L/a* - 7.611.L/b* - 10.743.a*/b*.

Since the P-value is less than 0.01, there is a statistically significant relationship between the variables at the 99% confidence level. The R-Squared statistic indicates that the model as fitted explains 99.29% of the variability in $L_{k,0}$.

By the method forward selection was evaluated new multiple linear regression model, where $L_{k,0}$ = 161.713+1.00256*Ys–1.470*L–2.571*ΔE+1.0423*R_280 -13.145*R_280/Ys – 16.108*Ys/b*.

Tab. 1: Optical properties of accelerated ageing at 105 °C and 100 °C

	Samples	$L_{k.0}$	t	B	Ys	L	a*	b*	ΔE	R_280	R_280/B	R_280/Ys	R_280/L
		(%)	(days)	(%)	(%)					(%)			
Accelerated ageing at 105°C according to STN ISO 5630-1	1	22.26	0	67	21	91.5	0.2	10.7	0	11.52	0.172	0.549	0.126
	2	0.048	0	81.7	9.2	94.8	0.2	4.7	0	0.72	0.009	0.078	0.008
	3	3.4	0	79.6	11.3	94.6	0.3	6	0	1.73	0.022	0.153	0.018
	4	5.7	0	77.6	12.8	94.2	0.1	7	0	1.8	0.023	0.141	0.019
	5	9	0	73.8	15.4	93	0.1	8.1	0	2.77	0.038	0.180	0.030
	6	14.52	0	71.8	16.8	92.4	0.1	9.1	0	6.18	0.086	0.368	0.067
	7	22.26	3	58.8	28.9	89.1	1	14.8	4.9	11.52	0.196	0.399	0.129
	8	0.048	3	78.7	11.8	94.7	0.2	6.5	2	1.13	0.014	0.096	0.012
	9	3.4	3	75.5	14.2	93.9	0.4	7.7	1.8	1.49	0.020	0.105	0.016
	10	5.7	3	72.8	17	93.3	0.4	9.3	2.5	2.03	0.028	0.119	0.022
	11	9	3	68.1	20.4	91.9	0.5	11	3.1	3.06	0.045	0.150	0.033
	12	14.52	3	63.1	24.6	89.9	0.9	12.8	4.5	6.72	0.107	0.273	0.075
	13	22.26	6	55.7	32.3	88.1	1.7	16.9	7.3	11.52	0.207	0.357	0.131
	14	0.048	6	76	13.7	94.5	0.1	7.3	2.7	1.05	0.014	0.077	0.011
	15	3.4	6	72.7	17.4	93.1	0.3	9.2	3.5	1.6	0.022	0.092	0.017
	16	5.7	6	69.4	20.8	92.5	0.5	10.9	4.3	1.87	0.027	0.090	0.020
	17	9	6	64	24.7	90.7	0.9	12.8	5.3	2.64	0.041	0.107	0.029
	18	14.52	6	60.6	28.9	89.9	1	14.7	6.3	6.18	0.102	0.214	0.069
	19	22.26	12	50.8	37.8	86.6	2.9	18.8	9.9	9.03	0.178	0.239	0.104
	20	0.048	12	75.2	15.3	94	0.2	8.3	3.7	1.29	0.017	0.084	0.014
	21	3.4	12	70.1	19.5	92.7	0.7	10.5	4.8	2.03	0.029	0.104	0.022
	22	5.7	12	67.1	22.2	92	1.1	11.7	5.3	2.3	0.034	0.104	0.025
	23	9	12	59.4	29.7	89.5	1.9	15.1	8	3.41	0.057	0.115	0.038
	24	14.52	12	56.1	32	88.3	2.4	16.1	8.5	6.18	0.110	0.193	0.070
	25	22.26	24	45.1	43.1	84.3	4.2	19.7	12.3	11.52	0.255	0.267	0.137
	26	0.048	24	72.6	18	93.2	0.1	9.5	5.1	2.21	0.030	0.123	0.024
	27	3.4	24	65.9	23.4	91.5	1.1	11.9	6.7	1.6	0.024	0.068	0.018
	28	5.7	24	61.1	28.5	89.8	1.9	14.6	9	2.77	0.045	0.097	0.031
	29	9	24	54.3	34	87.5	2.9	16.3	10.2	4.05	0.075	0.119	0.046
	30	14.52	24	48.8	39.6	85.7	3.6	19.6	13	5.29	0.108	0.134	0.062
Accelerated ageing at 100°C	31	22.26	2	41.6	43.1	81.8	4.2	20.3	14.2	11.52	0.277	0.267	0.141
	32	0.048	2	56.6	28.1	87.2	2.3	13.8	12	1.29	0.023	0.046	0.015
	33	3.4	2	63	24.3	90.1	1.4	12.6	8	1.8	0.029	0.074	0.020
	34	5.7	2	55.9	29.5	87.4	2.3	14.5	10.4	2.64	0.047	0.090	0.030
	35	9	2	49.2	35.7	84.8	3	17.1	12.5	4.6	0.094	0.129	0.054
	36	14.52	2	44.8	39.1	82.8	3.6	18.8	13.9	5.7	0.127	0.146	0.069
	37	22.26	5	16.8	73.9	63.9	11.4	28.3	34.6	11.52	0.686	0.156	0.180
	38	0.048	5	31.5	55.5	77.4	6.1	25.8	28	3.6	0.114	0.065	0.047
	39	3.4	5	36.9	49.7	80.4	5.4	22.3	22.2	4.92	0.133	0.099	0.061
	40	5.7	5	22	63.5	68.9	7.9	26.1	32.6	3.81	0.173	0.060	0.055
	41	9	5	21	67	67.5	9.9	27.1	33.3	8.12	0.387	0.121	0.120
	42	14.52	5	18.8	69.9	65.6	10.4	27.6	34	7.36	0.392	0.105	0.112
	43	22.26	8	21	69.2	69.4	8.7	29.4	30.2	11.52	0.549	0.167	0.166
	44	0.048	8	30.8	56.9	76.4	5.7	23.6	26.9	4.05	0.132	0.071	0.053
	45	3.4	8	30.2	55.9	74.8	6.3	24.9	28.1	5.7	0.189	0.102	0.076
	46	5.7	8	28.1	58.3	73.9	7.2	25.7	28.4	4.92	0.175	0.084	0.067
	47	9	8	22.2	64.3	69	8.6	26.6	31.4	6.18	0.278	0.096	0.090
	48	14.52	8	27.3	61.3	73.7	8.3	26.5	26.7	4.92	0.180	0.080	0.067
	49	22.26	0	67	21	91.5	0.2	10.7	0	11.52	0.172	0.549	0.126
	50	0.048	0	81.7	9.2	94.8	0.2	4.7	0	0.72	0.009	0.078	0.008
	51	3.4	0	79.6	11.3	94.6	0.3	6	0	1.73	0.022	0.153	0.018
	52	5.7	0	77.6	12.8	94.2	0.1	7	0	1.8	0.023	0.141	0.019
	53	9	0	73.8	15.4	93	0.1	8.1	0	2.77	0.038	0.180	0.030
	54	14.52	0	71.8	16.8	92.4	0.1	9.1	0	6.18	0.086	0.368	0.067

Tab 1 (cont.): Optical properties of accelerated ageing at 105° and 100 °C

	Samples	R_280/a*	R_280/b*	B/Ys	B/L	B/a*	B/b*	Ys/L	Ys/a*	Ys/b*	L/a*	L/b*	a*/b*
Accelerated ageing at 105°C according to STN ISO 5630-1	1	57.60	1.08	3.19	0.73	335.00	6.26	0.23	105.00	1.96	457.50	8.55	0.02
	2	3.60	0.15	8.88	0.86	408.50	17.38	0.10	46.00	1.96	474.00	20.17	0.04
	3	5.77	0.29	7.04	0.84	265.33	13.27	0.12	37.67	1.88	315.33	15.77	0.05
	4	18.00	0.26	6.06	0.82	776.00	11.09	0.14	128.00	1.83	942.00	13.46	0.01
	5	27.70	0.34	4.79	0.79	738.00	9.11	0.17	154.00	1.90	930.00	11.48	0.01
	6	61.80	0.68	4.27	0.78	718.00	7.89	0.18	168.00	1.85	924.00	10.15	0.01
	7	11.52	0.78	2.03	0.66	58.80	3.97	0.32	28.90	1.95	89.10	6.02	0.07
	8	5.65	0.17	6.67	0.83	393.50	12.11	0.12	59.00	1.82	473.50	14.57	0.03
	9	3.73	0.19	5.32	0.80	188.75	9.81	0.15	35.50	1.84	234.75	12.19	0.05
	10	5.08	0.22	4.28	0.78	182.00	7.83	0.18	42.50	1.83	233.25	10.03	0.04
	11	6.12	0.28	3.34	0.74	136.20	6.19	0.22	40.80	1.85	183.80	8.35	0.05
	12	7.47	0.53	2.57	0.70	70.11	4.93	0.27	27.33	1.92	99.89	7.02	0.07
	13	6.78	0.68	1.72	0.63	32.76	3.30	0.37	19.00	1.91	51.82	5.21	0.10
	14	10.50	0.14	5.55	0.80	760.00	10.41	0.15	137.00	1.88	945.00	12.95	0.01
	15	5.33	0.17	4.18	0.78	242.33	7.90	0.19	58.00	1.89	310.33	10.12	0.03
	16	3.74	0.17	3.34	0.75	138.80	6.37	0.22	41.60	1.91	185.00	8.49	0.05
	17	2.93	0.21	2.59	0.71	71.11	5.00	0.27	27.44	1.93	100.77	7.09	0.07
	18	6.18	0.42	2.10	0.67	60.60	4.12	0.32	28.90	1.97	89.90	6.12	0.07
	19	3.11	0.48	1.34	0.59	17.52	2.70	0.44	13.03	2.01	29.86	4.61	0.15
	20	6.45	0.16	4.92	0.80	376.00	9.06	0.16	76.50	1.84	470.00	11.33	0.02
	21	2.90	0.19	3.59	0.76	100.14	6.68	0.21	27.86	1.86	132.42	8.83	0.07
	22	2.09	0.20	3.02	0.73	61.00	5.74	0.24	20.18	1.90	83.63	7.86	0.09
	23	1.80	0.23	2.00	0.66	31.26	3.93	0.33	15.63	1.97	47.10	5.93	0.13
	24	2.58	0.38	1.75	0.64	23.38	3.48	0.36	13.33	1.99	36.79	5.48	0.15
	25	2.74	0.58	1.05	0.54	10.74	2.29	0.51	10.26	2.19	20.07	4.28	0.21
	26	22.10	0.23	4.03	0.78	726.00	7.64	0.19	180.00	1.89	932.00	9.81	0.01
	27	1.46	0.13	2.82	0.72	59.91	5.54	0.26	21.27	1.97	83.18	7.69	0.09
	28	1.46	0.19	2.14	0.68	32.16	4.18	0.32	15.00	1.95	47.26	6.15	0.13
	29	1.40	0.25	1.60	0.62	18.72	3.33	0.39	11.72	2.09	30.17	5.37	0.18
	30	1.47	0.27	1.23	0.57	13.56	2.49	0.46	11.00	2.02	23.81	4.37	0.18
Accelerated ageing at 100°C	31	2.74	0.57	0.97	0.51	9.90	2.05	0.53	10.26	2.12	19.47	4.03	0.21
	32	0.56	0.09	2.01	0.65	24.61	4.10	0.32	12.22	2.04	37.91	6.32	0.17
	33	1.29	0.14	2.59	0.70	45.00	5.00	0.27	17.36	1.93	64.36	7.15	0.11
	34	1.15	0.18	1.89	0.64	24.30	3.86	0.34	12.83	2.03	38.00	6.03	0.16
	35	1.53	0.27	1.38	0.58	16.40	2.88	0.42	11.90	2.09	28.27	4.96	0.18
	36	1.58	0.30	1.15	0.54	12.44	2.38	0.47	10.86	2.08	23.00	4.40	0.19
	37	1.01	0.41	0.23	0.26	1.47	0.59	1.16	6.48	2.61	5.61	2.26	0.40
	38	0.59	0.14	0.57	0.41	5.16	1.22	0.72	9.10	2.15	12.69	3.00	0.24
	39	0.91	0.22	0.74	0.46	6.83	1.65	0.62	9.20	2.23	14.89	3.61	0.24
	40	0.48	0.15	0.35	0.32	2.78	0.84	0.92	8.04	2.43	8.72	2.64	0.30
	41	0.82	0.30	0.31	0.31	2.12	0.77	0.99	6.77	2.47	6.82	2.49	0.37
	42	0.71	0.27	0.27	0.29	1.81	0.68	1.07	6.72	2.53	6.31	2.38	0.38
	43	1.32	0.39	0.30	0.30	2.41	0.71	1.00	7.95	2.35	7.98	2.36	0.30
	44	0.71	0.17	0.54	0.40	5.40	1.31	0.74	9.98	2.41	13.40	3.24	0.24
	45	0.91	0.23	0.54	0.40	4.79	1.21	0.75	8.87	2.25	11.87	3.00	0.25
	46	0.68	0.19	0.48	0.38	3.90	1.09	0.79	8.10	2.27	10.26	2.88	0.28
	47	0.72	0.23	0.35	0.32	2.58	0.83	0.93	7.48	2.42	8.02	2.59	0.32
	48	0.59	0.19	0.45	0.37	3.29	1.03	0.83	7.39	2.31	8.88	2.78	0.31
	49	57.60	1.08	3.19	0.73	335.00	6.26	0.23	105.00	1.96	457.50	8.55	0.02
	50	3.60	0.15	8.88	0.86	408.50	17.38	0.10	46.00	1.96	474.00	20.17	0.04
	51	5.77	0.29	7.04	0.84	265.33	13.27	0.12	37.67	1.88	315.33	15.77	0.05
	52	18.00	0.26	6.06	0.82	776.00	11.09	0.14	128.00	1.83	942.00	13.46	0.01
	53	27.70	0.34	4.79	0.79	738.00	9.11	0.17	154.00	1.90	930.00	11.48	0.01
	54	61.80	0.68	4.27	0.78	718.00	7.89	0.18	168.00	1.85	924.00	10.15	0.01

The R-Squared statistic indicates that the model as fitted explains 98.58% of the variability in $L_{k,0}$. As can be seen from figure 1 for error of measured of multiple linear regression models (forward selection) we have shown, that of lignin estimation is unsuitable when applied to archive documents with low lignin concentration. The lower the lignin content is, the higher the measurement error of this method. The lignocellulosics with higher content of lignin gives more reliable results, than measurements of paper with only low content of lignin, but they are still unsatisfactory. The measurement error of such obtained experimental results is still too large and error is up to 30 % for paper with high content of lignin. Even the results of destructive wet chemistry methods can be influenced by changing the quality and structure of the lignin, polyphenolics, polysaccharides and other components through the oxidation or ageing. So even the data of the wet chemistry methods measured in samples after certain period of ageing or oxidation may possibly not give reliable information on the lignin content, e.g. on the lignin content in the paper used for the production of historical books or archive documents.

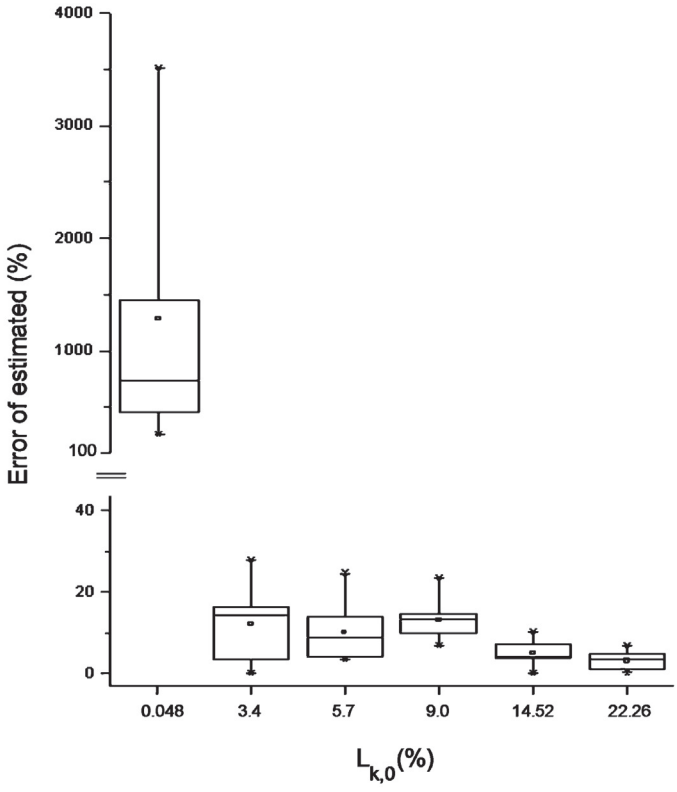

Fig. 1: Box and Wish diagram for error of estimated (%) at different initial lignin contents ($L_{k,0}$, %)

CONCLUSIONS

The aim of the work was to quantify the failure of lignin estimation by traditional UV-VIS method in models of historical documents. The results, presented in paper has shown that multiple linear regression model describes the relationship between initial lignin content and independent variables as yellowness, lightness, color difference, R_280, R_280/Yellowness and Yellowness/b* coordinate. The equation of the fitted model is

$$L_{k,0} = 161.713+1.003*Ys–1.470*L–2.571*\Delta E+1.042*R\_280 -13.145*R\_280/Ys – 16.108*Ys/b*$$

The R-Squared statistics indicates that the model as fitted explains 98.85 % of the variability in initial lignin content.

1. Using multiple linear regression model we have shown, that the conventional UV-VIS method of lignin estimation is unsuitable when applied to archive documents with low lignin content. The lower the lignin content is, the much higher the measurement error of this method.
2. The lignocellulosics with higher content of lignin gives more reliable results, than paper with low content of lignin ($L_{k,0} \approx 0$), but they are still unsatisfactory. The measurement error of such obtained experimental results is still too large.

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REFERENCES

1. Clarke, M., 2001: Review in Conservation, The International Institute for Conservation of Historic and Artistic Works, London, UK 2: 3 pp.
2. Davidson, R. S., 1996: The photodegradation of some naturally occurring polymers. J. Photochem. Photobiol. B: Biology 33(1): 3-25
3. Katuščák, S., Horský, K., Mahdalík, M., 1971: The oxidation of lignin with oxygene and peroxides. The examination of changes occuring in the initial stages of oxidation of methanol lignin. Paperi ja Puu 53(4a): 197-202
4. Katuščák, S., Hrivík ,A., Minárik, V., Mahdalík, M., 1973: Modification of oxidized lignins with styrene. J. Appl. Polym. Sci 17(5): 1919-1928
5. McCarthy, J. L., In: Glasser, W. G., Northey, R. A., Schultz, T. P., 2000: Lignin: historical, biological, and materials perspectives. American Chemical Society, Pp. 2–100 from acaba .bre. 1999: J. Sci. Food Agric. 79: 1091–1098
6. Missori, M., Righini, M., Selci, S., 2004: Optical reflectance spectroscopy of ancient papers with discoloration or foxing. Opt. Commun. 231: 99–106
7. Pouteau, C., Dole, P., Cathala, B., Averous, L., Boquillon, N., 2003: Antioxidant properties of lignin in polypropylene. Polym. Degrad. Stab. 81: 9–18

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