

It could be concluded that no significant differences occurred between characteristics of industrial grass containing and control papers.

Summary

Evaluating our experiments performed so far the industrial grass proved to be a hopeful yearly renewable raw material for energetic as well as for industrial application. It can be concluded from results of pilot and industrial scale production that the industrial grass cellulose was equivalent or even better in quality and value with papers produced from traditional resources.

Acknowledgement

Authors are very thankful to the National Develop-

ment Agency (GVOP-3.1.1.-2004-05-0066/3.0) for the financial support which enabled of fulfilment of the present work.

References

1. C. Ververis, K. Georghiou, N. Christodoulakis, P. Santas, R. Santas: *Industrial Crops and Products* (2004) 19(3) 245–254.
2. C. R. Wilke, R. D. Yang, A. F. Sciamanna, R. P. Freitas: *Biotechnology and Bioengineering* (1981) 23(1) 163–183.
3. www.cepi-sustainability.eu
4. www.recyclingportal.eu/
5. Smook G. A.: *Handbook for Pulp- and Paper Technologist* Angus Wilde Publications (2002)

FT-IR and UV/VIS analysis of classic and recycled papers

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Abstract

The properties of classic and recycled papers with and without surface coatings were investigated by several methods. With the infrared attenuated total reflection spectroscopy, the molecular structure on sample surfaces was identified and analysed. This way the filler and coating pigment were detected and their amount on classic and on recycled papers. Ultraviolet/visible spectroscopy enables the reflectance and transmittance measurements. The most important result was detection of the optical brighteners and comparison of its amount in our paper samples. These results were compared with the calcium carbonate and china clay content in the bulk of examined papers, as calculated from the ash contents. Furthermore, differences between classic and recycled materials are discussed in more details.

Keywords: Recycled paper, FT-IR spectroscopy, UV/VIS spectroscopy, ash content.

1. Introduction

The infrared (IR) absorption spectroscopy is frequ-

ently used to identify the molecular structure of a sample qualitatively and quantitatively. The most useful for the analysis is the mid-IR spectra, i.e. the region from 4,000 to 400 cm⁻¹; in the upper wavenumber part (up to 1300 cm⁻¹) vibrations of functional groups in molecules can be detected, whereas the region with lower wavenumbers represent the so-called molecular fingerprint region of the analyte [1, 2]. The IR absorption is analysed with the help of absorbance spectra by the position, intensity (height), half-width and the shape of individual peaks.

The peak position is the basic characteristic of the corresponding vibration. It reveals an effective mass of vibrating group of atoms, the vibration geometry and coupling with the immediate surroundings, i.e. the vibrational species in the neighbourhood. A different position can indicate different effective mass of vibrating group and/or their different surroundings. The first effect produce different characteristic peaks, whereas differences the potential field in the surrounding of vibrating species can, in

general, shifts the corresponding peak which may indicate small differences in net material under investigation. The height of the peak presents strong, medium or weak vibrations, which depends on vibrating dipole moment, i.e. on the intrinsic nature of the matter. The peak width demonstrates several phenomena; crystalline matter, in general, reveal narrower peaks than their amorphous counterparts [3]. Basic characteristics of spectra show the chemical composition of the investigated sample; this is most frequently obtained by comparison to existing IR database. Small differences between spectra of samples with the same database match is then addressed to differences in molecular surrounding and/or degree of ordering in the structure.

The ultraviolet/visible (UV/VIS) spectroscopy enables the measuring of reflectance and transmittance of solid or liquid materials. The measurements are performed using collimated beam; when it is detected in collimated form, specular reflectance or directional transmittance is measured. The integrating sphere enables the collecting of the light emerging from the sample in arbitrary direction; thus, the diffuse reflectance or diffuse transmittance could be obtained. Such analysis enables the surface characterisation of glossy or rough solids or the photometric analyses of turbid, colloidal, transparent and translucent samples in solid or liquid forms.

The absorbance in this spectral region give information about electronic transitions within the investigated material, which is of great importance in many applications in the material science research. The UV/VIS spectroscopy is widely used in several applications such as characterisation of materials used in solar applications, printing inks, colour of samples, dyes, food composition etc [4].

The combination of IR and UV/VIS spectroscopy offers to give complete data about the material under investigation, i.e. their molecular structure, fingerprint, electronic transitions and surface properties. This is the reason why we applied this combination of analytical methods for our work.

The main goal of the research was to analyse the differences among classic and recycled papers from intrinsic material point of view as well as from their surface characteristics over wide spectral region, covering the entire optic part of electromagnetic spectrum.

2. Materials and methods

The analysis was performed on the upper (A) and bottom (B) side of the following paper samples:

- classic uncoated paper (CUP),
- classic matte coated paper (CCP),
- recycled uncoated paper (RUP) and
- recycled matte coated paper (RCP).

The samples were measured with a FT-IR spectrometer, using the diamond attenuated total reflectance (ATR) measuring cell which is suitable for surface measurement (measuring penetration depth up to about 2 μm). All spectra were examined with the resolution of 4 cm^{-1} , obtaining absorbance spectra of all samples, for side A and B.

- Hardware: Spectrum GX, FT-IR System, PerkinElmer,
- Software: Spectrum v 5.3.1,
- ATR measuring cell, Golden Gate (Harrick Scientific),
- Database: Nicodom IR/NIR Libraries for polymers, fibres, dyes, pigments.

The ash content was determined at two different temperatures [5, 6]. About 2.8 g of paper pieces, smaller than 1 cm^2 were weighted in a heat-resistance crucibles. After that the paper pieces were put into muffle furnace at 525 ± 25 °C and 900 ± 25 °C, cooled in a desiccators and weighted again. Ash content was calculated from both masses with consideration of moisture content. The procedure was carried out in duplicate and the average value was calculated [7]. We determined the ash content to compare results with FT-IR measurements.

Using the UV/VIS spectrometer with integrating sphere accessory, we measured the transmittance and reflectance values in the wavelength region 200–900 nm. The measurements of all samples were conducted in 10-nm steps, preparing 5 specimens for each sample, separately for side A and B, the average values of reflectance and transmittance of which was calculated with software.

- Hardware: Lambda 800 with PELA-1000 integrating sphere accessory, PerkinElmer,
- Software: UV WinLab 6.0.2.0723.

3. Results and discussion

3.1. FT-IR database

The applied database detected calcium carbonate

(CaCO_3) for classic as well as recycled uncoated paper (CUP and RUP). It detected CaCO_3 only on side A of the paper, which most likely indicates that side B contains a smaller share of CaCO_3 . We were informed by the producers that they use CaCO_3 as the only filler in the production of classic and recycled uncoated paper. Due to the similarity of CaCO_3 with our uncoated papers, we compared their spectra (Figure 1). The peaks which are located in the same positions as they are in the spectrum of CaCO_3 (at 1420, 870 and 710 cm^{-1} , spectrum from the applied IR database) indicated the CaCO_3 presence in uncoated papers. These peaks are assigned as asymmetric stretching (at about 1425 cm^{-1}) and out-of-plane bending (at 870 cm^{-1}) vibrations of CO_3 group and to the in-plane bending vibration of CO_2 group (at 710 cm^{-1}) [8].

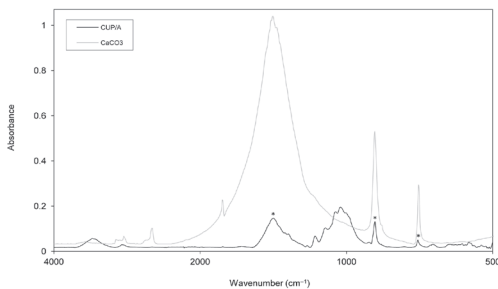


Figure 1: Spectra of CUP and CaCO_3 from the applied IR database. The peaks in CUP sample indicated by stars confirm the presence of CaCO_3 .

For classic coated paper (CCP), we obtained information from the producer that they also use CaCO_3 as a filler in the paper production. Moreover, for the coating, they use apart from CaCO_3 also kaolin as a pigment. The database listed in the first place kaolin and in the fifth place CaCO_3 for side A and B of the paper. Recycled coated paper (RCP) contains CaCO_3 as a filler, while it contains apart from CaCO_3 for the coating also size and latex.

The database lists in the first place CaCO_3 and slightly lower kaolin, which was not listed by the producers; nevertheless, the coating most likely contains a smaller amount of kaolin on both paper sides. We compared the spectra of coated papers with those of CaCO_3 and kaolin (Figure 2).

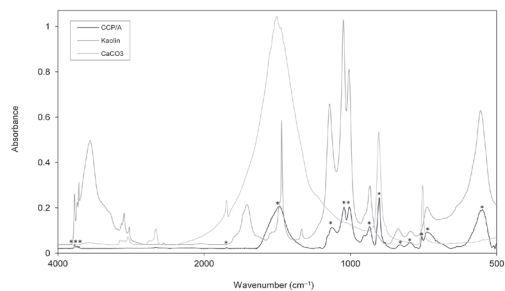


Figure 2: Spectra of CCP, kaolin and CaCO_3 from the applied IR database. The peaks in CCP sample indicated by stars confirm the presence of kaolin and CaCO_3 .

Even here, the peaks are detected for the CaCO_3 content as at uncoated papers, while some of these peaks are less and some more distinctive. The peaks are located at 1800, 1400, 870 and 710 cm^{-1} . According to the literature [9], the CaCO_3 peaks which appear in the coated paper spectrum are to be located at around 2550, 1800, 1500–1300 and 890 cm^{-1} . The latter also proved correct in our case, not exposing the peak at 2550 cm^{-1} for being so small (in our case it appears at 2510 cm^{-1}). Slightly more distinct are the peaks located in the same places as kaolin. The first three very distinct peaks are at 3690, 3650 and 3620 cm^{-1} , followed by the peaks at the wavenumbers 1400, 1090, 1030, 1010, 910, 790, 750, 700 and 540 cm^{-1} .

3.2. FT-IR spectra

A substantially more precise analysis followed in the research, i.e. the analysis of our FT-IR spectra. We compared the recycled and non-recycled papers (side A and B), separately for uncoated and coated papers.

Using the program Spectrum, we defined the baseline for each spectrum individually and subtracted it from the spectrum. Figure 3 shows the spectra of classic uncoated paper for side A and B, and of the recycled uncoated paper for side A and B.

Whereas Figure 4 shows the spectra of classic and recycled coated paper, separately for each side. It can be instantly noticed that the peak positions separately for uncoated papers and coated papers are almost identical, while they differ in their peak height ratios.

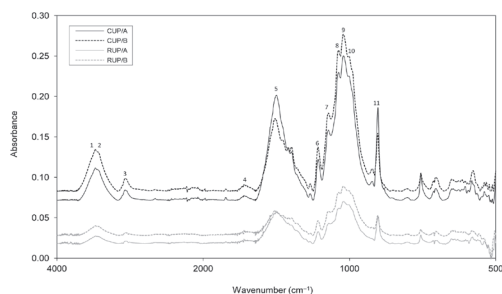


Figure 3: Spectra of classic (CUP) and recycled (RUP) uncoated papers for side A and B.

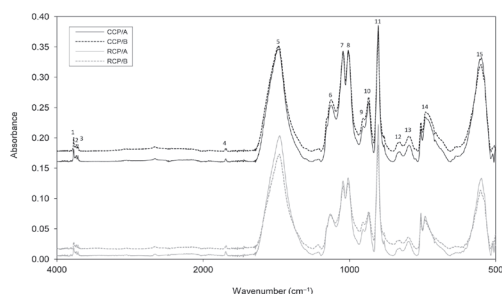


Figure 4: Spectra of classic (CCP) and recycled (RCP) coated papers for side A and B.

We defined the position ν_0 (cm^{-1}), height I_0 and half-width hw (cm^{-1}) of individual peaks which are standing out the most. The data were inserted into Tables 1 and 2, separately for uncoated and coated papers. Moreover, each of these tables was further divided into two parts. While the first part contains the peaks within the region of functional groups (from 4,000 to 1,300 cm^{-1}), the second part contains the peaks within the fingerprint region (from 1,300 to 600 cm^{-1}).

With a more detailed overview of Table 1, it can be established that regarding the peak position, samples CUP and RUP differ slightly more only in the position of peak 3 (C–H vibrations [1, 10]). CUP has by 13 and 12 cm^{-1} , respectively, higher wavenumber value than RUP, which could be attributed only to different potential energy of atoms as a consequence of various surroundings.

Regarding the peak height, Figure 3 and Table 1 demonstrate that all peaks of CUP are higher than

those of RUP, in some places more and in some less, which may indicate higher density of these molecular groups. However, the effect could also be a consequence of a different contact of the sample with the ATR crystal at the measurements due to unequal surface roughness, or different pressure applied when measuring.

Only at peak 4 (C=C, C=O, C=N vibrations [1, 10], water molecules vibrations [11]), it can be said that the heights are comparable. Comparing only side A and B, the differences are more substantial at peak 5 and 11 of both samples, i.e. CUP and RUP. Since these are the peaks typical of CaCO_3 , it can be said that side A of samples CUP and RUP has a higher content of CaCO_3 than side B. The difference in the peak width is bigger only at peaks 1 and 2, where CUP on side B has by 10 cm^{-1} greater width than on side A. Furthermore, CUP on side B has by 13 cm^{-1} greater width than RUP. Larger width means differences in effective surroundings, which could represent less symmetry of the local environment and therefore less uniform potential for vibrating species.

A note is in place here, namely that a slightly higher difference in the width could also be a consequence of overlapping peaks. In the region around 1000 cm^{-1} , we register more vibrations (stretching and deformations) of more groups: C–O–C, C–O, C–C, C–N. These groups are located in cellulose fibres. As this is a mixture of more substances, more peaks appear; thus the overlapping into a wide absorption band. This is a consequence of the vibration of more groups in variable molecular surroundings, which cause distinctive peaks shift and widen. The asymmetric stretching of the C–O–C groups is caused by the peak at 1160 cm^{-1} , whereas the stretching of C–O in cellulose/hemicellulose molecules is caused by the peaks at 1104 and 1028 cm^{-1} . The strongest peak at 1028 cm^{-1} is accompanied by two distinct peaks at 1051 and 1002 cm^{-1} [8].

At a more exact overview of Table 2, it can be instantly noticed that the differences in the position, height and half-width of peaks CCP and RCP are smaller than those for CUP and RUP.

At peak 5 between samples CCP and RCP, the difference in the position is slightly bigger (the corresponding peak shifts by 7 cm^{-1} for side A and B), as well as in the half-width (RCP has by 6 cm^{-1} bigger width on side A).

Table 1: Position (ν_0), height (l_0) and half-width (hw) of individual peaks of classic (CUP) and recycled (RUP) uncoated paper for side A and B.

* Half-width listed at peak 2 is actually half-width of peaks 1 and 2.

	Peak 1		Peak 2			Peak 3		Peak 4		Peak 5	
	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0
CUP/A	3333	0.040	3296	0.038	256*	2898	0.012	1649	0.006	1412	0.130
CUP/B	3332	0.051	3295	0.049	266*	2899	0.016	1648	0.008	1421	0.090
RUP/A	3332	0.009	3292	0.009	258*	2885	0.003	1649	0.006	1417	0.039
RUP/B	3332	0.012	3293	0.011	253*	2887	0.003	1649	0.006	1423	0.031

	Peak 6			Peak 7		Peak 8		Peak 9		Peak 10		Peak 11		
	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)
CUP/A	1160	0.051	30	1104	0.087	1052	0.158	1028	0.179	1003	0.154	873	0.115	14
CUP/B	1161	0.055	30	1104	0.097	1053	0.174	1029	0.194	1002	0.167	874	0.072	14
RUP/A	1160	0.015	25	1102	0.025	1051	0.044	1029	0.052	1003	0.048	873	0.034	15
RUP/B	1160	0.018	26	1103	0.030	1053	0.053	1029	0.061	1002	0.055	874	0.024	16

Table 2: Position (ν_0), height (l_0) and half-width (hw) of individual peaks of classic (CCP) and recycled (RCP) coated paper for side A and B.

	Peak 1		Peak 2		Peak 3		Peak 4			Peak 5		
	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)
CCP/A	3693	0.021	3649	0.011	3621	0.010	1797	0.005	11	1398	0.186	129
CCP/B	3692	0.023	3649	0.011	3621	0.011	1797	0.005	12	1400	0.174	128
RCP/A	3692	0.013	3649	0.007	3620	0.007	1797	0.007	12	1391	0.198	135
RCP/B	3692	0.011	3649	0.007	3620	0.006	1797	0.006	12	1393	0.156	131

	Peak 6		Peak 7		Peak 8		Peak 9		Peak 10		Peak 11		
	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)
CCP/A	1091	0.093	1030	0.182	1005	0.184	937	0.059	913	0.098	872	0.225	14
CCP/B	1090	0.085	1030	0.163	1005	0.164	937	0.054	913	0.089	872	0.198	14
RCP/A	1094	0.069	1030	0.123	1006	0.128	938	0.043	912	0.069	872	0.216	13
RCP/B	1094	0.055	1030	0.104	1006	0.109	937	0.044	912	0.061	872	0.172	14

	Peak 12		Peak 13		Peak 14		Peak 15		
	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	ν_0 (cm ⁻¹)	l_0	hw (cm ⁻¹)
CCP/A	789	0.016	753	0.027	697	0.073	535	0.172	34
CCP/B	789	0.015	753	0.025	697	0.065	536	0.143	34
RCP/A	788	0.012	756	0.023	698	0.065	535	0.128	31
RCP/B	789	0.014	756	0.019	698	0.049	537	0.097	31

Bigger differences in the peak height between side A and B of both samples (cf. Figure 4 and Table 2) appear at peaks 5, 7, 8, 11 and 15 (sides A have higher values), and between samples CCP and RCP at the height of peaks 7, 8 and 15 (CCP has higher values). The results show that side A has in comparison with side B higher kaolin and CaCO₃ content, and CCP compared to RCP higher kaolin content.

3.3 Ash content

The results of residues on ignition at 525 °C and 900 °C on oven-dry basis, calcium carbonate and kaolin content for all paper samples are presented in Table 3.

The percentages of calcium carbonate and kaolin in the papers were calculated by the following equations [7]:

$$CaCO_3 = (Ash_{525} - Ash_{900}) \times \frac{100}{44}$$

$$Clay = (Ash_{525} - CaCO_3) \times 1.13$$

where Ash525 and Ash900 are the residues on ignition expressed as mass percentage of the oven-dry samples, CaCO₃ is the calcium carbonate content and Clay is the content of the china clay also known as kaolin. The CaCO₃ content and the content of the china clay were determined to examine the FT-IR results.

Table 3: Content of ash on ignition at 525 °C and 900 °C, calcium carbonate and china clay in all paper samples.

	Ash ₅₂₅ (%)	Ash ₉₀₀ (%)	CaCO ₃ (%)	Clay (%)
CUP	23.4	13.4	22.8	0.7
CCP	39.7	28.3	26.0	15.5
RUP	31.2	19.3	27.2	4.6
RCP	39.6	25.5	32.1	8.5

The results from Table 3 show that both classic papers contain smaller amount of calcium carbonate than recycled papers. Classic uncoated paper (CUP) has 16% lower CaCO₃ content in comparison with recycled uncoated paper (RUP), while classic coated paper (CCP) has 19% lower CaCO₃ content compared to recycled coated paper (RCP). Both uncoated papers contain very small amount of kaolin. Meanwhile at coated papers it is clearly seen that classic paper (CCP) contains much larger amount of kaolin than recycled one (RCP), 82% larger. The latter is also proved with FT-IR analysis, where it was recognised that CCP has in comparison with RCP higher kaolin content.

3.4 UV/VIS spectroscopy

Figures 5 and 6 show the reflectance of uncoated and coated papers in dependence of the wavelengths. Particularly interesting are the reflectance values of uncoated papers, the values of which exceed 100%. This is a typical phenomenon of papers which contain optical brighteners, due to which paper emits light even more in the UV spectral region. The phenomenon is the strongest at classic uncoated paper (CUP), where the maximum reflectance value equals 250%. The phenomenon is smaller, yet still noticeable at recycled uncoated paper (RUP) on side B, the reflectance value being 120%.

The coating on paper partially suppresses the effect of brighteners, thus it is less distinct or not noticeable at all. In our case, the reflectance values of coated papers are lower than 100%, despite containing optical brighteners. Classic papers have in the UV spectral region higher reflectance values than recycled papers.

Apart from reflectance, we also measured the transmittance values of our samples (cf. Figures 7 and 8). The transmittance of recycled uncoated paper (RUP)

is in the UV spectral region smaller, while it increases in the visible region and is higher than classic uncoated paper (CUP).

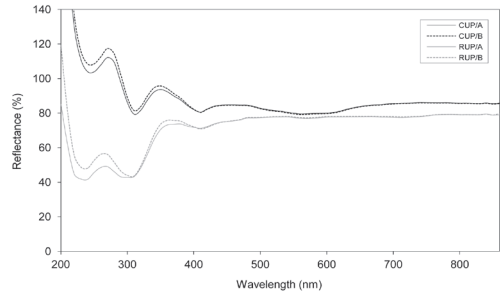


Figure 5: Reflectance spectra for uncoated papers.

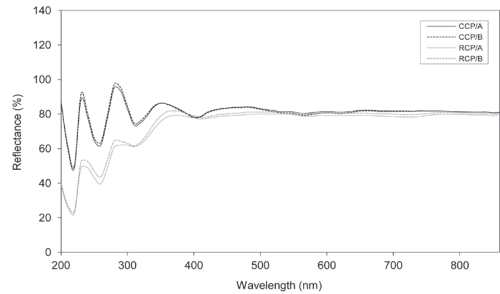


Figure 6: Reflectance spectra for coated papers.

At coated papers, by increasing the wavelength, transmittance increases as well. Classic coated paper (CCP) has higher transmittance than recycled coated paper (RCP) throughout the whole UV and visible spectrum. The differences between the reflectance and transmittance values for side A and B of uncoated and coated papers are extremely small.

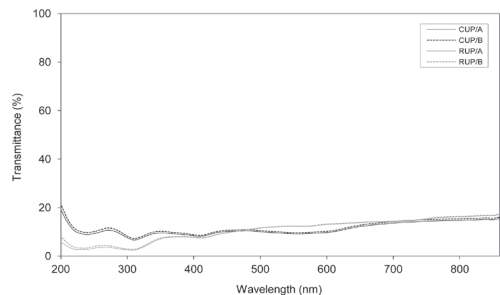


Figure 7: Transmittance spectra for uncoated papers.

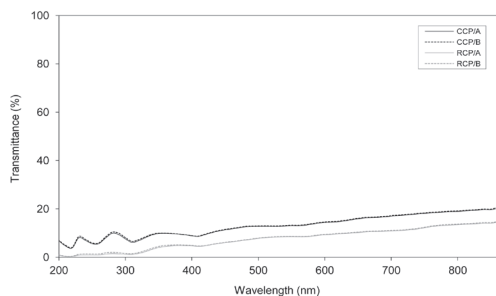


Figure 8: Transmittance spectra for coated papers.

4. Conclusions

With the help of FT-IR-ATR spectra, we detected the chemical structure on surfaces of the investigated classic and recycled papers.

By the help of IR database the calcium carbonate was shown in all papers, whereas on coated papers the additional presence of kaolin was obtained. Comparing IR spectra of samples, we established that the surface of classic coated paper contains more kaolin than the surface of recycled coated paper.

The ash content determination confirms the last finding and shows the percentages of calcium carbonate and kaolin in all paper samples.

However, it should be pointed out here, that this method yields for the presence of calcium carbonate in the bulk of samples which is therefore not directly comparable to the presence on the surface. With a UV/VIS spectrometer, we detected in the measured reflectance the content of optical brighteners in the paper samples, due to which paper additionally emits light in the UV spectral region which gives higher reflectance in the blue region and therefore a whiter surface appearance.

The reflectance values in the UV and visible spectral region were higher at classic papers in comparison with the recycled ones.

Acknowledgements

This work was supported by the Slovenian Research Agency (Project BI-HU/10-11-013). The authors would like to thank the paper manufacturer Papirnica Vevče for providing some paper samples. S. G. thanks the Ministry of Higher Education, Science and Technology for the PhD grant.

References

- [1] COLTHUP, N. B.; DALY, L. H. & WIBERLEY, S. E.: Introduction to Infrared and Raman Spectroscopy, Academic Press Boston, ISBN 012182554X, San Diego, New York, London, Sydney, Tokyo, Toronto, (1990)
- [2] TOWNSHEND, A.: Gast – Lip, In Encyclopedia of analytical science, Harcourt Brace & Company, ISBN: 0122267001, London, (1995), pp. 1915–2546
- [3] KLANJŠEK GUNDE, M.: UV/VIS/IR spektroskopija IR, presentation, internal material
- [4] PERKINELMER: Applications and Use of Integrating Spheres with the Lambda 650 and 850 UV/Vis and Lambda 950 UV/Vis/NIR Spectrophotometers, Available from http://shop.perkinelmer.com/content/ApplicationNotes/APP_LAMBDA650Integrating-Spheres.pdf, Accessed: 2010-02-01
- [5] ISO 1762: Paper, board and pulps – Determination of residue (ash) on ignition at 525 °C, (2001)
- [6] ISO 2144: Paper, board and pulps – Determination of residue (ash) on ignition at 900 °C, (1997)
- [7] PITA RAW MATERIALS WORKING GROUP: Commonly used Test Methods for Paper and Board, Available from <http://www.pita.co.uk/pdf/TestMethods.pdf>, Accessed: 2011-12-08
- [8] FERREIRA, P. J. et al: Application of FT-IR-ATR Spectroscopy to Evaluate the Penetration of Surface Sizing Agents into the Paper Structure, Ind. Eng. Chem. Res., Vol. 48 (2009) No. 8, pp. 3867–3872, ISSN: 0888-5885
- [9] BAKER, M.; REYDEN, D. & RAVENEL, N.: FTIR Analysis of Coated Papers, Available from <http://cool.conserva-tion-us.org/coolaic/sg/bpg/annual/v08/bp08-01.html>, Accessed: 2010-01-05
- [10] HUBLEY, C. E. & LEVI, L.: The Infrared Spectroscopic Method, Available from http://www.unodc.org/unodc/en/data-and-analysis/bulletin/bulletin_1955-01-01_1_page005.html, Accessed: 2010-01-10
- [11] PRONIEWICZ, L. M. et al: FT-IR and FT-Raman study of hydrothermally degraded cellulose, Journal of Molecular Structure, Vol. 596 (2001) No. 1, pp. 163–169, ISSN: 0022-2860