AGING OF NEWSPAPER SINCE 1959 UNDER ARCHIVE CONDITIONS – A QUANTIFICATION OF DIFFERENT EFFECTS USING FT-IR SPECTROSCOPY

J. TINTNER, F. REITER, E. SMIDT and B. HINTERSTOISSER

University of Natural Resources and Life Sciences, Vienna, Department of Material Sciences and Process Engineering, Peter Jordan Straße 82, 1190 Vienna, Austria
✉ *Corresponding authors: J. Tintner, johannes.tintner@boku.ac.at, E. Smidt, ena.smidt@boku.ac.at*

Received March 29, 2017

Aging of newspaper under archive conditions was investigated. The experimental design included issues of all the decades since 1959 to 2015. Newsprint and white parts of colored pages were characterized. The yellowed border and the area in the middle of the pages were characterized using ATR-FTIR spectroscopy. Principal component analysis (PCA) revealed two processes of paper aging: cellulose modification, which results in an increase of carboxyl/carbonyl content; and lignin degradation reactions, which is the main cause of paper yellowing. Cellulose aging was loaded on the first principal component (PC), accounting for about 90% of data variability. Yellowing effects were loaded on the second PC with an explanation rate of 5%. Yellowing was even found in newspapers from the year 2015 with only slight changes over time, whereas cellulose aging proceeded quite continuously. The effects were found for both newsprint and colored pages. Additionally, five samples from newspapers that had been buried in a sanitary landfill were included into the dataset. The organic bands followed the same aging process as in the archives; microbial degradation obviously had a minor effect on the aging process studied.

Keywords: newsprint, paper aging, ATR-FTIR spectroscopy, paper yellowing, cellulose modification

INTRODUCTION

Aging of paper depends on different factors. Under environmental conditions, biological activity plays a crucial role, but also chemical and physical processes can change and destroy paper after a certain time. Archives usually try to create conditions unfavorable for biological attack, especially, for mold and insects.[1] In addition, techniques to preserve paper against embrittlement and disintegration are widely known.[2,3] However, the study of aging is usually limited by different origins and fabrication methods of the paper and investigations of comparable time series are rare. In terms of chemical aging processes, cellulose and the remaining lignin content of the pulp play crucial roles.[4]

Because paper aging is a time-consuming process, in order to investigate it, paper samples are often subjected to a definite artificial aging process[13] or are taken from selected archive documents.[14] Until now, the different effects of paper aging have been investigated altogether, while only a definite aging process is put in the foreground in artificial aging studies. The present research work focuses on aging of newspaper over more than 55 years in an archive, investigating a time series of newspaper samples – from each decade since 1959 until 2015.

FTIR spectroscopy is a proven method to characterize complex organic materials. A wide range of different materials have been characterized by this method, *e.g.* soil organic matter,[5-7] clinical body materials[8] and wood.[9,10] However, FTIR is a common technique for paper investigation as well.[11,12] In the present study, the attenuated total reflection (ATR) technique was applied to observe the changes that newspaper underwent over time. Moreover, using a factorial design of the measurements, we separated the different effects of cellulose modification and yellowing, and compared them with the changes that paper underwent under the storage conditions of a sanitary landfill.

EXPERIMENTAL

Samples of naturally aged paper

Newspaper samples were obtained from the archives of Kronen Zeitung® in Vienna, the highest circulation daily newsprint in Austria. The archives contain all printed issues that are added hot off the press since December 1959. The exemplars issued during a month or half of a month are bound in a book. These books are stored in a closed windowless room on open shelves, without any rigorous control of the temperature and air humidity. Nevertheless, all the papers are subjected to the same conditions over time. The 2015 exemplars were not bound yet, so free duplicates were available. Every decade was represented by the December editions of one year – starting with 1959. Ten newsprints out of 31 were selected for the measurements. Supplements of weekend editions (in 1959 only two pages, later increasing to about 100 pages) contain multi-color printing. The term "colored paper" refers to newsprint with multi-color printing from weekend editions. In 1999 and 2009, additional TV-supplements were produced on high-gloss paper. The whole set of samples, including the number of samples is presented in Table 1.

Seven additional samples were collected from an old landfill of municipal solid waste in Styria. In the course of another project, landfilled material was dug out by an excavator. Newspaper (Kronen Zeitung® as well) was found stored under wet, anaerobic conditions, not mixed with other waste materials. After excavation, the newspaper was air-dried. Measurements were performed on the interior parts of the paper, which did not show any obvious contamination. Five samples were newsprint, two were colored weekend supplements. The newspapers were printed in 1984.

Characterisation methods

FT-IR spectroscopy

FT-IR spectra were recorded for all the samples, in the ATR mode, using a Bruker® FT-IR spectrometer (Tensor 27) with a diamond crystal. The spatial resolution was 250 µm; the spectra were corrected against ambient air; 32 scans were collected at a spectral resolution of 4 cm^{-1}. The replications were vector normalized and averaged with integrated OPUS® 7.2 software. Two areas of every newspaper were investigated: the border of the page, where yellowing was visible and at least a few centimeters inside on unprinted, ink-free parts. Five replicates were performed. All measurements were taken on interior pages to avoid potential surface contamination.

XRD analysis

XRD measurements were carried out with a PANalytical® X´Pert PRO diffractometer. The measurements were performed to identify the inorganic compounds of the color-printed weekend supplements from 2015 (6^{th}, 13^{th} and 20^{th} of December, 2015). The unprinted borders of three samples were cut and combusted at 420 °C. After the organic matter burned up, the ash was analyzed by X-ray diffraction (XRD) and FT-IR spectroscopy. The purpose of these measurements was to confirm the interpretation of the PCA (Fig. 1).

Principal component analysis

Principal component analysis (PCA) was performed with The Unscrambler® X 10.1 software to display the influencing factors.[15] The method calculates new coordinates out of the infrared spectra, explaining structures within the data set. PCA splits the spectral data into a scores plot and a loadings plot. The plots are connected *via* the principal components. The scores plot displays the structural pattern of the samples, whereas the loadings plot determines which regions of the spectrum are relevant for that pattern.

Table 1
Sample set of newspapers originating from an archive and from a landfill (1984)

Type	Location	1959	1969	1979	1984	1989	1999	2009	2015	Total
Newsprint	inside	10	10	10	5	10	10	11	9	145
(only black print)	border	10	10	10		10	10	11	9	
Colored paper	inside	4	4	5	2	5	4	4	3	61
	border	4	4	5		6	4	4	3	
TV supplement	inside						6	7		24
	border						6	5		
Total		28	28	30	7	31	40	42	24	230

RESULTS AND DISCUSSION

Characterization of all samples, using the whole IR spectrum

In a first step, the whole FT-IR spectra, from 4000 to 400 cm^{-1}, obtained for all the archive samples were used for the PCA. The results are displayed in Figure 1. The first PCs explained together 95% of data variability. The main drivers of the PCs were the inorganic compounds. PC 1 is dominated by kaolinite, whereas PC 2 is driven by calcite (Fig. 1c). These inorganic compounds were confirmed by ash analysis of the three weekend supplement samples (Fig. 2). The peaks between 3691 cm^{-1} and 3620 cm^{-1} are typical of OH stretching of kaolinite, the peaks between 1026 cm^{-1} and 1007 cm^{-1} originate from the in-plane Si-O stretch vibration, that at 912 cm^{-1} represents the OH deformation of kaolinite and those at 532 cm^{-1}, 465 cm^{-1} and 428 cm^{-1} originate from Al-O-Si, and Si-O deformation.[16] The peaks at 1796 cm^{-1}, 1421 cm^{-1}, 874 cm^{-1} and 712 cm^{-1} can be attributed to calcite.[17,18] The minerals were confirmed by XRD measurements (results not shown).

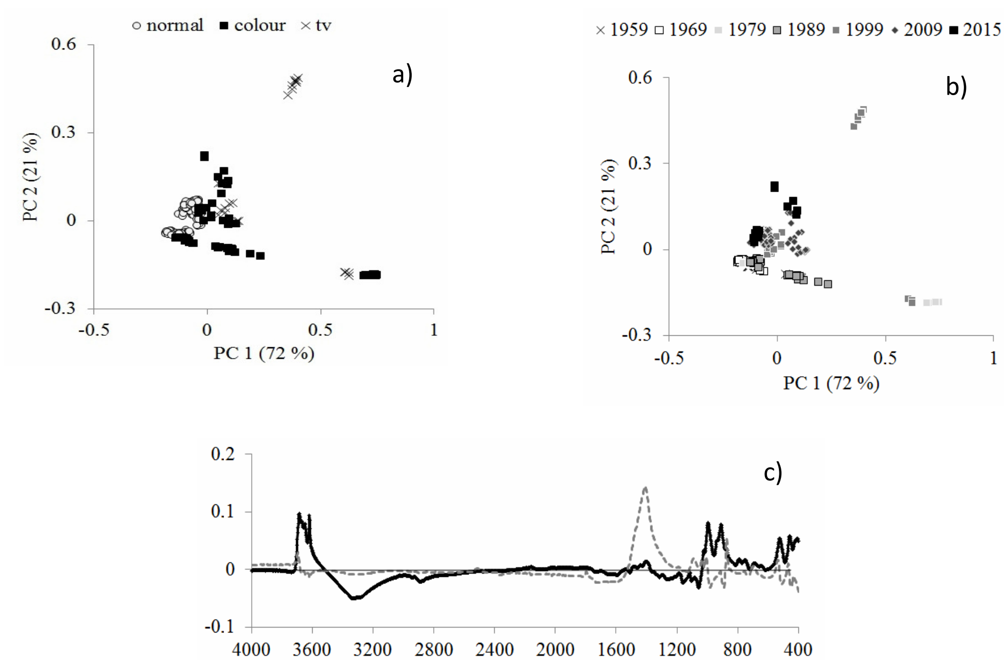

Figure 1: PCA based on infrared spectra (4000-400 cm^{-1}) of all archive samples $_{n=223}$: Scores plots with PC 1 and PC 2 marked a) according to the type of paper, b) according to the year; c) loadings plot of PC 1 and PC 2

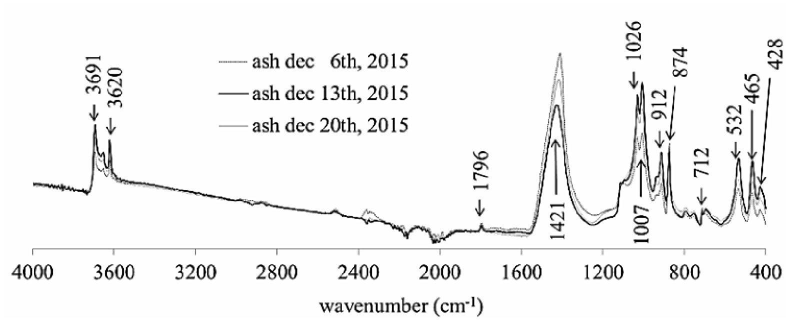

Figure 2: FT-IR spectra of the ash obtained from three weekend supplement samples by burning at 420 °C (prominent bands are indicated)

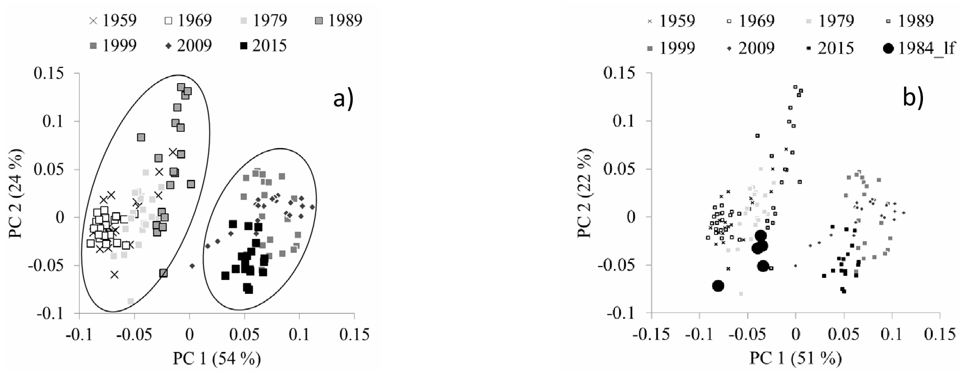

Figure 3: a) Scores plot with PC 1 and PC 2 based on infrared spectra (4000-400 cm^{-1}), all newsprint samples from the archive $_{n=140}$; b) Scores plot with PC 1 and PC 2, all newsprint samples including five samples from a landfill (1984_lf) $_{n=145}$

According to Figure 1a and b, TV supplements from 1999 are rich in inorganic compounds, partly only kaolinite, partly both. The colored pages from 1979 contained more kaolinite as well. Inorganic pigments, such as calcium carbonate and kaolin, are used as papermaking additives in the papermaking stock or in surface coating formulas to improve printing properties.[19] The types of inorganic compounds changed over time several times, so the differences between the TV supplements and the colored pages are not explained by aging. On the other hand, the newsprint paper was not affected that much by differences in inorganic compounds, since it is known that it is produced with low content of inorganic material or without it. Therefore, another PCA was performed focusing on only black print newsprint.

Characterization of newsprint samples only

Characterization of newsprints only, using the whole IR spectrum

Figure 3 displays the results obtained when only newsprints were subjected to PCA. The scores plot for all the archive samples is shown in Figure 3a. A segregation of the results into two parts was found: the samples of 2015, 2009 and 1999 were grouped together, and the other years were separated within the second group. In this second group, the sample from 1989 is located close to the border of its own group and towards the younger group, followed by 1979 and 1969. Only the samples of 1959 are intermingled.

It is known that the paper of Kronen Zeitung® is produced by a few paper mills. According to the information provided by one of these paper mills, the material composition changed considerably in the late 80s of the 20th century. Due to the increase in separate collection and recycling relevance, modern newsprint paper production is based on processing wastepaper as main raw material. Moreover, the pH in modern paper production shifted from predominantly acidic conditions to mainly neutral ones, which is correlated with the use of calcium carbonate as filler or coating material. The PCA presented in Figure 3b contains all the samples of newsprints, including five obtained from the landfill (marked as 1984_lf).

The landfilled samples are located in between 1989 and 1979. Landfill storage is characterized by anaerobic conditions. The temperature and moisture depend on the waste conditions and composition, as well as on the landfill construction, which altogether regulate microbial activity within the landfill. However, good preservation of newspaper and magazines in landfills even over decades is well known.[20] Our results confirmed that microbial activity might not play an important role, when paper is compacted and not mixed with other easily available organic material. Aging processes were comparable to those occurring in archives.

Characterization of newsprints only using specific spectral regions

To determine the aging process, a further PCA was performed with only two spectral regions of organic matter ranging from 2930 to 2785 cm^{-1} and from 1761 to 1570 cm^{-1}. The scores plot of this PCA, which separates the different decades continuously along the first PC, explained 92% of data variability (Fig. 4a). Only the samples from 1959 are situated between 1969 and 1979, while those from 2009 are intermingled within 2015 and 1999. The second PC, which separates the measurements from the border of the pages and from the inside (Fig. 4b), explained only 4% of data variability. The effect is stronger in the samples from the earlier decades, but can be found even in those of 2015. The difference between border and inside measurements was obviously caused by the color. At the outer borders of the pages, more or less strong yellowing occurred. According to the loadings plot (Fig. 4c), the first PC is dominated by changes in the spectral regions at about 1728 cm^{-1} and 1593 cm^{-1}.

Cellulose aging is usually described by two processes: hydrolysis induced by water and acids,[21] and oxidation induced by metal ions and air.[22] Both processes lead to an increase in carbonyl and carboxyl groups.[23] The band between 1740 cm^{-1} and 1690 cm^{-1} is characteristic of the carbonyl/carboxyl groups and is a good indicator for the aging of cellulose.[24] Therefore, our results confirm these aging processes. According to the archivist at Kronen Zeitung®, the archives moved to a closed windowless room in the late 90s of the 20th century. Furthermore, all the issues since 1994 are digitalized nowadays. Therefore, it can be assumed that older newspapers are taken out much more often. These two reasons could explain the distance between the samples from 1989 and 1999.

The yellowing of newsprint paper is due mainly to its high content of lignin, which can support various degradation reactions as a function of the environment conditions.[4] In our study, the yellowing effect at the border of the pages is reflected by a slight, but specific decrease of the aliphatic methylene bands at 2922 cm^{-1} and 2852 cm^{-1}. A further band indicates a relevant difference at 1686 cm^{-1} (Fig. 4c). No peak is visible in the average spectra of the border and inside measurements, but the valley between the peaks at 1736 cm^{-1} and 1655 cm^{-1} is less distinct for the measurements inside the pages (not shown). At 1686 cm^{-1}, the C=O stretch vibration of quinones can be found.[25] Demethylation and the formation of quinones are typical results of lignin degradation, which leads to newsprint yellowing.[26]

Average FTIR spectra of all archive newsprints

Figure 5 displays the average spectra of all the newsprints from the archive according to different decades. Figure 5a shows the whole spectrum used for the PCA in Figure 3, whereas Figure 5b displays the regions used for the PCA in Figure 4. In the whole spectra, the inorganic compounds, calcium carbonate and kaolinite, dominate the differences over the decades. In the selected regions, the carboxylates become especially prominent for differentiation.

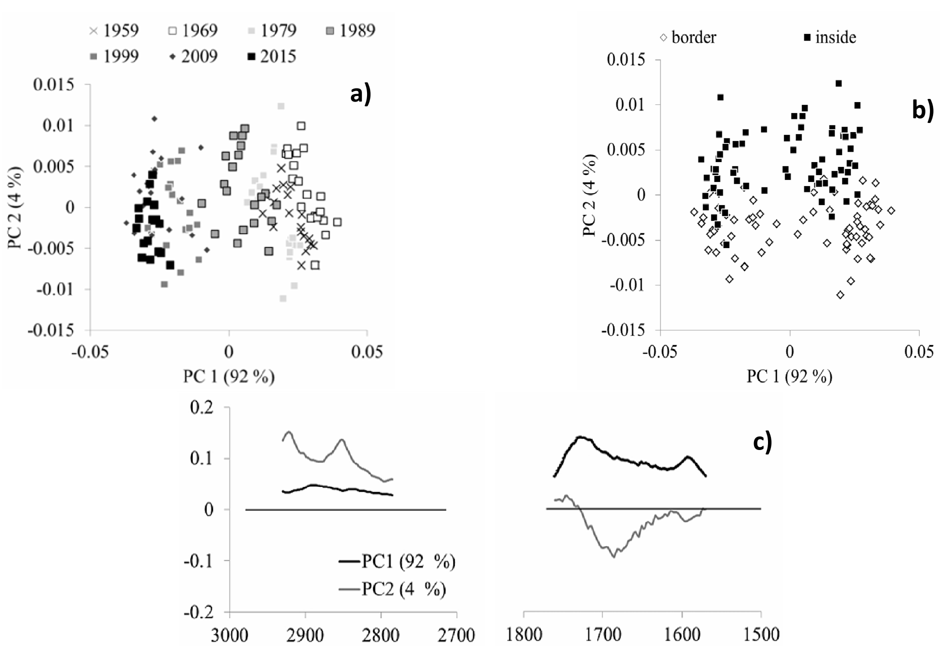

Figure 4: Scores plot (PC 1 and PC 2) of the PCA with all archive samples with newsprint $_{n=140}$, based on two spectral regions (2930 to 2785 cm^{-1} and 1761 to 1570 cm^{-1}) marked a) according to the decade, b) according to border/inside measurement; c) corresponding loadings plots of PC 1 and PC 2

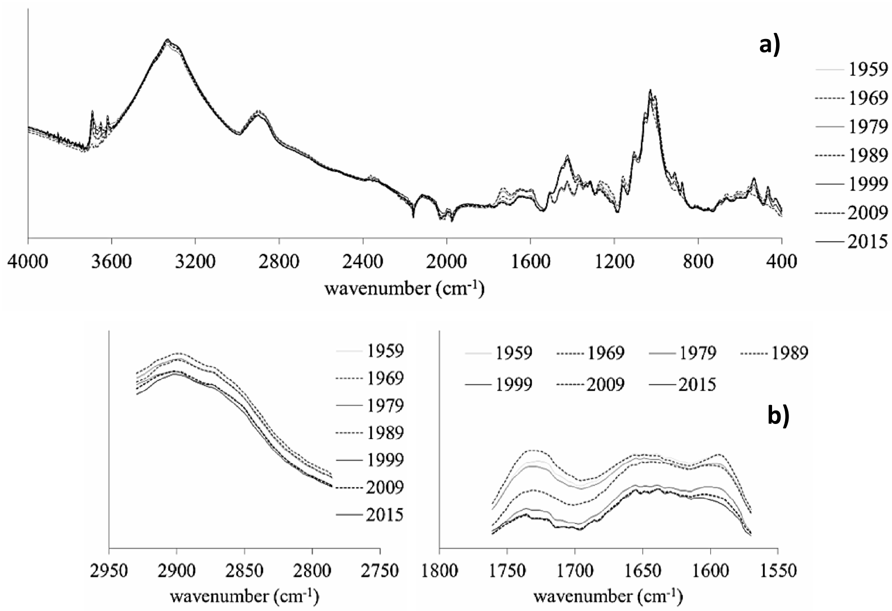

Figure 5: Average FTIR spectra of all newsprints from the archive; a) whole spectral range from 4000 to 400 cm^{-1}; b) spectral regions from 2930 to 2785 cm^{-1} and 1761 to 1570 cm^{-1}

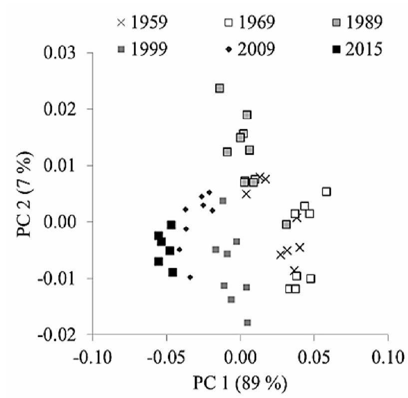

Figure 6: Scores plot (PC 1 and PC 2) of the PCA with all archive samples with colored pages, except the ones from 1979 $_{n=49}$, based on two spectral regions (2930 to 2785 cm^{-1} and 1761 to 1570 cm^{-1})

The PCA on the spectral regions from 2930 to 2785 cm^{-1} and from 1761 to 1570 cm^{-1} was additionally performed for the colored pages. The scores plot of the results is given in Figure 6. It displays the same results, the decades are separated as well mainly according to the first PC, but the year 1989 is shifted on the second axis. This might indicate a stronger yellowing effect on these pages. Therefore, the second PC has a slightly higher relevance for the colored pages than for newsprints (7%). The first PC accounts for 89% of data variability.

CONCLUSION

The main output of this work is the clear differentiation between the effects of cellulose modification by acid hydrolysis/oxidation reactions and those of the degradation reactions of lignin on newsprint paper aging. By means of PCA, cellulose modification was loaded on one axis and accounted for about 90% of data variability. The different decades were separated quite continuously with a certain gap after 1989. This gap can be explained first by a shift of the archives to a different location, and second, by the reduced handling of the documents during the later years due to digitalization. The yellowing effect was loaded on the second axis and accounted for only about 5% of data variability. It became clear that this yellowing effect obviously occurs very rapidly over the first weeks or months of storage. Considering the samples representing different decades, the distance between the results of border measurements and the ones measured inside the page becomes bigger, but the main driver of separation between the decades is triggered by another effect. This continuous aging over time is due to cellulose modification. This result was found for daily newspaper, but was also proven for the white parts of colored pages. Interestingly, the process of cellulose modification is comparable even under strongly differing storage conditions. Thus, the samples of newspaper from 1984, which had been buried in a sanitary landfill, were located on the axis of cellulose modification between those of 1989 and 1979, which had been stored in the archives. This result is remarkable although only 5 landfilled samples were used in the study. One could assume that totally different changes over time would dominate the paper aging process, but, at least in this case, this was not revealed by the data.

ACKNOWLEDGMENTS: We thank the Kronen Zeitung®, respectively Martin Kriegel from the archives for the possibility to measure the newspapers. Norbert Tuchny (Mediaprint®) and Dr. Herwig Kapeller (Norske Skog Bruck GmbH®) provided information about paper composition and production. We also thank Prof. Franz Ottner and Dr. Karin Wriessnig from the Institute of Applied Geology, BOKU, for the XRD measurements of the ashes and the reference data, as well as Andreas Zöscher (Mürzverband®) for his help with landfill sampling. The authors declare that they have no conflict of interest.

REFERENCES

[1] O. M. Bankole, *Libr. Rev.*, **59**, 414 (2010).
[2] N. Gurnagul, R. C. Howard, X. Zou, T. Uesaka and D. H. Page, *J. Pulp Pap. Sci.*, **19**, J160 (1993).
[3] J. W. Baty, C. L. Maitland, W. Minter, M. A. Hubbe and S. K. Jordan-Mowery, *BioResources*, **5**, 1955 (2010).
[4] M. Paulsson and J. Parkås, *BioResources*, **7**, 5995 (2012).
[5] A. Tinti, V. Tugnoli, S. Bonora and O. Francioso, *J. Centr. Eur. Agr.*, **16**, 1 (2015).
[6] K. Meissl, E. Smidt, M. Schwanninger and J. Tintner, *Appl. Spec.*, **62**, 873 (2008).
[7] D. Solomon, J. Lehmann, J. Kinyangi, B. Liang and T. Schäfer, *Soil Sci. Soc. Am. J.*, **69**, 107 (2005).
[8] A. A. Bunaciu, H. Y. Aboul-Enein and Ş. Fleschin, *Appl. Spec. Rev.*, **50**, 176 (2014).
[9] K. Fackler and M. Schwanninger, *J. Near Infrared Spec.*, **18**, 403 (2008).
[10] M. Schwanninger, J. C. Rodrigues and K. Fackler, *J. Near Infrared Spec.*, **19**, 287 (2011).
[11] P. Calvini and A. Gorassini, *Restaurator*, **23**, 48 (2002).
[12] T. Canals, J. R. Riba, R. Cantero, J. Cansino, D. Domingo *et al.*, *Talanta*, **77**, 751 (2008).
[13] J. Łojewska, A. Lubańska, P. Miśkowiec, T. Łojewski and L. M. Proniewicz, *Appl. Phys. A: Mater. Sci. Proc.*, **83**, 597 (2006).
[14] R. Ganzerla, A. Gambaro, E. Cappelletto, M. Fantin, S. Montalbani *et al.*, *Microchem. J.*, **91**, 70 (2009).
[15] K. Esbensen, "Multivariate Data Analysis – In Practice", Alborg University, Esbjerg, 2002.
[16] L. Vaculíková, E. Plevová, S. Vallová and I. Koutník, *Acta Geodyn. Geomat.*, **8**, 59 (2011).
[17] V. J. Bruckman and K. Wriessnig, *Environ. Chem. Lett.*, **11**, 65 (2013).
[18] E. Smidt, K. Meissl, J. Tintner and F. Ottner, *Environ. Chem. Lett.*, **8**, 217 (2010).
[19] M. Ciobanu, E. Bobu and F. Ciolacu, *Cellulose Chem. Technol.*, **44**, 379 (2010).
[20] L. Chen, M. A. Nanny, D. R. U. Knappe, T. B. Wagner and N. Ratasuk, *Environ. Sci. Technol.*, **38**, 3542 (2004).
[21] R. Feller, S. B. Lee and J. Bogard, in "Historic Textile and Paper Materials", edited by H. L. Needles and S. H. Zeronian, Adv. Chem. Series, Washington DC, American Chemical Society, 1986, vol. 212, pp. 329-347.
[22] J. Kolar, *Restaurator*, **18**, 163 (1997).
[23] A. Potthast, T. Rosenau and P. Kosma, *Adv. Polym. Sci.*, **205**, 1 (2006).
[24] M. Ali, A. M. Emsley, H. Herman and R. J. Heywood, *Polymer*, **42**, 2893 (2001).
[25] NIST, National Institute of Standards and Technology, U.S. Secretary of Commerce. http://webbook.nist.gov/chemistry, 2016 (accessed 2016-07-05).
[26] R. S. Davidson, *J. Photochem. Photobiol. B*, **33**, 3 (1996).