**R.O. Shabiev, A.S. Smolin, V.I. Ivanov-Omskii, T.K. Zvonaryova,
I.N. Trapeznikova**

A NEW HANDS-ON METHOD TO INVESTIGATE
THE SYSTEM OF HYDROGEN BONDS IN PAPER

Introduction. Usually the hydrogen bonds in cellulose macromolecules and cellulose containing materials are divided onto intra- and intermolecular bonds between hydroxyl (O–H) groups. This arrangement is well suitable for cellulose films, but a bit doubtful for cellulose fibers, because the reality of microfibrils structure in such a model is not considered. The hydrogen-bonding pattern between microfibrils is one of the key element in determining the structure and properties of cellulose containing materials [Ciolacu, Kovac and Kokol, 2010]. To study the phenomenon of hydrogen bonding, the Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy are conventionally used (Steiner, 2002). The vibrational frequencies of high-polarized functional groups like O–H groups appropriately fall in the infrared spectral range, maintaining FTIR spectroscopy as one of the best tool to study the formation of hydrogen bonds (Kondo, 2005). The area of O–H stretching vibration is subject to the greatest influence on hydrogen bonds in the range of 3700–3000 cm^{-1} [Ciolacu, Ciolacu, and Popa, 2011; Maréchal and Chanzy, 2000]. The assignment of infrared absorption in bands is typically achieved by the mathematical processing of a spectra. To resolve broadband, obviously derived from several overlapping bands, both deconvolution [Fengel, 1992; Kondo, 1997] and the second-derivative approach [Kondo, 2005] are typically suggested. The peak identification of O–H stretching regions by deconvolution is applied for analysis of paper contents (Calvini, P. & Gorassini 2002) and deinking pulp processing [Qinglin Meng et al., 2013], but obviously has not been used for paper stock.

Depending on the purpose, destructive (Daisuke, Tatsuo, and Murakami, 1995) and non-destructive techniques [Ivanova et al., 2015; Olsson and Salmén, 2004] are both used for paper FTIR spectroscopy. When investigating the system of hydrogen bonds any damage of samples should be taken with caution, because the energy spent for preparation of KBr tablet are comparable with the hydrogen bonding energy (approx. 10–20 kJ/mol). Even the technique with freeze-dried samples should be considered with warning. The procedure to

investigate the system of hydrogen bonds by means of preparation of thin laboratory samples is not wide-spread, because extraction of sorbed water absorbance from the spectrum requires special arrangement. Our hands-on approach allows investigation of hydrogen bonds in paper has a potential practical future for routine mill control.

There are the following objectives for this study:

1. To use the proposed FTIR spectrometry method for splitting up different types of hydrogen bonds in the region of O–H stretching vibration;

2. To identify to identify tolerances of proposed non-destructive FTIR spectroscopy technique some limitations of proposed hands-on method;

The whole procedure of recording, processing and peak deconvolution of infrared spectra into Gaussians was specified during the study. From a practical point of view, we hope that the proposed hands-on technique would be useful for mill control and feedforward prediction of paper properties. Moreover, studying the system of polysaccharides hydrogen bonding in paper offers new fundamental knowledge of important type of bonding in living nature and beyond.

Materials and Methods. The hydrogen bonds were investigated for eucalyptus bleached kraft pulp. The eucalyptus pulp was used due to enable uniform formation of short-fiber containing handsheets in the broad range of basis weights. The refined pulp was prepared in accordance with DIN 54360:2004-07. The degree of refining was measured in accordance with ISO 5267-1 and maintained at 40SR. All handsheets were formed in the screen section of Rapid Koethen sheet-former (ISO 5269-2), whereas handling, transferring and drying were done differently. For each individual trial 5 pcs handsheets were made with basis weights ranged from 13.6 to 47.2 g/m^2 and variable thicknesses. In order to obtain samples with basis weight below 20 g/m^2, the wet handsheets were placed with the forming screen disc on the corresponding diameter protection grid of industrial electric 3 kW fan heater. The handsheets became self-detachable from the forming screen in about 2-3 min as the drying was completed. This procedure prevents destruction of very thin handsheets. The handsheets become bulkier by hot air drying comparing to vacuum drying, but basis weight is lower. Prior to testing, all handsheets were conditioned for several hours at controlled environment with standard temperature (23^oC) and humidity (50% RH). Physical and mechanical properties were determined in accordance with ISO procedures, all samples of the same batch were tested on the same day. The tensile strength was measured by a PC-controlled vertical Hounsfield H1KS testing machine with 250 N load cell according to ISO 1924-1, to be able to measure all samples the width of specimens was varied depending on the basis weight. After the

measurement in paper testing laboratory, all handsheets were packed and transported to physical laboratory where they were studied as described below without maintaining the room humidity. The system of hydrogen bonds in paper was studied by transmission FTIR spectroscopy. Prior to this study, the approach given early for D-glucose – the building material for cellulose containing materials [Ivanov-Omskii, 2014], was modified and adopted. The infrared spectra were obtained with the Shimadzu FTIR-8400S spectrometer in the range of 3700–2400 cm^{-1} with resolution of 4 cm^{-1} in 20–40 scans. The measurement was performed at several locations of the same smooth side. The obtained spectra were processed in OriginPro 6.0. The transmission was converted into absorption. The transmission outside of absorption region, i.e. >3800 cm^{-1} or >2400 cm^{-1}, was considering as reflection and scattering within the samples. Their elimination was corrected as a baseline. Therefore, the baseline correction for reflection and scattering was altered depends on thickness and structure of handsheets. The deconvolution of characteristic absorption peaks was performed through a Gaussian function. Calculations of number and shape of elementary bands were obtained with $R^2 > 0.999$. The O–H stretching vibrations cause a frequency shift of characteristic absorption bands of hydrogen bonds determining the energy of bonding. A frequency shift of each Gaussian was compared with reference band of «free» non-bonded O–H group to estimate the energy of the hydrogen bond formation by using the numerous dependences available in the literature. The equation given below satisfies the experimental data:

$$E(kJ/mol) = 5 - 0{,}1 \times \upsilon_o + 8 \times 10^{-5} \times \upsilon_o^2,$$

where υ_o – is the absorption band of «free» or not covered primary O–H groups of native cellulose ($\upsilon_o = 3650$ cm^{-1}) (Kondo 1997).

Results and discussion. Although during investigation of the handsheets, normally more than 95% of incident light radiation was scattered and reflected, it did not restrict in obtaining clear and structured absorption spectra. Fig. 1 shows the baseline corrected 3700-2400 cm^{-1} infrared absorption spectrum (bold line) of 13.6 g/m^2 sample. The broad band fragment between 3700 cm^{-1} and 3000 cm^{-1} of absorption spectra is due to the O–H stretching vibration and is characteristic for cellulose containing materials (Fengel, 1992; Olsson and Salmén, 2004). The peak around of 2900 cm^{-1} [Kuptsov and Zhizhin, 1998] corresponds to C-H stretching which is a reference band in infrared spectra of carbohydrates and found normally in paper. The band of C-H stretching is required for initial identification and conformation of infrared spectra. Infrared spectra were resolved into 5 (4 out of 5 is shown) Gaussians with correlation

coefficient of $R^2 > 0.999$ of the overall approximation. Fig. 1 shows the spectrum of 13.6 g/m^2 handsheets. Each resolved band was assigned to stretching vibration of a certain type of O–H groups participating in hydrogen bonding. The 5th band of sorbed water was not depicted there intentionally due to no association with carbohydrate's hydrogen bonds. Each given band can be associated with characteristics of proton oscillators of O–H groups, by their area it is illustrated the integrity power of bonding. To be able to compare different samples, the sum of all areas was assumed to be as 100%, then the density of hydrogen bonds was calculated out of that (Table 1). Hinterstoisser and Salmen [Hinterstoisse and Salmen, 1999] first reported the hydrogen bonds found in non-destructive investigation of cellulose sheets by dynamic two-dimensional FTIR technique. They conventionally interpreted them regarding molecular hydrogen bonding, but not in terms of interfibre hydrogen bonding.
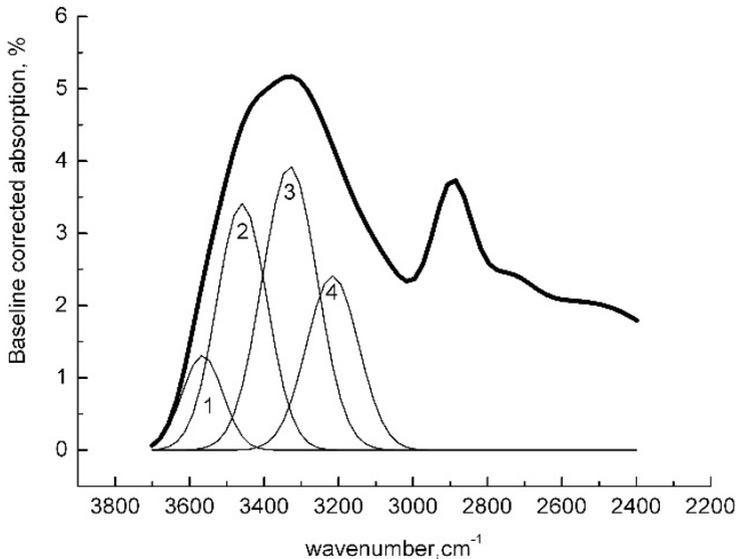

Fig. 1. An example of the baseline corrected infrared absorption spectrum (**bold line**) in the range of 3700-2400 cm^{-1} of 13.6 g/m^2 sample with deconvolution for O–H stretching region (numbered components)

Рис. 1. Пример ИК-спектра с коррекцией на поглощение вне спектра пропускания (**жирная линия**) в диапазоне 3700-2400 см$^{-1}$ отливок с массой 13,6 г/м^2 и результат деконволюции области валентных колебаний О-Н групп (пронумерованные контуры)

The results (Table 1) show that the energy of hydrogen bonds forming between cellulose O–H groups lies in the range between 10–23 kJ/mol. The «Content» column is the same as relative density of hydrogen bonds of particular type. The energy of hydrogen bonding between cellulose and water molecules is at least 3 times lower (approx. 3 kJ/mol). The proposed strong hydrogen bonds appeared at lower wavenumbers compare to intermolecular hydrogen bonds at 3230-3310 cm^{-1} which usually assign to native cellulose studied in film form [Kondo, 1997]. The similar peak at 3200 cm^{-1} was found for moist-dry handsheets in the work by Olsson and Salmén [Olsson and Salmén, 2004] without spectrum deconvolution assuming this band is responsible for a strongly bound cluster water. These evidences show that fiber bonding does a bit stronger that typical intermolecular bonding in cellulose.

Table 1

The deconvolution parameters of infrared spectra in the range of 3700–2400 cm^{-1} of 13.6 g/m^2 handsheets, where component No 1 – hydrogen bonds between cellulose and water, 2 – Intramolecular weak bonds, 3 – Intramolecular medium bonds, 4 – Intermolecular strong bonds (both intra- and interfibre)

Параметры деконволюции ИК-спектра в диапазоне 3700–2400 см$^{-1}$ отливок с массой 13,6 г/м^2, где контур №1 соответствует водородным связям между целлюлозой и водой, №2 – внутримолекулярным слабым связям, №3 – внутримолекулярным средним связям, №4 – межмолекулярным сильным связям (внутри- и межфибриллярным связям)

No	Gaussian peaks, cm^{-1}	Shift of the band, cm^{-1}	Area of Gaussians, dimensionless	Content, %	Energy, kJ/mol
1	3564	86	178	9.3	–3.01
2	3469	181	576	30.2	–10.48
3	3331	319	726	38.1	–18.76
4	3216	433	424	22.3	–23.30

The system of hydrogen bonds in paper governs by arrangement of hydrogen bonds in cellulose macromolecule (Kondo, 2005), taking into account the subtypes of hydrogen bonding between fibers at Fig. 2, it is shown the system of hydrogen bonds. Different subtypes should have different responsibilities and bond energies. The intramolecular hydrogen bonds are O(C3)H…O(C5) and O(C2)H…O(C6)H types. These hydrogen bonds are involved in macromolecule conformation within cellulose, therefore cannot
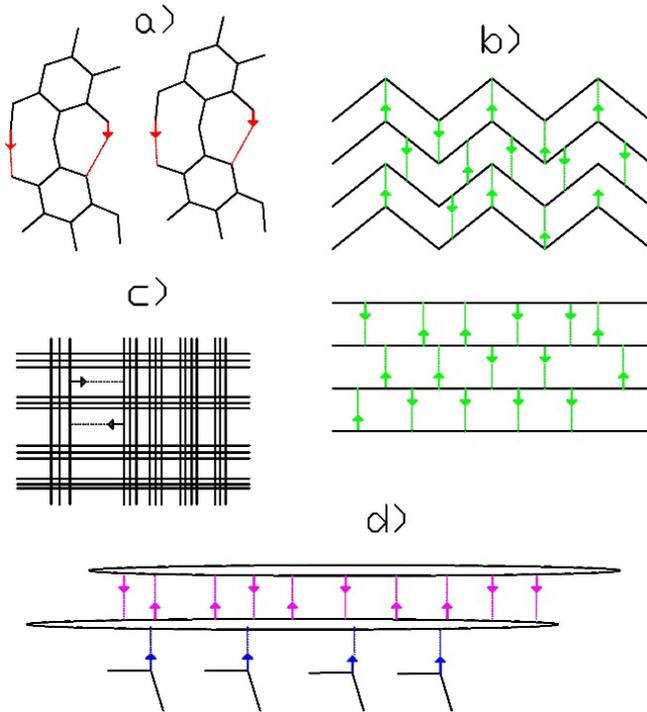
Fig. 2. The schematic view of the system of hydrogen bonds in paper, the arrows of certain color are bonds: a) intramolecular, b) intrafibrillar, c) single fiber interfibrillar, d) interfiber + «free» bonds between cellulose and water molecules are shown as well

Рис. 2. Схематическое представление системы водородных связей в бумаге, стрелками показаны связи: а) внутримолекулярные; б) внутрифибриллярные; с) межфибриллярные; д) межволоконные + показаны свободные связи между целлюлозой и молекулами воды

participate through paper stock preparation. The intramolecular hydrogen bonds are medium and weak bonds, their energy is low comparing to the intermolecular hydrogen bonds. These groups are depicted by bands No.2 and No.3 at Fig. 1. The primary O–H groups of O(C6)H…O(C3) type (the band No.4 at Fig. 1) are involved in the intermolecular hydrogen bonding [Ciolacu, Kovac, and Kokol, 2010]. Nevertheless, when considering the bundles of cellulose fibers and paper, there are possible several subtypes of intermolecular hydrogen bonds due to cellulose superstructure. Intermolecular hydrogen bonds

might be divided into intrafibrillar and interfibrillar subtypes (Fig. 2). The intrafibrillar bonds are hydrogen bonds formed between O–H groups of one fibril; they are located both in crystalline and amorphous part of cellulose. All interfibrillar bonds are to be divided into single fiber interfibrillar bonds (further mentioned just interfibrillar) forming between hydrogen bonds of fibrils of one single fiber and the interfibre bonds forming between different fibers. All intermolecular bonds are strong hydrogen bonds. We assume that these bonds should vary in the bonding energy due to different distances between oxygen atoms, while forming hydrogen bonds either between fibrils or fibers. Meanwhile only hydrogen bonds of O(C6)H…O(C3) type in amorphous part of cellulose might be influenced by stock preparation.
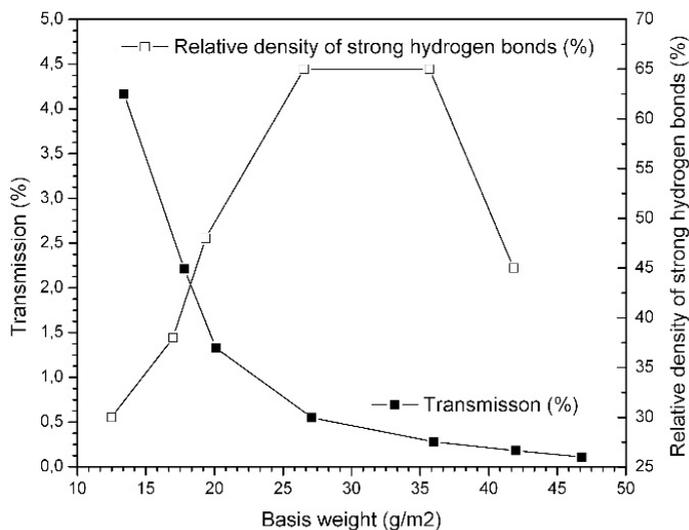

Fig 3. Basis weight of handsheets versus relative density of strong hydrogen bonds (or their content in paper) and the average sheet transmission in 3700–3000 cm^{-1} spectra band

Рис. 3. Зависимость массы 1 м^2 отливок и относительная плотность водородных связей (или их содержание в бумаге) и среднее пропускание в диапазоне 3700–3000 см$^{-1}$ ИК-спектра

In was revealed that the structure of handsheets should be counted as well. The increase of strong hydrogen bonds share was affected by sheet transmission (Fig. 3). The maximum of strong bonds 65% was reached for 27.1 g/m^2, herewith the average sheet infrared transmission was 0.5%. The next sample of

36 g/m^2 had the same content of strong hydrogen bonds, wherein the average sheet infrared transmission was 0.1%. The following sample of 42.0 g/m^2 had much lower number of strong hydrogen bonds. Finally, the 46.8 g/m^2 sample scattered infrared radiation so much that obtaining of infrared spectrum in the O–H stretching vibration range was not possible. These results clearly show that the number of strong hydrogen bonds increases with the growth in basis weight up to a certain value, then it decreases basically due to low infrared transmission rate and limitations of spectrometer being used. The minimum sheet infrared transmission in the range of 3700–3000 cm^{-1} for the method should be at least 0.10%, but it is better having 0.50%, what is confirmed from tendencies at Fig. 3. The average sheet infrared transmission and the number of strong hydrogen bonds depend on basis weight and paper structure expressed as thickness, due to transmission FTIR spectroscopy enables to investigate all fibers in paper, including the surface ones. Light handsheets have just a few fiber layers, therefore the outer fibers (top and wire layers) constitute the principal part of the whole substrate. The top and wire layers have less fiber sites to form interfibre bonding. Oppositely, the inner fibers are surrounded by the neighboring fibers; therefore, the greater number of O–H groups are available for bonding.
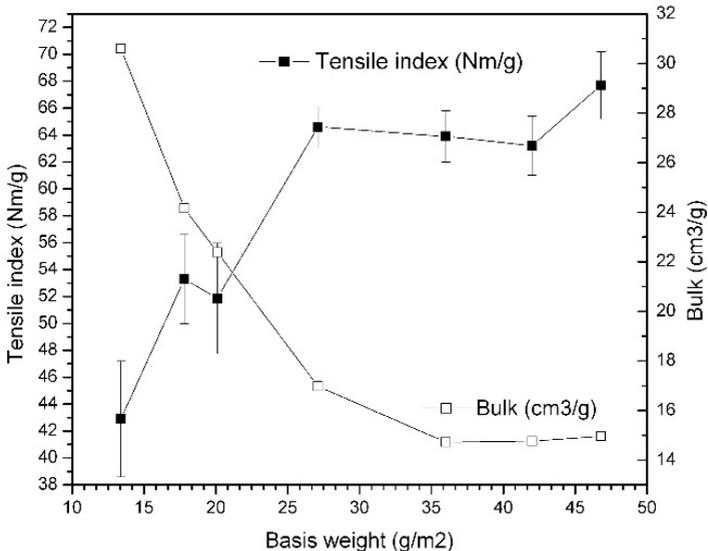

Fig. 4. Tensile index and bulk of handsheets varying in basis weight

Рис. 4. Зависимость индекса прочности при растяжении и удельного объема от массы 1 м^2 лабораторных образцов бумаги

The number of strong hydrogen bonds is correlated obviously with tensile strength. Fig. 4 shows that the heavier the samplers the higher tensile index, nevertheless, several samples had similar tensile index varied within the standard deviation. The handsheets with basis weight between 16–22 g/m^2 had tensile index of roughly 50 Nm/g, the handsheets with basis weight ranged between 26–46 g/m^2 had tensile index of roughly 65 Nm/g. The increase in both tensile index and basis weight reflects the increase in the number of strong hydrogen bonds. It should be noted that the standard deviation was lower for heavier handsheets due to obtaining more homogeneous paper structure as far as the more interfibre bonding occurs.

The bulk at Fig. 4 follows transmission, the bulkier the paper was the less transmission of infrared radiation occurred. At the same time, the extreme high bulk for handsheets up to 20 g/m^2 is a conformation that industrial tissue grades can be measured by this method, what is important in practical point of view. The handsheets heavier than 35 g/m^2 were similar in bulk of 15 cm^3/g, what is comparable with bulk of industrial tissue obtained through air drying (TAD). The tissue strength is usually expressed in tensile force instead of specific tensile values (tensile index etc.). As far as there is no straightforward correlation between tissue tensile and basis weight the measurement of strong hydrogen bonds might be considered as an alternative for this paper grade as strength parameter.

Conclusions. The schematic view of the system of hydrogen bonds in refined eucalyptus kraft pulp handsheets was confirmed by original non-destruction deconvolution method analyzing paper handsheets in the region of O–H stretching vibration 3700–3000 cm^{-1}. Infrared spectra were resolved into four Gaussians and characterized for the content of energy-varied hydrogen bonds. A frequency shift of Gaussians from the absorption frequency of «free» unbonded primary O–H groups was used to estimate the energy of hydrogen bonds. The energies of three types of hydrogen bonds were ranged from 10 to 30 kJ/mol. The band responsible for hydrogen bonds between cellulose and water shows the energy of around 3 kJ/mol. It was found that the essential requirement for the method is the minimum average sheet transmission of 0.10–0.50% in the range of 3700–3000 cm^{-1}. Although during investigation of the handsheets, normally more than 95% of incident light radiation was scattered and reflected, it did not restrict in obtaining clear and structured absorption spectra. In the case when the sheet transmission was >0.50% or <0.1% the share of strong hydrogen bonds was different, but it demonstrates the difference in the paper structure.

One of the main problems associated with transmission IR method is the prerequisite for thin paper sheets. The further development and improvement of the proposed method should go in the direction of deconvolution of infrared absorption spectra into combination of different functions as such Gaussians, Lorenzians and others what is possible in some latest versions of mathematical graphing software.

References

Calvini P., Gorassini A. FTIR – Deconvolution Spectra of Paper Documents. *Restaurator*, 2002, 23, pp. 48–66.

Ciolacu, Diana, Florin Ciolacu, and Valentin I Popa. Amorphous Cellulose – Structure and Characterization. *Cellulose Chemistry and Technology*, 2011, 45(1–2): 13–21.

Ciolacu Diana, Janez Kovac, Vanja Kokol. The Effect of the Cellulose-Binding Domain from Clostridium Cellulovorans on the Supramolecular Structure of Cellulose Fibers. *Carbohydrate Research*, 2010, 345(5), pp. 621–30.

Daisuke Tatsumi, Yarnauchi Tatsuo, Koji Murakami. FT-IR Spectroscopy in the Evaluation of Dry Handsheets with an Acrylamide-Based Dry-Strength Resin. *NPPRJ*, 1995, 10(2), pp. 94–97.

Fengel Dietrich. Characterization of Cellulose by Deconvoluting the OH Valency Range In FTIR Spectra. *Holzforschung*, 1992, 46(4), pp. 283–88.

Hinterstoisse Barbara, Lennar Salmen. Two-Dimensional Step-Scan FTIR: A Tool to Unravel the OH-Valency-Range of the Spectrum of Cellulose I. *Cellulose*, 1999, 6(3), pp. 251–63.

Ivanov-Omskii V.I. Characteristics of Hydrogen Bonds in D-Glucose. *Technical Physics Letters*, 2014. 40(8), pp. 690–92 (both English and Russian vesrions are available).

Ivanova Elena I., Alexander S. Smolin, Tatiana K. Zvonareva, and Vladimir I. Ivanov-Omskii. The Investigation of Hydrogen Bonds in Paper (in Russian). *Khimiya Rastitel'nogo Syr'ya*, 2015, 1, pp. 181–85.

Kondo Tetsuo. The Assignment of IR Absorption Bands Due to Free Hydroxyl Groups in Cellulose. *Cellulose*, 1997, 4(4), pp. 281–92.

Kondo, Tetsuo. Hydrogen Bonds in Cellulose and Cellulose Derivatives. *Polysaccharides: Structural Diversity and Functional Versatility*, ed. Severian Dumitriu. Marcel Dekker: N. Y., 2005, pp. 69–99. URL: https://doi.org/10. 1021/ja0410486.

Kuptsov A.H., Zhizhin G.N. Handbook of Fourier Transform Raman and Infrared Spectra of Polymers. 1998. 535 p.

Maréchal Y., Chanzy H. The Hydrogen Bond Network in Iβ Cellulose as Observed by Infrared Spectrometry. *Journal of Molecular Structure*, 2000, 523(1–3), pp. 183–96.

Olsson, Anne Mari, Lennart Salmén. The Association of Water to Cellulose and Hemicellulose in Paper Examined by FTIR Spectroscopy. *Carbohydrate Research*, 2004, 339(4), pp. 813–18.

Qinglin Meng, Jinquan Wan, Yongwen Ma, Yan Wang. Effects of Different Deinking Processes on Fiber Morphology, Hydrogen Bond Models, and Cellulose Supramolecular Structure. *BioResources*, 2013, 8(2), pp. 2398–2416.

Steiner T. The Hydrogen Bond in the Solid State. *Angewandte Chemie International Edition*, 2002, 41(2), pp. 265–71.

The knowledge of principles of hydrogen bonding build-up during stock preparation is useful additional information for better control of refined pulp. Nevertheless, there is no wide accepted, accurate and quick method to investigate these interactions regarding pulp refining. The principal objective of this paper was to describe the rapid method of non-destructive analysis of handsheets by FTIR spectroscopy in the region of absorption frequencies of hydroxyl groups and interpretation of the results obtained. The proposed method is based on deconvolution of handsheets FTIR spectrum into four Gaussian bands. The calculated energy of hydrogen bonding was ranged from 2 to 25 kJ/mol. The bond energy was classified on weak, medium and strong ones corresponding to inter- or interfibre subtypes. The minimum requirement for handsheets being analyzed by proposed method was found as infrared transmission ranged between 0.10% and 0.50% in the range of 3700–3000 cm^{-1}. Although during investigation of the handsheets, normally more than 95% of incident light radiation was scattered and reflected, it did not restrict in obtaining clear and structured absorption spectra. In the case when the sheet transmission was >0.50% or <0.1% the share of strong hydrogen bonds was different, but it demonstrates the difference in the paper structure. This method might be recommended for pulp and paper stock quality mill control.

K e y w o r d s : hydrogen bonds, hydroxyl groups, FTIR spectroscopy, deconvolution, curve fitting, handsheets, pulp, paper stock preparation

———

Знание принципов образования водородной связи при подготовке бумажной массы является полезной информацией для лучшего управления размолотой целлюлозы. Тем не менее не существует широко признанного, точного и быстрого метода для изучения этих взаимодействий по отношению к размолу целлюлозы. Основная цель представленного исследования заключается в описании быстрого неразрушающего метода анализа лабораторных образцов посредством ИК-Фурье-спектроскопии в области поглощения водородных групп и интерпретации полученных результатов. Предложенный метод основывается на деконволюции ИК-Фурье-спектров в четыре Гауссовы контура. Расчетная энергия водородных связей получилась в диапазоне от 2 до 25 кДж/моль. Энергия связи была классифицирована на слабые, средние и сильные связи, что соответствует меж- и внутрифибриллярным подвидам связи. Было определено, что минимальное требование к анализируемым лабораторным образцам для данного метода, это ИК-пропускание в диапазоне 3700–3000 cm^{-1} от 0,1% до 0,5%. Хотя во время анализа лабораторных образцов обычно более 95% подающего света рассеивается или отражается, это не ограничило в получении чистого и структурированного спектра поглощения. В случае, когда пропускание составило более 0,5% или менее 0,1% было обнаружено разное количество сильной связи, что показывает разницу в структуре бумаги. Предложенный метод моет быть рекомендован для производственного контроля целлюлозы и массоподготовительных процессов при производстве бумаги.

К л ю ч е в ы е с л о в а: водородные связи, гидроксильные группы, ИК-Фурье-спектроскопии, деконволюция, лабораторные образцы, эвкалиптовая целлюлоза.

———

SHABIEV Ruslan O. – associate professor of St-Petersburg State University of Industrial Technologies and Design.
198095. 4th Ivana Chernykh ul. Saint Petersburg. Russia. E-mail: ncjob@yandex.ru

ШАБИЕВ Руслан Олегович – доцент Санкт-Петербургского университета промышленных технологий и дизайна.
198095, ул. Ивана Черных, д. 4, Санкт-Петербург, Россия. E-mail: ncjob@yandex.ru

SMOLIN Alexander S. – professor of St-Petersburg State University of Industrial Technologies and Design.
198095. 4th Ivana Chernykh ul. Saint Petersburg. Russia. E-mail: smolin@grurp.spb.ru

СМОЛИН Александр Семенович – профессор Санкт-Петербургского университета промышленных технологий и дизайна.

198095, ул. Ивана Черных, д. 4, Санкт-Петербург, Россия. E-mail: smolin@grurp.spb.ru

IVANOV-OMSKII Vladimir I. – professor of Russian Academy of Sciences, the Ioffe Physical Technical Institute of Russian Academy of Sciences (Ioffe Institute).

194021. 26th Polytechnicheskaya ul. Saint Petersburg. Russia. E-mail: Ivanov-omsky@ioffe.mail.ru

ИВАНОВ-ОМСКИЙ Владимир Иванович – профессор РАН Физико-технического Института РАН им. Иоффе

194021, ул. Политехническая, 26, Санкт-Петербург, Россия. E-mail: Ivanov-omsky@ioffe.mail.ru

ZVONARYOVA Tatiana K. – scientist of the Ioffe Physical Technical Institute of Russian Academy of Sciences (Ioffe Institute).

194021. 26th Polytechnicheskaya ul. Saint Petersburg. Russia. E-mail: Ivanov-omsky@ioffe.mail.ru

ЗВОНАРЕВА Татьяна Константиновна – научный сотрудник Физико-технического Института РАН им Иоффе

194021, ул. Политехническая, 26, Санкт-Петербург, Россия. E-mail: Ivanov-omsky@ioffe.mail.ru

TRAPEZNIKOVA Irina N. – scientist of the Ioffe Physical Technical Institute of Russian Academy of Sciences (Ioffe Institute).

194021. 26th Polytechnicheskaya ul. Saint Petersburg. Russia. E-mail: Ivanov-omsky@ioffe.mail.ru

ТРАПЕЗНИКОВА Ирина Николаевна – научный сотрудник Физико-технического Института РАН им Иоффе

194021, ул. Политехническая, 26, Санкт-Петербург, Россия. E-mail: Ivanov-omsky@ioffe.mail.ru