Characterization of 17th Century Papers from Valvasor's Collection of the Zagreb Archdiocese

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Abstract

Valvasor's library is a unique example of a 17th-century personal library, which also includes over 7.300 prints. Today, it is part of the Metropolitan Library of the Archdiocese of Zagreb. In this study, the 17th-century papers in Valvasor's collection of unknown origin and composition were analysed. In order to determine the composition of these papers, a dual approach was used, by combining results obtained by non-destructive and destructive analyses from two sets of samples. On 144 paper sheets from Valvasor's collection only non-destructive analyses were performed, whereas both, non-destructive and destructive analyses were performed on the second set of samples, 10 historical paper fragments, dating from 16th to 19th centuries. Among non-destructive analyses, surface imaging, measurements of thickness, surface pH and optical properties (brightness, yellowness, opacity, and gloss) of papers were carried out. Optical properties characterized the samples as yellowish, opaque papers without gloss. Destructive analyses performed on the historical paper fragments went deeper into their composition and properties. Initially, spot tests were performed to determine absorbency, an identify lignin and starch in paper samples. Of the elementary analyses, SEM-EDS and XRF analyses for the identification of inorganic elements and FTIR analysis to identify chemical bonds in fibers, fillers, and sizes were applied. Microscopic analyses were performed in two ways - the paper surface was imaged with a digital microscope and the morphological characteristics of the fibers were studied using an optical microscope. Different fibers and components were discovered in fragments of historical papers, thus confirming their presence in handmade paper over four centuries. The dominant fibers were flax and hemp, with a smaller proportion of cotton. Also, thick and thin light brown fibers resembling straw were observed. The presence of calcium containing components, probably calcium carbonate as filler, gelatin and alumn could be confirmed. Relating the composition of historical papers with surface pH and optical properties of papers enabled us to predict the composition of 17th-century papers in Valvasor's collection.

Introduction

Janez Vajkard Valvasor (1641–1693), the famous Slovenian polyhistorian, possessed a very valuable library, which was stored in the Slovene castle of Bogenšperg [1]. In 1690, Aleksandar Ignacije Mikulić (1650–1694), the Bishop of Zagreb, bought this priceless book collection, which also held some 7.300 prints, and moved it to Croatia. This collection became part of the Metropolitana – the library of the Zagreb Archdiocese and is presently stored in the Croatian State Archives in Zagreb. Today, the book profession shows great interest in Valvasor as a person as well as in his work [2]. Valvasor's library is a unique example of a 17th century personal library whose contents show his interests. Most of the books are in German, which indicates that the papers were mostly produced in German-speaking countries.

Paper sheets from Valvasor's collection were created just before the major modernization of hand made paper production, when each stage of production had its carefully developed course. During the 16th and 17th centuries, these were smaller manufactories with fewer workers (and mostly whole families [3]), while the 18th century brought the elaboration of the production process into a whole series of stages

with specialized workers. Demand for paper grew, and production expanded and refined with it, which aimed to improve the quality and speed up the production process [4].

Throughout its history, paper's basic ingredient, fiber, has been supplemented by additives intended to improve its quality or adapt it to its purpose. The three basic additives were sizing, filler, and colors.

Sizing was used as the most common additive to interconnect the fibers and other ingredients better. Sizing was added and applied in two ways. Initially, it was coated on the already formed moist sheet of paper or immersed in it, but, later in the 18th century, the sizing was added to the paper pulp. The sizing improves the mechanical and surface paper properties, regulates the ability of paper to absorb ink, which improves the quality of writing or printing. Gelatine was introduced in Italy for sizing writing and printing paper, but in German speaking countries, gelatine was used just for writing paper. Gelatin was introduced in Italy for sizing paper that was used for both writing and printing, but in German-speaking countries gelatin was used just for writing paper. For printing paper, gelatin was commonly used for sizing paper after the printing process. Printing on unclassified paper was easier and cheaper, and that was extra work that would increase costs [10]. Fillers were added for a few reasons - to improve surface and optical properties, to improve the opacity of paper, to color paper (make it lighter) and to improve the calendering capability of papers [11]. Colored rags (source color) can be used to make colored paper. Blue and pink papers especially were manufactured in this way. When the raw material lacked the right color, the desired result could be achieved by adding a pigment (engine color) or dye (pulp color) to the pulp [11].

One of the first researchers who investigated the physical and chemical properties of historical papers and connected them to durability and resistance to aging was William Barow [4]. In his research he covered the period from 16th to 20th century and gave an overview of the paper making process and its compositon in this period. Timoty Barrett [5] analysed characteristics of handmade papers from 14th to 19th century. He used UV/Vis/NIR and XRF spectroscopy to determine the composition of the papers and explained relations between composition and paper properties. FTIR and Raman spectroscopy are another thechniques theat were used in testing historical papers [6, 7]. The structure and properties of Islamic paper [8] were analysed by using non-destructive and destructive reserch approaches commonly used when analysing historical papers. Changes in paper properties before and after the conservation-restoration procedure were investigated also by Jedert Vodopivec Tomažič. The research of general and optical properties, FTIR analysis, among other analysis of book and papers, was carried out on several copies of Valvasor's book The Glory of the Duchy of Carniola from 1689 [9, 10] .

The aim of this research is to describe and characterize historical papers from the 17th century from Valvasor's collection. The goal was to find out as much information as possible about the composition and properties of paper by comparing results obtained by non-destructive and destructive analyses. From the obtained results, the interdependencies and influences of the composition and properties of the paper could be predicted. This work is part of a broader study aimed at finding the right analysis to characterize historical handmade paper.

Methods

One of the main reasons for the characterization of the historical paper, in this case papers from Valvasor's collection, was to identify the composition of the paper for the purpose of the elaborated methods of the conservation-restoration procedure. This is important, because by knowing the paper composition it is possible to predict the changes that could occur in the paper during the conservation-restoration treatment. The first stage of our study consisted of thorough visual examination of historical papers from Valvsasor’s collection, followed by non-destructive analyses. In the second stage, destructive analyses were performed on a second set of samples, fragments of historical papers, to supplement the findings of non-destructive analyses. Paper samples were analysed by methods according to standards intended for newer, industrial papers. Such standards also provide for standardized samples that cannot be found among historical papers. For this reason, methods were selected according to acceptable standards with respect to sample size and as little destructiveness as possible.

Samples from Valvasor's collection (VC)

The first set of analysed samples are paper sheets from Valvasor's collection of the Metropolitan Library of the Archdiocese of Zagreb, covering the period from 1662 to 1689. Samples were selected randomly throughout the book taking care to make minor differences between them. In total, 144 paper sheets were analysed (Table 1). Unfortunately, no clear information is available about provenance or date for these samples exept one.

Table 1
Selected paper from seven books of VC arranged chronologically according to their origin

Sample mark	Title, date, author	Number of paper sheet analysed
1ND	Notary of the Kingdom of Dalmatia, Croatia and Slavonia, 1662, (author of the record Ivan Zakmardi (1600–1667), Croatian humanist, lawyer, protonotary of the Kingdom (1644), deputy ban and king in court affairs), manuscript	10
2ND	Topographia arcium Lambergianarum id est arces, castella et dominia in Carniolia habita possident comites a Lamberg; Bagenspergi, loannem Weichardvm Valvasor, 1679.g., print	10
3ND	A book of sketches for a book Topographia Archiducatus Carinthiae modernae, prije 1681.g., manuscript	14
4ND	Topographia Archiducatus Carinthiae modernae, Durch Johann Weichard Valvasor, Wagensberg in Krain im iahr 1681.g., Zu Laybach, Gedr. Bey Johann Baptista Mayr, print	14
5ND	Valvasor's graphic collection, 1685.g., print	61
6ND	Topographia Archiducatus Carinthiae antiquae & modernae completa: Das ist Vollkommene und gründliche Land – Beschreibung des berühmten Erz – Herzogthums Kärndten; Nürnberg,In Verlegung Wolfgang Moritz Endters, 1688.g., print	10
7ND	Die Ehre dess Hertzogthums Crain; Johann Weichard Valvasor, Volume3; Laybach, Zu finden bey W.M.Endter, Buchhändlern in Nürnberg, 1689.g., print	25

Historical papers (HP)

A second set of analysed papers are historical papers, mostly fragments. They were ment to be destroyed because only a fragment of the archival document remained and was not intended for storage. Unfortunately, no clear information is available about provenance or date for most samples. The historical papers are roughly dated (some fragments of paper on which the year of creation of the document was not found are dated approximately according to the type of manuscript or the date of the archival fund in which it was found) and cover the period from the 16th to the 19th century. They are listed in Table 2. Because only fragments were available it was not possible to determine the raw format of the paper sheets.

Table 2
Samples of HP fragments

Sample mark	Name of samples,	Origin of samples	Date
1D	Valvasor collection, shelf-mark M158; paper support for graphic collection	Metropolitan Library Archdiocese of Zagreb	1685; 17.century
2D	ARS; blotting paper	Archives of the Republic of Slovenia	1.half of 19.century
3D	HR-HDA, Found Križevci County, 1; fragment without manuscript	Croatian State Archives	16.-17. century
4D	HR-HDA, Found Križevci County, 2; fragment without manuscript	Croatian State Archives	16.-17. century
5D	HR-HDA, Found Križevci County, 3; fragment of letter	Croatian State Archives	1745; 18. century
6D	ARS, protocol 1763–1781; fragment without manuscript	Archives of the Republic of Slovenia	18. century
7D	ARS, form 1806 (458); form	Archives of the Republic of Slovenia	19. century
8D	ARS, 1807; fragment without manuscript	Archives of the Republic of Slovenia	19. century
9D	HR-HDA, Found Križevci County, 4; fragment without manuscript	Croatian State Archives	16.-17. century
10D	HR-HDA, Found Križevci County, 15; fragment of manuscript document	Croatian State Archives	16. century

Characterization

To determine properties of 17th century papers from VC only non-destructive analysis were performed. The thickness of paper sheets, microscopic imaging, surface pH and optical properties were determined. On HC fragments, destructive analysis were also performed, among them spot tests to obtain results about paper composition using different reagents. Microscopic analysis of the surface of the paper sheets, as well as morphological analysis of paper fibers, were conducted. The following instrumental analyses were performed: SEM-EDS (Scanning Electron Microscopy with Energy Dispersive Spectroscopy), XRF (X-ray fluorescence), and FTIR (Fourier-transform infrared spectroscopy).

Microscopic analysis

Microscopic analysis to identify fibers in a paper samples were performed on a Micros Austria type MCx500 optical microscope with 4x, 10x, 40x and 100x lenses and a 10x/22 eyepiece magnification under transsmited light with and without staining according to the TAPPI standard T 401 [12]. Fiber identification was based on morphological characteristics.

The imaging of the paper surface was performed with the digital microscope Dino-Lite Pro AMK 412Z-C200 at a magnification of 50x and 200x and imaging at a magnification of 500x with the model Dino-Lite AM4013MT5.

Thickness

The thickness of paper was measured with a micrometer according to the standard EN ISO 534:2005 [13] by inserting a sample between two parallel metals measuring in the range of 0–10 mm with an accuracy of 0.001 mm. Device model Enrico Toniolo S.r.l. DGTB001 Thickness Gauge was used.

Surface characterization

In addition to visual examination, microscopic imaging of the surface was carried out, surface pH and optical properties were determined. Among the optical properties of the paper, brightness, yellowness, opacity and gloss were measured. These properties are selected in order to see the connection with the composition of paper and compare the results of elemental analysis.

The pH of the paper surface was measured with a portable pH meter Mettler Toledo Seven 2Go Advanced with a surface measurement electrode InLab Surface PRO-ISM in 5 different places as prescribed by the TAPPI T529 standard [14].

The X-Rite EXact device was used to measure the optical properties of samples. The measurement of brightness was conducted according to the ISO standard ISO 2470:1999 [15]. ISO brightness of paper is defined as the ratio of the degree of reflection of diffuse blue light (λ = 457 nm) from the surface of an opaque paper sample (sheet of paper in a bundle) to the degree of reflection of an ideal reflecting body, and it is expressed as a percentage (%). Measurement of yellowness is used to estimate the white and almost white samples, and it is expressed as a percentage (%). The color of the paper gives, the degree of reflection (i.e., the ratio between the reflection of the paper sample and the white standard) of monochromatic light of a narrow wavelength range. The device automatically calculates the normalized values of the colors X, Y, Z (which represent the surface reflection curves for each curve from the spectral diagram of the sensitivity of the eye). Opacity measures light impermeability in paper and is expressed as a percentage (%). Opacity is the ratio of the degree of reflection of a single sheet of paper above one black base (< 0.5% of reflection) to the degree of reflection of the same sheet in a bundle (above such a bundle of identical paper that light cannot pass through). The opacity of paper and paperboard is determined according to the standard ISO 2471: 1998 [16].

The gloss of the paper is measured by directing a beam of constant power at an angle of 75° to the test surface and by monitoring the reflected light. Paper gloss measurement was carried out in accordance with ISO 8254-1:2009 standard [17] using an Elcometer 407 Statistic Glossmeter.

Spot Tests

Spot tests are short, quick tests that, under the influence of a reagent, cause changes in the test sample.

The Paper Sheet Absorption test was performed according to the TAPPI standard T492 pm-76 [18]. It is a method of detecting the time required to absorb water for uncoated or lightly coated papers. A drop of distilled water is droped from a height of 1 cm onto the surface of the paper, and the time until the water droplet is completely absorbed is measured.

Spot Test for Starch in paper was determined with the solution of potassium iodide according to TAPPI standard T419 [19]. The solution was dropped on a paper surface and the change in color was recorded.

The presence of lignin was determined using phloroglucinol solution as a reagent according to TAPPI standard T401 [12]. The phloroglucinol solution stains wood fibers and other lignin-containing fibers in proportion to the amount of lignin. Color change is assessed.

Herzberg Stain test was performed according to TAPPI standard T 401[12]. This test for fiber identification is based on the color change; the wood fibers are colored blue, while the flax and hemp fibers turn pink or yellowish.

Spectroscopic Analyses

Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)

SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy) is an analytical technique for elementary characterization of a sample. SEM-EDS Analyses were conducted on the device Coxem EM30AXPlus with the possibility of magnification from 20–100000 x and spatial resolution < 5 nm. The X-ray detector, EDS technique, is used to qualitatively determine the elemental composition of the sample that is visually identified by SEM. EDS is a surface technique compared with XRF, which is a semi-quantitative method.

X-ray fluorescence analysis (XRF)

The X-ray fluorescence analysis (XRF) is a method for qualitative and quantitative detection of inorganic elements in a sample. The samples were analysed by BruXRF spectrometer Artax, manufactured by Bruker. The recording conditions were 50 kV and 700 μA. The so-called Helium purge was also used during the recording to detect the fluorescence of low elements (Na-Si). The anode of the X-ray tube is Rh. The X-ray beam was directed by a 0.6 mm diameter pinhole collimator. The Rh and Zr visible in the spectra originate from X-ray tubes and collimators, so they are not present in the sample.

Fourier-transform infrared spectroscopy (FTIR)

Fourier infrared spectroscopy (FTIR) was used to identify major paper components and to assess the presence of other compounds. FTIR spectra of historical paper samples were recorded on an FTIR spectrometer Spectrum GX, I-Series. FTIR spectrometer Spectrum GX, I-Series (Perkin Elmer, Waltham, MA, USA) is equipped with an attenuated total reflection (ATR) cell and a diamond crystal (n = 2). The operation of the apparatus is controlled through Spectrum and Image software for FTIR. The spectra were recorded in the reflection mode over the spectral range 4000–500 cm^{-1}, with the resolution of 4 cm^{-1} in ATR technique and were averaged from 64 scans.

Results

Visual inspection

The VC was visually examined, dimensions of paper sheets were measured, as well dimensions and orientation of paper mold (Table 3). Photographs were taken in transmitted light to measured and defined watermarks and mold lines. The dimensions of the mold imprint in chain lines range from 22–32 mm, while the density of laid lines is from 7/1 cm to 10/1 cm. Most of the watermarks are the coat of arms, two of them identify the origin of the paper mill other the others were assigned a label according to the IPH standard [20]. The dimensions of the paper mold were measured on 10 samples of HP, chain lines in the range of 22–32 mm, and laid lines in the range of 7–10lines /1 cm. Six watermarks were found and one was identified. One watermark from VC depicting the coat of arms of Carinthia identified as a watermark from St. Ruprecht paper mill near Klagenfurt in Carinthia (Fig. 1a) [21] (present-day Austria) from 17.ct. The other one as from a group of HP samples from the paper mill of Valentino Galvani from Pordenone (Fig. 1b) [22] (Italy) from the 19th century.

Table 3
Dimensions of paper sheets and watermarks, dimensions and orientation of paper mold of paper from VC

Sample group label	Dating	Sheet width x height /mm	Place of origin or use of paper sheets	Appearance and type of watermark	Chain lines	Laid lines
1ND	1662	410–420 × 320	Zagreb	1 type of watermark Bishop's crosier IPH: R1/1 or R1/2	Chain lines vertical 20–21 mm	Laid lines 9.10 and 12/1 cm
2ND	1679	278 × 190	Bogenšperk	4 types of watermarks - coats of arms except one, endleaf watermark depicting the coat of arms of Carinthia	Chain lines horizontal 22, 23, 28 mm	Laid lines 9 and 10/1 cm
3ND	Prior to 1681	278 × 179	Bogenšperk	5 types of watermarks - coats of arms, endleaf watermark depicting the coat of arms of Carinthia	Chain lines horizontal 22–28 mm	Laid lines 7, 8, 9, 10/1 cm
4ND	1681	286 × 180	Bogenšperk	4 types of watermarks - coats of arms, endleaf watermark depicting the coat of arms of Carinthia	Chain lines horizontal 22, 23, 24 mm	Laid lines 9 and 10/1 cm
5ND	1685	360–370 × 420–440	Bogenšperk	18 types of watermarks; 12 coats of arms, 2 scales, 2 horns, 2 lions 1, Bishop's crosier IPH R1/1; covering sheets and endleaves coat of arms depicting the coat of arms of Carinthia	Chain lines horizontal, other vertical 16–28 mm	Laid lines 8, 9, 10, 11, 12/1 cm
6ND	1688	245 and 440 × 368	Nüremberg	2 types of watermarks - coats of arms and Hermes cross on 7 sheets IPH S3	Chain lines on the covering sheet and endleaf, horizontal. Book block sheets vertical; 28 and 29 mm	Laid lines 10 and 11/1 cm
7ND	1689	240 × 373–376	Nüremberg	3 types of watermarks - coats of arms	Chain lines horizontal 23–28 mm	Laid lines 8, 9, 10/1 cm

By analysing the dimensions of the sheets, the imprint of the paper mold, and the position of the watermark, it can be concluded that in all the researched books, the sheets of paper originate from two

paper mold formats. The dimensions of the smaller format are 245–278 × 360–380 mm and larger 360–370 × 420–440 mm.

By examining the dimensions, watermarks, and paper mold imprints, several conclusions were reached, so the same watermarks on different sheets do not have the same dimensions, which indicates that the manufacturer used several molds for the same type of paper. It has been observed in several examples that the covering sheets and endleaves are of the same type of paper with the same watermark while the other sheets of paper from the book block are of a different type with different watermarks. By examining the watermarks, it can be concluded that in most cases they are coats of arms.

Microscopy analysis

Inspection of papers using a digital microscope revealed some specific fibers that appear to stand out from the majority of white fibers. Several types of such fibers have been detected on both types of samples, VC and HP. Thus, blue, red, light brown, dark brown, and black - brown fibers appear in historical papers. By measuring the width of the fibers, it was observed that there are two types of fibers, thin and thick, seen in Fig. 2. Among historic papers samples, 2D stands out, where the largest amount of specific and different types of fibers is seen. In samples 3D, 4D, 6D and 8D thick, light brown fibers where found, which could indicate that these are straw fibers. Thin fibers are present in samples 5D, 7D and 10D. The most recorded fiber, found in all samples, is the thin light brown fiber. It can be described as a fiber less than 0.15 mm thick, light brown in color. Also, a blue thin fiber is found in most papers.

By examining the paper sheets, it can be concluded that the most characteristic fibers that appear can be described as *thin light brown fiber.* It is less than 0.15 mm thick, light brown in color. Blue and red fibers are found in many papers and according to width can be characterized as thin fibers (Fig. 1a, 1b).

Also, a thick light brown fiber, which, in some places, has a width of over 0.4 mm and looks like straw is present (Figs. 2c). In some places, thicker fibers were found deep in the structure of the paper (which made it difficult to measure them accurately) so that the white fibers were clearly visible on them and it was possible to measure their width (Fig. 3). The width of white fibers ranged from 0.011 mm to 0.029 mm, which would probably refer to two types of fibers specific to the 17th century period which are hemp and flax [23].

The presence of flax and hemp fibers and, in some cases, cotton can be confirmed in most samples. Flax fibers can be identified by the characteristics of their longitudinal image, they are thin long fibers, with a narrow lumen, and a saber-shaped tip [23]. A part of the fibers is thicker, with a wider and intermittent lumen, which are the characteristics of hemp fibers [23]. In addition to these fibers, short elements with pits as well as abnormal elements were found in the samples, which is mentioned in the literature as one of the cell types present in flax and hemp [23] fibers.

The fibers taken from HP were subjected to the Herzberg stain test for identification purposes [24]. Most of analysed fibers were colored in a reddish gray (Table 4) color, which confirms that they are hemp and

flax fibers, which is referred in the literature [24] as rag or fibers from old rags [24]. In most samples, the phloroglucinol lignin test [25] did not color the fibers.

Thickness

The thickness of paper is one of the basic properties of paper. The measurements of the thickness on the paper sheets in VC were limited to the area along the edges of the sheets and to the area without a plate imprint. As seen from Fig. 4a, the most of the measured values range from 0.16–0.2 mm, followed by a range of 0.1–0.15 mm, while there were only two paper sheets with thickness below 0.1 mm (sample 2ND and 5ND) and a smaller proportion of paper sheets larger than 0.2 mm. Values over 0.5 mm were determined on a composite sample, paper glued on the textile base material. It was also noted, that within the same book, a small difference in thickness was observed between the covering sheet and the endleaf and other papers within the bookblock.

The measured values of paper thickness in six samples of HP range from 0.16 to 0.2 mm, whereas at other four samples they are greater than 0.2 mm (Fig. 4b). These measurements gave as an overview of paper thicknesses over four centuries.

Surface characterization

pH

Acidity/alkalinity of paper is crucal information in order to preserve papers and protect them from degradation. Therefore, determination of acidity/alkinity is one of the most used method performed in the conservation-restoration procedure. First, we performed measurements of pH on the second set of samples in order to see if standard measuring procedure applies to microdestructive conditions. Measuring the pH on the surface of HP has revealed the destructive nature of the method, due to damage caused by the water. After drying the part of the paper on which the measurement was performed, the stains from the water droplets remained (Fig. 5).

Although the TAPPI standard T529[12] prescribes measurements by applying a drop of distilled water to the appropriate place and measuring pH in that drop, this was not possible in the case of papers from VC due to possible residual stains that may occur after applying the water drop. Therefore, measurements were performed directly on the surface of the paper, without using the water, which unfortunately influenced the obtained results. All measured values are in the acidic range, pH between 3 and 5, and only one paper sheet in the sample 5ND showed the measured pH value of 6 (Fig. 6a). The majority of paper sheets in all seven books (samples 1ND-7ND) have pH between 4 and 5. Lower pH (3–4) was determined in samples 3ND to 7ND, mainly in samples 5ND and 7ND, whereas higher pH (5–6) was obtained in samples 1ND, 3ND, 5ND and 7ND, preveling in sample 1ND.

In Fig. 6b, pH values measured on HP (samples from 1D to 10D) are presented as overview of surface pH over four centuries. It is evident that most of the measured values are in the neutral or slightly acidic

range, between 6 and 7. Three samples 2D, 3D, and 9D stand out as their values are less than 6 and one of them, namely sample 3D, has a pH value of 5. The values slightly above 7 were measured in two samples (1D and 6D). The values of standard deviations are very low, ranging from 0.07–0.55, which indicates a uniform pH of the measured samples.

Optical Properties

In order to complement the visual evaluation of papers with the analytical method, the optical properties were measured. Brightness, yellowness, opacity and gloss were determined on paper sheets from VC and on HP fragments. Measurements revealed low brightness, high yellowness, high opacity and very low gloss of analysed samples, as expected. As seen from Fig. 7a, the brightness of paper sheets in VC is mainly distributed in three groups, in the range between 40 and 50% (30 paper sheets), between 50 and 60% (37 paper sheets) and over 60% (24 paper sheets). Also, the brightness of six samles of HP falls in the range between 40 and 66% (Fig. 7b). For other samples, values below 40% were obtained, the lowest being 18.2% at HP from 16th century, and 13.4% at paper sheet from sample 5ND in VC. The highest values of yellownes were obtained in papers with lower brightness, whereas for samples 1ND and 7ND the lowest values were determined. The most paper sheets in VC, over 60%, have a degree of yellowness in the range between 20 and 30%, and over 25% of paper sheets analysed in the range between 30–40% (Fig. 8a). At HP, seven samples showed yellowness values between 20 and 40%, where the three samples from the 16th and 16-17th centrury had a darker color, with yellowness values over 45% (Fig. 8b). All measured papers have very low transparency and very high opacity. Some paper sheets in VC showed values over 100%, which is a measuring mistake, due to the inhomogeneity and uneveness of paper sheets resulting in higher reflection from one sheet than from the bundle of sheets. The measured opacity values are very high, over 90% in most cases. In allmost all samples, except in sample 2ND, opacity between 80 and 90% was determined for few paper sheets (Fig. 9a). Very high values of opacity, over 90% were determined in HP and can be classified into two groups, three sampes are in the range between 90–95%, remaining samples in the range between 95 and 100% (Fig. 9b).

Very low values of gloss, below 2.5%, tell us that papers are uncoated. The most representive values for the paper sheets in VC in all seven samples are between 1 and 1.5, followed by a range betwen 1.5 and 2 (Fig. 10a). The measured values of gloss on HP are around 1, with one exception. Paper from the 19th century (sample 2D) has the gloss value of 0.73 (Fig. 10b).

Spot Tests

The paper sheet absorption test belongs to destructive methods, as can be seen by the residual line spots formed after the measurement (Fig. 11). For this reason, the test was applied only to samples of HP. Papers showed a different behaviours regarding water absorption.

Thus, the least absorbent samples were 5D and 6D, which took between 6 and 7 minutes to absorb a drop of water, followed by four samples: 3D, 4D, 9D, and 10D which took about 3 minutes to absorb a drop of

water. It took about 2 minutes for samples 7D and 8D to absorb water while samples 1D and 2D took less than half a minute. Absorbency of the papers depends on paper structure and surface properties, and is influenced by sizing and coating.

A test to prove the presence of starch was carried out to see if the paper samples contained starch that could be used for sizing. In all ten tested samples, none matched the expected results for starch in paper [25].

The aim of determing the presence of lignin in papers from 16th – 19th century was to obtain indications that the paper pulp containe fibers with a higher amount of lignin. The test is primarily designed to see if there are wood fibers in the paper pulp as they contain a high proportion of lignin [25].

If the paper has a small amount of lignin containing fibers, the individual fibers turn red and can be seen with the naked eye [25]. The spot test for proving the presence of lignin with phloroglucinol (Fig. 12) showed a presence of fibers containing lignin in most HP. Ten tested samples showed four categories of results of the amount of colored fibers in the paper. In only one sample of paper, 10D, there were no colored fibers, then in two samples, 2D and 6D, there was a larger number of colored fibers. Two samples, 4D and 7D, contained a moderate amount of colored fibers and five samples, 1D, 3D, 5D, 8D, and 9D, contained a small number of dyed fibers. It can be concluded that all but one contain colored fibers and that a majority of samples contain a small number of colored fibers.

Microscopic and spectroscopic analyses

SEM-EDS

SEM-EDS analysis was applied in order to obtain the surface structure of paper, and to identify fibers and elemental composition. Because this method is destructive, only the second set of samples, HP were examined. Table 5 shows images of the paper surface and the elements found in the recorded location. The elements found are sorted according to the number of found elements, while trace elements are listed in parentheses.

According to the EDS results, in most samples the elements O (oxygen), C (carbon) and Ca (calcium) were detected, except in 3D, 4D and 9D samples in which Ca is not visible. Among other elements Si (silicon), Cu (copper), Al (aluminium) and Ni (nickel) were detected in most samples, but only as trace elements. Mg (magnesium) is also visible in traces in 7D, 8D, 9D and 10D, while S (sulfur), Ag (silver), and Au (gold) appear in one sample (4D), which may represent contamination.

The SEM micrographs show differences between the samples, so in some samples (5D and 8D) it is visible that the spaces between the fibers are filled, indicating that surface sizing was used during paper production and remained in some place until today. In other samples (1D and 10D), a larger number of unidentified particles is visible on the surface of the fibers.

XRF

The XRF analysis was used to characterize the composition of HP and to complement the results obtained by the SEM-EDS analysis. In all samples (Table 6) the element which is present is calcium (Ca), with the highest concentration/content determined in samples 5D, 6D and 8D, followed by 1D and 10D. In 4 samples (2D, 3D, 9D and 10D) also iron (Fe) was detected in addition to calcium. The presence in traces show silicon (Si), manganese (Mn), sulfur (S) in all samples, potassium (K) which is visible in seven samples, while aluminium (Al) is visible only in samples 3D and 4D.

FTIR

The identification of the characteristic absorption peaks was performed by the visual method [26] of comparing the obtained spectra with the reference spectra. Spectra were recorded only on HP. According to the literature on the composition of historical papers, the expected materials are cellulose fibers, among them also straw fibers [27], gelatin, gypsum, and calcium carbonate [28, 29, 30]. The reference spectra [28] of cellulose fibers have very similar absorption peaks in the fingerprint region. In all samples, the strong absorption peaks characteristic of flax, hemp and cotton fibers were detected at approximately 1050, 1110, and 1155 cm^{-1}. The characteristic absorption area around 3344 cm^{-1}, is difficult to compare, due to the overlaping with the bands characteristic of gelatin.

By examining the spectra of the individual samples and comparing them with the reference spectra, it can be noted that cellulose has two dominant regions. One of them is in the fingerprint region with one sharp peak, about 1000 cm^{-1}, with two smaller ones at about 1050 cm^{-1} and 1100 cm^{-1}. The second is in the area of stretching single bonds, about 3300 cm^{-1}. The spectra of additives (sizing and fillers) in paper such as gelatin, calcium carbonate and gypsum overlap with the spectra of cellulose in the fingerprint region, so it is difficult to confirm with certainty the presence of individual materials, i.e. their presence can only be assumed. Nevertheless, for gelatin the absorption peaks in the range 3400-3200cm^{-1} (N-H stretching band) and 3100-2800cm^{-1} (C-H stretching), peaks around 1640 cm^{-1}, 1550 cm^{-1}, and 1450 cm^{-1} (amide I, amide II and amide III) can be detected in the spectra of historical papers (Fig. 13). Gelatine was found in all samples, except in samples 1D and 2D. Calcium carbonate shows astrong absorbtion peak in the fingerprint region, around 1400 cm^{-1}, that was detected in six samples (4D, 5D, 6D, 7D, 8D, 9D) and two weak absorption peaks around 800 – 700 cm^{-1}, detected in samples 5D and 6D.

Gypsum has two dominant sharp peaks, one in the fingerprint region and the other in the area of asymmetric and symmetric OH single stretching bands, about 3300 cm^{-1}. In both areas, the peaks overlap with the cellulose peaks, making them difficult to identify. Nevertheeless, the absorption peak at around 660 cm^{-1} (SO_4^{2-} bending band) was detected in all samples, except in samples 2D and 1D.

By comparing all recorded ATR-FTIR spectra, it can be concluded that there is a very small difference between the samples in the fingerprint region, around 1550 and 1400 cm^{-1} and in the area of single bonds stretching at 3100 and 2800 cm^{-1}. The fingerprint region around 1050, 1110, and 1155 cm^{-1} characteristic of cellulose fibers is almost identical in all recorded samples, as can be seen in Fig. 12 where the ART-FTIR spectra of three samples (1D, 6D, and 8D) from different periods from 17th, 18th and

19th centuries are shown. According to the same spectrum, it can be seen that the peaks overlap only in the specified region, while other parts of the spectrum are different, which indicates the difference in the share of additives in the paper from the 17th to the 19th centuries. Although the amount of samples examined is small (10 samples), it is evident that there is a difference in the proportion of additives, which is confirmed by the research of William Barrow, who concludes that, over time, the amount of additives (sizing and fillers) in the paper changed, which affected the durability and stability of the paper [4].

Discussion

Analysis of historical papers

Although opacity values are very high and range from 90 to 98% (Fig. 9b), it has been shown that papers whose thicknesses (Fig. 4b) are lower also have lower opacity, as in examples 4D, 6D, and 8D. Such a conclusion is very logical because a smaller amount of fibers and fillers in the paper certainly contributes to greater transparency and lower opacity. Comparing the values of brightness and yellowness showed that they are inversely proportional, which means that when the brightness value is higher, the value of yellowness is lower and vice versa.

The brightness in the paper could depend on the proportion of filler that fills the space between the fibers in the paper as shown by a comparing the results of the XRF analysis with the brightness value. Thus, this comparison shows that samples with a higher proportion of calcium (Table 6) also have a higher brightness (Fig. 7b). This is best recognized in samples 1D, 5D, 6D, and 8D. Such a result suggests the opposite situation as well, i.e. that a lower brightness indicates a lower amount of calcium as the basic element of the filler, which is visible in samples 2D, 3D, 4D, and 9D. The exception is the 10D sample, which is visibly dark and has a brightness value of 18.16% and a yellowness value of 60.55% (Fig. 8b), while the calcium content according to the XRF analysis is high (Table 6). The cause of such values may lie in the aging of the paper or poor conditions in which the sample was stored, and not in the calcium content. An exception is also the 7D sample, whose brightness value is 65.32%, while its calcium content is low, which indicates that other factors also affect the brightness. In this case, it is possible that the better storage conditions are the reason why the paper has remained lighter.

The pH of the paper can also be related to the calcium content in the paper or filler that creates an alkaline environment. Thus, samples 2D, 3D, and 9D have an acidic pH between 5 and 5.45 (Fig. 6b), and the very low calcium content seen from XRF spectrum (Table 6). In the case where the calcium content is higher, the pH is neutral, around 7 [5]. This can be seen in samples 1D, 5D, 6D, and 8D. The gloss of paper surface (Fig. 10b) can be related to lower brightness and acidic pH, as obtained in samples 2D and 3D, where the measured gloss values were less than 1.

Spot tests performed for identification of starch in historic papers did not yield a positive result, proving that starch was very rarely used as a surface sizing additive from the 16th – 19th centuries on papers

produced in Europe [8].

A test to identify lignin with the reagent phloroglucinol indicated the presence of fibers that have a slightly higher proportion of lignin. Samples 2D and 6D had the most colored fibers, which could indicate the presence of lignin, while in the sample 10D from the 16th century there are no such fibers present. A paper absorbency test conducted with a drop of water showed that the most absorbing paper samples were 1D and 2D, and the least 5D and 6D. The results of the ATR-FTIR analysis showed that it is the 1D and 2D paper samples that have no additives of either gelatin as a coating or calcium as filler, which could be the reason for their higher absorbency.

Microscopic Analysis was performed on the surface of the paper samples and on the fibers. Analysis of the surface of the paper revealed specific fibers that stood out, so it could be concluded that most of the specific fibers are thick light brown fibers that look like straw [23, 27]. Also, a thin blue fiber was found in samples 1D, 2D, 5D, 6D, 8D, and 10D. The presence of blue dyed fibers was confirmed by analysis on an optical microscope in samples 1D, 2D, 3D, 4D, 5D, 6D, and 10D. Based on morphology, the blue fibers in samples 1D, 2D, 3D, and 5D are cotton fibers while in samples 4D, 6D, and 10D they are silk fibers. According to the data from the literature, it is assumed that the blue fibers were dyed with indigo dye, which, in the period from the 16th to the 19th century, was used in Europe for dyeing fabrics [32]. Most of the fibers in all samples were recognized as flax and hemp, the most represented fibers cultivated for the production of textiles in Europe in the period from the 16th to the 18th century, while cotton was less represented. Cotton was identified in only two samples from the 19th century (5D and 6D). Such a result can be supported by the historical fact that, in the 16th-17th centuries, cotton was mostly imported from India and then hand-spun in Europe [23, 11].

ATR-FTIR spectra confirmed the presence of both types of fillers in most samples except in 1D and 2D, which is significant, but when considering the purpose of these papers, such results are not surprising. 1D is the paper Valvasor used as the base for his collection of prints while 2D served as the blotting paper for the ink that was placed under the paper used for writing. Calcium as an element is visible in both elemental analyses of inorganic elements (Tables 5 and 6) except in SEM-EDS in three samples: 3D, 4D, and 9D. Comparing the results with XRF, it is clear that the calcium peaks on these samples are smaller, which would indicate that the calcium content is lower and which can be further related to other analysis results such as pH, absorption, brightness, etc.

In the SEM-EDS and XRF analyses, many trace elements have been recorded that can be related to the composition of the paper (Tables <link rid="tb5">5</link> and 5). Thus, sulfur (S), potassium (K), and in some samples iron (Fe) are visible in XRF spectra, while aluminium (Al) and copper (Cu) are visible in SEM-EDS spectra. Sulfur is an element that is part of the molecule of gypsum ($CaSO_4$ x H_2O) and alum ($KAl(SO_4)_2$ x $12H_2O$) as well as aluminium and potassium. Iron as an element is visible in traces in all XRF spectra and can be attributed to the composition of iron alum ($FeAl(SO_4)_2$ x $12H_2O$). Silicon (Si) is an element that was detected in both elemental analyses and, according to the literature, is associated with the presence of straw. Straw stalks contain silicon oxide (SiO_2) [25], 4–7% in wheat straw [21]. The

presence of most of the elements recorded in traces during elemental analyses could be interpreted, though for some, such as manganese (Mn), magnesium (Mg), titanium (Ti), copper (Cu) and nickel (Ni), we did not find any explanation for their presence. Such a result could be attributed to sample contamination.

Analysis of paper sheets from Valvasor's collection

With a comparison of the results of analyses performed on the paper sheets in VC and HP some similarities, as well as differences were observed. The thickness measurements revealed (Fig. 4) that the values range from 0.16 mm to a little more than 0.24 mm. The exception is the sample 5ND (collection of geographical maps [33]) where individual papers are glued to the fabric, so the measurements were carried out together with the fabric, and, as such, the result can be neglected. Although, afer we analysed only a small amount of historical papers, some conclusions could be made. It could be concluded that the thicknesses of the paper samples from the 16th and 18th centuries (10D, 5D, 6D) were somewhat lower compared to the papers from the 16th – 17th centuries (10D, 3D, 9D, 1D). Papers from the 19th century (2D, 7D, 8D) can have different thicknesses as a result of the development of production technology and the possibility of making different types of paper. Barrett in his research [5] shows that the thicknesses range from 0.15 mm to 0.3 mm and that towards the 19th and 20th centuries, thickness values increased.

The highest difference in properties between two set of samples was obtained for acidity/alkinity of papers (Fig. 6), probably due to different approaches to measurement. Measurement of paper pH on the surface with a drop of water, according to the TAPPI standard T529 [14], performed on HP fragments is compared with a non-destructive pH measurement directly on the surface, without a drop of water. It should be emphasized that later results, performed on the paper sheets from VC should not be taken as such, but should be considered only as an indicative value. In the non-destructive approach, the obtained pH values were in the acidic range, while in the destructive approach these values were broader. A comparison with the results of elementary analyses of SEM-EDS and XRF on paper fragments shows that the pH depends on the proportion of calcium or fillers in the paper. In this research, two things can be concluded - firstly, that the difference in results arose from different approaches to measurement and, secondly, that the papers from the 17th century have a lower proportion of calcium or fillers in the paper. There is another theory put forward by William Barrow [4] which was confirmed by Irene Brückle [34], where they stated that papers in the 17th century were coated with gelatin and alum, which remained on the surface of the paper due to which the surface of the paper has an acidic pH.

Observing the results of the brightness and yellowness (Figs. 7 and 8), a scattering of results may be noticed, the cause of which are different papers in the book marked 5ND, although most of the measured brightness values range from 40–60%. Comparing these values with the values of brightness of the tested samples historical papers fragments, it can be seen that the values in the 16th century were lower, then increased during the 17th century, and dropped a little during the 18th century, and, finally, increased in the 19th century. An attempt was made to explain the reason for such brightness in the proportion of calcium that could affect the brightness or yellowness of the paper. If we look at the oldest tested sample,

i.e. paper from the 16th century (10D), it can be seen that the brightness is very low (18.16%) (Fig. 7), while the calcium content is high (Tables 5 and 6). This indicates that we cannot fully confirm the claim that a high brightness also means a high proportion of calcium or fillers in the paper. The reason for the low brightness values despite the high calcium content should be sought in other factors that influence the brightness. The yellowness (Fig. 8) is inversely proportional to the brightness, so the scatter of the results at paper sheets in VC is repeated, as well as the yellowness in HP samples being high and then dropping in the in 17th century, after which it slightly increases and drops again in the 19th century.

The values of opacity determined in the paper sheets in the VC (Fig. 9) are very similar, around 90%. The situation is similar with the opacity of HP fragments shown through the centuries where values range from 90–98%. The comparison of the opacity and thickness over the centuries showed that they coincide; thinner papers have lower opacity and vice versa.

The gloss of paper sheets in VC (Fig. 10) is low, in the range between 1 and 1.5. Again, values determined for paper sheets in book marked 5ND (collections of geographical maps) show more scattering, on some papers the values are up to 2.5. Observing the diagram of HP fragments through the centuries, a slight increase in gloss towards the 19th century was noted, with the exception of blotting paper marked 2D. The low gloss is connected with a paper surface which is not coated or sized.

Conclusions

The topic of this research were papers from the 17th century, more exactly, papers in Valvasor's collection of unknown origin and composition. The determination of paper properties should be carried out in accordance with standardised testing methods, where the measurements are in most cases performed on sample pieces. On the other hand, the principles of the conservation-restoration profession dictate non-destructiveness in their work and do not allow sampling from the objects for scientific or any other research. For this reason, it was decided to conduct measurements on two sets of samples in order to link the results and supplement them to obtain the composition of papers from the 17th century. Non-destructive analyses were performed on papers in VC, while destructive analyses were conducted on fragments of HP obtained from two state archives.

The results of the analyses showed that most of the papers in VC originate from two paper mold formats – the smaller format is 245-278x360-380mm and larger 360-370x420-440mm. Papers can be characterized as a thick, with slightly acidic surface. The results of optical measurements show that the brightness of paper is relatively low and yellowness relatively high, while the opacity is extremely high, and the gloss of the paper is extremely low.

Combining microscopic analyses (digital, OM, SEM) with spot test and FTIR analyses, the fiber composition of paper was determined. Papers in VC were mainly manufactured from flax and hemp fibers, and cotton fibers were also present to a lesser extent. By imaging the surface of the paper on most samples, fibers defined as thick light brown and thin light brown, resembling straw, were observed. In addition to these fibers, blue fibers were also observed, indentified as cotton and silk fibers. Elemental

analyses performed with ESD and XRF confirmed the presence of calcium-based fillers and FTIR showed the presence of gelatin in historical paper fragments.

The amount of calcium present can be related to pH and brightness. It has been shown that acidic pH coinsides with a smaller peak of calcium in the XRF spectrum. The height of the calcium peak in the XRF spectrum coincides with the brightness of the paper, a higher proportion of calcium yields a higher brightness and lower yellowness.

Other trace elements noted in SEM-EDS and XRF spectra such as aluminium, potassium, and sulfur may suggest the presence of alum, while silicon may suggest the presence of silicates. This could be related to straw, whose stems contain silicates suggesting that straw could have been part of the pulp for paper production until wood pulp began to be used. Some other trace elements have been noted that could be defined as contamination, though future research may also define them as part of some added components in the paper.

In addition to determing the origin and composition of the papers in VC, some methods that could be used in preparation for conservation and restoration work on HP are highlighted in this study. They are quick, non-expensive, undemanding and easy to perfom tests. Measurements of thickness, surface pH, paper absorbency test with a drop of water, and spot tests to prove the presence of starch and lignin are methods which could be widely used in the conservation-restoration practice. Optical properties such as brightness, yellowness, and gloss could be of interest in research before and after conservation-restoration procedures to see the extent and manner in which individual procedures affect the paper.

Declarations

- Competing interests

- Not applicable

- Funding

-Not applicable

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Tables

Due to technical limitations, table 4, table 5 and table 6 are only available as a download in the Supplemental Files section.

Figures

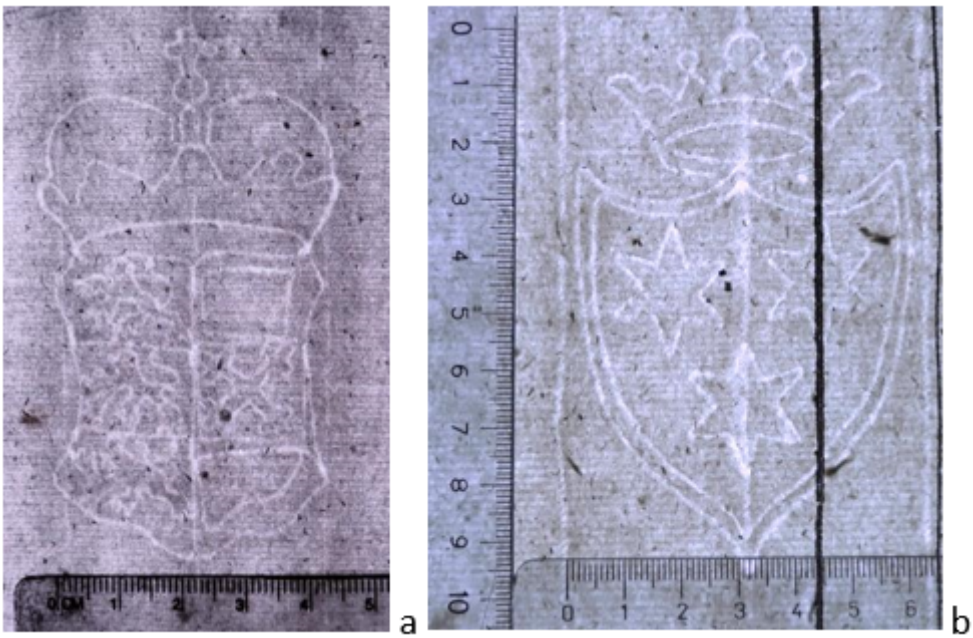

Figure 1

Identified watermark from a) VC paper 5ND b) HP sample 7D

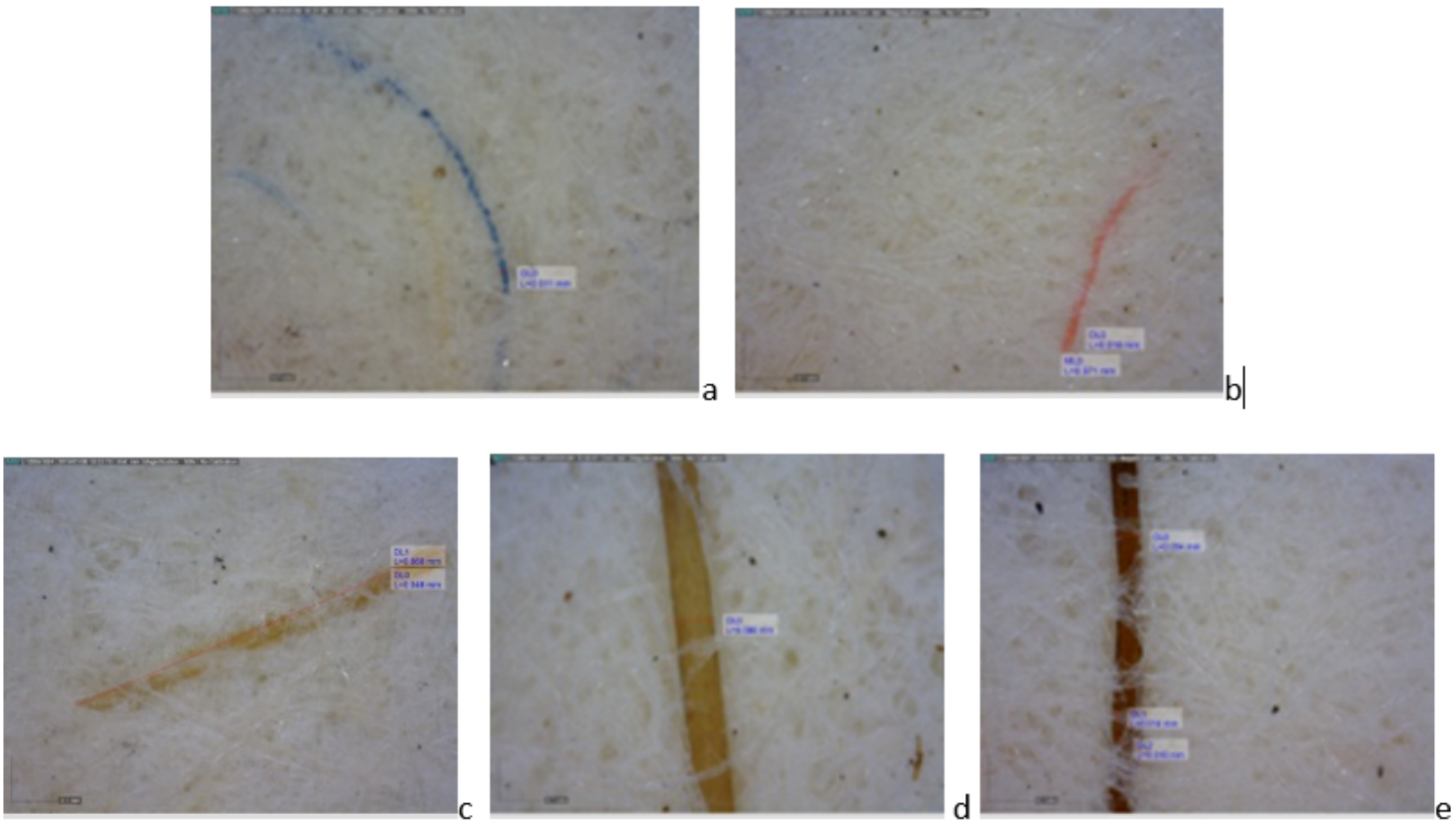

Figure 2

Image of fibers detected with digital microscope: a) blue, b) red, c) thin light brown, d) thick light brown and e) thin dark brown fiber

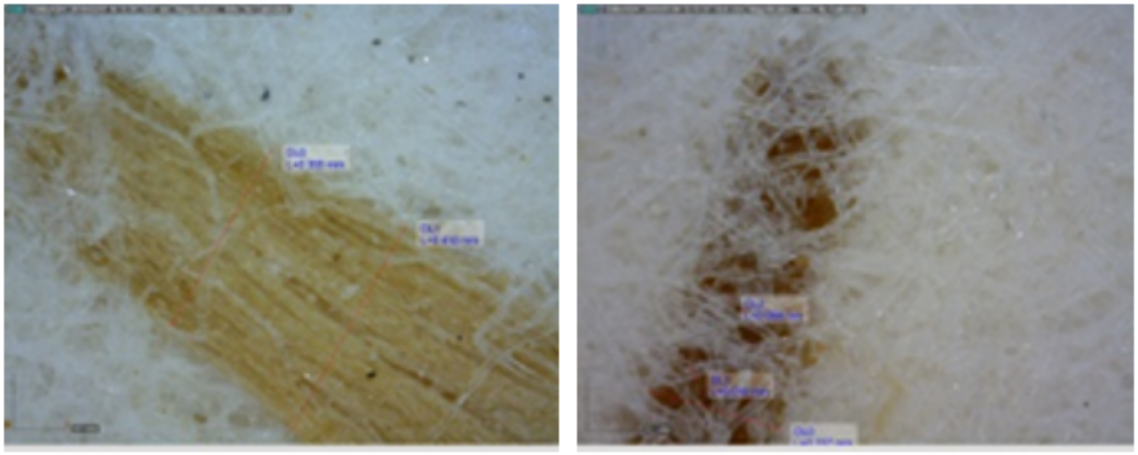

Figure 3

Images of thick light brown fiber in the paper structure

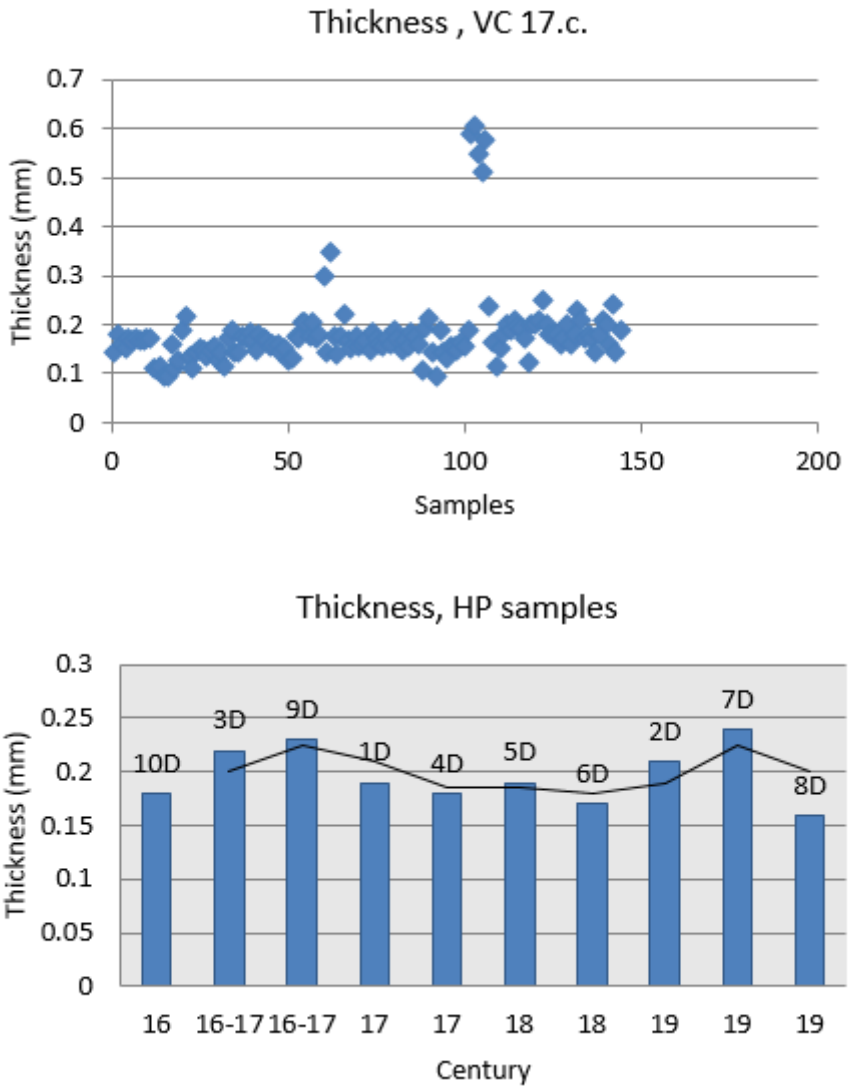

Figure 4

Paper thickness a) papers from VC b) HP samples sorted by dating

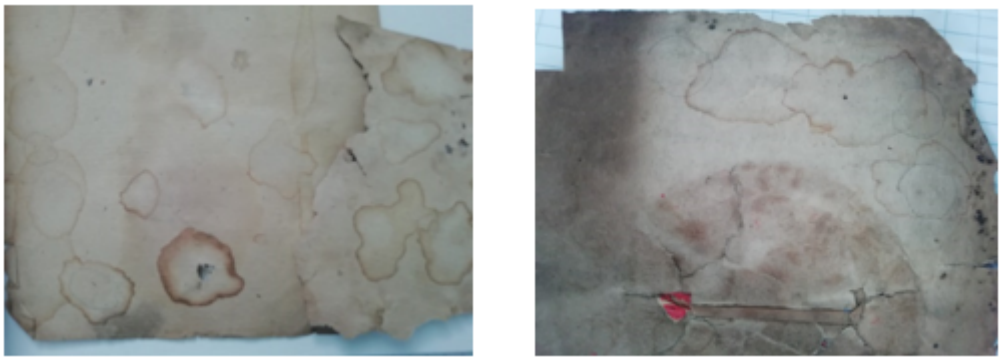

Figure 5

Details with stains on 3D and 10D paper samples after surface pH measurement

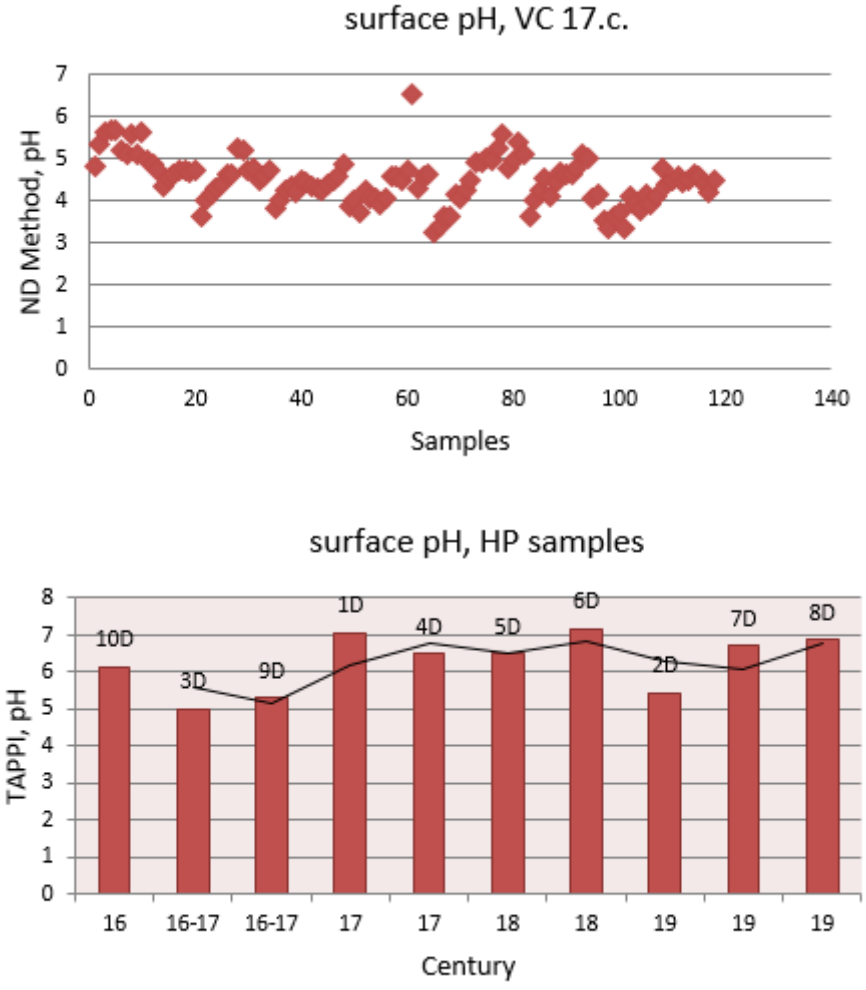

Figure 6

Surface pH a) papers from VC b) HP samples sorted by dating

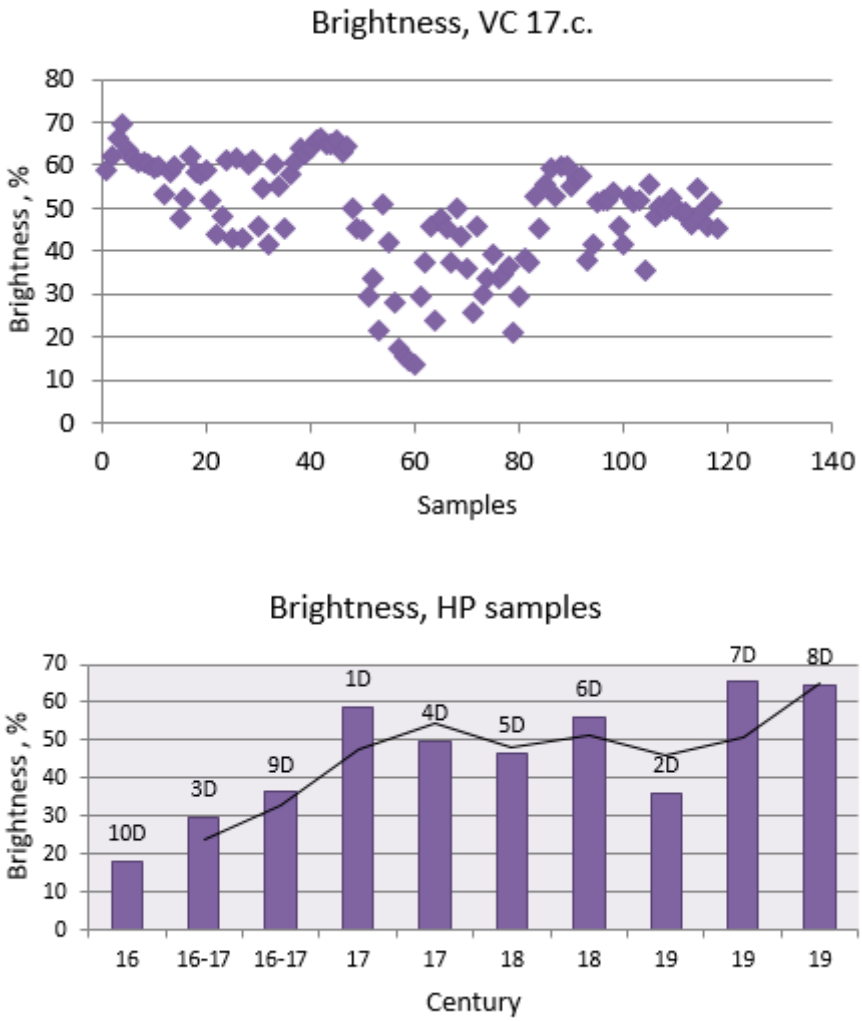

Figure 7

Paper brightness a) papers from VC b) HP samples sorted by dating

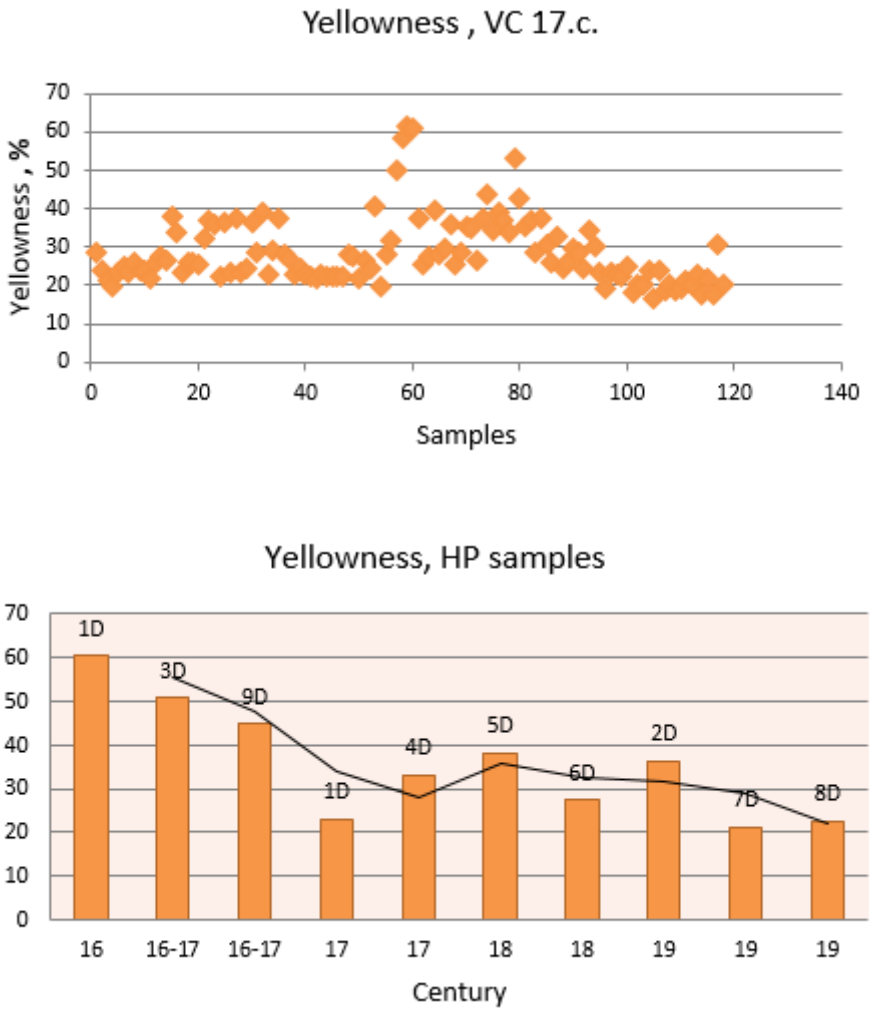

Figure 8

Paper yellowness a) papers from VC b) HP samples sorted by dating

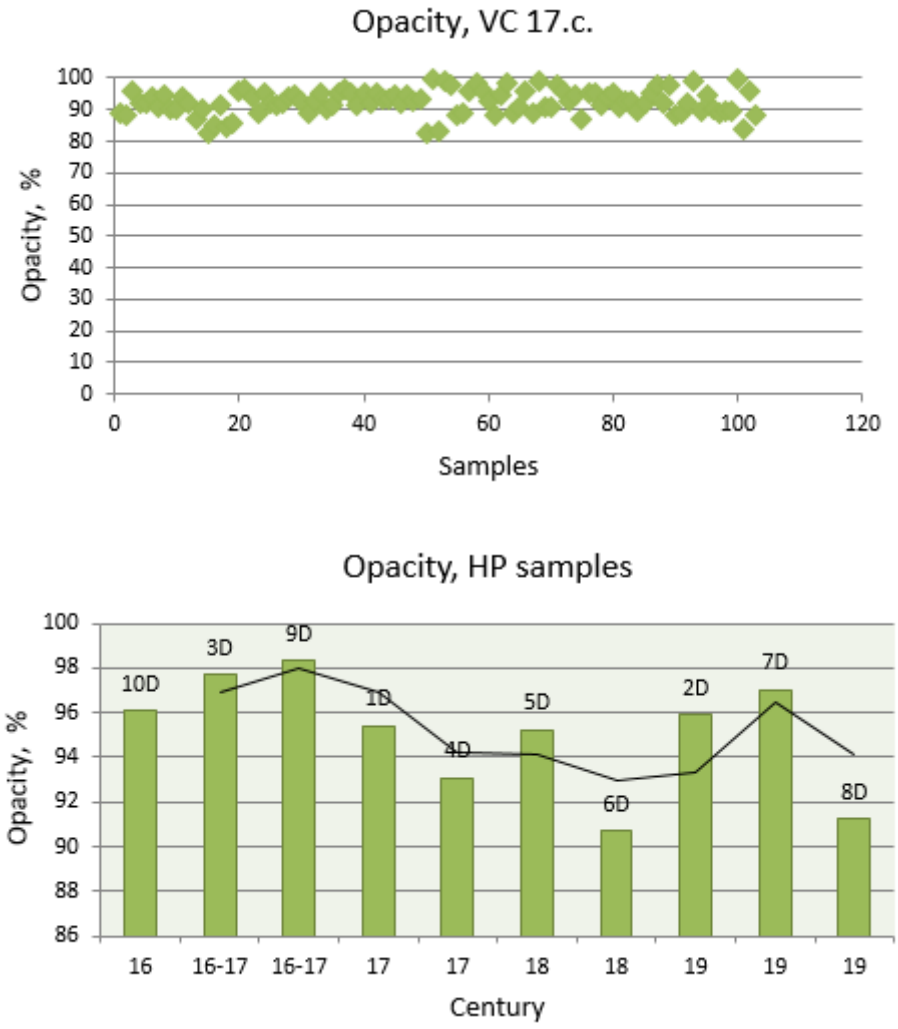

Figure 9

Paper opacity a) papers from VC b) HP samples sorted by dating

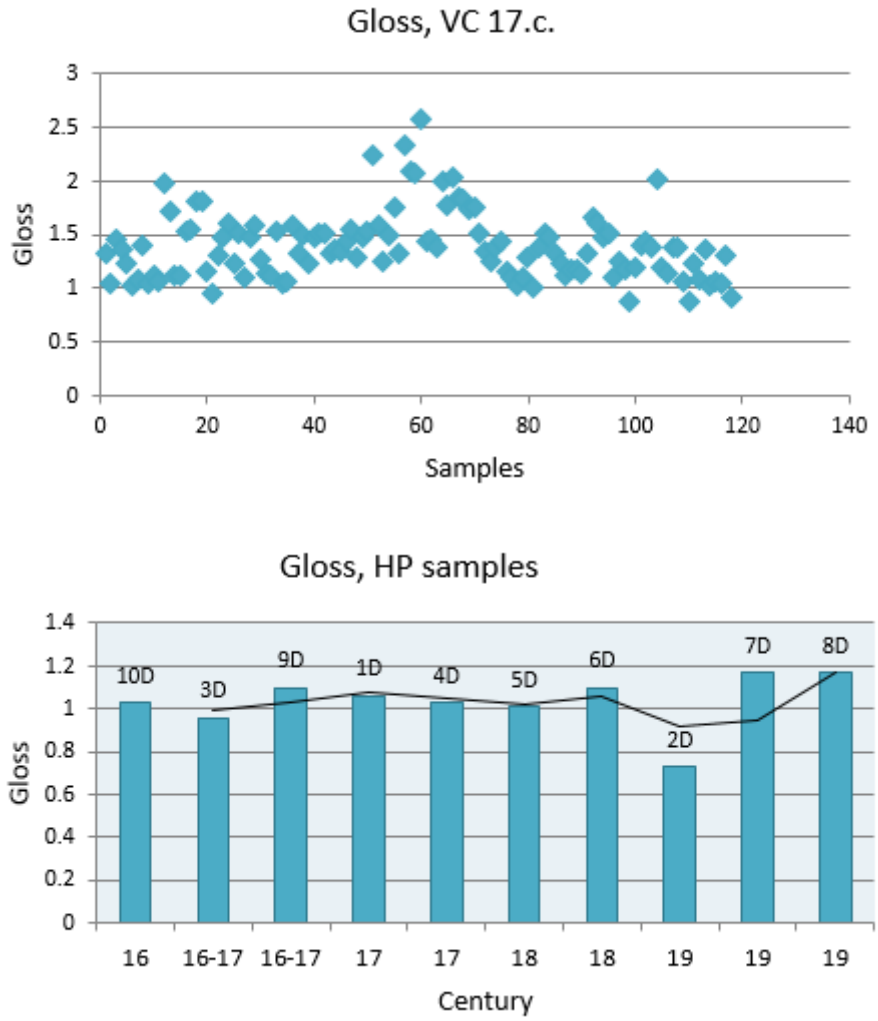

Figure 10

Paper gloss a) papers from VC b) HP samples sorted by dating

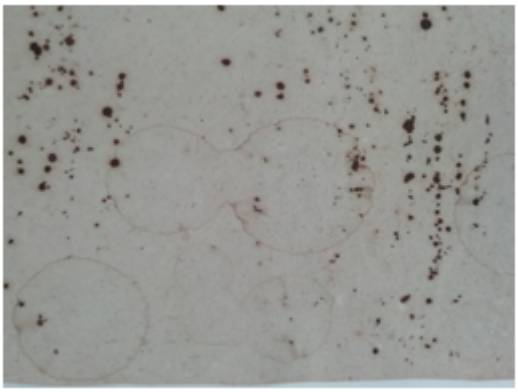

Figure 11

Line stains formed after measurement on sample 2D

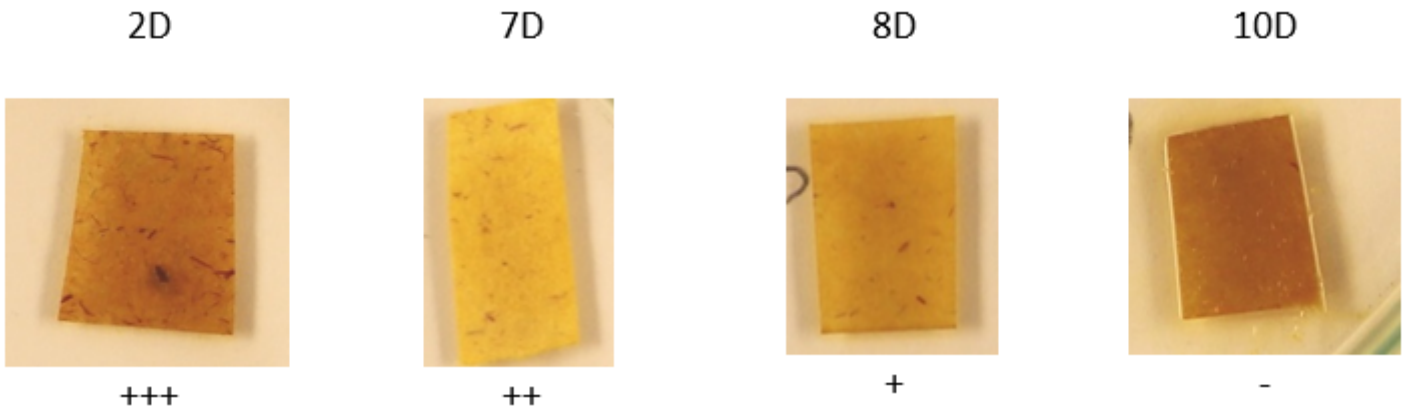

Figure 12

Results of the spot tests for starch and lignin in HP * display of the amount of colored fibers: –No colored fibers, + small amount of colored fibers, ++ moderate amount of colored fibers, +++ higher amount of colored fibers

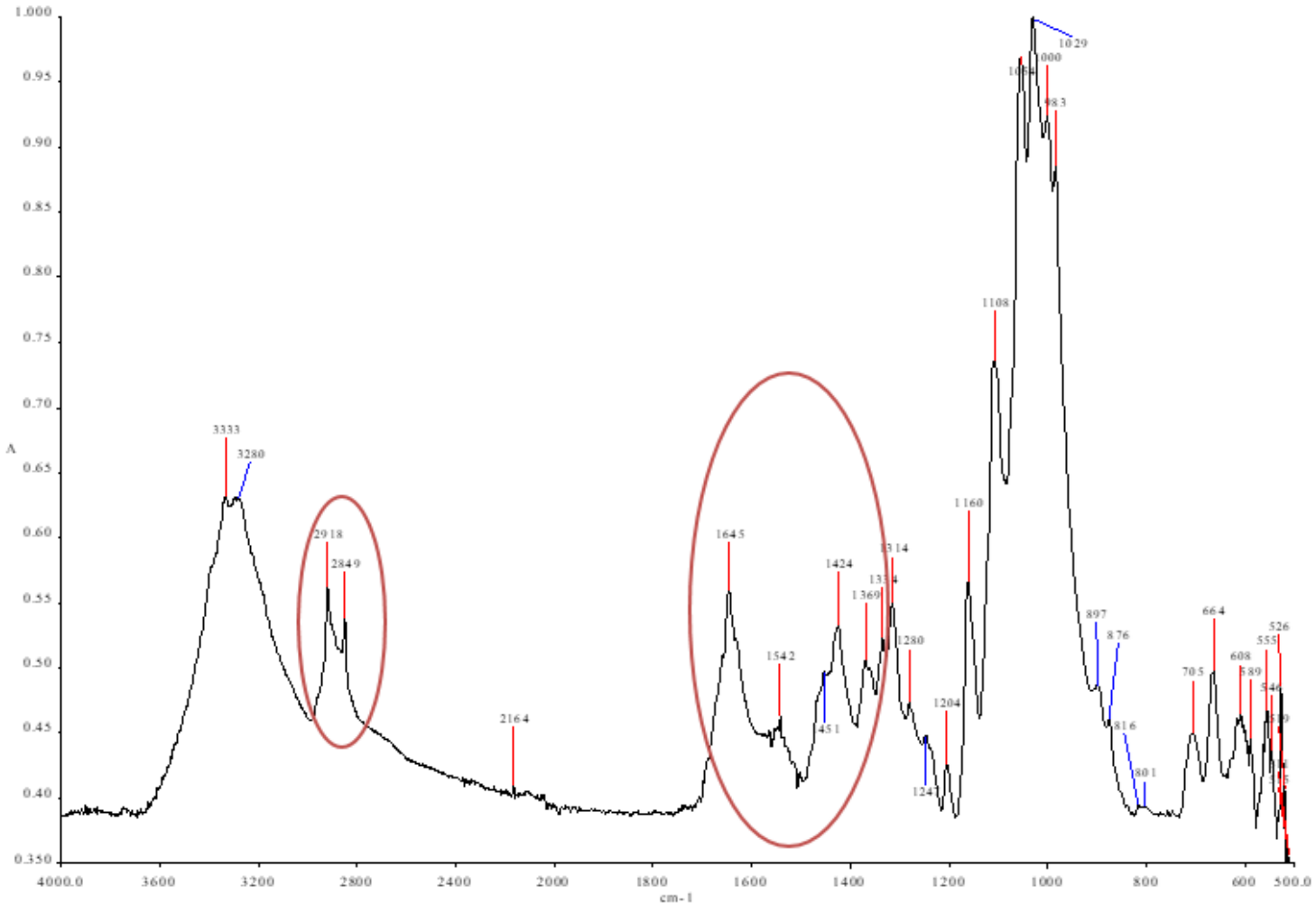

Figure 13

ATR-FTIR spectrum of sample 6D, with absorption peaks typical for gelatin.

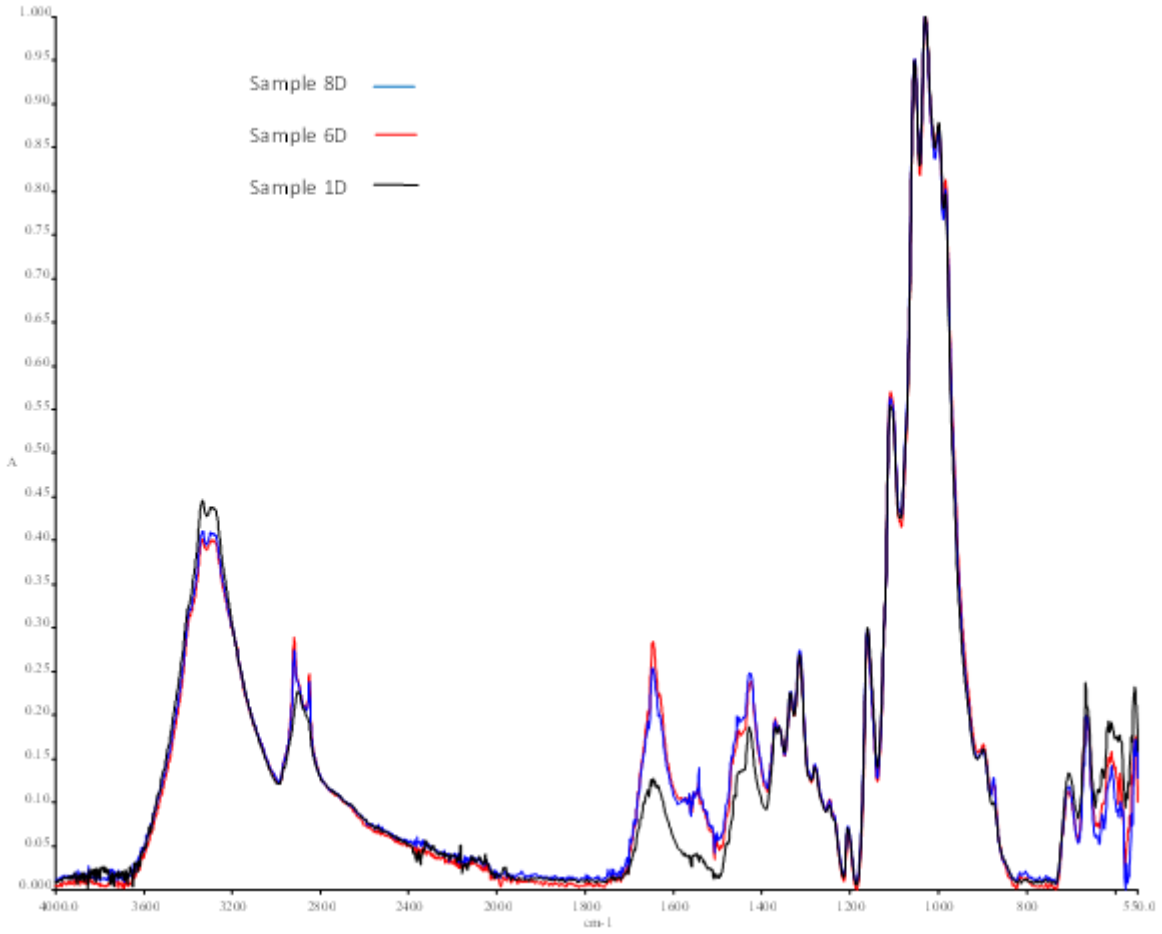

Figure 14

ATR-FTIR spectra of historic papers sorted by dates 1D (17th century), 6D (18th century) and 8D (19th century)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Table456.docx