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 includes over 7,300 prints and 1530 books. Today, it is part of the Metropolitan Library of the Archdiocese of Zagreb, kept in the Croatian State Archives. In this study, 17th-century papers from Valvasor's collection (*VC*) of unknown origin and composition were analysed. To determine the compositions of those papers, a dual approach was used, combining the results of analyses of two sets of samples. For the first set of samples, composed of 144 papers from *VC,* which are cultural heritage materials, only non-destructive analyses of paper properties were performed. Surface imaging, measurements of thickness, and determinations of optical properties (brightness, yellowness, opacity, and gloss) were carried out. According to the optical properties, papers from *VC* could be characterized as yellowish and opaque, without gloss. The second set of samples was composed of 10 historical paper (*HP*) samples collected from archival materials dating from the 16th to 19th centuries; non-destructive analyses of the paper composition were also performed. Initially, spot tests were performed to determine water absorbency and to identify the presence of lignin and starch in the paper samples. SEM-EDS and XRF were applied for the identification of inorganic elements. FTIR analyses were used to identify the chemical structures of the paper components. Microscopic analyses were performed in two ways: the paper surface was imaged with a digital microscope, and the morphological characteristics of the fibres were studied using an optical microscope. The dominant fibres present were flax and hemp, with a smaller proportion of cotton. Additionally, thick and thin light brown fibres resembling straw were detected. The presence of calcium-containing components, gelatine and alum could be confirmed with SEM-EDS, XFR and FTIR analysis. Comparing the results of analyses performed on two sets of samples enabled us to predict the composition of 17th-century papers from *VC*.

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, the Bishop of Zagreb (1650–1694), bought this priceless book collection and moved it to Zagreb (today 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. 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 could indicate that the papers were mostly produced in German-speaking countries [2].

Papers from Valvasor's collection (*VC*) were hand-made papers from an era when each stage of production had carefully developed steps. During the 16th and 17th centuries, there 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, aiming to increase the quantity and speed up the production process [3].

Throughout its history, paper's basic ingredient, fibre, has been supplemented by additives intended to improve its quality or adapt it to its purpose. Fibres were obtained by a fermentation process from well-worn cloth or rag textiles [3]. The three basic additives were sizing agents, filler, and colours [4]. Sizing was used to change a paper's resistance to the penetration of a liquid such as ink or other aqueous media. Surface sizing, such as

gelatine, also improved the paper's strength and abrasion resistance. Sizing was added and applied in two ways. Initially, it was coated on the already formed moist sheet of paper or immersed in it; later in the 18th century, sizing was added to the paper pulp. Gelatine was introduced in Italy for sizing writing and printing paper, but, in German speaking countries, gelatine was used only for writing paper [5]. For printing paper, gelatine was commonly used after the printing process [6, 7]. Fillers were added for a few reasons: to improve the surface and optical properties, to improve the opacity and brightness and to improve the calendaring capability [7, 8]. Coloured rags (the source of colour) can be used to make coloured paper. When the raw material lacked the right colour, the desired result could be achieved by adding a pigment (engine colour) or dye (pulp colour) to the pulp [8].

One of the first researchers studying historical book papers, Barrow, investigated the physical and chemical properties of papers and connected them to durability and resistance to ageing. The research provided an overview of the papermaking process, and its composition covered the period from the 16th to 20th centuries [9]. For characteristics of handmade papers from the 14th to 19th century Barrett et al. used UV/Vis/NIR and XRF spectroscopy to determine the composition of the papers and explained relations between composition and paper properties [10]. The combination of non-destructive and destructive research approaches was used by Maghoub et al. [11] to determine the structure and properties of Islamic paper. FTIR and Raman spectroscopy are other techniques that have been used in testing historical papers [12, 13]. Librando et al. [14] used FTIR for ancient and modern paper characterization to study the degradation process of cellulose papers. Trafela et al. [15] performed near- and mid-FT-IR analyses of historical papers. They related the obtained data to ash, lignin and aluminium content, degree of polymerization of cellulose and pH, which were determined with classical analytical methods. Non-destructive analyses of NIR spectroscopy and comparison with analyses of mechanical properties as a parameter of the state of usability were investigated by the same group of authors, which could be the basis for the elaboration of conservation procedures [16]. Ganzerla et al. [17] used various analytical techniques, including FTIR and SEM-EDS, for the characterization of fibres and additives used in paper production in the 19th century. In the study by Kostadinovska et al. [18], the combination of optical microscopy and ATR FTIR was shown to be a good tool to analyse historic paper artefacts of unknown composition. The optical properties of paper were investigated by a non-destructive method to discover certain materials in the paper. The relationship between the brightness of the paper filler and the brightness of the paper was investigated by Hubbe and Gill [19]. Investigation of the influence of light and temperature on optical properties to simulate the conditions of use and storage of documents led to results that showed a negative impact on the stability of paper with cellulose fibres [20]. Changes in paper properties before and after the conservation-restoration procedure were also investigated by Vodopivec Tomažič et al. [6]. The research of general and optical properties, FTIR analysis and other analyses of books and papers were carried out on several copies of Valvasor's book The Glory of the Duchy of Carniola from 1689.

Non-destructive analysis for the characterization of historical papers is an important approach in the analysis of cultural heritage objects [21]. The database on the mechanical and chemical properties of paper, which describes the interdependence between composition and degradation and may influence conservation research and practice, was researched by Strlič and coauthors [22]. In 1984, Lahavier [23] explained the application of scientific research on museum objects for the purpose of dating, information on provenance, and composition of materials. Rizutto et al. [24] elaborated the methodology of a proper approach to perform

research on cultural historical objects in three basic steps: visual inspection, non-destructive analysis, as well as semi-destructive and microscopic analysis. Kostadinovska et al. [25, 26] dealt with the study of historical papers with examples of books from the 18th and 19th centuries and artistic cartoons. In both cases, she compared the results of spot tests, ATR-FTIR and micro-Raman analysis for the purpose of elaborating the design of the conservation-restoration protocol on the above examples.

The research presented in this paper is part of a broader study focused on finding the most useful analyses for characterizing historical handmade papers that could assist future researchers and conservators in their work. The goal was to determine as much information as possible about the composition and properties of papers and the interdependencies between them by comparing the results obtained by non-destructive and destructive analyses performed on two sets of samples. Papers from Valvasor's collection/library were selected randomly [27] as a first set of samples for paper characterization by the non-destructive analyses. For comparison, 10 samples of historical papers were also analysed by destructive analytical methods.

Materials And Methods

The first stage of our study consisted of a thorough visual examination of papers from Valvsasor's collection (*VC*), followed by non-destructive analyses on these samples. In the second stage, destructive analyses were performed on the second set of samples, fragments of historical papers (*HP*), to supplement the findings of non-destructive analyses. For this reason, methods were selected according to acceptable standardized methods with respect to sample size and semi-destructiveness.

Papers from Valvasor's collection (*VC*)

The group of analysed papers with the non-destructive method is from Valvasor's collection of the Metropolitan Library of the Zagreb Archdiocese and covers the period from 1662 to 1689. All papers analysed are from the books of the Valvasor collection except the ones marked 1ND, which are archival documents from the Croatian State Archives. Four of them are printed books (2ND, 4ND, 6ND and 7ND), two of them are manuscripts (1ND and 3ND) and one of them is from Valvasor graphic collection (5ND). Analysed papers were selected randomly throughout each of the books. The number of selected analysed papers depended on the number of pages in the books. A total of 144 papers were analysed (Tab. 1).

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

Sample group mark	Type of material, Title, date, author, number of pages	Inventory number	No. of papers analysed
1ND	Document manuscript, Notary of the Kingdom of Dalmatia, Croatia and Slavonia, 1662, Ivan Zakmardi (1600 - 1667), 10	HR-HDA 11, box no. 3	10
2ND	Printed book, Topographia arcium Lambergianarum id est arces, castella et dominia in Carniolia habita possident comites a Lamberg; Bagenspergi, Ioannem Weichardvm Valvasor, 1679, 50	M11650	10
3ND	Manuscript, A book of sketches for a book, Topographia Archiducatus Carinthiae modernae, before 1681, 231	M 198	14
4ND	Printed book, Topographia Archiducatus Carinthiae modernae, Durch Johann Weichard Valvasor, Wagensberg in Krain im iahr 1681, Zu Laybach, Gedr. Bey Johann Baptista Mayr, 1681, 228	M11640	14
5ND	Graphics, Valvasor's graphic collection, 1685, 210	M158, Tomus VII	61
6ND	Printed book, 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, 274	M11527	10
7ND	Printed book, Die Ehre dess Hertzogthums Crain; Johann Weichard Valvasor, Volume 3; Laybach, Zu finden bey W.M.Endter, Buchhändlern in Nürnberg, 1689, 1129	M1124	25

ND: non-destructive

Historical paper samples (*HP*)

The second group of analysed paper samples, named historical papers (HPs), are fragments. These paper fragments were found in archive materials without classification and were not intended for storage and found separately in the archives. Five samples (3D, 4D, 6D, 8D, and 9D) are without manuscripts, two of them are fragments of manuscripts (5D and 10D) and the rest are paper support for the graphic collection and blotting paper for ink and print form. Historical paper samples are roughly dated (most of them are dated approximately according to the type of manuscript or the date of the archive in which they were found) and cover the period from the 16th to the 19th century. They are marked 1D to 10D for the purpose of this research and are listed in Table 2.

Table 2 Samples of HP fragments

Sample mark	Description	Origin of samples	Date
1D	Paper support for graphic collection Valvasor collection, inventory number M158	Metropolitan Library Archdiocese of Zagreb	1685; 17th century
2D	Blotting paper for ink	Archives of the Republic of Slovenia	The first half of the 19th century
3D	Fragment without manuscript; Found Križevci County, 1	Croatian State Archives	16th-17th century
4D	Fragment without manuscript; Found Križevci County, 2	Croatian State Archives	16th-17th century
5D	Fragment of a letter with manuscript; Found Križevci County, 3	Croatian State Archives	1745; 18th century
6D	Fragment without manuscript; Protocol 1763-1781	Archives of the Republic of Slovenia	18th century
7D	Fragment without manuscript; Print form; 1806	Archives of the Republic of Slovenia	19th century
8D	Fragment without manuscript; Print form; 1807	Archives of the Republic of Slovenia	19th century
9D	Fragment without manuscript; Found Križevci County, 4	Croatian State Archives	16th-17th century
10D	Fragment of the manuscript document; Found Križevci County, 15	Croatian State Archives	16th century

D: destructive

Characterization

Analyses performed on *VC* papers included measuring the thickness of papers, microscopic imaging of the paper surface, and measuring the optical properties. On *HP* fragments, in addition to the previously mentioned methods, micro-destructive spot tests using different reagents, pH measurements and morphological analysis of fibres were conducted. The following instrumental analyses were performed: SEM-EDS (scanning electron microscopy with energy dispersive spectroscopy), XRF (X-ray fluorescence), and ATR-FTIR (attenuated total reflection Fourier transform infrared spectroscopy). In Table 3, a list of methods performed on both sets of paper samples (*VC* and *HP*) is presented.

Table 3 List of analyses performed on the samples

	Microscopic analyses		Thickness	Surface characterization		Spot tests	Spectroscopic Analyses		XRF
	Digital microscope	Optical microscope		Surface pH	Brightness, Yellowness, Opacity, Gloss		SEM-EDS	ATR-FTIR	
VC	+		+		+				
HP	+	+	+	+	+	+	+	+	+

Microscopic analyses

Microscopic analyses to identify fibres in paper samples were performed on a Micros Austria type MCx500 optical microscope with 4x, 10x, 40x and 100x lenses and a 10x/22 magnification eyepiece under transmitted light with and without staining, according to the TAPPI standard T 401 [28]. Fibre identification was based on morphological characteristics [29, 30].

The imaging of the paper surface was performed with digital microscope imaging at a magnification of 500x with the model Dino-Lite AM4013 MT5.

Thickness

The thickness of paper was measured with a micrometre according to the standard EN ISO 534:2005 [31] by inserting a sample between two parallel metal plates, 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, and the surface pH and optical properties were determined. Among the optical properties of the paper, brightness, yellowness, opacity and gloss were measured.

The pH of the paper surface was measured with a Mettler Toledo Seven 2Go Advanced portable pH metre with an InLab Surface PRO-ISM surface measurement electrode in 5 different places as prescribed by the TAPPI T529 standard [32].

The X-Rite EXact device was used to measure the optical properties of the samples. The measurement of brightness was conducted according to the standard ISO 2470:1999 [33]. It is defined as the ratio of the reflection of diffuse blue light from the surface of a paper sample at 457 nm to the reflection of an ideal reflecting body and 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 (%). Opacity measures light impermeability in paper and is expressed as a percentage (%). The opacity of the paper was determined according to the standard ISO 2471: 1998 [34].

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 measurements were carried out in accordance with standard ISO 8254-1:2009 [35] 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 water absorption test was performed according to the TAPPI standard T492 pm-76 [36]. It is a method of detecting the time required to absorb water for uncoated or lightly coated papers. Distilled water was dropped from a height of 1 cm onto the surface of the paper, and the time until the water droplet was completely absorbed was recorded.

The spot test for starch in paper was determined with a solution of potassium iodide according to TAPPI standard T419 [37]. The solution was dropped on a paper surface, and the change in colour was observed with the naked eye.

The presence of lignin was determined using phloroglucinol solution as a reagent according to TAPPI standard T 401 [28]. The phloroglucinol solution stains wood fibres and other lignin-containing fibres in proportion to the amount of lignin. The colour change was assessed by the naked eye under a loupe.

The Herzberg stain test was performed according to TAPPI standard T 401 and ISO 9184-3 [28, 38]. A drop of reagent was added to the fibres pulled from the paper sample and placed on a microscope slide. This test for fibre identification is based on the colour change; chemical pulps acquire a blue tint, groundwood is yellow, while rag pulp fibres turn pink, light red or peach to deep red [38].

Spectroscopic Analyses

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

SEM-EDS is an analytical technique for elemental characterization of a sample. SEM-EDS analyses were conducted using a Coxem EM30AXPlus with magnification from 20 - 100000 x and spatial resolution <5 nm. The X-ray detection EDS technique is used to qualitatively determine the elemental composition of the sample that is visually identified by SEM. EDS is a surface technique while XRF is a semiquantitative method.

X-ray fluorescence analysis (XRF)

XRF is a method for qualitative and quantitative detection of inorganic elements in a sample. The samples were analysed using an Artax BruXRF spectrometer manufactured by Bruker. The recording conditions were 50 kV and 700 μA. A helium purge was also used during recording to detect the fluorescence of the lightest 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 the X-ray tubes and collimators, so they are not present in the sample.

Fourier transform infrared spectroscopy (FTIR)

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 (Perkin Elmer, Waltham, MA, USA) equipped with an attenuated total reflection (ATR) cell and a diamond crystal (n=2). The operation of the apparatus was controlled through Spectrum and Image software for FTIR. The spectra were recorded in reflection mode over the spectral range 4000–500 cm^{-1} with a resolution of 4 cm^{-1} in the ATR technique and were averaged from 64 scans. The recorded spectra of historic paper samples were compared with the selected reference spectra recorded for reference samples of cotton, flax, hemp, softwood and hardwood cellulose, gelatine, starch, clay and calcium carbonate. Additionally, the identification of the characteristic absorption bands was performed by comparing the obtained spectra with the published spectra [14, 18, 39].

Data analysis

Multiple regression and one-way analysis of variance (ANOVA) were performed on the data with the probability level for statistical significance set at p = 0.05. The thickness and optical properties of papers from VC and HP samples were compared using analysis of variance. The relationship between the properties of HP samples was assessed by regression analysis, where each of the optical properties was used as a dependent variable, whereas thickness and pH were independent variables. The correlation between the optical properties, thickness, pH content and water absorption was determined by the Pearson correlation coefficient.

Results And Discussion

Visual inspection

The *VC* papers were visually examined, the dimensions of the papers were measured, and the dimensions and orientation of the paper mould were determined (Tab. 4). Photographs were taken in transmitted light to define and measure mould laid and chain line spacing and watermarks. The chain line spacing ranged from 22-32 mm, while the density of the laid lines ranged from 7/1 cm to 10/1 cm. Most of the watermarks are a coat of arms, two of them identify the origin of the paper mill for historical hand-made papers, while the others were assigned a label according to the IPH standard [40]. The dimensions of the paper mould were measured on HP samples, chain line spacing was in the range of 22–32 mm, and laid lines were in the range of 7–10 lines/1 cm. Six watermarks were found, and two were identified. One watermark from VC depicting the coat of arms of Carinthia was identified as a watermark from St. Ruprecht paper mill near Klagenfurt in Carinthia (Fig. 1a) [41] (present-day Austria) from the 17th century. The other sample is from a group of HP samples from the paper mill of Valentino Galvani from Pordenone (Fig. 1b) [42] (present-day Italy) from the 19th century.

Table 4 Papers from VC: dimensions of papers, watermarks, dimensions and orientation of mould

Sample group mark	Dating	Paper width x height /mm	Place of origin or use of paper	Appearance and type of watermark	Chain lines	Laid lines
1ND	1662	410-420x320	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	278x190	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	278x179	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	286x180	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	360-370x420-440	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 440x368	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	240x373-376	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 papers, the imprint of the paper mould, and the position of the watermark, it can be concluded that, in all the researched books, the papers from *VC* originate from two paper mould

formats. The dimensions of the smaller format are 245-278 x 360-380 mm and those of the larger are 360-370 x 420-440 mm.

The above examinations by visual inspection led to several conclusions. The same watermarks on different sheets do not have the same dimensions, which indicates that the manufacturer used several paper moulds for the same type of paper. It has been observed in several examples (3ND, 4ND, and 5ND) that the endpapers in front and back of the book were made from the same type of watermarked paper (coat of arms of Carinthia), while the leaves or folios of the book block were from different types with different watermarks. By examining the watermarks, it can be concluded that in most cases, they are coats of arms. From 144 research papers, watermarks were found on 38, of which 29 were coats of arms.

Microscopy analysis

The surface of the paper was analysed with a digital microscope on both *VC* papers and *HP* samples, while fibres were analysed by an optical microscope only for *HP* samples. Inspection of papers using a digital microscope revealed some specific fibres that appear to stand out from the majority of white fibres, as shown in Fig. 2. Several types of such fibres have been detected on both sets of samples, *VC* and *HP*. Thus, blue, red, light brown, dark brown, and black-brown fibres appear in all samples examined. By measuring the width of the fibres, it was observed that there are two types of fibres, thin (<150 μm) and thick (>150 μm), as shown in Fig. 3. Among the *HP* samples, 2D stands out, where the largest amount of different types of fibres was detected, as seen in Fig. 2. In samples 3D, 4D, 6D and 8D, thick light brown fibres were found, which could indicate that these are straw fibres. Thin fibres are present in samples 5D, 7D and 10D.

From the non-destructive microscopic imaging of the raw historical papers of Valvasor's collection (*VC*), including the outstanding items as fragments (*HPs*), it can be concluded that the most specific fibres that appear can be described as *thin light brown fibres.* The fibre is less than 150 μm thick, and its colour is light brown. Blue and red fibres were found in many papers and, according to width, can be characterized as thin fibres (Fig. 3a, 3b).

In addition, a thick light brown fibre was observed, which, in some places, has a width of over 400 μm and looks like straw fibres (Fig. 3d, 4a). In some places, thicker fibres were found deep in the structure of the paper (which made it difficult to measure them accurately) so that the white fibres were clearly visible on them, and it was possible to measure their width (Fig. 4). The width values of white fibres ranged from 11 μm to 29 μm, which would probably refer to two types of fibres specific to the 17th century: hemp and flax [29].

Flax and hemp fibres and, in some cases, cotton fibres are visible under the optical microscope (Fig. 5a). The flax fibre cells appear as long transparent, cylindrical tubes that may be smooth or striated lengthwise. The width of the fibre may vary several times along its length. There are swellings or nodes at many points, and the fibres show characteristic cross-markings. The fibre cell has a lumen or canal running through the centre; the lumen is narrow but clearly defined and regular in width [30]. The individual cells of hemp are, on average, 13 – 26 mm long. They are cylindrical in shape, with joints, cracks, swellings and other irregularities on the surface.

The central canal or lumen is broader than that of flax, and the ends of the cells are blunt [29]. The fibres taken from *HP* samples were subjected to the Herzberg stain test for identification purposes [28,38]. Most of the analysed fibres were coloured reddish grey (Fig. 5a), which confirms that they are hemp and flax fibres, referred to in the literature as rags or fibres from old rags [3].

Thickness

The thickness of paper is one of its basic properties. The measurements of the thickness on the paper in *VC* were limited to the area along the edges of the papers and the area without a plate imprint. The thickness of the papers varied between 0.1-0.2 mm, while there were some papers in only two sample groups with thicknesses below 0.1 mm (2ND and 5ND) and few papers thicker than 0.2 mm. Values over 0.5 mm were determined on a composite sample, with 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 endpapers and papers within the book block.

The measured values of paper thickness in six samples of *HP* range from 0.16 to 0.2 mm, whereas, for the other four samples, they are greater than 0.2 mm.

ANOVA showed significantly different values for the thickness of papers in *VC* and *HP* samples ($p = 0.0077$), suggesting that papers in *VC*, which are thinner, differ from other historical papers analysed.

Surface characterization

pH

The acidity/alkalinity of the paper is key information to preserve and protect the paper from degradation. Therefore, the determination of acidity/alkalinity a common method for conservation treatment on paper.

A method according to the TAPPI T529 [32] standard was applied only to *HP* samples, which prescribes measurements by applying a drop of distilled water to an appropriate place and measuring the pH in that drop. 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 because their values are less than 6, and one of them, i.e., the 3D sample, has a pH value of 5. Values slightly above 7 were measured in two samples (1D and 6D).

Measurement of pH on the surface of *HP* samples revealed some destructiveness of the method due to damage caused by water. The stains occurred because of the water soluble components if paper or/and inks together with dust and dirt incorporated deep into the historical paper during a time, leaving tidelines. Such stains can be in some specific cases removed by conservation-restoration procedures, but because *VC* papers were not intended for further procedures, pH measurements were not applied to *VC* papers.

Optical Properties

To complement the visual evaluation of papers with the analytical method, the optical properties were measured. Brightness, yellowness, opacity and gloss were determined for *VC* and *HP* samples. These non-

destructive measurements help to characterize papers. As optical properties depend on the structure of the paper, they can be useful for comparison with other historic papers and help to create a conservation-restoration protocol.

The brightness of papers in *VC* is mainly distributed in two groups, in the range between 40 and 50 % (41 papers) and between 50 and 60 % (37 papers). Most *VC* papers have a degree of yellowness in the range between 20 and 30 %. The measured opacity values are very high, between 90 and 100 %. Very low gloss values, below 2.5, tell us that the papers are uncoated. The most representative values for *VC* papers are between 1 and 1.5 in 77 % of cases (Fig. 6).

The brightness values of six samples of historical papers were in the range between 40 and 66 % (Fig. 7). For other samples, values below 40% were obtained, the lowest being 18.2 % for a *HP* sample from the 16th century. Seven samples showed yellowness values between 20 and 40 %, where the three samples from the 16th and 16-17th centuries had a darker colour, with yellowness values over 45 %. Very high values of opacity, over 90 %, were determined in *HP* samples, which can be classified into two groups: three samples were in the range between 90-95 %, and the remaining samples were in the range between 95 and 100 %. The measured gloss values on *HP* were approximately 1; with the exception of papers from the 19th century (sample 2D) with a measured gloss value of 0.73.

The measurements of optical properties of *VC* and *HP* samples revealed low brightness, high yellowness, very high opacity and extremely low gloss. Among the optical properties, a significant difference was observed in the case of gloss ($p = 0.0001$) and opacity ($p = 0.0152$), whereas brightness with $p = 0.3268$ and yellowness with $p = 0.1365$ showed no significant difference in values between *VC* and *HP* samples.

The Pearson correlation coefficient was determined along with the optical properties, thickness, pH content and water absorption of *HP* samples (Fig. 8). A negligible correlation was obtained between optical properties, water absorption and thickness, with the exception of opacity, for which a high positive correlation ($r = 0.87$) was obtained. A weak linear relationship between the calcium content present in papers and their optical properties was observed. With increasing amounts of calcium in the paper, the brightness and gloss increase, and the yellowness and opacity decrease. A strong linear relationship between all optical properties and paper pH values was observed ($r > \pm 0.6$). Papers with higher pH values have higher brightness and gloss and lower yellowness and opacity. Additionally, a strong positive linear correlation ($r = 0.71$) between the amount of calcium in paper and its pH value was determined.

A multiple regression analysis was used to determine whether there is a statistically significant relationship between properties and how two independent properties, thickness and pH value, influence the optical properties of *HP* samples. The results are summarized in Table 5. A multiple regression coefficient shows a strong relationship between properties. On the other hand, R^2 and adjusted R^2 show an acceptable predicted outcome only for opacity. A p-value below 0.05 for brightness and opacity means that a significant relationship exists between thickness and pH value, whereas no significant correlation was obtained for yellowness and gloss. The p-values for each independent property show that a highly significant relationship

exists between the thickness and opacity (p = 0.009). The pH value showed a significant relationship with brightness (p = 0.015) and yellowness (p = 0.025) and marginal significance with gloss (p = 0.08).

Table 5 Results of multiple regression analysis for *HP* samples: multiple regression coefficient (R), coefficient of determination (R^2), adjusted R^2, p-values

	Brightness	Yellowness	Opacity	Gloss
Multiple R	0.78	0.74	0.89	0.63
R^2	0.61	0.55	0.80	0.40
Adjusted R^2	0.50	0.41	0.74	0.23
p-value	0.037	0.063	0.004	0.169
p-value - thickness	0.299	0.323	0.009	0.582
p-value - pH	0.015	0.025	0.256	0.08

Spot Tests

The water absorption test is a micro-destructive method, as shown by the residual line spots formed after the measurement (Fig. 9). For this reason, the test was applied only on *HP* samples. Papers showed 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 approximately 3 minutes to absorb a drop of water. It took approximately 2 minutes for samples 7D and 8D to absorb water, while samples 1D and 2D took less than half a minute. The absorbency of paper depends on the structure and surface properties of the paper and is primarily determined by the sizing.

A test to prove the presence of starch was carried out to determine whether the paper samples contained starch that was used for sizing in the production of handmade papers. In all ten tested *HP* samples (Fig. 10), none matched the expected results for the presence of starch in paper [43].

The aim of determining the presence of lignin in papers from the 16th - 19th century was to obtain indications if papers included fibres with more lignin. The test is primarily designed to determine the presence of wood fibres in paper, as wood contains a high proportion of lignin [43].

If the paper has a small amount of lignin-containing fibres, the individual fibres turn red and can be seen with the naked eye [43]. The spot test for determining lignin with phloroglucinol (Fig. 10) showed the presence of

fibres containing lignin in most *HP* samples. If we obtain 2-3 lignin fibres on a 1 cm^2 paper sample, this is evidence for a lignin content of less than <5%. Ten tested samples showed four categories of results regarding the amount of stained fibres in the paper. In only one sample, 10D (16th century), no stained fibres were found, whereas in two samples, 2D (19th century) and 6D (18th century), larger numbers of stained fibres were present (lignin content >5%). Two samples, 4D (16-17th century) and 7D (19th century), contained a moderate amount of stained fibres, and five samples (lignin content ≈5%), 1D (17th century), 3D (16-17th century), 5D (18th century), 8D (19th century), and 9D (16-17th century), contained small numbers of stained fibres (lignin content <5%). It can be concluded that all papers but one contain stained fibres and that a majority of samples contain a small number of stained fibres.

Microscopic and spectroscopic analyses

SEM-EDS

SEM-EDS analysis was applied to characterize the surface structure of paper and to identify fibres and elemental composition. Because this method is destructive, only the second set of samples, *HP,* were examined. SEM images of the paper surface and spectra with elements found in the recorded location are presented in the Supplement.

According to the EDS results, in most samples, O (oxygen), C (carbon) and Ca (calcium) were detected, except in samples 3D, 4D and 9D, in which Ca was not observed. Si (silicon), Cu (copper), Al (aluminium) and Ni (nickel) were detected in most samples as trace elements. Mg (magnesium) was also visible in trace quantities in samples 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; in some samples (5D and 8D), the spaces between the fibres are filled (Fig. 11a), indicating that surface sizing (Fig. 11b) was used during paper production and remained in some places until today. In other samples (1D and 10D), a larger number of unidentified particles are visible on the surface of the fibres.

XRF

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

In the SEM-EDS and XRF analyses, many elements have been recorded that can be related to the composition of the paper. Thus, sulfur (S), potassium (K), and in some samples, iron (Fe) were observed in the XRF spectra, while aluminium (Al) and copper (Cu) were observed in the SEM-EDS spectra. Sulfur is part of the molecular structure of gypsum ($CaSO_4 \times H_2O$) and alum ($KAl(SO_4)_2 \times 12H_2O$); aluminium (Al) and potassium (K) are also

present. Iron (Fe) was observed in trace quantities in all XRF spectra and can be attributed to the composition of iron alum ($FeAl(SO_4)_2$ x $12H_2O$). Silicon (Si) 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) at 4-7% for wheat straw [29, 44]. The presence of most of the elements recorded in trace quantities during elemental analyses could be explained, while some of them, such as manganese (Mn), magnesium (Mg), titanium (Ti), copper (Cu) and nickel (Ni), could be attributed to sample contamination.

FTIR-ATR

FTIR spectroscopy, a simple technique for rapidly obtaining information about the chemical structure and crystallinity of cellulose samples, is often used in research on historical papers. We used this technique to record ATR-FTIR spectra on HP samples. According to the literature on the composition of historical papers, the expected components are cellulose fibres, including straw fibres [44], gelatine, gypsum, and calcium carbonate [18, 39, 45]. The raw materials used in papermaking in Europe until the 19th century were rags from used textiles (flax, hemp, cotton). The reference spectra of cellulose fibres have very similar absorption bands in the wavenumber range of 3660 - 2900 cm^{-1} (the stretching vibrations of OH and CH bonds in polysaccharides), with the band at 3331 cm^{-1} is characteristic of the stretching vibration of OH groups [46]. Typical bands assigned to cellulose in the range of 1630 - 900 cm^{-1}, according to [46, 47, 48], are as follows:

- band at 1633 cm^{-1} corresponds to the vibration of water absorbed in cellulose,
- band at 1430 cm^{-1} corresponds to CH_2 vibrations, HCH and OCH in-plane bending
- band at 1367 cm^{-1} corresponds to COH and HCC vibrations,
- band at 1335 cm^{-1} corresponds to OH and CH_2 vibrations,
- band at 1155 cm^{-1} corresponds to COC asymmetric vibration,
- band at 1110 cm^{-1} corresponds to the asymmetric vibration of a glycosidic ring,
- band at 895 cm^{-1} corresponds to COC vibrations of glycoside bonds.

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 is in the fingerprint region with a sharp band at 1029 cm^{-1} with two smaller bands at approximately 1050 cm^{-1} and 1100 cm^{-1}, and the second region is in the area of stretching single bonds at approximately 3600-3000 cm^{-1}. Thus, *HP* samples showed characteristic FTIR spectral features of cellulose. Furthermore, in most samples, absorption bands at 2900 and 2849 cm^{-1}, attributed to CH stretching vibrations of cellulose and symmetric CH_2 stretching vibrations of noncellulose polysaccharides, were observed as peaks or as shoulders. The absorption band at 2918 cm^{-1} attributed to asymmetric CH_2 stretching vibrations in noncellulose polysaccharides was present as a sharp band in samples 5D, 6D, 7D, 8D, 9D and 10D, whereas, in four other samples , it was present as a shoulder (Fig. 12). This triplet is indicative of flax fibres [49]. In the study of Kostadinovska et al. [18], eight patterns were proposed to determine the prevailing type and quantity of fibres in the sample. By comparing the spectra of *HP* samples with the proposed patterns in all samples, the flax fibres were confirmed as the dominant component. In samples 2D and 3D, in addition to flax, a larger amount of hemp was identified, whereas, in sample 4D, a

larger amount of cotton was present. Sample 1D showing absorption bands at 2902, 1506, 1031, 1000 and 898 cm^{-1} and shoulders at 2900 and 2851 cm^{-1} suggested that, in addition to flax fibres, hemp prevailed over cotton (Fig. 13). A weak absorption band at 1735 cm^{-1} present in all *HP* samples is characteristic of the C=O ester band in pectins, confirming the presence of hemp, although it could also show the presence of carbonyl groups of oxycelluloses found in degraded materials [47].

The absence of an absorption band at 1595 cm-1 and a very weak absorption band at 1505 cm^{-1}, which are characteristic bands for lignin, confirm that all examined papers were made from pulped rags.

The spectra of additives (sizing agents and fillers) in paper, such as gelatine, starch, 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. The absorption bands related to proteins below 1400 cm^{-1} could be assigned to amide III, those in the region of 100 to 1500 cm^{-1} to amides I and II, and bands over 3000 cm^{-1} (characteristic for NH and CH stretching) to amides A and B [50]. For papers sized with animal gelatine, the absorption bands at approximately 1645/1650 cm^{-1}, associated with the C=O stretching vibration, and 1545/1550 cm^{-1}, associated with the NH in-plane bending vibration, were observed in the spectra. In all *HP* samples, doublets at 1648 and 1645 cm^{-1} and weak absorption bands at 1550/1548 cm^{-1} were found, which could indicate the presence of gelatine in papers (Fig. 12).

Calcium carbonate shows a strong absorption band in the fingerprint region at approximately 1425 cm^{-1} and two weaker absorption bands at 875 and 712 cm^{-1} [51]. The presence of an absorption band at 1425 cm^{-1} in all *HP* samples, in addition to indicating the presence of calcium carbonate, is assigned to CH_2 and CH vibrations in cellulose. The differences among samples were observed in the other two bands. The absorption band at 875 cm^{-1} was clearly observed in samples 5D, 6D and 8D and present as small peaks in samples 1D, 3D, 4D, 7D and 10D. In samples 2D and 9D, it was only a shoulder. A very weak absorption band at 711 cm^{-1} was observed in samples 5D and 6D and as a shoulder in samples 3D, 7D, 8D and 10D. Calcium in historic papers could be present in the form of calcium stearate, which shows an absorption peak at 2851 cm^{-1} and carboxylate bands at 1577 and 1541 cm^{-1} [12]. Both absorption bands (1575 and 1542 cm^{-1}) were present in all samples, except at 2D, where only a band at 1542 cm^{-1} was observed.

Gypsum has two dominant sharp bands, one in the fingerprint region and the other in the region of asymmetric and symmetric OH single stretching bands, at 3394 cm^{-1}. The other two bands typical for gypsum are at 667 and 595 cm^{-1}[52]. In both regions, the bands overlap with the cellulose bands, making them difficult to identify. Nevertheless, we identified a band at 3394 cm^{-1} present as a shoulder in all samples and in samples 9D and 10D as a small peak. The absorption band at approximately 660 cm^{-1} (SO_4^{2-} bending) overlaps with the OH out-of-plane bending vibration in cellulose and was detected at 667 cm^{-1} in all HP samples. The absorption band at 595 cm^{-1} was present as a small intensity peak in most samples and as a shoulder in samples 2D, 5D, 7D and 9D.

By comparing all recorded ATR-FTIR spectra, it can be concluded that there is a very small difference between the samples. As pulped rags were used for paper production, the presence of flax, hemp and cotton fibres in the samples is expected, with flax as the prevailing fibre component in most samples. In samples 1D, 2D and 3D, a larger amount of hemp was identified, and in sample 4D, cotton was also identified. In Fig. 12, the ART-FTIR spectra of three samples (1D, 6D, and 8D) from the 17th, 18th and 19th centuries are shown. The peaks mostly overlap, though in some parts of the spectrum they are different, which indicates the difference in the share of additives in the paper samples from the 17th to the 19th centuries. We can assume that gelatine was used for sizing in all cases. The presence of calcium compounds in the form of carbonate, sulfate or stearate could be predicted in all HP samples, though in different forms and quantities. Although the number 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 Barrow [9], who concludes that over time, the amounts of additives (sizing and fillers) in the paper changed, which affected the durability and stability of the paper.

Conclusions

Paper samples from the 17th century, more exactly, papers in *VC* of unknown origin and composition, were studied with the aim of collecting data for potential use in future research and conservation-restoration work. The principles of the conservation-restoration profession dictate the use of non-destructive methods and do not allow sampling of papers for scientific or any other research. For this reason, it was decided to conduct measurements on the fragments of *HP* to correlate the results and supplement them to determine the composition of papers from the 17th century.

Morphological analysis of the fibres showed that most of the fibres in the *HP* samples were flax and hemp, while FTIR analysis confirmed a higher proportion of flax fibres and cotton in addition to flax and hemp. The microscopic analyses showed the same type of fibres present in the *VC* and *HP* samples. Here, in addition to white fibres, wide light brown fibres (approximately 400 µm wide) most often appear. They resemble straw, and a spot test for lignin on *HP* samples showed that they contained fibres with a certain amount of lignin, which also may indicate straw. This can be confirmed by the SEM-EDS and XRF results, where Si (silicon) is present in trace quantities and may originate from silicon oxide, which is present in straw.

Analyses of optical properties and microscopic analyses of the paper surface can indicate the composition of the paper. This indication could be of interest in conservation-restoration research to predict how a particular phase of the process affects the paper, especially the wet cleaning stage. Based on the pH, optical properties and calcium content, the higher the calcium content, the higher the pH and the brightness of papers. It is evident from the results of SEM-EDS, XRF and FTIR analyses that a small proportion of calcium in *HP* samples affects the optical properties. This may then lead us to conclude that *VC* papers do not have a high calcium content due to lower brightness and gloss and a slightly higher yellowness and opacity. Although the differences are small, they are visible and confirmed with the statistical evaluation of the results.

In addition to determining the origin and composition of the papers in *VC*, some methods that could be used in preparation for conservation and restoration work on historic papers are highlighted in this study. They are quick, inexpensive, undemanding and easily performed tests. Measurements of thickness, surface pH, the paper absorbency test with a drop of water, and spot tests to prove the presence of starch and lignin are

methods that could be widely used in 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.

We also hope that the approach used to characterize the papers in *VC* can serve as a model for documenting other collections of historical papers. It served us to construct a database, named *Valper,* which will be presented in another article.

Declarations

- **List of abbreviations**

ATR-FTIR: Attenuated total reflection - Fourier transform infrared spectroscopy

HP: Historical paper samples

SEM-EDS: Scanning electron microscopy with energy dispersive spectroscopy

VC: Papers from Valvasor's collection

XRF: X-ray fluorescence analysis

- **Availability of data and materials**

All data generated or analysed during this study are included in this published article [and its supplementary information files].

- **Competing interests**

The authors declare that they have no competing interests

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- **Authors' Contributions**

AD designed the work, and made most of the measurements. DGS processed FTIR and made statistical evaluation of data. BL helped with the interpretation. JVT substantively revised the manuscript and designed the work. AD drafted the manuscript, DGS, JVT and BL helped to review and edit the manuscript. All authors read and approved the final manuscript.

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Figures

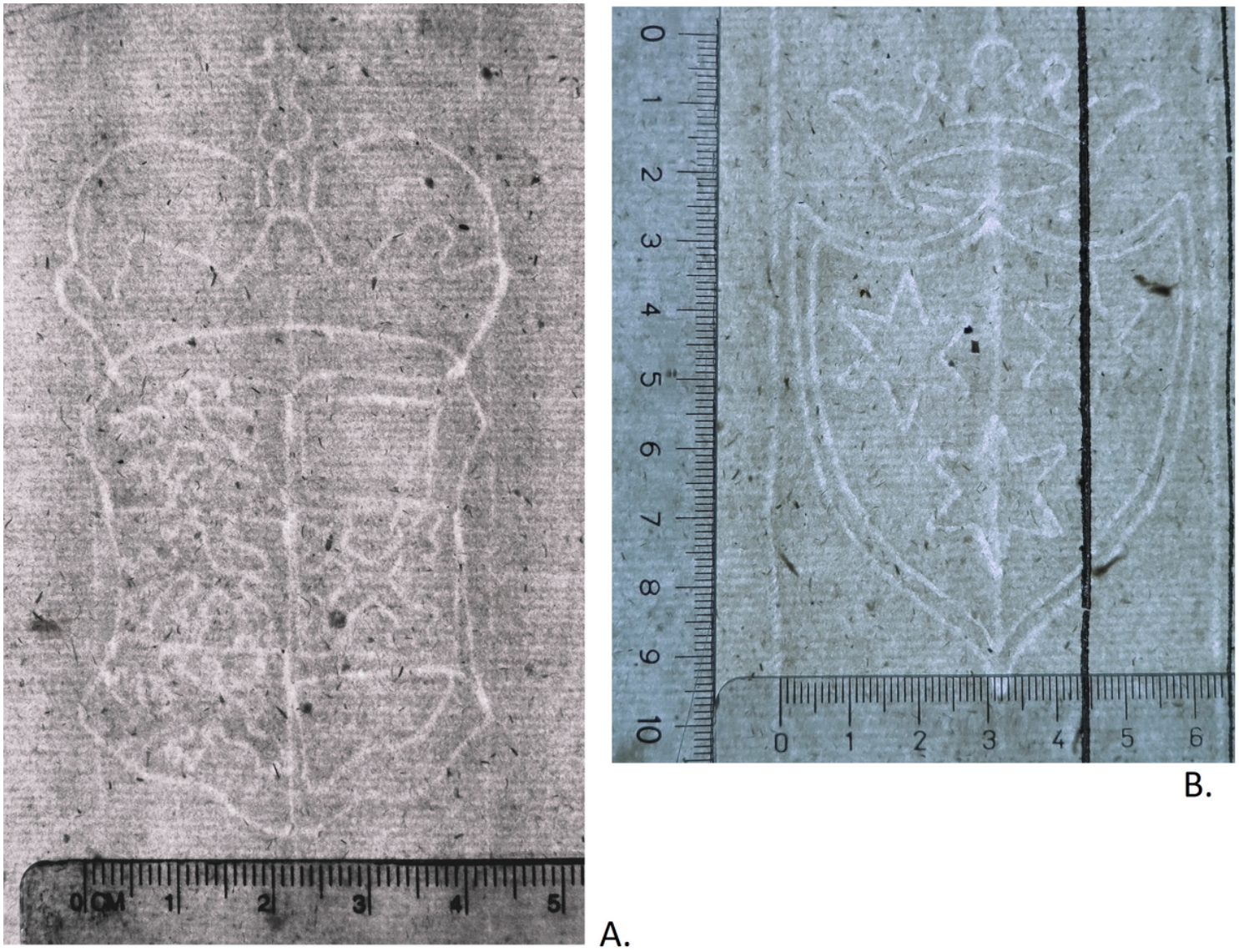


Figure 1

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

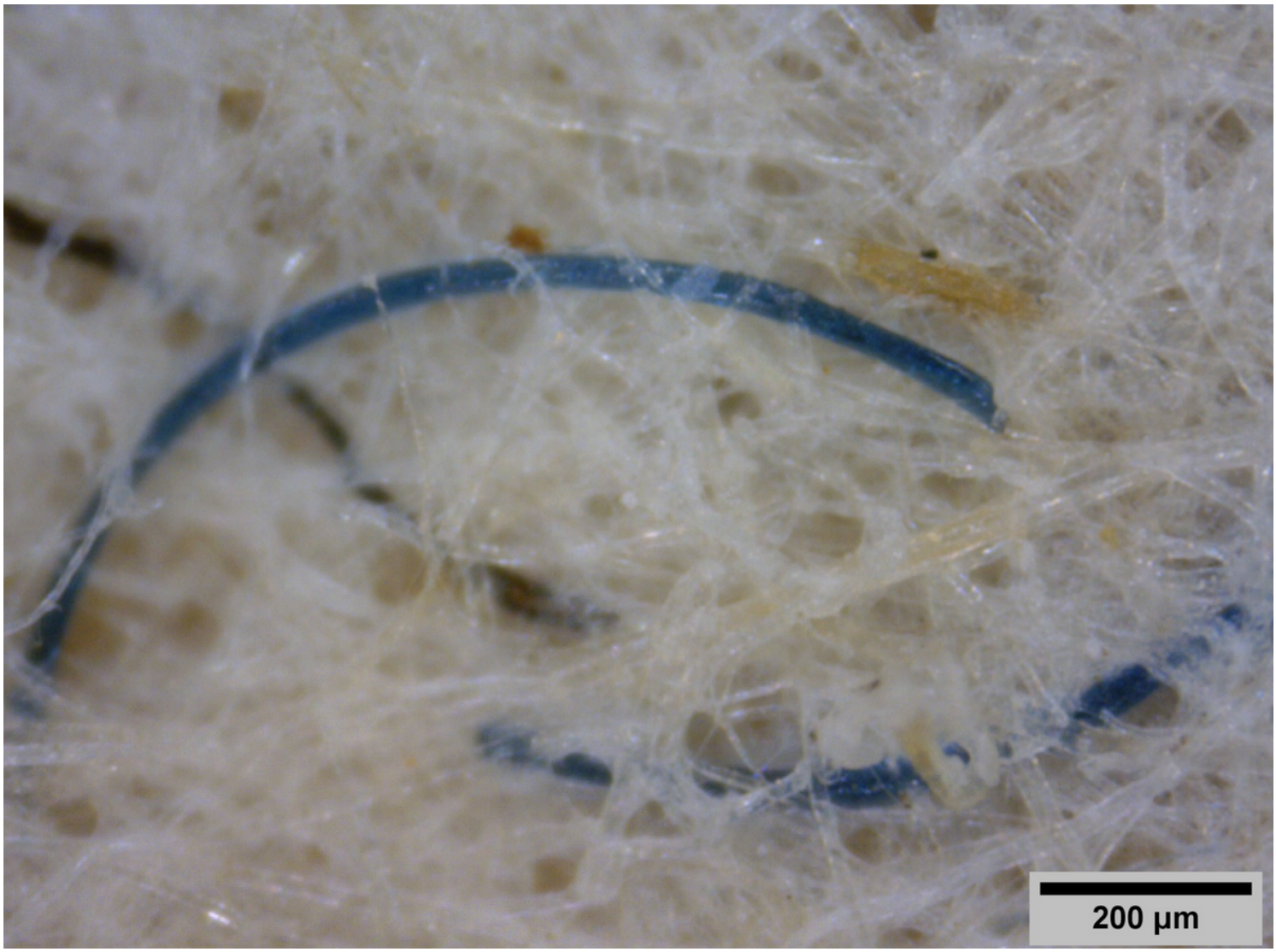


Figure 2

Surface of the HP sample 2D

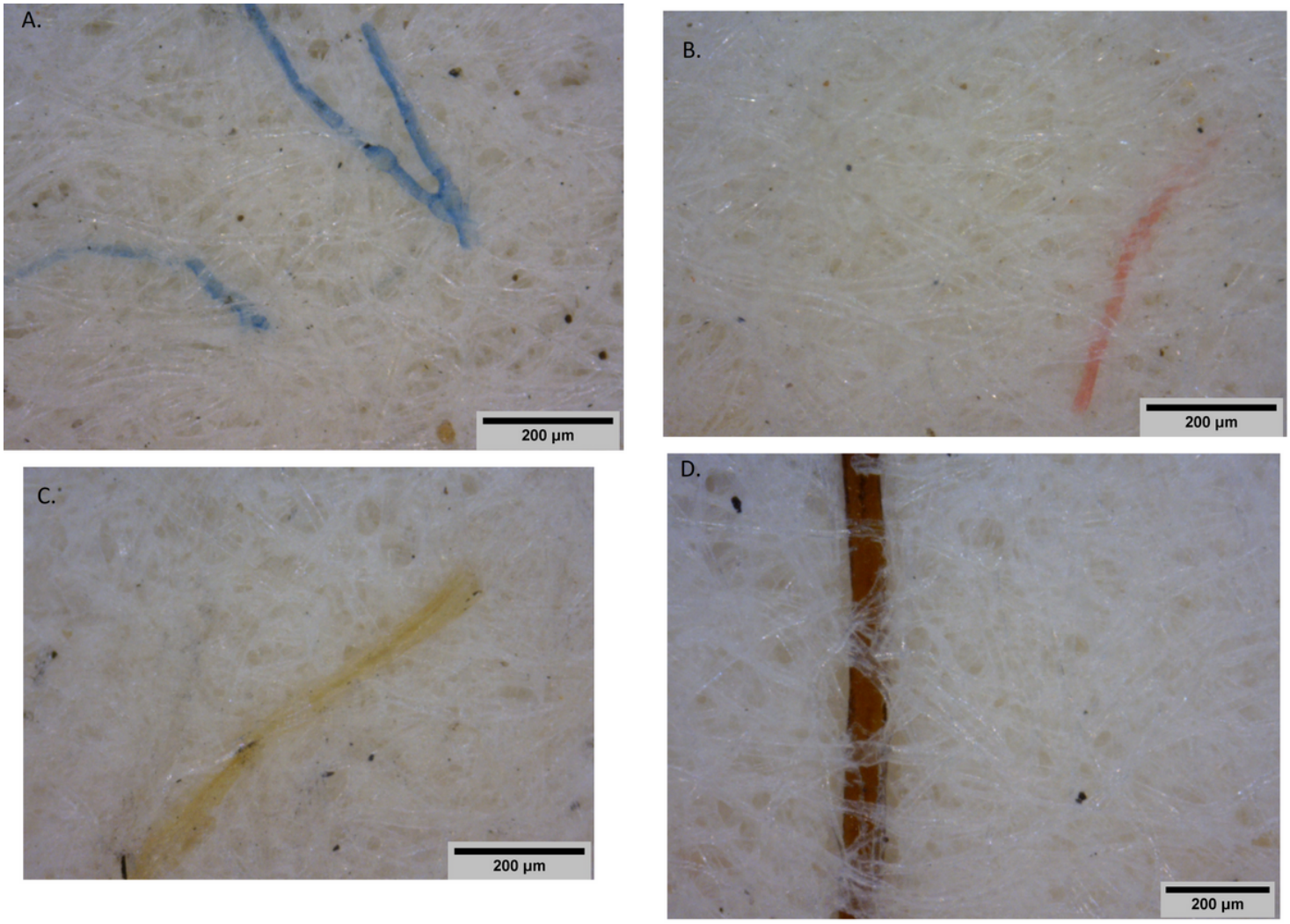
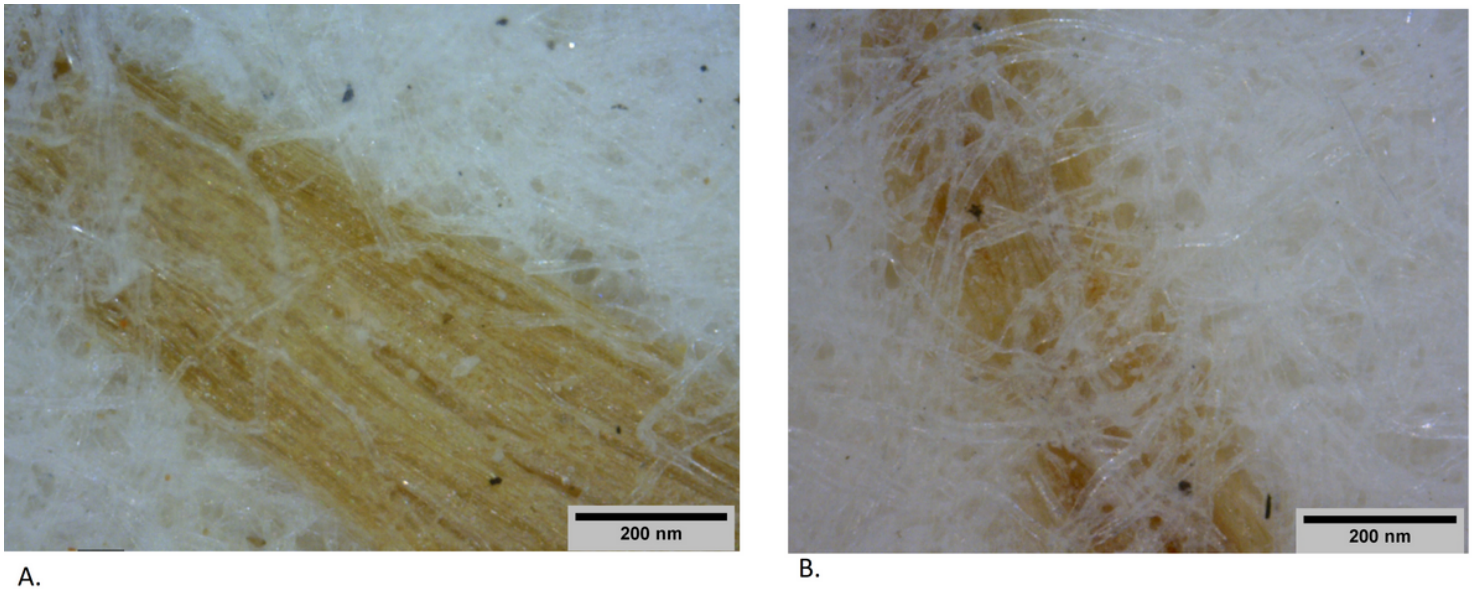


Figure 3

Image of fibers detected with digital microscopy: a) blue fiber (11 µm), b) red fiber (W=18 µm; L=371 µm), c) thin light brown fiber (W=48 µm), and d) thin dark brown fibre (14 µm – 54 µm)



A. B.

Figure 4

Images of a) thick light brown fibre (355 µm; 410 µm) and b) white flax and hemp fibres (9 µm; 18 µm).

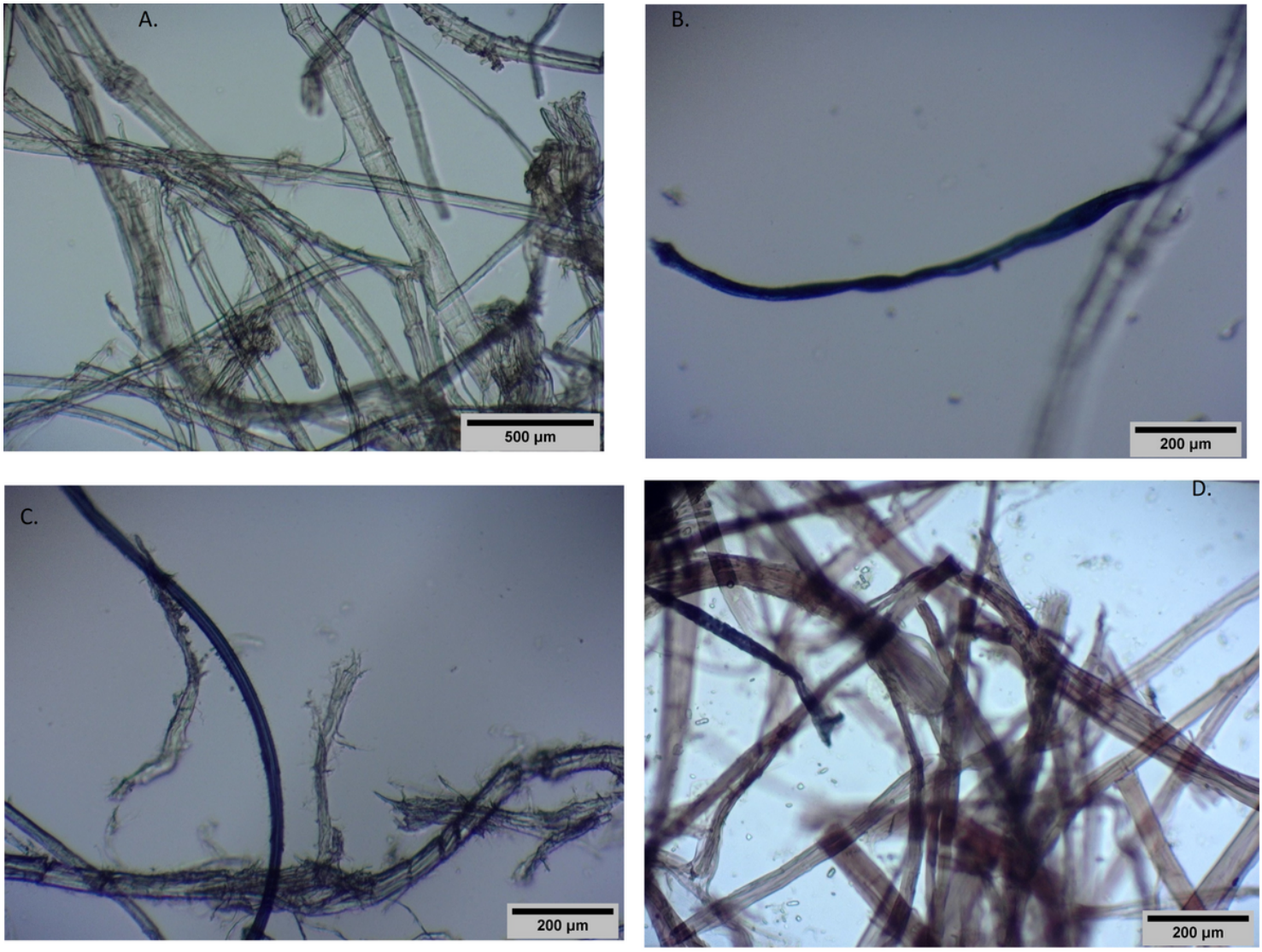


Figure 5

a) flax (1) and hemp (2) fibres in water, 100x, sample 3D; b) blue cotton fibre in water, 100x, sample 3D; c) blue silk fibre in water, 100x, sample 10D; d) flax and hemp in Herzberg reagent, 100x, sample 3D

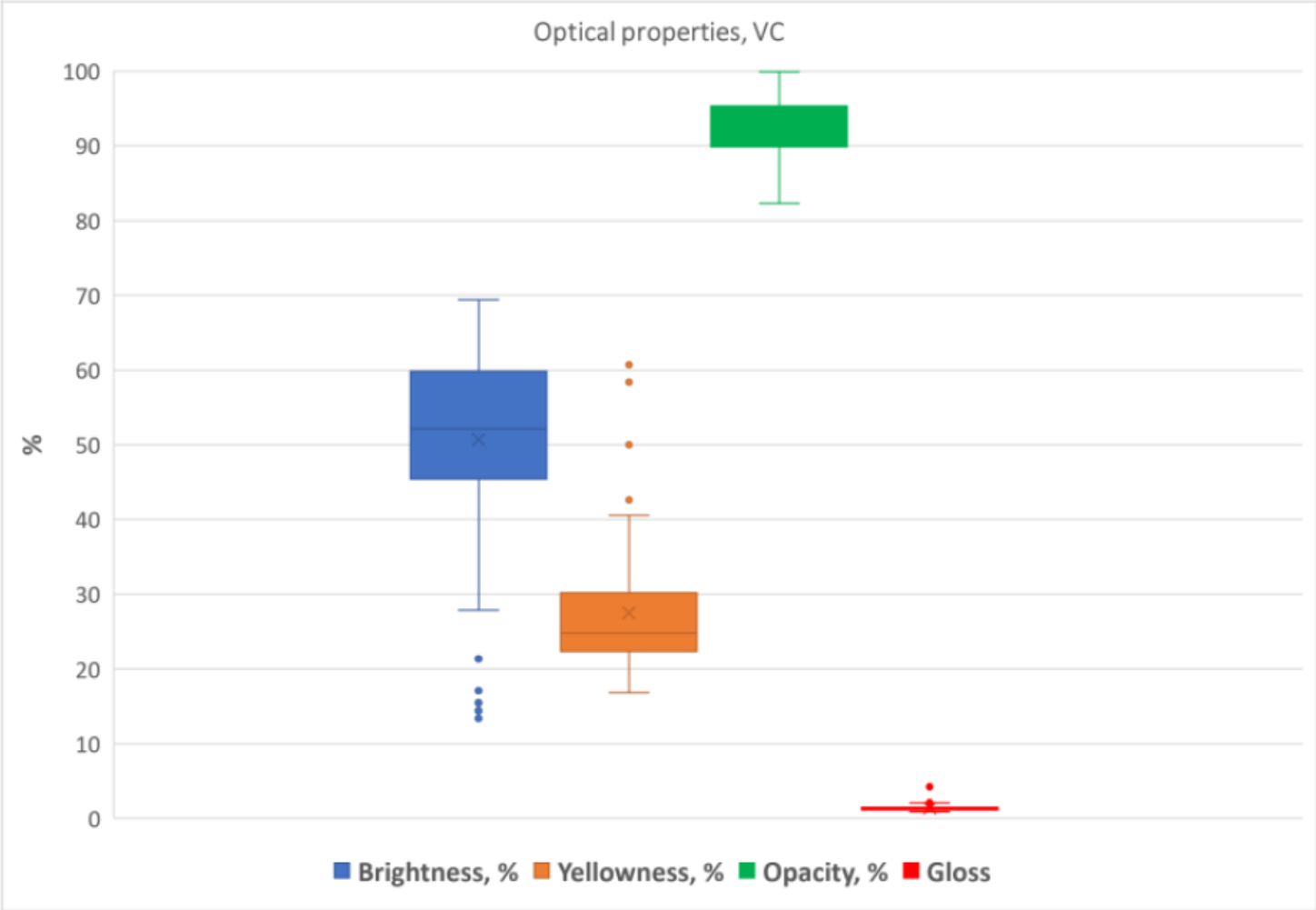


Figure 6

Optical properties of VC papers

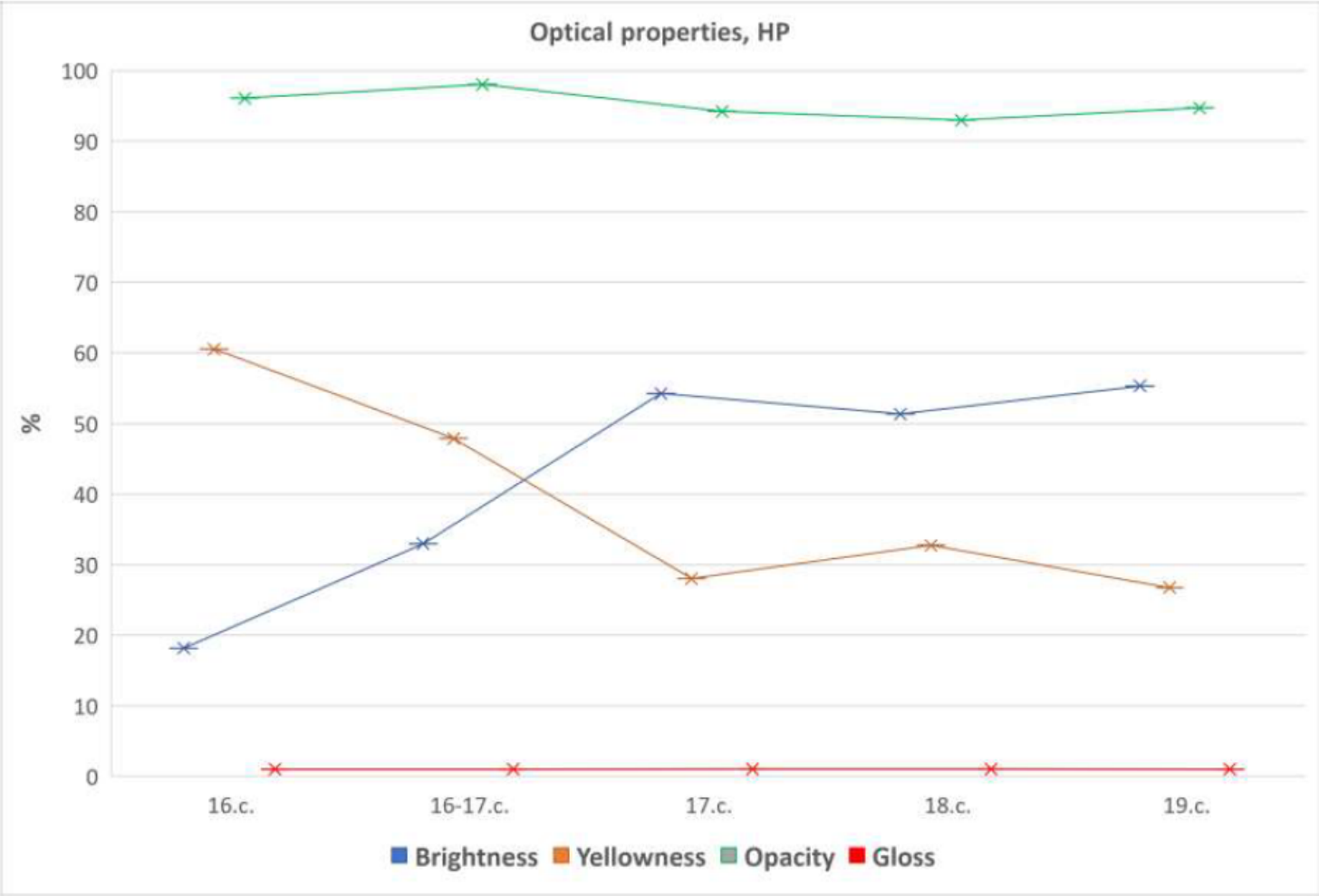


Figure 7

Optical properties of HP samples

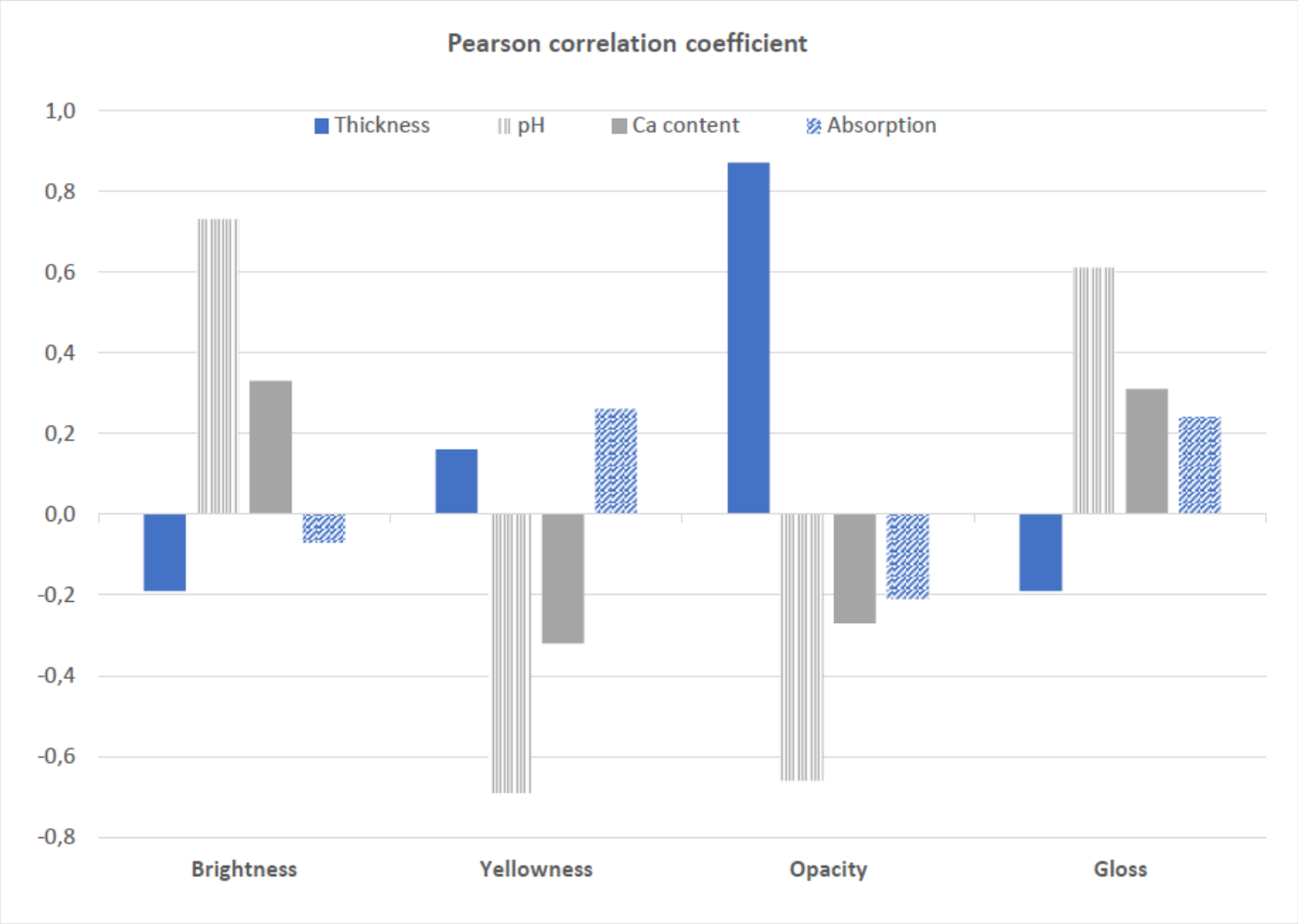


Figure 8

Pearson correlation coefficients between properties of HP samples

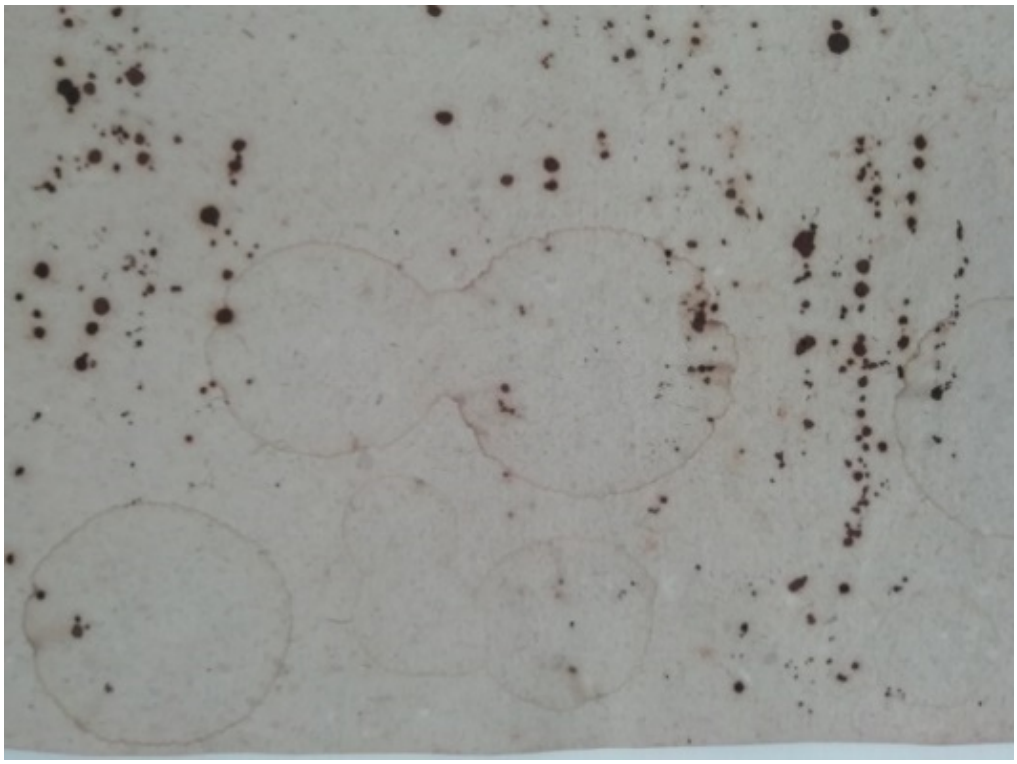


Figure 9

Line stains formed after measurement on sample 2D

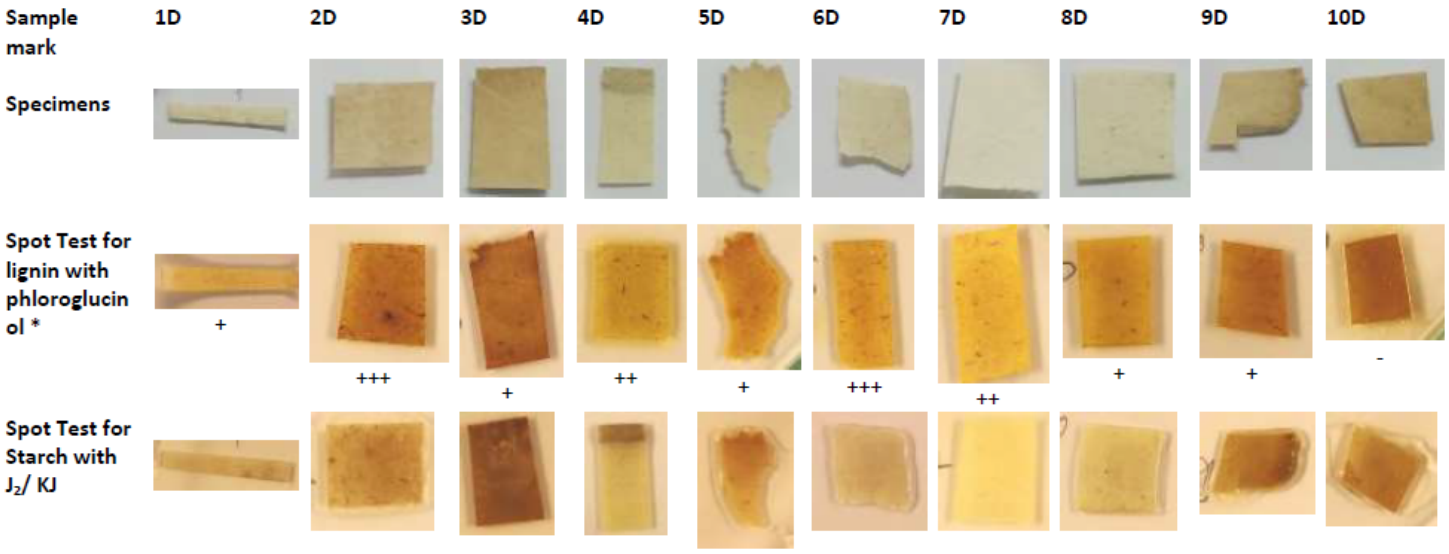


Figure 10

Results of the spot tests for lignin and starch in HP * display of the amount of stained fibers: −No stained fibers, + small amount of stained fibers (<5%), ++ moderate amount of stained fibers (≈5%), +++ higher amount of stained fibers (>5%)

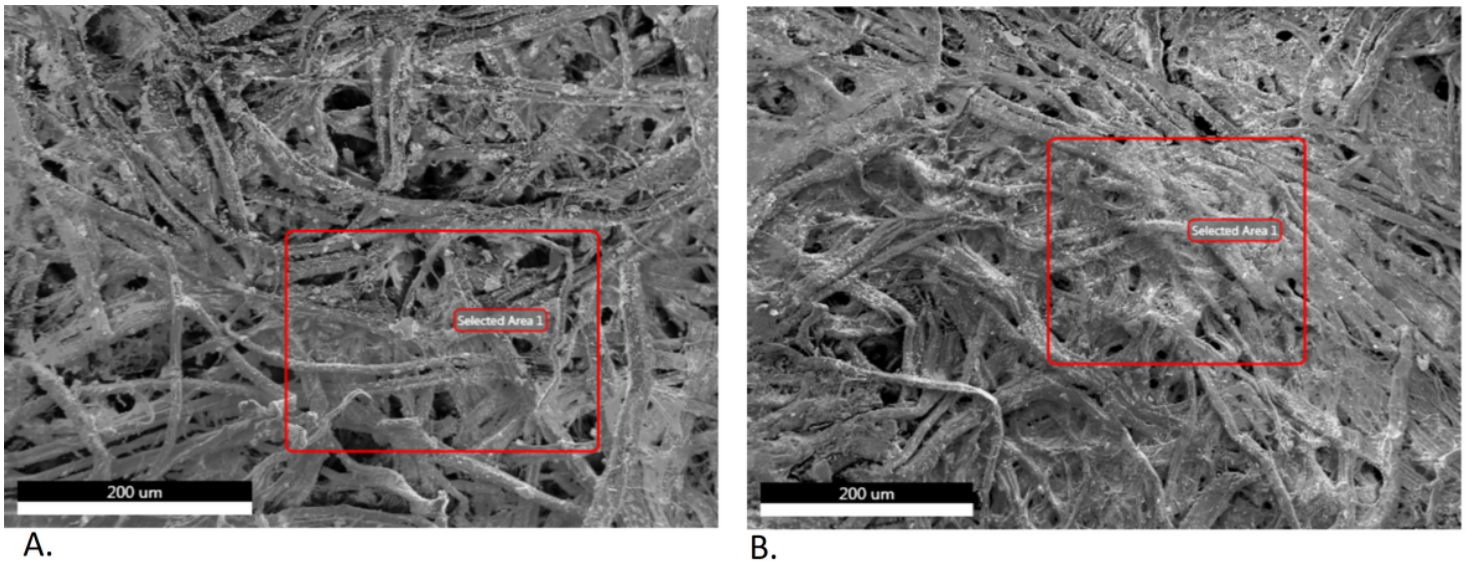


Figure 11

a) sample 3D unsized (16th-17th century), b) sample 5D sized (18th century)

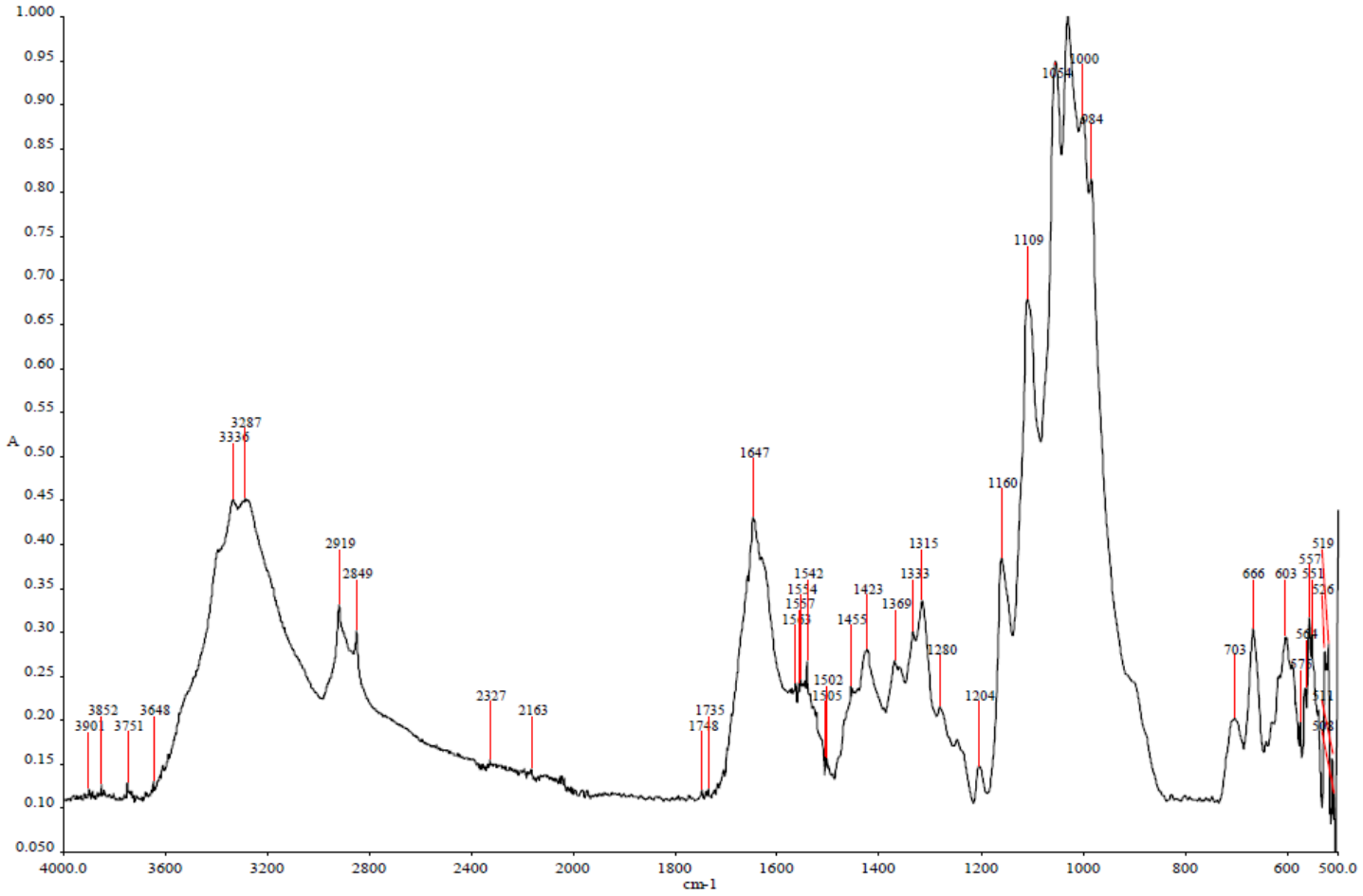


Figure 12

ATR-FTIR spectrum of 9D sample

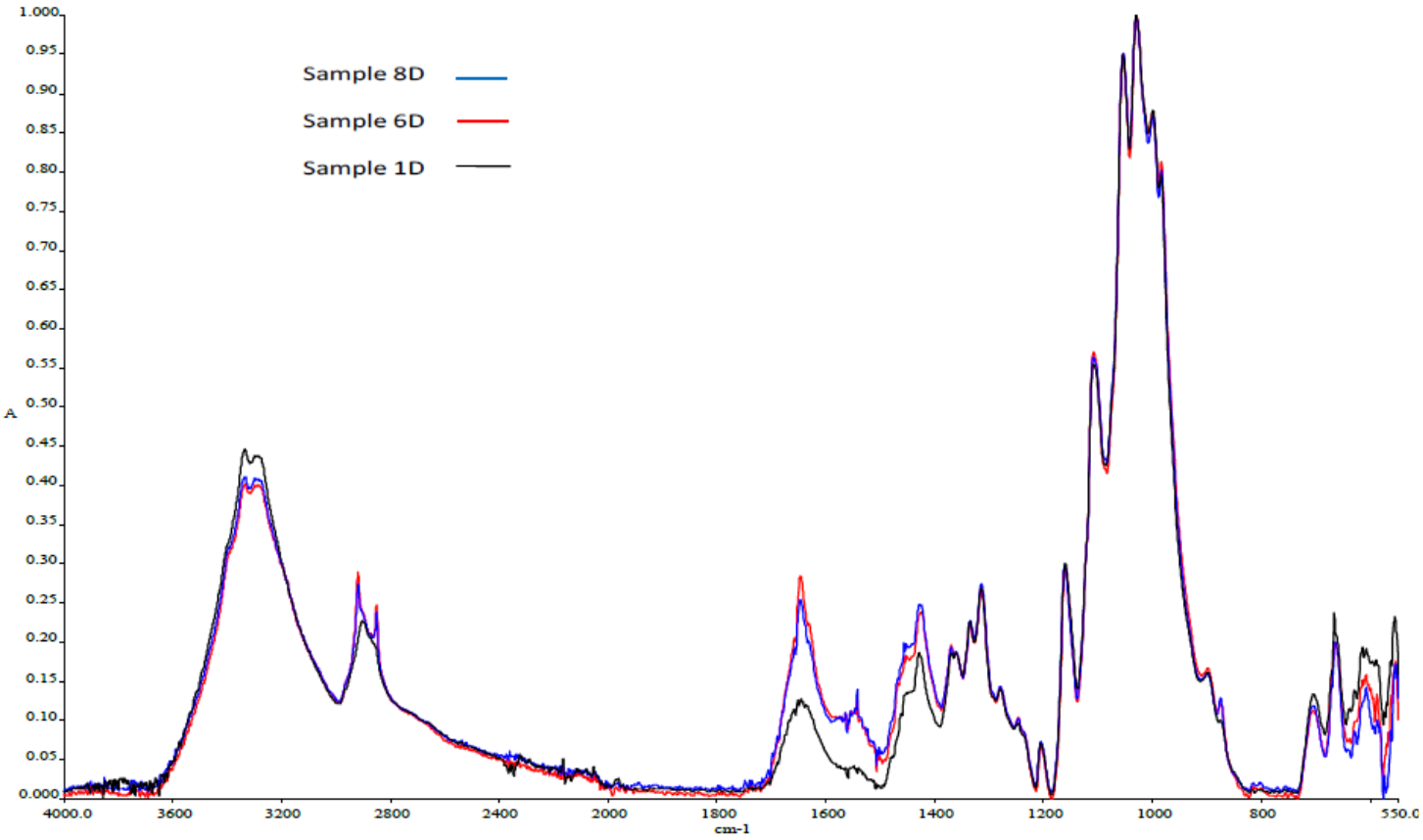


Figure 13

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

Supplementary Files

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