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Study and characterization of paper bookbindings from 16 to 18th stored in the Marciana National Library (Venice)

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Abstract

Paper bookbindings have been disregarded for centuries by scholars since they were only considered temporary covering materials for manuscripts and books. Recently, there is a willingness to reconsider these bindings and to evaluate their role. Thanks to the collaboration with the Marciana National Library in Venice, which stores an impressive collection of 849 detached bindings, the current research provides a chemical-physical elucidation about the composition and the manufacture of paper bookbindings realized between the 16th and the eighteenth century in the Venetian area. A selection of bookbindings was analysed by the means of complementary methods (thickness measurements, Attenuated Total Reflection—Fourier-Transform Infrared Spectroscopy (ATR-FTIR), Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC–MS) and X-Ray Fluorescence (XRF)). Data evidence the presence of cellulose as the main component of paper pulp; hemicellulose and lignin were identified too, probably related to the presence of linen/hemp rags in the paper production. Gelatine was detected muck likely related to paper sizing; among inorganic additives CaCO_3 was found in all samples. The presence of waxy material may be due to past undocumented conservation treatments.

Keywords Paper cover, Colourimetric measurements, ATIR-FTIR, Py-GC–MS, XRF, Marciana National Library, levoglucosan

Introduction

Originally, bookbindings made of paper were produced by Islamic binders and realized with paper boards [1] wrapped in a covering material similar to leather [2]. In this article, for clarity, binding is a general term

indicating the total structure of a bound book; boards or paper boards refer to the internal rigid or semi-rigid support of a binding (typical of semi-limp and stiff binding); paper cover refers to the outer structure with the potentially decorative part of the bound book when present [1].

The original intent of paper bindings [3, 4] was likely to create a lighter and less expensive protective layer [3, 5, 6]. First introduced in Europe in the sixteenth century, paper bookbindings gained rapid popularity thanks to the invention of the printing press. Printed books were economically affordable, easy to produce and immediately available to customers and not expected to last like manuscripts. Paper was the material of choice because it was less expensive and could readily accept ink in comparison to parchment. Paper gave lighter and easier to transport books; it was also less susceptible to deformations than

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parchment and did not need to be bound with wooden boards. Wooden boards were typical before the fifteenth century in the Western world and less common in the Islamic area [3, 4].

Specific studies of Islamic binding [7, 8] have demonstrated that in addition to construction peculiarities, paper bookbinding needs to be considered as an essential part of book production. Bindings can give essential information related to the historical trade, value, and function of books.

In the case of Italian productions, these aspects are even less investigated as bookbindings were often quite simple and made of strong papers, for instance the so-called “legatura alla rustica” [9]. The use of thick, heavily sized cover paper (often referred to as *cartonnage*), rather than parchment, was typical of Italian binders and reflects a peculiarity of this country for binding printed books [10–13]. The tradition of paper-making in Italy is often referred to as the Fabriano technique. In this well-documented tradition, lime (*addita calce*) or carbonate-based pigments were added either to the water pulp mix or to the wet sheet. Adding carbonates would give stiffer paper and partially solve issues related to reusing old or low-quality materials. Lime would also help in reducing the fermentation of paper pulp and the acidification of the final products. Besides calcium carbonate, the sizing of paper and covers with gelatine (with or without alum as preservative) is also well attested: the aim was to strengthen the paper and reduce its porosity [4, 9, 10, 13, 14].

In the latter part of the fifteenth century, the introduction of smaller formats (*octavo* books) also influenced the rise in popularity of paper bindings, as these formats did not need as much structural support as the larger ones. Aldo Pio Manunzio (1449/1452–1515), a well-known printer active in Venice in that period, was the one that introduced this format to the Venetian area [15].

The practice of rebinding books is well-documented among collectors, with the intent of matching the bindings of the new purchases to the bindings already owned. Sellers, often, used cheap or previously manufactured materials to avoid a time-consuming and elaborate binding process, which would eventually be redone by the owner. The creation of temporary bindings (made out of plain paper boards) eventually covered with printed paper or used parchment, was also a way to make books more attractive when stored in the shop [3, 4, 9]. This covering solution is in some cases linked to specific publications as pamphlets and music parts [1].

As for the materials used in the production of paper bindings, some historical sources are available in the form of Encyclopedias. In the “Dizionario delle arti e de’ mestieri” [16] by Francesco Grisellini (1717–1787) and

in the “Art de faire le papier” [15] by Joseph Jérôme de Lalande (1732–1807), specific definitions are given on the different materials employed in paper-making and on their production. Grisellini explains, for example, that *cartone* (Italian term for board, also commonly called *cartonnage* [16]) referred to lower-quality rags, often mixed with cut-outs and unusable paper sheets, treated with mallets to reduce them to a pulp again. The resulting sheet is often thick and characterized by long cellulose fibers. The dimension, form, and thickness of the resulting *cartone* were different depending on the mould and frame used [10, 13, 14, 17–20]. Under the definition of *papier*, Lalande also mentioned the production of a *cartonnage* obtained using old paper boiled in water. In this case, the glue used in the paper’s original production process would be retained and facilitate in obtaining a viscous paste [14, 15, 19, 21].

The abovementioned historical sources give very important information about how *cartonnage* was made.

Waste materials were mostly mixed with low-quality rags previously reduced to pulp with mallets. This process was very similar to the one employed to produce paper. Linen or hemp rags were submerged in a mixture of water and lime and left to soak for a time varying from few days to months. Once the fibers were completely saturated and swollen, they were beaten with mallets until a pulp was formed. Therefore, the main difference between *cartonnage* and paper seems just to be the raw starting materials. While higher-quality rags were used in the production of writing and printing paper, as high performance and whiteness were required, the same quality was not deemed necessary by the produce for *cartonnage* and low-quality papers [10, 13, 19, 22]. Once made, the pulp was spread over an assembled mould and frame, with a wire screen in the middle to create the chain and wire lines characteristic of handmade paper [14, 18, 19].

Gelatin-sizing was eventually added. Introduced by the paper mill of Fabriano in the thirteenth century, together with the hammer mills and the watermark [10, 13, 15, 18], gelatin-sizing became one of the most common practices between the fifteenth and eighteenth centuries since it produced more resistant paper sheets to ink bleeding [3, 9, 10, 23, 24].

After the mould, the sheet was pressed to remove the excess water and then hung to dry. The sheet would then be sized by dipping it in animal gelatin, obtained from boiling bones and skin residue mixed with alum, in the form of potash alum ($\text{AlK}(\text{SO}_4)_2$) [12, 14, 15].

Multiple layers of *cartonnage* could be pressed together to obtain a pasted or couched laminated board with different thicknesses. In the first case, an adhesive would be applied to keep the layers together, while, in the second case, the sheets would be wet and simply pressed

together to obtain couched *cartonnage* [6, 17, 21, 25]. This last case would encourage the formation of hydrogen bonds between layers and help keep the multilayer structure together.

In the production of paper between the fourteenth and eighteenth centuries, other additives were used in addition to the above-mentioned ones to improve or lessen the physical–chemical properties of the paper sheet. Magnesium, calcium and zinc have been identified in the best-quality papers, while sulphur, chlorine, potassium, aluminium, copper and iron were mainly found in the low-quality ones. Most probably, some elements were added intentionally (as in the case of alum during gelatin sizing) or unknowingly, as iron, which was presumably present in the water employed during the production. Previous studies have observed that, from the 16th to eighteenth century, the presence or absence of these elements might play a role in the quality and therefore in the conservation state of paper [24, 26].

Resuming, the main component expected in the paper bookbindings is cellulose from linen or hemp rags, but it would not be surprising to find other waste materials. Inorganic compounds are expected to be present as impurities from the water used and as additives to obtain specific characteristics. Finally, vegetal or animal glue may also be found in laminated paper boards or applied on paper as sizing.

Regarding paper bookbindings, it is still difficult to assess the actual materials used and the relative quantity due to a lack of dedicated studies but also of dedicated regulations [6, 27]. While paper quality was subjected to specific laws, for *cartonnage* any specific regulations have survived up to these days. The lack of control could have easily led to a large variation in the final products in terms of the quality and types of materials used. The producer could, in fact, easily adjust the mixture for convenience without having to account for that.

The lack of iconic or peculiar patterns has often led researchers to unjustly discount books with simple bookbindings, as they seem to provide no stylistic clues to their origin. Nevertheless, the analysis of materials and techniques employed to create the bindings can shed light on the book's history next to possible economic and socio-cultural aspects of the period in which it was made. Despite the work of many conservators and researchers in this field [4, 7, 19, 28], there is still a lack of clarity regarding the classification of bookbindings, describing the different parts, and preserving their peculiarities. While important publications [2, 4, 19, 29], projects [19, 30], and online sources [1, 19] are available on Islamic bookbindings, knowledge about European production methods is still lacking. For example, the idea that a bookbinding might just be a temporary solution decided

by the producer or the book owner is still debated [3, 4, 20, 29].

For all these reasons, paper bindings (as simple paper adhesive-laminated and couched-laminated boards [1]) have not been adequately considered by scholars and the conservation community yet. Over the centuries, due to their perceived low economic value and being considered as temporary solutions, paper bindings were often repaired, replaced, or discarded without much consideration for the original material. Very few studies, in particular to the Western area, have been dedicated to understanding their structure and the characteristics of the materials involved [3, 9, 19, 28]. These aspects are crucial for selecting appropriate conservation treatments and ensuring their preservation in the future.

The Marciana National Library Conservation Department in Venice owns an impressive and unique collection of 849 historical bindings detached from manuscripts and printed volumes. The collection varies in terms of materials (wood, paper, leather, parchment), age and place of production. Most of the bindings come from previous restorations carried out in the 1960s, when a common practice in book conservation was to undo the original sewing, detach the ancient bookbinding (even if slightly damaged) and make a new one. This practice persisted for centuries, but in this last decade, a few conservators decided to give back the original bindings to the Marciana. The original bindings were still in good condition, with even the endleaves still adhered.

This study will use the information acquired on the Marciana bookbinding as a starting point to give an insight into the materials used in their production.

Material and methods

Samples

This study considers paper bookbindings from text blocks printed between the sixteenth and eighteenth centuries in the Venetian area, since they constitute the most significant part of the collection.

The bookbindings are now stored in acid-free boxes and recorded in a database with references to the associated shelfmarks. Information about materials, binding technique, printing place and year of the book or of the manuscript, past conservation interventions and other general observations about the original binding and the new one is reported when available [31].

The paper bookbindings are divided into three main categories: limp, semi-limp and stiff paper bindings, depending on their structure [9, 19, 28]. Figure 1 reports an example of the outer and inside structure of the three categories.

Limp category refers to a single sheet of *cartonnage* folded to fit the text block (Fig. 1a/b). This style may have

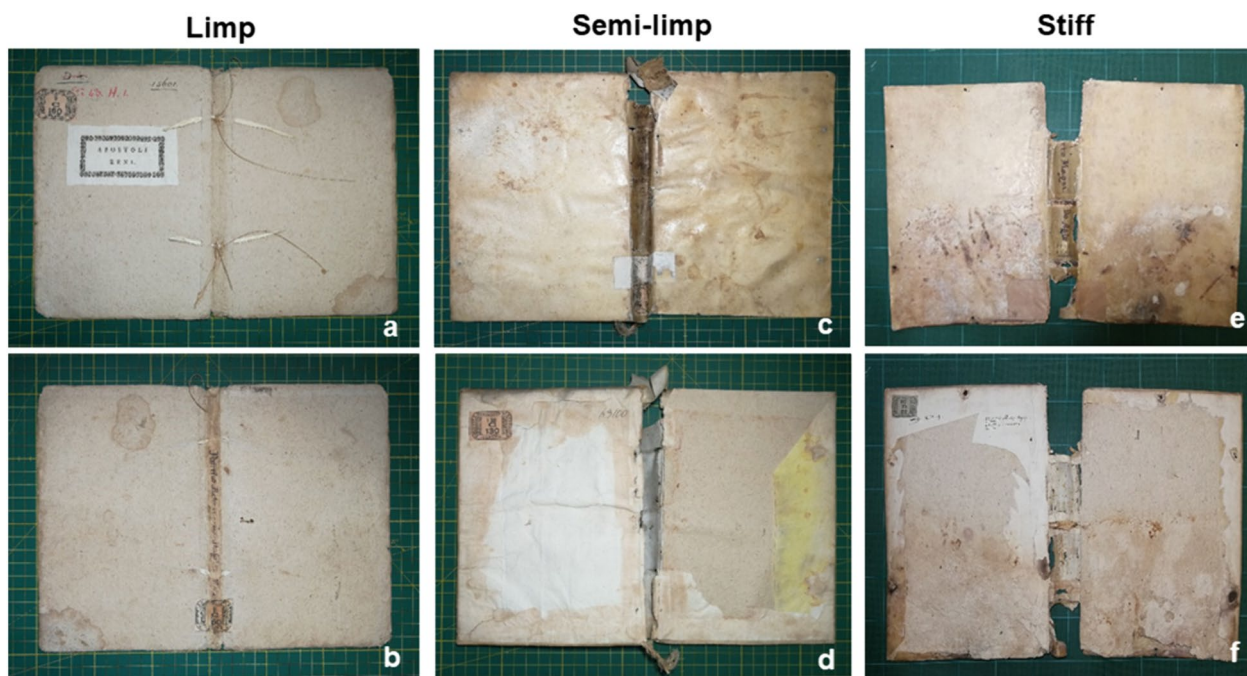


Fig. 1 Examples of the analyzed binding per group: limp binding sample 390D185 (a – outer, b—inner); Semi-limp binding 158C130 (c – outer, d – inner); Stiff binding sample 227D058 (e – outer, f—inner)

the edges tucked and untrimmed. This structure is a typical early Italian paper cover [27] and its use is attested from the 16th to the eighteenth century [6, 9]. Endpaper and endbands were also present in most of the examined samples as well as handwritten annotations and collocation labels.

In the semi-limp category (Fig. 1c/d), the paper binding is characterized by two flexible boards of *cartonnage* with variable thickness, placed inside an outer layer of paper or parchment as in the case of sample 158C130. This structure was mainly used during the sixteenth and seventeenth centuries [6, 25]. Endpapers, endbands and annotations were present as well.

Lastly, the stiff binding (Fig. 1e/f) sees the application of two boards, on both sides of the text block, covered up with materials similar to parchment, leather and, starting from the nineteenth century, paper and cloths [19]. As for the limp one, this type of structure is found as early as the 16th to the eighteenth century [25]. Annotations, endpapers, and endbands could also be present. The laminated boards usually look darker and thicker than the limp and semi-limp paper bindings, indicating two possible different preparations. In the stiff bindings, all the considered paper boards were laminated in contrast to the most common practice of obtaining boards with just one sheet made of a coarse paper mixture. Lamination could be achieved with an adhesive and by couching [17, 25].

The conservation state of the bindings was evaluated by the conservator of the Marciana Library, evidencing mainly colour inhomogeneities, possible paper oxidation, foxing, and in the worst conserved ones, detachments and defibring of the covers, in particular in the corner and in the spine.

As the main aim was to investigate the materials composing the bookbindings, analyses were taken in areas not affected by evident degradation according to the conservators. Seventy-one samples were studied to determine possible similarities or trends considering parameters such thickness, colour and construction aspects. Out of these, nineteen bindings were also micro-sampled and chemically analysed with Infrared Spectroscopy in Attenuated Total Reflection mode (ATR-FTIR), Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC–MS), and X-Ray Fluorescence (XRF).

In this study, bindings were organised based on the shelfmark and dated according to the associated book (Table 1). Dating bookbindings is always difficult, as pointed out by Pickwoad [9], as they may have been added after the book printing. However, after a careful examination of the materials and structure by the conservators, it was reasonable to claim that the bindings and books are contemporary. Table 1 reports the book bindings considered in this study for the ATR-FTIR, XRF and Py-GC–MS analysis.

Table 1 List of samples chosen from the main dataset of bindings for the analyses with the time period of the associated textbook

Limp		Semi-Limp		Stiff	
Time period	Shelfmark	Time period	Shelfmark	Time period	Shelfmark
1500–1550	010C130	≈1550	158C130	1500–1550	227D058
1550–1600	009C160	≈1600	175C066	1550–1600	213C023
	390D185				222D016
1600–1650	095C291			1600–1650	192C002
	023D178			1650–1700	172D175
1650–1700	143C180			1700–1750	006C024
	061D196				
1700–1750	390D018				
	164D228				
1750–1800	150D215				
	015C010				

Physical and morphological characterization

Colourimetric measurements

Colourimetric coordinates, in the CIE 1976 $L^*a^*b^*$ space, were acquired with a, Konica Minolta (Tokyo, Japan) CM-2600d Spectrophotometer (illuminant D65, observe 8 degree viewing angle geometry). A Teflon-based Spectralon metrological standard (Labsphere, North Sutton, NH, USA), diffusing 99% of incident light was used for calibration. The data were collected and processed with the program Spectra Magic NX 6 software.

For each sample, three different random points of the paper bookbindings were measured using a 3 mm diameter target area. For irregular materials such as hand-made paper, the value of specular reflectance (SCI) and diffuse reflectance (SCE) can change depending on the surface of the objects. The average SCI and SCE values were therefore compared, and any relevant differences in the values of L^* , a^* , and b^* were evidenced as the covers were neither coated or glossy. For this study, the Specular Component Excluded (SCE) values were, however, considered to reduce the influence of possible surface variations common for paper pulp [32, 33].

The colourimetric measurements were taken on all the seventy-one boards on the inner part as potentially less susceptible to modifications, avoiding evident stains, adhesive, or other degradation patterns. Among the colourimetric coordinates (L^* , a^* , b^*), this study considered only the white parameter (L^*), expressed in the CIE system as a pure number between 0 and 100, where 0 corresponds to total black and 100 to total white [34]. Next to gelatine and pH, the white parameter L^* was reported in different publications to play a role in combination with calcium on paper visual appearance and conservation. For this reason, in this work the L^* variations were investigated for highlighting possible modification on the raw

materials and production techniques among the years [23, 35].

Thickness measurements

The covers' thickness was measured on all seventy-one binders with a Käfer J 50 Tasterform dial thickness gauge, reading range between 0,01–10 mm and a jaw depth of 50 mm. Since the instrument is characterized by a flat contact point, it requires the *cartonnage* to be easily accessible from both sides and to have enough free space for the measurements. Unfortunately, this was not the case for four stiff bindings which were completely covered by parchment or other materials. Where the covering materials and endleaves were too adhered to the *cartonnage*, a AM4113T-FV2W Dino-Lite Special light digital microscope was used to measure both the *cartonnage's* thickness and the singular layers. The calibration and line functions available in the DinoCapture 2.0 version 1.5.32.B program was employed for these measurements.

A dataset with the thickness of the paper binding was obtained and the results explored with the help of RStudio. Min, Max, Mean and Standard Deviation (SD) were considered [36].

Chemical characterization

ATR-FTIR analysis

A portable Bruker ALPHA (Bruker Optics) spectrometer equipped with the Attenuated Total Reflection (ATR) modulus based on a single-bounce diamond ATR crystal was employed. The spectra were acquired using 64 scans and a range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . In accordance with past studies, three FTIR-ATR measurements were acquired per sample and then averaged

[37]. The data were processed with the proprietary software Opus 8.2.28 by Bruker Optics.

PY-GC-MS analysis

Selected samples from the different categories were investigated through single shot Py-GC/MS (SS-Py-GC/MS) to better identify their organic fraction. 40 ug of each sample were inserted in a Frontier eco-cup. In details, the bookbindings analysed were: 009C160, 023D178 and 164D228 for limp category, 158C130 and 175c066 for semi-limp, 213C023, 172D175 and 006C024 for the stiff ones.

40 ug of each sample were inserted in a Frontier eco-cup. According to specific literature on ancient papers Py-GC-MS analysis, the sample were not subjected to previous derivatization procedures [38–41].

A Py-3030D pyrolyzer (Frontier Lab, Koriyama, Japan) mounted on a Trace 1310 gas chromatograph (ThermoFisher Scientific, Waltham, MA, USA) combined with an ISQ7000 mass spectrometer (ThermoFisher Scientific, Waltham, MA, USA) was adopted.

According to preliminary tests and the specific literature related to Py-GC-MS [38–41], the pyrolysis furnace was set at 500 °C and the samples were pyrolysed for 0.20 min. The interface temperature was 300 °C. The pyrolysis unit was attached by a programmed temperature vaporization (PTV) injector to a HP-MS column (30 m, internal diameter 0.25 mm, film thickness 0.25 µm). Helium was used as carrier gas with a constant flow of 1 mL/min. The temperature program was set from 40 °C (held 5 min) to 280 °C (held 5 min), 10 °C/min. The interface temperature was 280 °C and the ion source temperature was 300 °C. The transfer line to the MS was kept at 280 °C. MS detection was carried out with electron impact ionization (70 eV) in full scan mode, in the range 30–600 m/z, 0.2 s dwell time.

Chromeleon 7 software was used for collecting and processing mass spectral data. The results were interpreted with NIST Libraries, F-Search software, and an ad hoc created ADMIS library with ESCAPE system [42].

XRF analysis

For the elemental analyses, a Philips Minipal PW4025 Philips (Maynards Industries Canada) was used at 20 kV and 70 µA power settings. The analyses were carried in open air and a Kapton filter was employed. Calcium resulted to be the most abundant element and its variation was evaluated among the analyzed samples. The presence of other elements (Si, S, K, Mn, Fe, Ni, Cu, Pb, Zn), due to their low amount, are here discussed in terms of presence/absence. As only minimum sample were available, only general trends are here discussed avoiding quantification. XRF data were normalized to

Rh peak and compared to a paper realised by the University of IOWA and Prof. Tim Barrett within the *Project Paper through time*; the handmade paper is realised with flax cooked in lime without fermentation to resample 15–18 century paper. This *cartonnage* is no longer in production [13, 43].

Results and discussion

Colourimetric measurements

Figure 2 shows the box plot obtained for the different bookbindings. The covers in the limp bindings have the highest degree of white (ranging from min 70.61 to max 86.99; mean 80.60 ± 4.47 SD, median 81.91) while the semi-limp ones reach a maximum of 79.28 (min 74.70; max 79.28; mean 76.80 ± 1.77 SD; median 76.31) and the stiff categories has a white values of 81.82 (min 66.96; max 81.82; mean 75.38 ± 4.03 SD; median 75.88). Comparison among the different categories is complex as the number of samples, their age and their production are different. Nevertheless, the semi-limp and stiff bindings present a normal distribution (Origin—Normality test—Shapiro -Wilk) where the median is close to the mean value and most of the values fit within the box. The limp bindings do not have a normal distribution and the median value is far from the mean showing an asymmetric distribution.

The lower values in L^* in semi-limp and stiff bindings could be due to the quality and type of materials employed: in fact, semi-limp and stiff bindings were commonly covered with parchment, paper or leather, as stated before [9, 28].

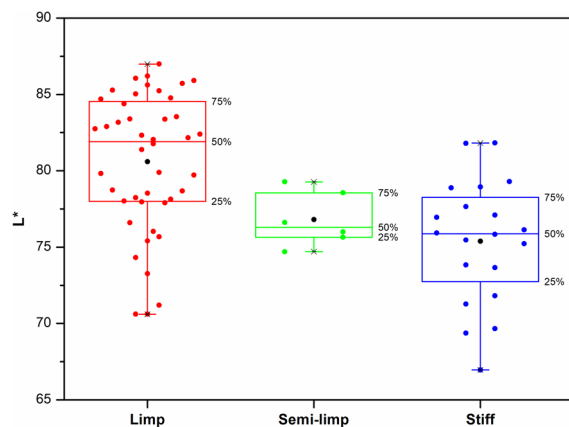


Fig. 2 Box plot of white parameter (L^*) for the bindings depending on the different category: limp, semi-limp, stiff. Lower and upper box boundaries are the 25th and 75th percentiles, respectively. Line inside the box in the median, black dots the mean values, the ends of the whiskers represent the minimum and the maximum values

Thickness measurements

For the limp bindings, the mean thickness was equal to 0.62 mm (with a SD of 0.25 mm, min 0.28 mm; max 1.59 mm), for semi-limp was 0.57 mm (SD 0.09 mm, min 0.47 mm; max 0.72 mm), and for the stiff ones 2.67 mm (SD 0.73 mm, min 1.29 mm; max 4.02 mm). In terms of thickness, there is a clear difference between the *cartonnage* used for the boards in stiff bindings, while limp and semi-limp ones share similar values.

Figure 3 shows the box plot obtained for the bindings. The limp bindings, despite the lower variability in thickness (lower dispersion of data), do not present a normal distribution (Origin—Normality test—Shapiro -Wilk) with a median value equal to 0.55 mm. In this case, most of the examined boards fall between the 25th and 50th percentile.

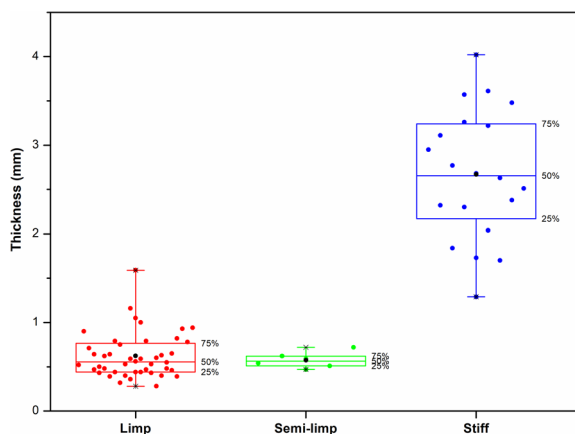


Fig. 3 Box plot of the thickness (mm) of limp, semi-limp and still boards. Lower and upper box boundaries are the 25th and 75th percentiles, respectively. Line inside the box in the median, black dots the average values, the ends of the whiskers represent the minimum and the maximum values

Boards in semi-limp and stiff bindings have a normal distribution with a median (0.56 for semi-limp; 2.65 for stiff) close to their mean values (0.55 for semi-limp; 2.65 for the stiff). Nevertheless, the boards of the stiff bindings show a spread distribution. The *cartonnage* employed for the stiff bindings is, in fact, characterized by variable thickness ranging from a minimum of 1.29 mm to a maximum of 4.02 mm. This spread-out distribution of the stiff bindings thickness is probably related to the production process. The boards are often realized, as in this study, with a different number of layers of *cartonnage* one on top of the other.

The measurement of the single layer’s thickness was sometimes complex, as the corners were often deteriorated and affected by peeling, making it difficult to discern the paper layers properly. Among the available stiff bindings, four samples were therefore investigated with a digital microscope to measure the thickness of the layers (Fig. 4).

The resulting observation showed that the *cartonnage* was obtained with a variable number of layers ranging from a minimum of 2 to a maximum of 6. The thickness of a single layer *cartonnage* was calculated as the mean of all the paper layers and is equal to 0.92 mm (SD ± 0.59 mm), showing again a pronounced variation among them.

ATR-FTIR and XRF analysis

Most of the investigated paper bookbindings showed similar IR spectra (Fig. 5). Between 3400 and 2800 cm^{-1} peaks associated with O–H and C–H stretching, typical of polysaccharides, are present.

Characteristic bands related to cellulose were also detected in the region between 1650–900 cm^{-1} . In particular, the peak at about 1630 cm^{-1} is related to water molecules absorbed in the cellulose. Between 1200 cm^{-1}

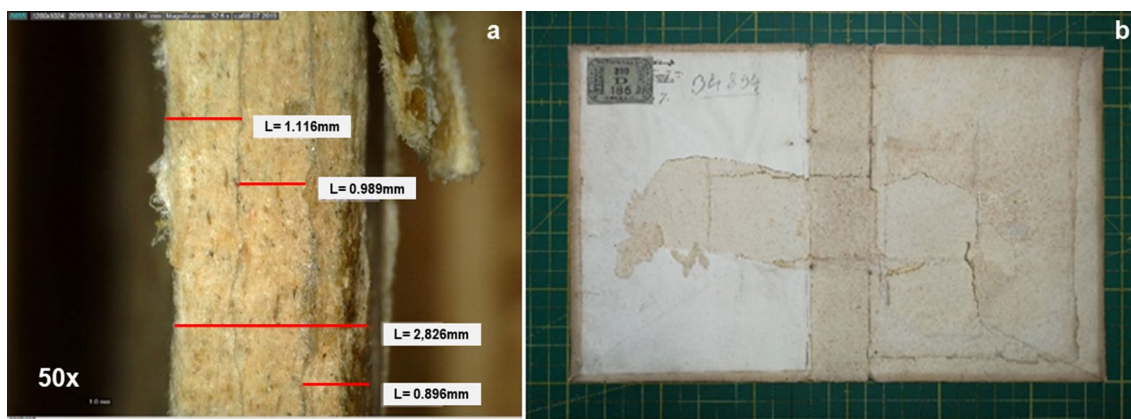


Fig. 4 Layers under microscope in the laminated 220D007 stiff paper cover (50x) (a), example of stiff paper binding 390D185 (b)

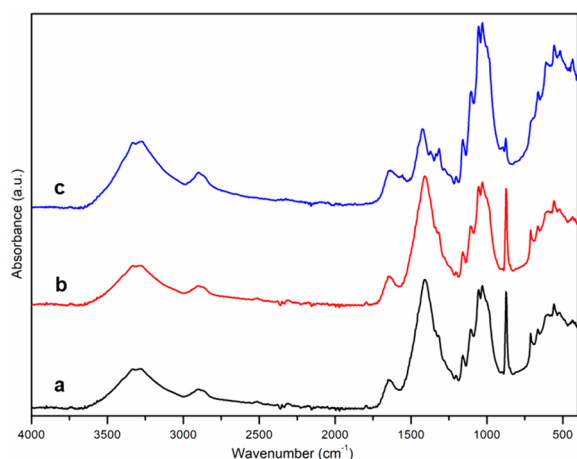


Fig. 5 ATR-FTIR spectra representative of **a** limp sample 164D228, **b** semi-limp sample 158C228 and **c** stiff sample 213C023

and 900 cm^{-1} , the ATR-FTIR spectra evidenced other typical peaks associated to the cellulose fingerprint: at 1208 cm^{-1} C–OH and C–CH bending, at 1157 cm^{-1} the C–C breathing ring asymmetric stretching, at 1105 cm^{-1} the asymmetric stretching of the C–O–C glycosidic ether band, at 1060 and 1030 cm^{-1} the stretching of the primary and secondary C–OH alcohols, and finally at 897 cm^{-1} the symmetric stretching of the C–O–C often associated to the amorphous region of cellulose [44]. The relative intensities of these peaks identify cellulose as the main component of the paper pulp for the binding production; this is in accordance with the literature since rag paper pulp, mixed with waste materials, was mainly employed in producing paper covers [10, 15, 17].

The peaks at 1640 cm^{-1} (Amide band I C=O stretching vibration of peptide groups) and 1540 cm^{-1} (Amide band II associated with C–N stretching and N–H bending vibrations of peptide groups) might be linked to the presence of gelatine [23, 45, 46]. Gelatine was commonly used as sizing either by tub dipping or surface application in traditional papermaking until the eighteenth century. Alum, often associated to gelatine sizing, was not detected, even though its presence cannot be excluded, as also discussed lately in literature [10, 13, 35].

Calcium carbonate (CaCO_3) was also detected in all the samples based on the characteristic peaks at about 1440 cm^{-1} and 870 cm^{-1} in all the samples. CaCO_3 is a common additive in paper pulp production and acts as an alkaline reserve and/or a thickener in handmade paper [14, 26, 35]. Additional signals were also depicted under 600 cm^{-1} and probably caused by inorganic compounds present as additives; this hypothesis was further investigated with X-Ray Fluorescence.

In the case of the limp covers (Fig. 6a), the sample 10C130 (dated 1500–1550) shows a lower intensity for CaCO_3 in comparison with the sample 164D228 (dated 1700–1750). Among the stiff covers (Fig. 6b), both the samples show possible traces of CaCO_3 in force of the shoulder at about 870 cm^{-1} but slightly noticeable respect to limp bindings.

In the case of papermaking, different publications have highlighted how variations of gelatine, alum and CaCO_3 have a role on the conservation and visual aspect of the documents. Additionally, their presence and content might be related to technological modification over the years or countries [10, 14, 35, 47]. Based on Fig. 6, the difference in CaCO_3 between the limp and stiff boards

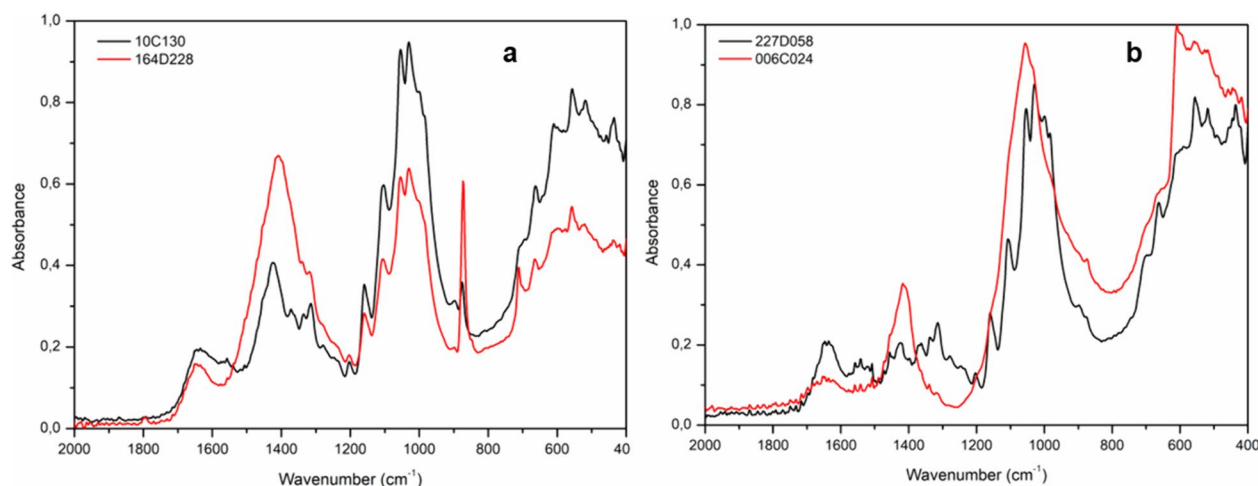


Fig. 6 ATR-FTIR spectra: limp bindings **(a)** 10C130 (dated 1500–1550) and 164D228 (dated 1700–1750); and stiff bindings **(b)** sample 227D058 (dated 1500–1550) and 006C024 (dated 1700–1750). All spectra in absorbance mode were normalized to a scale of 0 to 1

might suggest a different protocol for the board production. Stiff bindings may have been mainly produced with paper, while in the limp bindings a higher addition of CaCO_3 could help create a stiffer material. Besides, the different presence of CaCO_3 might indicate a modification over time which could be related to the introduction of other materials such as straw [19, 20, 29].

XRF analyses were carried to evaluate the elemental composition of the samples. Specifically, Fig. 7a shows the XRF spectra of samples 01C130 (limp binding) and 227D058 (stiff binding) respect to a modern paper (MP) used for binding conservation with a high content of Ca [13, 43]. Two bindings from the same period, as identified by the conservators, were selected. For the semi-limp category, there was not a sufficient amount of sample for carrying out XRF analysis.

The samples show a high signal for Ca, being the main element; CaCO_3 was already hypothesized based on literature and detected by ATR-FTIR results. Before the advent and spreading of mass pulp printing paper, the presence of elements such as Ca or Al has long been debated [14, 15, 35]. Specifically, various authors still disagree to whether Ca-based compounds could have been intentionally added, even in high amounts for obtaining stiffer and whiter papers, reducing gelatine or paper oxidation [24, 35, 48]. As visible in Fig. 7b, all limp bindings present a significant Ca content, that might be far from being a casual presence or a contamination. The presence of Ca seems to be an important characteristic in all XRF spectra. Ca-based compounds could have been added to get specific characteristics in terms of visual aspect or quality as often reported for Venetian paper production

[9, 26]. The use of CaCO_3 and alum in parchment treatments is attested as well and their presence should be carefully considered [3, 4, 28].

Aluminium (Al) was detected in limited cases and its co-presence with sulphur (S) and potassium (K) could presume the presence of alum, possibly mixed with gelatine [13, 14, 26]. Other elements, such as Mn, Fe, and Cu, were also detected. Ca is commonly associated with alkaline reserve, while metals as copper (Cu) and iron (Fe) might be related to paper production or presence of oxidative degradation [26, 35].

Py-GC-MS

Py-GC-MS analysis allowed for a better understanding of the organic compounds present in paper bindings, highlighting the complexity of their compositions and identifying related degradation products.

Table 2 lists all the compound detected in a sample taken from a limp binding (namely 009C160, dated 1550–1600), considered here as representative for all the samples analysed by Py-GC-MS. Figure 8 illustrates the pyrograms obtained from samples: a) 009C160 limp binding; b) 158C130 semi limp; c) 213C023 stiff binding.

Cellulose results as the core component of the paper pulp in force of the associated thermal degradation products obtained at 500 °C, confirming ATR-FTIR results.

As stated in literature [39, 41, 49, 50], it was possible to detect: furan-based structures (such as Furan, 2,5-dimethyl (peak 4), Furan-3methyl (5), Furfural (11), 2-furanmethanol (12), 2(5H) furanone (14), furfural, 5-methyl (16), 2,5-furandicarboxaldehyde (22), 2,5-dimethylfuran-3,4(2H,5H)-dione

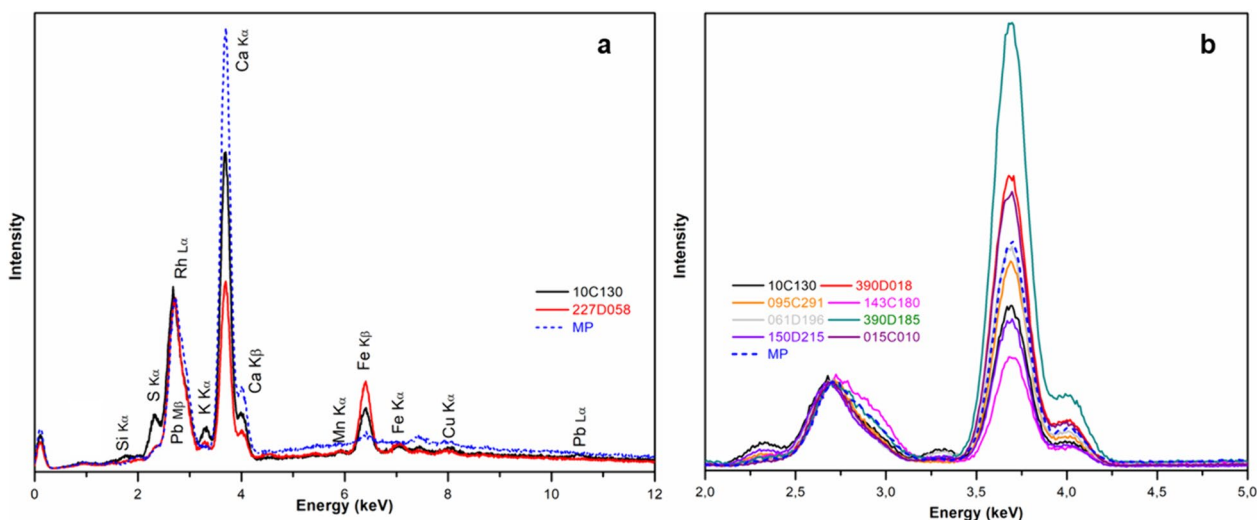


Fig. 7 XRF spectra obtained for samples: **a** 01C130 (limp binding) and 227D058 (stiff binding); **b** detail respect to Ca peaks for limp bindings. Spectra are compared to a modern paper (MP) realised within the Project “Paper through time”. Data were normalized respect to the Rh signal

Table 2 Summary of identified compounds in sample 009C160 by Py-GC-MS

Peak #	Retention Time	Compounds
1	2.96	1-hydroxy-2-propanone
2	3.22	Glyceraldehyde
3	3.57	1,2-ethanediol
4	3.70	Furan, 2,5-dimethyl
5	4.79	Furan-3methyl
6	5.01	Pyrrrole
7	5.44	Acetic acid
8	5.72	Butanedial
9	6.01	2- propanone 1-hydroxy
10	6.09	Methylpiruvate
11	7.26	Furfural
12	7.95	2-furanmethanol
13	8.28	Acetoxipropanone
14	9.36	2(5H) furanone
15	9.64	2-cyclopenten-1-one, 2-hydroxy
16	10.43	Furfural, 5-methyl
17	10.75	2-hydroxy-3-methyl-2-cyclopente-1-one
18	10.97	Phenol
19	11.75	1,2-cyclopentanedione
20	12.04	P-cresol
21	12.30	O- cresol
22	12.63	2,5-furandicarboxaldehyde
23	12.67	M-cresol
24	12.80	2,5-dimethylfuran-3,4(2H,5H)-dione
25	12.88	P-guaiacol
26	12.95	Pentanal
27	13.28	Maltol
28	13.41	2,4(3H,5H)-Furandione,3-methyl
29	13.90	2(3H)-Furanone, dihydro-4-methyl
30	14.50	Nonanal
31	14.88	1,4:3,6-Dianhydro- α -d-glucopyranose
32	15.04	3,4 anhydro-d-galactosan
33	15.16	5-hydroxy methylfurfural
34	15.34	Maltose
35	15.49	2,3-anhydro-d-mannosan
36	16.87	Syringol
37	18.21	D-Mannose
38	19.00	Levogluconan [(B-D-Glucopyranose, 1,6-anhydro)]
39	20.29	D-galactose
40	20.42	1,6-anhydro-B-D-glucofuranose
41	21.97	Glycyl-proline
42	22.40	Hydroxyproline
43	23.79	Palmitic acid
44	25.12	Oleic acid
45	25.68	Stearic acid
46	26.85	Nonadecane
47	27.68	Heneicosane
48	28.48	Tricosane

Table 2 (continued)

Peak #	Retention Time	Compounds
49	29.25	Pentacosane
50	29.43	Tetracosenoic acid
51	30.09	Heptacosane
52	31.03	Nonacosane
53	32.14	Hentriacontane
54	33.47	Tritriacontane

(24), 2,4(3H,5H)-Furandione,3-methyl (28), 2(3H)-Furanone, dihydro-4-methyl (29), 5-hydroxy methylfurfural (33)); light linear carbonyls (mainly 1-hydroxy-2-propanone (1), Methylpiruvate (10), 2-cyclopenten-1-one, 2-hydroxy (15), 2-hydroxy-3-methyl-2-cyclopente-1-one (17) and 1,2-cyclopentanedione (19)); anhydro-oligosaccharides (mainly 1,6-anhydro-beta-D-glucopyranose, better known as levoglucosan (38) and 1,6-anhydro-B-D-glucofuranose (40)) and anhydrosugar derivatives (mainly 1,4:3,6-Dianhydro- α -d-glucopyranose (31), 3,4-anhydro-d-galactosan (32), 2,3-anhydro-d-mannosan (35)); several sugars (maltose, mannose, galactose).

As concerns the “purity” of cellulosic paper, Py-GC-MS analyses show not only compounds originating from cellulose, but also derivatives from hemicellulose and lignin in all the pyrograms. The thermal degradation of cellulose and hemicellulose generally produces the same compounds (e.g. furans and pyrans), but those from hemicelluloses are hexose- and pentose-based [51]. Pyrolytic lignin derivatives detected in the paper bindings (Table 2 and Fig. 8) encompass: phenol (peak 18), p-cresol (20) o-cresol (21), m-cresol (23), p-guaiacol (25) and syringol (36) [52, 53].

As reported in the historical documents, these paper bindings were generally produced from linen or hemp rags. The chemical composition of both hemp and linen fibres includes the presence of cellulose, hemicellulose and lignin-based compounds [10, 54–56], making their distinction in aged lignocellulosic materials not very feasible.

Besides lignocellulosic compounds, Py-GC-MS analyses revealed the presence of different organic materials in the paper bindings analysed.

Traces of amino acids were detected, specifically glycine-proline and hydroxyproline (peaks 41 and 42, respectively in Fig. 8), although the Py-GC-MS conditions were not specifically set for proteinaceous compounds. Their presence may be linked to animal glue-based gelatine, as also indicated by ATR-FTIR analysis, being hydroxyproline the characteristic biomarker of animal glue [57–59].

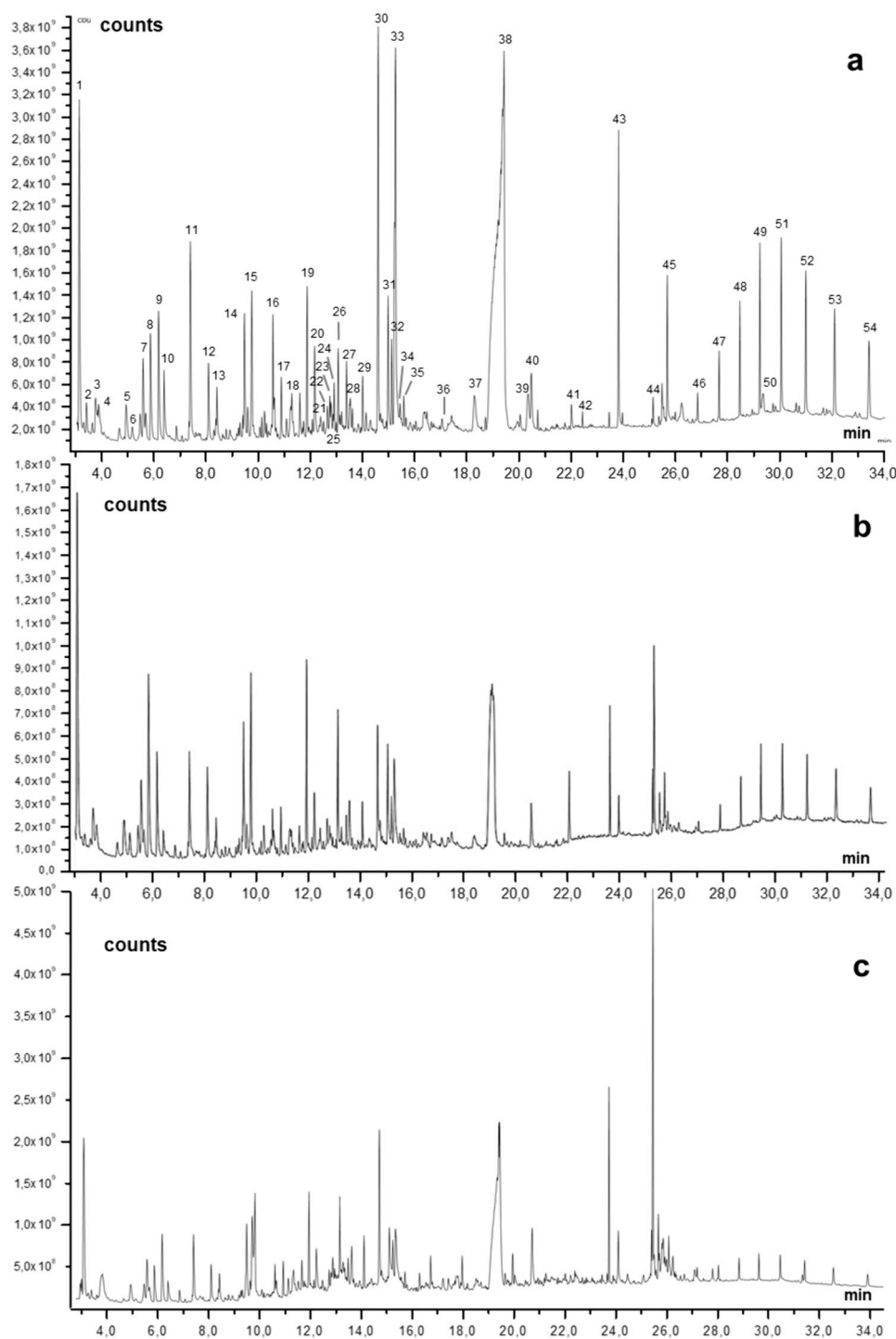


Fig. 8 Py-GC-MS results obtained from samples: **a** 009C160 limp binding; **b** 158C130 semi limp; **c** 213C023 stiff binding. The peaks identification is reported in Table 2

In all the samples, from 26 to 34 min, eight peaks are associated with a series of odd-numbered linear n-alkanes (C19-C33), being heptacosane (C27) the most abundant. According to literature [39, 60–62],

their peculiar disposition and the detection of fatty acids (in particular, high amounts of palmitic acid (43), stearic acid (45) and tetracosanoic acid (50)) may refer to the presence of wax, likely beeswax. Due

to the relatively high intensity of the abovementioned peaks, wax cannot be considered as a contaminant. Nevertheless, the typical beeswax marker, namely the 15-hydroxypalmitic acid was hardly detectable, and the chain alcohols could not be identified because of the methodology used (i.e. no sample pre-treatment with a derivatising agent). This leaves the possibility open to other waxy materials, such as microcrystalline/mineral wax, which would explain the presence of odd-numbered alkanes. These materials may have been adopted during undocumented conservation treatments, done before the 1960s.

On the other hand, the presence of different fatty acids could have a role linked to paper degradation.

One of the most prominent peaks in the pyrograms is the one at about 14.50 min. From the mass spectrum, it was identified as an aldehyde, specifically nonanal. Literature on the degradation of historical paper and books, reports that analyses of VOCs revealed the massive presence of acetic acid, furfural, and the straight chain aldehydes (such as hexanal, heptanal, octanal, nonanal, and decanal) [63–66]. In the pyrograms of the paper bindings, these compounds were detected. They naturally formed during the ageing process of paper. As suggested by [64, 65], acid hydrolysis can cause the chain scission of cellulose molecules, leading to the fragmentation of carbohydrates. These fragments can then be oxidized to form carboxylic acids, which increases the acidity of the paper, leading to well-known degradation phenomena. Furthermore, the identified aldehydes are proved to be prominent features in Py-GC-MS paper analyses, but more abundant when paper is obtained from cotton/linen rags: this indicates that oxidative pathways are more crucial for paper made of cotton or linen [63].

Levoglucosan is one of the most important products of depolymerization of cellulose and the pyrograms of the analysed paper bindings show its prominent presence. Generally speaking, the older the samples, the more easily they are subjected to the pyrolysis processes showing higher peaks of levoglucosan [39]. No direct correlation was found between higher levoglucosan content and the age of the paper bindings. There are, in fact, many factors that can influence the formation of levoglucosan (including the presence of inorganic additives such as alum and CaCO_3).

Interesting, however, is the correlation between the greater abundance of levoglucosan and that of nonanal, mentioned earlier, never reported in literature before to the best of our knowledge. The limited number of samples analysed in this study does not allow a further explanation than the formation of 'odorous' compounds is strictly related to the age of the paper (the so-called smell of books) [63, 65, 66].

Conclusions

This research provides an insight into the chemical and physical characteristics of a selection of paper bookbindings dated between the 16th and the eighteenth century and stored in the Marciana Library in Venice.

Among the three bookbinding categories, thickness measurements of the paper boards did not show any significant variability for limp and semi-limp bindings with values close to their mean. On the contrary, stiff bindings show a spread distribution: they are in fact realized with different number of layers of *cartonnage* one on top of the other.

From the colourimetric results (L^*), limp bindings show the highest values of whiteness in comparison to semi-limp and stiff bindings, which could be related to a different quality in the raw materials used for their production.

FTIR analyses evidenced cellulose as the main compound of the paper bindings, confirmed also by Py-GC-MS which identified emicellulose and lignin-based materials. These materials may suggest the use of linen / hemp rags in the paper bookbinding production. Gelatine was identified and probably related to paper sizing. CaCO_3 was detected in all the analysed samples, particularly in limp and semi-limp boards. Ca was confirmed by XRF next to other minor elements. The co-presence of S, Al and K, might indicate the addition of alum with gelatin, as also reported in the literature.

The detection by Py-GC-MS of a series of odd-numbered n-alkanes, palmitic acid and tetracosanoic acid may refer to wax, likely beeswax or microcrystalline/mineral wax. Far from being a contamination, the presence of wax is most probably linked to undocumented past conservation treatments.

This research paves the way for promoting the knowledge on paper bookbindings materials and their conservation and historic role. For examples, a geographical and technological classification of the bookbinders, which is possible only when the boards are subjected to conservation, would give important knowledge that a precise classification. These details together with an expanded dataset could help in applying multivariate tools for reconstructing historical, technical, and technological aspects.

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Author contributions

E. Paro: Conceptualization, Investigation, Methodology, Validation, Formal analysis, Writing – original draft, Writing—Review & Editing. C. Benvestio: Methodology, Writing—original draft, Writing—Review & Editing. S. Pugliese: Methodology, Writing—original draft, Writing—Review & Editing. F. C. Izzo: Investigation, Validation, Formal analysis, Writing—original draft, Writing—Review & Editing. E. Balliana: Investigation, Validation, Formal analysis, Writing—Review & Editing. E. Zendri: Conceptualization, Methodology,

Writing—original draft, Writing—Review & Editing, Supervision. All authors have read and approved the final version of the manuscript for publication.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publications

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Competing interests

The authors declare no competing interests.

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References

- Language of Bindings—Ligatus, (n.d.). <https://www.ligatus.org.uk/>. Accessed 11 April 2024.
- Scheper CH, The Islamic bookbinding tradition. A book archaeological study, Universiteit Leiden, 2014. <https://hdl.handle.net/1887/30100>.
- Pickwood N. Bookbindings and the History of the Book. *Arh Vjesn Bull d'archives*. 2016;59:157–76.
- Foot MM. *Bookbinders at work: their roles and methods*. London: British Library; 2005.
- Rudy KM. *Piety in pieces: how medieval readers customized their manuscripts*, Open Book Publishers, 2016. <https://doi.org/10.11647/OBP.0094>.
- Miller J. *Suave mechanicals, essay on the history of bookbinding*, Julia Miller Editor, Brookhaven, 2016.
- Scheper K. *The technique of Islamic bookbinding*. BRILL. 2015. <https://doi.org/10.1163/9789004387263>.
- Scheper K. Three very specific binding features, shedding new light on Islamic manuscript structures. *J Islam Manuscripts*. 2013;4:82–109. <https://doi.org/10.1163/1878464-13040103>.
- Pickwood N. Italian laced-case paper bindings. *J Pap Conserv*. 2019;20:122–51. <https://doi.org/10.1080/18680860.2019.1748416>.
- Dąbrowski J, Simmons J.S.G. Permanence of early European hand-made papers, *Fibres Text. East. Eur*. 11 (2003) 8–13.
- Erhardt D, Tumosa CS. Chemical degradation of cellulose in paper over 500 years. *Restaurator*. 2005. <https://doi.org/10.1515/rest.2005.26.3.151>.
- Gitat A, Michelin A, Belhadj O, Pellizzi E, Massiani P, Rouchon V. Paper sizing with gelatine: from the macro- to the nano-scale. *Cellulose*. 2021;28:2419–32. <https://doi.org/10.1007/s10570-020-03655-z>.
- Barret T. Background: European Papermaking Techniques 1300–1800, (n.d.). https://paper.lib.uiowa.edu/european.php#_ednref28. Accessed 11 April 2024.
- Dąbrowski J. Paper Manufacture in Central and Eastern Europe Before the Introduction of Paper-making Machines, 2008. <https://www.paperhistory.org/dabro.pdf> Accessed 11 April 11 2024.
- Lefrançois de Lalande JJ, Art of paper making. Of M. De La Lande (in French: Art de faire le papier. Par M. de La Lande), in: J. Desaint, C. Sailant (Eds.), *Descr. Des Arts Metiers, Faites Ou Approuv. Par Messieurs l'Académie R. Des Sci. Avec Fig. En Taille-Douce, chez Desaint & Saillant, libraires, rue Saint Jean de Beauvais, Paris, 1761*.
- Griselini F. Dictionary of arts and professions written by Francesco Griselini (in Italian: Dizionario delle arti e de' mestieri compilato da Francesco Griselini), 4 (1769) 216.
- Pickwood N. Onward and downward: How Binders Coped with the Printing Press before 1800, in: R. Myers, M. Harris (Eds.), *A Millenn. Book, Prod. Des. Illus. Manusc. Print 900–1900, Oak Knoll Pr, Delaware, 1994: pp. 61–106*.
- Lackner F. History and making of paper in middle ages (in Italian: Storia e fabbricazione della carta nel Medioevo), in: P. Rückert (Ed.), *Testa Di Bue e Sirena La Mem. Della Cart. e Delle Filigr. Dal Medioev. Al Seicento*, Landesarchiv Baden-Württemberg, Hauptstaatsarchiv Stuttgart, 2007: pp. 16–20.
- Cloonan MV. *Early binding in paper a brief history of European hand-made paper-covered books with a multilingual glossary*. Boston: G K Hall; 1991.
- Pearson D. *Books as history: the importance of books beyond their texts*. London: The British Library; 2008.
- Diehl E. *Bookbinding, it's background and technique*. New York: Hacker Art Books; 1979.
- Dupont AL. *Gelatine sizing of paper and its impact on the degradation of cellulose during aging: a study using size-exclusion chromatography*, Van 't Hoff Institute for Molecular Sciences (HIMS), 2003, PhD thesis. <https://hdl.handle.net/11245/1.215260> Accessed 11 April 2024.
- Barrett T, Mosier C. The role of gelatin in paper permanence. *J Am Inst Conserv*. 1995;34:173–86. <https://doi.org/10.2307/3179538>.
- Barrett TD, *Early European papers/contemporary conservation papers: a report on research undertaken from fall 1984 through fall 1987*, The Pap. Conserv. Vol 13 1989.
- Miller J. *Books will speak plain: a handbook for identifying and describing historical bindings*. Ann Arbor: Legacy Press; 2010.
- Albertin F, Balliana E, Pizzol G, Colavizza G, Zendri E, Raines D. Printing materials and technologies in the 15th–17th century book production: an undervalued research field. *Microchem J*. 2018;138:147–53. <https://doi.org/10.1016/j.microc.2017.12.010>.
- Carmencho A. Old Italian paper covers. *New Bookbind J Des Bookbind*. 2011;31:37–44.
- Pugliese S. When cover paper meets parchment: a non-adhesive variation of the limp parchment binding. *J Pap Conserv*. 2019;20:152–7. <https://doi.org/10.1080/18680860.2019.1746118>.
- Delbey T, Holck JP, Jørgensen B, Alvis A, Smith VH, Kavich GM, Harmon KA, Dorch BF, Rasmussen KL. Poisonous books: analyses of four sixteenth and seventeenth century book bindings covered with arsenic rich green paint. *Herit Sci*. 2019;7:91. <https://doi.org/10.1186/s40494-019-0334-2>.
- Poison Book Project, (n.d.). <https://sites.udel.edu/poisonbookproject/>. Accessed 11 April 2024.
- Benvestito C, Pugliese S. Detached bindings, forgotten bindings? The Aldine in the new database of the conservation interventions (in Italian: Legature staccate, legature dimenticate? Le aldine nella nuova banca dati degli interventi di restauro), in: Tiziana Plebani (Ed.), *Aldine Marciane, Biblioteca Nazionale Marciana, Venezia, 2015: pp. 41–44*. <https://biblioteca.nazionalemarciana.cultura.gov.it/sites/default/files/785-Aldine-Marciane-2015-web-B.pdf>. Accessed April 11 2024.
- Panda SS, Singh N, Singh MR. Development, characterization of traditional inks for restoration of ancient manuscripts and application on various substrates to understand stability. *Vib Spectrosc*. 2021;114: 103232. <https://doi.org/10.1016/j.vibspec.2021.103232>.
- Missori M. Optical spectroscopy of ancient paper and textiles. *NUOVO Cim*. 2016;39C:293–303. <https://doi.org/10.1393/ncc/12016-16293-x>.
- Deschl M, Hiller G, Franz W. Book three of color management. Color measurement – the CIE 1931 system, *Datacolor AG Eur. Rotkreuz*. 3 (2019) 1–16. <https://www.datacolor.com/wp-content/uploads/2022/06/color-management-ebook-3-en.pdf>. Accessed 11 April 2024.
- Barrett T, Ormsby M, Lang JB. Non-destructive analysis of 14th–19th century European handmade papers. *Restaur Int J Preserv Libr Arch Mater*. 2016;37:93–135. <https://doi.org/10.1515/res-2015-0017>.
- R Foundation, The R Project for statistical computing, (n.d.). <https://www.r-project.org>. Accessed 25 Sep 2023.
- Favaro B, Balliana E, Rigoni F, Zendri E. A preliminary evaluation of chemical interaction between sanitizing products and silk. *J Cult Herit*. 2021;51:1–13. <https://doi.org/10.1016/j.culher.2021.06.012>.
- Keheyani Y. PY/GC/MS analyses of historical papers. *Bio Res*. 3 (2008) 829–837. <https://doi.org/10.15376/biores.3.3.829-837>.
- Ortiz-Herrero L, Blanco ME, García-Ruiz C, Bartolomé L. Direct and indirect approaches based on paper analysis by Py-GC/MS for estimating the age of documents. *J Anal Appl Pyrolysis*. 2018;131:9–16. <https://doi.org/10.1016/J.JAAP.2018.02.018>.

40. Wang S, Guo X, Liang T, Zhou Y, Luo Z. Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies. *Biores Technol.* 2012;104:722–8. <https://doi.org/10.1016/j.biortech.2011.10.078>.
41. Lu Q, Yang X, Dong C, Zhang Z, Zhang X, Zhu X. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: Analytical Py-GC/MS study. *J Anal Appl Pyrolysis.* 2011;92:430–8. <https://doi.org/10.1016/j.jaap.2011.08.006>.
42. Van Keulen H, Schilling M. AMDIS & EXCEL: a powerful combination for evaluating THM-Py-GC/MS results from European lacquers. *Stud Conserv.* 2019;64(sup1):S64–80. <https://doi.org/10.1080/00393630.2019.1594580>.
43. Barrett T. Enzymatic pretreatment during 15th to 18th century papermaking in Europe. *BioResources.* 2016;11:2964–7. <https://doi.org/10.15376/biores.11.2.2964-2967>.
44. Garside P, Wyeth P. Identification of cellulosic fibres by FTIR spectroscopy—thread and single fibre analysis by attenuated total reflectance. *Stud Conserv.* 2003;48:269–75. <https://doi.org/10.1179/SIC.2003.48.4.269>.
45. Rouchon V, Pellizzi E, Janssens K. FTIR techniques applied to the detection of gelatine in paper artifacts: from macroscopic to microscopic approach. *Appl Phys A.* 2010;100:663–9. <https://doi.org/10.1007/s00339-010-5649-5>.
46. Gorassini A, Calvini P, Baldin A, Fourier transform infrared spectroscopy (FTIR) analysis of historic paper documents as a preliminary step for chemometrical analysis, in: CMA4CH 2008 multivariate analysis and chemometry applied to environmental and cultural heritage, Ventotene Island (Italy, 1–3 June 2008). <http://www.cma4ch.org/08/abstracts/A-Gorassini-Orad3cv7zcv9ref.pdf> Accessed in 11 April 2024.
47. Missori M, Righini M, Dupont AL. Gelatine sizing and discoloration: a comparative study of optical spectra obtained from ancient and artificially aged modern papers. *Opt Commun.* 2006;263:289–94. <https://doi.org/10.1016/j.optcom.2006.02.004>.
48. Stephens CH, Barrett T, Whitmore PM, Wade JA, Mazurek J, Schilling M. Composition and condition of naturally aged papers. *J Am Inst Conserv.* 2008;47:201–15. <https://doi.org/10.1179/019713608804539583>.
49. Zhao C, Jiang E, Chen A. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *J Energy Inst.* 2017;90:902–13. <https://doi.org/10.1016/j.joel.2016.08.004>.
50. Shen DK, Gu S. The mechanism for thermal decomposition of cellulose and its main products. *Biores Technol.* 2009;100:6496–504. <https://doi.org/10.1016/j.biortech.2009.06.095>.
51. Lourenço A, Gominho J, Pereira H, Lourenço A, Gominho J, Pereira H, Chemical characterization of lignocellulosic materials by analytical pyrolysis, in: *Anal. Pyrolysis Chap.2*, Ed. Kusch P. (2018) 1–22. <https://doi.org/10.5772/INTECHOPEN.80556>.
52. Lucejko JJ, Tamburini D, Modugno F, Ribechini E, Colombini MP. Analytical pyrolysis and mass spectrometry to characterise lignin in archaeological wood. *Appl Sci.* 2020;11:240. <https://doi.org/10.3390/APP11010240>.
53. Mullen CA, Boateng AA. Catalytic pyrolysis-GC/MS of lignin from several sources. *Fuel Process Technol.* 2010;91:1446–58. <https://doi.org/10.1016/j.fuproc.2010.05.022>.
54. Liu M, Thygesen A, Summerscales J, Meyer AS. Targeted pre-treatment of hemp bast fibres for optimal performance in biocomposite materials: a review. *Ind Crops Prod.* 2017;108:660–83. <https://doi.org/10.1016/j.indcrop.2017.07.027>.
55. Korenberg C. The effect of ultraviolet-filtered light on the mechanical strength of fabrics. *Br Museum Tech Res Bull.* 1 (2007) 23–27. <https://www.researchgate.net/publication/312952564>. Accessed 29 April 2024.
56. Dehabadi L, Karoyo AH, Soleimani M, Alabi WO, Simonson CJ, Wilson LD. Flax biomass conversion via controlled oxidation: facile tuning of physicochemical properties. *Bioeng.* 2020;7:38–56. <https://doi.org/10.3390/BIOENGINEERING7020038>.
57. Schellmann NC. Animal glues: a review of their key properties relevant to conservation. *Stud Conserv.* 2007;52:55–66. <https://doi.org/10.1179/SIC.2007.52.SUPPLEMENT-1.55>.
58. Ntasi G, Sbriglia S, Pitocchi R, Vinciguerra R, Melchiorre C, Dello Iorio L, Fatigati G, Crisci E, Bonaduce I, Carpentieri A, Marino G, Birolo L. Proteomic characterization of collagen-based animal glues for restoration. *J Proteome Res.* 2022;21:2173–84. <https://doi.org/10.1021/acs.jproteome.2c00232>.
59. Mikhailov OV. Molecular structure design and soft template synthesis of aza-, oxaza- and thiazamacrocyclic metal chelates in the gelatin matrix. *Arab J Chem.* 2017;10:47–67. <https://doi.org/10.1016/J.ARABJC.2016.10.014>.
60. Namdar D, Neumann R, Sladetzki Y, Haddad N, Weiner S. Alkane composition variations between darker and lighter colored comb beeswax. *Apidologie.* 2007;2007(38):453–61. <https://doi.org/10.1051/APIDO:2007033>.
61. Waś E, Szczesna T, Rybak-Chmielewska H. Hydrocarbon composition of beeswax (*Apis Mellifera*) collected from light and dark coloured combs. *J Apic Sci.* 2014;58:99–106. <https://doi.org/10.2478/JAS-2014-0026>.
62. Waś E, Szczesna T, Rybak-Chmielewska H. Determination of beeswax hydrocarbons by gas chromatography with a mass detector (GC-MS) technique. *J Apic Sci.* 2014;58:145–57. <https://doi.org/10.2478/JAS-2014-0015>.
63. Clark AJ, Calvillo JL, Roosa MS, Green DB, Ganske JA. Degradation product emission from historic and modern books by headspace SPME/GC-MS: evaluation of lipid oxidation and cellulose hydrolysis. *Anal Bioanal Chem.* 2011;399:3589–600. <https://doi.org/10.1007/S00216-011-4680-5>.
64. Gibson LT, Ewlad-Ahmed A, Knight B, Horie V, Mitchell G, Robertson CJ. Measurement of volatile organic compounds emitted in libraries and archives: an inferential indicator of paper decay? *Chem Cent J.* 2012;6:1–22. <https://doi.org/10.1186/1752-153X-6-42/FIGURES/17>.
65. Gaspar EM, Santana JC, Lopes JF, Diniz MB. Volatile organic compounds in paper—an approach for identification of markers in aged books. *Anal Bioanal Chem.* 2010;397:369–80. <https://doi.org/10.1007/S00216-010-3520-3>.
66. Strlič M, Thomas J, Trafela T, Csefalvayová L, Cigić IK, Kolar J, Casar M. Material degradomics: on the smell of old books. *Anal Chem.* 2009;81:8617–22. <https://doi.org/10.1021/AC9016049>.

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