INSIDE THE PARCHMENT

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ABSTRACT
Even though parchment has been applied as library and archive substrate for centuries, this material's structure and degradation patterns are less explored than paper's ones. In this preliminary work vibrational studies highlighting distinction between parchment components are presented. Advances in conservation methods can in fact be achieved by an improved knowledge of the microscopic and spectroscopic features of the parchment components.

Studies of the chemical interactions with the products used in manufacturing and writing will be presented. Standard glycine, proline and hydroxyproline FTIR spectra were compared to different kind of parchment and other collagen-based materials. Some samples were inked with different kind of inks (carbon black, iron-gall, carbon black mixed with iron II sulfate or iron-gall) other subjected to invasive treatments so as to simulate damages induced by catastrophes or by a recently developed restoring treatment. Spectral variations due to artificially induced modification of parchment were monitored and analyzed.

INTRODUCTION
Since antiquities parchment has been a widely applied writing support, actually the major one until the advent of paper, and still widespread even afterwards [13]. Differently from paper, however, no industrial of semi-industrial process for parchment production has ever been outlined: still nowadays parchment is only manufactured and, therefore, every specimen is unique. The lack of reproducibility is why research on parchment behavior at a structural level is still ongoing [4,13,15].

The aim of this work is providing insight about the main structural aspects of parchment and the most effective non-destructive techniques in its characterization, by means of spectroscopic analysis of several laboratory and some original samples. We also focused our study on the identification of historical inks and pigments.

The manufacturing of parchment follows different procedures depending on the geographical area and historical period. The commonly intended meaning of the word "parchment" is related to the Western procedure carried out since Middle Age with extensive use of calcium hydroxide.

On the other hand, different ways to treat skin, including the use of tannin and alum, led to what is today the support of many worthy documents. According to Ryder [15] the Jewish tradition is unique in finishing the parchment with vegetable tannin and oil: of course, tannin was applied in amounts much smaller than the ones needed in leather tanning.

From the chemical point of view, parchment major component is collagen: this protein is constituted mainly of three amino acids (~33% glycine, 20-30% of proline and

hydroxyproline). Collagen basic unit is a triple-helix: helices are arranged in fibrils and, at an upper hierarchical level, fibrils are arranged into the final collagen fibers.

Internal and external factors -chemical, physical and biological- contribute to parchment deterioration, causing an appearance very stiff, brittle, undulated and darkened or, on the contrary, relaxed or gelatinized [5,6,10].

MATERIALS AND METHODS

- Glycine, L-proline and trans-4-hydroxy-L-proline standards from Aldrich were used to characterize single major aminoacidic components of collagen.
- Modern parchment were immersed in hydrochloric acid 6M solution for 40 minutes, quickly rinsed in water, then left soaking in deionized water for 24 hours. They were then treated -on the hair side- with a tannic acid aqueous solution at two concentrations, 2 and 10 g/l. The samples were let to dry under tension at room temperature and used in order to obtain spectroscopic information on parchment degradation after partial removal of $CaCO_3$. Other samples were partially burned and other subjected to a restoring treatment [11].
- One fragment of ancient Jewish ritual parchment and four fragments of contemporary ones, courtesy of Rav Amedeo Spagnoletto, were measured. The samples were used to investigate the spectral behavior of original degraded and modern parchment manufactured according to the Jewish tradition.
- Laboratory samples were inked with carbon black, iron-gall ink, carbon black mixed with iron II sulfate or iron-gall ink, for a complete spectroscopic characterization of the graphic medium. The inks were prepared in laboratory according to ancient recipes.
- A Medieval ink (in MS Piana 3.207 - Biblioteca Malatestiana di Cesena) and an Arabic one (in a 16^{th} century fragment) were analyzed for comparison with the laboratory inks.

Amino acids powders were dispersed in KBr pellets and FTIR transmission measurements were performed with a Nexus Nicolet interferometer, equipped with KBr beam splitter and DTGS KBr detector. The system was operated in dry air, in the 4000-450 cm^{-1} range with a resolution of 4 cm^{-1} averaging 200 acquisitions on each sample. Parchments were measured by means of ATR-FTIR. To such an extent, the above-mentioned instrument was extended with a ZnSe cell and a liquid nitrogen cooled MCT/A detector. Measurements were performed in the 4000-650 cm^{-1} range with a resolution of 8 cm^{-1}, averaging 400 acquisitions on each sample.

Transmittance and reflectance spectra were converted into optical densities and peak centers and amplitudes were computed as overlapped Lorentzian curves.

A Renishaw In-Via Reflex Raman microscope equipped with a Renishaw diode LASER at 785 nm (output power 300 mW) was used. The LASER power on the sample was kept at about 7 mW. The backscattered light was dispersed by a 1200 lines/mm grating and the Raman signal was detected by a Peltier cooled (-70° C) deep depletion CCD (576x384 pixel). Spectral acquisitions (5 accumulations, 50 s each for ink analysis and 3 accumulations, 300 s each for the parchments) were performed with a 50X objective. Spectra were elaborated with background subtraction for a better visualization.

XRF spectra were recorded by means of an Assing Lithos 3000 portable spectrometer, equipped with a Mo X-ray tube. In this experiment a 2 mm collimator was used together with

a Zr filter. Measurements were performed with the tube operating at 25 kV, 0.300 mA, in the 0-25 keV range, and a resolution of 160 eV at 5.9 keV.

RESULTS AND DISCUSSIONS

Parchment Analysis

FTIR analysis of the amino acids was in agreement to several available literature and acknowledged data [8,16]. On the other hand, when comparing the parchment fiber spectra to literature [3] on collagen and to samples obtained from different kinds of animal tissue (see Table 1), some discrepancies were observed, confirming that slightly different amino acids arrangements can be found, depending on the collagen origin.

In particular parchment peaks at about 1028, 1080 and 1165 cm^{-1} are not reported and assigned elsewhere. The peak at 1028 cm^{-1} is common to all considered amino acids and it is interpretable as C-N stretching. Peaks at about 1080 cm^{-1} are found in L-proline, trans-4-hydroxy-proline and gelatine [12]: it can be interpreted as a C-O stretching or skeletal stretching [12]. Eventually, the peak at 1165 cm^{-1} is only found in L-proline and probably belongs to the range of the NH_3^+ residual modes [14].

Modern parchment		Bone tissue		Collagen from literature		Peaks assignments
peak center	σ	peak center	σ	peak center	peak center	
1028	13					Found in glycine, proline and hydroxyproline, probable stretching CN [14,16]
		1034	48			
1080	18					Found in proline, hydroxyproline [16]
		1104	35			
1165	26					Found in proline [16]
1239	32				1235	bending NH [12]
		1251	11			
		1333	6			wagging CH_2 [14]
1340	40					
		1408	26			
1432	45					bending CH_2 [8]
				1445		
		1456	37		1457	(amide III) bending CH_2 [12]
1532	44	1531	56	1535		Amide II coil [8]
					1542	coupl. bending NH stretching CN [12]
				1555		Amide II, elicoid [8]
				1570		COO [8]
				1630		Amide I, coil [8]
					1650	Amide I coupl. To stretch C=O e COO- [12]
1659	40	1656	41	1660		Amide I, elicoid [8]
				1675		C=O [8]

Table 1: Parchment and collagen from other sources: peaks in the 1000-1500 cm^{-1} region

To the extent of our research -that included non-destructive ATR-FTIR and Raman measurements and comparison to original parchment samples, achieved with different procedures- a critical issue has been the removal of $CaCO_3$ from laboratory samples.

This had to be accomplished for two major reasons: firstly, the $CaCO_3$ present on surface affects the ATR-FTIR spectra, that are taken with a low (a few micrometers) penetration inside the sample, preventing recognition of parchment peaks; moreover, some of the original samples had not been treated with lime. Parchment surfaces spectra before and after $CaCO_3$ removal are shown in Figure 1.

The tannic acid treatment on the hair side is visible in IR at both concentrations (Figure 2), even though the effect is more neat with the higher one: in particular, the typical peaks [7] at about 1710, 1327 and 1205 cm^{-1} are well distinguishable from the parchment spectra. While

the peak at 1710 cm^{-1} persists in the tannate residuals, the other two peaks can vanish when the tannic acid form complexes [7].

The tannic acid treatment is detected by Raman spectroscopy (Figure 3) only at the higher used concentration (10 g/l).

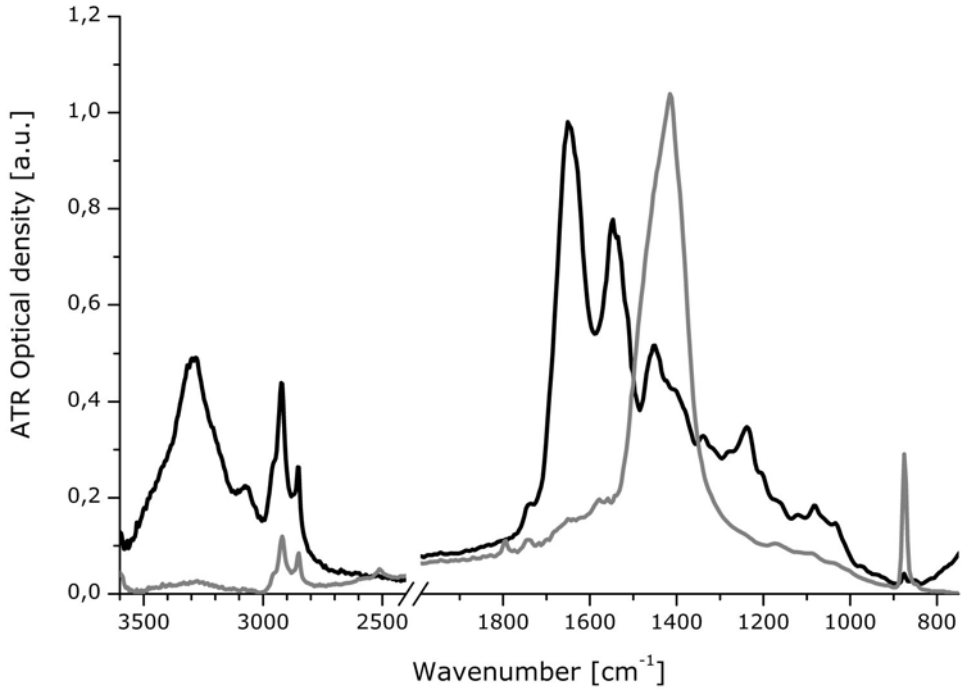

Figure 1: ATR/FTIR spectra of parchment samples prepared in laboratory. Untreated (grey) and after removal of $CaCO_3$ (black)

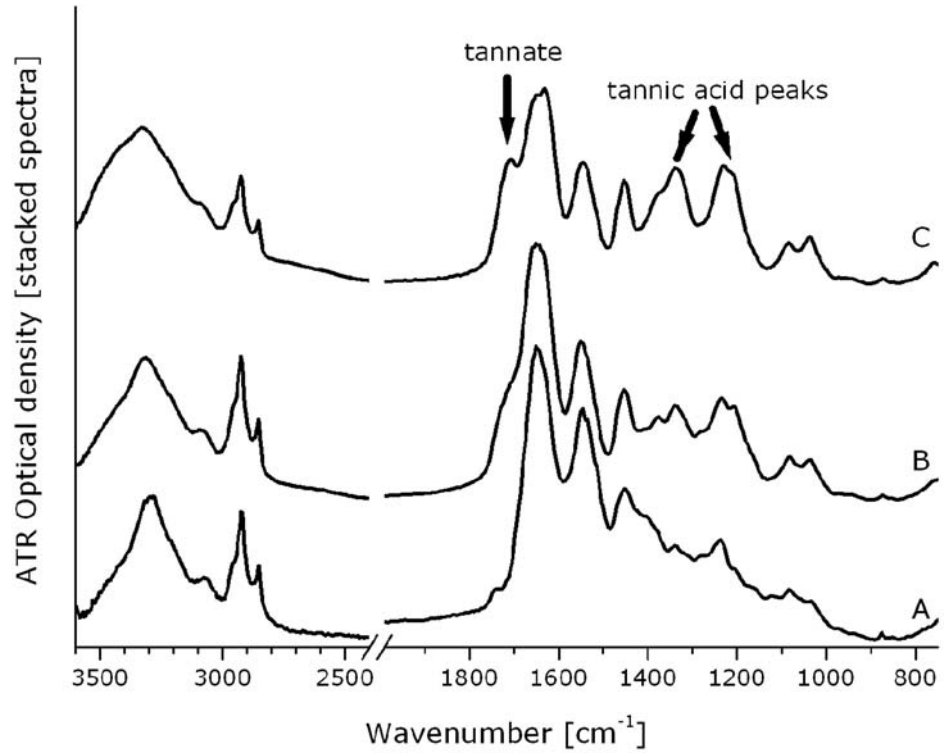

Figure 2: ATR/FTIR spectra of parchment samples -hair sides- after removal of $CaCO_3$ (spectrum A), after removal of $CaCO_3$ and addition of tannic acid 2 g/l (spectrum B), after removal of $CaCO_3$ and addition of tannic acid 10 g/l (spectrum C).

The treatment induces modification in the 1640 and 1668 cm^{-1} parchment broad band with formation of a shoulder at 1610 cm^{-1}, that matches one of the tannic acid band (attributable to aromatic C=C) and a broadening at higher wavenumbers, in correspondence with the 1710 cm^{-1} tannin acid peak (attributable to C=O and COO groups).

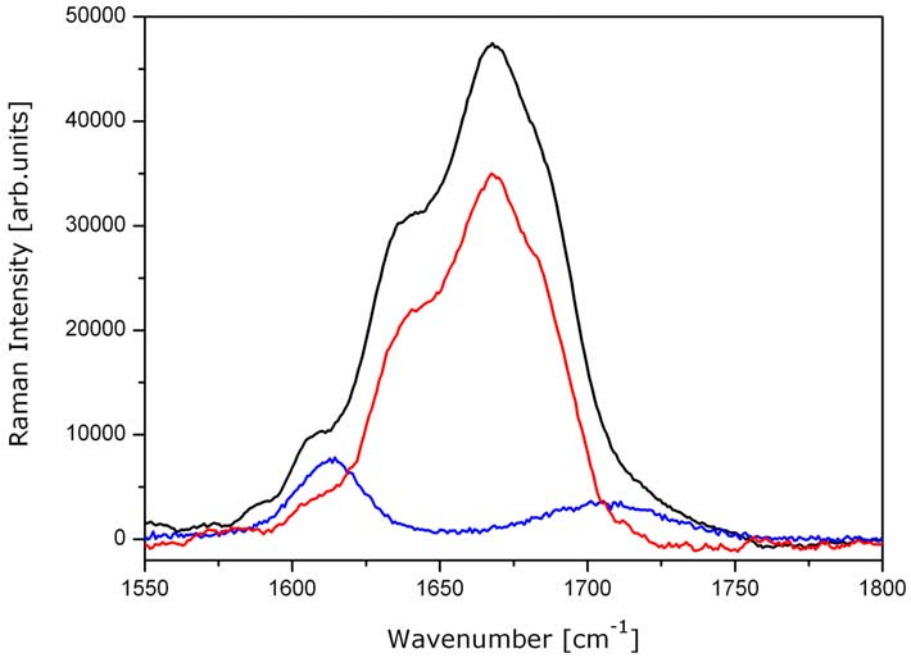

Figure 3: Raman spectra of parchment samples -hair sides- after removal of $CaCO_3$ (red line), after removal of $CaCO_3$ and addition of tannic acid 10 g/l (black line) compared to tannic acid (blue line).

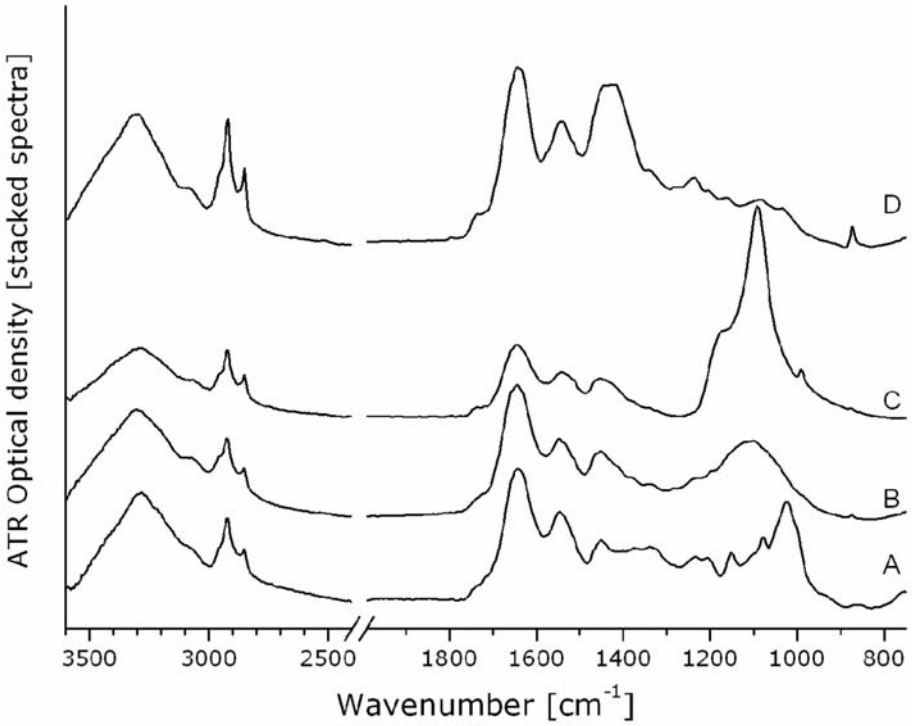

Figure 4: ATR/FTIR spectra of ancient Jewish ritual parchment (A) and contemporary Jewish ritual parchment: treated with gallnuts and alum (B and C), with gallnuts and lime (D). Spectra are stacked.

IR spectra of original samples are reported in Figure 4. Modifications in spectral features could be ascribed to different manufacturing and/or degradation. An extensive analysis for band attribution is in progress.

Ink Analysis

Raman investigation allows for the identification of several different inks. Spectra on laboratory samples are plotted in Figure 5. Carbon black ink is characterized by the typical bands at 1334 and 1588 cm^{-1}; iron-gall ink by the peaks at about 1472 and 572 cm^{-1} and iron sulfate by the peak at 1454 cm^{-1}. The difference in wavenumber lead to a clear identification of the two iron based compounds and is important to select specific conservation methods. Iron sulfate, in fact, was sometimes added to carbon black in order to obtain a particular hue.

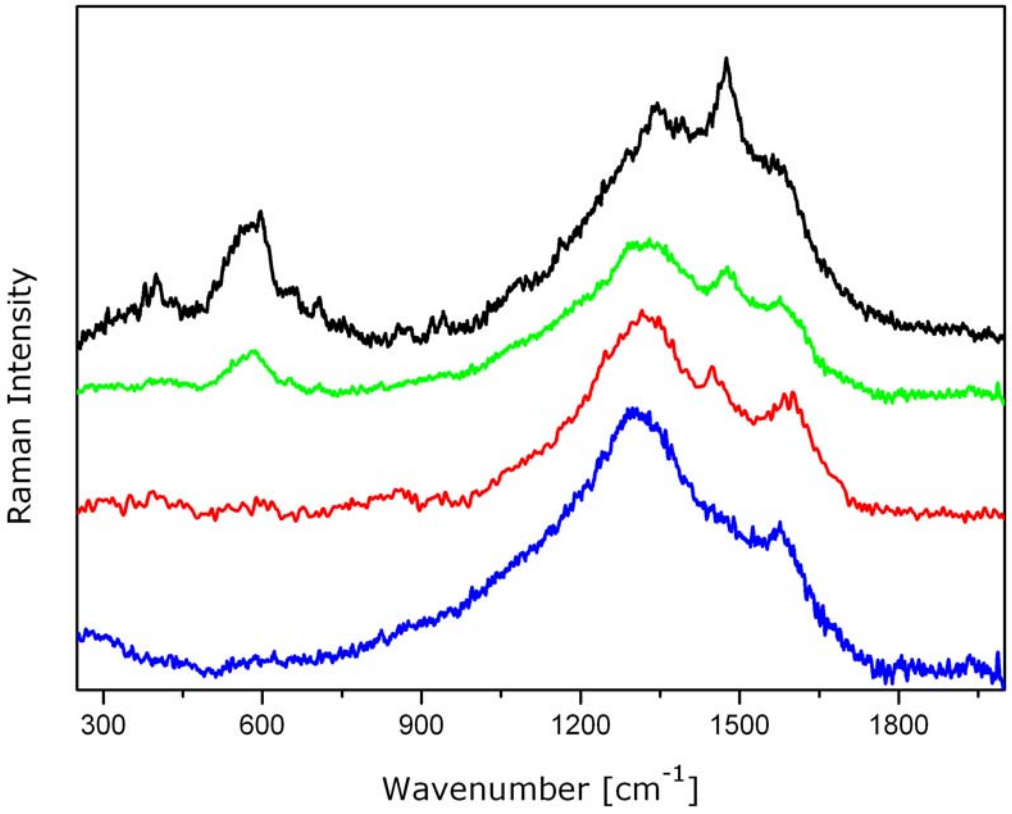

Figure 5: Raman spectra (stacked) of different inks on the laboratory samples. Carbon black (blue line); carbon black with iron II sulfate (red line); carbon black with iron-gall ink (green line); iron-gall ink (black line).

These spectra were compared to the ones obtained on medieval manuscript MS Piana 3.207 and on the 16th century Arabic fragment (Figure 6).

Micro-Raman measurements on the Medieval ink showed the presence of amorphous carbon (broad bands at 1334 and 1588 cm^{-1}) and two bands at 1472 and 572 cm^{-1}.

The peak at 1472 cm^{-1} is characteristic of the iron-gall ink [9], the other band is independent of the ink composition and is characteristic of an iron-organic substrate complex [2]. The broadening of the 572 cm^{-1} band could be related to the presence of other metallic salts.

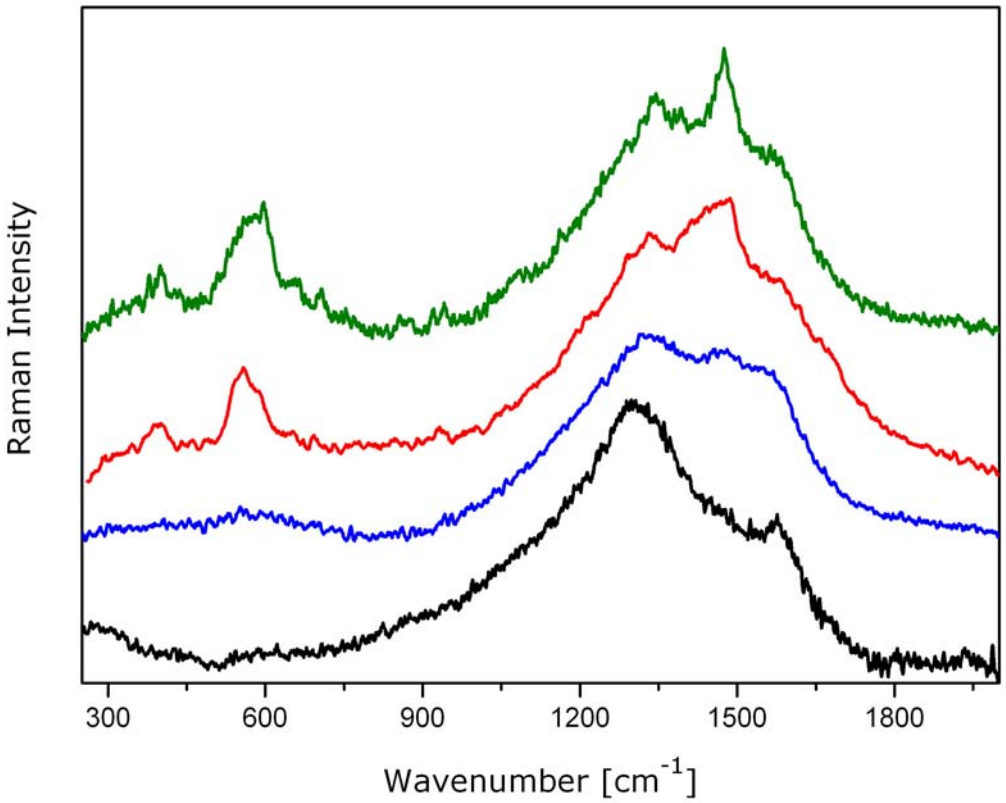

Figure 6: Raman spectra of original inks compared to standards. MS Piana 3.207 (blue line); Arabic ink (red line); carbon black (black line); iron-gall ink (green line).

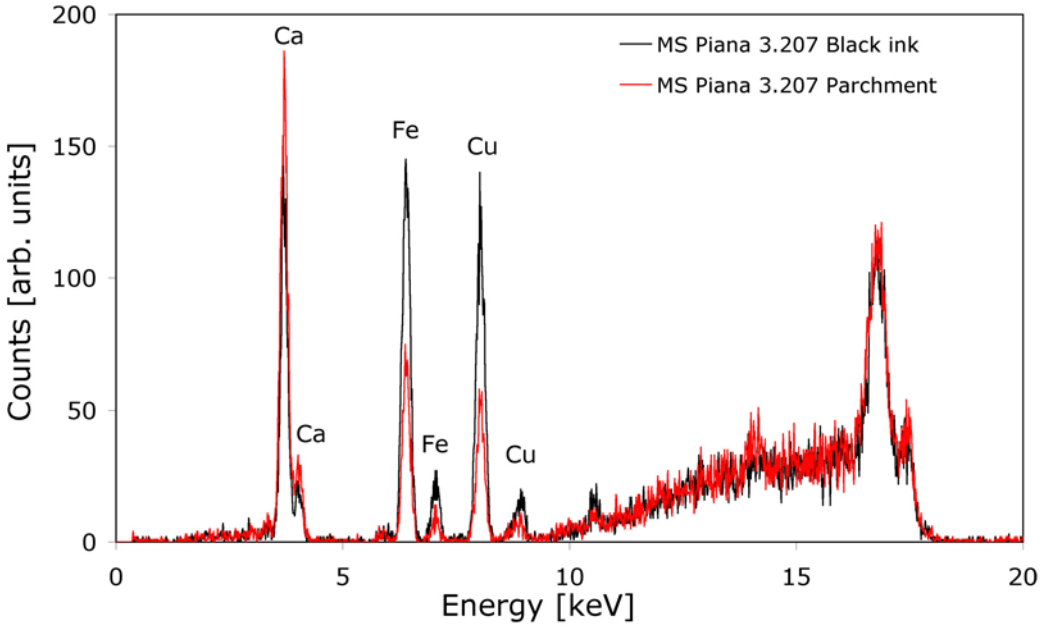

Figure 7: XRF spectra of MS Piana 3.207. Black line: ink; red line: parchment.

XRF analysis of the same sample (Figures 7) showed, in fact, an iron and copper content in the ink considerably higher than in the parchment, confirming the Raman hypothesis.

Raman measurements on the Arabic fragment clearly showed the presence of pure iron-gall ink, without addition of other salts or compounds. The attribution is confirmed by XRF

measurements (Figure 8). Mercury presence in XRF spectrum is due to the extensive use of cinnabar in the manuscript, that contaminates the whole fragment.

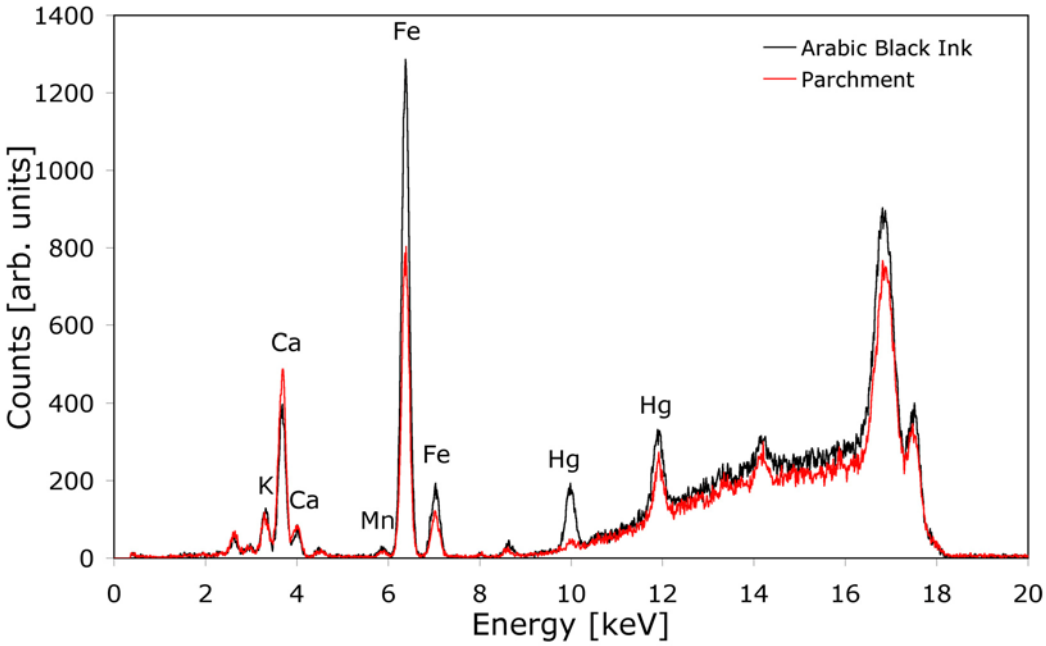

Figure 8: XRF spectra of an Arabic fragment. Black line: ink; red line: parchment.

Catastrophes and Restoring Procedures

FTIR spectra of samples artificially and partially burned then treated with water, in order to simulate the damages induced by fire and subsequent use of water as fire extinguisher, are reported in Figure 9-Left.

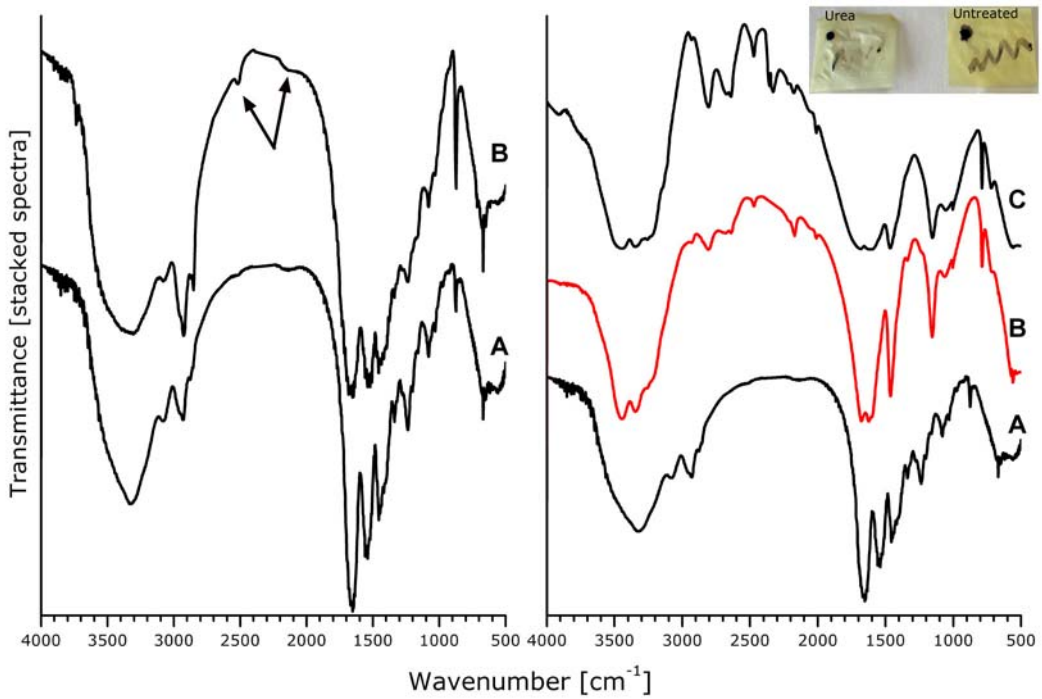

Figure 9. Left: FTIR spectra in KBr of an intact (A) and a burned (B) parchment. Right: FTIR spectra of parchment treated with urea (B) and reference materials, pure urea (C) and untreated parchment (A).

After burning, the parchment spectrum clearly shows the formation of oxidised functions (broad weak peak at 2150 cm^{-1}, triple C-C bond). The appearance of a peak at about 2515 cm^{-1} is compatible with the shift of NH_3^+ stretching when an acidic amino acid salt is formed [14]. Both effects could be expected in the event of fire damage. The fingerprint of the parchment remains substantially unaltered.

To test a restoring treatment recently developed by other researchers [11], some samples were immersed in an aqueous solution of urea (2%), NaCl (2%) and ethanol 48% for 30' then washed with 1:1 ethanol/water mixture. The treatment has been set up for the recovery of items with a huge extent of fire damage. We wanted to test whether the same products could be used as softening agents in the same way as PEG 200 [17,18] on stiff parchment.

For this reason we compared untreated and treated parchment and spectra are shown in Figure 9-Rigth together with a pure urea spectrum. It is evident that urea is strongly permanent on the substrate.

CONCLUSIONS

This work allowed us to set up a standard procedure in order to investigate parchments from different origin and differently treated.

The first methodological conclusion is that it is necessary to face the problem with a multidisciplinary approach that includes several and complementary techniques. Furthermore it is crucial to investigate, as a first step, standard samples prepared *ad hoc* to optimize measurements conditions to be extended to the original documents. Further development of this work foresees the application of the standardized methods to the artificially aged samples.

From the analytical point of view:

- IR spectroscopy enables to recognize the contribution of the most representative amino acids in collagen that is different depending on collagen source.
- A good identification of parchment treated on the surface with tannic acid at relative high concentration (> 2 g/l) is possible coupling Raman and IR spectroscopies.
- IR spectra obtained after removal of $CaCO_3$ are likely comparable to the ones recorded from degraded original documents [1].
- In order to choose correct conservation strategies and for a complete characterization of the graphic medium and to predict the life expectancy of the original documents, conclusions drawn from observations with the naked eye are likely to be as faulty as those drawn from limited diagnostics. The analyses on inks present in the literature are often based only on elemental techniques and not on molecular spectroscopies. XRF is only a semi-quantitative, penetrating technique that gives information essentially on higher atomic number elements. Protonic PIXE, another commonly used elemental technique, is not superficial, even though it allows the detection of lower atomic weight elements. These methods are unable to determine the real ink composition because of the lack of information about molecular formula and about carbon presence. Furthermore due to penetration of protons in the material, it is impossible to differentiate the surface composition from the bulk one. A molecular spectroscopy is indeed necessary for a correct interpretation of ink composition.
- Possible use of urea solutions in restoration of parchment needs further and deeper investigation.

The complex parchment and parchment-ink system needs further investigation and studies are in progress.

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