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Research Article

Characterization and Digital Restauration of XIV-XV Centuries Written Parchments by Means of Nondestructive Techniques: Three Case Studies

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Parchment is the primary writing medium of the majority of documents with cultural importance. Unfortunately, this material suffers of several mechanisms of degradation that affect its chemical-physical structure and the readability of text. Due to the unique and delicate character of these objects, the use of nondestructive techniques is mandatory. In this work, three partially degraded handwritten parchments dating back to the XIV-XV centuries were analyzed by means of X-ray fluorescence spectroscopy, μ-ATR Fourier transform infrared spectroscopy, and reflectance and UV-induced fluorescence spectroscopy. The elemental and molecular results provided the identification of the inks, pigments, and superficial treatments. In particular, all manuscripts have been written with iron gall inks, while the capital letters have been realized with cinnabar and azurite. Furthermore, multispectral UV fluorescence imaging and multispectral VIS-NIR imaging proved to be a good approach for the digital restoration of manuscripts that suffer from the loss of inked areas or from the presence of brown spotting. Indeed, using ultraviolet radiation and collecting the images at different spectral ranges is possible to enhance the readability of the text, while by illuminating with visible light and by collecting the images at longer wavelengths, the hiding effect of brown spots can be attenuated.

1. Introduction

Parchment was one of the most important writing supports used in the Middle Ages [1, 2]. Several kinds of animal skins were used (sheep, goat, and calf); the most precious skin was that obtained from the foetuses of lambs, named *charta-virginea*, due to its high white colour, thin thickness, and strength. The dermis, which is an intermediate layer of the skin constituted by fibrillar collagen, was the most used for obtaining parchments [3, 4].

In the manufacturing of the parchments, the removal of derma from vellum and the weakening of the epidermis involved mechanical and chemical practices in which vegetal infusions, dung, flour, lime, and sodium sulphide were used. Often, tanning procedures were required. The addition of sodium chloride permitted the conservation of the skin (salting process).

In the Mediterranean areas, gypsum powder was added to accelerate drying of parchments and to increase the absorption of ink. In some cases, the parchment surface was treated with egg white, fats, vegetal oils, tannin, and alum to obtain more stability of the support to the hygrometric variations and it was subjected to a smoothing process with pumice [1].

Regarding the written parchments, pigments or colorant mixed with vegetal gum (arabic gum, cherry tree gum, and tragacanth gum) or egg white or egg yolk was used to produce red and blue inks. Cinnabar or vermillion was used

for the red inks and azurite or lazurite (or ultramarine blue) for the blue ones [5].

The first black inks used were based on carbon pigments (charcoal, bone black, and vine black) mixed with thickening agents such as arabic gum, animal glue, egg white, honey, linseed oil, and olive oil. The conservation of these mixtures could be ensured by the addition of camphor, cloves, vinegar, and garlic juice. Although these inks were known to impart a deep black colour, they were also very sensitive to moisture and could easily be destroyed by contact with water [6]. Iron gall inks arose as an alternative to the carbon-based ones, and there is proof of several "homemade" recipes from the 5th century until around 18th century, when trade manufacturing started [7]. It is difficult to fix the exact date in which carbon inks were superseded by iron gall inks though it can be stated that the latter was the first choice for writing purpose by the end of the late Middle Ages. Evidently, the more fluid character that ensured permeability into parchments and the brilliance of the black colour have led to the gradual replacement of carbon with iron gall inks [7].

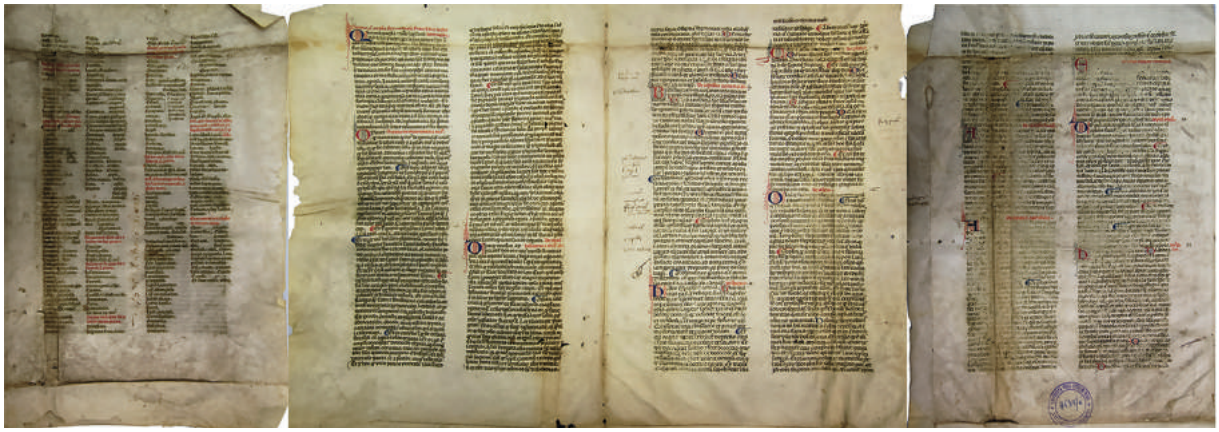
These inks were mainly obtained from the extraction of tannic and gallic acids from several kinds of galls (usually oak galls) by soaking and/or boiling them in water and wine with the addition of ferrous sulphate (known as vitriol or copperas) [6–11]. Addensants (arabic gum, egg white, tragacanth gum, etc.), fluidifiers (hydrochloric acid, sulphuric acid, etc.), and antifermentatives (vinegar) were usually added to bind the ink to the writing surface and to make it more stable, leading to a great brilliance and deep colour. The gallic acid reacts with the ferrous sulphate forming the ferrous gallate, which is colourless until the complete oxidation in air (ferric pyrogallate) [12]. The main benefit of the iron gall ink lies in its real difficulty in removal from the support, making this the ink of choice for writing official and important documents until the first years of the 20th century, when it was replaced by other types of inks with less corrosive properties. However, iron gall ink was made with a very wide variety of recipes and ingredients that varied with geographic areas and time period. Indeed, two inks can be chemically heterogeneous and suffer different degradation processes, even if they are produced following the same recipe. Iron gall ink corrosion is the result of two generally accepted mechanisms that interact and feed each other: acid hydrolysis and iron-catalyzed oxidation. According to Banik [13], the more destructive is the iron-catalyzed oxidation, which is strongly influenced by natural ageing, storage, temperature, and relative humidity. This process can be caused by an excess of iron in the ink and/or by the presence of other transition metals, such as copper or zinc (impurities in the vitriol or intentional addition) [14]. Research has shown that a stable ink can be obtained with a 1 : 3 ratio of iron to tannin [15]. Indeed, an excess of ferrous sulphate leads to a change of the ink's colour from black to brown due to chain reactions with oxygen and the formation of iron oxides, while the excess of tannin and a high level of humidity implicate the bleaching of the inks and the migration of sulphuric acid in the parchment. Furthermore, the permanence of iron gall ink depends on the manner in which they have been applied on the writing support [16]. For these reasons, documents written with iron gall ink frequently degrade to the point where it becomes challenging to read the text.

In the last 15 years, hyperspectral and multispectral imaging technique has been widely used for the imaging of fine art paintings [17, 20] and ancient documents, aiming at the analysis of the materials used [21, 22] and the digital restoration of degraded or erased parts [23]. Hyperspectral and multispectral imaging has been developed by combining both digital imaging and spectroscopy. These imaging techniques provide better image quality than may be obtained from a colour digital camera, revealing specific spectral ranges and/or infrared wavelengths that cannot be detected by the human eye. In case of erased inks on ancient manuscripts, UV fluorescence images can improve the readability of the text. This phenomenon is related to the presence of ink or its traces that attenuate the visible fluorescence of the support [23, 24]. In case of coloured spots covering the text, it is sometimes possible to select some spectral ranges in which they are transparent, enabling to stand out the ink. This means that spectral images may help palaeographers read old manuscripts by enhancing the contrast between the under- and overwriting texts or inks that have partially or completely disappeared.

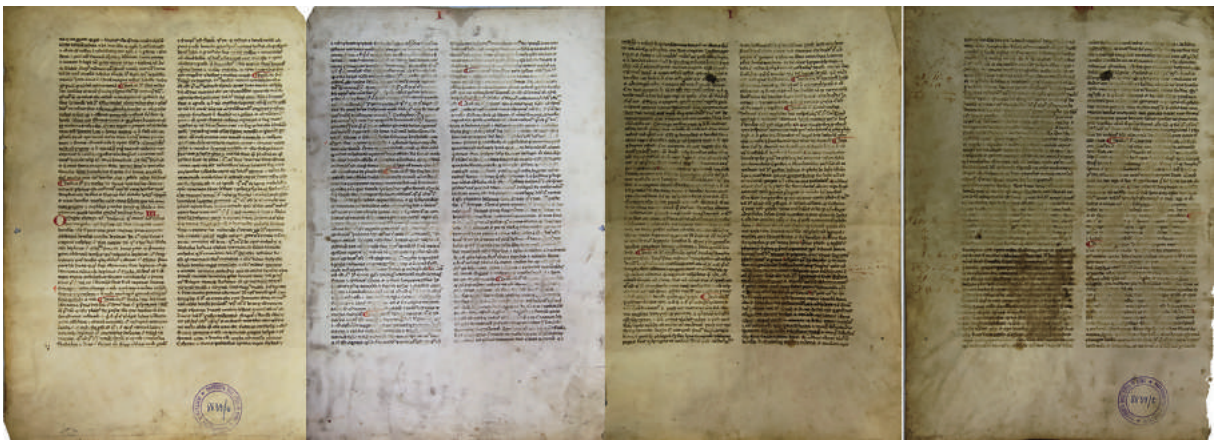
In this context, our goal is to use nondestructive techniques to characterize three written parchments dating back to the XIV-XV centuries: "Provvisorio 34 bis 8839/c" (XIV century), "Provvisorio 37 8839/o and 8839/t" (XIV century), and "Provvisorio 38" containing a fragment of "Filocolo" by Giovanni Boccaccio (XV century). The nondestructive techniques are energy dispersive X-ray fluorescence spectroscopy, μ-attenuated total reflectance Fourier transform infrared spectroscopy, and reflectance and UV-induced fluorescence spectroscopy. Furthermore, in order to perform a digital restoration of the texts, multispectral UV fluorescence imaging and VIS-NIR multispectral imaging were used.

2. Materials and Methods

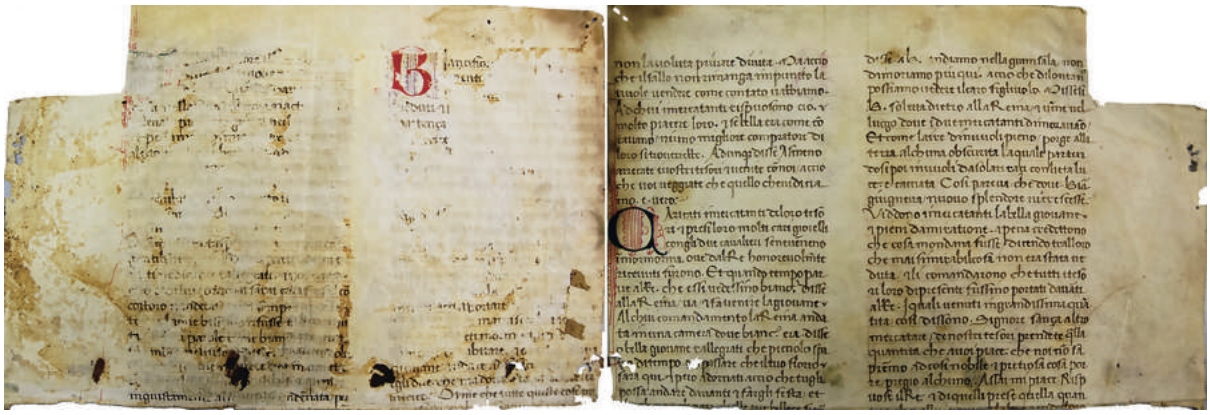
2.1. The Parchments. The three handwritten parchments belong to the collection of the Library of the Department of History, Cultures and Religions at University of Rome Sapienza (Figure 1): (i) The "Provvisorio 34 bis 8839/c" (labelled in this paper "Parch. 34"), dating back to the 14th century, is a two-sheet fragment written in Latin. The text is a medical treatise written with black/brown ink, with blue and red painted initials and red ink used for the rubrics (lat. rubrum, red). Red and blue flourished initials were added. The black ink has disappeared in some areas of the last folio. (ii) The "Provvisorio 37 8839/o and 8839/t" (labelled in this paper "Parch. 37"), dating back to the 14th century, is a two-sheet fragment written in Latin. The text is a commentary on Seneca's plays written by Nicholas Trevet with black/brown ink and red painted initials. Some written areas are covered by brown spots that do not allow the text to be read. (iii) The "Provvisorio 38" (labelled in this paper "Parch. 38"), dating back to the 15th century, is a one-sheet fragment written in



(a)



(b)



(c)

Figure 1: Images of the studied parchments: (a) Provvisorio 34 bis 8839/c ("Parch. 34"), (b) Provvisorio 37 8839/o and 8839/t" ("Parch. 37"), and (c) Provvisorio 38 ("Parch. 38").

Italian. It contains a fragment of "Filocolo" by Giovanni Boccaccio. The text is written with black/brown ink, and initials are painted in blue and red ink with red and violet flourished decorations, respectively. The black ink on the verso side appears extremely degraded.

2.2. Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF). The spectrometer consists of an X-ray tube (Amptek Mini-X) with an anode target of rhodium and a beryllium window of thickness 127 μm and was powered with an accelerating potential difference of 30 kV and an electronic current of 100 μA. The detector is a Peltier-cooled silicon drift with amplifier and integrated multichannel analyser (Amptek 123-SDD), providing for any detected X-ray photon a current pulse with amplitude proportional to the energy of the photon. The detector has a surface area of 25 mm^2, a thickness of 500 μm, and a beryllium window of thickness 12.5 μm. The energy resolution is 140 eV, full

width half maximum (FWHM) of the manganese Kα line at 5.9 keV. The geometry between primary beam, sample, and detector is fixed at 0°/45° relative to the normal of the sample surface. The X-ray beam collimation was 1 mm, and the acquisition time was 200 seconds.

2.3. Micro-Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (μ-ATR-FTIR). Analyses were performed with an FTIR spectrometer (Vertex 70v, Bruker Optik GmbH) coupled with an infrared microscope (Hyperion 2000, Bruker Optics GmbH) equipped with a standard single element midband photoconductive mercury-cadmium-telluride (MCT) detector cooled by liquid nitrogen, a 20x Cassegrain objective, and a Ge ATR crystal. Spectra were collected with a spectral resolution of 4 cm^{-1} in the range 4000–600 cm^{-1} using 256 scans.

2.4. Reflectance and UV-Induced Fluorescence Spectroscopy. Reflectance spectroscopy was performed with an Avantes AvaSpec spectrophotometer equipped with a halogen lamp (HL-2000 FHSA, Avantes). The spectrometer uses a diffraction grating of 300 lines/mm, blazed at 500 nm, which allows coverage of the spectral range from 300 nm to 1100 nm, and a CCD linear sensor (2048 pixels). The spectral resolution is 0.8 nm. We illuminated and collected the light at 90° with respect to the surface with a reflection probe constituted by 7 optical fibers, 200 μm core, 6 for illuminating and 1 for collecting the diffuse light (FCR-7UV200-2, Avantes). The reflectance spectra were collected from 350 to 800 nm. In some cases, the reflectance spectra were converted in absorbance following this formula: $A = \log(1/R)$.

Fluorescence spectroscopy was performed with an LED UV (emitting at 365 nm; High Power LED M365D1, Thorlabs) as excitation source and the previously described spectrometer. The surface was illuminated at 45° using a bifurcated fiber (diameter of 600 μm), connected to the source; the fluorescence emission from the surface was collected with a 200 μm diameter fiber at 90° with respect to the surface. The fluorescence spectra were collected over the wavelength range from 400 to 800 nm. Since the fluorescence emission on parchments presents different intensities due to the superficial inhomogeneities, the normalization of the spectra was performed to compare the spectral features of the investigated materials.

2.5. Multispectral Imaging. The multispectral imaging was performed with a monochromatic camera (QSI 583-w) equipped with a Leica optical system and eleven Thorlabs narrow-band interference filters (FWHM = 10 nm), with the central wavelengths at 380 nm, 390 nm, 400 nm, 410 nm, 420 nm, 450 nm, 470 nm, 500 nm, 550 nm, 600 nm, and 680 nm. All images were properly calibrated using dark and flat frames. For the visible imaging, two halogen lamps and two white LED lamps were used, while two UV lamps composed of three UV LEDs (High Power LED M365D1, Thorlabs), characterized by a spectral emission peaked at 365 nm with a FWHM of 10 nm and an optical output power of 190 mW for each LED were used for the UV fluorescence imaging. The sources were placed at 45° with respect to the normal samples, following the standard illumination geometry used for imaging. The multispectral UV fluorescence images were radiometrically calibrated; namely, all the images were corrected for the spectral sensitivity of the CCD camera, the spectral transmittance of the optical lens, and the filters [17]. Principal component analysis (PCA) was performed as chemometric tool for the analysis of multiple images [25–28]. The image calibration and processing were performed by using Matlab 2017a (the MathWorks Inc., USA) and HYPER-Tools (Free Graphical User Interface for Hyperspectral Image Analysis) software.

3. Results and Discussion

After the characterization of the parchments, the assessment of the inks is presented and discussed colour by colour. The results of EDXRF analysis are reported in Table 1.

3.1. The Parchments. The three parchments are characterized by the presence of calcium (Ca), sulphur (S), chlorine (Cl), iron (Fe), and potassium (K), as shown in Table 1. The occurrence of calcium is linked to the use of lime (CaO, $CaCO_3$, $Ca(OH)_2$) for the dehairing and the weakening of the skin and chalk ($CaSO_4$) to accelerate the drying and to raise the writability of the surface [1]. The presence of sulphur can be attributed to the use of chalk, as mentioned above, and/or sodium sulphide, added to accelerate the pretreatment procedure of the parchment. However, sulphur is also a constituent of the proteinaceous structures (i.e., cysteine). The chlorine content is probably related to the sodium chloride bath performed to avoid the putrefaction of the skins. Two of the parchments (Parch. 34 and Parch. 37) show the presence of silicon (Si), probably ascribed to the smoothing processes performed by means of pumices [1]. The other elements, among which iron, can be considered as contaminants. The ATR-FTIR spectrum of the "Parch. 34" is shown in Figure 2(a). Most of the general patterns of collagen are identified: the Amide A bands, the Amide B bands, and the Amide I, II, and III bands. The ATR-FTIR spectrum revealed that parchment support was gelatinized, as confirmed by the presence of a band at 1030 cm^{-1} due to C–O–C stretching of the saccharide structure of the gelatin [29, 30]. In this parchment are present also gypsum ($CaSO_4 \bullet 2H_2O$) with the absorption bands at 3523 cm^{-1}, 3394 cm^{-1}, 1113 cm^{-1}, 670 cm^{-1}, and 602 cm^{-1} and calcite ($CaCO_3$) with the absorption bands at 1796 cm^{-1}, 1414 cm^{-1} (partially overlapped by the collagen bands), and 874 cm^{-1} [31]. The presence of gypsum can be attributed to different sources: (a) it can be added during the treatment of the parchment [1], and (b) it can be formed from the reaction between the sulphates migrated from the ink to the ink-free parchment and the Ca ions [4, 6]. "Parch. 37" and "Parch. 38" show ATR-FTIR spectra similar to the one of the previous parchments; an example is reported in Figures 2(b)–2(d), respectively.

Table 1: EDXRF counts.

Sample	Si K	P K	S K	Cl K	K K	Ca K	Ti K	Cr K	Mn K	Fe K	Co K	Ni K	Cu K	Zn K	As K	Br L	Sr K	Ba L	Hg L	Pb L
34_parchment	36	66	1269	540	662	12298	121	142	129	1019	n.d.	177	170	289	n.d.	n.d.	n.d.	136	n.d.	380
37_parchment	39	73	344	n.d.	414	12965	131	n.d.	70	811	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	349	n.d.	n.d.	188
37_parchment	59	83	502	669	969	12271	93	n.d.	117	775	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	274	191	n.d.	n.d.
38_parchment	n.d.	n.d.	443	728	146	6323	117	n.d.	n.d.	325	n.d.	n.d.	100	n.d.	n.d.	n.d.	n.d.	202	n.d.	n.d.
34_black ink	42	112	2005	104	837	11098	141	112	547	4536	n.d.	n.d.	17026	7137	n.d.	n.d.	114	186	163	315
34_black ink	171	74	2203	119	1261	11947	184	61	514	4996	n.d.	105	14106	5880	n.d.	n.d.	124	94	n.d.	351
34_black ink	106	84	1921	n.d.	1828	16255	224	n.d.	258	8951	n.d.	164	376	535	n.d.	n.d.	135	n.d.	183	456
37_black ink	73	85	1449	483	1321	15769	140	n.d.	212	5974	n.d.	119	2705	1217	n.d.	n.d.	456	227	n.d.	170
37_black ink	84	122	1070	610	827	16269	154	n.d.	127	3232	n.d.	n.d.	1392	603	n.d.	n.d.	423	257	n.d.	113
37_black ink	63	92	1422	209	1130	11786	n.d.	n.d.	131	4741	n.d.	n.d.	2234	1074	n.d.	n.d.	319	327	n.d.	136
37_brown ink	64	71	1059	895	1377	11182	216	n.d.	159	3558	n.d.	n.d.	117	n.d.	n.d.	n.d.	215	n.d.	n.d.	n.d.
38_black ink	33	82	516	358	508	10380	215	n.d.	123	3167	n.d.	n.d.	1462	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
34_red ink	84	154	3119	208	356	5909	125	n.d.	126	1531	n.d.	n.d.	3863	1781	n.d.	n.d.	n.d.	170	41613	n.d.
34_red ink	86	300	6261	n.d.	n.d.	3626	262	96	n.d.	1091	295	n.d.	7110	n.d.	383	2199	n.d.	n.d.	228186	n.d.
37_red ink	128	285	4910	310	n.d.	9451	108	n.d.	n.d.	2447	181	71	1287	710	n.d.	n.d.	n.d.	170	60315	n.d.
37_red ink	95	229	5004	n.d.	7502	1231	n.d.	118	n.d.	1242	213	n.d.	651	161	n.d.	191	208	n.d.	108960	n.d.
38_red ink	111	388	7374	n.d.	n.d.	2601	n.d.	n.d.	n.d.	1119	214	n.d.	552	118	4647	302	n.d.	514	238820	n.d.
38_red ink	n.d.	101	1885	227	n.d.	7389	125	n.d.	n.d.	1097	n.d.	91	447	n.d.	591	n.d.	n.d.	200	41682	n.d.
34_blue ink	115	77	935	214	928	11490	258	150	100	1816	n.d.	129	16453	343	194	n.d.	115	199	412	451
34_blue ink	371	66	1643	n.d.	219	4513	460	n.d.	334	5328	160	306	320155	2869	3082	n.d.	103	779	19885	379
38_blue ink	95	92	2206	191	144	3149	1099	n.d.	300	4360	n.d.	n.d.	216958	620	n.d.	n.d.	91	2257	29917	n.d.
38_purple ink	37	45	647	302	201	10024	104	n.d.	n.d.	1417	n.d.	98	506	n.d.	921	n.d.	n.d.	288	2052	n.d.

n.d.: not detected.

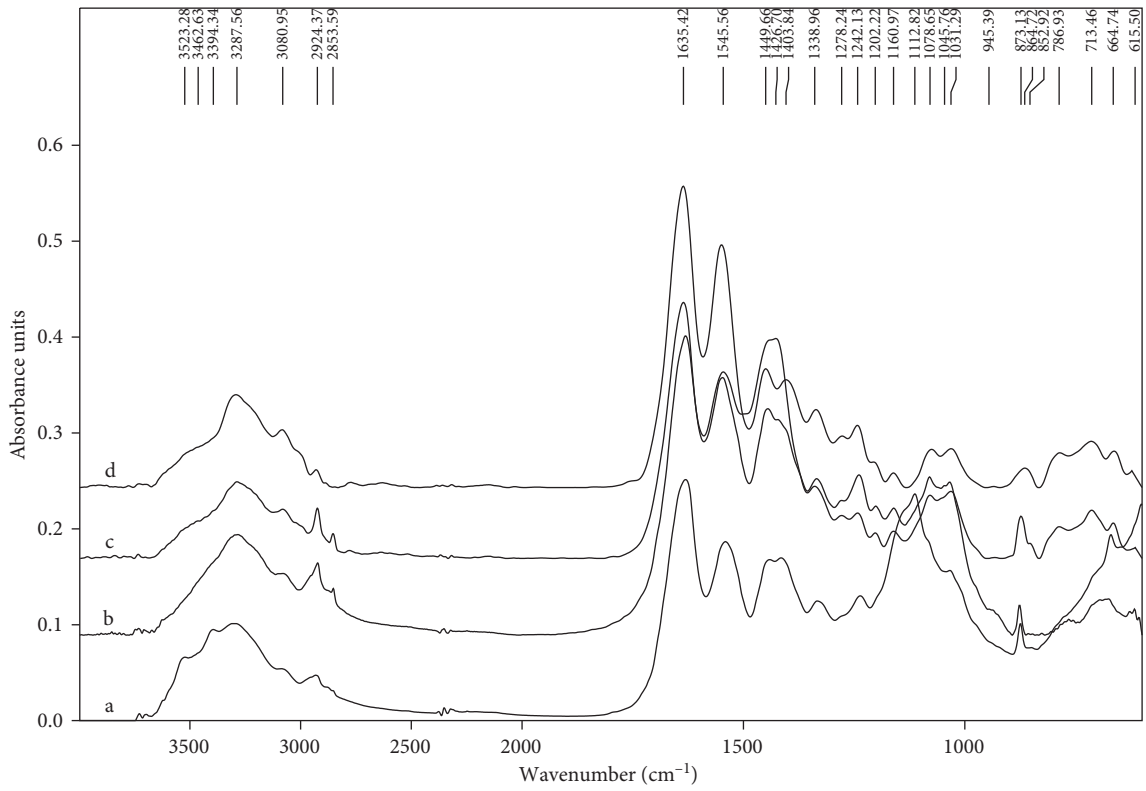


Figure 2: ATR-FTIR spectrum of parchments: (a) Parch. 34, (b) Parch. 37, and (c, d) two areas of Parch. 38.

Table 2: Assignment of the main ATR-FTIR bands of the three parchments.

Wavenumber (cm^{-1})			Band assignments
Parch. 34	Parch. 37	Parch. 38	
3523; 3394			Gypsum (νOH)
3294	3291	3291	Collagen (Amide A) [4]
3087	3076	3078	Collagen (Amide B) [4]
2932; 2854	2919; 2854	2924; 2854	Collagen (νC–H) [4]
1796			$\nu_1 + \nu_4$ combination band of $CO_3^{=}$ [31]
1631	1631	1642	Collagen (Amide I) [overlapping with δH–O–H (approx. 1610) of structural H_2O] [4]
1541	1548	1545	Collagen (Amide II)
1440	1430	1430	δCH_2 [4]
1415	1413	1413	δipC–O–H (carboxylic side chains), δNH_2 [4], ν_3 asymmetric of $CO_3^{=}$ [3, 31]
1333	1337	1323	$\omega CH_2/\delta$C–H (methine) [4]
1236	1240	1242	Amide III [3]
	1200	1200	νC–O–C and δC–H [3]
	1162	1162	NH_3 + residual modes [30]
1140 (sh)			ν_3 calcium sulphate [4]
1113			Gypsum (ν_3 $SO_4^{=}$) [4]
1080 (sh)	1081	1081	νC–O or skeletal ν [30]
1034	1034	1034	νC–N [30]or νC–O–C and νC–O [3]
874	874	874	ν_2 asymmetric of $CO_3^{=}$ [3, 25]
711 (sh)			ν_4 symmetric of $CO_3^{=}$
670		662	Gypsum (δ_{antis} $SO_4^{=}$)
602		602	Gypsum (ν_{4as} $SO_4^{=}$) [4]

ν = stretching; δ = bending; d = deformation; ip = in-plane; sh = shoulder.

The absence of a band at 1730 cm^{-1} suggests that tannins, historically employed in the surface treatment of the parchment, were not used [3]. All the band assignments are reported in Table 2.

3.2. The Inks

3.2.1. Black. The inks of Parch. 34 and Parch. 37 present similar elemental composition, characterized by zinc (Zn),

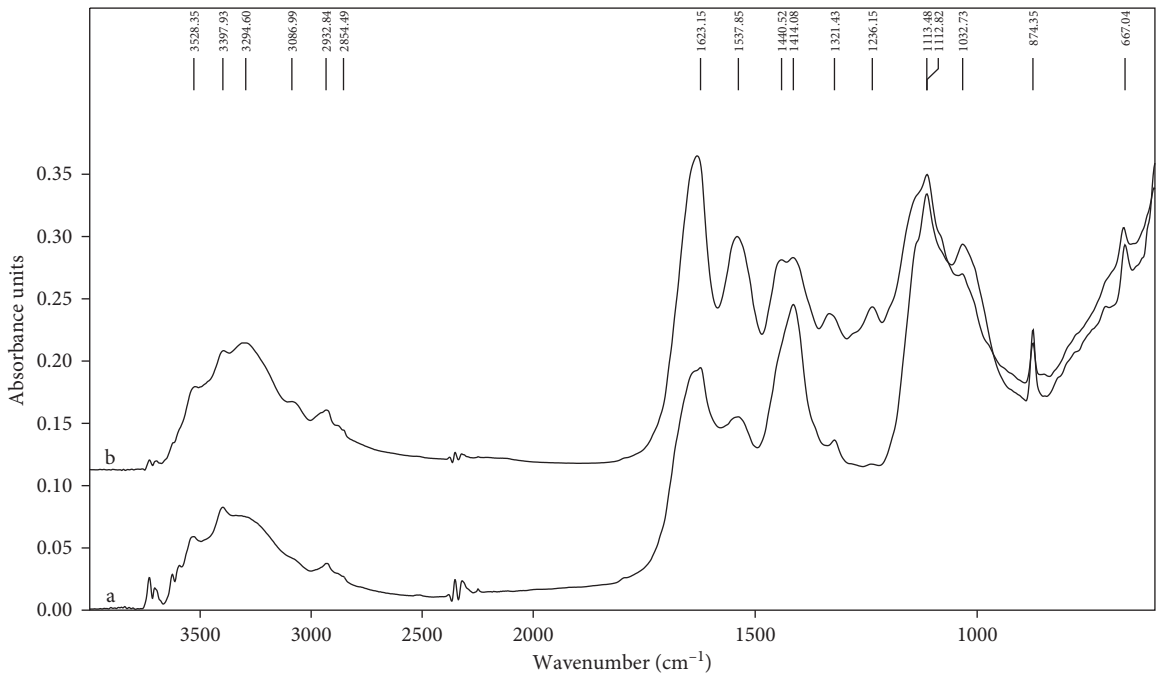


Figure 3: ATR-FTIR spectra of the inked area: (a) Parch. 34 and (b) related parchment.

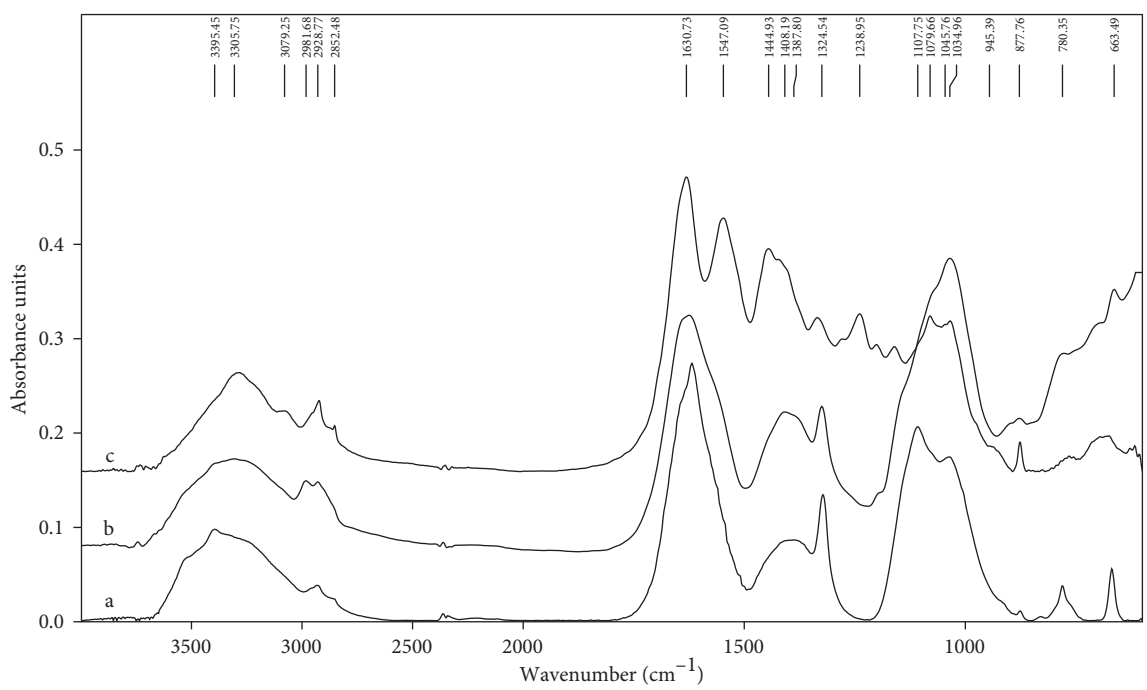


Figure 4: ATR-FTIR spectra of two black inked areas: (a, b) Parch. 37 and (c) related parchment.

iron (Fe), manganese (Mn), barium (Ba), and lead (Pb), as shown in Table 1, except for Parch. 34, in which higher counts of copper (Cu) occur, probably related to the intentional addition of copper sulphate in the manufacturing of the ink. The ink of Parch. 38 is characterized by copper (Cu) and iron (Fe). Zinc, barium, and lead were not detected. The presence of calcium (Ca) in all the inks could come from the support. The ATR-FTIR spectra of the inked areas on Parch. 34 are dominated by the parchment infrared bands, but we assisted at the increasing of the band at 1031 cm^{-1} indicating the presence of tannins [3, 4], as shown in Figure 3. Furthermore, gypsum and calcite were detected [3, 32]. For Parch. 37, the spectra of the black inked areas differ from the one of the parchments in the presence of the absorption bands of the oxalates (1620 cm^{-1}, 1316 cm^{-1}, and 780 cm^{-1}) [33] and gypsum, as shown in Figure 4. The presence of oxalates can suggest a biological attack due to fungal species that can reprecipitate secondary carbonates

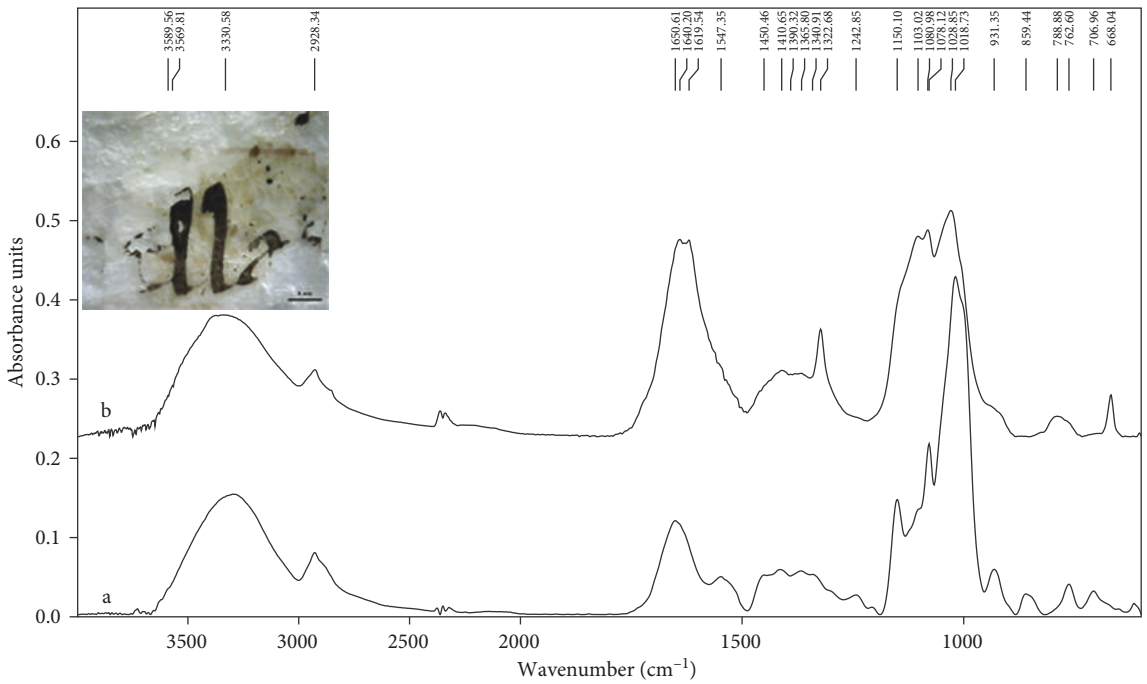


Figure 5: ATR-FTIR spectra of two black inked areas: (a, b) Parch. 38. The inset shows the yellowing effect due to a superficial treatment.

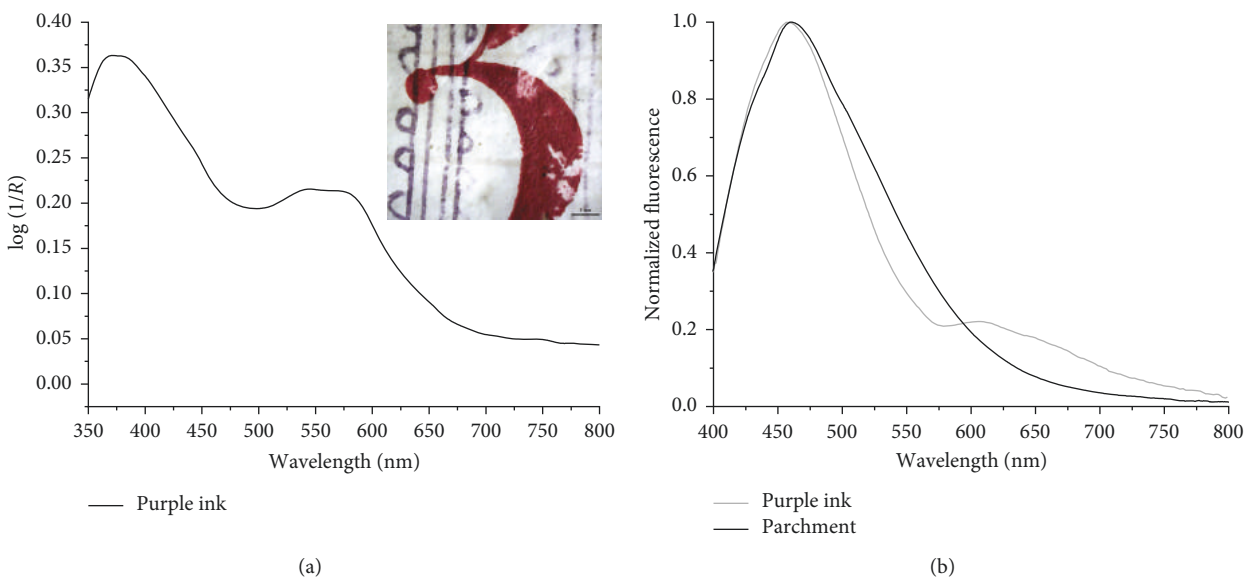


Figure 6: Reflectance spectrum in log (1/R) coordinates of the purple lines (shown in the inset, 150x magnification): (a) Parch. 38 and (b) fluorescence spectra of the purple ink and the related parchment.

and biomineralize hyphae with both calcite and whewellite [29]. Both the inked areas show a strong band at 1038 cm^{-1}, indicating the presence of gallic acid, and a shoulder at 1730 cm^{-1}, indicating the presence of gallic acid or tannins [3, 4]. Also, the ink of parchment 38 presents oxalates (1620 cm^{-1} and 1322 cm^{-1}) and gypsum (1109 cm^{-1} and 670 cm^{-1}), but we also detected starch (1150 cm^{-1}, 1081 cm^{-1}, and 1017 cm^{-1}), as shown in Figure 5. This substance could be added on the parchment in order to improve the writability of the surface [34], or it could be used as a restoration adhesive [1, 14, 35]. Indeed, as can be seen in Figure 5 (inset), an area of the parchment conserving the black ink shows a strong yellowing compared to the not-visible inked areas, suggesting a superficial treatment.

Moreover, images of all written parchments taken with the CCD camera equipped with a band-pass filter centered at 1000 nm reveal almost no contrast between the inks and the parchment (Figure S1 in Supplementary Materials). This spectral feature is typical of iron gall inks [26, 27]. Thus, from the results obtained by the multianalytical approach adopted in this study, it can be stated that the three parchments are written with iron gall inks.

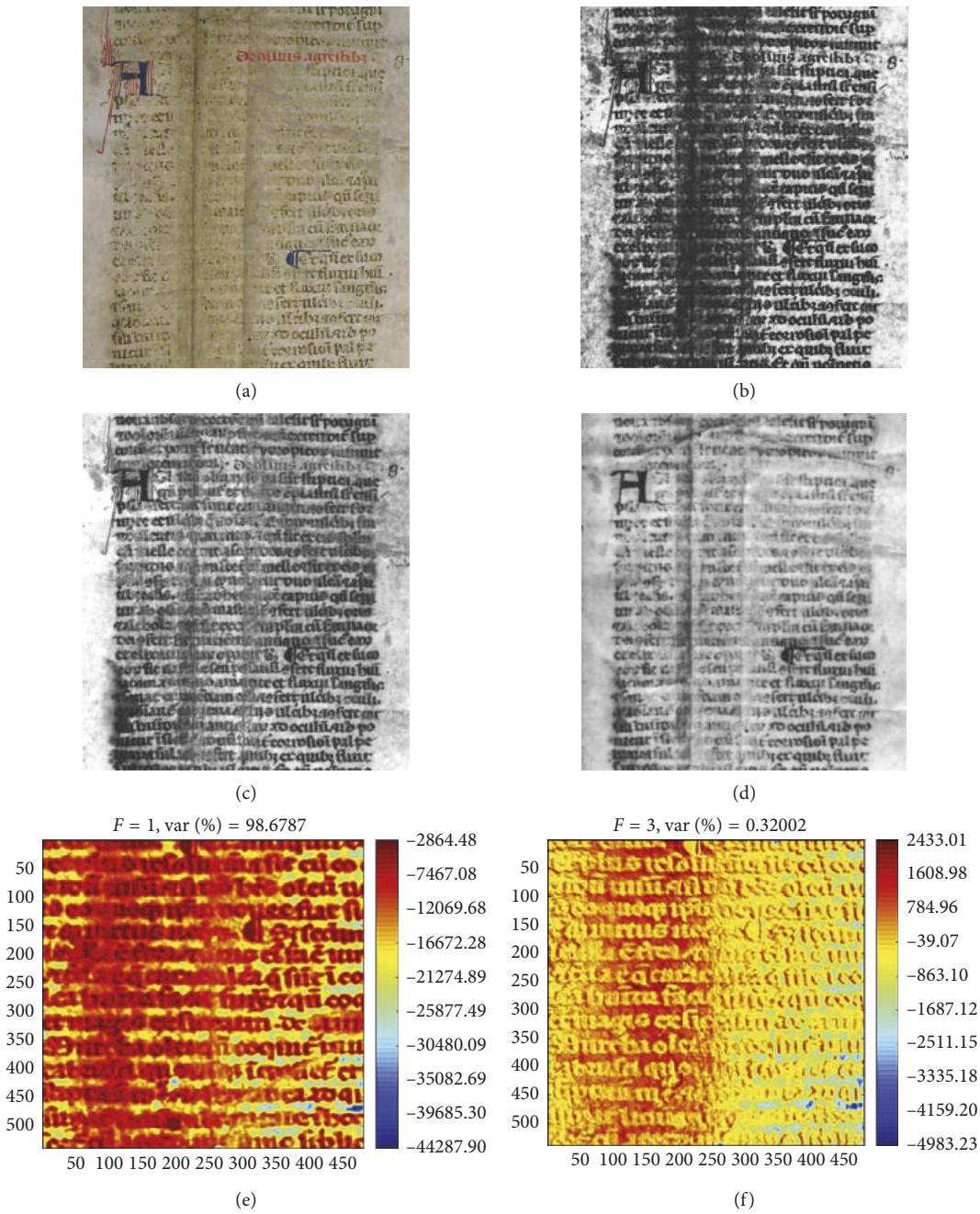


Figure 7: Photography (a) and UV fluorescence images taken at 420 nm (b), 680 nm (c), and 800 nm (d) of details of Parch. 34. (e, f) Image processing results by PCA: score image of PC1 (variance 98.68%) and score image of PC3 (variance 0.32%).

3.2.2. Red. All red inks are made of cinnabar or vermillion (HgS) as suggested by the high counts of mercury (Hg) detected by EDXRF (Table 1) and reflectance measurements (Figure S2 in Supplementary Materials) [36, 37]. The red inks of Parch. 38 and 34 show the presence of arsenic (As). In the latter, arsenic also is present in the blue ink, suggesting contamination or a residue of a conservation treatment [38]. Instead, in Parch. 38, this element is present only in the red ink, suggesting the use of cinnabar with accessory minerals, such as realgar (As_4S_4) and/or orpiment (As_2S_3) [37]. Parch. 38 presents starch, as shown in the ATR-FTIR spectra (Figure S3 in Supplementary Materials), that has been probably spread on the whole surface of the writing support. The use of this substance is also supposed for Parch. 34 although its characteristic band partially overlaps with that of gypsum. In the red ink of "Parch. 37," ATR-FTIR analysis reveals the presence of calcite (Figure S3 in Supplementary Materials), but no other compounds linked to the red ink are detected due to the presence of the black ink on the other side of the parchment which modifies the spectrum. Bromine (Br) was detected in some red initials of the three parchments (Table 1) and could be related to the presence of

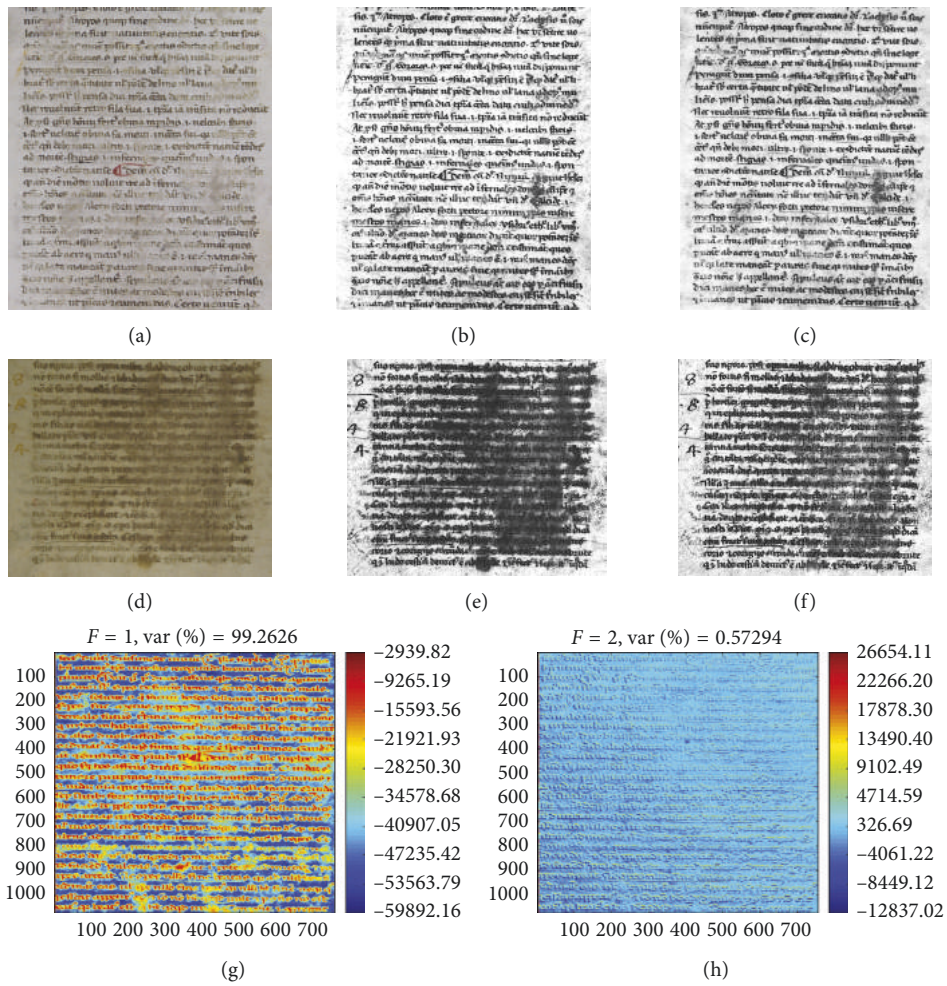


Figure 8: Photography (a, d) and UV fluorescence images taken at 420 nm (b, e) and 680 nm (c, f) of two details of Parch. 37. (g, h) Image processing results by PCA: score image of PC1 (variance 99.26%) and score image of PC2 (variance 0.57%).

a purple dye [39, 40] or to a conservation product, containing bromine, commonly used on ancient manuscripts [41]; however, it was not detected in the related parchments.

3.2.3. Blue. All blue inks include copper (Cu) (Table 1) as well as the typical ATR-FTIR (see Figure S4 in Supplementary Materials) and reflectance spectra of azurite (Figure S5 in Supplementary Materials). The blue ink of Parch. 34 also included arsenic (As), probably due to conservation treatments.

3.2.4. Purple. The purple ink has been used in Parch. 38 in the red initials. The EDXRF analysis revealed the presence of mercury (Hg), which could be a contamination from the nearest initial letter inked with cinnabar. Bromine is not detected, suggesting that the Tyrian purple has not been used. The ATR-FTIR spectrum shows the presence of starch (Figure S6 in Supplementary Materials), as in the other inks of Parch. 38. The reflectance spectrum shows two absorption bands at 540 nm and 580 nm (Figure 6(a)) that could be related to the presence of folium (or turnsole), a colorant produced by *Chrozophora tinctoria* plant, widely used on manuscripts [42]. The fluorescence spectrum of the parchment (Figure 6(b)) exhibits a strong emission at shorter wavelengths (λ_{max} =460 nm), while the purple ink also shows an emission at 605 nm that confirms the use of folium, as reported by Aceto et al. [40].

3.3. Multispectral Imaging for Digital Restoration. Parch. 34 appears to be strongly degraded in the last folio with the loss of some written areas, as shown in Figure 7(a). The text is more visible after illuminating the parchments with ultraviolet (UV) radiation and capturing the fluorescence at shorter wavelength ($\lambda = 420$ nm) for the flat surface of the parchment and at longer wavelengths ($\lambda = 680$ nm) for the folds of the parchment, as shown in Figures 7(b) and 7(c), respectively. In the near-infrared (NIR) range, the black areas and the ink in the fluorescence images disappear, as shown in Figure 7(d). Moreover, from the fluorescence images, we find that the number reported in the upper right side, which seems to be a "3" in the visible image (Figure 7(a)), is certainly a "8." In order to improve the readability of the text, taking into account the spectral behavior of the entire set of multiple images, a principal component analysis (PCA) via singular values decomposition (SVD) and without mean centering was performed, as shown in Figures 7(e)–7(f).

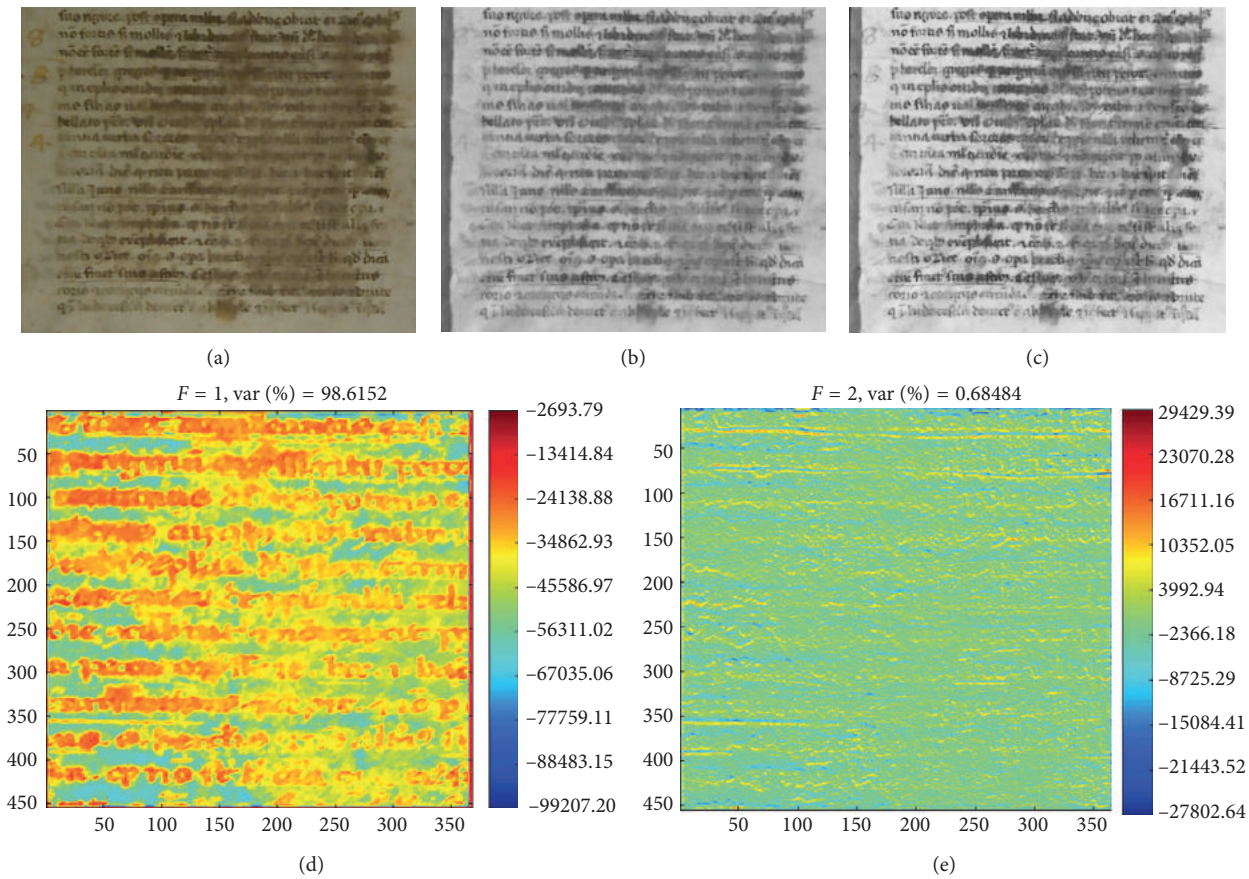


Figure 9: Photography (a) and visible images taken at 600 nm (b) and 680 nm (c) of details of Parch. 37. (d, e) Image processing results by PCA: score image of PC1 (variance 98.62%) and score image of PC2 (variance 0.68%).

A similar result was obtained from the lost inked areas on Parch. 37 (Figure 8(a)), but in this case, the text is readable with filters at short wavelengths, as shown in Figure 8(b). In the presence of brown spots, the use of filters at long wavelengths can improve the contrast between the text and the backgrounds in the UV fluorescence images, as shown in Figure 8(f). However, by illuminating with visible light and collecting images at long wavelengths, we can exploit the transparency of the brown pigmented areas in these spectral ranges, improving the readability of the text, as shown in Figure 9. In this case, the image processing by PCA improves the contrast between the parchment and the written areas, as shown in Figures 8(g) and 9(d).

Parch. 38 exhibits a strong loss of the text, which is completely restored by illuminating the parchment with UV radiation. All the images, taken at different spectral intervals, led to a better readability of the text, and some examples are reported in Figure 10. Moreover, the purple ink used for the flourished initials exhibits fluorescence in the NIR spectral range, as shown in Figures 10(f)–10(h).

4. Conclusions

The elemental and molecular techniques used in this work have proven to be useful for characterizing the parchments, inks, and pigments of three written fragments dating back to the XIV-XV centuries. The ATR-FTIR band at about 1030 cm^{-1} indicates gelatinization of the parchment 34. Moreover, the presence of many salts and impurities was detected, suggesting a fungal attack on almost all the inks. The presence of starch, detected on Parch. 38, indicates a conservation treatment spread over the whole surface. The texts were written with iron gall inks that present different elemental composition; particularly, Parch. 38 does not show impurities. Red and blue inks are based on pigments such as cinnabar (or vermillion) and azurite, but no binders could have been identified due to the interference of the parchments and contaminants.

Multispectral imaging proved to be a good approach for the digital restoration of manuscripts that suffer from the loss of inked areas or from the presence of brown spotting. In particular, in the first case, the readability of the text is achieved by illuminating the manuscript with ultraviolet radiation and collecting the images at different spectral ranges, while in the second case, the hiding effect of brown spots can be overcome by illuminating with visible light and collecting the images at longer wavelengths. Although the selection of single spectral band could be sufficient to increase the contrast between the parchment and the text, the principal component analysis (PCA) has proved to be a useful processing technique to further increase the readability of the text.

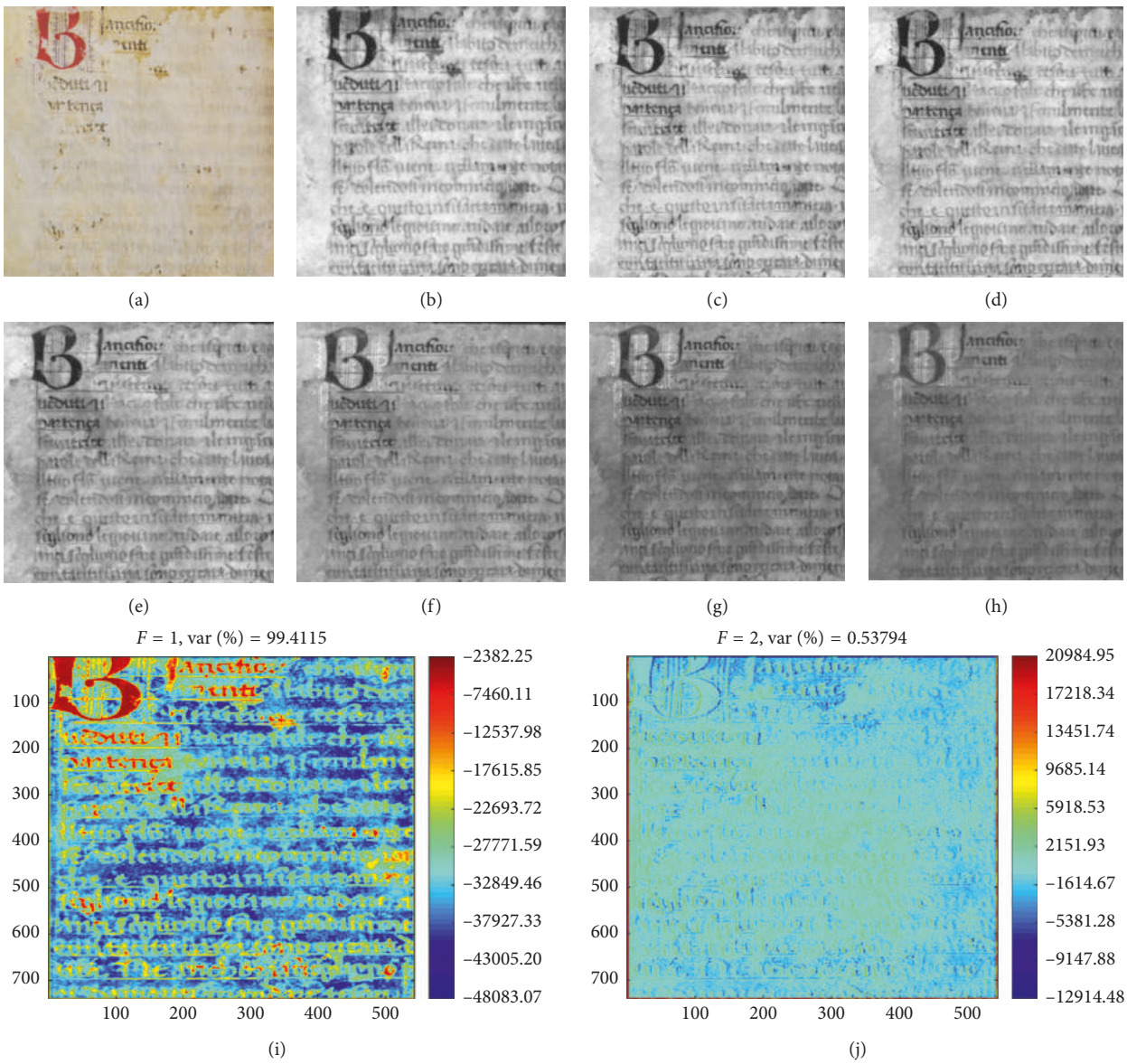


Figure 10: Photography (a) and UV fluorescence images taken at 470 nm (b), 500 nm (c), 532 nm (d), 600 nm (e), 680 nm (f), 700 nm (g), and 750 nm (h) of a detail of Parch. 38. (i, j) Image processing results by PCA: score image of PC1 (variance 99.41%) and score image of PC2 (variance 0.54%).

Data Availability

The authors declare that all data supporting the findings of this study are available within the article and supplementary materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Supplementary Materials

For the sake of completeness, the Supplementary Materials contains the reflectance and FTIR spectra that are not shown in the text. In Figure S1 are shown images of all written parchments taken with the CCD camera equipped with a band-pass filter centered at 1000 nm. Figures S2 and S5 show the reflectance spectra of the red (cinnabar or vermillion) and blue (azurite) inks detected on Parch. 38 and 34, respectively. In Figures S3, S4, and S6 are shown the μ-ATR-FTIR spectra of the red, blue, and violet inks on the three written parchments analyzed. (*Supplementary Materials*)

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