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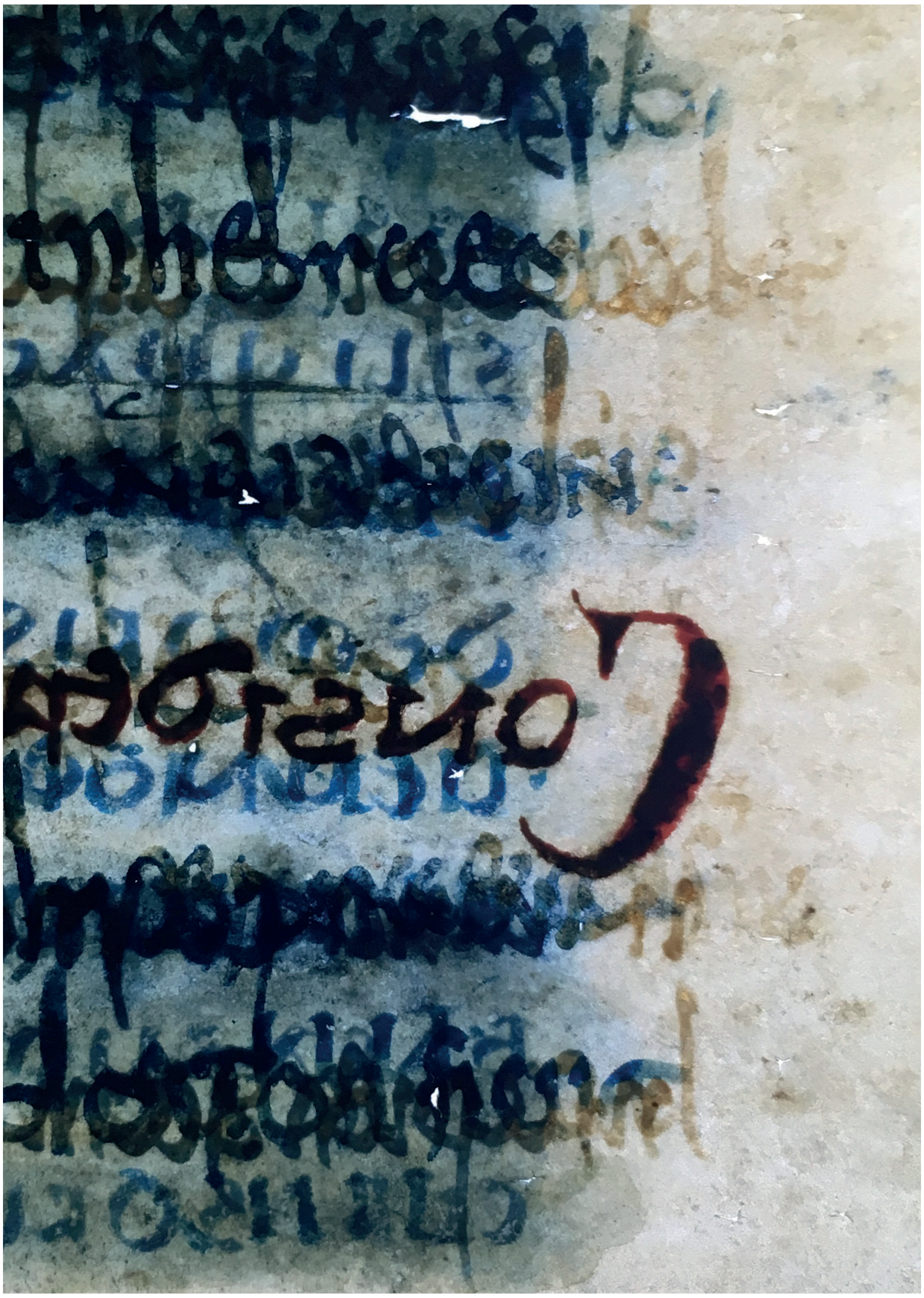

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Article

Ignatius of Loyola's *Exercitia Spiritualia*: Spectroscopic Monitoring and Nanomaterials for an Integrated Conservation Methodology on Ink-degraded Manuscripts

Melania Zanetti, Alfonso Zoleo, Luca Nodari, and Maddalena Bronzato | Venice, Padova

Abstract

This work concerns the analytical investigation and the conservation treatment of the oldest evidence of Ignatius of Loyola's *Exercitia Spiritualia* [*Spiritual Exercises*], which represent the cornerstone of Ignatian spirituality and are still the foundation of the Jesuits' training program.

The paper manuscript, held by the Archivum Romanum Societatis Iesu (ARSI) in Rome, includes many autograph annotations by the founder of the Society of Jesus (Fig. 1). Iron gall inks used to write the text induced a severe degradation, resulted in discoloration and ink diffusion through the leaves and burn-through. In the first half of the twentieth century, each leaf was lined with silk recto/verso to prevent fragmentation of the paper in the inked areas. Nothing was done to neutralise the chemical aggression, which has continued to cause damage.

In winter 2015, a new complex conservation project for the *Exercitia Spiritualia* was carried out to inhibit the degradation catalysed by acidity and to improve the general chemical, physical and aesthetic condition of the volume. The work was conceived as an open project that would be gradually outlined on the basis of data acquired from the analysis performed before, during and after the conservation steps by means of non-destructive and non-invasive spectroscopic techniques, in order to get information and to plan a swift and suitable intervention procedure.

Fig. 1: Hieronymus Wierix, engraving showing Ignatius of Loyola, Flemish, sixteenth century.

1. Introduction

The corrosive effects of iron gall inks endanger many Western historical manuscripts, due to the wide use of these inks up to the second half of the nineteenth century. It is well known that the Fe(III) and Fe(II) species occurring in these

Fig. 2: *Exercitia Spiritualia,* cc. 2v–3r, before the conservation treatment.

inks are powerful catalysers of paper degradation reactions.[1] As a consequence, iron gall inks are a main concern for paper conservators: iron migration from the inked areas has been related to degradation of the paper;[2] migration from the written text to the surroundings, or iron penetration into the leaf, is a frequent unwanted situation. The water solubility of Fe(II) ions requires a careful approach to aqueous treatments – even to gentle humidification procedures – that can induce halo formation. A mixture of water and alcohol is often suggested to limit the risk of ion migration. However, both water and hydroalcoholic treatments have been recently questioned: in fact, the increase of the alcoholic fraction hampers iron migration, but the efficiency of hydroalcoholic treatments depends largely on the type and nature of the paper and ink, and a reliable, general protocol is far from being set up.[3]

At present, there is no consensus on the use of water-based treatments; and more data on iron migration in iron gall ink occurring in different procedures are required, particularly with respect to discoloration and transverse (recto/verso) and lateral diffusion. However, most of the experimental work (ink diffusion, paper degradation etc.) to test the performance of water/hydroalcoholic treatments has been carried out on mock-ups. We propose to address a case where an original, very important manuscript has undergone a conservation treatment, leaf by leaf, with the results of spectrochemical analyses. In the paper, we focus firstly on the treatments involving the paper humidification, in particular for the silk removal, for the sizing of the damaged areas and for the re-hydration of the leaves; secondly, we introduce a deacidification treatment that involves the use of $Ca(OH)_2$ nanoparticle suspension in a non-aqueous solvent.

[1] Hey et al. 1979.

[2] Kolar et al. 2006.

[3] Rouchon et al. 2009.

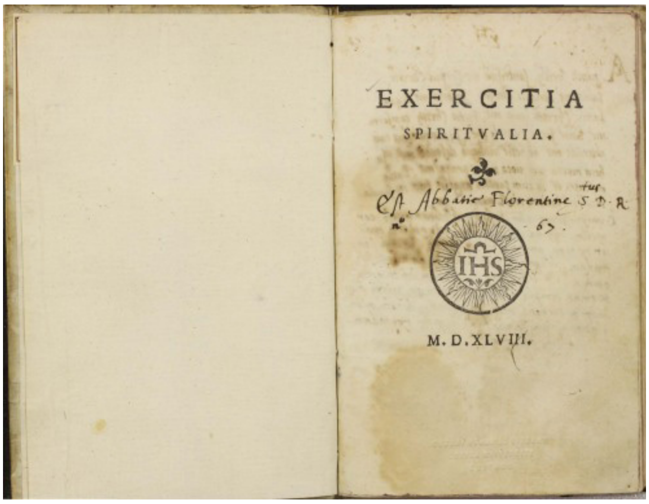
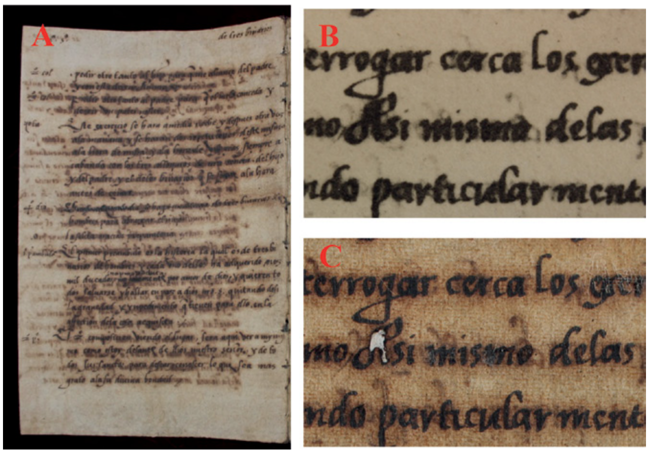


Fig. 3: First edition of the *Exercitia spiritualia*, Rome 1548. This copy belonged once to the Benedictine abbey Badia Fiorentina and belongs today to the Archives & Special Collections of the Loyola University Chicago.



Figs 4A, B, and C: *Exercitia spiritualia*, c. 24: c. 24 verso (A), showing the recto-verso ink passage. A detail of c. 3 recto, as it appeared in 1908 (B), and as it appeared nowadays before repair (C). Recto-verso ink passage, holes and the fine network of the silk lining are evident.

Certainly, the conservation treatment included several other steps (documentation, paper and binding repair, rehousing of the volume etc.) that are clearly outside the scope of the present work.

The *Exercitia Spiritualia* (Fig. 2) (230 × 157 × 28 mm) are composed of two distinct paper manuscripts, written independently of each other in the early decades of the sixteenth century. The first one (cc. 2–65) is the Spanish text of the *Exercitia*, annotated and corrected by Saint Ignatius' own hand; the second one (cc. 69–108) contains the translation from Spanish into Latin. The Latin text was then printed by Antonio Blado in Rome in 1548 (Fig. 3) and approved by Pope Paul III in the same year. The Spanish and the Latin manuscripts of the *Exercitia* were already bound together in 1908, when the only Spanish text and a brief description of the book were reproduced by phototype:

> Es un volumen encuadernado, en pasta de piel verdosa… En el lomo léese, en letras doradas, el siguente titulo: Exercitia S. P. Ignatii. Consta de dos partes: la primera… comprende los Ejercicios que reproducimos… La segunda parte… contiene una traducción latina de los Ejercicios, que parece ser el borrador de la versión literal é inédita, aprobada, juntamente con la versión vulgata y por los mismos jueces, el año 1548.[4]

> It is a volume bound in greenish leather … on the spine of the book one reads in golden letters the following title: [...]

The case binding was similarly illustrated in the *Monumenta Historica*, except for the gold tooled decorations of both the boards:

> Corio coloris viridis compositum et auratis laminis ornatum.[5]

In the meantime, probably in the thirties or forties of the last century, the manuscript underwent a deep repair aimed at limiting the effects of the corrosive iron gall inks used for writing, which were inducing discolorations and severe burn-through. The volume was unbound and each leaf was roughly lined on both sides with silk to prevent the loss of paper fragments. The gatherings were sewn and bound anew; portions of the old tanned leather cover were reused, fit and moulded into place on the boards, directly onto a new blue synthetic leather cover.

Unfortunately, no measures were taken to combat the chemical aggression of the inks, which have continued to emit persistent VOCs (volatile organic compounds) and to cause damage. The use of hot, liquid, water-based gelatine for the silk application has rather accelerated the burn-through process, producing crackling and perforation in the inked areas: it induced ink lines overlapping recto/verso, transversal and lateral migration of the coloured ink compounds (with halo formation around the writing), paper browning and adhesive stains, thus dramatically affecting the readability of the text (Fig. 2). The poor con-

[4] *Ejercicios Espirituales*, 1908, IX.

[5] *Monumenta Ignatiana series secunda. Exercitia Spiritualia*, 1969, 39.

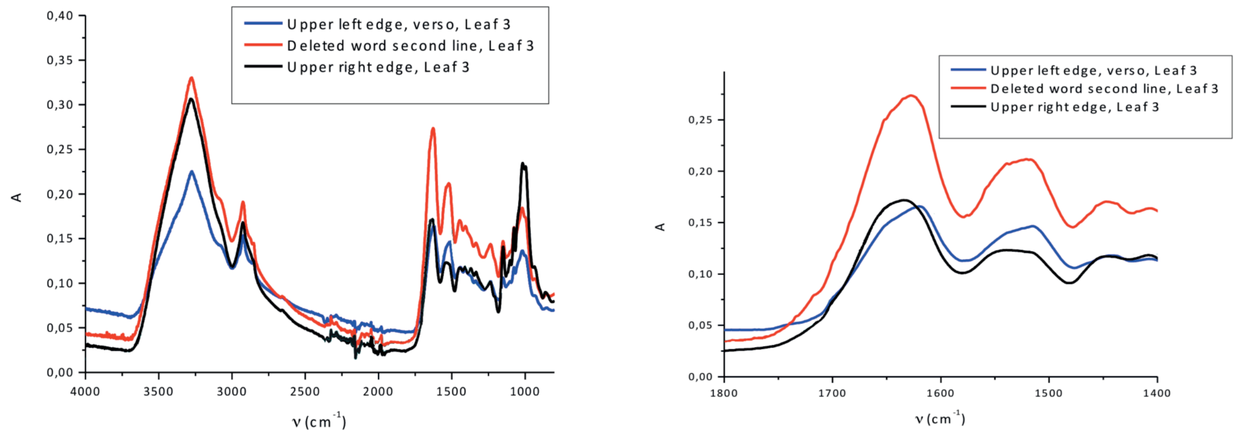


Fig. 5: ATR–IR spectra of c. 3 (left panel) and the region between 1400 and 1800 cm^{-1} magnified (right panel). Spectra of the upper left edge, verso, and upper right edge, recto, are shown in blue and black respectively. An inked deteriorated area is shown in red.

dition of the manuscript was worsened by tears and losses, repaired in the past with paper patches.

2. Experimental setup

Archivists, chemists and conservators took part in the complex conservation project for the *Exercitia Spiritualia*, carried out in 2015. It was conceived as an open project that would be gradually outlined on the basis of data acquired from a combination of complementary analytical methods and several tests carried out on the leaves.

In designing the treatment, we considered that a controlled humidification, in particular in vapour phase, is an essential step in rag pulp papers. The treatment is necessary to re-hydrated the paper fibres to make them flexible and mechanically resistant, features that had already been partially compromised by the application of silk on each leaf side in the previous repair. Furthermore, the inks were in contact with abundant aqueous-based materials, i.e. the hot, liquid, water-based gelatine used for the silk application in the previous conservation study, which left several coagulated gelatine drops on the leaf edges. Nevertheless, there was still the risk that a wet treatment could reactivate the inks and trigger further degradation of the manuscript.

Starting from these assumptions, we did not exclude the application of a careful, controlled wet treatment of the manuscript, under a continuous check, collecting spectroscopic data before, during and after any aqueous step, in order to assess variations, to evaluate their impact and to develop new methods aimed at stabilizing damaged manuscripts.

Non-invasive investigations were carried out by means of infrared spectroscopy in attenuated total reflection mode (ATR-IR), UV-visible reflectance spectroscopy with an optical fibre set-up (FORS) and X-ray fluorescence spectroscopy (XRF). IR is an effective tool in conservation science and was used to characterize the paper components and their degradation.[6] Before, during and after any aqueous treatment, FORS, also widely employed in the examination of works of art,[7] was used to establish possible colour variations in inks and paper, and XRF was used to monitor iron and metal ion migration on and around the inked areas.[8]

ATR-IR measurements were performed on a Bruker Equinox 55 spectrometer equipped with an ATR sampling accessory (diamond cell) and a liquid nitrogen-cooled MCT detector. IR spectra were ATR-corrected to display the correct absorption mode. XRF measurements were carried out on an XRF system consisting of an X-ray tube with Mo anode (operated at 20 kV and 1.2 mA current). FORS spectra were recorded with an Ocean Optics HR2000+ UV-visible spectrometer, equipped with a Xenon lamp and quartz optical fibres to carry the light onto the sample and to collect the diffuse radiation from the sample. The light spot was 1 mm in diameter. A standard white in Teflon® was used for calibration.

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[6] Derrick et al. 1999.

[7] Picollo et al. 2002.

[8] Hahn et al. 2005.

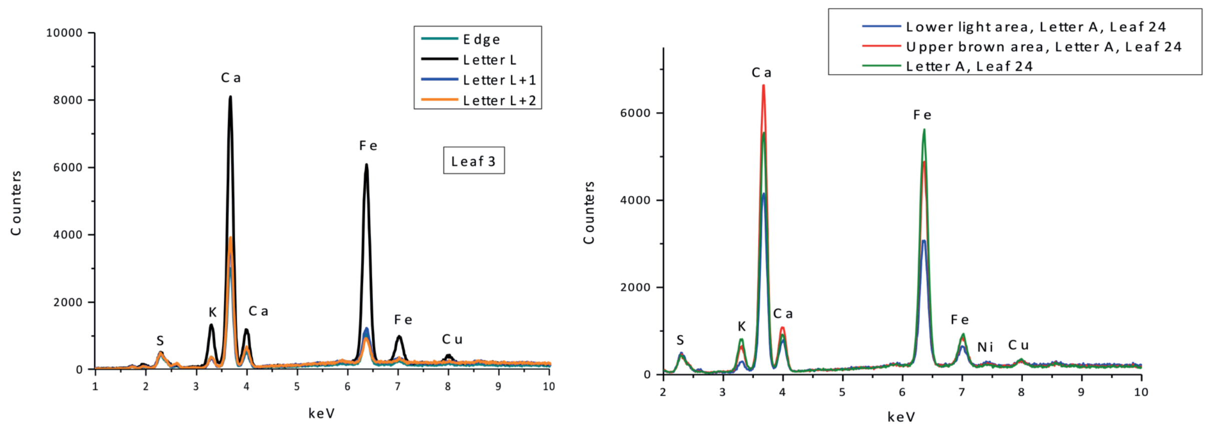

Fig. 6: Left panel, XRF spectra of c. 3: in black, spectrum of an inked area ('Letter L'), 1 mm away from the inked area (blue, 'L+1') and 2 mm away from the inked area (red, 'L+2'); in green, XRF spectrum of the edge. Right panel, XRF spectra of c. 24: an inked, degraded point (green), brown area above the inked point (red), light brown area below the inked point (blue).

Five bifolia were initially selected to undergo further investigations, aimed to develop the most suitable intervention protocol. Based on visual examination, cc. 3–24, cc. 5–22, cc. 8–19, cc. 35–36 and cc. 72–91 were considered a representative sample of different paper qualities, ink types and colours and of the current condition of the manuscript.

Inks were assessed in daylight, raking light and UV light and rated according to the ICN system[9], which helps classify the condition of inks, even though not predicting their behaviour over time. Inks showing the worst degradation – belonging to the Spain text – were rated rank 3 (poor condition, cracks occurring; this was the case with cc. 5–22 and cc. 8–19) and 4 (bad condition, severe losses; for example in cc. 3–24 and cc. 35–36).

2.1 Pre-treatment analysis

Once the manuscript was unbound, the single bifolia were analysed by means of infrared spectroscopy in attenuated total reflection mode (ATR-IR), UV-visible reflectance spectroscopy with an optical fibre set-up (FORS) and X-ray fluorescence spectroscopy (XRF).

ATR-IR and XRF were used to investigate the paper composition and conditions and to characterize the metal composition of the inks used in the main text and in Saint Ignatius' annotations/corrections.

Analyses confirmed that the most degraded bifolium of the selected ones was cc. 3–24 (Figs 4A–C), where ink passage from one side of the leaf to the other, perforations in inked areas and stains were observed. As the conservation operations had a more relevant impact on this bifolium, we propose it as an example of the methodology adopted in the project and of the results obtained.

Figure 5 shows the ATR-IR spectra recorded on leaf 3, recto and verso, and on a deleted word on the same leaf. The main observable peaks are: a structured peak at 1016 cm^{-1}, which is due mainly to the cellulose present in paper and generally attributed to C–O vibrations; a couple of peaks at 1516 and 1620 cm^{-1} (amide I and II), which are due to a protein, usually present in the gelatine used to size the paper;[10] a strong band at 3275 cm^{-1}, which is due to the overlap of two bands, one due to gelatine (N–H stretching, triangular band) and one due to water (O–H stretching, almost Gaussian-shaped).[11] The region between 1400 and 1800 cm^{-1} is particularly investigated, because in this region peaks indicative of paper degradation occur.[12] Specifically, in the region between 1600 and 1680 cm^{-1} there are overlapped peaks due to conjugated carbonyl or carboxylate groups present in cellulose and water-bending vibrations.[13] When gelatine is present, these peaks overlap at the amide I peak.

The two spectra acquired on the sheet margins show some differences in the intensity ratio of the double peak amide I and amide II: the IR spectrum of the upper right

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[9] Netherlands Institute for Cultural Heritage 2001.

[10] Barret et al. 1989; Rouchon et al. 2010.

[11] Derrick et al. 1999.

[12] Calvini et al. 2006.

[13] Łojewska et al. 2006; Łojewski et al. 2010.

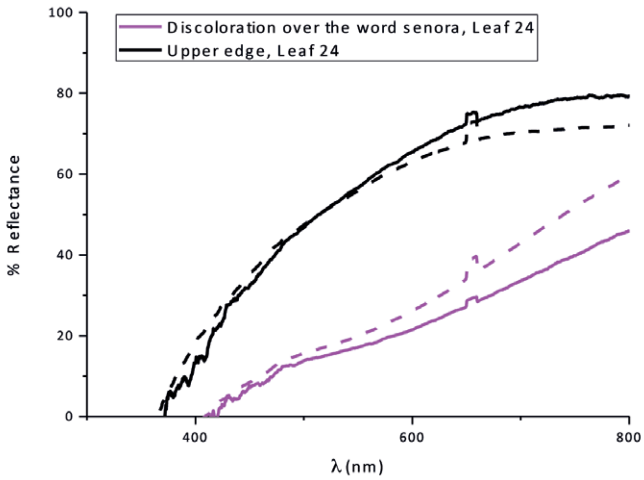

Fig. 7: FORS curves before (continuous line) and after (dotted lines) silk removal. Black line: a spectrum taken on the upper leaf edge. Pink line: a spectrum taken on a discoloration above an inked point.

margin on the recto side (black) is quite similar to the IR spectrum of pure cellulose with a thin layer of gelatine, while the upper left margin spectrum (blue, verso side) shows a comparative high signal in the region around 1600 cm^{-1} and a weaker signal around 1000 cm^{-1}. This suggests that sheet deterioration has likely reduced the gelatine size cover on the recto size, making the paper signal more evident. A further confirmation of this hypothesis can be found in the differences in the IR range between 3000 and 3500 cm^{-1}: the triangular peak at 3300 cm^{-1} is typical of N–H stretching, with some overlapped contribution from O–H stretching. All the spectra show almost the same profile, but the shoulder at 3100 cm^{-1}, which is an overtone of the N–H bending vibration, is weaker in the black spectrum. The deteriorated inked area shows a strong increase of the peak around 1630–1650 cm^{-1} compared with the margin spectra: this indicates degradation in the paper, because this peak is mainly contributed by cellulose by-products like carboxylate and conjugated carbonyl, deriving from the hydrolysis and oxidation of the paper.

XRF measurements on inked areas show a high amount of iron and traces of copper, confirming the use of iron gall ink in the text (Fig. 6, left panel). On some leaves, blank areas (green spectrum, 'edge') show much less iron than the inked areas (black spectrum, 'Letter L'), comparable to areas close to text ('L+1', blue and 'L+2', yellow, with L+1 closer than L+2). This indicates that iron diffusion from the text is very limited and iron is well embedded in the ink matrix.

In other sheets, in contrast, as in the case of leaf 24 of bifolium cc. 3–24 (Fig. 6, right panel), the halos present in the discoloured and degraded inked areas around the text ('Letter A, brown area', red line and 'Letter A, white area', blue line) show amounts of iron comparable to those in the inked areas ('Letter A', green line).

A small amount of Ni has been detected in the ink used on some pages and in particular in some correction notes, indicating the use of different inks. These data have been confirmed by Raman analysis (not reported here).

2.2 Spot tests

Sensitivity to water was evaluated with spot tests on a representative sample of papers and inks.

Despite the large amount of gelatine used for mounting the silk, protecting the paper from water penetration, the spot results were almost always positive and precluded the use of aqueous washing or spraying.

2.3 Silk removal

A Teflon® microspatula was used to test the adherence of the silk lining. Silk could be manually removed from bifolia in better condition (i.e. cc. 8–19, cc. 72–91 and almost 1/3 of the total amount). In the other cases (including bifolia cc. 3–24, cc. 5–22 and cc. 35–36), it was necessary to soften the adhesive to allow a safe mechanical retraction of the silk. As is well known, gelatine is a water-based adhesive and therefore very sensitive to applied moisture, which can affect its tenacity.

In this sense, a controlled humidification was achieved with a local application of Kelcogel® CG–LA gellan gum, a hydrogel usually assessed at 2–3% in demineralized and recalcified water and normally employed in paper conservation to wet specific areas by means of a gradual release of water.[14] As we did not want to wet the papers, but only to affect the gelatine's tenacity, we prepared the Kelcogel® at a higher concentration (4%) and applied it for a maximum of a few minutes (3–5) on small ink areas (3–4 inked lines at a time) in order to reduce the impact of the water on the bifolia as much as possible. Under these conditions, only water vapour moved from the thickener to the paper (vapour diffusion). Moreover, the gel transparency made it possible to check the ink's response during the

[14] Iannuccelli et al. 2012.

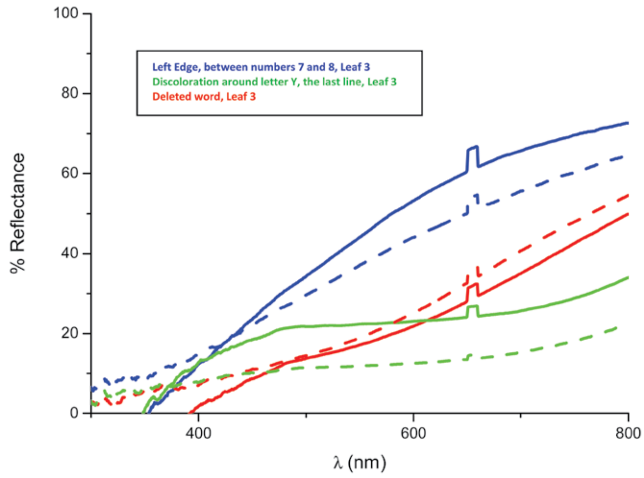

Fig. 8: FORS curves recorded before (continuous line) and after (dotted lines) the treatments on inked areas and on the margin of c. 3. Blue line: a spectrum taken on the left leaf edge. Red line: a spectrum taken on a discoloration around an inked point. Green line: a spectrum taken on an inked point.

treatment. As a result, the gelatine softened, allowing the silk to be removed without any risk.

2.3.1 Analyses: results and discussion

Humidification was a critical step in the conservation treatment: by using moisture, the dissolution of water-soluble products could drastically modify the chemical composition of the paper and the inks, significantly changing the appearance of the manuscript. Moreover, moisture could trigger the oxidative degradation of the paper, inducing the migration of metal species within the paper, especially iron and copper ions, paramagnetic centres known to act as catalysts for the degradation reactions on paper.[15]

The risks connected to humidification procedures in the presence of iron gall inks do not depend only on ink composition (e.g., when the ratio of iron ions to the added gallic acid is too high) or on the general manuscript condition, but also on the penetration depth of the inks. Deeper penetrations can lead the corrosion to spread to the substrate's verso side. Moreover, the humidification effect on the inks depends also on the duration of the treatment.[16]

The ATR–IR measurements performed before and after the quick application of the gellan gum hydrogel and the removal of the silk showed an expected decrease in the silk signal (amide I and II), but no other difference. FORS curves recorded before and after the intervention were fully overlapped; only slight differences in the total reflectance could be detected in the darkest areas, due to a change in the paper surface properties related to the removal of the lining. As regards the bifolium cc. 3–24, for example, XRF measurements were performed to check a possible iron migration from the text to the surrounding area. Measurements were taken of some inked areas ('L'), as well as of areas 1 mm away from the ink ('L+1') and of some marginal points. The ratio between the values taken from 'L' or 'L+1' and values taken from the margin was calculated. In this way, it was possible to obtain corrected values, independent of the specific instrumental conditions. Variation of the ratio before and after the treatment could indicate a migration/diffusion of different ions induced by the treatment. For instance, the iron migration from the inked area to the leaf margin would imply a ratio decrease. We must point out that, due to ink/paper heterogeneity, an error up to 20% can be estimated in the repeated measurements. In all cases, the ratios presented only very small variations, well below the experimental error. Therefore, we conclude that the treatment had no significant impact on iron migration, within the XRF sensitivity.

FORS measurements were carried out to characterize the bifolium cc. 3–24 and the other bifolia before and after all steps. Indeed, this analysis turns out to be useful for characterising halo variations by their colour change. In particular, specific attention was paid to possible profile variations, which could indicate variations in the chemical structure of the analysed samples due to the treatment they underwent. Increase and decrease in the total reflectance were not considered, as they are mainly due to instrumental effects. The FORS curves overlapped very well before and after removal of the silk: Figure 7 shows the FORS curves for two areas on leaf 24.

2.4 pH measurement

After removing the silk, the surface ink pH was measured by means of a Hanna pH-meter equipped with a surface electrode and a minimal amount of bidistilled water. The results varied between 4.25 and 4.79 for the inks used in the Spanish text (thus including cc. 3–24 and cc. 35–36) and were above 5 for those in the Latin manuscript.

2.5 Lining and acidity neutralization: a combined treatment

In the areas of the bifolia presenting brittleness, crackling or fragmentation due to ink corrosion, once the silk was

[15] Zoleo et al. 2010, Bronzato et al. 2013.

[16] Rouchon et al. 2009.

Fig. 9: Combined treatment (reinforcement and acidity neutralization).

removed it was necessary to increase the paper's mechanical strength. Most of the Spanish manuscript needed to be lined on the recto or verso side, fully (the whole written area) or partially (some written lines). The lightest-weight Japanese paper made from long kozo fibres (Tengujo, 2 gr/m^2) was chosen to be applied with gelatine B 250 Bloom (hide gelatine, pH 6.5–7.0).[17] To avoid the impact of the liquid water-based animal glue, a 2% solution was prepared by swelling the dry adhesive in cold water, heating it, letting it cool down and then pushing it repeatedly through a steel sieve to obtain a creamy gel suitable for brushing.[18]

There is a general consensus that historical paper gelatine-sized during manufacture lasted longer and better than unsized paper or paper treated with vegetable sizing.[19] It has been demonstrated that gelatine application on leaves, in particular on written areas, to enhance the mechanical properties of paper can stabilize mobile iron ions present in the inks, bonding them in an elastic film, making them inert. Gelatin B 250 Bloom at low concentration in water turned out to be suitable for applications on unbalanced iron gall inks: it does not induce halo formation and therefore causes no chemical diffusion from the text area.[20]

FORS curves recorded before and after the treatments on inked areas and on the margin of leaf 3 of bifolium cc. 3–24 are shown in Figure 8. Changes in the UV region can be observed before (continuous lines) and after (dotted lines) gelatine application, on a blank area (blue line), a brown area (red line) and a text point (green line). Changes show the same trend for all the areas and can be attributed to the contribution of the fresh gelatine layer. In any case, the visible region is almost unaffected, and the minima/maxima position is the same in the inked/brown areas, indicating that no migration of ink or brown degradation by-products occur, within the limit of the analysis. Also, after the gelatine

[17] Barrett et al. 1989.

[18] Charles et al. 2008.

[19] Garlick et al. 1986, Barret et al. 1989, Barret et al. 1994, Stephens et al. 2007.

[20] Kolbe et al. 2008.

Fig. 10: Deacidification using $Ca(OH)_2$ nanoparticles in 2-propanol.

layer was completely dried, the reflectance in the UV region decreased to the value before gelatine application.

As the analyses verified gelatine's suitability, a combined treatment was developed reinforce the leaf structure and to neutralize acidity, avoiding traditionally employed aqueous processes.[21]

A calcium-based deacidifying agent for cellulosic materials was chosen: it usually works very well as an alkaline reserve thanks to its transformation into calcium carbonate. Moreover, calcium carbonate is physicochemically compatible with the support; western paper mills have used it in the paper-making process since the thirteenth century.

Calcium hydroxide, a strong alkali commonly used in the past to treat acidic papers, is not recommended for use on acidic inks and oxidized papers, as it can dramatically increase the paper's pH (pH>10), triggering alkaline hydrolysis of the cellulosic support.

In the last years, the use of calcium propionate to deacidify manuscript papers has become pretty common:[22] calcium propionate is soluble in polar solvents (normally it is dissolved in ethanol) and it is a mild alkali, which promotes the neutralization of paper and ink acidity without any risk of alkaline hydrolysis of the cellulose.

However, this chemical tends to make treated papers release an unpleasant and long-lasting smell, due to the propionic acid that forms during neutralization and carbonation.

Recent studies have been developing and testing the application of a $Ca(OH)_2$ nanoparticle suspension in solvent (ethanol or isopropanol) on different historical materials.[23] Initially, the product was used mainly as a stabilizer for wall paints and stone surfaces. Later, the formulation was redesigned and made suitable also for paper treatment: Nanorestore Paper® is a dispersion of calcium hydroxide

[21] Netherlands Institute for Cultural Heritage 2001, Iannuccelli et al. 2012, Tamburin 2009, 103; Gelatine Handbook 2012; Charles et al. 2008.

[22] Plossi Zappalà et al. 1997, Bicchieri et al. 2012.

[23] Reissland et al. 1999, Rouchon et al. 2011.

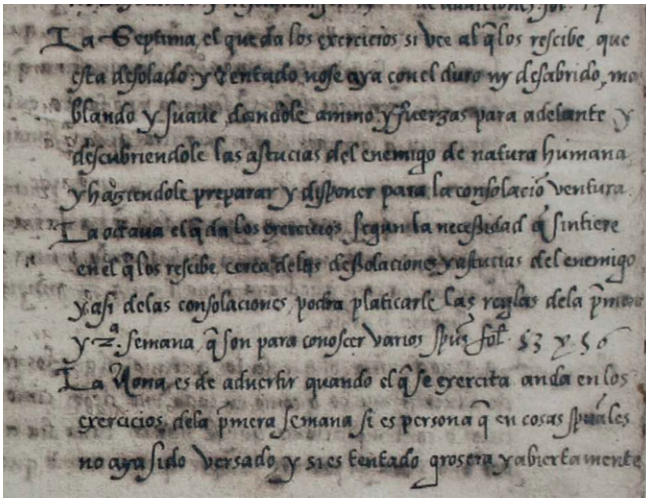

Fig. 11: Reported details of c. 3, before treatment.

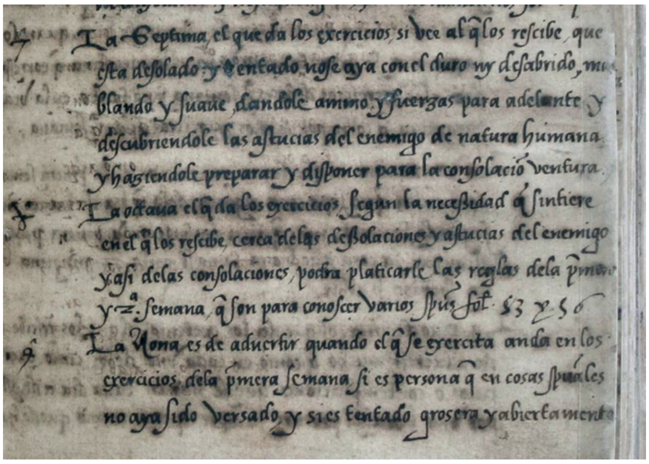

Fig. 12: Reported details of c. 3, after the combined treatment and deacidification.

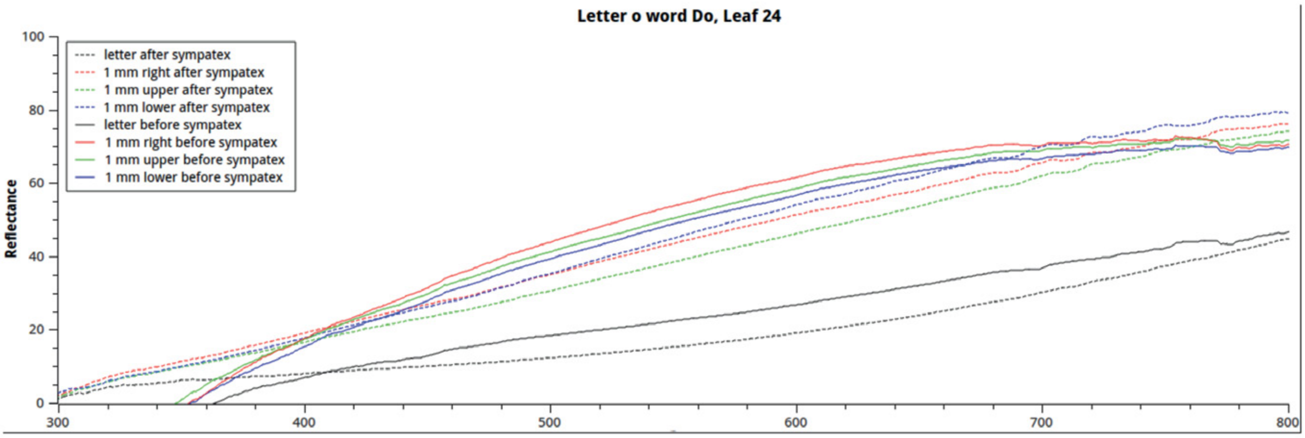

Fig. 13: FORS curve before (continuous line) and after (dotted lines) Sympatex humidification on c. 24. Black line: a spectrum taken on an inked point. Red, green, blue lines: 1 mm on the right, on the left and above the inked point.

nanoparticles developed by the Department of Chemistry and CSGI of the University of Florence. The product is available in ethanol or 2-propanol and is applied to deacidify paper artefacts and historical manuscripts affected by ink corrosion.[24]

The use of the nanoparticle suspension offers many advantages over the $Ca(OH)_2$ solutions normally used in conservation treatments. Firstly, the nanoparticle size promotes a deep dispersion of the calcium hydroxide, allowing for a total carbonation of the paper; secondly, the application of alkaline-earth metal hydroxide nanoparticles dispersed in non-aqueous solvents induces a slow, long-term deacidification process that gradually results in a neutral pH. This implies a significant increase in the inked paper's resistance to aging and the avoidance of a dramatic increase in the paper's pH, which could trigger alkaline hydrolysis of the cellulose.[25]

To perform the combined treatment, the Nanorestore® suspension (calcium hydroxide nanoparticles in 2-propanol at a concentration of 5g/l) was added to the 3% gelatine prepared in water; the ratio between water and alcohol was 1:1. The mixture – showing a milky appearance and an almost fluid consistency – was used to apply the Japanese paper (2 gr/m^2) over most of the bifolia of the Spanish manuscript recto or verso and limited to the written lines (Fig. 9). The bifolia were allowed to air dry to favour the calcium hydroxide carbonation (Fig. 11 and Fig. 12).

[24] Poggi et al. 2016.

[25] Poggi et al. 2016.

Fig. 14: *Exercitia Spiritualia,* cc. 2v–3r, after the conservation treatment.

The pH, measured 72 hours after the treatment, had increased in the treated areas up to a 5.00 value. In particular, the average pH on the inked area of c. 24 (part of the bifolium we are proposing as an example) was 4.24 before treatment and 4.90 in the same areas after the treatment.

2.6 Deacidification

The main goal of the conservation treatment of the *Exercitia Spiritualia* manuscript – to counteract acidity connected to the iron gall inks – was only partially achieved by applying the alkaline reinforcement to the bifolia in the worst condition. The pH values had slightly risen, but were still far from neutral; moreover, it was necessary to provide an alkaline reserve acting as a buffer in the paper to counteract acids in the future.

The Nanorestore® suspension (with a concentration of 5g/l in 2-propanol) was therefore used to deacidify both the already treated bifolia and those that presented halos but did not need to be reinforced with Japanese paper.

The calcium hydroxide nanoparticle suspension was applied by brushing (Fig. 10) and the pH was checked 24, 48 and 72 hours after each application, keeping the treated leaves at 57–60% RH and 21°C room temperature; four applications were needed to reach neutrality (pH 7.20–7.50) on bifolia showing a pre-treatment pH around 5, as in the case of cc. 24.

Deacidification was not achieved in cc. 94–105: the general condition of these leaves was acceptable, the inks were assessed at rank 1 and rank 2 on the ICN scale (good or fair condition, no crackling or perforation) and the average pH of the inked area was between 5.50 and 6.50.

2.7 Moisture content restoration

A minimal amount of moisture had to be introduced to rehydrate the treated leaves, realigning deformations and restoring a planar surface, so that the gatherings could be bound in the previous leather case binding. An indirect humidification by Sympatex was performed, laying the felt side on a wet cotton towel and placing the bifolia on the membrane side, permeable to water vapour, with a Mylar sheet in order to reduce the risk of significant chemical diffusion around the ink line and towards the paper verso side together with halo formation.[26]

Special attention was paid to the duration of the treatment, which was reduced to some minutes, enough to uniformly relax the paper fibres. It should be emphasized that the permeability of the paper and inks was noticeably reduced by the presence of a large quantity of animal glue in and on the leaf. This animal glue is composed mainly of the gelatine added during manufacture, the proteinaceous glue of the silk lining and the gelatine B used in the conservation treatments.

2.7.1 Analysis: results and discussion

The FORS measurements were applied to test the impact of indirect humidification. Figure 13 shows that no reflectance profile variations emerged after the rapid humidification of the leaves, apart from the variations in the UV region, which are attributable to the contribution of the wet gelatine layer.

3. Conclusions

As previously stated, this work describes some steps of the conservation treatment carried out on the manuscript of Ignatius of Loyola's *Exercitia Spiritualia*, specifically the actions involving close cooperation between chemists and conservators, in order to evaluate the impact of aqueous treatments on the manuscript: these latter can be critical due to the presence of iron gall ink in bad condition. The investigations were carried out not only before and after the complete treatment (as usual), but also before, during and after the most critical steps addressing the intervention on the leaves in different conditions and therefore needing different conservation procedures. A step-by-step analytical protocol allowed a proper evaluation of the efficiency of each of them (Fig. 14).

On the other hand, we must point out that the proposed spectroscopic methods have limitations to be taken into account. E.g., the ink layer on the manuscript was almost undetectable by ATR-IR, and XRF suffers from matrix effects. FORS curves are more useful in evaluating the effects of ink migration/diffusion, but adding or removing components (e.g., silk removal and gelatine adding) leads to spectral variations that are not always simple to interpret.

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[26] Rouchon et al. 2009.

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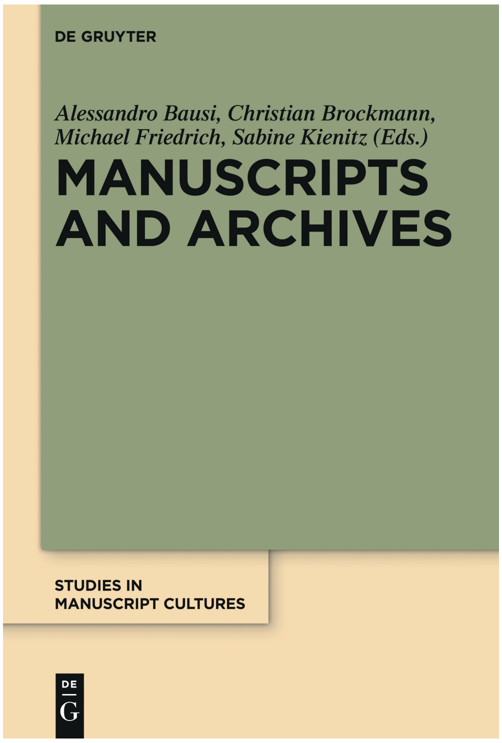

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