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A MULTIDISCIPLINARY APPROACH TO CONSERVATION: A CASE STUDY OF IGNATIUS OF LOYOLA'S AUTOGRAPH *DIARIO SPIRITUALE*

Riassunto

Il *Diario spirituale* è un frammento autografo scritto da S. Ignazio fra il 1544 e 1545 e fortunosamente recuperato dopo la morte del fondatore della Compagnia di Gesù. Conservato–presso l'*Archivum Romanum Societatis Iesu* (ARSI) a Roma, il *Diario* presentava seri problemi di conservazione, in particolare a causa dell'azione acida degli inchiostri ferrogallici. Il restauro di manoscritti in presenza di questi inchiostri risulta sempre problematico e, di conseguenza, il progetto di intervento realizzato nel 2017 ha previsto il monitoraggio dell'opera prima, durante e dopo le diverse fasi del restauro tramite analisi non invasive (XRF e FORS) mirate a valutare innanzitutto l'eventuale reazione degli inchiostri ai trattamenti.

Keywords: Conservation treatment, chemical hydrogel, spectroscopy, manuscript, iron-gall ink

Introduction

The manuscript *Diario spirituale* is the only surviving autograph by Ignatius of Loyola, written in the years 1544-1545. The Diario was not intended for readers, and only a part of the original work was retrieved after Ignatius' death. The manuscript was therefore soon given the veneration due to a sacred object.

The surviving autograph written in Spanish by the founder of the Society of Jesus (the Jesuits) is today kept in the *Archivum Romanum Societatis Iesu* (ARSI) in Rome, bound in a volume (two sections: ff. 2-15 and ff. 16-27), together with the Italian version of the same text, written by the cleric Jean Viset in the first half of the 17th century (two sections: ff. 29-44 and ff. 45-56; f. 28 is a single blank leaf bound together with the third section).

The volume has a late tissue binding in silk, manufactured in the first half of the 18th century (Fig. 1).

The manuscript is composed of papers of various quality, and almost six different watermarks are observed in the autograph text (eagle, bird, anchor in the circle, siren and so on, Fig. 2, upper row). Iron gall inks used to write the text induced severe paper degradation, resulting in discolouration, ink diffusion through the leaf, and burn through, depending on paper quality and ink composition (Fig. 2, lower row).

In the first half of the 20th century, the manuscript underwent a deep repair aimed at limiting the corrosive effects of the iron gall inks: all the leaves, other than the blank

Fig. 1: *Diario's* silk cover (18th century)

Fig. 3: Detail of the silk lining on the text

ff. 42, 43 and 44, were lined on both sides with silk to prevent the risk of paper fragmentation (Fig. 3).

Unfortunately, nothing was done to counter the chemical aggression of the inks, and they 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 somewhat accelerated the burn-through process, producing cracking and perforation in the inked areas: it induced overlap of *recto/verso*, transversal and lateral migration of the coloured ink compounds (with halo formation around the written), paper browning and adhesive stains, thus dramatically affecting the readability of the text.

This is why, in 2017, the manuscript underwent a new conservation treatment aimed at inhibiting the degradation and improving the general chemical physical and aesthetic condition.[1]

The project involved the participation of archivists, chemists and conservators and was conceived as an open project, which 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 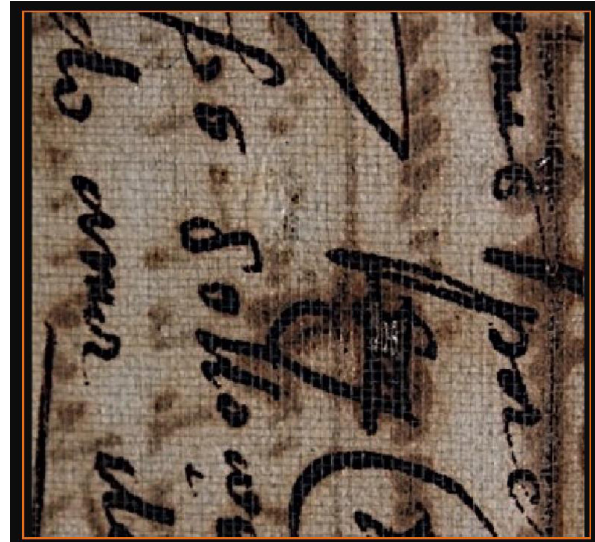to obtain information and to plan a punctual and suitable intervention procedure. This type of open project was already successfully tested in a previous intervention on the Ignatius of Loyola's *Exercitia Spiritualia*.[2]

In this work, we are focusing on paper and ink treatments, although the conservation intervention consisted of several steps, from documentation to binding repair and rehousing of the volume.

Results and discussion

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 discolouration, and transverse (*recto/verso*) and lateral diffusion.[3,4] Our analysis was based on a two-step approach: firstly, the

1   M. ZANETTI, 'Il restauro del manoscritto autografo *Diario spirituale* di Sant'Ignazio di Loyola', in: *Dalla tutela al restauro del patrimonio librario e archivistico* (Atti del convegno, ed. by M. Zanetti, Ca' Foscari editions, Venezia, 2018), 231-256.

2   M. ZANETTI, A. ZOLEO, L. NODARI, M. BRONZATO, 'Ignatius of Loyola's *Exercitia spiritualia*: Spectroscopic Monitoring and Nanomaterials for an Integrated Methodology on Ink-degraded Manuscripts', in: *Manuscript cultures-Natural Sciences and Technology in Manuscript Analysis*, 11 (2018), 49-62.

3   B. REISSLAND, S. DE GOOT, 'Ink corrosion: Comparison of currently used aqueous treatments for paper objects', in: *IADA preprints* (Preprints of 9th IADA Congress: Internationale Arbeitsgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren, Copenhagen 1999), 121-129.

4   V. ROUCHON, B. DUROCHER, E. PELLIZZI, J. STORDIAU-PALLOT, 'The water sensitivity of iron gall ink and its risk assessment', in: *Studies in Conservation*, 54 (2009), 236-254.

Fig. 2: Leaf fragments showing watermarks (first row, transmitted light) and degradation induced by iron gall inks (second row, reflection light). The images were taken after silk removal (see text)

characterization of iron-gall inks and paper was carried out to evaluate the reasons for the different degradation levels of the leaves. The second step was the evaluation of iron and ink distribution on the leaves before and after each intervention step to establish the impact, specifically for the water-based steps. To this purpose, we used X-Ray fluorescence (XRF) to probe iron distribution/diffusion, as well as the type of metallic ions present in the ink.[5]

XRF is a non-invasive spectroscopy widely applied to assess the distribution of metal ions in artefacts. It works only for elements with an atomic number larger than aluminium and is semiquantitative, i.e., it is able to quantify the relative amount of a specific ion in the same or similar material. It is based on the X-ray irradiation of a sample, which emits back X rays characteristic of the sample atoms.

To evaluate colour changes, we used reflectance spectroscopy in the ultraviolet-visible region with fibre optic equipment (Fibre Optic Reflectance Spectroscopy (FORS)). FORS is a straightforward, quick, non-invasive technique: a light in the ultraviolet-visible region is conveyed to a sample point, and the back-reflected light is analysed at each wavelength. The resulting spectrum can be compared with reference spectra of pigments and inks. Also, colour variations before and after specific treatments, as artificial ageing, wetting, oxidation, and so on, can be easily determined by means of this technique.

Seven *bifolia* from the autograph text (2-3, 6-13, 9-10, 16-27, 17-26, 19-24, 21-22) and three from the Italian translation (30-43, 34-39, 45-46) were selected for the analysis. The most damaged *bifolia* were 2-3, 6-13, 9-10, 16-27 and 21-22, all in the autograph part.

For each *bifolium*, 30 XRF points were sampled, 20 on the inked and 10 on the blank areas. Blank areas were on the leaf edges. On the most damaged *bifolia* (i.e.,

5   A. Zoleo, 'Le analisi spettroscopiche sul *Diario spirituale* di Sant'Ignazio in occasione del suo restauro', in: *Dalla tutela al restauro del patrimonio librario e archivistico* (Atti del convegno, ed. by M. Zanetti, Ca' Foscari editions, Venezia, 2018) 257-274.
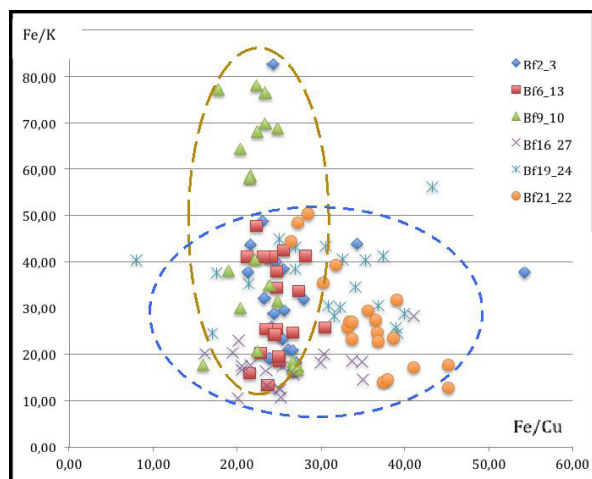
Fig. 4: Diagram showing the different clustering of the XRF-mapped points for the first three *bifolia* (2-3, 6-13, 9-10, in the brown circle) compared to the other *bifolia* (blue circle)
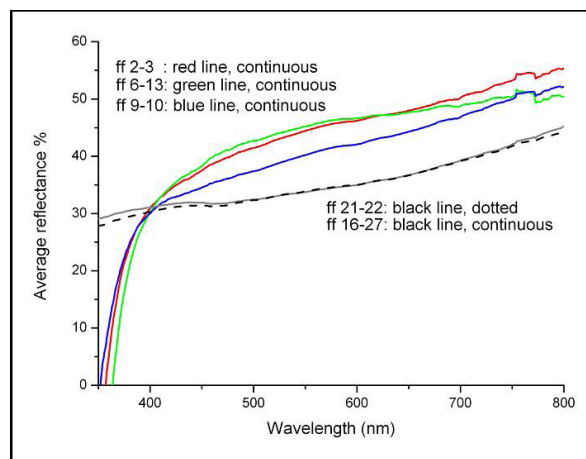

Fig. 5: Comparison between FORS spectra of the first three *bifolia* (2-3, red line; 6-13, green line; 9-10, blue line) and other two *bifolia* (21-22, 16-27) of the autograph text

the ones in the worst conditions), 20 out of 30 points were examined before and after each treatment. Globally, more than 300 XRF points were acquired.

As a first step, we applied XRF to evaluate the amount of the different ions in the ink writings before the intervention and in order to establish, if possible, a correlation between ink type and conservation condition of the *bifolium*. First of all, the best parameters to be used for the reliable identification of the inks were selected. A reliable identification should be based on robust and well-reproducible XRF signals. Since iron-gall inks were prepared with vitriol (i.e., iron sulphate, and gall extract), iron, copper, sulphur and potassium are the XRF-detectable, more abundant, and likely representative ions. Iron and sulphur come from vitriol, while potassium is commonly found in plants. Copper is commonly present with iron in the natural vitriol. The strongest XRF signals are from calcium and iron. A comparison between iron signals in blank and inked areas shows that iron is ten times more abundant in inks. Furthermore, its signals are well reproducible. Iron, therefore, gives an ink-representative XRF signal. Calcium is abundant, but its XRF signals are highly variable. Moreover, it is about twice as present in ink than in blank areas. It comes from a variety of sources, and it is not suitable for

ink identification. In contrast, while copper is not very abundant, it is four times more abundant in ink and, overall, its amount is very well reproduced in inked areas. Therefore, its XRF signal is suitable as a representative parameter.

Potassium comes from the organic part of the ink. Potassium is found almost only in the ink and not on the leaf and therefore is indicative of ink. Furthermore, its amount is well reproduced in inked areas and is suitable for ink identification. Although sulphur could be an excellent ion for ink identification, it is almost undetectable in our conditions, and could not be used.

Based on these considerations, we used the XRF ratios of iron-copper and iron-potassium as identifying parameters for inks. We used XRF ratios of ink iron and leaf iron to evaluate iron diffusion before and after treatments.

The diagram in Fig. 4 reports the iron-potassium ratios against iron-copper ratios for the various *bifolia*.

Clearly, different clusters of points can be identified. Specifically, the *bifolia* 2-3 and 6-13, belonging to the first part, showed very similar iron-copper and iron-potassium ratios, indicative of similar recipes and material for the inks. The *bifolium* 9-10 has a slightly different iron-potassium ratio, indicative of different amounts, probably of

the same materials as for *bifolia* 2-3 and *bifolia* 6-13 (maybe a different preparation from the same materials).

However, no clear relation between ink type and *bifolium* conservation state was found, since the damaged *bifolia* 2-3, 6-13, 9-10, 16-27, 21-22 belonged to different cluster groups, although they were all in the autograph part.

Reflectance spectra were acquired on the inked areas of the *bifolia*. The spectral profile was very similar for the first three *bifolia* and was indicative of a black-brown ink (Fig. 5, red, green and blue lines). In contrast, for the other *bifolia* of the autograph text, the spectra of the inks were very flat, indicative of black-grey inks (Fig. 5, continuous and dotted black lines). This confirms what was already observed with XRF, i.e. the first three *bifolia* were written with similar inks.

After this first spectroscopic evaluation, the *Diario* underwent the first step of the intervention. Because of the critical condition of papers and inks, it was necessary to soften the adhesive to allow the safe mechanical traction of the silk. Controlled humidification was therefore achieved with the local application of a water-based chemical gel, characterized by a nanostructured network having very high water retention.

The action of this nanomaterial is limited to the interface: the penetration of water into paper and inks is gradual and controlled. Moreover, the gel transparency allows one to check the ink response during the treatment.[6,7] As a result, the gelatine softened, and the silk could be removed by gentle mechanical action.

After this first step, on the more damaged *bifolia*, XRF and FORS measurements were carried out again on 20 points (15

Fig. 6: A bifolium positioned on the steel frame for drying at natural ventilation, magnetic pads all around its perimeter

inked + 5 blank) already sampled before the intervention.

In the areas of the *bifolia* presenting embrittlement, cracking, and fragmentation due to ink corrosion, once the silk was removed, it was necessary to increase the paper mechanical strength to allow the most damaged ink areas to undergo the following conservation steps, avoiding any additional risk related to the handling of paper and inks. The lightest-weight Japanese paper made from long kozo fibres (Tengujo, 2 g/m^2) was chosen to be applied with gelatine B 250 Bloom (hide gelatine, pH 6.5–7.0). It has been demonstrated that gelatine application on leaves can enhance the mechanical properties of paper and stabilize mobile iron ions present in the inks, bonding them into an elastic film and making them inert. 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 through a steel sieve to obtain a creamy gel suitable to be used with brushing. After removing the silk, the surface pH was measured: the results varied between 4.20 and 5. We considered it necessary to counteract acidity connected to the iron gall inks by using a nonaqueous system and by providing an alkaline reserve acting in the paper as a buffer to contrast acids in the future.

To this aim, a dispersion of calcium hydroxide nanoparticles in isopropanol

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6   *Nanotechnologies in the Conservation of Cultural Heritage. A Compendium of Materials and Techniques*, ed. by P. Baglioni, D. Chelazzi, R. Giorgi (Dordrecht: Springer, 2015), 117-144.

7   G. Poggi, N. Bonelli, R. Giorgi, P. Baglioni, 'La chimica dei nanocompositi e la loro applicazione al restauro dei manoscritti', in: *Dalla tutela al restauro del patrimonio librario e archivistico* (Atti del convegno, ed. by M. Zanetti, Ca' Foscari editions, Venezia, 2018).

Table 1: Average XRF counts for the ions K, Fe, Cu (chosen as representative parameters for the inks) before and after water-based treatments: the suffix *sv* means after silk removal; the suffix *da* after deacidification treatment.

	Bifolia						
	2-3	*2-3sv*	*6-13*	*6-13sv*	*6-13da*	*9-10*	*9-10sv*
Blank							
K	982	1344	546	715	464	354	807
Fe	4758	4430	5317	4223	3959	6122	6984
Cu	1017	996	811	564	519	941	631
Ink							
K	4042	4468	5229	6577	6092	2679	3800
Fe	92828	93530	142290	142079	142761	107945	118520
Cu	3520	3767	5637	5971	6053	4649	5317

at a concentration of 5 g/L was applied by brushing, granting a good penetration into the paper fibres.[8] Four applications were needed to reach neutral or slightly alkaline pH values (i.e., pH values between 7.50 and 8.50). The pH was checked on the same points 48–72 hours after treatment (i.e., the minimum time necessary for calcium hydroxide to turn into calcium carbonate) and the values remained constant. The introduction of a minimal amount of moisture was necessary to rehydrate the treated leaves, realigning deformations and restoring a planar surface. Indirect humidification by Sympatex was, therefore, performed.

As indirect humidification techniques are known to induce potentially significant chemical diffusion around the ink line and towards the paper *verso* side together with halo formation, special attention was paid to the duration of the treatment, reduced to some minutes, enough to uniformly relax the paper fibres. It should be emphasized that the permeability of paper and inks was sensibly reduced by the presence of high quantities of gelatine in and on the leaves. Once humidified, the leaves were positioned on a stainless steel frame (Fig. 6) employing magnetic pads all around their perimeter: this method induces paper fibres to flatten gently, reducing the risk of further mechanical damage.

Starting from a very slightly damp state, paper fibre stretching induced by drying was minimum; moreover, weight pressure was avoided together with the risk of crackling fragile inked areas.

After this critical step, XRF measurements were carried out on the 20 sampled points of the most damaged *bifolia* (2-3, 6-13, 9-10, 16-27, 21-22).

The data in table 1 are the average of the XRF ion counts (XRF ion intensities) for the inked and blank points of each leaf: within the experimental error (which can be estimated around ±10% from repeated measurements), no variation of the XRF iron counts, and therefore no variation in the iron amount, are observed before and after the critical steps of silk removal and Sympatex humidification. As far as the ions in the inked areas are concerned, similar conclusions also hold for copper and potassium. To evaluate ink diffusion before and after Sympatex, FORS spectra were also acquired on the inks and nearby halos (1 mm from inked areas) for the most damaged *bifolia*. Within the experimental error, the FORS lines before and after treatment matched well. Minor variations were observed, mainly related to spectrum offset changes, which are due to small calibration errors, whereas ink diffusion should result in real changes in the spectral profile. This indicates that the wetting Sympatex treatment did not cause ink diffusion.

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8   G. POGGI, R. GIORGI, A. MIRABILE, H. XING, P. BAGLIONI, 'A Stabilizer-Free Non-polar Dispersion for the Deacidification of Contemporary Art on Paper', in: *Journal of Cultural Heritage*, 26 (2016), 44-52.

Conclusions

In this work, a case study of a conservation project conceived as intervention followed by step-by-step spectroscopic monitoring was proposed. Modern hydrogel-based treatments combined with XRF/FORS single point analysis also provided a reliable and general protocol for future interventions in critical cases, such as interventions on manuscripts with iron-gall ink corrosion. Spectroscopic analyses showed that the "soft" hydrogel-based approach prevented the effect of ink and iron diffusion during the critical water-based conservation steps. XRF/FORS also provided a tool to distinguish different types of ink.

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