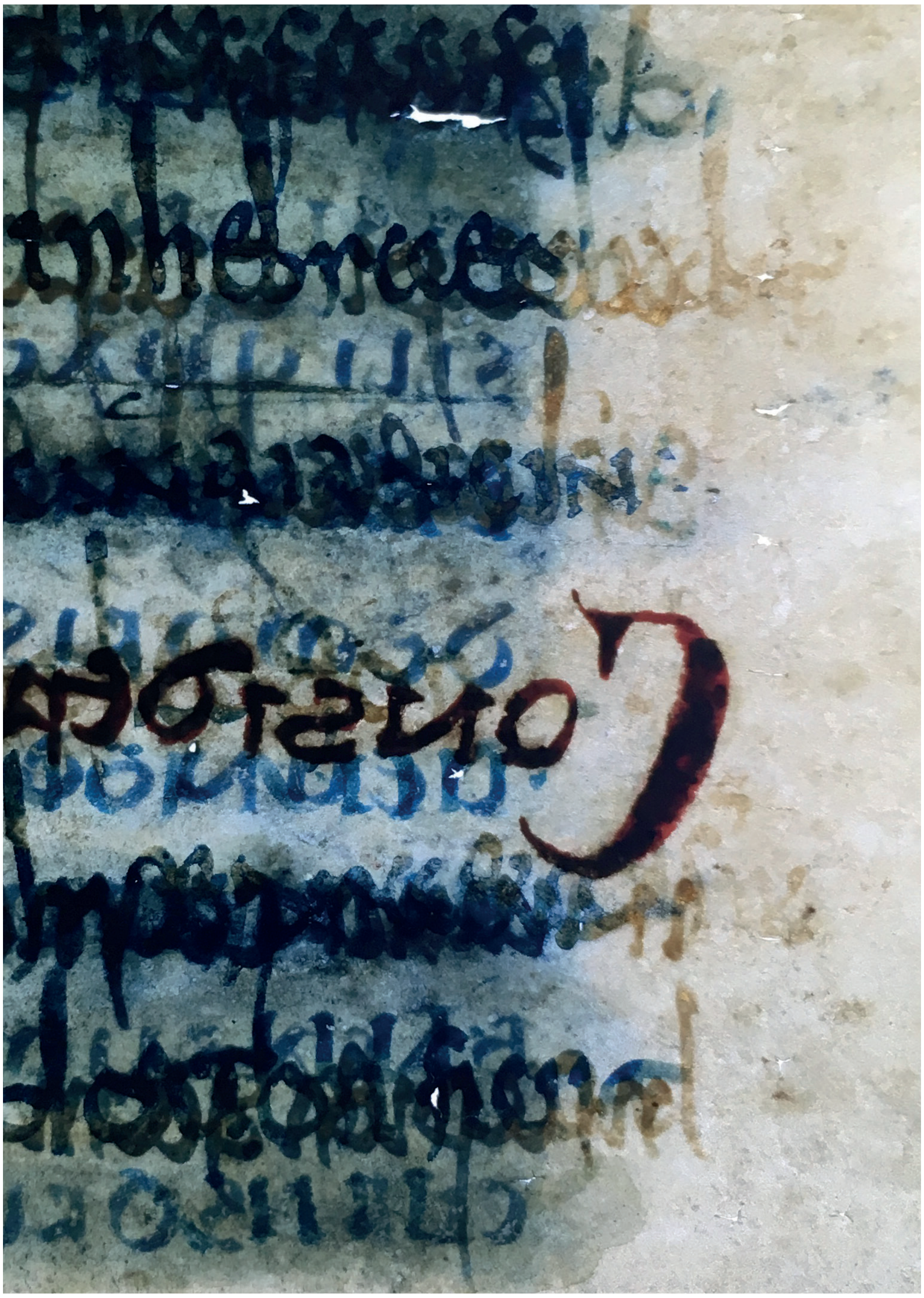
mc Nº 11 2018

manuscript cultures

Hamburg | Centre for the Study of Manuscript Cultures ISSN 1867–9617



Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG
CENTRE FOR THE STUDY OF MANUSCRIPT CULTURES
DFG

Publishing Information

Editors
Prof Dr Michael Friedrich
Universität Hamburg
Asien-Afrika-Institut
Edmund-Siemers-Allee 1/ Flügel Ost
D-20146 Hamburg
Tel. No.: +49 (0)40 42838 7127
Fax No.: +49 (0)40 42838 4899
michael.friedrich@uni-hamburg.de

Prof Dr Jörg Quenzer
Universität Hamburg
Asien-Afrika-Institut
Edmund-Siemers-Allee 1/ Flügel Ost
D-20146 Hamburg
Tel. No.: +49 40 42838 - 7203
Fax No.: +49 40 42838 - 6200
joerg.quenzer@uni-hamburg.de

www.manuscript-cultures.uni-hamburg.de

Editorial Office
Dr Irina Wandrey
Universität Hamburg
Sonderforschungsbereich 950
'Manuskriptkulturen in Asien, Afrika und Europa'
Warburgstraße 26
D-20354 Hamburg
Tel. No.: +49 (0)40 42838 9420
Fax No.: +49 (0)40 42838 4899
irina.wandrey@uni-hamburg.de

Layout
Astrid Kajsa Nylander

Cover
Transmitted light image (detail) of Codex 3/1 (5th century Luxueil or 7th–8th century Italy), Benedictine Abbey St Paul in Lavant Valley, Austria. Hieronymus, *Commentarius in Ecclesiasten*; Plinius Secundus, *Historia naturalis.* Photography by Thomas Drechsler, Berlin.

Translations and Copy-editing
Mitch Cohen, Berlin

Print
AZ Druck und Datentechnik GmbH, Kempten
Printed in Germany

ISSN 1867–9617

CONTENTS

Editorial

Natural Sciences and Technology in Manuscript Analysis

The Centre for the Studies of Manuscript Cultures in Hamburg strives to enhance the field of manuscript studies by providing a forum for dialogue between the humanities and the natural sciences. This dialogue leads to well-defined new tasks for the natural and applied sciences and very often provides answers to questions that could not be solved by historical and philological methods alone.

In recent years, multi- and hyperspectral imaging to recover erased text in palimpsests has made considerable progress. Various institutions have acquired dozens of the imaging systems. However, image processing still requires serious development and the establishment of standard procedures. In addition to non-destructive material analysis of pigments and dyes, which has become standard in the studies of illuminated manuscripts, the interdisciplinary teams of the CSMC are currently working on establishing guidelines for studies of writing inks. Finally, digital image processing and analysis techniques are also gaining recognition in the fields of palaeography and codicology.

The second International Conference on Natural Sciences and Technology in Manuscript Analysis was held on the premises of the Centre for the Study of Manuscript Cultures in Hamburg from 29 February to 2 March 2016. Like the first conference, it brought together scientists and scholars engaged in this field of research and provided a forum for discussion and for presenting new methods and results.

This special issue of *manuscript cultures* once again contains a selection of extended papers presented at that conference in Hamburg 2016 and some additional contributions presenting unique case studies. The articles were solicited for original research work illuminating the role of the natural sciences and technology in manuscript analysis.

All in all, this special issue represents the state of the art, illustrating how different techniques and varying methodologies can be successfully applied to analytical investigations in the field of manuscript analysis. We hope that it will help to integrate the natural and applied sciences into the field of manuscript studies.

The research at the University of Hamburg for this volume was sponsored by the German Research Foundation (Deutsche Forschungsgemeinschaft) at SFB 950 'Manuscript Cultures in Asia, Africa and Europe' and undertaken within the scope of the Centre for the Study of Manuscript Cultures (CSMC). We would like to express our gratitude to all the authors for submitting persuasive, up-to-date papers, to all the anonymous reviewers for their valuable and constructive comments and finally to the editorial office for their own fruitful contribution to this issue.

Christian Brockmann, Oliver Hahn, Volker Märgner, Ira Rabin, and H. Siegfried Stiehl

Article

Hard Science and History

Marina Bicchieri | Rome

1. Introduction

Books, archival documents and graphic works of art are amongst the most invaluable patrimony in human history. Each single document is an open window on our history, and its preservation is paramount.

The value of books is often evaluated merely on the basis of their content, either textual or graphic, neglecting the history of the physical support, the paper used, the kind of ink chosen, their provenience, what they are made of and the fabrication procedures. All of this information, stored between the pages and somehow hidden to the eye, tells us of the long travel of the paper used, the technological and scientific discoveries made at the time the book was written or drawn, and the genius of those who invented an ink or a specific paper treatment; it reveals the evolution of the aesthetics, morals, and costumes of the time.

In brief, it is a carrier of our story, of human history.

This entire incommensurable heritage is unfortunately destined to a slow death.

Supports, media and binding are subject to aging, and they lose their mechanical characteristics; inks can fade or induce acidity in the support, damaging it to the point of complete destruction.

Natural aging is a spontaneous and irreversible process, quite slow by itself in the absence of external interference such as storage in unsuitable places, when other degradation processes – physical, biological or chemical – can take place.

The function of scientists in the field of conservation of cultural heritage is manifold. On the one hand, by investigating the structure of materials, they can understand the nature and causes of degradation and find solutions to prevent further decay. On the other hand, they can solve problems or questions related to the manufacture of the object or to its past life, thus helping scholars in their historical studies. Moreover, each discovery also permits us to explore issues of the history of science.

In this paper, two case studies – a self-portrait by Leonardo da Vinci and the Purple *Codex Rossanensis* – will be presented to underline the positive or negative synergy between different expertises.

2. Instruments

Raman measurements were performed with a Renishaw In-Via Reflex Raman microscope equipped with a Renishaw diode laser at 785 nm. The laser spot measured about 20 μm$^{2;}$ the resolution was 3 cm^{-1}, and the laser power on the sample was 0.03–1 mW, depending on the characteristics of the sample investigated.

Micro-FTIR measurements were executed with a Nexus Nicolet interferometer and a Continuμm™ Microscope equipped with an Infinity Reflachromat™ 15X ∞/V objective. The measurements were performed on a surface of 100 x 100 μm^{2} in the 4000–650 cm^{-1} range at a resolution of 8 cm^{-1}, averaging 200–400 acquisitions per sample. No ATR spectra were collected, in order to avoid any direct contact with the original documents.

XRF spectra were recorded by means of an Assing Lithos 3000 portable spectrometer, equipped with a Mo X-ray tube. The measurements were carried out with a 2-mm collimator and a Zr filter. The tube operated at 25 kV, 0.300 mA in the 0-25 keV range with a resolution of 160 eV at 5.9 keV, lasting 10–60 minutes for each acquisition. Long-time acquisitions were performed to obtain information on the elements present in minor amounts.

The AFM measurements were performed with the AFM easyScan 2 Nanosurf instrument with FLEX-AFM head and conical tip (thickness 7 μm, height 17 μm, radius <10 μM) covered with 'aluminium reflex'. The instrument was provided for the measures by Lot-Oriel-Nanosurf. The tip, inserted in the measuring head, vibrates with an oscillation frequency of 190 kHz and, when approaching the area to be analysed, is sensitive to short-range forces, due to the interaction with the surface of the sample (non-contact mode). When applied to 'soft' samples, such as paper, the non-contact mode is more suitable, because it avoids removing fibrils and modifying the surface, which would compromise the analysis. The non-contact method allows a completely non-destructive way of working, obtaining a real three-dimensional reconstruction of the roughness of the analysed surface and avoiding any contact with it.

3. Materials

Apart from the measurements performed directly on the original documents, for the study of the *Codex Rossanensis* some laboratory samples were prepared.

a. Historical samples of lake pigments, belonging to the collection of the Icrcpal chemistry laboratory (gift of Lorilleux, Milan, 1938) obtained from *Rubia Tinctorum* (red) and *Porphyrophora hamelii* (Armenian cochineal, red) were applied to the surface of a parchment following the indication of Bisulca.[1]

b. Aluminium lake pigments from *Crocus Sativus* (red) and *Sambucus Nigra* (pink-mauve) were prepared following ancient recipes reported in Carriera and in Caffaro.[2] Each pigment was then mixed with egg white, as reported in Caffaro[3] and in *De Arte Illuminandi*[4], and then applied to the parchment.

c. Two different kinds of purple-dyed parchment samples were prepared by treating the parchment with: a) an aqueous solution of *Roccella Tinctoria* prepared as described in the Stockholm papyrus,[5] recipe 131; and b) an aqueous solution of *Roccella Tinctoria* and sodium carbonate, as described in recipe 123 in the same manuscript.

4. Results and discussion

4.1 Leonardo da Vinci self-portrait

In 2012, the very famous self-portrait of Leonardo da Vinci, conserved in the Biblioteca Reale di Torino, was subjected to a completely non-destructive diagnostic campaign at Istituto Centrale Restauro e Conservazione del Patrimonio Archivistico e Librario (Icrcpal), Chemistry Laboratory. The purpose of the analyses was to assess the conservation status of the drawing, which presented an apparent fading of the graphic medium and diffuse foxing. To this end, surveys were accomplished in the chemistry laboratory using molecular (Raman and Infrared) and elemental (X-Ray Fluorescence) spectroscopies. At the same time, Atomic Force Microscopy (AFM) was applied to obtain a topographic description of the paper in damaged and less-damaged areas. The topography of the paper is, in fact, related to its state of preservation.[6] The other laboratories of the Institute performed microbiological studies, codicological investigation, measures in FORS and Multispectral Reflectance.

Only the comparative analysis of experimental results obtained with different techniques and methods can actually provide scientific information to correctly characterize the work and predict how time will alter its chemical-physical characteristics and what the life expectancy of the work of art is.

I summarize below the results obtained by the laboratories of the Institute before examining in depth the results from the chemical laboratory.

The codicological analyses consisted of the measurements of the portrait (33.2 cm high × 21.2 cm wide; average paper thickness: 230 µm) and the characteristics of the manufacturing wire. The latter were obtained by collecting images of the paper under grazing light. The wire used had 8–9 wire lines/cm and the distance between the chain lines was equal to 2.7 cm; no watermarks were present. These technological characteristics are compatible with the wires typically used in the sixteenth century. Moreover, it was possible to recognize – without any sampling – the pulp composition as a mixture of hemp and flax fibres with the addition of some coloured wool fibres, indicating a low quality of paper.[7]

The analysis under UV light evidenced a considerable presence of glue, leftover of a previous arrangement of the drawing, which had been glued directly to a piece of cardboard. Part of the glue had penetrated the paper; moreover, thick residues of glue were still present on the perimeter of the sheet, inducing undulation.[8]

Optical measurements in visible and ultraviolet light, followed by TDDFT (Time Dependant Density Functional Theory) analysis and interpretation evidenced the presence

[1] Bisulca et al. 2008

[2] Carriera 2005; Caffaro 2004.

[3] Caffaro 2004.

[4] *De Arte Illuminandi*, ed. Brunello 1976.

[5] Caley 2008.

[6] Piantanida et al. 2005.

[7] Pascalicchio 2014.

[8] Botti et al. 2014.

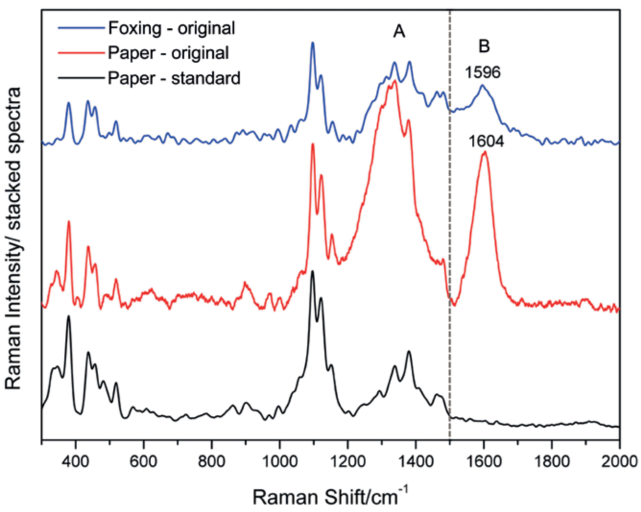


Fig. 1: Raman spectra collected from Leonardo's self-portrait. From top: foxed areas, not foxed paper, cellulose standard reported for comparison. In the figure, A indicates the spectral features related to superimposition of collagen and paper, and B to the formation of carbon-carbon double bonds; the dotted line indicates the separation between the signals characteristic of the pure cellulose (Raman shift lower than 1500 cm^{-1}) and those typical of oxidisation of the chain, at higher Raman shift.

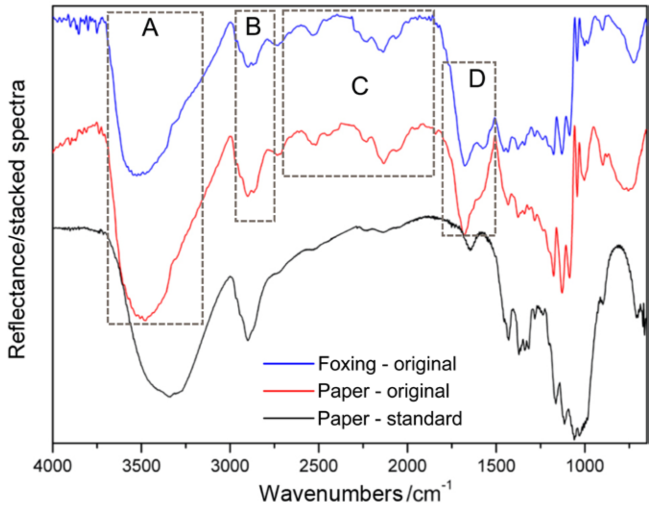


Fig. 2: FTIR reflectance spectra collected from Leonardo's self-portrait. From top: foxed areas, not foxed paper, cellulose standard reported for comparison. In the figure, A indicates the spectral features related to dehydration of the paper, B to gelatine size, C to the formation of carbon-carbon triple bonds, and D to carbon-carbon double bonds and carbonylic functions.

in the paper of a great amount of oxidised groups, indicating a serious degradation of the paper, compatible with storage in a closed and humid environment.[9]

Meanwhile, the microbiological analyses showed diffuse traces of fly's catabolites and the absence of active fungal attacks, but a massive presence of fungal remains – mostly *Eurotium Halophilicum* – on the back of the portrait and in the region with glue. A previous fungal attack could be hypothesised as causing the formation of oxidised function in the cellulose (chromophores), giving rise to spots and discolouration of the paper.[10]

The Chemistry Laboratory analysed the drawing using Raman, FTIR in reflectance, XRF and AFM.

Raman spectroscopy can identify the functional groups characterizing degradation, and previous researches allowed the evaluation of the modification induced in the spectra of cellulose after oxidative degradation.[11] The investigations of the self-portrait indicated a severe oxidation, both of the cellulosic support and of the areas affected by foxing. Double carbon-carbon bonds were, indeed, detected, and their amount was so great as to produce a very intense peak, normally absent in the Raman spectra of undamaged cellulose, at 1596 cm^{-1} and 1604 cm^{-1} in the foxed areas and in the paper support, respectively (Fig. 1).

This behaviour was confirmed by infrared analysis (Fig. 2), which, indeed, showed an even worse situation, highlighting the formation of carbon-carbon double bonds and carbonyl groups (1500–1700 cm^{-1} region) and even of triple carbon-carbon bonds (2100–2300 cm^{-1} region), which implies the breaking of the anhydroglucose ring. Moreover, the peak of the OH stretching, centred at around 3500 cm^{-1}, was not as broad as usual; this behaviour is typical of a severe dehydration of the support.

Very interesting results were obtained by applying, in a completely non-destructive way, atomic force microscopy (AFM) to the self-portrait.

Previous researches performed at the Chemistry Laboratory made it possible to correlate the morphological changes of the paper's surface to its aging,[12] the hydrolytical or oxidative degradation of cellulose[13] and the biological or chemical origin of foxing[14].

[9] Missori et al. 2014.

[10] Pinzari et al. 2014.

[11] Bicchieri et al. 2000.

[12] Piantanida et al. 2005.

[13] Coluzza et al. 2008.

[14] Piantanida et al. 2006.

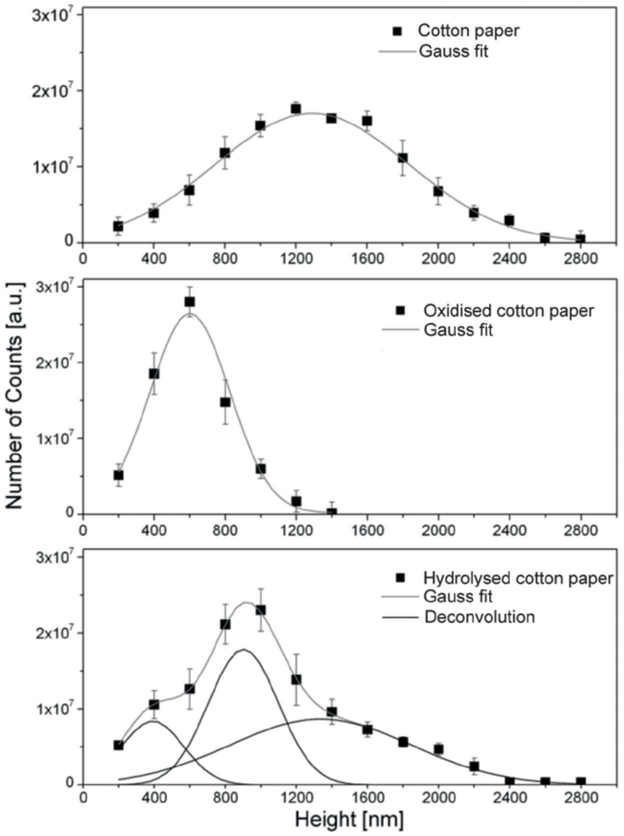


Fig. 3: AFM surface corrugation of (from top): not damaged, oxidised and hydrolysed papers. Oxidation produces a unique peak at lower dimension in respect to paper. The fragmentation of the cellulose, caused by hydrolysis, give rise to a superimposition of different surface distributions.

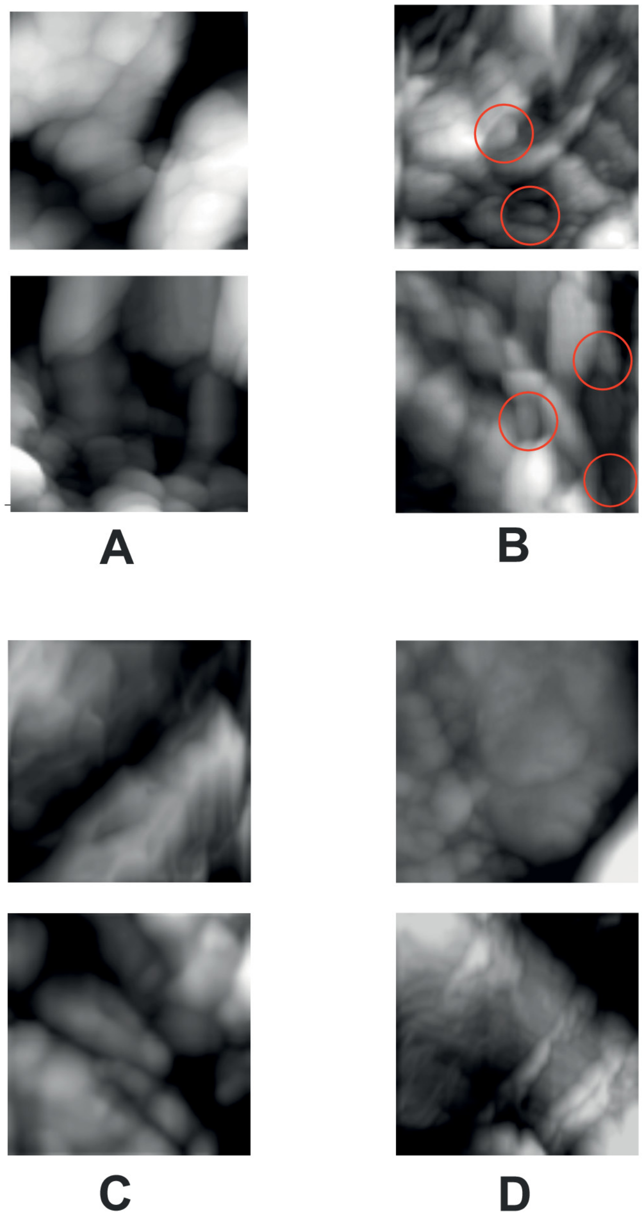


Fig. 4: AFM morphologies (15 μm x 15 μm) of A: paper in an original document (Original A in Fig. 5) at 3 mm distance from a foxing spot. B: foxing spot – induced in the same document by iron – in which repeated morphologies are evidenced by red circles. C: paper in an original document (Original B in Fig. 5) different from A at 3 mm distance from a foxing spot. D: foxing spot – induced by *Aspergillus terreus* in the same document – in which no repeated morphologies are visible.

A dominant oxidation causes a surface height distribution easily distinguishable from the one induced by a mainly hydrolytical degradation. Oxidative processes give rise to the formation of a single peak in dimensions lower than those observed in well-preserved paper. After hydrolysis, the fragmentation is an expected effect and causes, firstly, a random spread of the surface distribution and, eventually, an increase in the lower dimensions (Fig. 3).

When foxing spots are analysed by AFM, it is possible to distinguish whether they were produced by a biological or a chemical attack. In the case of chemical foxing, some morphologies are repeated regularly, whereas biological foxing produces morphologies randomly distributed on the surface of the stains and the paper (Fig. 4).

This behaviour reflects the distribution of the surface corrugation (Fig. 5).

In chemically induced foxing, the roughness of the spot does not increase, but decreases slightly. Paper and foxing stain surfaces are each described by a unique peak; moreover, stain and paper peaks are well separated. This is consistent with the strong oxidation usually found in foxed areas (Fig. 5, Original A).

In biological foxing, the roughness variation is caused by the presence of two peaks: one is consistent with the peak found in the paper; the other is well separated from this and is a marker of the stain, a completely independent colorimetric aspect of the foxing spot (Fig. 5, Original B).

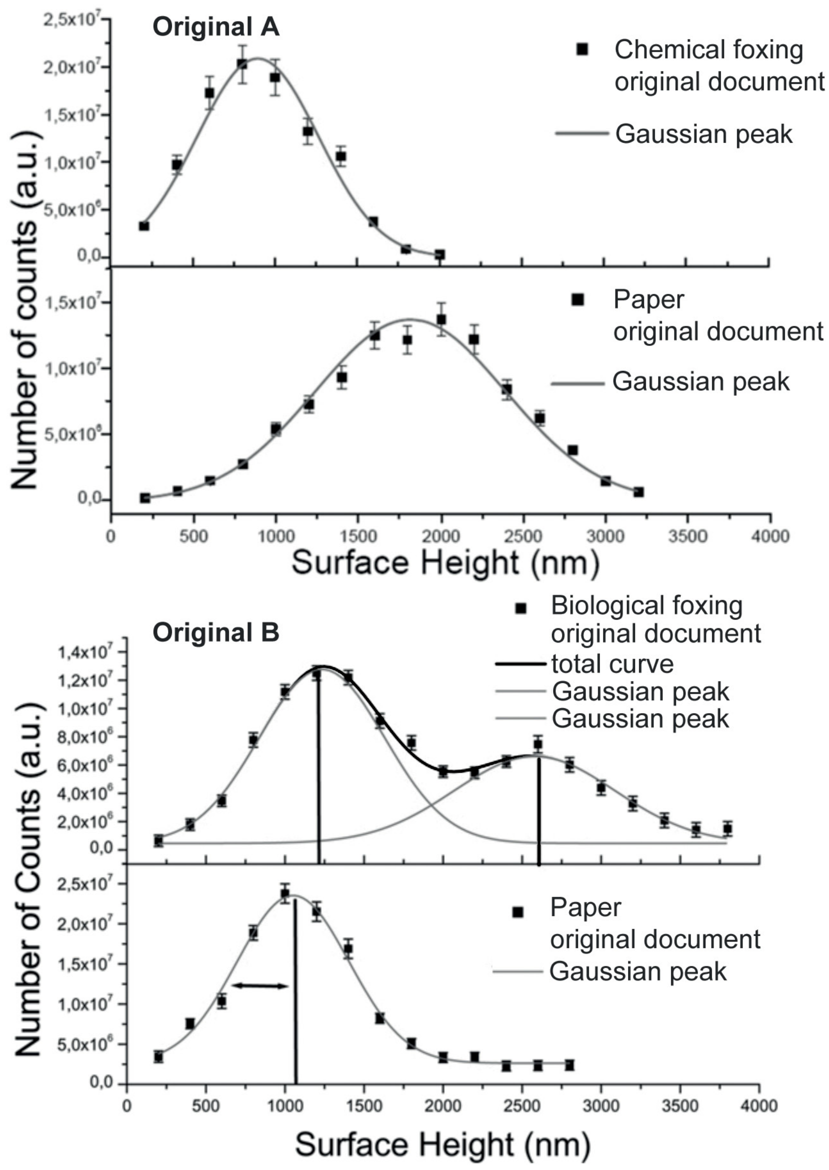


Fig. 5: AFM surface corrugation of (from top): chemical foxing spot on an original document, not-foxed paper of the same document; biological foxing spot on an original document, not-foxed paper of the same document.

A restoration project, including chemical treatment to stabilise the paper, was proposed, but the art historians rejected it for purely 'philological' reasons, in this way condemning the drawing to its destruction. In this case, the positive synergy between the different branches of science did not correspond to a positive synergy with the world of the humanities, thus leading to negative results.

4.2 The purple Codex Rossanensis

The *Codex Rossanensis* is a sixth-century illuminated manuscript written on purple parchment, conserved at the Museo Diocesano di Rossano (Cosenza, Italy).

In 1917–19, the codex was subjected to a restoration treatment, carried out by Nestore Leoni, a famous miniaturist active from the end of the nineteenth century to the mid-twentieth century. Leoni's intervention irreversibly modified the aspect of the illuminated sheets. Nestore Leoni never wrote which materials he used for the restoration.

In June 2012, the Codex arrived at Icrcpal for a complete characterization of the pigments, support and materials Nestore Leoni used and to ascertain its state of conservation to determine the real restoration needs.

A scientific commission was established, including palaeographers, Bible scholars and historians specialized in the study of illumination.

In the analysis of Leonardo's self-portrait, AFM topographies of the paper showed a very corrugated surface, indicating a coexistence of hydrolysis and oxidation. In the foxed spots, AFM topographies demonstrated a severe decrease in the thickness of the paper, ranging on average from 20% on the whole foxing spot to 60% in some parts of the spot, where the spectroscopic measures showed the presence of triple carbon-carbon bonds (Fig. 6).

All the techniques applied in the different laboratories of the Institute showed a very dramatic oxidation of the paper, caused by chemical, physical and biological attacks.

The challenge of the analysis of the *Codex Rossanensis* lies in the lack of analytical information on the pictorial media used in the Early Middle Ages (fourth–ninth centuries). Old-medieval illuminated manuscripts have been deeply studied from the historical standpoint, but their material composition has rarely been described.[15]

The results obtained at the Icrcpal Chemistry Laboratory are based on micro-Raman (378 spectra), micro-Fourier Transform Infrared (80 spectra) and X-Ray Fluorescence (35 spectra) spectroscopic analyses, performed on the

[15] Aceto et al. 2012.

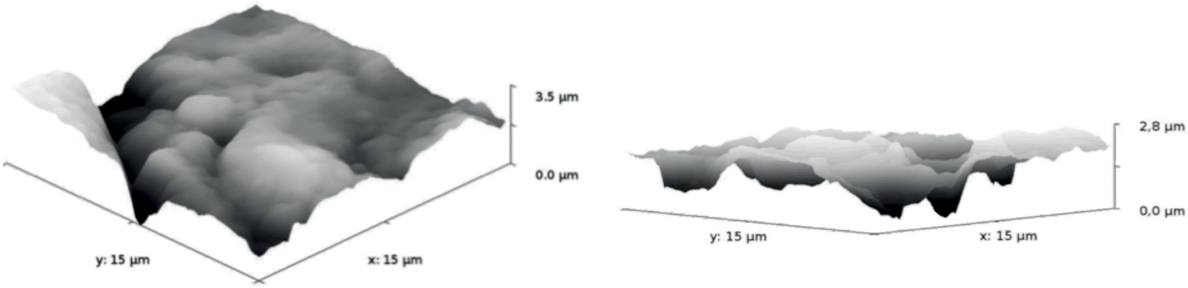


Fig. 6: Leonardo self-portrait. Left: AFM topography of the paper. Right: AFM topography of the paper in a foxing spot. In this case there is an evident decrease of the thickness of the paper as well as the formation of holes on the surface.

whole volume, the pigments, the support and the previous restoration. For a better understanding of some spectra acquired on red lakes, laboratory samples were prepared, using historical lake samples belonging to the collection of the Icrcpal chemistry laboratory or newly synthesized samples, on which spectroscopic analyses were performed. For the analysis of the purple substrate, FORS technique was also applied to originals and laboratory samples, in collaboration with the physics laboratory of the Institute.

Many questions were posed to the chemistry laboratory about the nature of the products applied by Leoni during the restoration, the composition of the pictorial palette used by the miniaturist(s) and the composition of the different inks present in the manuscript. The laboratory also had the task to provide scientific information that could help solve a problem of paramount historical importance. Some scholars[16] supposed that the illumination of Mark inspired by Sophia did not belong to the original manuscript, but could be dated to the twelfth century. The question needing an answer was whether the scientific tools could be useful to confirm or reject this hypothesis.

For clarity, each point will be discussed in a separate paragraph.

4.2.1 Materials used in the previous restoration (1917–19)

The first 20 pages of the codex show a clearly evident layer of an unknown material applied during the restoration performed by Nestore Leoni, who never revealed any details about the compounds he used, not even in the technical reports (conserved at the Archivio Centrale dello Stato, Rome, Italy) he had to present to the Ministry at the end of his work.

These materials deeply penetrated into the support, modifying its optical characteristics: the restored pages are now completely transparent and their colour is brown instead of purple. Sometimes the applied layer was partially detached.

When some regions of the applied layer were observed under the Raman microscope, some fibres were visible; from which spectra of cellulose were then collected. In the remaining part of the pellicle, both Raman and infrared analyses showed the spectrum of collagen. The analyses directly executed on other pages showed the presence of cellulose nitrate in some restricted areas, usually close to blue pigments. This lets us suppose that the first step of the restoration was an attempt to protect the more damaged pigments with cellulose nitrate.

The last 15 pages of the codex showed insect damage and extensive corrosion caused by the silver ink. Here the parchment pages were particularly fragile, and, instead of a gelatine layer, Leoni applied a fabric with a loose weave, crêpeline[17], made of silk, as confirmed by Raman. Results are shown in Fig. 7.

Between the end of the nineteenth century and the beginning of the twentieth century, three products were mainly used to reinforce damaged parchments:[18] gelatine mixed with formaldehyde, directly applied on the parchment or reinforced with Japanese paper; Archiv-Zapon (cellulose nitrate dissolved in amyl acetate with the addition of camphor or formaldehyde); and Cellit (cellulose acetate mixed with acetic ether, ethanol, acetic acid and camphor). No traces of cellulose acetate were found in the codex.

At that time, the mentioned methods were supposed to be safe and reversible, although many scholars had

16 Kresten, Prato 1985.

17 Anonymous 1900-1901.

18 Schill 1899; Frederking 1910; Casanova 1928.

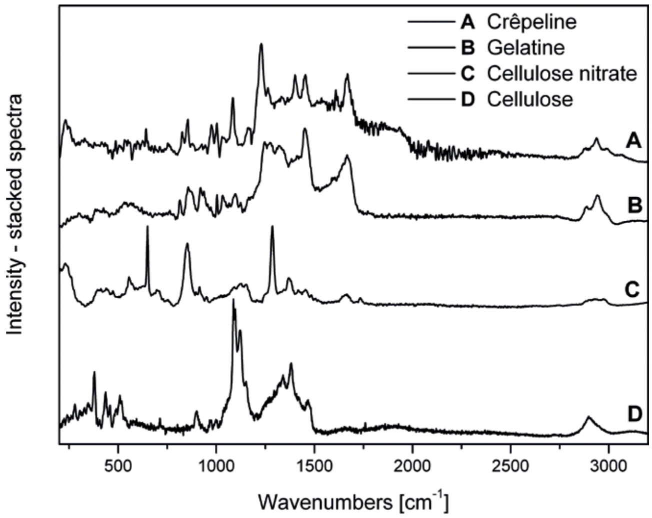


Fig. 7: Raman spectra collected from the materials applied in the previous restoration of the *Codex Rossanensis*. A: spectrum of silk (crêpeline) used in the last 15 pages of the codex; B: spectrum of gelatine applied as a thick layer to reinforce the parchment support; C: spectrum of cellulose nitrate found in restricted areas near the blue colours; D: spectrum of cellulose collected from fibres dispersed in the restoration layer.

already expressed doubts about their long-term effects. As an example of the debate, I have translated here the words of Eugenio Casanova,[19] concerning the use of gelatine. Casanova examines the restoration methods used in his time, which he was able to directly observe and record, thereby experiencing the underlying relative merits and defects of the various methodologies. In his description of the methods, Casanova expresses a strongly negative opinion about Marré gelatine, which gives documents a 'brilliant varnish', but in a short time leads to their total ruin:

> I am horrified at the thought that, if that bright patina is not removed soon, it will quickly destroy the manuscripts. It is, in fact, composed of siccative materials; under the influence of the temperature, this film cracks and detaches in pieces, at the same time removing fragments of the membrane to which it sticks. Using such gelatine simply adds more troubles to something that was already damaged.

Manifestly, Nestore Leoni, although aware of the debate, as evidenced by his preliminary reports (unpublished; conserved at the Archivio Centrale dello Stato, Rome, Italy), which he wrote to obtain the assignment of the restoration work, did not take into account the problem. The results are evident in

Table 1: Palette of the *Codex Rossanensis:* attribution to specific pigments/dye

Colour	Compound
Pictorial palette	
White	White lead [$2PbCO_3 \cdot Pb(OH)_2$]
Black	Carbon black [amorphous C]
Red	Red lead [$2PbO \cdot PbO_2$] Cinnabar [HgS]
Orange	Red lead mixed with goethite
Yellow	Goethite [α-$Fe^{3+}O(OH)$] Orpiment [As_2S_3]
Green	Goethite mixed with lapis lazuli Goethite mixed with indigo Orpiment mixed with indigo
Blue	Lapis lazuli [$Na_3Ca(Al_3Si_3O_{12})S$]
Indigo	Indigo[$C_{16}H_{10}N_2O_2$]
Violet	Red lead mixed with lapis lazuli Pink lake mixed with lapis lazuli
Pink	Red lead mixed with white lead
Mauve	Pink lake from *Sambucus Nigra* *
Gold	Gold [Au], traces of iron [Fe]
Writing inks	
Original black inks	Carbon black [C]
Black inks added on top of silver inks	Carbon black [C]
Posterior inks	Iron-gall inks [$C_{14}H_6O_{10}Fe_2$]
Silvery inks	Silver [Ag] as main component
Golden inks	Gold [Au] as main component
Purple dye	
Purple support	Purple lake from *Roccella Tinctoria* [mainly orcein** $C_{28}H_{24}N_2O_7$]

* The composition of the lake is very complex. No single formula can be attributed to the lake (European Medicines Agency 2013).

** Orcein comprises a mixture of three major chromophores: 7-hydroxy-phenoxazone, 7-aminophenoxazone and 7-aminophenoxazine (Elix 1996). Being an extract from lichen, lake can also contain other organic compounds, such as erythrolitmin, lecanoric acid, erythrolein, α,β,γ-amino orcein, hydroxyl orcein.

[19] 1908, 'Report to the Interior Minister' published by Spadaccini 2013.

the codex: huge and irreversible damage to the pages treated with products that irreversibly penetrated into the support, which had become transparent and brittle by aging. The main problem in the use of gelatine and cellulose nitrate is the transparency of the parchment support. These products migrate into the porous parchment structure, causing transparency; furthermore, the brittleness of the support correlates with the penetration of the these products into the parchment. Filling the air cavities in the collagen structure with polymers able to link with the collagen reduces the softness of the parchment, making it brittle.

4.2.2 The pictorial palette

Many colours are present in the precious manuscript, from white to black and passing through all possible hues of visible light. Moreover, gold and silver were used for the text of the Gospels, as well as black inks in the title, the explanations of the miniatures and in the posterior notes. Some parts of the faded text in silver were rewritten in black ink at an unknown time.[20]

Fortunately for the scientist in charge of the analyses, the miniaturist(s) did not finely grind the pigments used for the illuminations. That made it possible to collect individual Raman spectra from each pigment, even when applied in a mixture, thus aiding in the identification of the colouring substances. In some cases, XRF spectra were recorded to confirm the Raman attribution. For the organic dyes, lakes and purple, infrared technique was employed, being complementary to Raman. The black inks were analysed using the three cited techniques. No preparatory layer for the pigments (Armenian bole or lead white or gypsum) was present in the manuscript, though this was common in the Byzantine area where the codex was written and decorated. Table 1 summarizes the results of the analyses.

White lead was the unique source of white in the manuscript and was also used as heightening; carbon black was applied both as black colour and as a darkener for other pigments; minium for all red hues or in mixture with other pigments (Table 1) to obtain orange, pink and some violet tones. Only one exception needs to be mentioned: on page 241 (Mark the Evangelist and Sophia), cinnabar, an expensive mineral, was used to write the name of the Evangelist.

Throughout the whole manuscript, yellow areas were drawn with goethite, which was also applied mixed with blue to obtain green shades. There are only two occurrences of the use of another yellow. On pages 3 (The cleansing of the Temple) and 241 (Mark the Evangelist and Sophia), a dark green was obtained by mixing orpiment and indigo. The presence of arsenic in the pigment was confirmed by XRF.

No *true* green pigments, such as malachite, verdigris, copper resinate or green earths, were found in the manuscript; all the different greens were obtained by mixing blue and yellow.

Raman analyses showed the use of lapis lazuli and indigo for the light and dark blue areas, respectively.

Violet was obtained by mixing minium with lapis lazuli, sometimes with an addition of carbon black. For a brown-violet colour, goethite was mixed with carbon black and lapis lazuli.

No silver areas were found in the miniatures, whereas very pure gold was used in all the illuminations.

The mauve colour needed more complex work to be characterised: identical Raman spectra of an unknown organic compound were collected from all the illuminations drawn in mauve. Manifestly, the dye used was a lake; in fact, in the false colour images the mauve pigment acquired a yellow hue, typical of organic red lakes (inset in Fig. 8).

Identification of lakes with infrared spectroscopy is usually almost impossible, due to the very low concentration of the dye: the spectral features of the support – parchment or paper – dominate in the collected data. For the same reason, the direct Raman analysis of dyes and lakes is particularly difficult; moreover, these colourants are poor Raman scatterers. Usually, when molecular spectroscopies are chosen, the lakes are analysed by using SERS (Surface Enhanced Raman Spectroscopy), but this involves direct contact with the original work of art, which should be avoided. A detailed discussion of the differences between Raman and SERS spectra of lakes can be found in Bicchieri, as well as an analysis of the composition of *Sambucus Nigra* extracts.[21]

Even though the spectra of the original miniatures presented features that could correspond to an anthocyanic compound, it was decided to compare the original spectra with those obtained from some red and red-violet lakes prepared in the laboratory with different chromophores.

The chosen lakes contain as principal compounds: alizarin (*Rubia Tinctorum*), carminic acid (*Porphyrophora hamelii*),

[20] Bicchieri 2014.

[21] Bicchieri 2014

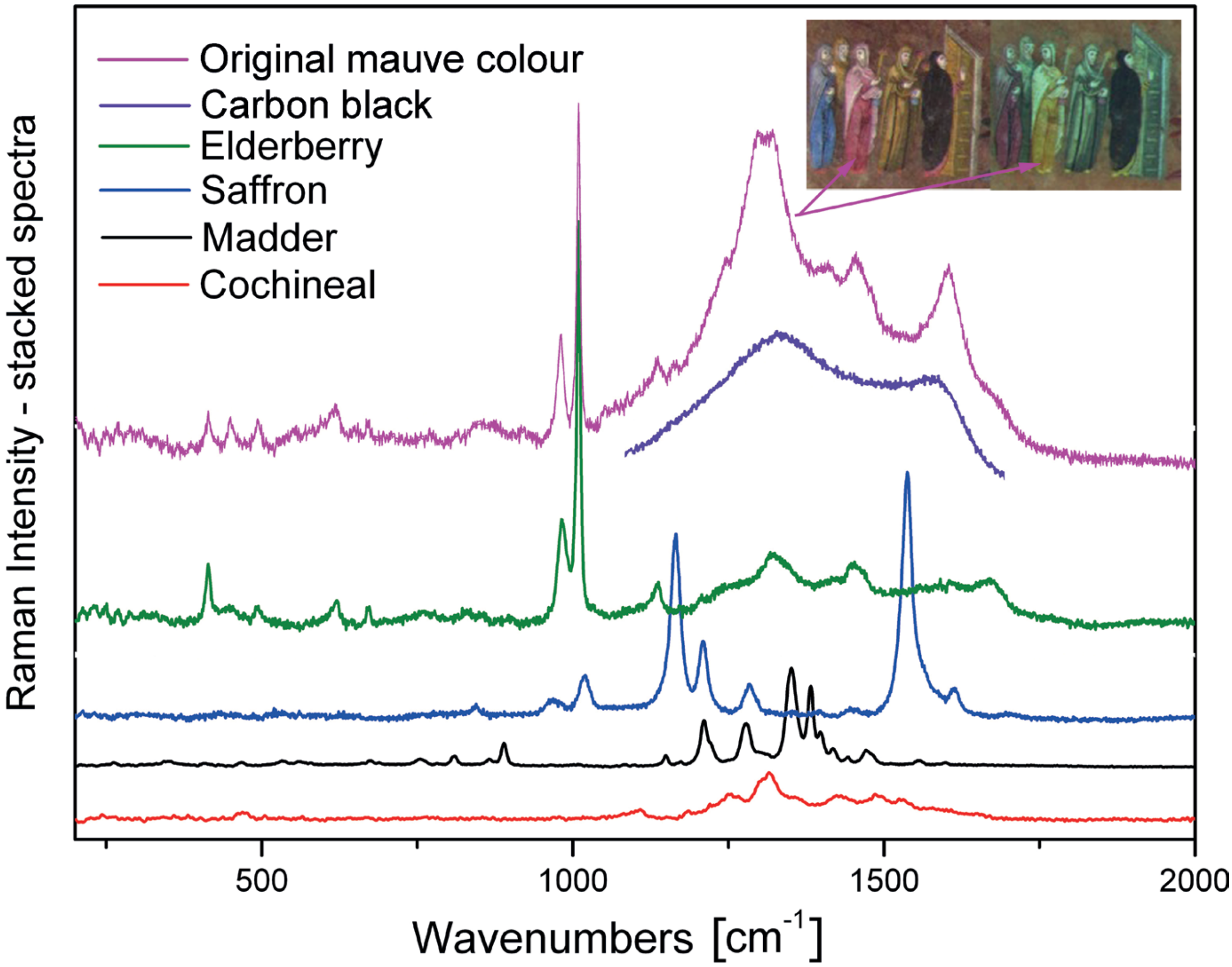


Fig. 8: Raman spectra of lakes (from bottom): cochineal (*Porphyrophora hamelii*), Madder (*Rubia Tinctorum*), Saffron (*Crocus Sativus*), (Carbon black), Elderberry (*Sambucus Nigra*), original mauve colour. Carbon black spectrum is reported to support the discussion in the text. The inset shows, marked with an arrow, the measurement point on the original (left) and the elaboration in false colours (right), courtesy of TEA s.a.s.

crocetin (*Crocus Sativus*) and anthocyanines (*Sambucus Nigra*).

Fig. 8 reports the Raman spectra of four laboratory samples compared with a typical spectrum collected from the original mauve areas. As can be seen, the best correlation was obtained for elderberry lake.

The differences between Raman spectra of the laboratory elderberry lake and the original mauve colour are due to the presence of a small amount of carbon black in the original lake that causes an enlargement of the bands in the 1200–1600 cm^{-1} region, as can be seen in Fig. 8, where the spectrum of carbon black is plotted only in the region where it shows characteristic bands. The two intense peaks at 981 and 1009 cm^{-1} in the elderberry lake are related to the presence of aluminium sulphate, necessary for its manufacturing.

To confirm the Raman data, FORS spectra (Fiber Optics Reflectance Spectra with a Zeiss MCS 600 spectrometer) were recorded from the original mauve colour and the prepared elderberry lake, in collaboration with the Physics Laboratory of Icrcpal.

There was a perfect concordance between the spectra. In the visible part of the spectrum, both show characteristic signals at 496, 524 and 564 nm, confirming the attribution of the mauve colour to elderberry lake.

4.2.3 Inks

All the black inks presented the characteristic Raman spectra of carbon black. Only the posterior comments to the text were written with iron-gall ink, detected by Raman and infrared and confirmed by the intense iron peak in XRF.

Table 2: (semi)quantitative calculation for the concentration of elements found in the silver-ink.

Element	Non-corroded ink (%)	Corroded ink (%)
Ag	69.83	69.79
Ca	28.64	28.11
Fe	0.23	0.64
Cu	1.11	1.16
Zn	---	0.22
Au	0.06	0.03
Pb	0.14	0.06

Table 3: Position of the characterising bands (nm) of original purple-dyed page, laboratory parchment sample dyed with orchil + sodium carbonate, and laboratory parchment sample dyed with orchil.

Sample	Peak 1	Peak 2	Correlation
original parchment	547.6 ± 0.4	594.6 ± 0.2	$R^2 = 0.999$ $\chi^2 = 3 \cdot 10^{-6}$
orchil + sodium carbonate	545.1 ± 0.8	592 ± 2	$R^2 = 0.995$ $\chi^2 = 7 \cdot 10^{-5}$
orchil	555 ± 2	589.6 ± 0.5	$R^2 = 0.998$ $\chi^2 = 2 \cdot 10^{-5}$

The golden ink had the same composition as the gold used for the illuminations. The gold was quite pure, containing only a small amount of iron.

The silver used for the text presented a different conservation state in the manuscript. XRF spectra (Fig. 9) showed that the silver had a different composition, in relation to its state of degradation, as can be seen in Table 2. It always contained copper, which is suspected to be responsible for the corrosion of the parchment substrate,[22] particularly evident in the last 15 pages that Leoni had reinforced with crêpeline.

A quantitative analysis of the XRF data, within the limitation of such a technique applied to thin supports, shows that the concentration of copper is not higher in the more corroded areas; but in these areas there is a greater amount of iron (about 3 times that found in the non-corroded regions), and zinc is also present. A more complicated degradation mechanism, involving contemporary redox reactions catalysed by iron and copper in the presence of zinc, should be imagined and investigated to understand the different behaviours of the two inks.

The presence of traces of gold (Au) is attributable to a contamination of the ink, whereas lead (Pb) and calcium (Ca) arise from the manufacture of the writing support.

4.2.4 Tyrian purple: truth or legend?

Scholars and art historians supposed that the parchment of such a precious manuscript must have been dyed with Tyrian purple (6,6'-dibromoindigo extracted from *Murex*), which is extremely expensive.

[22] van der Most et al. 2010.

XRF analyses did not reveal the presence of bromine, even after a prolonged acquisition time of 1 hour, suggesting the use of a dye other than Tyrian purple.

Raman spectra collected from many pages were of very low quality because they were affected by an intense fluorescent band that masked all Raman signals; and infrared spectra could not help characterise the dye, as they were dominated by the signals of the collagen substrate. Even FORS spectra collected from the Codex at the Icrcpal physics laboratory did not match those of Tyrian purple.[23]

A perfect match was found with the parchment samples dyed with orchil, prepared in the chemistry laboratory.

The deconvolution (Origin software, Gaussian multipeaks fit) of the region 500–700 nm allowed us to find the exact position of the bands for the analysed samples of parchment dyed with orchil, of those dyed with orchil and sodium carbonate and of the original parchment. The results are reported in Table 3.

The band positions reported in the literature for orchil are located at 549 and 595 nm and are in good agreement with the positions calculated for the original purple-dyed parchment and the parchment dyed with orchil with sodium carbonate added.[24] Pure orchil has a band position different from that found in the original parchment.

In a previous work carried out at the Icrcpal Chemistry Laboratory during the restoration of some pages of another

[23] Aceto et al. 2014a.

[24] Aceto et al. 2014 a.

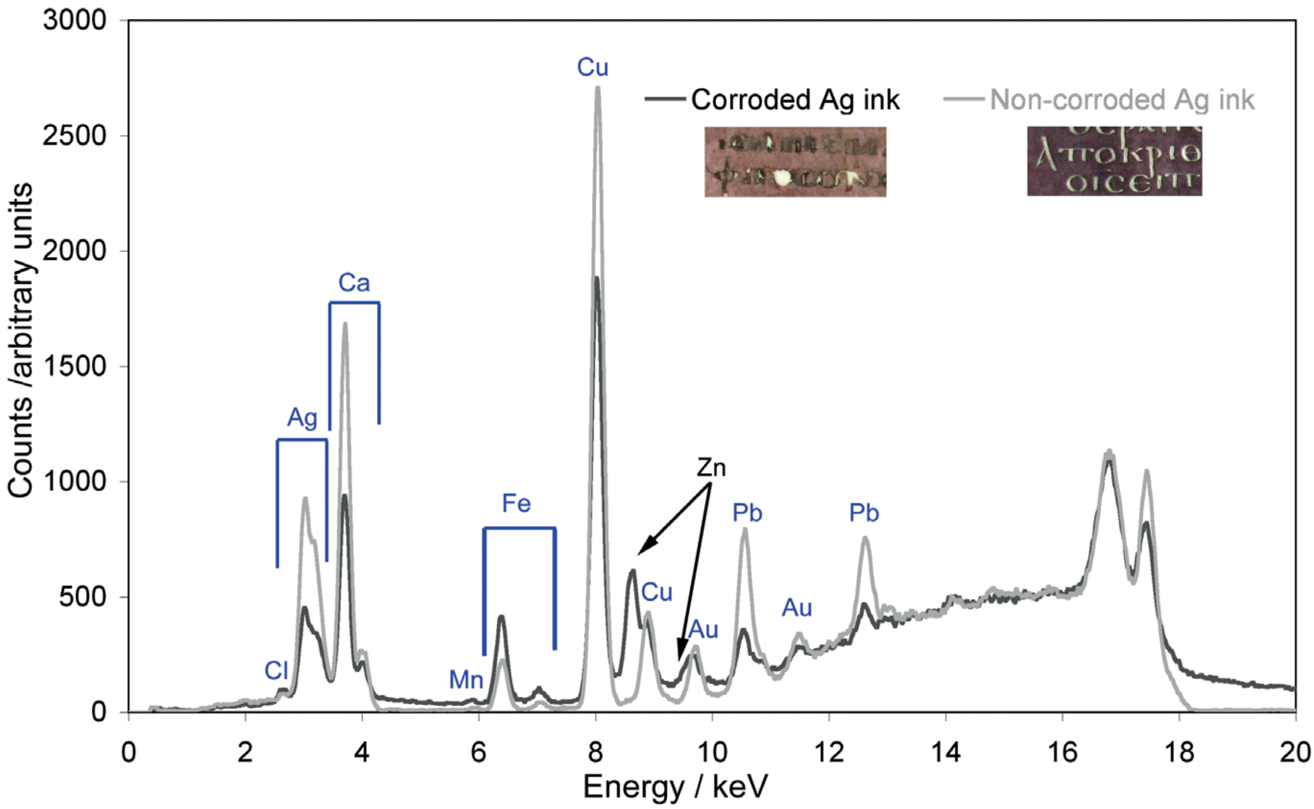


Fig. 9: XRF spectra of two different silver-inks. Black line: corroded. Gray line: non-corroded. In the figure the common elements are written in blue, whereas the element present only in the corroded areas is written in black.

purple codex, the *Sarezzano Codex* (fols 72ff., Tortona, Archivio Diocesano, fifth–sixth century), XRF showed a noticeable presence of bromine in the dyed parchment, but the infrared spectra did not show the typical features of 6,6'-dibromoindigo. In this case, Tyrian purple was not used to dye the parchment, as confirmed by the FORS analyses reported in.[25]

It seems indeed very important, from the historical point of view, to extend the analyses of purple codices, in order to elucidate whether a real Tyrian purple could have been used.

Until now, in fact, there is no evidence of its use for writing purposes.

In the case of the *Codex Rossanensis*, the positive synergy between all the different approaches allowed the complete characterisation of the manuscript, its dating (in particular on the basis of the biblical text) and the attribution of the discovered pictorial palette to a specific geographical area. Moreover, the chemistry laboratory was able to discover, replicate and characterize a peculiar lake, elderberry lake. To the author's knowledge, this was the first time that experimental evidence has been shown for the use of that lake in such an ancient document.

Furthermore, the characterisation of the illumination of Mark the Evangelist inspired by Sophia (p. 241) gave a scientific answer to the scholars who supposed that the illumination did not belong to the original manuscript, but could be dated to the twelfth century and realised with pigments different from those applied in the remaining manuscript. What differentiates such a miniature from the others present in the codex is that it maintains the freshness of the original colours, because it was not subjected to any previous invasive restoration.

All the experimental results show that the same palette was used throughout the entire codex. In particular, Raman and FORS results show the peculiar use of elderberry lake and of orpiment mixed with indigo to obtain, in the supposed posterior miniature, the precise shade of green, already found on page 3, that was considered original.

As a result of all the documented analyses, the findings of the historians and Bible scholars, the careful restoration and the valorisation, UNESCO has added the codex to the World Heritage List, and it is now conserved in the renewed Museo Diocesano di Rossano.

[25] Aceto et al. 2014 b.

5. Conclusions

The few examples presented in this paper allow us to draw some conclusions.

Methodologically, all problems related to cultural heritage artefacts must be addressed with a multidisciplinary approach that includes several and complementary techniques and competences.

It should also be emphasised that no single non-destructive technique can be claimed to be the 'resolving' one and that the cooperation between all the 'souls' involved in conservation, from scientists to humanists, can add important information to the knowledge of our history.

REFERENCES

Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Pietro Baraldi, Paolo Zannini, Christa Hofmann, and Ernst Gamillscheg, (2012), 'First analytical evidences of precious colourants on Mediterranean illuminated manuscripts', *Spectrochim Acta A*, 95: 235–245.

Aceto, Maurizio, Ambra Idone, Angelo Agostino, Gaia Fenoglio, Monica Gulmini, Pietro Baraldi, Fabrizio Crivello (2014a) 'Non-invasive investigation on a VI century purple codex from Brescia, Italy', *Spectrochim Acta A,* 117: 34–41.

Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Monica Gulmini, Pietro Baraldi, Fabrizio Crivello, and Cheryl Porter (2014b), 'On the colouring of purple codices'. <http://www.associazioneaiar.com/cms/sites/default/files/Extended_abs_2014/CeD_oral/Aceto%20et%20al.pdf> (last accessed 15 April 2018).

Anonymous (1900–1901), 'La conservazione dei manoscritti', *La Bibliofilia*, 2: 42.

De arte illuminandi e altri trattati sulla tecnica della miniatura medievale (1976), 'De clara ovorum et quomodo preparetur (rubr. XVI)', in Franco Brunello (ed.) (Vicenza: Neri Pozza), 94–97.

Bicchieri, Marina (2014), 'The purple Codex Rossanensis: spectroscopic characterization and first evidence of the use of the elderberry lake in a 6th century manuscript', *Environmental Science and Pollution Research*, 21.24: 14146–14157.

Bicchieri, Marina, Michele Nardone, and Armida Sodo (2000), 'Application of micro-Raman spectroscopy to the study of differently degraded papers', in *Proceedings of 2nd International Congress on Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin* (Parigi: Elsevier), 969–972.

Bisulca, Christina, Marcello Picollo, Mauro Bacci, and Diane Kunzelman (2008), 'UV-VIS-NIR reflectance spectroscopy of red lakes in paintings' in *Proceedings of the 9th International Conference on Non- destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage*. <http://www.ndt.net> (last accessed 15 April 2018).

Botti, Lorena, Daniele Ruggiero, and Maria Teresa Tanasi (2014), 'L'Autoritratto di Leonardo: imaging ed indagini FORS', in Maria Cristina Misiti (ed.), *I disegni di Leonardo: diagnostica, conservazione, tutela* (Livorno: Sillabe), 50–55.

Caffaro, Adriano (2004), *De Clare: Manuale medievale di tecnica della miniatura* (Salerno: Arci Postiglione), 16–102.

Caley, Earle Radcliffe (2008), *The Leyden and Stockholm Papyri Greco-Egyptian Chemical Documents From the Early 4th Century AD: An English Translation with Brief Notes* (Cincinnati, OH: University of Cincinnati).

Carriera, Rosalba (2005), *Maniere diverse per formare i colori*, in Manlio Brusatin, Vittorio Mandelli (eds) (Milan: Abscondita Srl), 13–14.

Casanova, Eugenio (1928), *Archivistica 2a edizione* (Siena: Stabilimento Arti Grafiche Lazzeri).

Coluzza, Carlo, Marina Bicchieri, Michela Monti, Giovanna Piantanida, and Armida Sodo (2008), 'Atomic force microscopy application for degradation diagnostics in library heritage', *Surface and Interface Analysis* 40.9: 1248–1253.

Elix, J. A. (1996), 'Biochemistry and secondary metabolites', in Thomas H. Nash III (ed.) *Lichen Biology*, (Cambridge: Cambridge University Press), 154–180.

European Medicines Agency (2013), *Assessment report on Sambucus nigra L., fructus*. <http://www.ema.europa.eu/docs/en_GB/document_library/Herbal_-_HMPC_assessment_report/2013/04/WC500142245.pdf> (last accessed 15 April 2018).

Frederking, Heinrich (1910), 'Zapon oder Cellit?', *Korrespondenzblatt des Gesamtvereins der deutschen Geschichts- und Altertumsvereine*, 58: 578–589.

Kresten, Otto, Giancarlo Prato (1985), 'Die Miniatur des Evangelisten Markus im *Codex Purpureus Rossanensis*: eine spätere Einfügung', *Römische historische Mitteilungen*, 27: 381–399.

Missori, Mauro, Lorenzo Teodonio (2014), 'Una nuova metodologia d'indagine per la carta antica: applicazione all'Autoritratto di Leonardo' in Maria Cristina Misiti (ed.), *I disegni di Leonardo: diagnostica, conservazione, tutela* (Livorno: Sillabe), 67–71.

Pascalicchio, Francesca (2014), 'La carta dell'Autoritratto: Osservazioni al macroscopio', in Maria Cristina Misiti (ed.), *I disegni di Leonardo: diagnostica, conservazione, tutela* (Livorno: Sillabe), 45–49.

Piantanida, Giovanna, Marina Bicchieri, and Carlo Coluzza (2005), 'Atomic Force Microscopy characterization of the ageing of pure cellulose', *Polymer,* 46.26: 12313–12321.

Piantanida, Giovanna, Flavia Pinzari, Mariasanta Montanari, Marina Bicchieri, and Carlo Coluzza (2006), 'Atomic force microscopy applied to the study of Whatman paper surface deteriorated by cellulosolytic filamentous fungus', *Macromolecular Symposia,* 238: 92–97

Pinzari, Flavia, Maria Carla Sclocchi, Piero Colaizzi, and Paola Valenti (2014), 'Indagini microbiologiche e microscopiche', in Maria Cristina Misiti (ed.), *I disegni di Leonardo: diagnostica, conservazione, tutela* (Livorno: Sillabe), 56–66.

Schill, Ernst Georg (1899), *Anleitung zur Erhaltung und Ausbesserung von Handschriften durch Zapon-Imprägnierung* (Dresden: Verlag des 'Apollo', F. Hoffmann).

Spadaccini, Roberta (2013), 'Il segreto del "restauratore di antichi documenti": Eugenio Casanova e Cristoforo Marino fra "specialità di arte" e restauro di Stato', in *Atti Accademia Pontaniana N.S.,* 60.63: 80–84.

van der Most, Peter, Peter Defize, and John Havermans (2010), 'Archives Damage Atlas'. <http://www.nationaalarchief.nl/sites/default/files/docs/nieuws/archives_damage_atlas.pdf> (last accessed 15 April 2018).

Article

Ink study of Herculaneum Papyri

Ana S. Leal, Silvia Romano, and Vito Mocella | Naples

In recent years, various studies have applied advanced techniques to explore the texts on rolled Herculaneum papyri.[1] Non-destructive technology such as X-ray Phase Contrast Tomography (XPCT) and 3D visualization software are applied to the extremely fragile carbonized Herculaneum papyrus scrolls to visualize the letters written in carbon-based ink. The radiation used by XPCT can penetrate through several windings and may reveal some letters in the dense structure of the charred papyrus without unwrapping and damaging the rolls. The results of these studies show that it is possible to visualize the internal structure of the carbonized Herculaneum papyrus, including the texture, shapes, damaged area, density and some contaminations of the fibres of papyrus sheets. In some cases, however, it is difficult to completely decipher the letters. Therefore, it is important to understand the contrast between the carbonized papyrus surface and the carbon-based ink, the composition of the ink used by the scribes and the concentration of the ink in each letter of the text.

One of the most valuable heritages in Naples, Italy is a collection of hundreds of papyrus scrolls, buried during the eruption of Mount Vesuvius in 79 CE and belonging to the only library passed on from Antiquity. This library was discovered between 1752 and 1754 in Herculaneum.[2] This inestimable treasure, which was discovered in a small room in a huge villa, comprises texts mainly concerning Epicurean philosophy. The scrolls were stored on shelves covering the walls of that room and are presently stored in the Officina dei Papiri section of the National Library of Naples.[3]

Over the years, curiosity and the inestimable value of the texts hidden in the carbonized scrolls have driven researchers to try to open the scrolls by various mechanical methods, which imposed physical stress on the structure of the fragile papyrus.[4] Among these methods, it is worthwhile to mention the Oslo method applied in the 1980s to two scrolls.[5] However, these mechanical techniques have been abandoned due to their low efficiency and in order to maintain and preserve the physical integrity of this important cultural heritage.[6] In recent years, with the progress of technology, some texts on unrolled fragments of the Herculaneum papyrus scrolls have been read using microscopes, digital photography (with multispectral filters) and multispectral techniques.[7] However, when applied to the rolled papyrus, the same techniques have failed because of the radiation's low capacity to penetrate several layers. Additionally, the level of carbonization makes it very difficult to distinguish the ink from the papyrus' supporting texture when using conventional X-ray source and techniques.[8]

Since Antiquity, the alphabetic writing process and the evolution of the chemical composition of the inks used were historical steps.[9] Pliny the Elder reports the use of carbon-based ink in his lifetime and described how it was obtained from residues of smoke from wood burnt in furnaces, without adding any metals.[10] Further, according to the literature, ancient Greek and Latin papyri may have been written using carbon-based ink until the fourth to fifth centuries CE.[11]

[1] Mocella et al. 2015, Seales and Delattre 2013.

[2] See the letter from Camillo Paderni to Dr Mead concerning the Antiquities dug up from the ancient Herculaneum, dated Naples, 18 November 1752;Paderni 1753. Also see Mocella et al. 2015; Tack et al. 2016; Mattus 2005.

[3] Mocella et al. 2015, Gigante 1979.

[4] Angeli 1994.

[5] Mocella et al. 2015, Delattre 2009.

[6] Mocella et al. 2015.

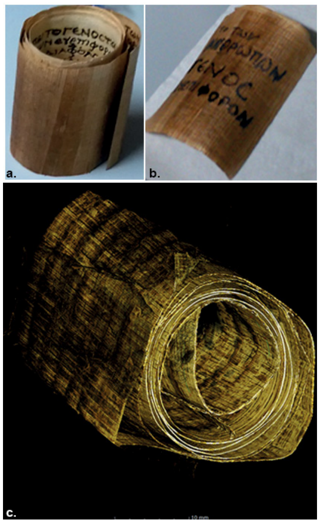
[7] Chabries et al. 2003.

[8] Mocella et al. 2015.

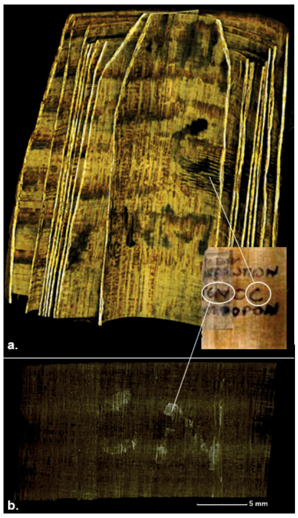
[9] Brun et al. 2016.

[10] *Natural History*, ed. Eichholz et al. 1938.

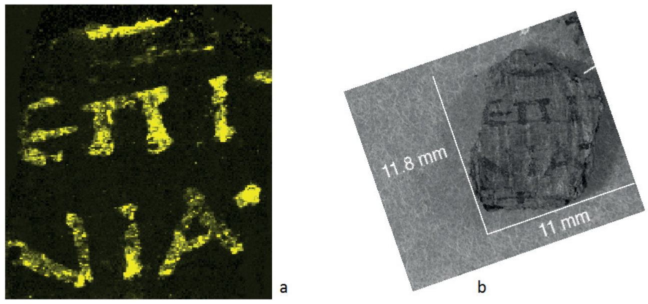
[11] Brun et al. 2016, Thompson 2007.



Figs 1a, b and c



Figs 2a and b



Figs 3a and b

Fig. 1: Pictures of phantom 1 (a) and phantom 2 (b) used for the study of the ink. Phantom 2 was placed within phantom 2, but only the ink with lead added was decipherable using XPCT + 3D visualization.

Fig. 2: Two portions of letters visualized by using VGStudio MAX 2.2 software. The large amount of ink with Pb is visible on the fibres of phantom 2 scroll. Letters with a greater concentration of Pb in the ink reflect more radiation.

Fig. 3: X-Ray Fluorescence map of Pb (a) perfectly matches the ink distribution of the visible photograph (b)

However, Brun et al.[12] recently showed that the ink of two Herculaneum fragments, Fig. 3, exhibits a high concentration of lead, which is deemed strong evidence that the lead was intentionally used in the ink on the Herculaneum papyri.

On the other hand, accordingly to Tack et al.,[13] lead could have been introduced unknowingly in different ways, for instance by the contamination of the water used as a solvent for the ink, or from the bronze container in which the ink was stored. It might also gave been introduced to the ink with the lead-based pigments galena (PbS), lead white (cerusite, $PbCO_3$, hydrocerusite ($2PbCO_3 \cdot Pb(OH)_2$) and/or minium ($Pb^{2+}_2Pb^{4+}O_4$). Furthermore, the lead could originate from a binding medium in the ink utilised as an agent to speed the process of drying, in the same way as for paintings. We can also surmise that lipid-based ink was used to draft the writing on papyri.[14] Knowing the chemical composition of the ink makes it possible to make a targeted choice of the imaging technique to be used or to optimize the selection of X-ray wavelengths used.[15] An additional difficulty is that the individual scribes made their own inks and variations in the materials can be expected.[16] A considerable amount of work has been done to enable the virtual unrolling and visualization of the ancient texts,[17] including X-ray computed tomography (XCT), which also finds many applications in medicine,[18] material science, palaeontology and archaeology.[19] However, XCT has some limitations when applied to the Herculaneum scrolls. Recently, Mocella et al.[20] discovered some letters inside a charred roll by applying XPCT to two of the six Herculaneum scrolls (one unrolled and the other still rolled), which were a 'gift' to Premier Consul Napoléon Bonaparte in 1802 and currently belong to the collection of the Institute de France. Phase contrast imaging technique exploits variations in the refractive indexes of structures that absorb quite uniformly within a composite object, thus significantly enhancing image contrast.[21] Moreover, according to the literature, XPCT shows suitability for discriminating

12 Brun et al. 2016.

13 Tack et al. 2016.

14 Tack et al. 2016.

15 Brun et al. 2016.

16 Brun et al. 2016.

17 Shutthanandan et al. 2008.

18 Allegra et al. 2015.

19 Mocella et. al. 2015.

20 Mocella et. al. 2015.

21 Mocella et. al. 2015.

among different materials of similar composition within a single object, as in the case of the black charcoal ink and carbonized papyrus.[22] The results of Mocella et al. show that XPCT is the first technique that enables us to read many Greek letters and some words on the rolled Herculaneum papyri without any physical damage.[23] These discoveries are very promising, but new experiments are needed to increase the image quality using future synchrotron beamlines with better coherence and other phase contrast techniques.[24]

On the other hand, there are doubts about the composition of the ink on the rolled Herculaneum papyrus, such as the possible addition of metal, i.e. the high concentration of lead found by Brun et al., as mentioned above.[25] The results of XPCT imaging of the rolled Herculaneum papyrus to decipher the letters are also unconfirmed. We studied two facsimiles (phantom) of Herculaneum papyrus made of modern materials – a present-day papyrus support and commercial ink. The virtual unrolling of the phantom was performed with advanced imaging software (VGStudio MAX). In the larger phantom (phantom 1), a black commercial Chinese ink was used to write a portion of text in the Greek alphabet, reproducing the ancient technique, Figure 1a. In the shorter phantom (phantom 2), Figure 1b, a blue commercial Chinese ink was used, to which lead(II) acetate was added. The text written with this ink used Greek letters, too. This blue ink was made with the aim of simulating the amount of lead found in the original Herculaneum papyrus studied by Brun et al. and Tack et al.[26] Phantom 2 was placed in phantom 1, Figure 1c, so that they looked like a single scroll. When XPCT + 3D visualization software was applied, the results from the phantom showed that it is possible to decipher the letters on the contemporaneous phantom 2, which is written with commercial ink with lead added. In Figures 2a and 2b, some letters were clearly visible.

The results show that more extensive research is needed to develop a method for virtually unrolling ancient carbonized papyrus scrolls using the experimental, non-destructive technique XPCT and the 3D visualization software to elucidate the contrast between the carbonized papyrus surface and the carbon-based ink, as well as the composition and concentration of ink, i.e. the question of the presence of lead (or other metals). Additional knowledge will make it possible to adapt future XPCT experiments specifically to Herculaneum scrolls.

22 Mocella et. al. 2015.

23 Mocella et. al. 2015.

24 Mocella et. al. 2015.

25 Brun et al. 2016.

26 Brun et al. 2016, Tack et al. 2016.

REFERENCES

Allegra, D., E. Ciliberto, P. Ciliberto, F. L. M. Milotta, G. Petrillo, F. Stanco, and C. Trombatore (2015), 'Virtual Unrolling Using X-ray Computed Tomography', *23rd European Signal Processing Conference (EUSIPCO)*. <doi:10.1109/EUSIPCO.2015.7362908>.

Angeli, A. (1994), 'Lo svolgimento dei papyri carbonizzati', *Papyrologica Lupiensi*, 3: 43–84.

Brun, E., M. Cotte, J. Wright, M. Ruat, P. Tack, L. Vincze, C. Ferrero, D. Delattre, and V. Mocella (2016), 'Revealing Metallic Ink in Herculaneum Papyri', *Proceedings of the National Academy of Sciences*, 14.113: 3751–3754.

Chabries, D. M., S. W. Booras, and G. H. Bearman (2003), 'Imaging the Past: Recent Applications of Multispectral Imaging Technology to Deciphering Manuscripts', *Antiquity*, 77: 359–372.

Delattre, D. (2009), 'Le point sur les travaux relatifs au P. Herc. Paris 2', *Comptes rendus des séances de l'Académie des Inscriptions et Belles-Lettres*, 152–153: 925–943.

Eichholz, D. E, W. H. S. Jones, and H. Rackham (eds) (1938), *Pliny the Elder*, *Natural History* (Cambridge, MA: Harvard University Press).

Gigante, M. (1979), *Catalogo dei Papiri Ercolanesi* (Naples: Bibliopolis).

Mattusch, C. C. (2005), *The Villa dei Papiri at Herculaneum: Life and Afterlife of a Sculpture Collection* (Los Angeles: J. Paul Getty Museum).

Mocella, V., E. Brun, C. Ferrero, and D. Delattre (2015), 'Revealing Letters in Rolled Herculaneum Papyri by X-ray Phase-contrast Imaging', *Nature Communications*, 6: 5895. <doi:10.1038/ncomms6895>.

Paderni, C. (1753), 'Extract of a Letter from Signor *Camillo Paderni*, to Dr *Mead*, concerning the Antiquities Dug up from the Ancient *Herculaneum*, Dated from *Naples*, Nov. 18, 1752', *Philosophical Transactions*, 48: 71–73.

Seales, W. B. and D. Delattre (2013), 'Virtual Unrolling of Carbonized Herculaneum Scrolls: Research Status (2007–2012)', *Cronache Ercolanesi,* 43: 191–208.

Shutthanandan, V., S. Thevuthasan, E. Iuliano, and W. B. Seales (2008), 'Pixe Analysis on an Ancient Scroll Sample', *International Journal of Pixe*, 18.3&4: 279–284.

Tack, P., M. Cotte, S. Bauters, E. Brun, D. Banerjee, W. Bras, C. Ferrero, D. Delattre, V. Mocella, and L. Vincze (2016), 'Tracking Ink Composition on Herculaneum Papyrus Scrolls: Quantification and Speciation of Lead by X-ray Based Techniques and Monte Carlo Simulations', *Scientific Reports*, 6: 20763. <doi:10.1038/srep20763>.

Thompson, E. M. (2007), *Handbook of Greek and Latin Paleography* (Whitefish, Mont.: Kessinger Publishing).

Article

The 'Decorative Style' Group of Byzantine Manuscripts Seen with Different Eyes: Initial Explorations, Further Thoughts, Implications and New Avenues for Research

Marina Toumpouri | Thessaloniki

Introduction

Losses of manuscripts over several centuries from natural disasters and accidents (fires, floods, liquidations, relocations of institutions or individuals, extinctions of monastic or parochial communities etc.), combined with the wide-scale systematic looting of mainly the religious institutions of the Eastern Mediterranean,[1] resulted in the deprivation of these institutions' patrimony as well as their intellectual and cultural property. Another, equally important consequence of the destruction or dispersion of libraries and the often wide geographical scattering of their holdings was the loss of a body of indirect evidence concerning the identity, interests and practices of their owners, as well as the network of their relationships, the way they were transmitted from one place to the other, the significance of acquiring and/or collecting books and, more generally, the history of libraries and archives.

The fate of the manuscript heritage of the island of Cyprus does not present a significantly diversified picture, since events such as the fleeing of the nobility and members of the clergy after the change of political systems,[2] catastrophic fires[3] and the sacking of the major cities and religious institutions[4] reduced the number of volumes significantly. Finally, the estimated small portion of manuscripts – compared to what once existed – that survived the accidents of history and was still found on the island was transferred massively to the West by the acquisition missions in the Levant that were organized by zealous collectors.[5] It is, however, necessary to signal that during the medieval period Cyprus was never a prominent learning or literary centre.[6] Being the eastern frontier of the Byzantine Empire and later the eastern sea border between the Christian and Muslim worlds, it rather played a central role in military and commercial matters in the

[1] Constantinides and Browning 1993, 23–28.

[2] The mediaeval history of Cyprus covers four periods, i.e. the period of the Arab raids (from the seventh to the tenth century); the Byzantine period (965–1191); the Frankish era (1192–1489); and the period of Venetian rule (1489–1571), which ends with the conquest of the island by the Ottomans in 1571. Examples of manuscripts that were moved out of Cyprus with their owners are: Vatican, Biblioteca Apostolica Vaticana, gr. 1231, which belonged to the Dukas of Cyprus Leon Nikerites who later transferred it to Constantinople. In 1470, the manuscript came into the possession of Anna Notara, daughter of Loukas Notaras, last Megas Dukas of the Byzantine Empire (fol. 456v: dated ownership entry); Vatican, Biblioteca Apostolica Vaticana gr. 1158 and gr. 1208 were offered by Queen Charlotte de Lusignan (reg. 1458–1475) to Pope Innocent VIII. Charlotte moved to the court of Savoy after her second marriage (1459), to Louis de Savoie, and following the deprivation of her throne in 1463, which was preceded by her three-year blockade in the castle of Kyrenia by her brother James II. The bilingual (Greek-Latin) manuscript Berlin, Kupferstichkabinett, 78.A.9 (also known as the Hamilton Psalter) also belonged to Charlotte.

[3] For instance, the royal and stavropegic monasteries of the Virgin of Machairas and Kykkos were completely destroyed by fires, the first in 1530 and in 1892 and the second four times, in 1365, 1542, 1751 and 1813. Both monasteries were patronized by the members of the secular ruling elites of the island and received grants from the Byzantine emperors. It is most probable that they possessed a large number of manuscripts. See: Constantinides, and Browning 1993, 37. In the case of the monastery of Machairas, the Greek scholar C. Papadopoulos, who visited it in 1890, signalled the necessity to prepare a catalogue of its important holdings, which included manuscripts, chrysobulls and archival material. See: Papadopoulos 1890, 315.

[4] For instance, the Monastery of Stavrovouni was taken over by Benedictine monks when Cyprus became a Frankish kingdom. It was also looted by the Mamelukes in 1426, like many other Orthodox and Catholic monasteries. For the monastery of Stavrovouni, see: De Mas Latrie 1852, 512. More generally on the looting of the Cypriot monasteries, see: Papadopoulos 1995, 644.

[5] Such missions were organized by Nicolas-Claude Fabri de Peiresc (1580–1637); Cardinal Mazarin (1602–1661), le Chancelier Séguier (1643–1663), the king of France (1671–1675) and Jean-Baptiste Colbert (1619–1683). See: Constantinides and Browning 1993, 23–27.

[6] Constantinides 1982, 25; Constantinides and Browning 1993, 5–13; Galatariotou 2004, 157–163; Grivaud 2005, 221.

region.[7] Excellence in education and the flourishing of the sciences and the letters were never among the priorities of the rulers of Cyprus.[8] This fact, combined with the worldwide scattering of the manuscripts, the absence of catalogues of Cypriot manuscript collections and the inaccessibility of the island during the period of Ottoman rule (1571–1878), significantly retarded any scholarly interest in the manuscript culture of the island, while it also led to continuing losses of evidence. Efforts in this direction are relatively recent. Combined with the vastness of the indirect sources and the variety of evidence that has to be gathered,[9] our knowledge of specific production centres and practices as well as of the book collections of individuals and institutions is still limited.

The 'decorative style' group of manuscripts is a notable exception. The items in this group – over one hundred fifteen deluxe illuminated manuscripts – have come to be connected to Cyprus, or more precisely, to a broader geographic area that comprises also Palestine, Syria and even Egypt. They were either produced there or their history of ownership and transmission indicates that they belonged to local institutions or individuals originating from or residing in the region, either permanently or for shorter periods.

Research on the 'decorative style' group has revealed a multifaceted and complex picture of production, while hypotheses and assumptions about the time span and locality of production, as well as about interrelationships between its members, have changed over time, emphasizing the necessity to address the same issues with new methods. This group and the questions it addresses in fact advocate for the application of a holistic approach integrating different methods and areas of research. This paper will present some preliminary thoughts and new insights that led to the pilot experiments of the exploratory phase of the study of the 'decorative style', which will be discussed in conjunction with opportunities and strategies for future research.[10]

1. The 'decorative style' group of manuscripts: the corpus and its historiography

The twelfth and thirteenth century group consists today of some one hundred fifteen manuscripts. It was given the name 'decorative style' based on the stylistic features of their illumination (decoration and miniatures).[11] It is in fact almost all that is known of Byzantine illuminated manuscript production in the twelfth century and the only group of deluxe Greek manuscripts from the first half of the thirteenth century.[12]

It is notable that, though service books were the ones usually receiving illumination, they are a minority in the case of the 'decorative style' group, given that they account for just less than ten per cent of the whole (four Gospel Lectionaries,[13] five *Menaia* and one *Octoechos*).[14] The number of the Tetraevangelia is much larger (seventy), followed by the Psalters (thirteen), the volumes combining New Testament and Psalter (seven), the Gospel Lectionaries (four), the copies of the Book of Job with *catenae* (four) and the complete Old Testament in four volumes (one set). Moreover, throughout the non-liturgical manuscripts the liturgical equipment, the section and the canon numbers are insufficient and inconsistent, while the deficiency and sometimes even emptiness of the canon tables contrasts with their profuse illumination.[15]

---

[7] Galatariotou 2004, 40–67; Grivaud 2012, 182–189; Malamut 2012, 98–100.

[8] Further investigation is needed to complete our knowledge of textual production in Cyprus. It should therefore be noted that literary, scientific and legal texts were produced. See, for instance: Grivaud 2005, 219–284; Malamut 2012, 102.

[9] The evidence used in tracking the ownership of manuscripts produced in or associated with Cyprus is quite varied. It comes from inscriptions, catalogue records, sales catalogues, the association between scribal hands, stylistic evidence etc.

[10] The exploratory phase of the project conducted on the manuscripts of the 'decorative style' was planned and led by Dr Marina Toumpouri within the framework of STAR-Lab project (ΝΕΑ ΥΠΟΔΟΜΗ/ΣΤΡΑΤΗ/0308/30), co-financed by the European Regional Development Fund and the Republic of Cyprus through the Research Promotion Foundation.

[11] Weyl Carr 1982, 39–81.

[12] Maxwell 2014, 11.

[13] Gospel Lectionaries and Tetraevangelia are two modalities of the four canonical Gospels. The Tetraevangelion contains the Gospels in their traditional order (Matthew, Mark, Luke and John). A Gospel lectionary is a recomposed Tetraevangelion. It contains lessons for the ensemble of the days of the ecclesiastical year. More precisely, it comprises the four Gospels in the form of lessons organised in two series of readings. The first is arranged according to the movable structure of the Byzantine calendar. The second follows the fixed structure of the Byzantine calendar. The Gospel lectionaries can also include readings for particular occasions and commemorations.

[14] Weyl Carr 1987, 1–2.

[15] Weyl Carr 1987, 1–2; Weyl Carr 1988–1989, 126.

Palaeographically, the group adheres to the 'style epsilon à pseudo-ligatures basses' defined by Paul Canart.[16] It embraces both of the style's modes, the diminutive and cursive called 'epsilon arrondi' and the bold, blocky and more angular one called 'epsilon rectangulaire'.[17] The script distinguished also by the use of a deep black ink is characterized by its impetuous ductus, the high proportion of uncials, a large variation in letter forms and sizes and the interplay between small regular forms and considerably enlarged letters or combinations of letters and ligatures[18].

Among its key features is the *mise-en-page*, seen especially well in the case of the openings of the Gospels. This is characterized by the presence of full-page author portraits preceding each Gospel; the carpet headpieces filled with vigorous lattice, palmette and vine scroll patterns; the titles below the headpieces with the sonorous majuscule letters written with a dark red ink; and the animated or ornate initials found below the titles.[19] The same dark red ink carries over into the text. The opening verses, the initials and the liturgical equipment found in the margins all over the manuscripts were also written with this ink.[20]

From a codicological viewpoint, the manuscripts are composed of a thick, rather heavy parchment.[21] The quires that make up the books are usually quaternions. They were often modified, however, to permit the beginning of a new text and/or of a major text division to coincide with the beginning of the gathering.[22] Full-page miniatures were painted on inserted single folia or bifolia some of which are purple-tinted.[23] The beginnings of the quires were designated by a number found in the upper corner of the first folio (recto), occasionally in addition to or replaced by a dagger in the middle of the upper margin of the same first folio.[24]

The artistic character of the manuscripts confirms the coherence of the group. Stylistically it is characterized by lavish miniatures coloured in dark red, pink, green and blue, the same tones used for the decorative elements on the openings of the Gospels.[25] The decorative method of the composition of the miniatures also defines the group. It is seen in particular in the case of the full-page portraits of the Evangelists. The big, centrally placed figures with strong contours are depicted in profile view. They are surrounded by ornate furniture and architecture painted on the same surface plane. As a result, they are all compressed into a decorative pattern fusing figure and setting on the same plane.[26]

The group's membership grew significantly compared with when a group of New Testament text criticism scholars and art historians initially identified it in the early 1930s. It then comprised only thirteen manuscripts[27] coalesced around Gregory's 'codex 2400',[28] whose palaeographic, stylistic, iconographic and decorative features turned out to characterize a larger group of manuscripts, dubbed 'Family 2400'.[29] The conjunction of these identifiable features in so many illuminated manuscripts led to the ascription of the initial cluster to imperial origin and a single workshop, presumably one active in the capital, after its recovery in 1261.[30] Even though palaeographic and iconographic

[16] Canart 1981, 17–76; Canart 1988–1989, 33–36.

[17] On the differentiation between the two modes, see: Canart 1981, 17–76; Canart 1988–1989, 33–36.

[18] Canart 1981, 17–76; Canart 1988–1989, 33–36.

[19] Weyl Carr 1987, 3.

[20] Weyl Carr 1987, 3.

[21] Weyl Carr 1987, 2.

[22] Weyl Carr 1987, 2.

[23] Purple-tinted parchment can be found in: Paris, Bibliothèque Nationale de France, sup. gr. 1335; Jerusalem, Greek Orthodox Patriarchate, Taphou 47; Athos, Monastery of Dionysiou, 12; London, British Library, Add. 37002; Saint Petersburg, State Public Library, gr. 644; Moscow, State Historical Museum, Mus. 3646; Oxford, Bodleian Library, Auct. T.5.34; Münster, Bibelmuseum, gr. 10; and probably Athos, Monastery of Stavronikita, 56. See: Weyl Carr 1987, 143.

[24] Weyl Carr 1987, 2.

[25] Weyl Carr 1987, 4.

[26] Weyl Carr 1987, 4.

[27] The initial identification of the group was done by Goodspeed et al. 1932, 30. The list of manuscripts, however, was first presented in: Colwell and Willoughby 1936, vol 2., 4. For a list of the manuscripts included initially in the group, see: Weyl Carr 1987, 156.

[28] Now Chicago, University Library, 965. The manuscript was named 'codex 2400' after its number in Gregory's standard listing of New Testament texts. It is also known as the 'Rockefeller McCormick New Testament', since Edith Rockefeller McCormick purchased it in 1928 for the University of Chicago. Weyl Carr 1973, 1–3.

[29] The title was introduced by Willoughby in 1940–1941, 126–132.

[30] It was suggested that the workshop in question was set up by Michael VIII Palaeologus somewhere between 1261 and 1269 in the imperial palace, after the Byzantines regained control of Constantinople and as a result of the re-establishment of the court. On the evidence on which this attribution was supported, see: Weyl Carr 1973, 11–13. On whether or not the manuscripts of the 'decorative style' group were the products of a workshop, see: Dufrenne 1981, 450–451.

comparisons with dated works from the second half of the thirteenth century were seen to confirm the early Palaeologan[31] dating, this attribution was stylistically problematic.[32] As an alternative place of production, Der Nersessian then proposed post-conquest Lascarid Nicaea, which served as the functional capital of the Empire from 1204 until the recovery of Constantinople.[33] This new attribution yielded the group's famous name 'School of Nicaea' which allowed, above all, the option for an earlier date, i.e. the first half of the thirteenth century, that could better explain the stylistic incompatibility of the group's illuminations with the early Palaeologan works.[34] The title was upheld in the catalogue that accompanied the 1964 exhibition of the Council of Europe in Athens, which focused particular attention on the group, which numbered almost forty manuscripts by then.[35]

The group continued to expand, and by the early 1970s it consisted of over sixty manuscripts.[36] With this significant growth, the character of the group and the problems posed were no longer the same. More reliable inscriptions, notably a number of dated ones, replaced the evidence provided by the initial cluster by pushing a portion of the group back to the second half of the twelfth century.[37] As a consequence, this date severed the bond with the Nicaean attribution, or at least the Nicaean origin of the group.[38] It also disproved its imperial origin, since the well-documented metropolitan illumination of the second half of the twelfth century differs significantly.[39] Moreover, the label 'School' was no longer suitable, since the group was too large and its members clearly gathered into interrelated but distinguishable groups with significant differences in quality, each with its own stylistic traits, iconographic patterns and palaeographic variations.[40] It was not clear whether these differences were due to the territorial diffusion of the group, its chronological duration, the means of its dissemination or the source of its unifying features.[41] The descriptive, more flexible title by which the group is still known today, i.e. the 'decorative style', replaced the name 'School of Nicaea', since many problems have yet to be solved before its historical place is understood and, consequently, a firm historical title can be established.[42]

By 1987, when Annemarie Weyl Carr published her monograph, the group's membership had almost doubled, since the list of manuscripts under consideration then comprised one hundred eight items.[43] This was in fact the first effort to consider the group as a whole. It was based on the classification of the manuscripts into three groups and, within them, eight subgroups,[44] based on the study of their iconography and style. The four major questions addressed were: i. the kinds and degrees of kinships existing among the members of each subgroup, as well as the character and strength of the qualities uniting the subgroups; ii. the chronological relation of subgroup to subgroup embracing the duration of the whole group and the distribution of each manuscript within that span; iii. the clientele to which this production was addressed; and, iv. the range of territory within which the decorative style was practiced.[45] Weyl Carr concluded that the group constitutes the only provincial manuscript tradition with a century's duration (1150–1250), whose coherence emanates from the comprehensive characteristics embracing the ensemble of its members. Yet, rather than a single scriptorium, she put forward that the pattern of production emerging is a more complex and unstable one, allowing for constantly

---

31 The Byzantine Empire was ruled by the Palaeologoi dynasty from 1261 to 1453. The artistic production of that period is therefore referred to as Palaeologan. The 'early Palaeologan period' spans from 1261 to 1300.

32 Weyl Carr 1973, 11–15; Weyl Carr 1987, 4.

33 Der Nersessian 1936, xxvi–xxxvi (Introduction).

34 An attribution to the first half of the thirteenth century was also defended by Buchthal 1964, 224. On this attribution, see also: Weyl Carr 1973, 14; Weyl Carr 1982, 40.

35 The Council of Europe's exhibition in Athens was accompanied by a catalogue. See in particular the entries Nos. 295, 298, 299, 300, 323, 341 and 348 of the catalogue *Byzantine Art, An European Art*.

36 Weyl Carr 1973; Weyl Carr 1987, 4–5.

37 Weyl Carr 1973, 21–22; Weyl Carr 1987, 5.

38 Weyl Carr 1973, 22–24; Weyl Carr 1987, 5.

39 Weyl Carr 1987, 5.

40 Weyl Carr 1973, 35; Weyl Carr 1982, 41; Weyl Carr 1987, 5.

41 Weyl Carr 1982, 41; Weyl Carr 1987.

42 Weyl Carr 1987, p. 5; Weyl Carr 1988–1989, 124.

43 The list of manuscripts can be found in: Weyl Carr 1987, 184–290.

44 I. The Initial group (a. the Chicago subgroup; b. the Taphou subgroup; c. the London subgroup); II. The Central group (a. the Ludwig subgroup; b. the Harley subgroup; c. the Seraglio subgroup); III. The Late group (a. the Dionysiou and Berlin subgroup; b. the Interregnum subgroup). See: Weyl Carr 1987.

45 Weyl Carr 1987, 6–10.

varying collaborations between scribes, illuminators and patrons. The territorial diffusion of such a large group, however, appears to be limited to the region of the Eastern Mediterranean, and more precisely, Cyprus and Palestine, which assumed importance following the Crusader conquest of Jerusalem. The availability of patrons and resources due to the Comnenian involvement in the region were indicated as the conditions conducive to the expansion of production of luxury illuminated manuscripts oriented towards private consumption.[46]

Weyl Carr's subsequent contributions reaffirmed the likelihood of the Cypro-Palestinian origin of the group. They furthermore provided additional insights into the milieu of production of the manuscripts of the group, the kinships of the group with contemporary Constantinopolitan and Levantine – mainly Cypriot, Cilician Armenian and Syro-Palestinian – comparanda (manuscript, mural and panel painting) and those between groups and subgroups[47].

2. Verifying Weyl Carr's conclusions: the contribution of the textual evidence

Although few if any Byzantine groups of illuminated manuscripts have been so extensively studied, the outline of the scholarship that dealt with this group indicates clearly the complexity of the interrelationships of the members of the group. But above all, it bespeaks the limitations of traditional methodologies in providing, if not definite answers, at least more objective and reliable qualitative and quantitative evidence that could shed further light on or at least open up discussion about the relationships of the manuscripts, as well as various matters relevant to their production.[48]

Recognizing the necessity to provide new unbiased and objective knowledge, the most recent inquiries into the manuscripts of the 'decorative style', undertaken almost concurrently, were the first attempts to verify Weyl Carr's conclusions by applying automated text analysis.[49] Their aim was to observe from a text-critical approach the questions addressed by Weyl Carr, in an effort to shed light on issues of kinship between single manuscripts and groups and relations between scribes and illuminators and to clarify whether the manuscripts of the group represent a textual tradition that could be defined as provincial. The overall conclusion was that, despite ornamental, scribal and stylistic ties between the manuscripts of the different subgroups, these connections could not be confirmed in most of the cases, suggesting that the boundaries of the subgroups are blurred.[50] It was also revealed that the manuscripts of the group continued to be used as textual exemplars, long after the assumed demise of the 'decorative style' around ca. 1260.[51] This was hardly a surprising discovery, since the chronology of the group had previously been challenged, in consequence of the emergence of new dated manuscripts from the end of the thirteenth century that fit squarely into the conceptual scheme of the 'decorative style'.[52] The most interesting outcome, however, was that certain of the manuscripts demonstrate compelling textual affinities with deluxe Constantinopolitan products, suggesting that, in spite of their provincial script, ornamentation and miniatures the members of the group may be more integral to Byzantine mainstream manuscript production than Weyl Carr thought.[53]

[46] Weyl Carr 1987, 142–154 (Conclusions).

[47] Weyl Carr 1988–1989; Weyl Carr 1989; Weyl Carr 1991a; Weyl Carr 1991b; Weyl Carr 1993; Weyl Carr 2012.

[48] On a number of questions that the 'decorative style' group addresses, see also: Fonkič 1980–1982, 108–112.

[49] Langford 2009; Maxwell 2014, 11–38; Maxwell 2016, 33–34. They were of course subsequent to the pioneer work of the Chicago University scholars, Goodspeed, Riddle, and Willoughby 1932; Colwell and Willoughby 1936, which dealt with the text of the initial thirteen members of the group.

[50] Langford 2009, 158–161; Maxwell 2014, 11–38; Maxwell 2016, 33 and 57. The necessity to reassess Weyl Carr's groupings was also pointed out in: Canart 1988–1989, 35.

[51] It is assumed that at least for two centuries the manuscripts of the group continued to serve as exemplars. See: Maxwell 2014, 35. In an analogous manner, the 'style epsilon' script seems to survive until the end of the thirteenth century. See: Canart 1988–1989, 38.

[52] This is for example the case of Sofia, Centre Ivan Dujčev, gr. 339 (olim. Drama, Monastery of Eikosifinissa, 219). It contains the date 1285 on fol. 307v. On this manuscript, see: Džurova 2002, 179; Džurova 2008, 283–291. It is expected that the attribution of further manuscripts to the group will continue since manuscripts or important repositories still remain inaccessible, or because, a catalogue of the manuscripts they hold was not published. In fact, several manuscripts were discovered after the publication of Weyl Carr's monograph in 1987. Such is the case of Paris, Bibliothèque Nationale de France, gr. 88; or, of the most recently discovered one: Athens, Benaki Museum, 2. See: Maxwell 2014, 10.

[53] Maxwell 2014, 35–36. Constantinople has been suggested as a more plausible place of execution of a number of manuscripts. For example, see: Marinis 2004, 284. The exhibition catalogue entry in question deals with Malibu, The J. Paul Getty Museum, Ludwig II.5, a manuscript of very high quality. Indicatively, Weyl Carr characterized the portraits of the Evangelists as 'definitive monuments of the decorative style'. See: Weyl Carr 1987, 44.

3. New approaches and new tools: some preliminary results and future prospects

With the aim to overcome the conspicuous absence of evidence about the production circumstances of the 'decorative style' group, a holistic approach was envisaged, combining traditional arts and humanities methodologies with advanced scientific analyses to obtain new, otherwise inaccessible data preserved in the different components of the manuscripts.[54] Two main directions of research were thus chosen: i. material analyses; and, ii. document image analyses. Given that the two approaches do not contrast with, but complement each other; this was considered essential to unfold the full interpretative potential of the material under investigation.

As already mentioned, the research group addresses a wide range of questions such as: the organisation of production, the materials' procurement and the identification of chronological changes in the overall patterns of production, provenance determination and consumption patterns.[55] This initial stage of inquiry was not expected to provide answers to the aforementioned questions. The general objectives of this exploratory work were: i. to establish the foundations for the multidisciplinary range of approaches and techniques intended to be subsequently applied; ii. to initiate the creation of a corpus of new and original data, which would include both archaeological information (i.e. on material and codicological aspects of the manuscripts) and analytical information, which was expected to expand through time; iii. to generate new assumptions and ideas; iv. to develop new hypotheses; v. to determine the feasibility of the study of the group in the future; and vi. to refine specific questions for a further and more systematic investigation.

The design and piloting of the documentation process was unprecedented and fundamental. A model was thus created, including all the characteristics of a manuscript, which can provide information about the types of materials, procurement and manufacturing processes at a macroscopic and a microscopic level. They were organized in series that could also facilitate recording information at every following stage of the work. Table 1 shows two sections of the documentation model in question.[56]

Due to the exploratory character of the study, it concentrated mainly on five purposefully selected manuscripts[57] still located in Cyprus.[58] The ensuing paragraphs are therefore intended to raise a number of questions generated by the knowledge recently acquired[59] that will hopefully be refined by future work on the manuscripts of the 'decorative style', as well as on items outside the group comparatively studied, with the aim to extend their meaning and interpretative value. A variety of analytical techniques, i.e. digital microscopy, FORS, XRF and FTIR, were applied to examine the parchment's preparation and to identify the inks and pigments used. Multispectral imaging was employed as a complementary and, in some cases, as an alternative technique. Biomolecular information was also recovered from the parchment folios of the manuscripts to identify the species of the animals used for their confection.[60] Interesting

[54] It has to be noted that analytical investigation was previously undertaken in the case of two manuscripts belonging to the 'decorative style' group. The two manuscripts, belonging to Russian libraries, are: Saint Petersburg, State Public Library, gr. 105 and Moscow, State Public Library, F181, gr. 9. See: Mokretsova 2003, 279–281.

[55] One has to signal the lack of Byzantine compilations of and treatises on art technology. In a recent publication, a large number of texts treating relevant issues were edited and commented. See: Schreiner and Oltrogge 2011.

[56] For purposes of brevity, only an abridged version of the parchment and ink sections of the documentation model prepared were included here. The complete documentation model will be made available in a forthcoming publication.

[57] The selected manuscripts were: Paphos, Museum of the Monastery of Kykkos, Ms. R8; Paphos, Museum of the Monastery of Kykkos, liturgical scroll; Paphos, Monastery of Saint Neophytos, Ms. 11 (unfinished manuscript); Paphos, Monastery of Saint Neophytos, Ms. 12; Paphos, Monastery of Saint Neophytos, Ms. 31. Although impossible to confirm given the absence of substantial evidence, the place of origin of the manuscripts studied could be Cyprus or the broader Eastern Mediterranean region. The presumed dates of creation of all the manuscripts in question fall within the chronological limits of the 'decorative style' group. Finally, two of the manuscripts studied were attributed to the group, i.e. Paphos, Museum of the Monastery of Kykkos, Ms. R8; and, Paphos, Monastery of Saint Neophytos, Ms. 11. On their attribution to the group, see Weyl Carr 1993; Constantinides 1988–1989.

[58] I would like to acknowledge Father Neophytos Enkleistriotis, librarian of the Monastery of Saint Neophytos and Stylianos Perdikis, Director of the Museum of Kykkos, for their help and cooperation. Additional thanks go to Leontios, Bishop of Chytroi and Abbot of the Monastery of Saint Neophytos and to Nikiphoros, Bishop of Kykkos and Tylliria and Abbot of the Monastery of Kykkos, for allowing the study of the manuscripts. The monasteries of Iviron and Dionysiou and the General Experimental Lyceum of Mytilini (G. Skalochoritou and A. Kalamatas) are here gratefully acknowledged for making digital images of their manuscripts available to me. I am grateful to Father Hieronymos, Abbot of the Monastery of Mega Spilaion (Kalavryta, Greece) for allowing the study and digitization of Ms. 4 (olim. Ms. 17). I would finally like to thank all the monasteries and institutions for permitting the publication of the images that illustrate this paper.

[59] The results obtained are currently being prepared for publication.

[60] The analyses were performed by Dr Sarah Fiddyment and her colleagues at the Department of Bio-archaeology of the University of York. I would like to thank Professor Matthew Collins and Dr Fiddyment for their contribution. On the method used and its contribution to manuscript studies,

Table 1: Two sections of the documentation model prepared during the first phase of the project.

1. PARCHMENT			
Dimensions of single folios			
Dimensions of bifolia			
Thickness			
Animal	- type		
	- follicle patterns		
	- skeletal marks	- shape	
		- depth	
	- scarring	- shape	
		- depth	
Preparation	- washing and bathing	- materials used	
Manufacturing features	- veining	- intensity	
	- striation marks	- shape	
		- depth	
	- holes	- shape	
		- dimensions	
Pre-use treatment	- pouncing		
	- coating	- materials	
2. INKS			
Black/brown	- main text	- pigments/ingredients	- preparation method
		- binding media	
	- corrections	- pigments/ingredients	- preparation method
		- binding media	
	- annotations	- pigments/ingredients	- preparation method
		- binding media	

	- quire numbering	- pigments/ingredients	- preparation method
		- binding media	
	- canon table numbers	- pigments/ingredients	- preparation method
		- binding media	
Red	- layout design	- pigments/ingredients	- preparation method
		- binding media	
	- decorated/animated initials design	- pigments/ingredients	- preparation method
		- binding media	
	- simple initials	- pigments/ingredients	- preparation method
		- binding media	
	- headtitles	- pigments/ingredients	- preparation method
		- binding media	
	- *incipits*	- pigments/ingredients	- preparation method
		- binding media	
	- liturgical indications	- pigments/ingredients	- preparation method
		- binding media	

as they are, however, the results obtained will not be presented extensively here, since forthcoming publications will have this purpose. Instead, we will attempt to provide some first thoughts about the work undertaken during the past years, its contextualisation and comparisons with relevant evidence, as well as a number of possible strands of investigation that shall be envisaged by future research on the 'decorative style' manuscripts.

The issue of the groupings of the manuscripts, addressed since the discovery of the group, is still open. The textual analyses undertaken have already drawn attention to the fact that, despite strong stylistic affinities and iconographic similarities between the miniatures and decoration of the manuscripts, great variability can be revealed by material, technological and document image analyses. The question that therefore remains is the extent to which the groupings of the manuscripts of the 'decorative style' that were based on subjective criteria must continue being the basis for the planning and realization of future undertakings. The answer cannot be straightforward, for many reasons. The main one is that there can be no doubt that an already existing classification of the members of such a large group is of great interest to anyone working or planning to work on specific manuscripts belonging to it or on issues relevant to the group as a whole. The groupings offer, above all, the possibility to re-examine specific issues and to conduct tests performed on a restricted number of manuscripts to confirm or reject hypotheses. The investigation undertaken by Elisabeth Yota can be mentioned here as an example of a study that benefitted from Weyl Carr's groupings in this respect.[61] More precisely, in her Ph.D. dissertation on London, British Library, Harley 1810, Yota strove to verify the attribution of

see: Fiddyment et al. 2015, 15066–15071; Teasdale et al. 2017.

[61] Yota 2001.

the Harley subgroup to a single scribe, Manuel Boukellaros Hagiostephanites,[62] one of the rare scribes who signed their work. That the name of Hagiostephanites is found only in two colophons of manuscripts belonging to the Chicago subgroup[63] and that the whole Harley subgroup was finally attributed to him aroused Yota's suspicion and prompted her to re-examine this attribution.[64] Hence, comparisons between the script of the manuscripts of the Harley and the Chicago subgroup showed that Hagiostephanites could not have been the person who copied all the manuscripts in question.[65] Yota furthermore identified strong palaeographic kinships between the members of the Harley subgroup that she attributed, not to a single hand, but to scribes who worked conjointly and had a reciprocal influence on each other.[66]

Likewise, the groupings and subgroupings make the manuscripts of the group very attractive as case studies aiming at improving and testing existing or creating new tools and solutions. For example, the systematic study of the characteristics of the animals' skin (species, age, size) from which the parchments were made, as well as of the different traces attributable to their preparation (materials, processes, tools and gestures used) and that can still be detected, would lead to the creation of a computerized tool. Its purpose would be to assist scientific description of manuscript parchment; and, through the creation of an extensive databank in which the characteristics of parchment specimens would be recorded, it might eventually contribute to provenance studies, since it could provide further evidence for dating manuscripts and identifying connections between localities and production centres.[67] To achieve such an objective, it would be much more beneficial to include specimens that can cover as large a geographical – and possibly also cultural – spectrum as possible and that are able to reveal variations and craft production on local, regional and inter-regional scales. The exploratory tests on manuscripts of the 'decorative style' could therefore fill the knowledge gap regarding twelfth- and the thirteenth-century parchment production in the Eastern Mediterranean, a period and region historically significant due to the Crusader presence in the area. The groupings and subgroupings make the manuscripts of the 'decorative style' a particularly suitable case study for improving the tool created, since they provide not only the possibility to go a step further and identify variances between parchment specimens produced within the same region, but also variances between manuscripts belonging to the same group and even to the same subgroup. It goes without saying that the development of such a tool could provide more insightful information about the relationships among the manuscripts. For instance, the examination of the members of a subgroup or of those having been characterized as 'codicological twins'[68] would reveal codicological evidence equally important as that provided by the rest of the parchment folia features (rulings, pricking marks, structure and dimensions). Questions such as whether the parchment used was qualitatively (size, age, species of the animal, same production process etc.) uniform throughout one manuscript or even within two 'twin manuscripts' could be therefore answered and the new evidence generated could fill knowledge gaps.

But though there cannot be any doubt that these groupings have resulted from a titanic and admirable effort to address the 'decorative style' manuscripts, both stylistic and iconographic evidence depend on subjective judgement, i.e. temporally evolving expertise in visual inspection. Given that subjectivity means higher hypotheticality and that higher hypotheticality means lower probability, it is clear that Weyl Carr's groupings remain subject to debate

62 On Manuel Boukellaros Hagiostephanites, see: Weyl Carr 1987, 51–52.

63 The manuscripts are: Vatican, Biblioteca Apostolica Vaticana, Barb. gr. 44934, dated May 13, 1153; and the manuscript (dated July 1156) *olim* New York, Kraus Collection, *olim* Oslo, Schøyen Collection, 231, now belonging to an unknown private collector (Martin Schøyen, personal communication, March 11, 2016).

64 The other manuscripts are: Athos, Monastery of Megali Lavra, B 24; Kiev, Library of the national Academy of Sciences of Ukraine, A 25 4; Saint Petersburg, National Library of Russia, gr. 644; Leyden, University Library, gron. 137; London, British Library, Add. 39595; and London, British Library, Harley 1810. See: Weyl Carr 1987, 51–52.

65 Yota 2001, 37–46.

66 Yota 2001, 29–39.

67 Jiří Vnouček (Department of Bio-archaeology, University of York) is currently working towards the creation of such a tool. For more information, see: <https://www.york.ac.uk/archaeology/research/research-students/vnoucek/#tab-4> (last accessed 25 Octobre 2017). The type of evidence that can be gathered from the study of parchment is also discussed in: Harris 2014, 9–21.

68 Weyl Carr uses the term 'codicological twins' for the manuscripts that have the same size, the same justification dimensions, the same type of lineation and the same number of lines per folio. Examples of manuscripts presenting these characteristics are: London, British Library, Add. 37002; Moscow, State Public Library, F181, gr. 11; and the four volumes that formed the complete Old Testament, i.e. Athens, National Library of Greece, 44; Oxford, New College, 44; Istanbul, Topkapi Saray, 13; and Oxford, Bodleian Library, Auct. E.2.16. See: Weyl Carr 1987, 38; 70.

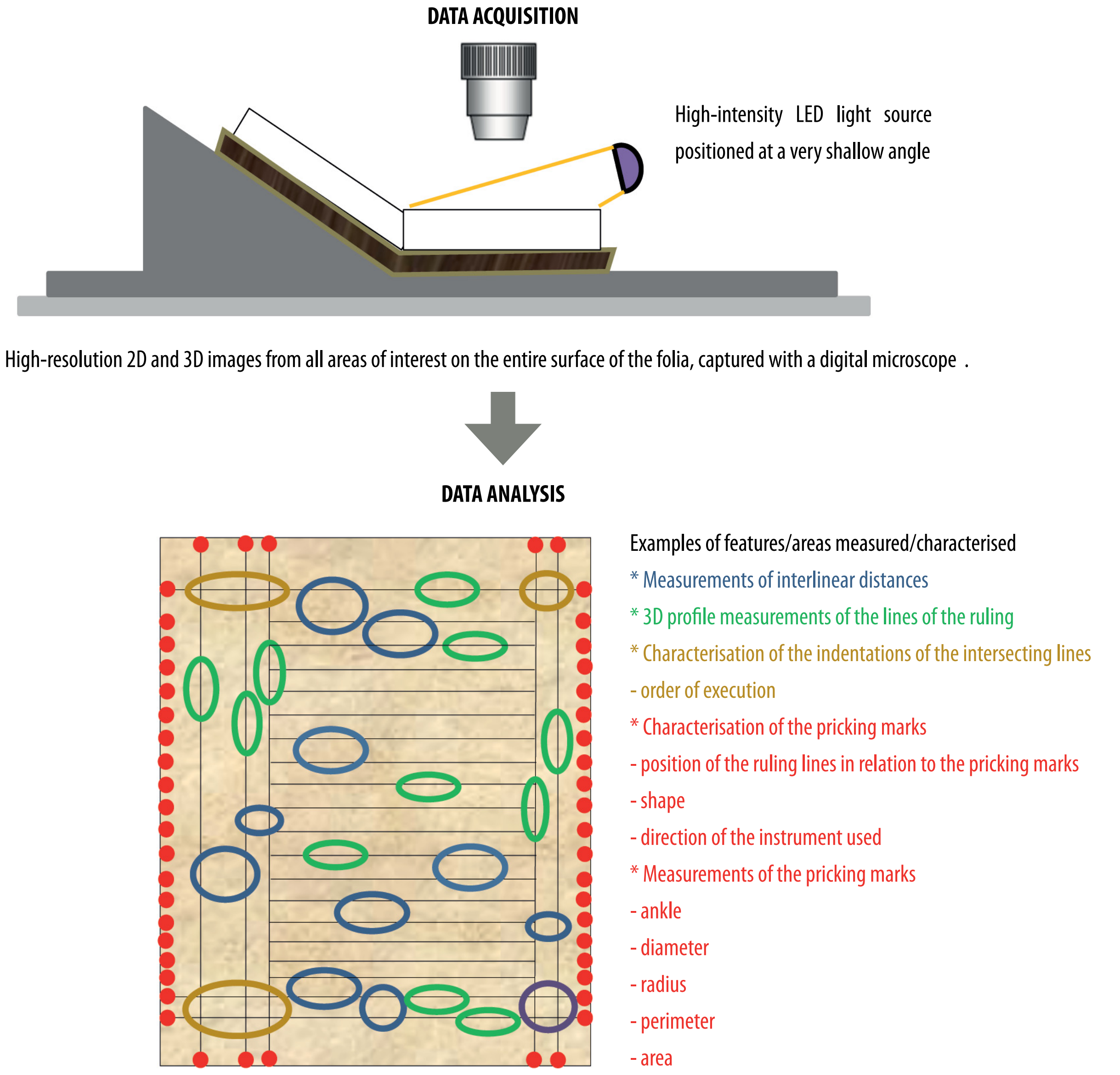


Fig. 1: Schematic description of the parchment documentation process including data acquisition and data analysis.

and discussion and that, in the future, subjective evidence should be gradually replaced by objective criteria. Thus, the study and/or analysis of style and iconography, as of every material and/or characteristic of the manuscripts, has the potential to establish or invalidate different hypotheses or assumptions, including those regarding associations between manuscripts, to the degree that the evidence generated comes from objective assessment and/or quantitative measurements.

All the characteristics and/or features of the manuscripts of the group shall therefore be seen as interrelated segments of an ensemble. Consequently, to deal satisfactorily with this large ensemble and the complex questions it poses, the task of its study and analysis must be broken into smaller, less complex and more manageable sub-tasks, whose results must be finally brought together. The approach in question presents considerable advantages. For instance, it provides the ability to fully investigate each feature/component of the manuscripts and to obtain information that is not otherwise accessible. It could also improve the accuracy of a new classification. Finally, it could promote the development of specific protocols, for example for collecting data, preparing suitable reference collections etc. The ensuing examples can illustrate the advantages of this approach.

The first example concerns the development of a protocol that was deemed necessary during the parchment documentation process (Fig. 1). This protocol was developed with the following objectives: i. to enable the identification

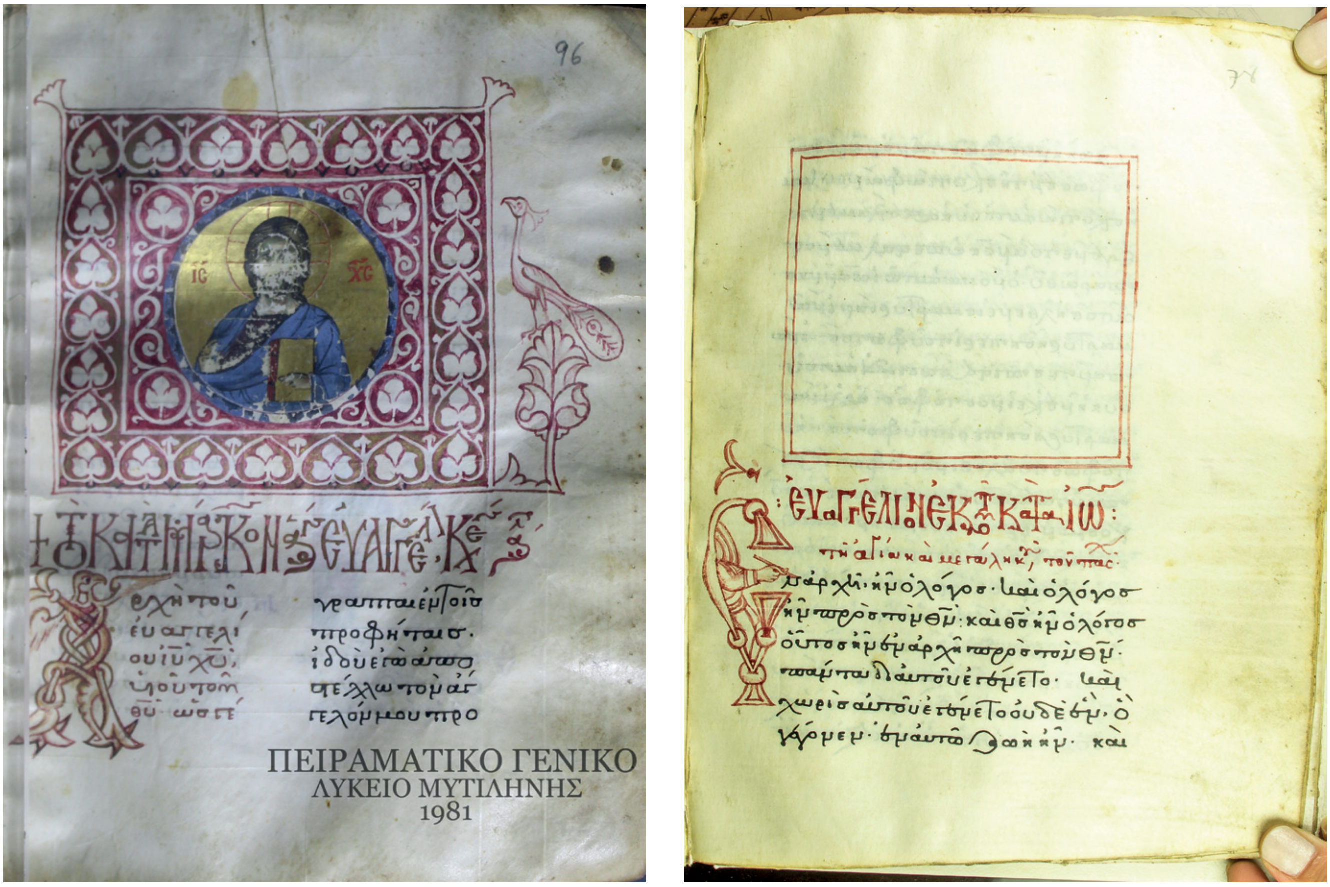


Fig. 2a: Lesbos, General Experimental Lyceum of Mytilini, 9, fol. 96r; Fig. 2b: Paphos, Monastery of Saint Neophytos, Ms. 11, fol. 78r. Opening folios of two uncompleted 'decorative style' manuscripts where the characteristic dark red ink was amply used by their planner(s) and/or scribe(s).

of the ruling system(s) of the manuscripts analysed and ii. to record and characterize the rulings and the pricking marks of the folios of the manuscripts, in an effort to define the sequence of procedures in the production of the quires that immediately precede the copying stage.[69]

The second example concerns the analysis of the dark red ink, referred to in the literature as the magenta ink used extensively in the manuscripts of the group, that came to be considered one of its main characteristics.[70] The red ink in question was used by the planners of the manuscripts for the design of the openings of the major divisions of the texts and for writing the head titles and the *incipits* (Fig. 2). The pervasiveness of this feature prompted its analysis in two of the examined manuscripts, i.e. Paphos, Museum of the Monastery of Kykkos, Ms. R8 and the unfinished Paphos, Monastery of Saint Neophytos, Ms. 11 (Fig. 2b). Though it proved difficult to identify with precision all the ingredients of the red inks in the two aforementioned manuscripts using the non-invasive techniques applied,[71] it was evident that they were composed mainly of an organic dye. In the case of the opening page of John's Gospel in Ms. Kykkos R8, the detection of As lines of considerable intensity through XRF analysis ultimately prompted several measurement campaigns aiming at a more in-depth investigation of the red areas (script and illumination) on all the folios.[72] Combined with codicological and art historical evidence, the distribution of the different red compounds throughout the manuscript finally made it possible to reshape the narrative of its history, a more complicated task than initially assumed.[73]

[69] The protocol in question is still at the stage of development. On the importance of an in-depth study of the rulings of the manuscripts of the group, see also: Fonkič 1980–1982, 110–111.

[70] First characterized thus in: Weyl Carr 1973.

[71] The techniques used were: digital microscopy, FORS, XRF, FTIR and multispectral imaging.

[72] The results and the hypotheses formulated will be made available in a forthcoming publication.

[73] The codicological and art historical study of Kykkos Ms. R8 is in preparation. The manuscript was the subject of a short publication in the past. See: Constantinides 1988–1989, 169–186.

Fig. 3a: Kalavryta, Monastery of Mega Spilaion, 4 (*olim* 17). Opening folio of the Gospel of Matthew.

Fig. 3b: Athos, Monastery of Iviron, 55, fol. 112r. Opening folio of the Gospel of Luke.

Fig. 3c: Athos, Monastery of Dionysiou 4, fol. 5r. Opening folio of the Gospel of Matthew.

While the tools and efforts mentioned above concentrate mainly on the evidence acquired by applying analytical techniques to the materials, an equally dynamic array of information is preserved in the layout and the script of the manuscripts. Indicated already as one of the trademarks of the 'decorative style' group, the layout of the opening of the major text divisions in the manuscripts must have been the outcome of careful planning. Layout analyses not only of the opening pages, but also of the rest of the instances encountered in the manuscripts of the group, will undoubtedly be capable of illuminating the complex picture of its manufacture. There are five main categories of layout: i. the folios with the Evangelists' portraits; ii. the folios with the openings of the major text divisions (see: Fig. 3); iii. the folios with figural illuminations found within the text; iv. the folios with text without any illumination; and v. the folios that contain the decorated canon tables.

In all the aforementioned cases, the first task is to detect the position of each entity within the page(s). It is then necessary to provide their exact dimensions for the following two reasons: i. this allows comparisons between corresponding entities within different manuscripts of the group and ii. the ratio between each entity and the surface of the folio on which it is found can expand our knowledge of the criteria and the intention behind the decision-making of the planners and the patrons of the manuscripts. For example, three different texts, i.e. the Gospels, the Psalters and the Book of Job, have figural miniatures inserted within the column of the script. It would therefore be essential to know whether the aspect ratio remains identical throughout a single manuscript containing different texts or if variations can be detected. The fluctuations in question could have been motivated by complex and versatile criteria. These could be, for instance, the subject matter of the miniature (a more or less important feast of the Orthodox Church, a feast enjoying high status locally or with the patron of the manuscript, a passage with specific significance either to the monastic community owning the manuscript or its patron etc.); the financial possibilities of the patron; or the iconographic formulation of the scene depicted (accordingly, more details requiring a larger surface and fewer details requiring a smaller surface).

The openings of the major text divisions in the Gospel books and the folios that accommodate the canon table can also be further explored. Though most of them conform to a standardised pattern (see: Fig. 3), the information gained by the layout analyses of large datasets can provide additional evidence of relationships between manuscripts. It is expected that this evidence will also increase our knowledge about the unfinished manuscripts and those preserving only one of their illuminated folios, which are otherwise difficult or impossible to classify, and will enable us to establish associations between them and other more complete manuscripts or manuscript groups.[74]

Relationships between manuscripts can furthermore be elucidated by providing answers to authorship-related questions, which can also benefit considerably from automated document analysis. The issue of authorship involves two different tasks: i. the identification of different sub-styles within the 'style epsilon à pseudo-ligatures basses' and, if possible, the identification of different hand(s)/scribe(s) and ii. the identification of the salient features that distinguish between individual painters or group of painters. In the case of the script, the possibilities provided by the capacity to detect variations between different handwritings are numerous.[75] Some of the case studies can therefore stand on their own. Others are expected to benefit the wider study of the group. The corpus being extremely large, however, a first grouping based upon a first differentiation shall precede the more specific tasks. Manuel Boukellaros Hagiostephanites and the manuscripts ascribed to him, as already mentioned, are unquestionably one of the particularly apposite cases for the application of an automated analysis, since they pose straightforward questions, i.e. whether the unsigned

[74] This, for example, is the case with Athens, Gennadius Library, gr. 259 and with Paphos, Museum of the Monastery of Kykkos, Ms. R8. They each preserve only one illumination. The Gennadius manuscript preserves the opening of Matthew's Gospel, while the Kykkos manuscript preserves the opening of John's Gospel.

[75] The advantages of extensive and in-depth palaeographic analyses of the manuscripts of the group were also highlighted in: Fonkič 1980-1982, 110–111.

manuscripts attributed to him on palaeographic evidence were copied indeed by him.[76]

An example of a more challenging task is the validation of the existence of the two distinct variants within the 'style epsilon', the 'arrondi' and the 'rectangulaire', and the identification of their respective discriminative variations. The final objective, however, will be to show how each evolved, without, however, overlooking that they constitute variants of the same style. The core dataset for investigating the development of the script in question will be the dated manuscripts not only of the group, but also the unilluminated ones Canart includes in his study of the 'style epsilon'.[77] The rest of the unilluminated 'style epsilon' manuscripts and all the members of the 'decorative style' group will complete the inquiry, in this way ensuring that all the different variations are represented.[78]

In the case of the painted surfaces (miniatures including surfaces covered by both figural and decorative motifs; decorative elements such as headpieces; decorated/animated initials etc.) rigorous computer methods can finally address many purely art historical issues by enhancing and extending traditional methods of art historical connoisseurship. They can cover a large range and variety of tasks, from an iconographic to a stylistic analysis. The computer methods can therefore rely on numerous features, such as colour, texture, shading, stroke patterns, line styles, geometry, perspective, iconographic formulation etc.[79] Some of these traits, such as texture, are difficult or impossible to perceive with the naked eye. Others, such as stroke patterns, are described by art historians qualitatively and therefore necessitate quantification. Finally, some others, such as iconographic formulations, need to be automatically identified to process large numbers of images. As previously mentioned, the information obtained depends on the scope and the target of the analysis. Thus, general tasks can establish a classification of the manuscripts of the whole group, while more specific ones can provide authorship-relevant answers or generate new knowledge of production patterns or stylistic traits.

The portraits of the Evangelists form an ideal case study, since every Tetravengelion and every Gospel Lectionary includes four portraits, found before the beginning of each Gospel section. Though in most of the cases the Evangelists are represented seated, their gestures, the background details, the furniture, the frame of the miniatures and the decoration of all the aforementioned elements differ significantly. The compositional and decorative similarities and divergences between the portraits could contribute to the assessment of important issues of the production of the manuscripts of the group, such as the models used and the relationships between these portraits. Thus, taking into account that the Evangelists' portraits were painted on separate folios inserted between the quires, the evidence gathered from these analyses can be particularly significant, since it might provide much deeper insight into the production patterns.

The question of linearism is particularly relevant when it comes to the stylistic examination of the miniatures of the members of the group. Characteristic of the Komnenian tradition, to which the group clearly adheres, linearity is considered a stylistic trend, whose evolution can be traced throughout the ensemble of the manuscripts of the 'decorative style'[80] Linearism in fact refers to two distinct traits of the figural miniatures of the manuscripts, i.e. the contour of the figures often traced with a dark, usually black pigment, and the linear webs of – mainly white – highlights found almost exclusively in the draperies of the depicted figures. Considering their orientation and the measurements of their various characteristics (length, width, corner, contour curvature, intensity, homogeneity etc.), the aim would initially be to validate the existence of such a stylistic distinction between the miniatures or even between hands and, if possible, prove quantitatively the stylistic evolution traced.[81] For the second task, since it seeks to gather diachronic evidence, once again the core dataset will be formed from the group's dated manuscripts.

A plethora of further case studies can be cited to make it more overt that the possibilities provided by the existing

[76] Among the rare names of scribes found in the manuscripts of the group are: Basil, the notary of the Monastery of Kellion, who copied two manuscripts (Mount Sinai, Monastery of Saint Catherine, Ms. 220 and 232); and a scribe from Rhodes working in Cyprus (Paris, Bibliothèque Nationale de France, gr. 301). Weyl Carr 1987, 127–128.

[77] Canart 1981, 17–76.

[78] The necessity to have a dataset representing all the possible variants of the script was also stressed in: Canart 1988–89, 33.

[79] For a classification of the features in question, see: Arora and Elgammal 2012, 3541.

[80] Weyl Carr 1987; Weyl Carr 1988–89 134. See furthermore: Yota 2001; Džurova 2008, 288.

[81] Various research teams have undertaken computer-based analyses for art historical purposes. See for example: Stork 2009; Arora and Elgammal 2012; Li et al. 2012; Vieira et al. 2015.

tools and methods, which are expected to be further improved and created in the future, are unlimited. They can make it conceivable to address a variety of questions whose answers can enhance our knowledge about a range of very specific to general issues about individual manuscripts, subgroups or even the 'decorative style' group as a whole. But it is crucial that future endeavours be undertaken by collaborative networks, not only for purposes of implementation-specific requirements, but foremost because the large size of the corpus necessitates a well-concerted venture. Libraries and repositories in the possession of the group's manuscripts should hence be actively involved, since they can act as the point of reference for researchers. With this capacity, they could also initiate and coordinate foundational work. For instance, digital surrogates of the manuscripts corresponding to standards that will be mutually accepted and established by the institutions in possession of the manuscripts will make them accessible and hence attractive to research teams wishing to deal with them, since physical presence is not required for a great variety of tasks. This is particularly the case for tasks applying automatic document image analyses. Layout analyses require particular mention here. Their feasibility being high, they have the potential to prove profitable as foundational work, since they can constitute the initial step in an attempt to provide an automatic clustering of the group's manuscripts, on which future undertakings could be based. Planning the layout is the step that precedes the execution of a manuscript, a further argument in support of the aforementioned initiative and its value.

Restorative interventions carried out on the group's manuscripts in the various institutions can generate material to be collected, stored and used for future analyses, in particular destructive analyses, which are otherwise forbidden. Close collaboration with conservators and restorers in Cyprus led to the constitution of a collection of pigments that had peeled and were lying between the folios of the manuscripts, along with pieces of parchment and threads from the sewing of the bindings.[82]

Finally, the necessity to create and maintain a digital workspace from the very beginning of a project addressing the 'decorative style' should not be overlooked, since it will allow scholars from the humanities and the natural and computer sciences to collaborate and to discuss and share expertise, data and results.

Conclusion

This paper argued that a holistic approach is necessary for the effective study of the 'decorative style' group of manuscripts. A selection of preliminary results and a number of remarks that derived from the experimental work undertaken during the exploratory phase of the project were presented and discussed. Suggestions for avenues of future research were also provided. However, the concluding remarks of this article will be concerned with a paramount aspect of future work on the group, i.e. reflecting upon going beyond its boundaries, outside the investigated period of the production of Byzantine illuminated manuscripts, with the aim to develop interpretative frameworks and to adequately contextualise the results obtained.

The first remark concerns the place of the group within the more general context of artistic production during the Komnenian era in Cyprus. The period in question saw the foundation of a large number of monuments decorated with wall paintings.[83] Though written testimony is absent, art historians have suggested that artists from Constantinople moved to Cyprus along with their Byzantine patrons, while others sailed to Cyprus and the Levantine coasts in search of a new clientele after the Crusaders' capture of Constantinople in 1204. The answer to the question whether the production of manuscripts of the 'decorative style' was one branch of the industry of art of the island and more generally in the region, which included not only monumental painting, but also panel and manuscript painting, cannot yet be provided. Nor is it possible to know whether the painters involved in manuscript illumination were specialized in that medium alone or if they were capable of crossing freely between different media (fresco, icon painting and manuscript illumination). It is notable that art historical inquiries put forward stylistic and iconographic kinships between the manuscripts of the group and the mural paintings of a

82 I would like to thank here the restorer of the Kykkos Foundation Souzanna Agathokli, as well as the museum of the monastery of Kykkos, the monastery of Saint Neophytos, the monastery of the Virgin of Trooditissa and the Holy Bishopric of Kition for providing me with the 'scraps' resulting from restorative interventions in their manuscripts.

83 Among the well-known Komnenian generals who founded monasteries in Cyprus are: Eumathios Philokales (Saint John Chrysostomos of Koutsoventis), Nikiphoros Ischyrios (Monastery of the Panagia of Asinou), Manuel Boutoumites (Monastery of the Panagia of Kykkos) and Epiphanios Paschalis (Monastery of the Panagia of Alypou).

number of contemporary monuments in Cyprus.[84] On the other hand, the technical studies of Komnenian frescoes, again in Cyprus, i.e. the Enkleistra of Saint Neophytos, the church of Panagia Amasgou and the church of Panagia of Asinou, revealed very interesting results, since they managed to identify the painters' choices of materials and work methods.[85] At this very rudimentary stage, though, it is impossible to make hypotheses about connections between the different branches of the local artistic production. Endeavours planned in this direction will certainly contribute extensively to our knowledge.

But if we then consider that the manuscripts were produced in the Eastern Mediterranean by Byzantine and/or Levantine scribes and illuminators, is it feasible to deal with the issue of the provenance of the manuscripts? How relevant is the question of provenance in cases like the 'decorative style' group, given that its members were the products of a mobile world? To which aspect would provenance finally refer? To the quantitative prominence of one specific local production centre over another or possibly over all the others, for example of Cyprus over Palestine? Would provenance refer to the locality where the manuscript was copied and/or illuminated? In that case, can we ignore that the rest of the stages of the composite chaîne opératoire might have been executed elsewhere? And what about local production centres working independently and existing within a single locality, each specialized only in a very specific stage of the manufacturing procedure? Would locality refer to the source location of the various raw materials used? Would it refer to the origin of the scribes and the miniaturists or to the prevailing cultural milieu of the place where they were trained? Furthermore, if we consider the multiple and parallel evolution of traditions of manuscript illumination and production within the Byzantine oecumene, how different or how similar were the materials used and the methods of production, assuming that significant differentiations can be detected? Could the analyses reveal far more complex production patterns and a different situation in the case of the manuscripts of the 'decorative style' group compared with the products of copying/illuminating ateliers centred on a single and very specific locality, as in the case of the 'Palaeologina group', the 'Kokkinobaphos group' or the works produced by the scriptorium of the Prodromos-Petra monastery? Can we attribute these differences to looser production patterns? Or did the contexts of production – lay or monastic – affect the manufacturing processes?

At this point, the questions can be multiplied, and though we can try to give answers based on qualitative evidence, they cannot be definitely provided. What is hoped is that the implementation of the next phase of the project will benefit from a collaborative research network that will contribute greatly and meaningfully to the study of the 'decorative style' group of manuscripts.

[84] Indicatively, some of the monuments on Cyprus drawn into art historical discussion about the manuscripts of the 'decorative style' group are: the church of Panagia tou Arakos at Lagoudera, the church of Panagia Amasgou at Monagri, the church of Panagia of Asinou, the church of Archangel Michael at Kato Lefkara, the church of Christ Antiphonitis at Kalogrea, the church of Saint John Lampadistis at Kalopanayiotis, the Enkleistra of Saint Neophytos in Paphos. Apart from Weyl Carr's already cited papers, see for example: Weitzmann 1975, 4763; Yota 2001.

[85] Jenssen and Majewski 1974; Kakoulli et al. 2012; Kakoulli et al. 2014; Radpour et al. 2014. Furthermore, the results of the technical study of the frescoes of the church of the Transfiguration of Sotira (Famagusta, Cyprus) will be soon published by Prof. Ioanna Kakoulli (Materials Science and Engineering Department, University of California, Los Angeles) in a volume dedicated to this monument.

REFERENCES

Arora, Ravneet Singh, Ahmed Elgammal (2012), 'Towards automated classification of fine-art painting style: A comparative study', in *21st International Conference on Pattern Recognition (ICPR), Tsukuba 11–15 Nov. 2012* (Tsukuba: IEEE), 35413544.

Buchthal, Hugo (1964), 'An unknown Byzantine manuscript of the thirteenth century', *Connoisseur*, 115: 217–224.

'Byzantine Art: An European Art', 9th Exhibition of the Council of Europe (Athens, Zappeion Exhibition Hall, April 1st-June 15th 1964) (Athens: Office of the Minister to the Prime Minister of the Greek Government and Department of Antiquities and Archaeological Restoration of Greece).

Canart, Paul (1981), 'Les écritures livresques chypriotes du milieu du XIe siècle au milieu du XIIIe et le style palestino-chypriote 'epsilon'', *Scrittura e Civiltà*, 5: 17–76.

—— (1988–1989), 'Les écritures livresques chypriotes du XIe au XVIe siècle', Επετηρίς του Κέντρου Επιστημονικών Ερευνών Κύπρου, 17: 27–53.

Colwell, Ernest, Harold Willoughby (eds) (1936), *The Four Gospels of Karahissar*, 2 vols (Chicago: University of Chicago Press).

Constantinides, Costas (1982), *Higher education in Byzantium in the thirteenth and early fourteenth centuries (1204–ca.1310)* (Nicosia: Cyprus Research Centre).

—— (1988–1989), 'An unknown manuscript of the 'Family 2400' from Cyprus', *Επετηρίς του Κέντρου Επιστημονικών Ερευνών Κύπρου*, 17: 169–186.

Constantinides, Costas, Robert Browning (1993), *Dated Greek Manuscripts from Cyprus to the Year 1570* (Washington D.C. and Nicosia: Dumbarton Oaks Research Library and Collection and Cyprus Research Centre).

De Mas Latrie, Louis (1852), *Histoire de l'île de Chypre sous le règne de la Maison de Lusignan* (Paris: Imprimerie Impériale).

Der Nersessian, Sirarpie (1936), 'Introduction', in Ernest Colwell, Harold Willoughby (eds), *The Four Gospels of Karahissar*, 2 vols (Chicago: University of Chicago Press), xxvi–xxxvi.

Dufrenne, Suzie (1981), 'Problèmes des ateliers de miniaturistes byzantins', *Jahrbuch der Österreichischen Byzantinistik*, 31: 445–470.

Džurova, Axinia (2002), *Byzantinische Miniaturen: Schätze der Buchmalerei vom 4. bis zum 19. Jahrhundert* (Regensburg: Schnell und Steiner).

—— (2008), 'La production des manuscrits à l'époque des Croisades (Cod. D. Gr. 358 et 339)', in Marina Koumanoudi, Chryssa Maltezou (eds), *Dopo le due cadute di Constantinopoli (1204, 1453): Eredi ideologici di Bisanzio (Atti del Convegno Internazionale di Studi (Venezia, 4–5 dicembre 2006)* (Venice: Istituto Ellenico di Studi Bizantini e Postbizantini di Venezia), 273–325.

Fiddyment, Sarah, Bruce Holsinger, Chiara Ruzzier, Alexander Devine, Annelise Binois, Umberto Albarella, Roman Fischer, Emma Nichols, Antoinette Curtis, Edward Cheese, Matthew Teasdale, Caroline Checkley-Scott, Stephen Milner, Kathryn Rudy, Eric Johnson, Jiří Vnouček, Mary Garrison, Simon McGrory, Daniel Bradley, and Matthew Collins (2015), 'Animal origin of 13th-century uterine vellum revealed using noninvasive peptide fingerprinting', *Proceedings of the National Academy of Sciences*, 112 (49): 15066–15071.

Fonkič, Boris (1980–1982), 'Scriptoria Bizantini: Risultati e prospettive della ricerca', *Rivista di Studi Bizantini e Noellenici*, 17–19: 73–118.

Galatariotou, Catia (2004), *The making of a Saint: The life, times and sanctification of Neophytos the Recluse* (Cambridge: Cambridge University Press).

Goodspeed, Edgar, Donald Riddle, and Harold Willoughby (eds) (1932), *The Rockefeller McCormick New Testament*, 3 vols (Chicago: University of Chicago Press).

Grivaud, Gilles (2005), 'Literature', in Angel Nicolaou-Konnari, Chris Schabel (eds), *Cyprus, Society and Culture 1191–1369*, (Leiden: Brill), 219–284.

—— (2012), 'Le doux royaume de Chypre (1192–1474)', in Jannic Durand, and Dorotta Giovannoni (eds), *Chypre entre Byzance et l'Occident: IVe–XVIe siècle* (Paris: Louvre editions), 182–189.

Harris, Susanna (2014), 'Leather in archaeology: between material properties, materiality and technological choices', in Susanna Harris, André Veldmeijer (eds), *Why Leather? The Material and Cultural Dimensions of Leather* (Leiden: Sidestone Press), 9–21.

Jenssen, Victoria, Lawrence Majewski (1974), Appendix to Susan Boyd, 'The Church of the Panagia Amasgou, Monagri, Cyprus and its Wall-paintings', *Dumbarton Oaks Papers*, 28: 329–345.

Kakoulli, Ioanna, Michael Schilling, and Joy Mazurek (2012), 'The Murals of the Panagia Phorbiotissa: A Technical Examination', in Annemarie Weyl Carr, Andreas Nicolaides (eds), *Asinou across time: Studies in the Architecture and Murals of the Panagia Phorbiotissa, Cyprus* (Washington D.C: Dumbarton Oaks Research Library and Collection), 313–359.

Kakoulli, Ioanna, Sergey Prikhodko, Andrew King, and Christian Fischer (2017), 'Earliest evidence for asbestos composites linked to Byzantine wall paintings production', *Journal of Archaeological Science*, 44: 148–153.

Langford, Warren (2009), *From Text to Art and Back Again: Verifying A. Weyl Carr's Manuscript Groupings through Textual Analysis* (New Orleans Baptist Theological Seminary, Unpublished Ph.D. dissertation).

Li, Jia, Lei Yao, Ella Hendriks, and James Wang (2012), 'Rhythmic Brushstrokes Distinguish van Gogh from His Contemporaries: Findings via Automated Brushstroke Extraction', *IEEE Transactions on Pattern Analysis and Machine Intelligence*, 34.6: 1159–1176.

Malamut, Elisabeth (2012), 'Chypre nouvelle province byzantine (965–1191)' in Jannic Durand, Dorotta Giovannoni (eds), *Chypre entre Byzance et l'Occident: IVe–XVIe siècle* (Paris: Louvre editions), 96–102.

Marinis, Vasileios (2004), '169. Tetraevangelion: Four Gospels' in Helen Evans (ed.), *Byzantium: faith and power (1261–1557)* (New Haven and London: Yale University Press and the Metropolitan Museum of Art), 284–285.

Maxwell, Kathleen (2014), 'The Afterlife of Texts: Decorative Style Manuscripts and New Testament Textual Criticism', in Jones Lynn (ed.), *Byzantine Images and their Afterlives. Essays in Honor of Annemarie Weyl Carr* (Surrey: Ashgate), 1138.

—— (2016), 'The Textual Affiliation of Deluxe Byzantine Gospel Books', in Robert Nelson, Derek Krueger (eds), *The New Testament in Byzantium* (Washington D.C.: Dumbarton Oaks Research Library and Collection), 33–85.

Mokretsova, Inna, Maya Naumova, Vilena Kireyeva, Elina Dobrynina, and Boris Fonkitch (2003), *Materials and techniques of Byzantine manuscripts* (Moscow: Ministry of Culture of Russian Federation).

Papadopoulos, Chrysostomos (1890), 'Περιγραφὴ μονῶν τινῶν τῆς νήσου Κύπρου μετὰ τῶν ἐν αὐταῖς χειρογράφων', *Σωτὴρ* 13: 314–320.

Papadopoulos, Theodoros (1995), 'Η Εκκλησία Κύπρου κατά την περίοδο της Φραγκοκρατίας', in Papadopoulos Theodoros (ed.), *Ιστορία της Κύπρου. Μεσαιωνικόν Βασίλειον-Ενετοκρατία*, vol. 4 (Nicosia: Archbishop Makarios III Foundation), 543–666.

Radpour Roxanne, Neha Bajwab, James Garritano, Shijun Sung, Magdalena Balonis-Santa, Priyamvada Tewari, Warren Grundfest, Ioanna Kakoulli, and Zachary Taylor (2014), 'THz Imaging Studies of Painted Samples to Guide Cultural Heritage Investigations at the Enkleistra of St. Neophytos in Paphos, Cyprus', in Manijeh Razeghi, Alexei Baranov, John Zavada, and Pavlidis Dimitris, *SPIE Optics and Photonics Proceedings, Terahertz Emitters, Receivers and Applications V*, 91990Q-1–9.

Schreiner Peter, Doris Oltrogge (2011), *Byzantinische Tinten, Tuschen und Farbrezepte* (Vienna: Österreichische Akademie der Wissenschaften).

Stork, David (2009), 'Computer Vision and Computer Graphics Analysis of Paintings and Drawings: An Introduction to the Literature', in Jiang Xiaoyi and Petkov Nicolai (eds), *Proceedings of the International Conference on Computer Analysis of Images and Patterns* (Munster: Springer), 9–24.

Teasdale, Matthew, Sarah Fiddyment, Jiří Vnouček, Valeria Mattiangeli, Camilla Speller, Annelise Binois, Martin Carver, Catherine Dand, Timothy Newfield, Christopher Webb, Daniel Bradley, and Matthew Collins (2017), 'The York Gospels: a one thousand year biological palimpsest', Royal Society Open Science 4.10, 170988. <http://doi.org/10.1098/rsos.170988> (last accessed 25 Octobre 2017).

Vieira, Vilson, Renato Fabbri, David Sbrissa, Luciano Da Fontoura Costa, and Gonzalo Travieso (2015), 'A quantitative approach to painting styles', *Physica A: Statistical Mechanics and its Applications*, 417.1: 110–129.

Weitzmann, Kurt (1975), 'A group of early twelfth-century icons attributed to Cyprus', in Robertson Giles, and Henderson George (eds), *Studies in memory of David Talbot Rice* (Edinburgh: Edinburgh University Press), 47–63.

Weyl Carr, Annemarie (1973), *The Rockefeller McCormick New Testament: Studies toward the reattribution of Chicago, University Library, ms. 965* (University of Michigan, Unpublished Ph.D. dissertation).

—— (1982), 'A Group of Provincial Manuscripts from the Twelfth Century', *Dumbarton Oaks Papers,* 36: 3981.

—— (1987), *Byzantine Illumination 1150–1250: The Study of a Provincial Tradition* (Chicago and London: University of Chicago Press).

—— (1988–1989), 'Cyprus and the "Decorative Style"', *Επετηρίς του Κέντρου Επιστημονικών Ερευνών Κύπρου*, 17: 123–167.

Weyl Carr, Annemarie (1989), 'Illuminated musical manuscripts in Byzantium: A note on the late twelfth century', *Gesta*, 28.1: 41–52.

—— (1991a), 'Thoughts on the production of provincial illuminated books in the twelfth and thirteenth centuries', in Guglielmo Cavallo, Giuseppe De Gregorio, and Marilena Maniaci (eds), *Scritture, libri e testi nelle aree provinciali di Bisanzio (Atti del Seminario di Erice, Biblioteca del Centro per il collegamento degli studi medievali e umanistici nell'Universita di Perugia, 18–25 settembre 1988)* (Spoleto: Centro italiano di studi sull'alto medioevo), 661688.

—— (1991b), 'The Production of Illuminated Manuscripts: A View from the Late Twelfth Century', in Dieter Harlfinger, Giancarlo Prato, Marco D'Agostino, and Alberto Doda (eds), *Paleografia e codicologia greca: atti del II colloquio internazionale (Berlino-Wolfenbüttel, 17–21 ottobre 1983)* (Alessandria: Edizioni dell'orso), 325–338.

—— (1993), 'Two Illuminated Manuscripts at the Monastery of Saint Neophytos: Issues of their Cypriot Attribution', in Anthony Bryer, Georgios Georghallides (eds), *'The Sweet Land of Cyprus': Papers Given at the Twenty-Fifth Jubilee Spring Symposium of Byzantine Studies (Birmingham, March 1991)* (Nicosia: The Cyprus Research Centre), 281–318.

—— (2012), 'Reading Styles of Use: The Rockefeller McCormick New Testament and Christian Kalam'; in Jean-Michel Spieser, Elisabeth Yota (eds), *Donation et donateurs dans le monde byzantin. Actes du colloque international de l'Université de Fribourg (Fribourg, 13–15 mars 2008)* (Paris: Desclée de Brouwer), 235–264.

Willoughby, Harold (1940–1941), 'Vagrant Folios from Family 2400 in the Free Library of Philadelphia', *Byzantion,* 15: 126–32.

Yota, Elisabeth (2001), *Le tétraévangile Harley 1810 de la British Library: Contribution à l'étude de l'illustration des tétraévangiles du Xe au XIIIe siècle* (University of Fribourg,Switzerland, and University Paris I Panthéon-Sorbonne, France, Unpublished Ph.D. dissertation).

PICTURE CREDITS

Fig. 1: © The author.

Fig. 2a: © General Experimental Lyceum of Mytilini (Lesbos, Greece). Courtesy.

Fig. 2b: © The author, by permission of the Monastery of Saint Neophytos (Paphos, Cyprus).

Fig. 3a: © The author, by permission of the Monastery of Mega Spilaion (Kalavryta, Greece).

Fig. 3b: © Athos, Monastery of Iviron. Courtesy.

Fig. 3c: © Athos, Monastery of Dionysiou. Courtesy.

Article

The Quest for the Mixed Inks

Claudia Colini, Oliver Hahn, Olivier Bonnerot, Simon Steger, Zina Cohen, Tea Ghigo, Thomas Christiansen, Marina Bicchieri, Paola Biocca, Myriam Krutzsch, and Ira Rabin | Hamburg, Berlin, Paris, Rome, Turin

In this article, we would like to share our observations concerning the inks produced by intentionally mixing soot or charcoal with tannin extracts or iron-gall ink. Aside from Zerdoun's mention in her outstanding review of written sources, *Les encres noires au Moyen-Âge*[1], this ink category has received little if any attention from scholars and scientists. And yet, if analytically attested, the use of such inks could serve as an additional category to classify and distinguish the writing inks on the historical socio-geographic map of the writing inks we are trying to build.

In the collection of recipes from Arabic sources that one of us investigated, we found that explicit recipes for mixed inks constitute some 20% of the collection[2]. It would be extremely interesting and important for our enterprise to obtain a chronological and geographic attribution of the recipes from the Orient, beyond those of Dioscorides[3] and Philo of Byzantium[4]. However, the overall scarcity of copies per treatise and the young age of the manuscripts make it difficult for the current state of the art to understand when and where a certain formula was introduced and changes were made. In addition, we observed that the transmission of recipes from one treatise to another is massive, but at the same time extremely fluid, since small but mostly reasonable changes are introduced every time, often resulting in modifications to the formulas (concerning the quantities, ingredients, or technique employed). Although great respect was accorded to the authors, especially if they were eminent figures, their texts and words were not untouchable and unchangeable. This 'active' transmission[5] suggests at the same time a living tradition with practical applications, as otherwise there wouldn't be the need to change the content and the formulas, but only the form. For this reason, a more detailed study not only of the origin, but also of the transmission of these texts[6] will contribute to establishing a chronology of the modifications of the single recipes, which will be useful when comparing with specific manuscripts.

Mixed inks appear also in the Jewish sources associated with the Jewish Diaspora in the Orient. The best-known among these recipes was suggested in the twelfth century by Maimonides, a Jewish philosopher from Spain and Egypt, for inscribing phylacteries.[7] It is very similar to the one attributed to Ibn Muqla, a famous calligrapher from the Abbasid period.[8] However, Maimonides argued against the practice of adding iron-gall ink to carbon, another popular mixed ink. It is also interesting to notice that none of the five Maimonides autographs we analyzed contained inks that followed his recipe. Analysis of the codices in the Jewish National Library in Jerusalem (Heb. 5703_2) and the Bodleian Library in Oxford (Huntington 80, fol. 165r, signature) revealed that these manuscripts were written using pure iron-gall inks. But the letter preserved in Cambridge University Library (T-S 12.192) was penned in carbon ink. Most interestingly, the manuscript containing 'The guide for the perplexed' (T-S 10 Ka 4.1) displayed both carbon and iron-gall ink on different pages and corrections both written by Maimonides himself.

These results correlate well with the study of the inks used in the legal documents found in the Cairo Genizah, which stated that both ink types were employed in mediaeval Fustat.[9]

In our study of the inks of the manuscripts produced in the Diaspora, we have found indication that Jews used the same

[1] Zerdoun 1983.

[2] Colini to be published in the PhD thesis 2018.

[3] *Materia Medica* V.181; Zerdoun 1983, 80.

[4] Zerdoun 1983, 92.

[5] Meaning the copyist's deliberate intervention in the text; Varvaro 1970, 87.

[6] Few contributions started a research in this sense: Zakī 2011, Fani 2013, Raggetti 2016.

[7] Zerdoun 1983, 111.

[8] Zerdoun 1983, 124; Schopen 2006, 130.

[9] Cohen, PhD thesis to be published in 2019.

writing materials as their non-Jewish neighbors.[10] Therefore, the Jewish records might be an excellent source for studies of the technology that corresponds to the place and time of the source. In this respect, it is interesting to compare the ink of Rashi (Rabbi Salomon ben Isaac), a Jewish author who lived in Northern France in the eleventh century, with the commentaries of Maimonides. In the Orient, Maimonides was familiar with the palette of all possible inks: carbon, plant, iron-gall, and mixtures of carbon inks with plant or iron-gall inks. In contrast, the arguments of Rashi allow us to conclude that mostly plant and maybe iron-gall ink were in use in northern Europe during the eleventh century. It is noteworthy that mixtures of carbon and iron-gall ink were found in some drawings of German artists in the fifteenth and sixteenth centuries.

The wealth of recipes for the black mixed inks in the Orient, on the one hand, and the absence of analytical evidence of their existence, on the other, raises two questions:

1. Is there a simple method for recognizing these inks?
2. Why would one use a mixture of two black inks?

Let us start by looking at the methods employed in the ink studies. Raman spectroscopy has been extensively used to identify materials such as pigments in paintings and archeological artefacts.[11] Generally, Raman spectroscopy probes the change in the wavelength of light that occurs when a light beam interacts with molecular vibrations (Raman scattering). Reliable Raman identification of mediaeval black inks started to emerge during the past decade[12] and shows that soot, logwood, and iron-gall inks have characteristic Raman spectra that provide a recognition pattern.[13] Therefore, Raman spectroscopy presents the cleanest and the most straightforward method to identify carbon and iron-gall inks and is therefore well suited to document a mixture of both. In the example below, mixed carbon and iron-gall inks were found in addition to the pure iron-gall inks of the main text of a Syriac manuscript (a sacred text, fourteenth century). The amount of added carbon was variable: ink A in Fig.1 contains less carbon than ink B, so that the features related to iron-gall (blue curve) are more evident in spectrum A, whereas spectrum B look similar to the carbon ink (black). The Raman peak at about 577 cm^{-1} and the XRF control test on both inks confirmed the presence of iron in the ink.

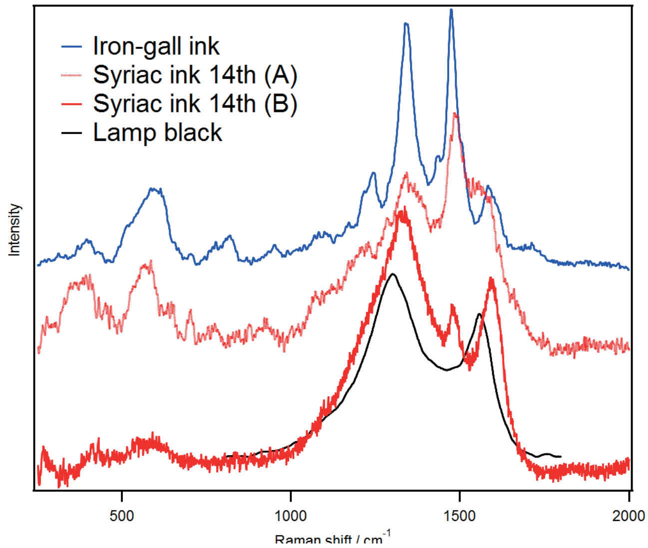


Fig.1: Raman spectra of Syriac inks (red), 14th century. The spectra of a standard laboratory sample of iron-gall ink (blue) and lamp-black ink (black) are reported for comparison. The spectra are stacked for the sake of the presentation.

Unfortunately, despite the recent development of portable Raman spectrometers, black ink analysis using Raman technique still often requires a bench instrument or the extraction of samples in addition to trained personnel.

Furthermore, Raman measurements on plant inks, i.e., inks based on tannin but not containing metals, yield no conclusive spectra with lasers in the VIS wavelength range whereas better results can be obtained by exciting the sample with a laser in the near-infrared.[14] In many cases strong fluorescence (= emission of light after excitation) of organic molecules considerably disturbs the spectrum. To overcome this difficulty, it has become customary to use Surface-Enhanced-Raman-Spectroscopy (SERS) in studies of modern paints and dyes.[15] SERS is a powerful technique in which the Raman scattering of molecules is enhanced by several orders of magnitude (up to a factor of 10^{11}) due to their adsorption by plasmonic metal surfaces (e.g. gold or silver nanoparticles) or nanostructures.[16] The simultaneous quenching of fluorescence allows measurements of strongly

[10] Rabin et al. 2014

[11] Smith and Clark 2004; Vandenabeele et al. 2007.

[12] Lee et al. 2008.

[13] Bicchieri et al. 2008.

[14] Bicchieri t al. 2017.

[15] Pozzi and Leona 2015.

[16] Schlücker 2014; Pozzi and Leona 2015; Lee and Meisel 1982.

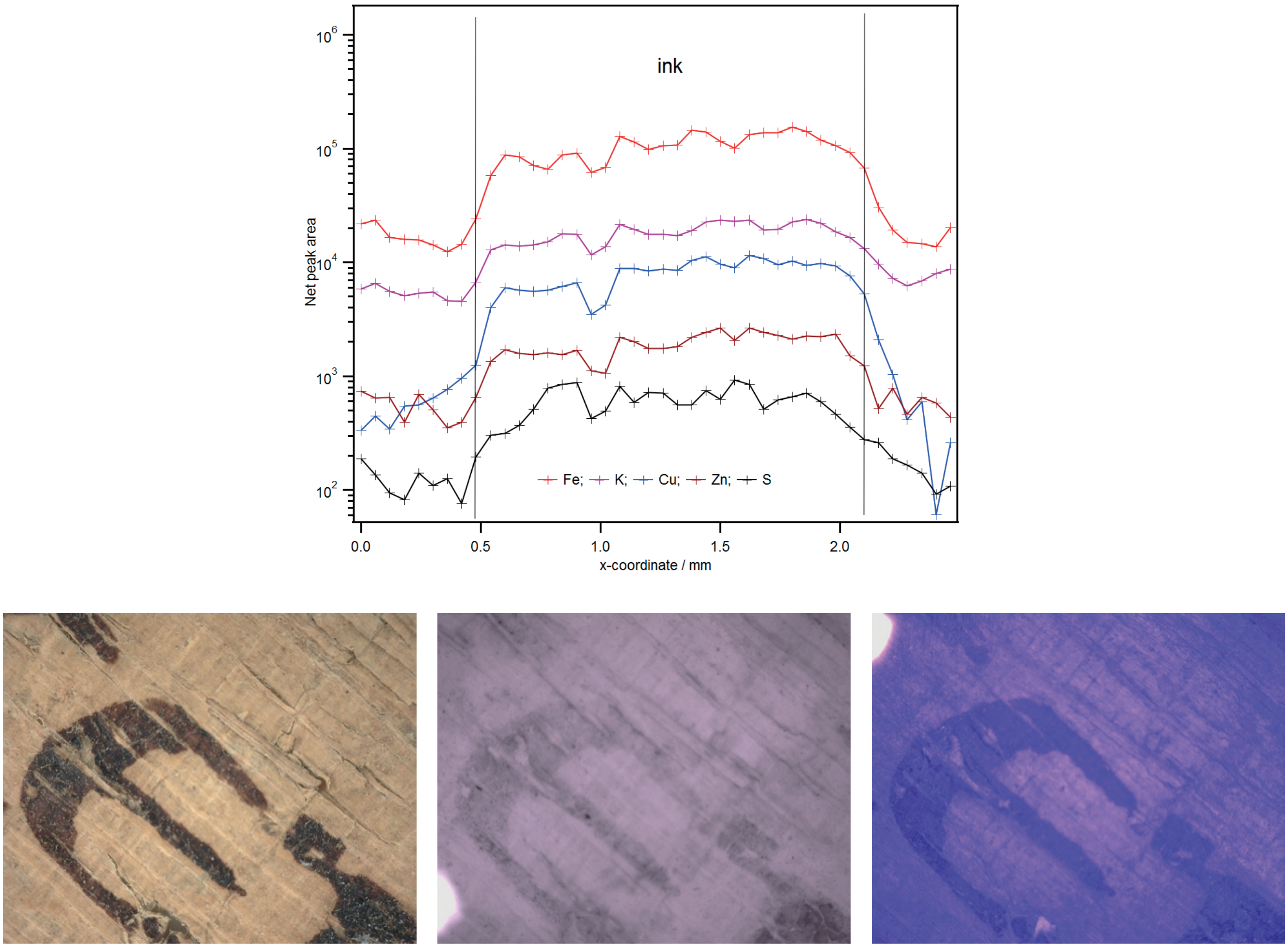


Fig. 2: Sahidic papyrus fragment Ms. Thompson HT 110.1. Fig. 2a (top): Intensities of the ink components extracted from an XRF line scan across the letter shown in the bottom images. Figs 2b, 2c and 2d (bottom): micrographs under white (left), near-infrared light (middle), and ultraviolet light (right).

fluorescent materials as well. Many different procedures for synthesizing and modifying SERS substrates have been described to optimize SERS for different kind of materials.[17] SERS is a micro-invasive technique that, depending on the selected substrate, requires a certain amount of sample. Attempts have been made, for cultural heritage purposes, to reduce the sample amount to a minimum and to optimize it.[18] In the case of tannin and iron gall ink, our first SERS tryouts yielded positive results. However, an optimized substrate and procedure for SERS on tannins and mixed inks need still to be defined. This means that, for the time being, we cannot use Raman technique to detect mixed inks on a large scale in situ and have to find a simpler way to conduct a primary classification similar to the one adopted in our ink test protocol.[19]

In short, we use the comparison of the images recorded under white and near-infrared light to quickly classify the inks by type (carbon, plant, or iron-gall). The simplicity of the test encouraged many codicologists and paleographers to adopt our methodology and share with us the results of their own field studies. As a result, a considerable number of papyri from the turn of the era started undergoing routine reflectographic checks in various collections. The knowledge of the ink type helps select which inks to study more closely. In such cases, following the reflectographic screening, we perform X-ray fluorescence analysis (XRF) on selected inks to determine their elemental composition and, in the case of the iron-gall inks, their fingerprint.[20] For the carbon inks,

[17] Pozzi and Leona 2015; Fan et al. 2011; Le Ru and Etchegoin 2009.

[18] e.g. Pozzi and Leona 2015; Lofrumento et al. 2012; Gomez and Lazzari 2014.

[19] e.g. Ghigo et al., present volume.

[20] Hahn et al. 2004; Rabin 2014.

we have used XRF to identify trace elements that could indicate characteristic contaminations. It was XRF analysis of the carbon inks that led to a successful identification of metals whose amounts hinted at intentional admixture rather than unintentional contamination.[21] In general, NIR reflectography is a quick and perfect method when dealing with an ink of a pure class, since carbon, plant, and iron-gall inks have very distinct optical properties. However, no unequivocal identification of mixed inks seems possible, since a considerable amount of carbon ink should mask the presence of any other component when illuminated with NIR light. On the other hand, tannin's property of quenching fluorescence and enhancing the contrast between a fluorescing background and the text makes UV reflectography a fine tool for identifying tannins or tracking the texts written with inks containing tannins. Since tannin solution deeply penetrates the substrate, it stays in it even if the text is removed from the surface. Therefore, the contrast enhancement achieved by UV light illumination has been widely used to recover lost writing done in iron-gall ink.[22] In the example below, we analyzed the ink in the Sahidic papyrus fragment from Cambridge University Library (Ms. Thompson HT 110.1). In the top part of Fig. 2, we present the individual intensities of the elemental components resulting from a line scan across a heterogeneously degraded letter shown in the three bottom images. Note that the curve form of each element in the graphics follows that of iron, the main component of iron-gall ink, revealing the composition of the ink. Iron, copper, and zinc represent the vitriol used in the recipe, sulfur indicates that the ink indeed contained vitriol, i.e., a mixture of metallic sulfates, and potassium is strongly associated with the tannins and gum arabic that was traditionally used as a binder. The varying thickness and degradation of the ink are reflected by the variability of the signal for iron and its satellites within the inked area. The changes in the opacity of the iron-gall inks can be seen in the bottom part of the same picture. Here the left, middle, and right images present micrographs taken under white, near-infrared (NIR), and ultraviolet (UV) light, respectively. The text penned in iron-gall ink that is perfectly visible under normal illumination becomes almost transparent when illuminated with NIR light, but regains its opacity under UV light. The latter picture shows the presence of tannin in the iron-gall ink.

We hope that tannins or the carbon/plant or carbon/iron-gall inks would be also detectable if they suffered damage and have been partially removed from the surface. Meanwhile, we started employing XRF for a routine screening of carbon inks to identify metals in metal-containing carbon inks. The fragment below is part of a demotic text concerning dream divination. It comes from Tebtynis and dates to c. 100–200 CE. It derives from clandestine excavations and was acquired by the Carlsberg Foundation on the antiquities markets of Cairo sometime between 1931 and 1938.[23]

The images in the top row of Fig. 3 show that there is no change in the opacity and intensity of the black color when the illumination is switched to NIR, proving the carboniferous nature of the ink. At the same time, the images in the bottom row show that the distributions of Ca and Fe correlate with the text, suggesting their presence in the ink. Strictly speaking, the presence of iron can't be considered unequivocal proof of iron-gall ink, since iron could have wandered into the ink as unintentional contamination. Here, however, ink contains also the element Ca, which has been detected many times in iron-gall inks. Therefore, we can assume here that we are dealing here with a mixed carbon and iron-gall ink, even though no Raman test for an unequivocal identification of iron-gall ink has been conducted.

The very early date of this ink correlates well with the detection of iron-gall ink coeval with the Coptic codex.[24] Therefore, we can assume that iron-gall ink was indeed in use in Egypt as early as the third century CE. However, it is not clear whether the production technology was always based on vitriol. In our example above, no copper, zinc, or other common iron satellites from vitriol could be detected. It is possible that metallic iron from nails was used: when soaked for a prolonged time in vinegar, the oxidation will result in the production of iron ions ready to react with tannins. We find that some of the oldest recipes in the Arabic collection prescribe using iron filings with or without acid.[25]

After establishing that the scarcity of analytical evidence results from the difficulties of unequivocal identification, we are left with a historical question of the emergence of the

[21] Nir-El and Broshi 1996; Brun et al., 2016; Christiansen et al., 2017; Rabin 2017.

[22] Rabin et al. 2015.

[23] Christiansen et al. 2017.

[24] Ghigo et al., present volume.

[25] Schopen 2006, 98–101, 124–125.

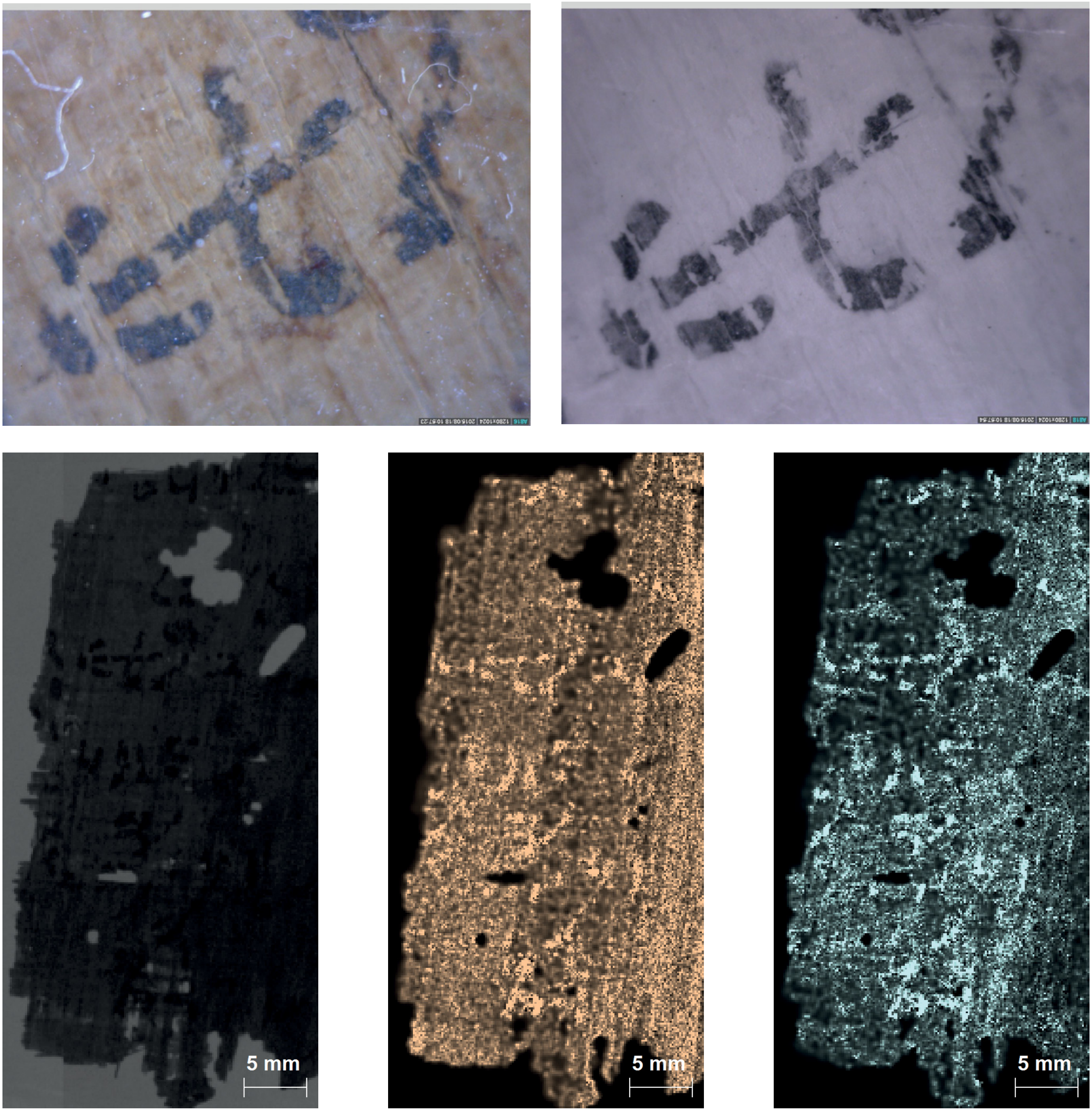


Fig. 3: Images of the papyrus P. Carlsberg 649. Top: micrographs under white (left) and near-infrared light (right). Bottom: visual image (left), calcium (middle) and iron (right) maps of the fragment.

mixed inks. The very early appearance of iron-gall inks and a high number of papyri inscribed with this ink overturn the generally accepted opinion that iron-gall ink accompanied the change of the substrate from papyrus to skin-based writing surfaces.[26] Moreover, thousands of the Dead Sea Scroll fragments inscribed with carbon inks speak strongly against this theory.

We believe that the explanation can be found in the entry 'Atramentum' of the very first encyclopedia preserved in the Western world: *Natural History* of Pliny (35.25). He recounts a number of ways to obtain black writing inks, where salts or dried leaves could be used in addition to soot. In other words, in the late Roman period, inks produced according to different recipes were in use. Given that Pliny mentions blue vitriol (copper sulfate) as 'shoemaker black' (34.123), it is rather obvious that the Romans had not yet arrived

[26] Diringer 1982, 551.

at the understanding that only green vitriol (iron sulfate) reacts with tannins to produce black substance. It is highly probable that early iron-gall ink was brown like tannin inks, so that carbon was added to obtain black ink. Alternatively, expensive carbon ink could have been adulterated by adding various dark liquids.

In any case, once we are aware of the existence of the mixed inks, we will be able to develop a suitable method for detecting them.

ACKNOWLEDGEMENT

A considerable part of the research presented in this article was carried out in the context of the SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa' funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC).

We would like to acknowledge the help of the personnel of the museums, archives and libraries who permitted us access and supported our work. Our special thanks go to the Cambridge University Library: to the scholars, Ben Outhwaite and Yasmin Faghihi, the staff of the conservation department, especially Anna Johnson and Jim Bloxam for preparing the documents and the literature, and every member of the digital contents unit, especially to Blazej Mikula and Maciej Pawlikowski for hosting us and taking care of the equipment transport.

REFERENCES

Bicchieri, M., Monti, M., Piantanida, G., Sodo, A. (2008), 'All that is Iron-ink is not always Iron-gall!', *Journal of Raman Spectroscopy* 39: 1074–1078. <https://doi.org/10.1002/jrs.1995>.

Bicchieri M., Sodo A., Rabin I., Kohl A., Piantanida G. (2018), 'New Results in Dead Sea Scrolls non-destructive characterization: Evidence of different Parchment Manufacture in the Fragments from Reed Collection' (corrected proof), *Journal of Cultural Heritage* (in press). <https://doi.org/10.1016/j.culher.2018.01.014>.

Brun, E., Cotte, M., Wright, J., Ruat, M., Tack, P., Vincze, L., Ferrero, C., Delattre, D., Mocella, V. (2016), 'Revealing Metallic Ink in Herculaneum Papyri', *Proceedings of the National Academy of Sciences*, 113: 3751–3754. <https://doi.org/10.1073/pnas.1519958113>.

Colini C., *From Recipes to Material Analysis: the Arabic Tradition of Black Inks and Paper Coatings (9th to 20th century)* (PhD thesis)

Cohen Z., *Composition Analysis of Writing Materials in Geniza Fragments* (PhD thesis)

Christiansen, T., M. Cotte, R. Loredo-Portales, P. E. Lindelof, K. Mortensen, K. Ryholt, and S. Larsen (2017), 'The Nature of Ancient Egyptian Copper-containing Carbon Inks is Revealed by Synchrotron Radiation Based X-ray Microscopy', *Science Reports*, 7: 15346. <https://doi.org/10.1038/s41598-017-15652-7>.

Cristiansen, T., Buti, D., Dalby, K.N., Lindelof, P.E., Ryholt, K. & Vila, A. (2017), 'Chemical Characterization of Black and Red Inks Inscribed on Ancient Egyptian Papyri: the Tebtunis Temple Library', *Journal of Archaeoloical Science: Reports,* 14: 208–219. <https://doi:10.1016/j.jasrep.2017.05.042>.

Diringer, D. (1982), *The Book before Printing* (New York: Dover Publications Inc).

Fan, C., Hu, Z., Mustapha, A., Lin, M. (2011), 'Rapid Detection of Food- and Waterborne Bacteria Using Surface-enhanced Raman Spectroscopy Coupled with Silver Nanosubstrates', *Applied Microbiology and Biotechnology*, 92: 1053–1061. <https://doi.org/10.1007/s00253-011-3634-3>.

Fani, S. (2013), *Le arti del libro secondo le fonti arabe originali. I ricettari arabi per la fabbricazione degli inchiostri (sec. IX-XIII): loro importanza per una corretta valutazione e conservazione del patrimonio manoscritto*, PhD dissertation, (Naples: Università L'Orientale).

Gómez, M., and M. Lazzari. (2014), 'Reliable and Cheap SERS Active Substrates', *Materials Today*, 7: 358–359. <https://doi.org/10.1016/j.mattod.2014.08.001>.

Hahn, O., W. Malzer, B. Kanngiesser, and B. Beckhoff (2004), 'Characterization of Iron-gall Inks in Historical Manuscripts and Music Compositions Using X-ray Fluorescence Spectrometry', *X-Ray Spectrometry*, 33: 234–239. <https://doi.org/10.1002/xrs.677>.

Le Ru, E.C., and P. G. Etchegoin (2009), 'Phenomenological Local Field Enhancement Factor Distributions around Electromagnetic Hot Spots', *Journal of Chemical Physics*, 130: 181101. <https://doi.org/10.1063/1.3138784>.

Lee, A. S., V. Otieno-Alego, and D. C. Creagh (2008), 'Identification of Iron-gall Inks with Near-infrared Raman Microspectroscopy', *Journal of Raman Spectroscopy*, 39: 1079–1084. <https://doi.org/10.1002/jrs.1989>.

Lee, P. C., and D. Meisel (1982), 'Adsorption and Surface-enhanced Raman of Dyes on Silver and Gold Sols', *The Journal of Physical Chemistry*, 86: 3391–3395.

Lofrumento, C., M. Ricci, E. Platania, M. Becucci, and E. Castellucci (2013), 'SERS Detection of Red Organic Dyes in Ag-agar Gel', *Journal of Raman Spectroscopy*, 44: 47–54. <https://doi.org/10.1002/jrs.4162>.

Nir-El, Y.,and M. Broshi (1996), 'The Black Ink of the Qumran Scrolls', *Dead Sea Discoveries*, 3: 157–167.

Pozzi, F., Leona, M. (2015), 'Surface-enhanced Raman Spectroscopy in Art and Archaeology', *Journal of Raman Spectroscopy*, 47: 67–77. <https://doi.org/10.1002/jrs.4827>.

Rabin, I. (2015), 'Instrumental Analysis in Manuscript Studies', in Bausi, Alessandro et al. (eds), *Comparative Oriental Manuscript Studies: An Introduction* (Hamburg: CoMSt; Tredition), 27–30.

Rabin, I. (2017), 'Building a Bridge from the Dead Sea Scrolls to Mediaeval Hebrew Manuscripts', in I. Wandrey (ed.), *Jewish Manuscript Cultures: New Perspectives* (Berlin: De Gruyter), 309–322. <https://doi.org/10.1515/9783110546422-012>.

Rabin, I., O. Hahn, and M. Binetti (2014), 'Tintenarten in mittelalterlichen hebräischen Manuskripten: eine typologische Studie / Inks Used in Mediaeval Hebrew Manuscripts: a Typological Study', *manuscript cultures*, 6: 119–130.

Rabin, I., O. Hahn, R. Easton, Jr., G. Heyworth, K. Knox, K. Boydston, G. Heyworth, T. Leonardi, and M. Phelps (2015), 'Initial Inspection of Reagent Damage to the Vercelli Book', *COMSt Bulletin*, 1: 34–45.

Raggetti, L. (2016), '*Cum grano salis*: some Arabic Inks Recipes in Their Historical and Literary Context', *Journal of Islamic Manuscripts,* 7: 294–338.

Schlücker, S. (2014), 'Surface-Enhanced Raman Spectroscopy: Concepts and Chemical Applications', *Angewandte Chemie International Edition,* 53: 4756–4795. <https://doi.org/10.1002/anie.201205748>.

Schopen, A. (2006), *Tinten und Tuschen des arabisch-islamischen Mittelalters: Dokumentation, Analyse, Rekonstruktion: ein Beitrag zur materiellen Kultur des Vorderen Orients* (Göttingen: Vandenhoeck & Ruprecht).

Smith, G.D., Clark, R.J.H. (2004), 'Raman Microscopy in Archaeological Science', *Journal of Archaeological Science*, 31: 1137–1160. <https://doi.org/10.1016/j.jas.2004.02.008>.

Vandenabeele, P., Castro, K., Hargreaves, M., Moens, L., Madariaga, J.M., Edwards, H.G.M. (2007), 'Comparative Study of Mobile Raman Instrumentation for Art Analysis', *Analitica Chimica Acta*, 588: 108–116. <https://doi.org/10.1016/j.aca.2007.01.082>.

Varvaro A. (1970), 'Critica dei testi classica e romanza: problemi comuni ed esperienze diverse', *Rendiconti dell'Accademia di Archeologia, Lettere e Belle Arti di Napoli*, 45: 73–117.

Zakī, M. (2011), 'Early Arabic Bookmaking Techniques as Described by al-Rāzī in His Recently Rediscovered *Zīnat al-Katabah*', *Journal of Islamic Manuscripts*, 2: 223–234.

Zerdoun Bat-Yehouda, Monique (1983), *Les encres noires au Moyen Âge: jusqu'à 1600* (Paris: CNRS).

SOURCES

Dioscorides, *De materia medica*: *Codex Neapolitanus, Napoli, Biblioteca nazionale, Ms. ex. Vindob. Gr. 1*, vol. 1: *Facsimile*, vol. 2: *Commentarium* by Carlo Bertelli, Salvatore Lilla, and Guglielmo Cavallo (Rom: Salerno Editrice / Graz: Akademische Druck- und Verlagsanstalt, 1988/1992).

Plinius Secundus, *Natural History*, ed. and transl. by Harris Rackham, vol. 9: *Books XXXIII – XXXV* (The Loeb Classical Library, 394) (Cambridge, Mass.: Harvard Univ. Press, 1995).

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.

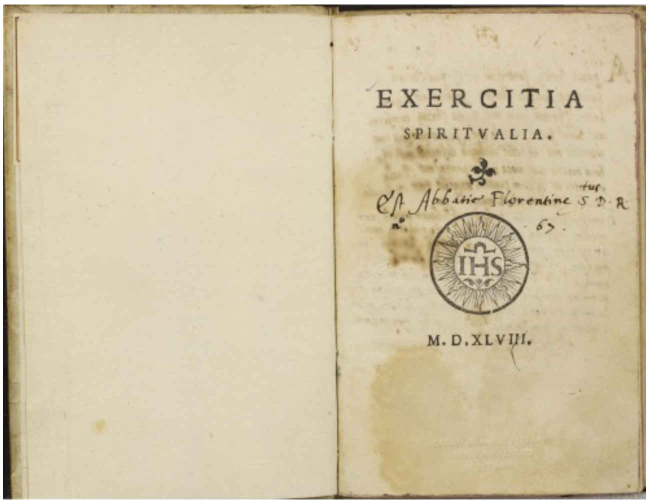
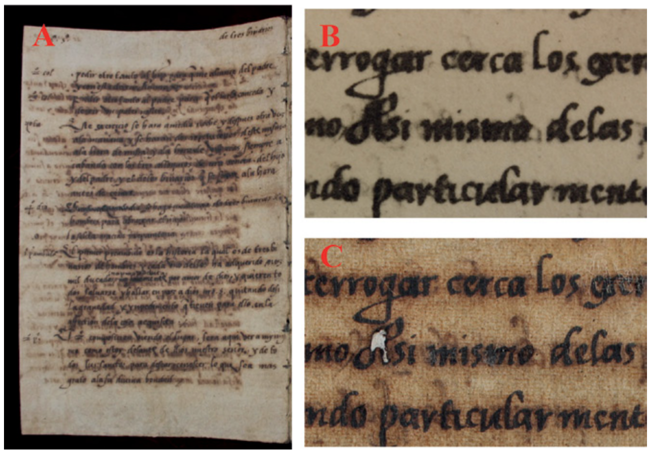


Fig. 3: First edition of the *Exercitia spiritualia*, Rome 1548. This copy belonged once to the Benedictine abbey Badia Fiorentina and belongs today to the Archives & Special Collections of the Loyola University Chicago.



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.

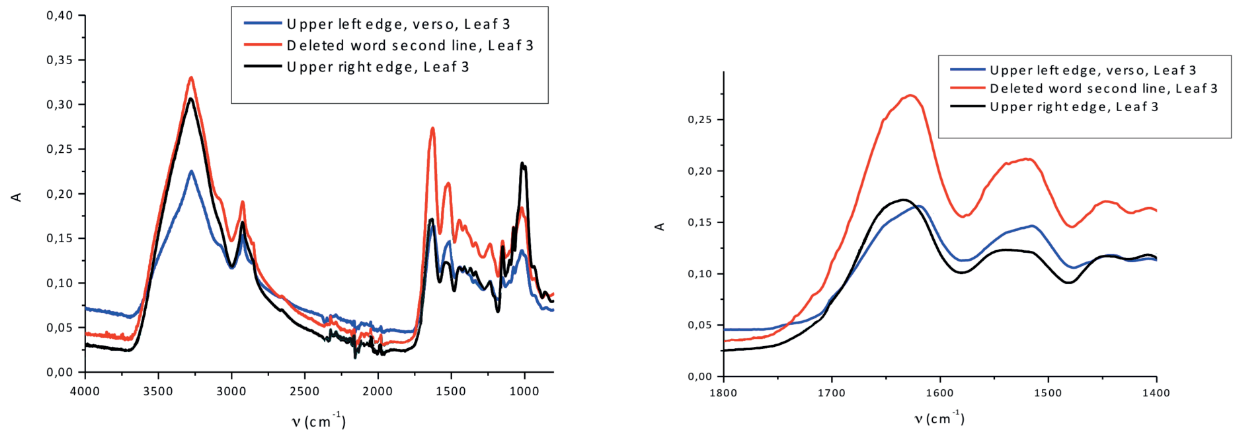


Fig. 5: ATR–IR spectra of c. 3 (left panel) and the region between 1400 and 1800 cm^{-1} magnified (right panel). Spectra of the upper left edge, verso, and upper right edge, recto, are shown in blue and black respectively. An inked deteriorated area is shown in red.

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.

[6] Derrick et al. 1999.

[7] Picollo et al. 2002.

[8] Hahn et al. 2005.

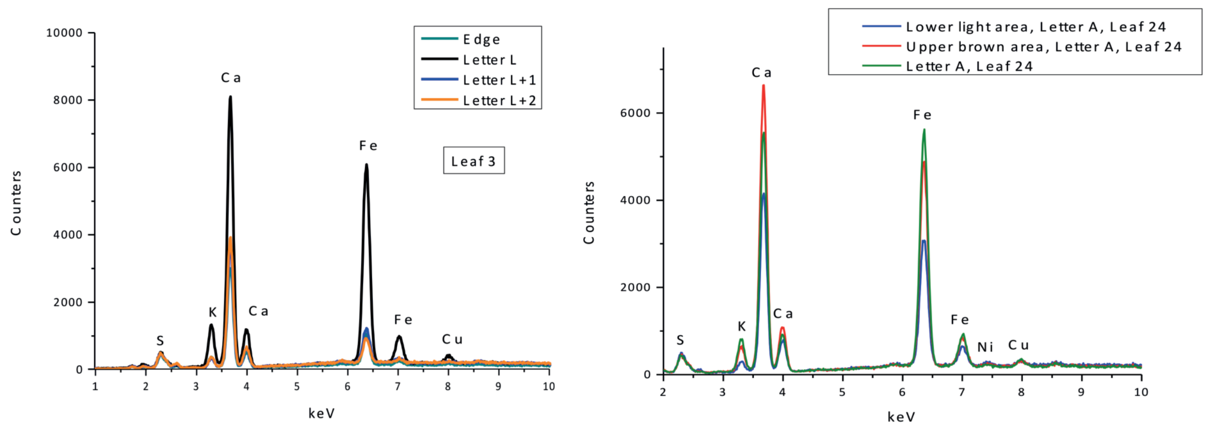


Fig. 6: Left panel, XRF spectra of c. 3: in black, spectrum of an inked area ('Letter L'), 1 mm away from the inked area (blue, 'L+1') and 2 mm away from the inked area (red, 'L+2'); in green, XRF spectrum of the edge. Right panel, XRF spectra of c. 24: an inked, degraded point (green), brown area above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

[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.

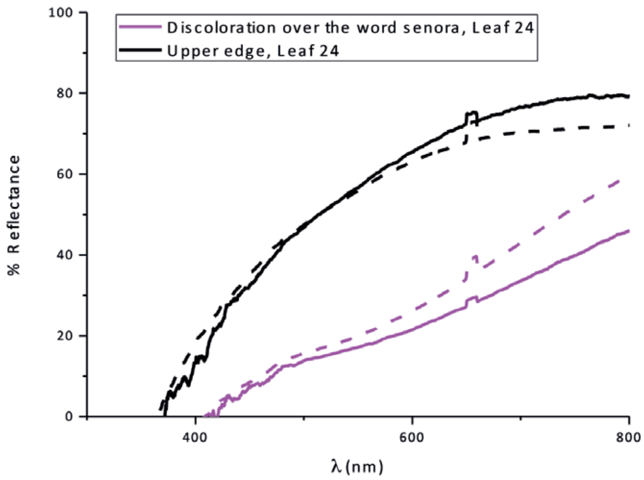


Fig. 7: FORS curves before (continuous line) and after (dotted lines) silk removal. Black line: a spectrum taken on the upper leaf edge. Pink line: a spectrum taken on a discoloration above an inked point.

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.

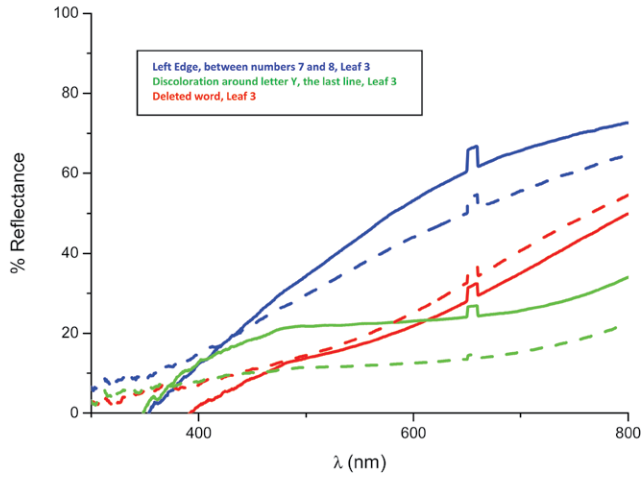


Fig. 8: FORS curves recorded before (continuous line) and after (dotted lines) the treatments on inked areas and on the margin of c. 3. Blue line: a spectrum taken on the left leaf edge. Red line: a spectrum taken on a discoloration around an inked point. Green line: a spectrum taken on an inked point.

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.

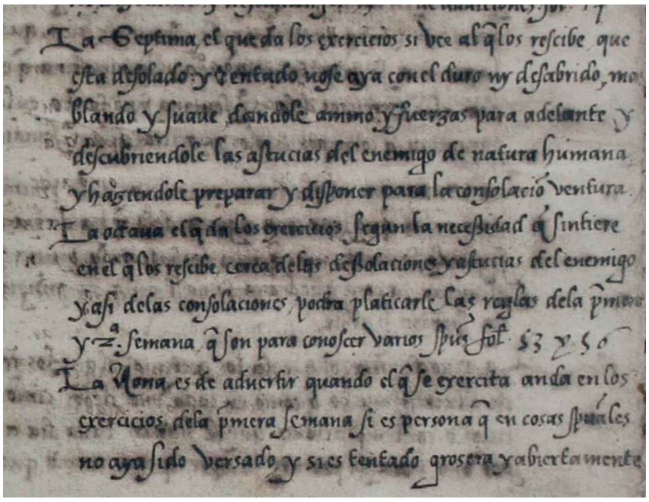


Fig. 11: Reported details of c. 3, before treatment.

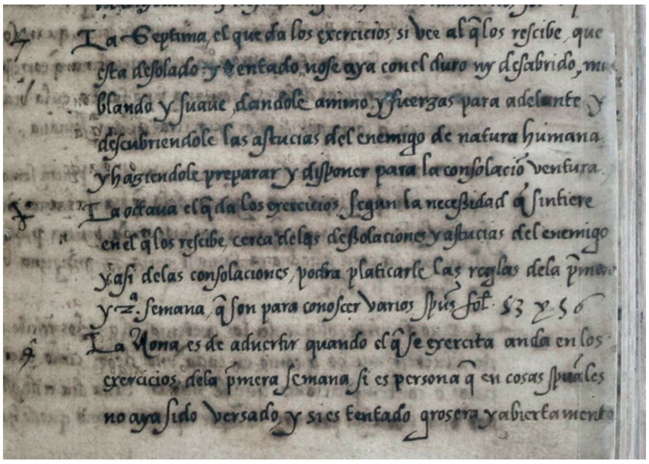


Fig. 12: Reported details of c. 3, after the combined treatment and deacidification.

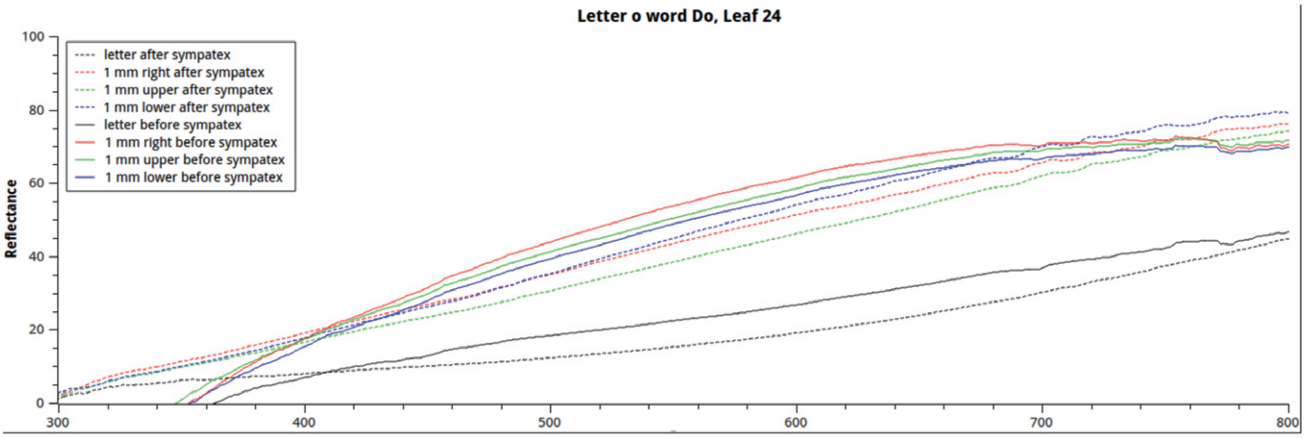


Fig. 13: FORS curve before (continuous line) and after (dotted lines) Sympatex humidification on c. 24. Black line: a spectrum taken on an inked point. Red, green, blue lines: 1 mm on the right, on the left and above the inked point.

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. 2^v–3^r, 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 re-hydrate 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.

ACKNOWLEDGEMENTS

The authors are grateful to P. Ignacio Echarte SJ, Secretary of the Society of Jesus, who made this project possible; to Mauro Brunello, the archivist of the Archivum Romanum Societatis Iesu, for his kind assistance; and to the Fundación Gondra Barandiarán in Guecho (Vizcaya, Spain) for funding the work.

Special thanks also to Aldo Barsi from Italgelatine S.p.A. for the free supply of samples of gelatine B (different Bloom) to be evaluated for the application in the conservation treatment.

[26] Rouchon et al. 2009.

REFERENCES

Barrett, T. D. (1989), 'Early European papers/contemporary conservation papers: A report on research undertaken from fall 1984 through fall 1987', *The Paper Conservator*, 13: 1–108.

Barrett, T. and C. Mosier, (1994), 'The Role of Gelatine in Paper Permanency II', *The Book and Paper Group Annual*, 13: 5–8.

Bicchieri, M., M. Monti, G. Piantanida, F. Pinzari, S. Iannuccelli, S. Sotgiu, and L.Tireni (2012), 'The Indian drawings of the poet Cesare Pascarella: non-destructive analyses and conservation treatments', *Analytical and Bioanalytical Chemistry*, 402.4: 1517–28.

Bronzato, M., P. Calvini, C. Federici, S. Bogialli, G. Favaro, M. Meneghetti, M. Mba, M. Brustolon, and A. Zoleo (2013), 'Degradation Products from Naturally Aged Paper Leaves of a 16th-Century-Printed Book: A Spectrochemical Study', *Chemistry*, 19.29: 9569–9577.

Calvini, P., A. Gorassini, G. Luciano, and E. Franceschi (2006), 'FTIR and WAXS analysis of periodate oxycellulose: Evidence for a cluster mechanism of oxidation', *Vibrational Spectroscopy*, 40: 177–183.

Charles, V. (2008), 'Cold Gelatine Adhesive', *Papierrestaurierung*, 9.3: 11–12.

Exercitia spiritualia: textuum antiquissimorum nova editio lexicon textus Hispani (1969), in *Monumenta Ignatiana ex autographis vel ex antiquioribus exemplis collecta Ignatius de Loyola*, Series 2, Part 1 (Monumenta Historica Societatis Jesu, 100) (Rome: Institutum Historicum Societatis Iesu).

Derrick, M., D. Stulik, and J. M. Landry (1999), *Scientific Tools for Conservation. Infrared Spectroscopy in Conservation Science* (Los Angeles: The Getty Conservation Institute).

Ejercicios Espirituales de S. Ignacio de Loyola fundador de la Companìa de Jesus. Reproducion fototipica del original (1908) (Rome: Stabilimento Danesi).

Garlick, K. (1986), 'A Brief Review of the History of Sizing and Resizing', *The Book and Paper Group Annual*, 5: 94–107.

Gelatine Manufacturers Institute of America (GMIA) (ed.) (n.y.), *Gelatine Handbook*. <http://www.gelatin-gmia.com/> (last accessed 15 April 2018).

Hahn, O., B. Kanngießer, and W. Malzer (2005), 'X-ray fluorescence analysis of iron gall inks, pencils and coloured crayons', *Studies in Conservation*, 50: 23–32.

Hey, M. (1979), 'The Washing and Aqueous Deacidification of Paper', *The Paper Conservator*, 4: 66–79.

Iannuccelli, S. and Sotgiu, S. (2012), 'Generalità sul gellano: struttura chimica, proprietà, applicazioni', in S. Iannuccelli and S. Sotgiu (eds), *La pulitura a umido di opere d'arte su carta con gel rigidi di gellano: presupposti teorici, metodologia applicative e verifica analitica* (Padua: Il Prato), 23-57.

Kolar, J. and Strlic, M. (eds) (2006), *Iron Gall Inks: On Manufacture, Characterisation, Degradation and Stabilization* (Ljubljana: National University Library).

Kolbe, G. (2008), 'Gelatine in Historical Paper Production and as Inhibiting Agent for Iron-Gall Ink Corrosion on Paper', *Restaurator*, 25: 26–39.

Łojewska, J., Lubańska, A., Miśkowiec, P., Łojewski, T., and Proniewicz, L.M. (2006), 'FTIR in situ transmission studies on the kinetics of paper degradation via hydrolytic and oxidative reaction paths', *Applied Physics A*, 83: 597–603.

Łojewski, T., Miśkowiec, P., Missori, M., Lubańska, A., Proniewicz, L.M. and Łojewska, J. (2010), 'FTIR and UV/vis as methods for evaluation of oxidative degradation of model paper: DFT approach for carbonyl vibrations', *Carbohydrate Polymers*, 82: 370–375.

Netherlands Institute for Cultural Heritage (ICN) (ed.) (2001), 'Condition rating for paper objects with iron-gall ink', *ICN-Information*, 1: 1–4. <https://www.scribd.com/document/27703598/Condition-rating-for-paper-objects-with-iron-gall-ink-ICN-info-1> (last accessed 15 April 2018).

Plossi Zappalà, M. (1997), 'Conservation of Acid Paper: Studies carried out in the Chemistry Laboratory of the Istituto Centrale per la Patologia del Libro', *Restaurator*, 18: 12–24.

Picollo, M., M. Bacci, A. Casini, F. Lotti, S. Porcinai, B. Radicati, and L. Stefani (2002), 'Fibre Optics Reflectance Spectroscopy: A Non-destructive Technique for the Analysis of Works of Art', in S. Martellucci, A.N. Chester, A.G. Mignani (eds), *Optical Sensors and Microsystems. New Concepts, Materials, Technologies* (NY: Kluwer Academic Publisher), 259–265.

Reissland, B., S. de Goot (1999), 'Ink corrosion: Comparison of currently used aqueous treatments for paper objects', in *IADA-Preprints* (9th IADA Congress, Copenhagen: Internationale Arbeitsgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren).

Rouchon, V., B. Durocher, E. Pellizzi, and J. Stordiau-Pallot, (2009), 'The water sensitivity of iron gall ink and its risk assessment', *Studies in Conservation*, 54: 236–254.

Rouchon, V., E. Pellizzi, and K. Janssens (2010), 'FTIR techniques applied to the detection of gelatine in paper artifacts: from macroscopic to microscopic approach', *Applied Physics A*, 100: 663–669.

Rouchon, V., E. Pellizzi, M. Duranton, F. Vanmeert, and K. Janssens (2011), 'Combining XANES, ICP–AES, and SEM/EDS for the study of phytate chelating treatments used on iron gall ink damaged manuscripts', *Journal of Analytical Atomic Spectrometry*, 26: 2434–2441.

Poggi, G., M. C. Sistach, E. Marn, J. F. Garcia, R. Giorgi, and P. Baglioni (2016), 'Calcium hydroxide nanoparticles in hydroalcoholic gelatine solutions (GeolNan) for the deacidification and strengthening of papers containing iron gall ink', *The Journal of Cultural Heritage*, 18: 250–257.

Stephens, C., T. Barrett, P. Whitmore, P., J. Mazurek, M. Schilling, and W. Rantanen (2007), 'Composition and Condition of Naturally Aged European Papers', *The Book and Paper Group Annual*, 26: 107–11.

Tamburin, M. (2008–2009), *Le gelatine animali: tecnologia di produzione e caratteristiche igienico–sanitarie* (Thesis, Università di Padova: Facoltà di Medicina Veterinaria).

Zoleo, A., D. Confortin, N. Dal Mina, and M. Brustolon (2010), 'The role of metal ions in the study of ancient paper by electron paramagnetic resonance', *Applied Magnetic Resonance*, 39: 215–223.

PICTURE CREDITS

Fig. 1: © Rijksmuseum Amsterdam.

Fig. 2: © The authors.

Fig. 3: © Loyola University Chicago, Archives & Special Collections.

Figs 4–14: © The authors.

Article

Image Processing Software for the Recovery of Erased or Damaged Text

Keith T. Knox | Kihei, Hawaii

1. Abstract

An imaging processing software package is being developed to recover erased or damaged text from multispectral images of ancient documents written on parchment or paper. The software is being written in the Java programming language to make it portable to many different computer platforms. The goal of the software project is to make this package of image processing routines available for use anywhere in the world by researchers, students, and potentially even scholars. The architecture of the software has been designed to make it modular, easily expanded, and easy-to-use with an intuitive graphical user interface. The capabilities of the software are demonstrated with examples of recovered text from manuscripts from the library of the Holy Monastery of St Catherine at Mount Sinai in Egypt.

2. Multispectral Imaging

The multispectral imaging system used in this project at St Catherine's Monastery was developed by MegaVision. Called the EurekaVision system, it includes a 50 megapixel panchromatic camera, and two panels of LEDs (light-emitting diodes) with diffusers, at several wavelengths across the spectrum from the ultraviolet to the near infrared.[1]

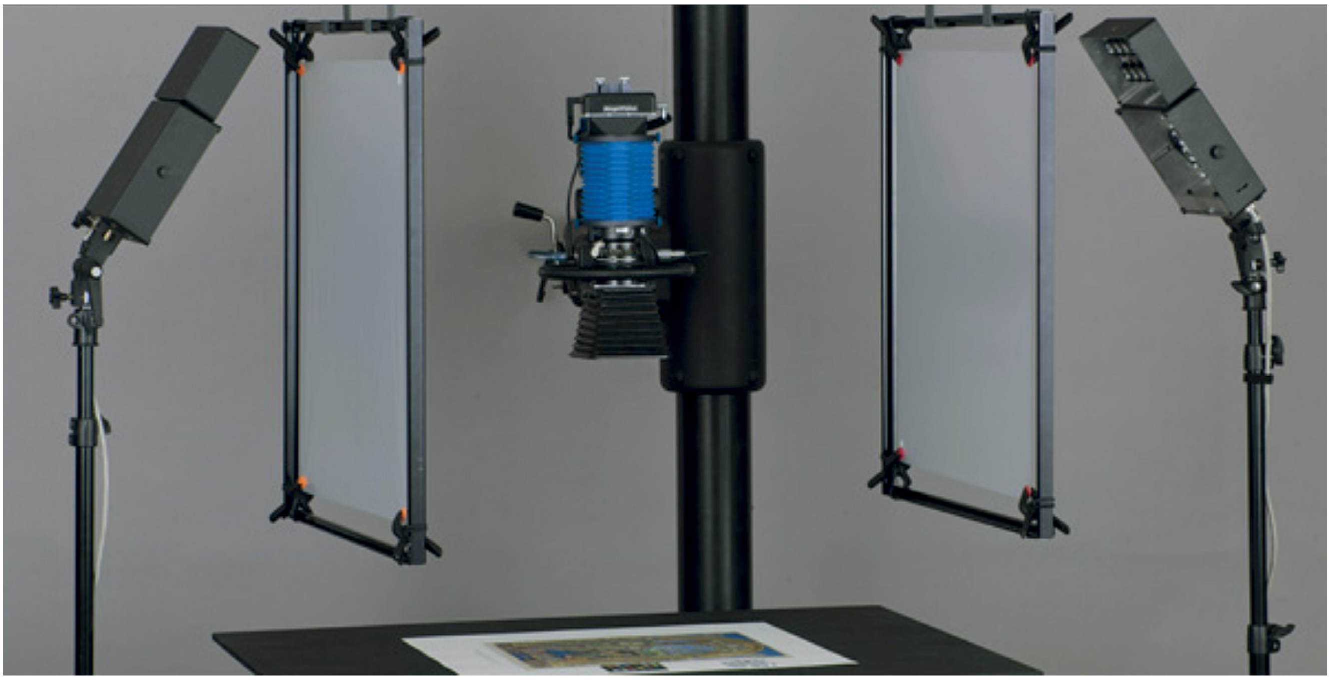


Fig. 1: EurekaVision cultural heritage imaging system from MegaVision.

[1] *MegaVision Archival and Cultural Heritage Imaging* <http://www.megavision.com/cultural_heritage.html>.

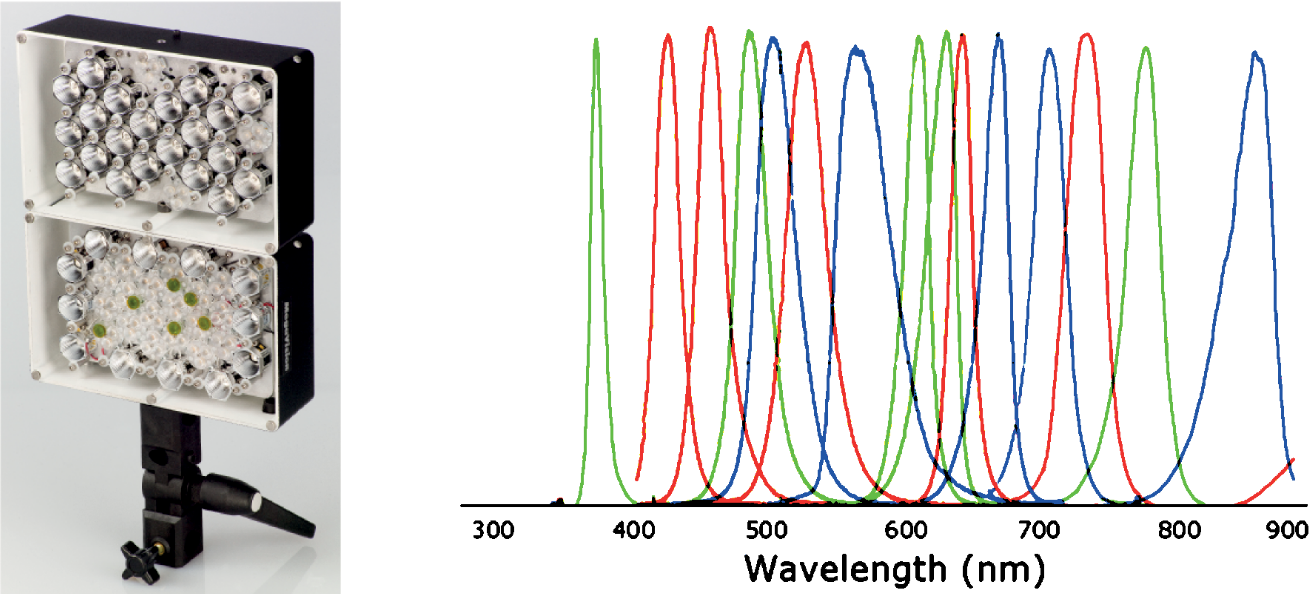


Fig. 2: A light panel from the EurekaVision system with several LEDs and their corresponding spectra.

A MegaVision imaging system is shown in Fig. 1. An early version of this system was used to image the Archimedes Palimpsest.[2] There are two light panels at either side of the copy stand, with diffusers suspended in front of the lights to spread the light uniformly across the manuscript. The LEDs are narrow-band light sources at specific wavelengths across the spectrum from the ultraviolet, through the visible region, and into the near infrared. A single LED panel, with the accompanying spectra of the LEDs, is shown in Fig. 2. During the course of the Sinai Palimpsests Project, LEDs of 12 different wavelengths were used. Since then, the number of wavelengths has been expanded to 15, as shown in Fig. 2.

To image the manuscript and gather the multispectral data, the manuscript is illuminated with light from the LEDs of individual wavelengths. During a single exposure, only the light from LEDs of one wavelength is used. Subsequent exposures capture the response of the manuscript from each of the different wavelengths sequentially. Given that the manuscript and the imaging systems (lights and camera) do not move from exposure to exposure, then all of the multispectral images are registered with respect to each other. This is achievable, because there is no heat generated by the LEDs that might cause the manuscript page to expand or contract between exposures.

In addition to these wavelengths, an option to capture the color variation of the fluorescence is also available. Typically, due to exposure with ultraviolet light, the substrate of the leaf fluoresces, while the inks do not. This increases the contrast of the writing against the background of the leaf. When the leaf fluoresces, it absorbs the ultraviolet light and re-emits light at lower wavelengths, typically in the visible region. A series of filters are rotated into the light path to filter the fluorescence and record its color variation. Most of these filters are very thin films, and as a result, there is little to no translation of the images due to the thickness of the filters and an arbitrary tilt of the filter within the light path. This maintains registration of the fluorescence-filtered images with the rest of the image set.

Further study of targets specifically designed to test the registration has shown that slight variations do exist in the captured imagery. Although this study has only just been started, initial results show that there are some very slight translations and magnifications induced by the very thin Wratten filters. There are also two glass filters used, one to block and one to pass the reflected ultraviolet light. These thicker filters do induce a noticeable magnification to the images, which needs to be corrected to avoid introducing edge effects in processed results that use those two images. It is beyond the scope of this paper to detail these effects or their mitigations, which will be addressed in future publications.

The spectral response of the parchment and inks can be seen in Fig. 3. The contrast of the images has been adjusted so that the parchment appears to be the same across the

[2] Easton, Knox, et al. 2010.

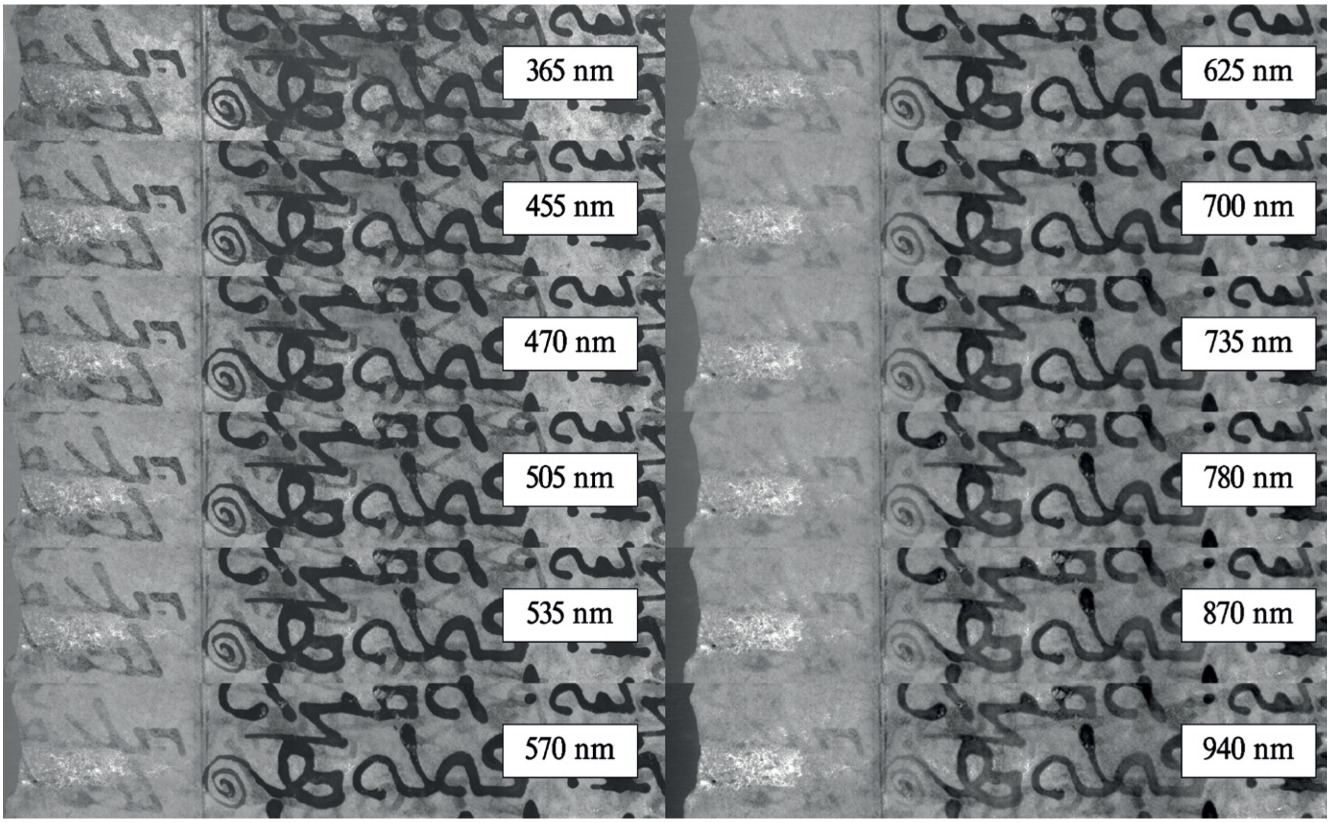


Fig. 3: Several images at different wavelengths of a manuscript parchment containing erased and overwritten handwriting.

wavelengths. Of course, the actual reflectance of the parchment varies across the spectrum. With this contrast adjustment, though, one can see that, in relation to the parchment, the erased ink stains in the parchment (seen on the left in each image) fade rapidly and practically disappear in the near infrared. On the other hand, the overwriting (seen on the right side of each image) maintains high contrast across the spectrum, although it does fade a little bit into the infrared.

Gathering the multispectral data is only the first step in recovering the erased (or damaged) text. The goal is to record the differences in the reflectance or fluorescence of the different inks and the parchment under different wavelengths of illumination. If these differences are easily visible at one or more of the wavelengths, then the text can be easily separated. On the other hand, these differences might manifest themselves in slight, low-contrast variations spread across the wavelengths, and not readily visible to the eye at any one wavelength. This is where sophisticated methods of extracting low contrast differences, through the image processing of the multispectral data, are needed to make the erased writing visible for the scholar to read.

Simple image processing methods that utilize the visible differences in wavelength response between the visible and the red, or near infrared, exposures were developed for the Archimedes Palimpsest Project and expanded for the Sinai Palimpsests Project. These methods are implemented in custom software, written for UNIX in C, and are the subject of this paper.

On the Sinai Palimpsests Project, other methods have been explored that use algorithms such as Principal Components Analysis (PCA) and Independent Components Analysis (ICA). These algorithms are capable of extracting image differences that are not readily visible to the eye, making them a subsequent step in processing, when simple processing methods do not yield sufficient results.

It is an art to use these sophisticated algorithms and the other image processing team members of the Sinai Palimpsests Project have spent several years honing their skills in this area. These other scientists are Dr Roger Easton, Jr of the Rochester Institute of Technology, Dr David Kelbe of the Oak Ridge National Laboratory and Dr William Christens-Barry of Equipoise Imaging LLC. The use of these sophisticated algorithms is not within the scope of this paper.

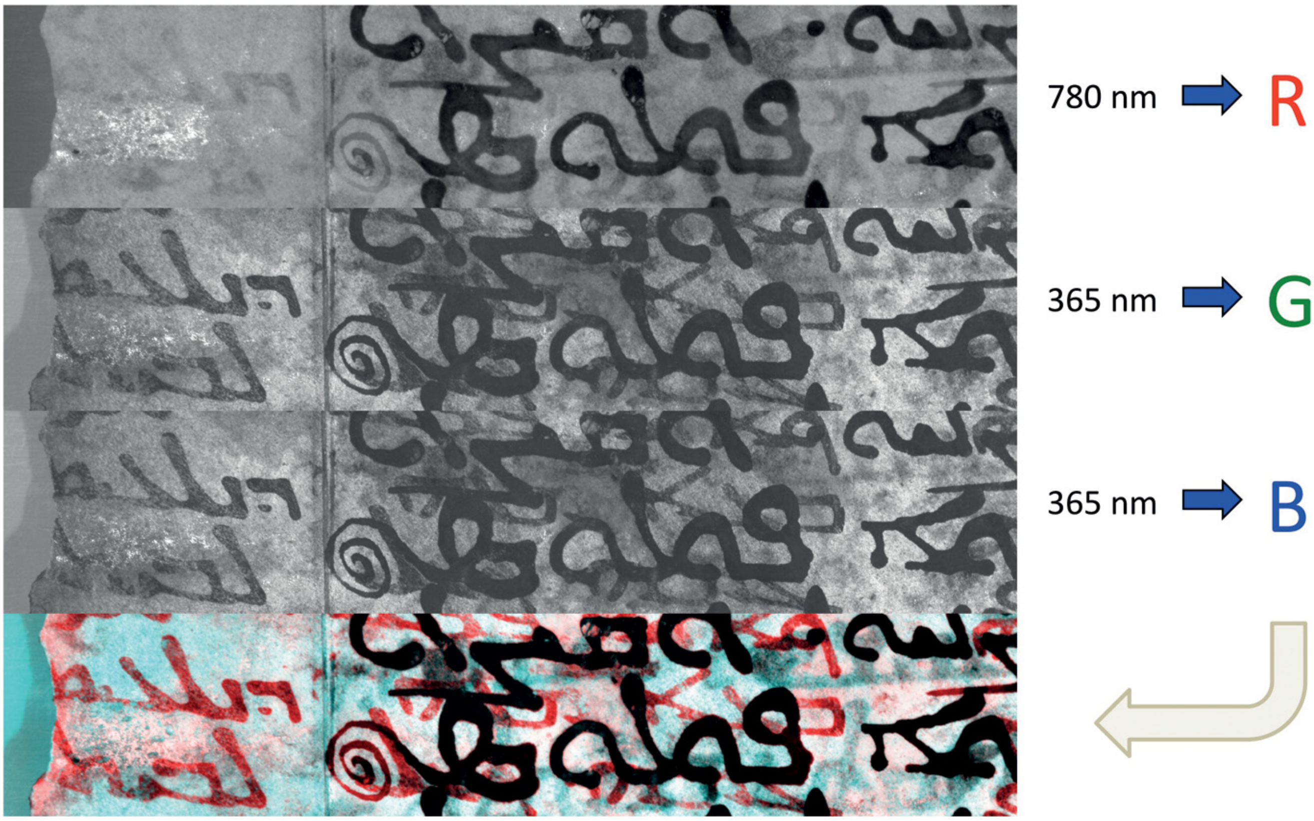


Fig. 4: A pseudocolor image is formed by combining two images into a single color image.

3. Sinai Palimpsests Project

The Sinai Palimpsests Project is a 5-year project that started in 2011. It is a joint effort of the Holy Monastery of St Catherine at Mount Sinai, the Early Manuscripts Electronic Library of California, and the Arcadia Foundation of the United Kingdom, to image palimpsests within the monastery's library and make them available to scholars.[3]

There are approximately 160 known palimpsests in the library of the Holy Monastery of St Catherine. Around 72 of these palimpsests have been imaged and processed by the project team. All images have been processed with the standard processing methods that will be described here.

The primary method is to form a pseudocolor image from two wavelengths of the multispectral image set.[4] The primary wavelengths that are combined are an ultraviolet image and a visible image. The ultraviolet image may be the 365 nm image shown in the upper left corner of Fig. 3, or it may be one of the filtered ultraviolet images, not shown in that figure. The second image is a visible image that is typically taken from the red to infrared region, perhaps the 625 nm image or the 780 nm image.

These two images are combined into a single RGB color image, as shown in Fig.4. The visible image, in this case at 780 nm, shows the overwriting, but the erased writing has almost completely disappeared into the parchment background. On the ultraviolet image, the erased writing stands out, along with the overwriting. By this method, the erased writing appears bright in the red separation and dark in the green and blue separations, making it appear to be red in the pseudocolor image. On the other hand, the overwriting is dark in all three color separations, making it appear neutral gray or black in the pseudocolor image. As a result, the erased writing shows up in high color contrast with respect to both the overwriting and the parchment background. This makes it easy for the scholar to read, even though some of the letters are partially obscured by the overwriting.

One additional step is done to each of the two images (the ultraviolet image and the visible image) before the two images are combined. That step is a locally-adaptive, normalization of the contrast of the image detail. A sliding window is moved across the image. Within the window, the

[3] *Sinai Palimpsests Project* <http://sinaipalimpsests.org>.

[4] Knox 2008.

Fig. 5: The natural light image of Holy Monastery of St Catherine at Mount Sinai, Ms. Syriac 30, fol. 4r on the left, compared to the pseudocolor image on the right.

Fig. 6: Natural light, Holy Monastery of St Catherine at Mount Sinai, Ms.Georgian NF 13, fol. 59r.

mean and the variance are measured. With these statistics, the center pixel of the sliding window is put through a linear stretch that adjusts the mean value to 127.5 and stretches the contrast so that ±3 standard deviations extend linearly between black and white (0–255).

This is a local adjustment, because the amount of contrast stretching depends on the image values within the sliding window. This tends to smooth out the variations in the background levels across the leaf and to equalize the contrast of the characters against the parchment background. That makes it easier to make the overwriting a neutral color, while enhancing the color contrast of the erased writing. The final result of the pseudocolor process can be seen for the whole leaf in Fig. 5.

A second standard processing method that was applied to all of the images on the Sinai Palimpsests Project is called a transmission ratio image. Images captured in transmission were taken of each leaf with a custom sheet illuminator on which each leaf is placed. Light from LEDs is fed into the clear transparent illuminator and it radiates uniformly out of the sheet, through the leaf and into the camera above. This enables the camera to see light, in wavelengths through the visible and into the infrared, that travels through the leaf from the back of the parchment. The reflectance images, as described earlier, are taken along with the transmission images. Since the leaf does not move during either process, the transmission images are registered with all of the other images.

The transmission ratio image is formed by taking the ratio of the transmission image at 940 nm by the reflectance image at 940 nm. Since the overwriting shows up in both images, this ratio tends to reduce the contrast of the overwriting. A contrast enhancement and a localized sharpening are then performed. The importance of the transmission ratio image can be seen in the next example. In Fig. 6 is shown a natural light image of Georgian NF 13, fol. 59 recto. The erased writing is very difficult to see. There appear to be some horizontal smudges where the erased characters should be. On the right-hand side of the image, in the center of the leaf, there are some characters that are barely visible.

The pseudocolor image of this page is shown in Fig. 7. There are some characters visible at the top of the image in

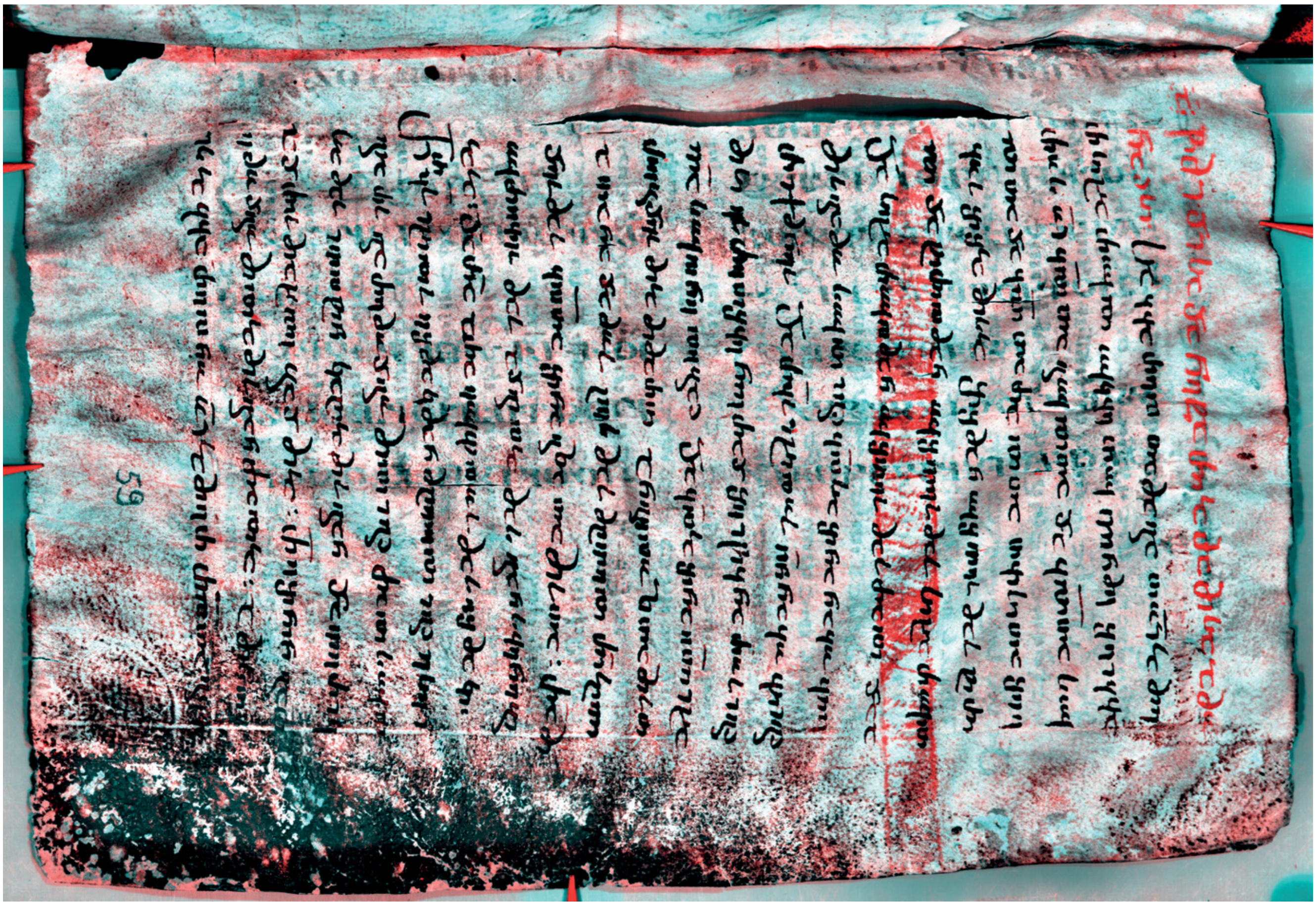


Fig. 7: Pseudocolor, Holy Monastery of St Catherine at Mount Sinai, Ms. Georgian NF 13, fol. 59r.

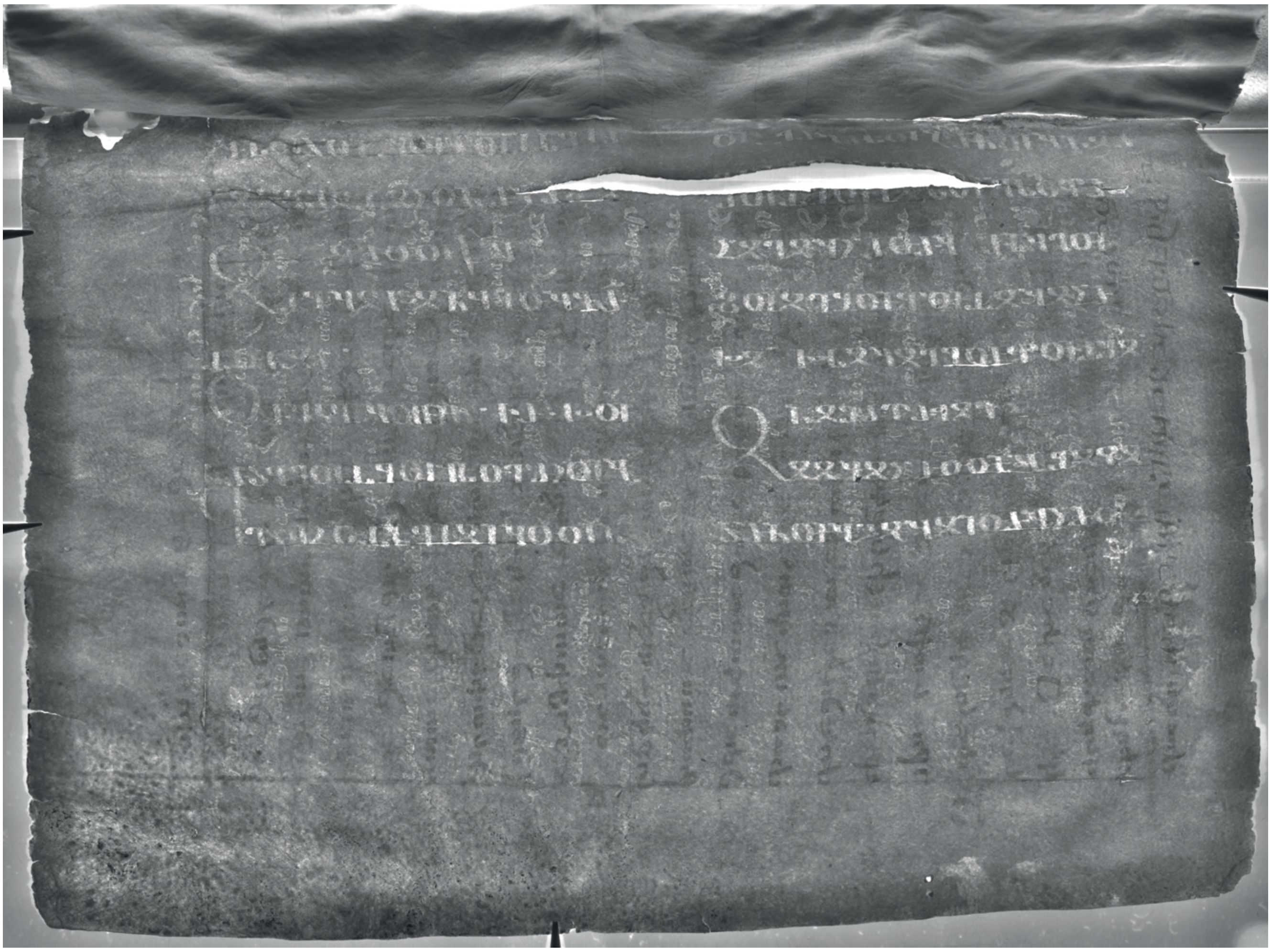


Fig. 8: Transmission ratio, Holy Monastery of St Catherine at Mount Sinai, Ms. Georgian NF 13, fol. 59r.

the gutter. For the rest of the leaf, though, there are hints of cyan colored characters, but nothing like the red characters typical of a fluorescence image taken under ultraviolet illumination.

The problem is that the residual acid of the original ink has eaten into the parchment. The parchment is a little thinner in the region of the character and no stain exists there to inhibit the fluorescence. As a result, the region of the character fluoresces along with the parchment, resulting in very low contrast characters in the pseudocolor image.

The fact that the parchment is thinner, though, means that the transmission image is now very valuable. In the transmission image, more light makes it through the leaf specifically in the regions where the erased characters have eaten into the parchment. This produces an image that shows clear characters that are otherwise very difficult to see. Since this process of eating away at the parchment tends to happen preferentially on the flesh side of the parchment, only the characters from one side are visible in the transmission ratio image.

The transmission ratio image of Georgian NF 13, fol. 59 recto is shown in Fig. 8. Now the characters that were barely visible in some regions, and not visible at all in most regions, are now clearly visible in transmission. Although this is a very simple process, the transmission ratio image has turned out to be a very valuable addition to the image processing toolkit for the Sinai Palimpsests Project.

4. Image Processing Software

The software to produce the pseudocolor and the transmission ratio images in this paper is part of a UNIX-based package of image processing routines, written in C by the author, between 2000 and 2013, to process the multispectral images of the Archimedes Palimpsest project.[5]

The UNIX operating system has the advantage that processing modules can be created (each implementing a

[5] *The Archimedes Palimpsest* <http://www.archimedespalimpsest.org>.

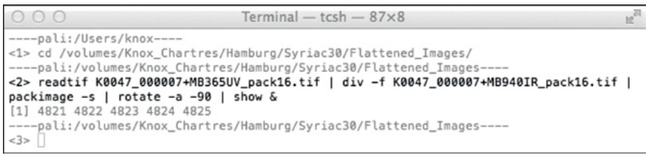


Fig. 9: Text-based interface of the UNIX-based, C-language image processing system. In this example, a ratio of two images is displayed.

single algorithm), that run independently and simultaneously, and communicate with each other by exchanging image scanlines over UNIX pipes. The use of UNIX pipes to exchange image scanlines, means that only a few scanlines of the image are in memory at any one moment. Each module receives a scanline, processes it and passes it onto the next module, before retrieving its next scanline. In this way, a very large image can be easily processed without running out of memory or requiring a computer with large memory stores.

Since each algorithm is implemented in its own module, standard algorithms can be implemented and tested separately, and then used without change at a later time. To add a new algorithm, a new module is written and tested without introducing errors in the implementations of the existing algorithms. To use the new module, it is simply included in the UNIX command line. This is easy for a software researcher to do, but is beyond the capabilities of a non-technical user.

For example, a command line to take the ratio of two images, using the UNIX-based software, is shown in Fig. 9. A file is read and piped to a routine that reads a second image and takes the ratio. This result is piped to a routine that adjusts the contrast and lastly to a routine that rotates the image for display. For the expert, this is easy to set up, but tedious to type into a text window. For the non-expert, this tends to be too complicated to be useful.

To make the software available to more people, a new version of the software, called Hoku, is being created in the Java language. The move to the Java programming language was made for two reasons. First, Java is a portable language that is available on almost all computers and operating systems. Secondly, Java comes with tools that make it easy to create graphical user interfaces. These two features make it possible to create an image processing package that can be used by a large number of people with varying degrees of technical expertise.

Although Java does not implement UNIX pipes, within Hoku, a modular architecture was created to enable each module to be run as an independent software 'thread' with an interface that enables modules to retrieve and send processed scanlines. As a result, a new image processing capability can be easily incorporated into the package. Since each module runs as an independent 'thread', different modules can run on different processors of a multi-processor computer, shortening execution times.

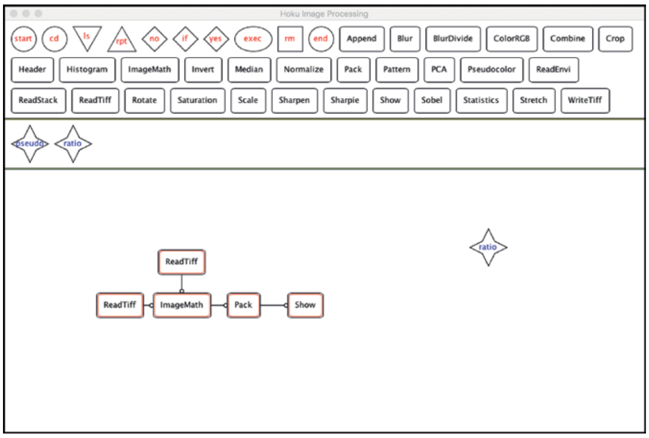


Fig. 10: User interface for the Java-language based Hoku image processing system.

The Java software package is still under development, but a preliminary user interface is shown in Fig. 10. The interface consists of three regions, a 'cupboard' on the top, a 'shelf' in the middle and a 'desktop' on the bottom. A list of available routines is automatically created as the package starts up and is displayed along the top in the 'cupboard'. To use one of the modules, the user simply drags it into the 'desktop' with the mouse or track pad. As multiple modules are added to the processing task, links are automatically connected between modules. A small circle on the link acts like an arrow and indicates the direction of flow of the image scanlines. The non-rectangular modules at the top left, with names in red, are control modules, which will enable jobs to be run on complete directories of images.

In the example shown below, two images are read, fed to a module called ImageMath, where a ratio is taken. The ratio is contrast adjusted and displayed on the screen. This job can be run in batch mode. If one draws a box around the collection of modules, that collection is collapsed into a 'star' figure containing the name of the job, in blue letters. This job can be dragged to the 'shelf', where it can be retrieved at a later time. When dragged to the 'shelf', a command file containing a source description of the job is saved to disk for later use. The job can be re-opened on the 'desktop' by drawing a box around the job icon. This expands the job into its set of linked modules allowing additional editing.

On the 'desktop', a job can be executed by right-clicking within the job icon and selecting 'Execute' from the pop-up menu that appears. When this task is executed, each ReadTiff module opens its image file, reads and feeds individual scanlines to the next module down the pipeline. Every other module, all of them running independently and simultaneously, gets a new scanline (from the module before it), processes the scanline, and then passes the processed scanline to the next module in the pipeline. In this way, images of arbitrary sizes can be processed with this software, without requiring large amounts of computer memory. Any module can buffer a few input scanlines as needed to produce an output scanline. Multiple jobs can be created, edited and executed on the 'desktop' at the same time.

There are commercial image processing systems available to process multispectral imagery. For example, ENVI is a software package developed for remote sensing image data.[6] While these commercial packages contain many image processing features, typically, they are complicated and the cost of the software can put it out of the reach of many potential users.

An open source Java software package, called ImageJ, also exists.[7] This software is freely available and has many algorithms available through plug-ins. It would be possible to implement the image processing software described in this paper with ImageJ, but it would lack one main advantage, that of small memory. The ImageJ software reads the whole image into memory, requiring a computer with a lot of memory to hold large images. The Hoku software package will have the advantage of being able to operate on computers with a small amount of memory, but still process large images.

In comparing the amount of memory required, ENVI typically will create an image cube that contains all of the images for a given leaf, stored in 64-bit pixels, or floating-point doubles. The raw images from MegaVision are currently 100 MB each, i.e. 16 bits/pixel and 8176 × 6132 pixels. Currently, 50 images are taken for each leaf. That means that one image cube requires 20 GB of image memory just to hold one copy of it in ENVI's memory. ImageJ typically reads the 16-bit pixels, but that still requires 5 GB for one image cube. Any processing within ImageJ, might require additional copies of that image cube. On the other hand, Hoku holds one or maybe a few scanlines at a time in memory in each module. For example, a job with 10 modules, where each module has an input buffer, a working buffer and an output buffer, would require 30, let's say 100 scanlines. If each of those 100 scanlines were floating point, Hoku would require 300 MB of memory to process the 20 GB image cube.

Today, computers with large memories, such as 32 GB, are becoming more readily available. Such a computer could hold one 20 GB image cube in memory. Why not write the software to hold everything in memory to take advantage of the new computer capability? One reason is that not everyone can afford to purchase such computers. Secondly, when the prices of computers eventually do come down to affordable levels, new camera technology will also be available. That new camera technology will have increased resolution and will produce captured image data of increased size. As a result, once again the amount of memory needed to process the new image cubes will exceed the capability of affordable computer memory. It is far better to have an image processing system for which the size of the computer memory does not limit the size of the image that can be processed.

Hoku, the Java package described in this paper, will be distributed free of charge. Initially, it will not contain much of the sophisticated capability of the ENVI system, or of ImageJ, but it will provide the capability described in this paper. Currently, only the author is developing this software package. By the end of 2018, the package will be sufficiently developed to enable additional developers to join the effort. At that time, the Hoku Java jar file and Hoku sources will be released on GitHub. As other people add modules, the available capability will grow. In addition, because the system is versatile and easily adaptable, the software package can be tailored to any image processing requirements, not just the software described here.

[6] Harris Geospatial Solutions, *Linear Spectral Unmixing* <http://www.harrisgeospatial.com/docs/LinearSpectralUnmixing.html>, <https://www.exelisvis.com/docs/linearspectralunmixing.html>.

[7] *Wikipedia*, 'ImageJ'<http://en.wikipedia.org/wiki/ImageJ>.

REFERENCES

Easton, Jr., R. L., K. T. Knox, W. A. Christens-Barry, K. Boydston, M. B. Toth, D. Emery, and W. Noel (2010), 'Standardized System for Multispectral Imaging of Palimpsests', *Proceedings of SPIE 7531, Computer Vision and Image Analysis of Art, San Jose, California*. <doi:10.1117/12.766679>.

Harris Geospatial Solutions, *Linear Spectral Unmixing* <http://www.harrisgeospatial.com/docs/LinearSpectralUnmixing.html>, <https://www.exelisvis.com/docs/linearspectralunmixing.html> (last accessed 15 April 2018).

Knox, K. T. (2008, February), 'Enhancement of Overwritten Text in the Archimedes Palimpsest', *Electronic Imaging 2008* (International Society for Optics and Photonics), <doi:10.1117/12.766679>, 681004–681004.

MegaVision Archival and Cultural Heritage Imaging <http://www.mega-vision.com/cultural_heritage.html> (last accessed 15 April 2018).

Sinai Palimpsests Project <http://sinaipalimpsests.org> (last accessed 15 April 2018).

The Archimedes Palimpsest <http://www.archimedespalimpsest.org> (last accessed 15 April 2018).

Wikipedia, 'ImageJ' <http://en.wikipedia.org/wiki/ImageJ> (last accessed 15 April 2018).

PICTURE CREDITS

Figs 1–3: © The author.

Figs 4–8: © Holy Monastery of St Catherine at Mount Sinai.

Figs 9 and 10: © The author.

Article

High Performance Software in Multidimensional Reduction Methods for Image Processing with Application to Ancient Manuscripts

Corneliu T. C. Arsene, Stephen Church, and Mark Dickinson | Manchester

Abstract

Multispectral imaging is an important technique for improving the readability of written or printed text where the letters have faded, either due to deliberate erasing or the ravages of time. Often the text can be read by illumination under a single wavelength of light, but in some cases the multispectral images need enhancement to improve the text clarity. There are many possible enhancement techniques: this paper compares an extended set of dimensionality reduction methods for image processing. We assess 15 dimensionality reduction methods applied to two different manuscripts. This assessment was performed subjectively, by asking the opinions of scholars who were experts in the languages used in the manuscripts, and also by using the Davies-Bouldin and Dunn indexes for evaluating the quality of the resultant image clusters. We found that the Canonical Variates Analysis (CVA) method, implemented in Matlab was superior to all the other tested methods. However, the other approaches may be more suitable in specific circumstances, so we would still recommend that a variety are tried. For example, CVA is a supervised clustering technique and therefore it requires considerably more user time and effort than a non-supervised technique such as the Principle Component Analysis approach (PCA). If the results from PCA are adequate to allow a text to be read then the added effort required for CVA may not be justified. For the purposes of comparing the computational times and the image results, a CVA method is also implemented in the C programming language and using the GNU (GNU's Not Unix) Scientific Library (GSL) and the OpenCV (OPEN source Computer Vision) computer vision programming library. Therefore high performance software was developed using the GNU GSL library, which drastically reduced the computational complexity and time for the CVA-GNU GSL method. For the CVA-Matlab technique, vectorization was used in order to reduce the respective computational times (i.e. matrix and vector operations instead of loop-based).

1. Introduction

Multispectral/hyperspectral image analysis has undergone much development in the last decade:[1] it has become a popular technique for imaging hard-to-read documents, as it is a non-invasive and non-destructive way of analyzing such documents by fully utilizing the full light spectrum. Multispectral images are obtained by illuminating the document or manuscript with narrow band light sources at a set of different wavelengths ranging from ultraviolet (300 nm) to infrared (1000 nm). This technique was applied to *Archimedes Palimpsest*[2], which was imaged over several years and in several stages with different imaging systems as technology was developed. A palimpsest is an old manuscript for which the initial writing (i.e. the underwriting) was deleted and new writing (i.e. the overwriting) was written on the same parchment. In the most recent work, 16 spectral images were selected, which included one waveband centered in the near Ultra Violet (UV) region of the spectrum (365 nm), seven visible bands (445 nm, 470 nm, 505 nm, 530 nm, 570 nm, 617 nm and 625 nm) and three infrared bands (700 nm, 735 nm, 870 nm). In addition, images were obtained under illumination with a tungsten lamp and under raking illumination using separate lighting units from two sides and at two wavelengths (470 nm and 870 nm). The inks used in the writing of the manuscript such as iron-gall

---

[1] Kwon et al. 2013; Wang and Chunhui 2015; Shanmugam and SrinivasaPerumal 2014; Chang 2013; Zhang and Du 2012.

[2] Easton, Christens-Barry, and Knox 2011; Easton and Noel 2010; Netz et al. 2010; Easton et al. 2010; Bergmann and Knox 2009; *OPenn: Primary Digital Resources Open to Everyone*, 'The Archimedes Palimpsest', <http://www.archimedespalimpsest.net> (last accessed 15 April 2018).

inks, have a relatively low reflectance at UV wavelengths[2]. Since the parchment is highly reflective in the UV, the ink can appear dark against a brighter background, which has a high reflectance at UV wavelengths. This distinction would be lost in conventional images, which are formed by integrating over larger wavelength ranges, and any variations in wavelength dependent reflectance or absorption, tend to average out.

The application of these multispectral/hyperspectral image analysis methods to old manuscripts and palimpsests[3] has produced significant results, enabling researchers to recover texts that would be otherwise lost, by improving the contrast between the text and the manuscript.

A number of important old manuscripts and ancient palimpsests have been processed in the last decade with significant results by using not only multispectral imaging systems and enhanced image processing techniques but also synchrotron facilities.[4] The *Archimedes Palimpsest*[5] was processed between 2000 and 2011 with great success. The *Archimedes Palimpsest* is a circa tenth century parchment manuscript that was deleted in the early of the thirteenth century and overwritten with a Christian prayer book called the *Euchologion*. The palimpsest was named as such because in the early of the twentieth century it was identified to be partial copies of seven scientific documents by Archimedes, the oldest surviving reproductions of his writings. During the respective project, an extended number of multispectral imaging techniques and processing methods were developed and successfully applied on the respective palimpsest. Multispectral imaging techniques[6] and image processing were carried out for manuscripts originating from Mount Sinai in Egypt, which were written between the 10th and 12th centuries in Glagolitic, the oldest Slavonic script. A number of palimpsests[7] which originated from the New Finds at Saint Catherine's Monastery in Sinai in today's Egypt were also analysed using multispectral imaging techniques. A number of old manuscripts or documents[8] (e.g. paintings) were multispectral imaged and processed namely the documentation of Heinrich Schliemann's (1822–1890) copybooks, Nikolas Gyzis's oil sketches, who was an important Greek painter of the nineteenth century, and an old papyrus dated 420/430 BCE, which is the Oldest Greek text, discovered in Daphne, Greece. In the *San Lorenzo Palimpsest*[9], multispectral imaging revealed underwriting, which contained over 200 secular musical compositions dated from the fourteenth and the beginning of the fifteenth century. The overwriting contained the church properties until the seventeenth century in Florence in Italy (i.e. document named *Campione dei Beni*). It is worth mentioning that other methods have been used to study old manuscripts. For example, X-ray fluorescence analysis[10] was performed to discover the history of making of the *Codex germanicus 6*, which is a combination of twelve different texts forming a 614-page manuscript created around 1450 in Germany. The X-ray Phase-Contrast Tomography (XPCT) technique [11]was used to uncover letters and words in two papyrus rolls, which were buried by the eruption of Mount Vesuvius in 79 CE, belonging at that time to a library in Herculaneum, Italy. A combination of X-ray fluorescence and multispectral imaging[12] was applied to the study of Leonardo da Vinci's *The Adoration of the Magi* drawing. Synchrotron radiation X-Ray Fluorescence (srXRF)[13] has been used also in the study of other old manuscripts.

The image processing techniques discussed in this paper have been applied, for the purposes of image enhancement, to two old manuscripts. The first manuscript is with regard to Aelius Galenus (ca. 129–216 CE), who was an important Greek physician and philosopher in the Roman empire and influenced the development of various scientific disciplines such as anatomy, physiology, pathology and pharmacology. For many centuries, the book written by Galen *On Simple Drugs*, was required to be known while seeking to become a physician as the book contained ancient knowledge about

[3] Bhayro, Pormann, and Sellers 2013; Pormann 2015; Hollaus, Gau, and Sablatnig 2012.

[4] Rabin, Hahn, and Geissbühler 2014; Mocella et al. 2015.

[5] Walvoord and Easton 2008; Easton, Christens-Barry, and Knox 2011; Easton and Noel 2010; Netz et al. 2011; Easton et al. 2010; Bergmann and Knox 2009.

[6] Camba et al. 2014.

[7] Easton and Kelbe 2014.

[8] Alexopoulou and Kaminari 2014.

[9] Janke and MacDonald 2014.

[10] Rabin, Hahn, and Geissbühler 2014.

[11] Mocella et al. 2015.

[12] Stout, Kuester, and Seracini 2012.

[13] Glaser and Deckers 2014; Manning et al. 2013.

pharmaceutical plants and medicine. The Syriac *Galen Palimpsest*[14] is an important ancient manuscript, which put many challenges to researchers as the undertext contains the Syriac translation[15] by Sergius of Reshaina of Galen's *On Simple Drugs*. Sergius of Reshaina was a Christian physician and priest (d. 536 CE). This palimpsest is especially important because it contains more text than in the other historical copy of the Syriac translation made by Sergiu of Reshaina, which exists in London, British Library (BL), Ms. Add. 14661. There are also better readings than in the other historical copy existent in BL. The text has relevance to both the Greek source text, the Arabic target texts and the development of Greco-Arabic translation technique. Finally, it is able to address the role of Sergius' Syriac versions on Hunayn ibn Ishaq's school.[16]

The second manuscript on which image processing techniques will be applied is an old Latin Roll titled *John Rylands Library, University of Manchester, United Kingdom, Latin Ms. 18*, with its catalogue entry dating from 1921[17] and entitled *Arbor Caritas at Misericordiae*. Although this roll does not have any underwriting (i.e not a palimpsest), some of the text has been almost deleted on account of water damage and the effects of age. This roll is also peculiar as it contains many illuminations/drawings, such as Church Fathers and saints, and biblical images from the Old and New Testaments.

2. Dimensionality Reduction Methods

There are various ways to improve the quality of an image of a page of a manuscript such as deblurring, enhancement or dimensional reduction methods.

Deblurring[18] of images involves of removing out blurring items from images which are caused, for example, by the fact that the image is out of focus. Deblurring can be done in several ways, such as by using a Wiener filter, a regularized filter, a blind deconvolution algorithm or the Lucy-Richardson algorithm[19]. Image enhancement can be achieved by modifying the histogram of pixel values in the image to adjust the contrast, thereby improving the clarity of details within the picture. This is typically achieved by linearly scaling the pixel values between two reference points, however, in some cases significant improvements can be made by using polynomial scaling to higher orders, ie. L2, L3 or L4, which can place more emphasis on the variation within features of interest. Color images can be also enhanced by transforming the RGB images to L*a*b* color space and then by altering the luminosity L* of the image. Techniques to improve the image contrast between the manuscript and the written text were developed elsewhere[20] and included, for example, the implementation of a custom image look-up table to display the text in false-color, the automatic contrast adjustment of the image based upon the quartic scaling of pixel values and the removal of variation in the manuscript pixels by blurring out the image details and subtracting the original image. These methods allowed an inexperienced user to maximize the clarity of text, but were heavily dependent upon required sampling and could produce artifacts and incoherent results due to large scale image variation and sampling mistakes. Therefore additional methods were developed to carry out the study with no user input. This included the calculation of localized variances, which provide a distinct outline for any text based upon the large change in pixel value between the text and other image components, and 2 dimensional spatial autocorrelation indexes, which distinguished between text and the manuscript based on the degree of variation in each region.

Color image enhancement in multispectral images can also be achieved by using the Karhunen-Loeve transform[21], a linear contrast stretch or a decorrelation stretch. Moreover, contrast enhancement techniques based on histograms for multispectral images have been developed in the past.[22] This method was further developed and applied to multispectral images[23] to enhance the images which are not in the visible range. Multispectral image enhancement techniques based on PCA and Intensity-Hue-Saturation (IHS) transformations have also been developed and applied.[24]

---

[14] Bhayro et al. 2013; *OPenn: Primary Digital Resources Open to Everyone*, 'The Galen Syriac Palimpsest', <http://www.digitalgalen.net> (last accessed 15 April 2018).

[15] Montgomery 2000; Montgomery 2001.

[16] Khurshid 1996.

[17] James 1921.

[18] Shao and Elad, 2015.

[19] Fish et al. 1995.

[20] Church 2015.

[21] Mitsui et al. 2005.

[22] Mlsna and Rodriguez 1995; McCollum and Clocksin 2007.

[23] Hashimoto et al. 2011.

[24] Lu et al. 2011.

For palimpsests such as the *Archimedes Palimpsest*, image enhancing techniques have been applied to the acquired multispectral images.[25] Initially, spectral segmentation techniques were developed[25] based on a least-squares supervised classification, but the scholars assessed that the results were not clear enough. Following this, the contrast of each image band was enhanced using the neighborhood information of a pixel and then subtracting two resultant channels (i.e. called sharpies method). However, the subtraction increased the noise, so a new method called 'pseudocolor' was developed. In this technique, the red channel under tungsten illumination was placed in the red channel of a new composite image, while the ultraviolet-blue image was placed in the blue and green channel. In this way, the overwriting appeared gray while the underwriting was red in the composite image. Finally, the PCA method was employed, which provided further enhancement to the multispectral images. The application of a combination of the PCA method with the pseudocolor method provided the best quality in the investigations.

An example of a regular and simple image enhancement technique for image processing briefly used herein is a Double Thresholding (DT) technique, which consists of the following: the darker overtext is carefully identified by the human operator and colored in white (threshold 1), and then the remaining undertext, which is slightly lighter than the initial overtext is made darker (threshold 2). This technique showed some initial interesting results but its success depends on both the human operator, who has to select suitable cutting values, and on the characteristics of the respective image. Therefore, this simpler method would not work for any page of an ancient manuscript. However, these image processing methods, although able to provide workable images of undertext, for example in the gutter region of a folio, are unable to show when there is undertext beneath the overtext. More complex methods[26] have been developed and are available for image processing (i.e. image reconstruction, image restoration, image segmentation) based, for example, on Artificial Neural Networks[27] (ANNs). These are information processing models, which try to mimic the way the brain works.

One solution is to use dimensionality reduction methods, which reduce the number of features or random variables under consideration by transforming the data to a space of a fewer dimensions.[28] There are two types of dimensionality reduction methods: unsupervised methods, which use a number of points to determine the model without knowing the classes (e.g. parchment, overwriting, underwriting) to which the input data points belong to, and supervised methods, which use a number of input points to determine the model while knowing the classes (e.g. parchment, overwriting, underwriting). In general, the supervised methods produce better results as they use class information and so the mathematical model is able to better reflect the sample. However, selecting a number of input points is time consuming,[29] so the unsupervised methods could be advantageous, especially if an automatic method of choosing the input points could be provided.

There are a large number of dimensionality reduction methods that have been developed in the last decade and implemented in various computer programming languages. An extended number of dimensionality reduction methods have been tested in this paper by using a Matlab toolkit[30], the ones presented below are those which provided meaningful image results.

The Canonical Variates Analysis[31] (CVA) supervised method, with an independent implementation in Matlab[32], tries to maximize the distance between the different classes, whilst minimizing the size of each class. This is performed for multiple classes. The covariance matrixes within each class and between the classes are calculated and eigenanalysis is performed based on these two matrixes. The eigenvectors calculated by this eigenanalysis are the canonical vectors, which are used to produce new grayscale images. The Linear Discriminant Analysis (LDA) is similar to CVA but it is usually applied to 2 classes. The methods are robust, producing very good results, since they are both supervised. In addition, this process of maximizing the distance between

[25] Easton and Noel 2010.

[26] Zhenghao et al. 2009; Doi 2007; Egmont-Petersen, de Ridder, and Handels 2002.

[27] Graves et al. 2009; Lisboa et al. 2009; Arsene, Lisboa, and Biganzoli 2011; Arsene and Lisboa 2011; Arsene and Lisboa 2007; Arsene et al. 2006.

[28] Freeden and Nashed 2010.

[29] Hollaus, Gau, and Sablatnig 2013.

[30] Van der Maaten and Hinton 2008, <https://lvdmaaten.github.io/drtoolbox/> (last accessed 15 April 2018).

[31] Macfie, Gutteridge, and Norris 1978; Maxwell 1961; Rao 1948; Fisher 1936; Campbell and Atchley 1981; Peltier, Visalli, and Schlich 2015.

[32] Bohling 2010.

the different classes while minimizing the size of each of the classes, is of key importance in the present analysis. As they are supervised methods, the human operator selects a number of points to be used and also provides the classifications of the respective points (i.e. class manuscript, class underwriting, etc). In this work, the LDA method can be applied to multiple classes and its implementation from the Matlab toolkit[30] is slightly different from the CVA's[33] implementation.

The Neighborhood Component Analysis (NCA) supervised method, taken from the Matlab toolkit[30], is a learning algorithm for classifying multivariate data into distinct classes by using a distance metric over the data. Typically the Mahalanobis distance measure is used. The method consists of learning a linear transformation of the input space, which in this case are the multispectral images, such that in the transformed space the k-Nearest Neighbors (kNN) algorithm performs well.

From the same toolkit, the supervised General Discriminate Analysis (GDA) applies the methods of the general linear model to the discriminant function analysis problem. The advantage of doing this is that it is possible to specify complex models for the set of predictor variables continuous or categorical (e.g. factorial regression).

Both NCA and GDA are expected to deliver some good image results as they are supervised methods and have previously been reported as effective methods in the context of multispectral/hyperspectral image analysis.[33] However, the NCA method is based on optimization algorithms (i.e. line search optimization method) for calculating the models parameters and sometimes, depending on the optimization algorithms being used, a local minimum point can be reached, which means that the image results might not be optimal. In such situations, re-running the respective dimensionality reduction method (e.g. NCA, GDA) might avoid reaching a point of local minimum.

Other dimensionality reduction methods will be used from the Matlab toolkit[30] in a supervised way, with the user selecting points as with the supervised methods, but without providing the class information.

Isomap is a nonlinear dimensionality reduction technique and a priori chosen points are used as input information, hence this is a supervised method. Here, a matrix of shortest distances between all of the input points is constructed and multidimensional scaling is then used to calculate a reduced-dimension space. To perform the multidimensional scaling, various nonlinear methods are applied, which map the high dimensional data to a low dimensional space by attempting to maintain the original distances between points. The quality of mapping is given by a stress function, which is a measure of the error between the distances in the initial high dimensional representation and the distances in the new lower dimensional representation.

The Landmark Isomap algorithm is a variant of the Isomap, which uses landmarks to increase the speed of the algorithm. It addresses the computational load with regard to the calculations of the shortest path distances between points when reducing the dimensionality of the data and calculating the eigenvalues. A smaller number of landmark points are chosen, for which the shortest distances between the respective points and each of the other data points are calculated. This results in a reduction of the computational time. In the literature, the Isomap type of methods which are nonlinear, local and geodesic methods were reported as having good performance when tested on multispectral images.[34]

The Principal Component Analysis (PCA) method is a statistical method, which performs an orthogonal transformation of the input data in order to change a number of observations of possibly correlated variables into a number of linear uncorrelated variables named Principal Components (orthogonal). The first principal component has the largest variance and therefore is responsible for most of the variation in the data. There are several stages in this well established method: subtract the mean of each variable from the dataset, calculate the covariance matrix, calculate the eigenvectors and eigenvalues of this matrix, orthogonalize the set of eigenvectors and normalize them. In the Probabilistic Principal Component Analysis (PPCA) method the principal components are calculated through maximum-likelihood estimation of parameters in a latent variable model, which offers a lower dimensional representation of the data and their correlations. The Gaussian Process Latent Variable (GPLV) model is a probabilistic dimensionality reduction method that uses a Gaussian Process Latent Variable model to find a lower dimensional space for the high dimensional data. It is an extension of the PCA. The latent variable models use, for example, one latent variable to aggregate

[33] Goldberger et al. 2005; Imani and Ghassemian 2014.

[34] Journaux et al. 2006; Journaux, Foucherot, and Gouton 2008.

several observable variables, which are dependent somehow (e.g. 'sharing' variance). The PCA types of dimensionality reduction methods have been applied with success to more general multispectral/hyperspectral images[35] but also to old manuscripts[36].

In this work, three variants of the PCA method will be used. One variant will be used in a supervised way by providing a set of input points chosen to represent the classes of interest (i.e. underwriting, overwriting, manuscript) and two unsupervised PCA methods implemented in ImageJ and Matlab, which will use an entire manuscript page/folio as an input without any supervised information.

The Diffusion Maps (DM) model is a nonlinear dimensionality reduction method, which uses a diffusion distance as a measure between the different input points, and so builds a map, to provide a global description of the dataset. An analogy can be seen between a diffusion operator on a geometrical space and a Markov transition matrix operating on a graph whose nodes are sampled from the respective geometrical space (i.e. dataset). The algorithm is robust to errors and it is computationally less expensive. The DM has been applied to image processing with some success[37] and here it will be used as a supervised method.

The t-Distributed Stochastic Neighbor Embedding (t-SNE) method is another dimensionality reduction method in which the Kullback-Leibler divergence distance between two probability distributions is minimized. In the first distribution the nearby points have higher probability than the other points in the higher initial dimensional space, while the second distribution contains the lower desired dimensional space of data. The model has only been recently developed and therefore its properties are still being heavily investigated[38] in order to improve its performances and it will be used here as a supervised technique.

The Neighborhood Preserving Embedding (NPE) method tries to maintain the local neighborhood structure in the data in order to be less influenced by errors than other techniques. It is similar to the Locality Linear Embedding (LLE) method which also attempts to find a linear combination of neighbors for each input point. In addition, the LLE method implements an eigenvector-based optimization method, which is different from the one used by NPE, in order to find a low-dimensional embedding of the points in such a way that each input point is still represented by the same mixture of its neighbors. In effect, a neighborhood map is realized in the two methods (NPE, LLE), which map creates a new point in the new lower dimensional space for each point in the higher initial dimensional space. The Hessian Locally-Linear Embedding (HLLE) method is based on the LLE method in the way that it achieves a linear embedding by minimizing the Hessian functional on the data space. The HLLE algorithm involves the second derivative and therefore the algorithm is sensitive to noise.

Other methods from the same Matlab toolbox, but which resulted in poor image results, were the Factor Analysis (FA) method and the Laplacian Eigenmaps (LE) method. The FA method depicts the diversity of input data as a function of some unseen variables called factors. The observed variables are depicted as linear mixtures of the unseen factors and some error variables are also included. The information extracted with regard to the relationships between the observed variables (i.e. the correlation matrix), is used to calculate both the factors and the new reduced dimensional space by minimizing the difference between the correlation matrix of the initial input data and the correlation matrix of the new reduced space. The LE method employs spectral techniques to implement the dimensionality reduction. A graph is built in which each node represents a data point, the connections with the other graph nodes are given by the distance between such a data point and the initial data point in the higher dimensional space. The lower dimensional space is represented by the eigenfunctions of the Laplace-Beltrami operator, while the minimization of an error function based on the graph ensures that the new points in the lower dimensional space maintain the proximity characteristic of the initial data points. The calculation of the connections in the graph is difficult, which reduces the robustness of the method. The FA and LE results are not shown herein as the image results were poor.

The above extended set of dimensionality reduction methods implemented by the Matlab toolbox[30], together with the previous results[39] obtained with the Canonical Variates Analysis (CVA) method, and the unsupervised PCA method

[35] Journaux, Foucherot, and Gouton 2008; Baronti et al. 1997; Ricotta and Avena 1997.

[36] Easton, Christens-Barry, and Knox 2011; Easton and Noel 2010.

[37] Gepshtein and Keller 2013; Xu et al. 2009; Freeden and Nashed 2010.

[38] Bunte et al. 2012.

[39] Pormann 2015.

implemented in ImageJ software and Matlab, were applied to the 102v–107r_B page of the *Galen Palimpsest*.

Image data consisted of large 8-bit TIFF image files. There were 23 multispectral images in total, obtained through Light-Emitting Diode (LED) illumination at wavelengths of 365 nm, 450 nm, 470 nm, 505 nm, 535 nm, 570 nm, 615 nm, 630 nm, 700 nm, 735 nm, 780 nm, 870 nm, 940 nm, images obtained at raking light under illumination at 940 nm (raking infrared with illumination from the right and then from the left), 470 nm (raking blue with illumination from the right and then from the left) and ultraviolet images (365 nm) and blue illumination (450 nm) with red, green and blue color filters. The multispectral images were normalized with values between 0 and 255 and were used as an input to the all the image processing methods used in this work without any further pre-processing.

In this experiment, for all the techniques except the unsupervised PCA methods, 50 points there were selected from each of the images to represent the overwriting (Class Overwriting), the underwriting (Class Underwriting), the parchment (Class Parchment) and both overwriting and underwriting (Class Both). In the case of Class Both, the scholar could infer the presence of the underwriting from the overlapping (i.e. the structure) of the overwriting and the underwriting. There were 200-classification input points in total used by each supervised dimensionality reduction method. The input data matrix consisted of 23 rows and 200 columns. For the CVA, LDA, GDA and NCA methods information about the classes was also provided to the Matlab software. Moreover, the number of points for each class could be varied to put more emphasis on a particular class and the number of classes could also be varied, such as to exclude Class Both or to include another class representing, for example, the region outside the manuscript (Class Outside).

For the unsupervised PCA methods implemented in ImageJ and Matlab, no a priori known information was used except the entire manuscript page/folio. In ImageJ the Multivariate Statistical Analysis (MSA) 514 plugin was used, which implements the PCA method. The 23 multispectral images were loaded as a stack in ImageJ, then the Crop function from ImageJ was used to exclude everything outside the folio of the manuscript. The MSA514 plugin was then run and was told how many images to produce (i.e. 5 in this case). An image stack is produced by the MSA514 plugin and by scrolling through the produced grayscale images it was seen that the undertext was mostly visible in channels 1, 4 and 5. The stack to RGB command was then used to produce a color image.

Each dimensionality reduction method produces a number of regression coefficients that are multiplied with the entire set of 23 multispectral images. This results in a new set of 23 arrays of floating point numbers which are further processed by rescaling the floating point numbers into the range of (0–255). This array will become a new 8 bit grayscale image.

A second set of 23 arrays of floating point numbers is produced based on the same multiplication between the regression coefficients and the entire set of multispectral images. The newly calculated minimum and the maximum values of the input points are scaled between 0 and 255 and the arrays of floating point numbers are rescaled based on this range. The scope of these two different processes is to map the new numbers to the range 0 and 255 by taking into account either the new scores of the input points or the new floating point numbers obtained from the above multiplication.

Finally, a third set of grayscale images can be obtained also for exploratory purposes by taking out the 0.01, 0.1, 1 or 5 percentiles of the data obtained from the multiplication of the regression coefficients with the entire set of multispectral images and following the same rescaling explained above. In this way it is possible this way to see the importance of the removed segments of the data.

The post-processing steps described above were applied identically to all the results obtained with the various dimensionality reduction methods.

All the grayscale images produced by the dimensionality reduction methods were investigated.

There were no pre-processing steps applied on the input data matrix, which consisted of the 23 rows by the 200 columns. However, some of the dimensionality reduction methods apply some pre-processing steps on the input data before applying the technique. Recentering the data on the mean and with variance 1 is applied in several techniques, such as NCA, GPLVM, LDA, t-SNE, PCA and DM. All the dimensionality reduction methods were used with the default input parameters. Most of these dimensionality reduction methods also calculate the eigenvectors in one of their inner computational steps, such as: CVA, PCA, DM, HLLE, t-SNE, GDA, GPLVM, LDA, NPE, Isomap, Landmark Isomap, LLE and Laplacian Eigenmaps.

Furthermore, a color image can be produced by combining three grayscale images. Normally, for each of the dimensionality reduction method, the grayscale image with the clearest underwriting was placed in the Green channel before producing the color image by combining Red, Green and Blue grayscale images. Further image enhancement can be achieved, for example, by adjusting the contrast on the grayscale images.

For the purposes of comparing the computational times with the CVA method implemented in Matlab, a CVA function was implemented in the C programming language using a software library for numerical computations called GNU (GNU's Not Unix) Scientific Library (GSL). For ease of use, ImageJ software[40] was employed, which is open architecture image processing software, which gives the possibility to add new functions/procedure/macros by writing Java plugins. By using a JNILIB library file, which is Java framework that allows Java to integrate with other programming languages, the CVA function implemented in C programming language as a JNILIB library file is called. The CVA-GNU GSL method is able to process and to produce both 8-bit and 16-bit images and the OpenCV[41] (OPEN source Computer Vision) computing programming library was used with this scope.

3. Evaluation of dimensionality reduction methods for ancient manuscripts

We used two approaches to evaluate the success of the image processing techniques. Firstly, the relative success of these methods was determined visually by seven experts in the Syriac language based on how well the scholars could read the undertext by distinguishing it from the parchment and the overtext. No further changes were made to the resulted images to directly assess the quality of the results of the dimensionality reduction methods. The scholars/experts were also able to identify the improvements the different dimensionality reduction methods achieved when compared to the original multispectral images.

Secondly we calculated two different indices that are commonly used for evaluating the success of multidimensional clustering techniques to see whether either of these agreed with the qualitative evaluations. The assessment made by the scholars is the standard way of evaluating these images, but for exploratory purposes the numerical comparison was also investigated (i.e. interferometric visibility another numerical method for quantitative assessment of manuscripts).[20] The first is the Davies-Bouldin Index (DBI),[42] which is one of the standard measures for evaluating clustering algorithms.[43] It is calculated using the following equation:

$$S_i = \frac{1}{T_i}\sum_{j=1}^{T_i}\left\|X_j - A_i\right\|_p \quad (1)$$

where S_i is a measure of scatter within the cluster i (i.e. the average distance between each point in the i cluster and the centroid of the i cluster), T_i is the size of cluster i, A_i is the centroid of cluster i, X_j are values forming a cluster and p is usually 2.

Equation (2) describes $M_{i,j}$, the Euclidian distance between the centroids of the two clusters i and j.

$$M_{i,j} = \left\|A_i - A_j\right\|_p = \left(\sum_{k=1}^{n}\left|a_{k,i} - a_{k,j}\right|^p\right)^{\frac{1}{p}} \quad (2)$$

where in this case the two clusters are the underwriting cluster and the parchment cluster, n is the size of the centroids A_i and A_j, $a_{k,i}$ and $a_{k,j}$ are the kth element of clusters A_i or A_j.

The measure of the effectiveness of clustering technique (i.e dimensionality reduction method) is given by $R_{i,j}$ where lower values, result from better the separation between the parchment cluster and the underwriting cluster:

$$R_{i,j} = \frac{S_i + S_j}{M_{i,j}} \quad (3)$$

where S_j is a measure of scatter within the cluster j (i.e. the average distance between each point in the j cluster and the centroid of the j cluster).

For exploratory purposes a second well-known measure is used, which is known as the Dunn Index (DI)[44]. This index is suggested for clusters, with small variance between the different items of the clusters and with the mean values of different clusters being at a sufficiently large distance, which might be expected if our multispectral enhancement methods have performed well.

[40] Schneider, Rasband, and Eliceiri 2012.

[41] *OpenCV* (*Open Source Computer Vision Library*) <http://opencv.org>. (last accessed 15 April 2018).

[42] Bouldin and Donald 1979.

[43] Franti, Rezaei and Zhao 2014.

[44] Dunn 1973.

Therefore DI is expected to prefer the CVA or LDA results, which are very likely to produce sets of clusters of the above type. However, the DI might be not so suitable for all the dimensionality reduction methods, hence the interest in exploring this index as well. The DI is defined by:

$$DI = \frac{Minimum\ Distance\ Between\ Cluster\ i\ and\ j}{Maximum\ Distance\ Within\ a\ Cluster\ Over\ All\ Clusters} \qquad (4)$$

The minimum distance between cluster *i* and *j* is taken as the difference between $M_{i,j}$ and the scatters of the two clusters S_i and S_j. Furthermore the maximum distance within a cluster and over all the clusters is taken as the maximum over the scatters of the two clusters S_i and S_j, therefore:

$$DI = \frac{M_{ij}-S_i-S_j}{\max(S_i,S_j)} \qquad (5)$$

Figure 1 shows a geometrical interpretation of the minimum distance between cluster *i* and *j*, which was taken as the difference between $M_{i,j}$ (i.e. the Euclidian difference between the means/centroids of the two clusters) and the scatters of the two clusters S_i and S_j.

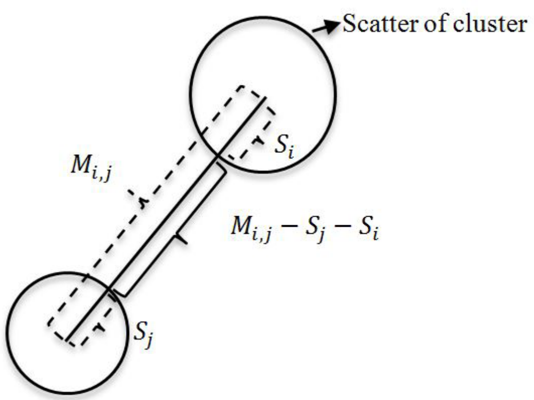


Fig. 1: Geometrical interpretation of the minimum distance between cluster *i* and *j* taken as the difference $M_{i,j}$ (i.e. the Euclidian difference between the centroids of the two clusters) and the scatters (i.e. the average distance between each point in the cluster and the centroid of the respective cluster) of the two clusters S_i and S_j.

4. Results

We chose 12 methods from the Matlab toolbox[30] and applied them to the 102v-107r_B page[45] of the *Galen Palimpsest* and also applied the CVA method[39] used previously. In total, 13 supervised methods were investigated, from which 4 methods used both a number of user selected input points and the class information: Canonical Variates Analysis (CVA) method, Generalized Discriminant Analysis (GDA), Linear Discriminant Analysis (LDA) and Neighborhood Component Analysis (NCA). 6 supervised methods were also applied which used only the user selected input points: Gaussian Process Latent Variable Model (GPLVM), Isomap, Landmark Isomap, Principal Component Analysis (PCA), Probabilistic Principal Component Analysis (PPCA) and Diffusion Maps (DM). Another three supervised methods, which used only the user selected input points but did not give good results in this work, were Neighborhood Preserving Embedding (NPE) method, the t-Distributed Stochastic Neighbor Embedding (t-SNE) and the Hessian Locally-Linear Embedding (HLLE).

Finally, a regular image enhancement method known as the Double Thresholding (DT) method was applied and two independent implementations of the unsupervised PCA method in ImageJ and Matlab (i.e. making a total of 15 dimensionality reduction methods being used). The image results of the DT method vary function of the thresholds used.

In Figure 2 is shown an area of the color or grayscale images of the 13 supervised methods, the two unsupervised PCA methods (ImageJ, Matlab), the DT technique (an initial result), the ultraviolet illumination with green color filter and the original page seen by the human eye for the 102v–107r_B page of the *Galen Palimpsest*.

[45] *OPenn: Primary Digital Resources Open to Everyone*, 'The Galen Syriac Palimpsest', <http://www.digitalgalen.net/Data/102v-107r/> (last accessed 15 April 2018).

Fig. 2a: Canonical Variates Analysis method.

Fig. 2b: Linear Discriminant Analysis.

Fig. 2c: Neighborhood Component Analysis.

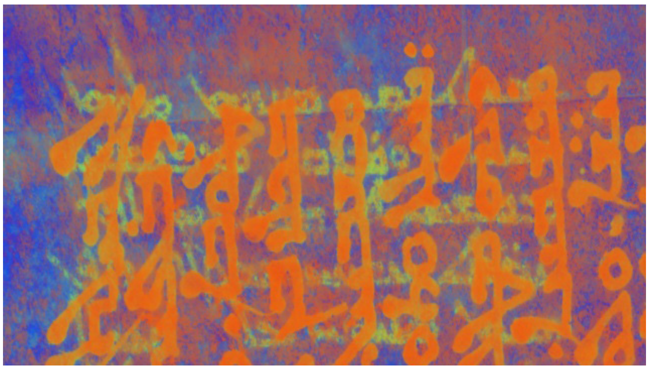


Fig. 2d: Generalized Discriminant Analysis.

Fig. 2e: Diffusion Map.

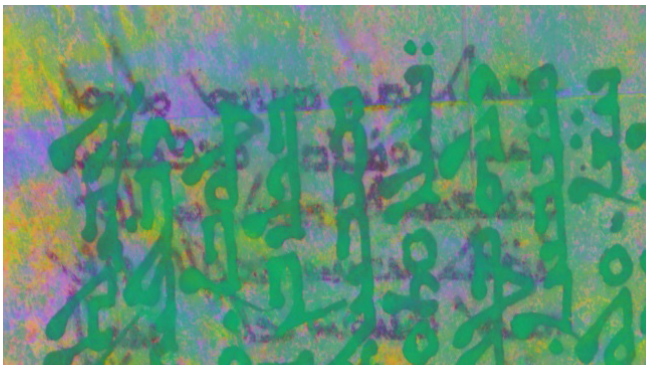


Fig. 2f: Isomap.

Fig. 2g: Landmark Isomap.

Fig. 2h: Principal Component Analysis-Unsupervised (ImageJ implementation).

Fig. 2i: Principal Component Analysis.

Fig. 2j: Gaussian Process Latent Variable Model.

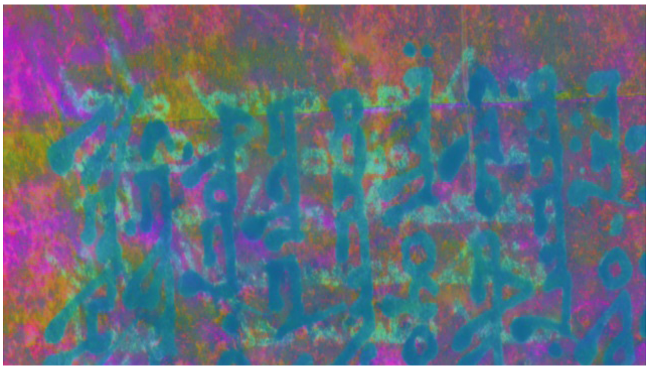


Fig. 2k: Probabilistic Principal Component Analysis.

Fig. 2l: Double thresholding (i.e. obtained initially in this project).

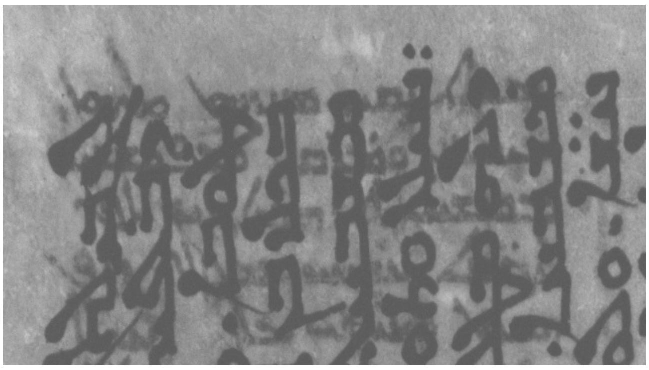


Fig. 2m: ultraviolet illumination with green color filter (i.e. CFUG).

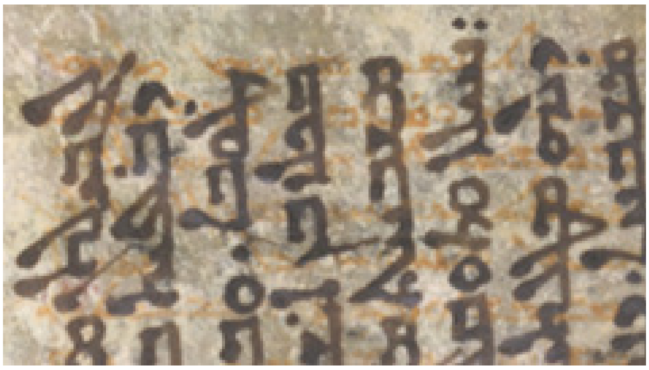


Fig. 2n: original page seen by the human eye.

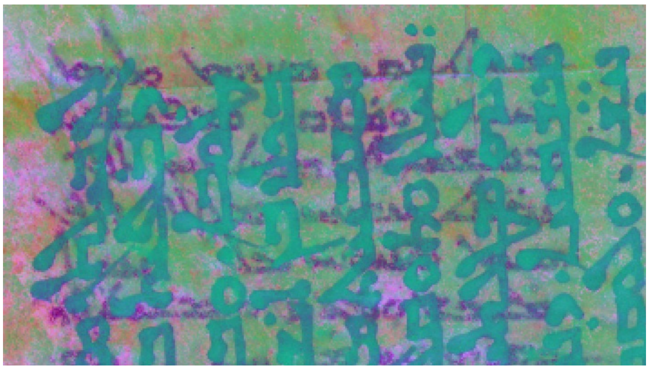


Fig. 2o: PCA – Unsupervised (Matlab implementation).

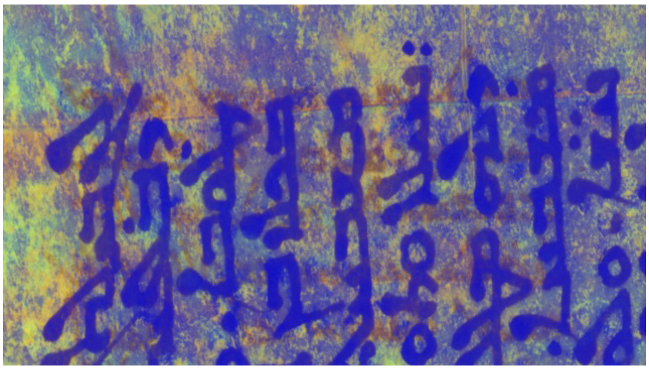


Fig. 2p: TSNE2.

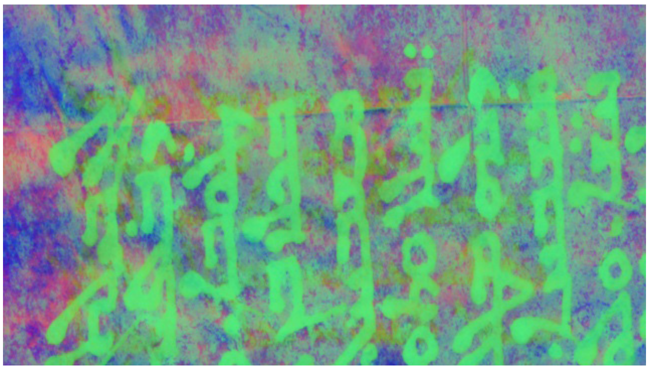


Fig. 2r: HLLE.

Fig. 2s: NPE.

Figs 2a–s: Color image results obtained with 13 supervised dimensionality reduction methods, a simple double thresholding technique, two unsupervised PCA dimensionality reduction methods and in comparison with the original page seen by the human eye and the image obtained with the ultraviolet illumination with green color filter for a section of 102v–107r_B page.

Table 1: Scores between 5 and 0 given by the 7 scholars (P1–P7) experts in Syriac language
(5 – excellent, 4 – good, 3 – moderate, 2 – fair, 1 – poor, 0 – no readability).

	P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**Total**
CVA	4	5	5	5	5	5	5	34
PCA unsupervised (Matlab)	4	4	5	2	5	4	4	28
GDA	4	4	3	3	5	3	4	26
Isomap	4	3	4	3	5	3	4	26
LDA	4	4	3	2	5	4	2	24
PCA unsupervised (ImageJ)	3	3	4	3	4	2	4	23
NCA	2	4	3	2	4	4	3	22
DM	2	3	3	2	5	2	4	21
PCA	1	3	4	2	4	2	3	19
GPLVM	1	3	4	2	4	2	3	19
PPCA	1	3	4	2	4	2	3	19
Landmark Isomap	3	3	3	2	3	3	3	18
CFUG (ultraviolet)	3	1	3	2	3	3	3	18
Original Page	0	0	2	0	2	2	1	7
DT	0	1	1	1	0	1	2	6
NPE	0	0	1	1	1	2	1	6
TSNE2	0	0	1	0	1	1	0	3
HLLE	0	0	0	0	0	0	0	0

Table 2: Ranking positions (1 to 18) given by the 7 scholars (P1–P7) experts in Syriac language.

	P1	P2	P3	P4	P5	P6	P7	Total
CVA	1	1	1	1	1	1	1	1
PCA unsupervised (Matlab)	5	9	2	3	3	2	4	28
NCA	9	3	8	2	7	3	2	34
Isomap	4	6	3	4	4	5	8	34
LDA	2	2	10	9	2	4	6	35
GDA	3	4	9	5	6	7	3	37
DM	10	5	11	7	5	9	5	52
PCA unsupervised (ImageJ)	7	8	4	8	8	11	7	53
Landmark Isomap	6	7	12	6	12	8	9	60
PCA	11	10	5	10	9	12	10	67
GPLVM	11	11	6	11	10	13	11	74
CFUG (ultraviolet)	8	14	13	13	13	6	13	80
PPCA	13	12	7	12	11	14	12	81
Original Page	16	15	14	14	15	10	14	98
DT	18	13	17	15	14	15	16	108
TSNE2	14	16	15	16	17	17	17	112
NPE	15	18	16	18	16	16	15	114
HLLE	17	17	18	17	18	18	18	123

As previously described, for the 13 supervised methods 50 points (i.e. 50 different x and y image pixel coordinates) were selected from each of the multispectral images for each of the classes Overwriting, Underwriting, Parchment and representing both overwriting and underwriting. 200 input points were used from each multispectral image, which resulted in an input matrix of 23 rows by 200 columns. This was used as the input data for each supervised dimensionality reduction method. In this case, the PCA, PPCA and GPLVM methods (Figure 2) gave similar visual and numerical results as can be seen above.

The visual assessment of the images in Figure 2 made by the 7 scholars, experts in the Syriac language, was done in two ways. First, by giving a score between 0 and 5 for the readability of the underwriting in each photo. The scores used were 5 – excellent, 4 – good, 3 – moderate, 2 – fair, 1 – poor, 0 – no readability and the images with the highest scores were deemed the best by the scholars in terms of underwriting. The total score was summed through the 7 lists produced by the 7 scholars. The first four images which scored best were CVA, PCA Matlab (unsupervised), GDA and Isomap (Table 1).

Running an Analysis of Variance (ANOVA) test for each column, where each column represents a different scholar, resulted in a p value of 0.0591. This result means that there are overall no significant differences between the different persons. Calculating the standard deviation of the Total column gives a value of 9.4903. We define the most effective methods as lying within one standard deviation of the top value, which is CVA (34), giving the following four methods: CVA, PCA Matlab (unsupervised), GDA and, Isomap.

Finally, a second ANOVA test was performed on each row. The calculated p-value of 5.1596e-23 means that there

Table 3: DB index.

Method	Score	Method	Score
CVA	0.0522	PCA	0.3
Double Thresholding	0.13	PPCA	0.3
LDA	0.2	GPLVM	0.3
Ultraviolet illumination with green color filter	0.21	PCA unsupervised (ImageJ)	0.331
DM	0.22	PCA unsupervised (Matlab)	0.38
GDA	0.235	Original Image	0.4194
Isomap	0.25	TSNE2	0.6614
Landmark Isomap	0.283	HLLE	1.61
NCA	0.29	NPE	3.85

are statistically significant differences between the scores given to the different images, which is obviously what was expected as some methods produced much better images than the others.

The second way in which the scholars assessed the images was to assign a rank from 1 to 18 based on how well the underwriting was readable and then to sum up the ranks for each image. The first six images which scored best (Table 2) corresponded to the methods CVA, PCA Matlab (unsupervised), NCA, Isomap, LDA, GDA. The standard deviation is 34.39 for the last column from Table 2 (Total) and the value of the best scoring method was added to this, yielding 41.39. The methods up to the value of 41.39 are in order CVA, PCA Matlab (unsupervised), NCA, Isomap, LDA and, GDA, which are exactly the same as the first six methods from above. It can also be observed that there are some strong similarities with the first four methods from Table 1.

For exploratory purposes, a numerical assessment of the color images from Figure 2 was done based on the grayscale images which had the clearest underwriting. A color RGB image is usually obtained by combining three of these grayscale images.

The grayscale image for which the underwriting is most visible after the application of a dimensionality reduction method, is, as already described, usually located in the green channel of the resultant color RGB image. 200 points from the underwriting cluster were compared with 200 points from the parchment cluster using the DB index, for the best looking grayscale image. Figure 3 shows the ranking of the grayscale images and the best looking grayscale image has the smallest value of the DB index.

The DB index (Table 3) partly agreed with the visual assessment as the CVA method was the best (0.0522), followed in order by the Double Thresholding technique (0.13), LDA (0.2), the original 102v-107r_B page with ultraviolet illumination and green color filter (0.21), DM (0.22), GDA (0.235), Isomap (0.25), Landmark Isomap (0.283), NCA (0.29), PCA (0.3), PPCA (0.3), GPLVM (0.3), PCA unsupervised-ImageJ implementation (0.33), PCA unsupervised-Matlab implementation (0.38), Original page (0.4194), TSNE2 (0.6614), HLLE (1.61) and NPE (3.85). The CVA method gave a much better result (0.0522) than the 102v-107r_B folio with ultraviolet illumination with green color filter (0.21).

For exploratory purposes, the DI (Table 4), was also used to assess the respective grayscale images, which resulted in the rankings shown in Figure 4. The DI is suitable especially for CVA or LDA methods. Although the DI confirmed the superiority of the CVA method, overall the DB index was more conservative. The DI ranking of the methods was CVA (32.90), Double Thresholding (10.52), LDA (7.65), DM (6.45), NCA (4.78), GDA (4.39), Landmark Isomap (3.93), PCA (3.83), PPCA (3.83), GPLVM (3.83), Isomap (3.18), PCA unsupervised-Matlab implementation (3), PCA unsupervised-ImageJ implementation (2.94), Original image (2.46), TSNE2 (0.9963), HLLE (-0.69) and NPE (-1.191).

Table 4: Dunn index.

Method	Score	Method	Score
CVA	32.90	GPLVM	3.83
Double Thresholding	10.52	PCA	3.82
LDA	7.65	Isomap	3.18
DM	6.45	PCA unsupervised (Matlab)	2.94
Ultraviolet illumination with green color filter	6.30	Original page	2.46
NCA	4.78	PCA unsupervised (ImageJ)	2.26
GDA	4.39	TSNE2	0.9963
Landmark Isomap	3.93	HLLE	-0.69
PPCA	3.83	NPE	-1.191

It has to be stressed again that although the indices are useful to be implemented for exploratory purposes, the standard way of assessing the resultant images is visually by scholars/experts in the respective language(s).

Comparing the numerical assessments based on DB and Dunn indexes versus the visual assessments, it is clear that there are a number of differences between the two assessments. The scholars did not find the DT method or the ultraviolet illumination with green color filter (i.e. CFUG) very useful, even though the numerical indexes indicated the two results were of better quality. This is because that, although the differences between the underwriting and parchment were significant compared with the underwriting, overall the images were not clear enough for the scholars. On the other hand, the PCA unsupervised method with the two different implementations in Matlab and ImageJ produced good images in terms of underwriting and were assessed positively by the scholars, even though the numerical indexes did not provide the same good results. This, suggests that, while the differences between the points representing the underwriting and the parchment were not significant in terms of the underwriting, there were not enough classification

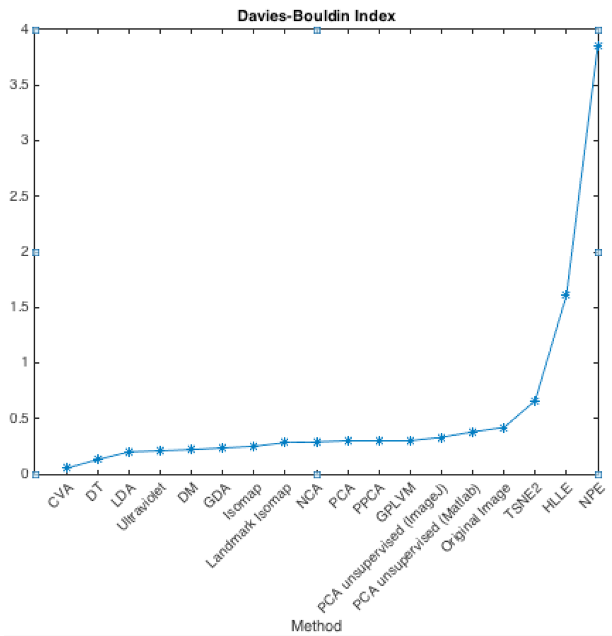


Fig. 3: Numerical assessment of images based on Davies-Bouldin index.

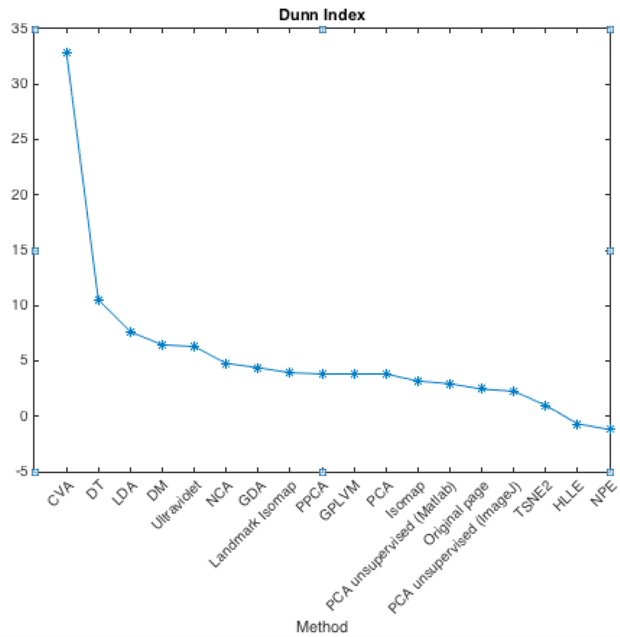


Fig. 4: Numerical assessment of images based on Dunn index.

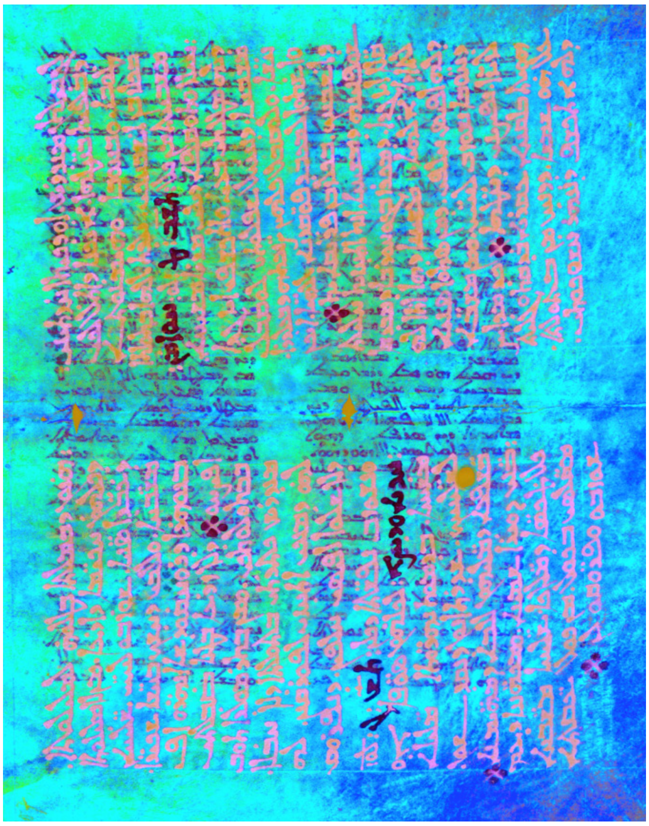


Fig. 5a: CVA-Matlab.

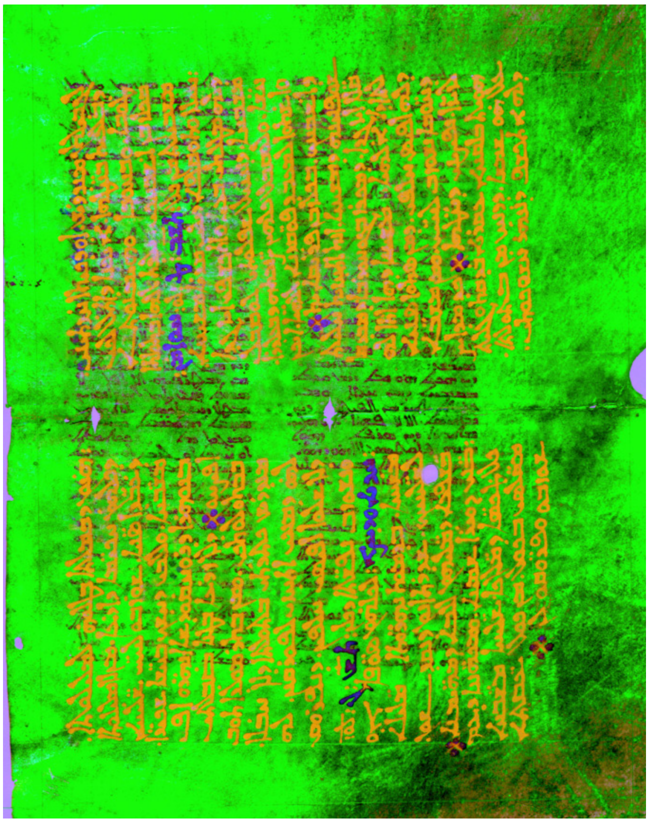


Fig. 5b: CVA-GNU GSL.

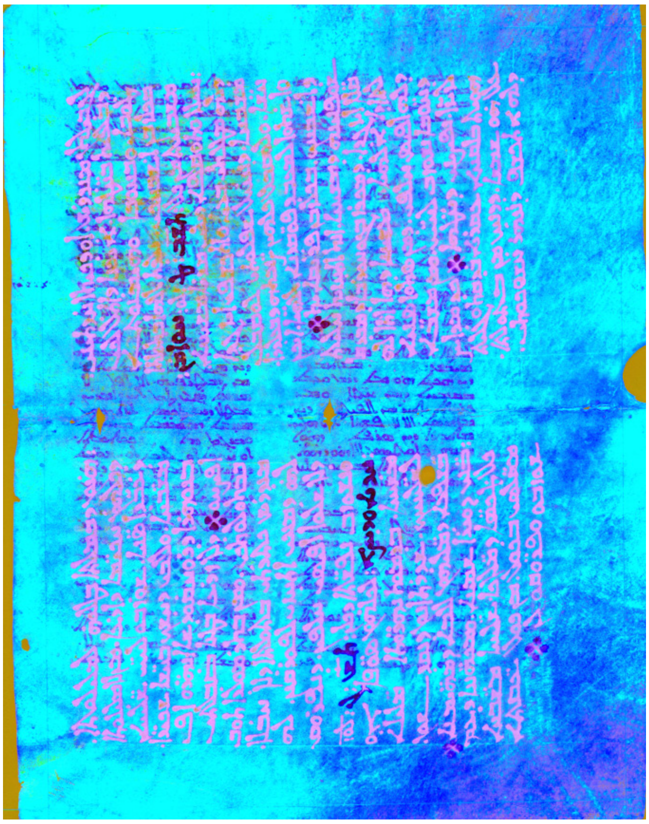


Fig. 5c: Inverting the first two channels of the three channel image (Red, Green and Blue) of the CVA-GNU GSL image result produces a photo similar to the CVA-Matlab result.

Figs 5a–c: Color image results obtained with CVA-Matlab and CVA-GNU GSL.

points being used (i.e. 200) in order to obtain important numerical results with the respective indexes.

Confidence intervals could be added to the results shown in Figure 3 and Figure 4 by applying the dimensionality reduction methods to a number of other palimpsest pages. However, the visual assessment done by the scholars was sufficient as the results were superior in terms of assessment quality than the numerical assessments with or without confidence intervals.

For the purposes of comparing the computational times and the image results, a CVA method is also implemented in C programming language using the GNU Scientific Library (GSL) and OpenCV computer vision library. High performance software was developed by using the GNU GSL library, which drastically reduced the computational complexity and time for the CVA-GNU GSL method. When run on a 3.5 GHz Intel Core i5 with 16 GB RAM memory, the CVA-Matlab function together with the creation of the new color images (i.e. writing on the SSD hard drive), had a computational time of 111 seconds. On the same computer, the computational time for the CVA-GNU GSL was 80 seconds, which is 31 seconds shorter than the CVA-

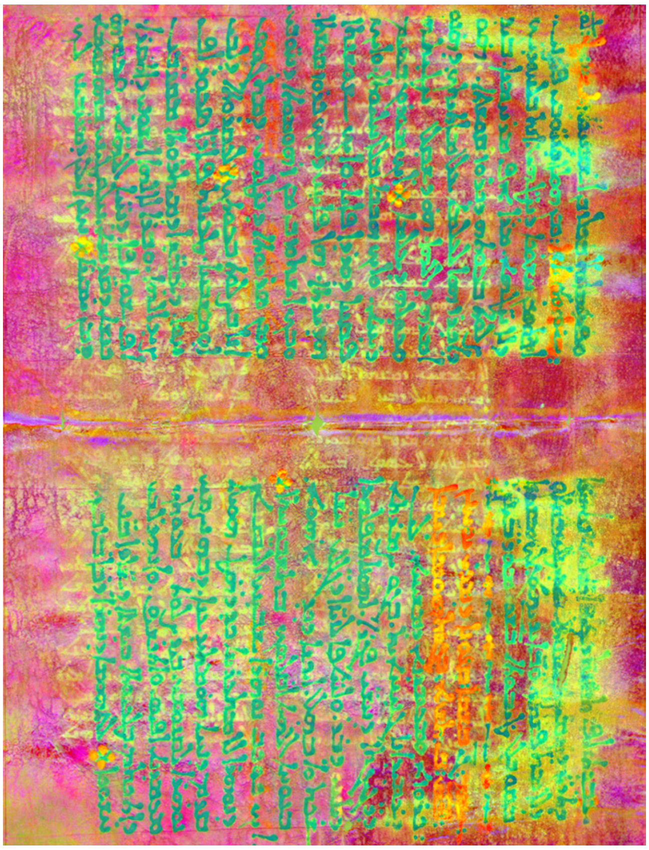


Fig. 6a: The CVA-GNU GSL processed page.

Fig. 6b: Original page seen by the human eye.

Figs 6a–c: Comparison for folios 040v–045r between the CVA-GNU GSL page and the multispectral and the original page seen by the human eye.

Maltab version, but this does not represent a critical time difference. This reduction of the computational time can be extended by using a computing programming library such as OpenMP[46] (OPEN MultiProcessing), which may further speed up the CVA-GNU GSL software by parallelizing the software code.

The eigen analysis functions in Matlab, eig, and GNU GSL, gsl_eigen_gensymmv, result in different calculated eigenvectors, for example, there can be different signs for the significant eigenvectors. This can be seen in Figure 5. Figure 5a is produced by the CVA-Matlab and Figures 5b and 5c are produced by CVA-GNU GSL. A similar result to Figure 5a was obtained by inverting the first two channels of the color image from the CVA-GNU GSL method (i.e. Figure 5b) and which is shown in Figure 5c. The majority of scholars (i.e. three out of five) considered the CVA-GNU GSL result (Figure 5b) better in terms of underwriting than the CVA-

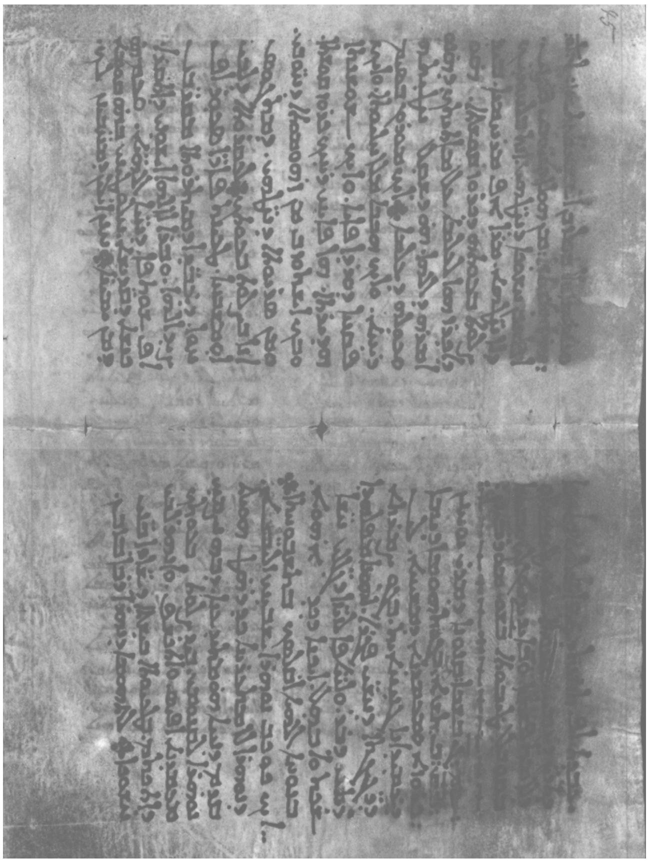


Fig. 6c: Ultraviolet illumination with green color filter.

[46] *OpenMP* <http://www.openmp.org> (last accessed 15 April 2018).

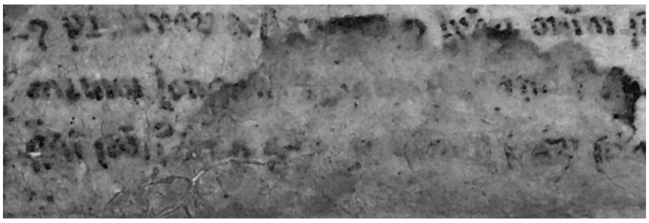


Fig. 7a: Section obtained with CVA-Matlab for a grayscale image.

Fig. 7b: Section obtained from the multispectral image of the *Latin Ms. 18* manuscript.

Figs 7a–b: Comparison between a section of one of the grayscale images produced by the CVA-Matlab method and the same section obtained from one of the multispectral images.

Matlab (Figure 5a), however, one scholar considered all the three results were of comparable high quality.

The entire *Syriac Galen Palimpsest*, which consists of about 240 pages, was processed with the CVA-GNU GSL, in less than 2 months and was able to produce both 8-bit and 16-bit images using the OpenCV computer vision programming library. Some pages were processed several times by varying the number of training input points to search for improvements in terms of the underwriting.

Figure 6 shows another folio of the palimpsest processed with the CVA-GNU GSL software library and the original page seen by the human eye for comparison (i.e. folio 040v–045r). This result shows how the underwriting is revealed to the scholars after multispectral imaging and the application of CVA-GNU GSL method. In Figure 6 there is no underwriting in the original page that can be seen by the human eye, while in the multispectral image, acquired with ultraviolet illumination with the green color filter, the underwriting starts to be revealed. In the image result obtained with the CVA-GNU GSL the underwriting becomes quite clear all over the page.

The study carried out on the *Galen Palimpsest* identified a smaller set of dimensionality reduction methods which provided the best image results. From this smaller set of methods, based on the visual and the numerical evaluation of the produced images, the CVA method produced the best result.

Therefore we wanted to test the CVA on a second manuscript written in Latin language and entitled *John Rylands Library, University of Manchester, Latin Ms. 18*. The authorship and provenance are currently unknown so hence there is a high degree of interest in identifying the respective manuscript. The manuscript does not have any underwriting, so it is not a palimpsest, but some of the text has been almost deleted because of passing of time and water.

In Figure 7 a result is shown, which was processed with CVA-Matlab with 200 points for the classes manuscript/parchment and text, for comparison with the multispectral image. For some sections of the page a slight improvement can be noticed with the CVA method, such as in Figure 7a.

In Figure 8, a comparison can be seen between the color image obtained with the CVA-Matlab and one of the multispectral images acquired for the *Latin Ms. 18* manuscript.

In Figure 9 a screen capture can be seen with the plugin[47], developed for the ImageJ software, with which the various dimensionality reduction methods implemented in Matlab or C-GNU GSL can be called.[48] The methods can be run with various numbers of input points and classes (e.g. class underwriting, class overwriting, etc). The methods that are available at the present time in the plugin and implemented in Matlab are CVA (i.e. processing 8 and 16 bit images), LDA, DM, GDA, Isomap, Landmark Isomap, NCA, PCA, PPCA, GPLVM and the CVA-GNU GSL method implemented in C programming language is also available (i.e. processing 8 or 16 bit images).

The image results and their visual and numerical assessment confirmed that the methods CVA and LDA seem to be always in the leadership position with regard to the image quality. The CVA/LDA methods find the linear combinations of variables that maximize the separation of data classes which were defined a priori. This means that, given a set of input points representing the different data classes (i.e. class parchment, class overwriting, class underwriting), the CVA method should be able to produce

[47] Arsene 2016a <https://zenodo.org/record/154127#.WVD12WgrJEY> (last accessed 15 April 2018).

[48] Arsene 2016b <https://github.com/corneliu25/GalenProject> (last accessed 15 April 2018).

Fig. 8a: Color image obtained with CVA-Matlab.

Figs 8a–b: Comparison between color image obtained with the CVA-Matlab and one of the multispectral images acquired for the *Latin Ms. 18* manuscript.

images which provide the best visual distinction between the different classes representing parchment, overwriting and underwriting. This characteristic of the CVA method, which is distinct from the other dimensionality reduction methods being tested here, was the most successful method studied and should be used further.

The use of supervised methods may involve the additional step of selecting the input points, but, as already envisaged in the previous sections, an automated technique for choosing the input points and classes to which the respective points belong to, has been recently devised[49]. Further work will be to include a quick automated process for choosing the input points and the classes to be used with the CVA method, and to further speed up the processing of multispectral images. Moreover, it was noted that when the unsupervised PCA method (i.e. Matlab, ImageJ) was used without selecting any input points, the image results obtained by PCA provided very good and important results in terms of underwriting. However, it must be stressed again that there is a need for an automated process to choose the input points and the classes to be used with supervised or unsupervised methods. More recently[49], another method was devised by which the overtext and the parchment were masked for a small section of a page of a palimpsest (i.e. a tile) and only the underwriting was used to train the PCA method. This last method resulted in very good image results and could also be considered for other supervised or unsupervised training methods.

[49] Hollaus et al. 2015.

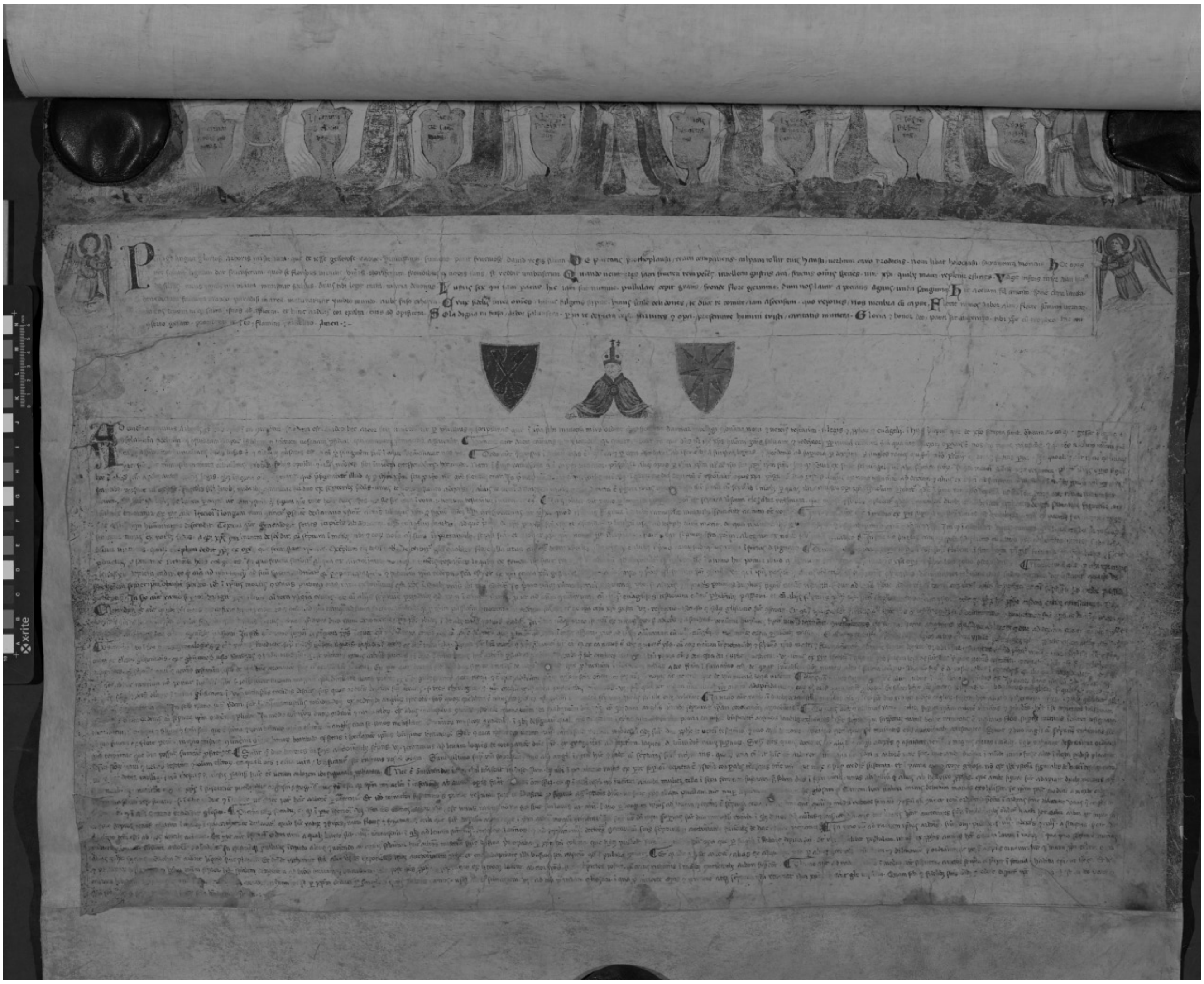


Fig. 8b: Multispectral image acquired for the *Latin Ms. 18* manuscript.

Some other methods proved to give good results such as Isomap and Landmark Isomap, which confirmed similar findings from literature[34]. Hence there is an interest to investigate other dimensionality reduction methods as sometimes they could provide good image results.

Other image enhancement methods could be applied to the grayscale images obtained from using the dimensionality reduction methods. One way would be to further improve the contrast via linear or polynomial scaling, as discussed previously. Another technique can be implemented, similar to the pseudocolor technique described above, where the grayscale image with the clearest underwriting is used in two channels rather than one to improve the appearance of the resulted color RGB image, which is usually obtained by combining three different grayscale channel images.

Finally, several dozen more images produced with the CVA method in Matlab or GNU GSL for the *Syriac Galen Palimpsest* showed at least the same quality, if not better, when compared with images produced by other image processing methods[50], in most of the cases. The entire *Syriac Galen Palimpsest*[51] was processed with the CVA-GNU GSL method and OpenCV library together with the developed ImageJ plugin, which consists of a number of Java files. These files are called by ImageJ software and also call the developed software library implementing the CVA-GNU GSL method. More than a quarter (i.e. 68 folios) of the *Syriac Galen Palimpsest* processed with the CVA-GNU

[50] Easton et al. 2010; Bergmann and Knox 2009; Hollaus et al. 2015.

[51] Afif et al. 2017; Afif et al. 2016.

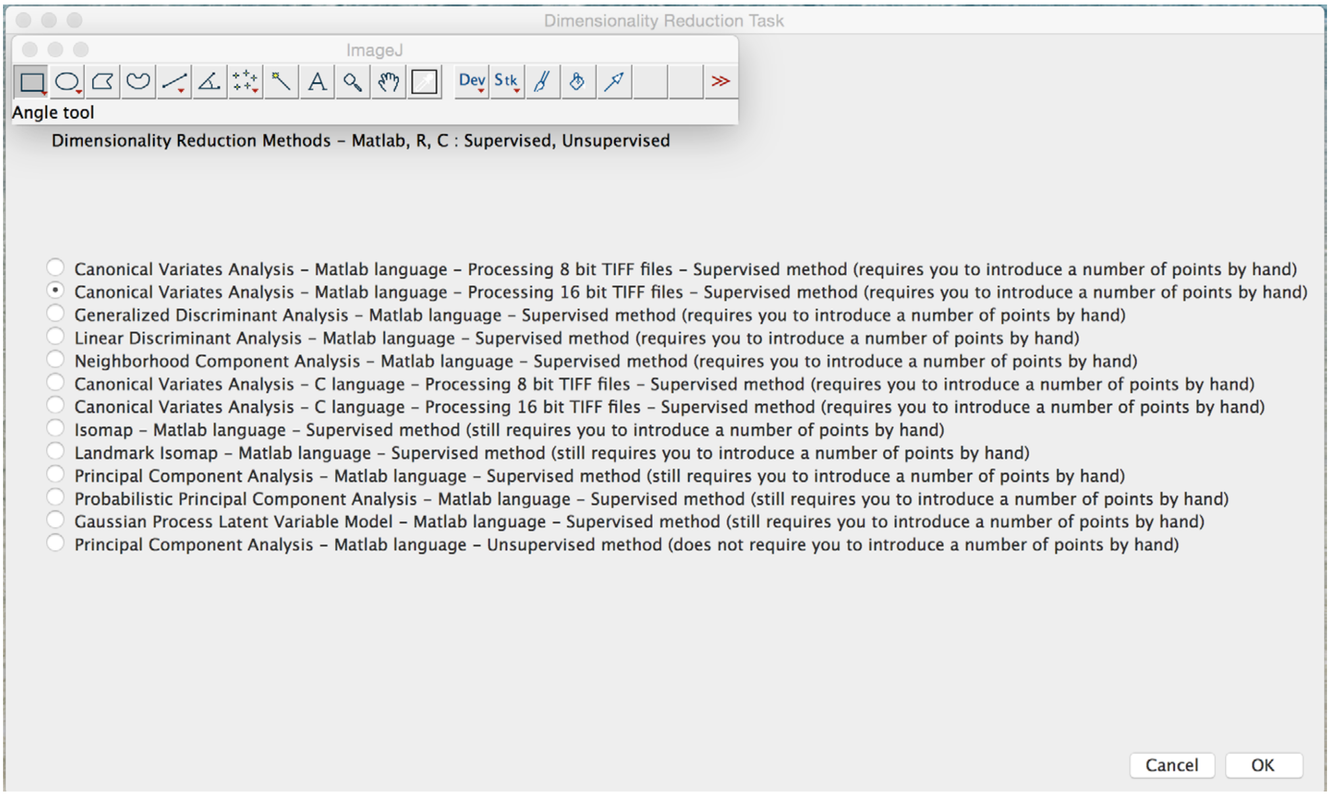


Fig. 9: Screen capture with the plugin developed for the ImageJ software with which the various dimensionality reduction methods implemented in Matlab or C-GNU GSL can be called for the purposes of image processing.

GSL method is freely available online[52] for any scholar to download and study.

5. Conclusions

Our findings suggest that a supervised dimensional reduction technique, such as CVA, is an excellent processing tool for multispectral images. The choice of method is ultimately based on the preferences of the person trying to read the manuscript, the precise makeup of the original document and obviously the quality of the images produced by the respective dimensionality reduction method. In addition to these, easy access to an appropriate toolset software was clearly highly desirable to provide quick processing of the multispectral images. The use of existing software for image processing, ImageJ, and the addition of the extra functionalities in course of this work, provided fast and remarkably good processing of the multispectral images of the *Galen Palimpsest*, of the second unidentified Latin manuscript and a number of other manuscripts.

Further work will consist of applying these dimensionality techniques and the software developed to enable the recovery of the undertext or hard-to-read texts in various other palimpsests and ancient manuscripts.

ACKNOWLEDGMENT

The authors would like to thank the Arts and Humanities Research Council, United Kingdom, for supporting this work (Research Grant AH/M005704/1 – The Syriac Galen Palimpsest: Galen's On Simple Drugs and the Recovery of Lost Texts through Sophisticated Imaging Techniques). The authors would like to thank to Prof. Dr Peter Pormann, Dr Naima Afif, Dr William Sellers, Dr Natalia Smelova, Dr Siam Bhayro, Dr Taro Mimura, Dr Kamran Karimullah, Dr Grigory Kessel, Dr Elaine Van Dalen, Dr Irene O'Daly, Dr Michelle Magin, Dr William Christens-Barry, Mr Michael Toth, Dr Chloe Jeffries, Mrs Gwen Riley Jones and Mrs Carol Burrows in supporting this work.

[52] Arsene 2017 <https://zenodo.org/record/252293#.WVEeaGgrJEY> (last accessed 15 April 2018).

REFERENCES

Afif, N., B. Siam, P. Pormann, W. I. Sellers, and N. Smelova (2016), 'The Syriac Galen Palimpsest: Research Methods and Latest Discoveries', *Comparative Oriental Manuscript Studies Bulletin*, 2: 5–16.

——, C. Arsene, S. Bhayro, I. Cala, J. Daccache, R. Hawley, G. Kessel, P. Pormann, W. Sellers, and N. Smelova (2016), 'Continuing Research on the Syriac Galen Palimpsest: Collaborative Implementation within the Framework of Two European Projects', *Semitica et Classica*, 9: 261–268.

Alexopoulou, A. and A. Kaminari (2014), 'The Evolution of Imaging Techniques in the Study of Manuscripts', *manuscript cultures*, 7: 58–68.

Arsene, C. T. C., P. J. G. Lisboa, P. Borrachi, E. Biganzoli, and M. S. H. Aung (2006), 'Bayesian Neural Networks for Competing Risks with Covariates', *The Third International Conference in Advances in Medical, Signal and Information Processing, MEDSIP* 2006, IET.

—— and —— (2007), 'Artificial Neural Networks Used in the Survival Analysis of Breast Cancer Patients: A Node Negative Study', in A. F. G. Taktak and A. C. Fisher (eds), *Perspectives in Outcome Prediction in Cancer* (Amsterdam: Elsevier Science).

—— and —— (2011), 'PLANN-CR-ARD Model Predictions and Non-parametric Estimates with Confidence Intervals', *Proceedings of the International Joint Conference on Neural Networks (IJCNN)*, San Jose, CA (San Jose, CA: IEEE).

——, ——, and E. Biganzoli (2011), 'Model Selection with PLANN-CR-ARD', in J. Cabestany, I. Rojas, and G. Joya (eds), *IWANN* 2011, Part II, (*Lecture Notes in Computer Science, LNCS*, 6692) (Berlin, Heidelberg: Springer), 210–219.

—— (2016a) 'Canonical Variates Analysis Software for Dimensionality Reduction with Application to Image Processing', *Zenodo* <doi 10.5281/zenodo.596199>, <https://zenodo.org/record/154127#.WVD12WgrJEY> (last accessed 15 April 2018).

—— (2016b), 'Image Enhancement of the Galen Palimpsest – Software Tools/Plugin for ImageJ', *GitHub* <doi 10.5281/zenodo.154127>.,<https://github.com/corneliu25/GalenProject> (last accessed 15 April 2018).

—— (2017), 'Processing a Quarter (68 folios) of the Syriac Galen Palimpsest http://www.digitalgalen.net', *Zenodo* <doi.org/10.5281/zenodo.252293>, <https://zenodo.org/record/252293#.WVEeaGgrJEY> (last accessed 15 April 2018).

Baronti, S., A. Casini, F. Lotti, and S. Porcinai (1997), 'Principal Component Analysis of Visible and Near-infrared Multispectral Images of Works of Art', *Chemometrics and Intelligent Laboratory Systems*, 39.1: 103–114.

Bergmann, U. and K. T. Knox (2009), 'Pseudocolor Enhanced X-ray Fluorescence of the Archimedes Palimpsest', *SPIE*, 7247: 724702.

Bhayro, S., R. Hawley, G. Kessel, and P. Pormann (2013), 'The Syriac Galen Palimpsest: Progress, Prospects and Problems', *Journal of Semitic Studies*, 58.1: 131–148.

—— , P. E. Pormann, and W. J. Sellers (2013), 'Imaging the Syriac Galen Palimpsest: Preliminary Analysis and Future Prospects', *Semitica et Classica*, 6: 297–300.

Bohling, G. (2010), 'Dimension Reduction and Cluster Analysis', *Report, EECS* 833, The University of Kansas, 6 March 2010.

Bouldin, D. L. and W. Donald (1979), 'A Cluster Separation Measure', *IEEE Transactions on Pattern Analysis and Machine Intelligence*, PAMI-1.2: 224–227.

Bunte, K, S. Haase, M. Biehl, and T. Villmann (2012), 'Stochastic Neighbour Embedding (SNE) for Dimension Reduction and Visualization Using Arbitrary Divergences', *Neurocomputing*, 90.1: 23–45.

Camba, A., M. Gau, F. Hollaus, S. Fiel, and R. Sablatnig (2014), 'Multispectral Imaging, Image Enhancement, and Automated Writer Identification in Historical Manuscripts', *manuscript cultures*, 7: 83–91.

Campbell, N.A and W. R. Atchley (1981), 'The Geometry of Canonical Variate Analysis', *System Zoology*, 30.3: 268–280.

Chang, C.-I. (2013), *Hyperspectral Data Processing: Algorithm Design and Analysis* (Hoboken, N.J.: Wiley).

Church, S. (2015), *Image Processing and Reflectance Recovery of Carbonised Papyri from Multispectral Images, MPhys report* (School of Physic and Astronomy, University of Manchester).

Doi, K. (2007), 'Computer-aided Diagnosis in Medical Imaging: Historical Review, Current Status and Future Potential', *Computerized Medical Imaging and Graphics*, 25.4–5: 198–211.

Dunn, J. C. (1973), 'A Fuzzy Relative of the ISODATA Process and Its Use in Detecting Compact Well-Separated Clusters', *Journal of Cybernetics*, 3.3: 32–57.

Easton, R. L., W. A. Christens-Barry, and K. T. Knox (2011), 'Spectral Image Processing and Analysis of the Archimedes Palimpsest', *19th European Signal Processing Conference (EUSIPCO 2011)*.

—— and W. G. Noel (2010), 'Infinite Possibilities: Ten Years of Study of the Archimedes Palimpsest', *Proceedings of the American Philosophical Society*, 154.1, 50–76.

—— and D. Kelbe (2014), 'Statistical Processing of Spectral Imagery to Recover Writings from Erased or Damaged Manuscripts', *manuscript cultures*, 7: 35–46.

——., K. T. Knox, W. A. Christens-Barry, K. Boydston, M. B. Toth, D. Emery, and W. G. Noel (2010), 'Standardized System for Multispectral Imaging of Palimpsests', *SPIE*, 7531: 753112.

Egmont-Petersen, M., D. de Ridder, and H. Handels (2002), 'Image Processing with Neural Networks — a review', *Pattern Recognition*, 35.10: 2279–2301.

Fish D. A., A. M. Brinicombe, E. R. Pike, and J. G. Walker (1995), 'Blind Deconvolution by Means of the Richardson-Lucy Algorithm', *Journal of the Optical Society of America A*, 12.1: 58–65.

Fisher, R. A., (1936), 'The Use of Multiple Measurements in Taxonomic Problems', *Annals of Eugenics*, 7.2: 179–188.

Freeden, W. and M. Z. Nashed (2010), *Handbook of Geomathematics* (Berlin, Heidelberg: Springer).

Franti, P., M. Rezaei, and Q. Zhao (2014), 'Centroid Index: Cluster Level Similarity Measure', *Pattern Recognition*, 47: 3034–3045.

Gepshtein, S. and Y. Keller (2013), 'Image Completion by Diffusion Maps and Spectral Relaxation', *IEEE Transactions on Image Processing*, 2983–2994.

Glaser, L. and D. Deckers (2014), 'The Basics of Fast-scanning XRF Element Mapping for Iron-gall Ink Palimpsests', *manuscript cultures*, 7: 104–112.

Goldberger, J., S. Roweis, G. Hinton, and R. Salakhutdinov (2005), 'Neighbourhood Component Analysis', *19TH Annual Conference on Neural Information Processing Systems, NIPS*.

Graves, A., M. Liwicki, S. Fernandez, R. Bertolami, H. Bunke, and J. Schmidhuber (2009), 'A Novel Connectionist System for Improved Unconstrained Handwriting', *IEEE Transactions on Pattern Analysis and Machine Intelligence*, 31.5: 855–868.

Hashimoto, N., Y. Murakami, P. A. Bautista, M. Yamaguchi, T. Obi, N. Ohyama, K. Uto, and Y. Kosugi (2011), 'Multispectral Image Enhancement for Effective Visualization', *Optics Express*, 19.10: 9315–9329.

Hollaus, F., M. Gau, and R. Sablatnig (2012), 'Multispectral Image Acquisition of Ancient Manuscripts', *Progress in Cultural Heritage Preservation, Lecture Notes in Computer Science, 4th International Conference, EuroMed 2012, Limassol, Cyprus, October 29 – November 3, 2012, Proceedings* (Berlin, Heidelberg: Springer), 30–39.

—— , —— , —— (2013), 'Enhancement of Multispectral Images of Degraded Documents by Employing Spatial Information', *12th International Conference on Document Analysis and Recognition (IEEE)*, 145-149.

—— , —— , —— , W. A. Christens-Barry, and H. Miklas (2015), 'Readability Enhancement and Palimpsest Decipherment of Historical Manuscripts', in O. Duntze, T. Schaban, and G. Vogeler (eds), *Codicology and Palaeography in the Digital Age 3* (Schriften des Instituts für Dokumentologie und Editorik, 10) (Norderstedt: BoD), 31–46.

Imani, M. and H. Ghassemian (2014), 'Band Clustering-based Feature Extraction for Classification of Hyperspectral Images Using Limited Training Samples', *IEEE Geoscience and Remote sensing Letters*, 11.8: 1325–1329.

James, M. R. (1921), A *Descriptive Catalogue of the Latin Manuscripts in the John Rylands Library at Manchester* (Manchester: University Press), reprinted 1980 with an introduction and additional notes and corrections by F. Taylor (Munich).

Janke, A and C. MacDonald (2014), 'Multispectral Imaging of the San Lorenzo Palimpsest (Florence Archivio del Capitolo di San Lorenzo, Ms. 2211)', *manuscript cultures*, 7: 113–125.

Journaux, L., X. Tizon, I. Foucherot, and P. Gouton (2006), 'Dimensionality Reduction Techniques: An Operational Comparison on Multispectral Satellite Images Using Unsupervised Clustering', *IEEE 7th Nordic Signal Processing Symposium (NORSIG), Reykjavik, Iceland, June 7-9, Proceedings (IEEE)*, 242–245.

—— , I. Foucherot, and P. Gouton (2008), 'Multispectral Satellite Images Processing Through Dimensionality Reduction', *Signal Processing for Image Enhancement and Multimedia Processing, Multimedia Systems and Applications Series*, 31, 59–66.

Khurshid. A. (1996), 'Hunain bin Ishaq on Ophthalmic Surgery', *Bulletin of the Indian Institute of History of Medicine*, 26: 69–74.

Kwon, H., X. Hu, J. Theiler, A. Zare, and P. Gurram (2013), 'Algorithms for Multispectral and Hyperspectral Image Analysis', *Journal of Electrical and Computer Engineering*, 908906.

Lisboa, P. J. L., T. Etchells, I. Jarman, C. T. C. Arsene, M. S. H. Aung, A. Eleuteri, A. F. G. Taktak, F. Ambrogi, P. Boracchi, and E. Biganzoli (2009), ‘Partial Logistic Artificial Neural Network for Competing Risks Regularized with Automatic Relevance Determination’, *IEEE Transactions on Neural Networks*, 20.9: 1403–1416.

Lu, S, L. Zou, X. Shen, W. Wu, and W. Zhang (2011), ‘Multispectral Remote Sensing Image Enhancement Method Based on PCA and IHS Transformations’, *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 12.6: 453–460.

Macfie, H. J., C. S. Gutteridge, and J. R. Norris (1978), ‘Use of Canonical Variates Analysis in Differentiation of Bacteria by Pyrolysis Gas-liquid Chromatography’, *Journal of General Microbiology*, 104.1: 67–74.

Manning, P.L., N. P. Edwards, R. A. Wogelius, U. Bergmann, H. E. Barden, P. L. Larson, D. Schwarz-Wings, V. M. Egerton, D. Sokaras, R. A. Mori, and W. I. Sellers (2013), ‘Synchrotron-based Chemical Imaging Reveals Plumage Patterns in a 150 Million Year Old Early Bird’, *Journal of Analytical Atomic Spectrometry*, 28: 1024–1030.

Maxwell, A. E. (1961), ‘Canonical Variates Analysis when the Variables are Dichotomous’, *Educational and Psychological Measurement*, 21.2: 259–271.

McCollum, A.J. and W. F. Clocksin (2007), ‘Multidimensional Histogram Equalization and Modification’, *14th International Conference on Image Analysis and Processing – ICIAP 2007*, 659–664.

Mitsui, M., Y. Murakami, T. Obi, M. Yamaguchi, and N. Ohyama (2005), ‘Color Enhancement in Multispectral Image Using the Karhunen-Loeve Transform’, *Optical Review*, 12.2: 69–75.

Mlsna, P.A. and J. J. Rodriguez (1995), ‘A Multivariate Contrast Enhancement Technique for Multispectral Images’, *IEEE Transactions on Geoscience and Remote Sensing*, 33.1: 212–216.

Mocella, V., E. Brun, E., C. Ferrero, D. Delattre (2015), ‘Revealing Letters in Rolled Herculaneum Papyri by X-Ray Phase-Contrast Imaging’, *Nature Communications*, 6: 5895.

Montgomery, S. L. (2000), *Science in Translation: Movements of Knowledge Through Cultures and Time*, (Chicago: University Chicago Press).

—— (2001), ‘Gained in the translation’, *Nature*, 409: 667.

Netz, R., W. Noel, N. Wilson, and N. Tchernetska (2011), *The Archimedes Palimpsest* (Cambridge: Cambridge University Press).

Peltier, C., M. Visalli, and P. Schlich (2015), ‘Comparison of Canonical Variate Analysis and Principal Component Analysis on 422 Descriptive Sensory Studies’, *Food Quality and Preference*, 40(B): 326–333.

Pormann, P. E. (2015), ‘Interdisciplinary: Inside Manchester’s “Arts Lab”’, *Nature*, 525: 318–319.

Rabin, I., O. Hahn, and M. Geissbühler (2014), ‘Combining Codicology and X-Ray Spectrometry to Unveil the History of Production of Codex Germanicus 6’, SUB Hamburg, *manuscript cultures*, 7: 126–131.

Rao, R. C. (1948), ‘The Utilization of Multiple Measurements in Problems of Biological Classification’, *Journal of the Royal Statistical Society, Series B*, 10.2: 159–203.

Ricotta, C. and G. C. Avena (1999), ‘The Influence of Principal Component Analysis on the Spatial Structure of a Multispectral Dataset’, *International Journal of Remote Sensing*, 20.17: 3367–3376.

Schneider, C. A., W. S. Rasband, and K. W. Eliceiri (2012), ‘NIH Image to ImageJ: 25 years of Image Analysis’, *Nature Methods*, 9.7: 671–675.

Shao, W. and M. Elad (2015), ‘Bi-l0-l2-Norm Regularization for Blind Motion Deblurring’, *Journal of Visual Communication and Image Representation*, 33: 42–59.

Shanmugam, S. and P. SrinivasaPerumal (2014), ‘Spectral Matching Approaches in Hyperspectral Image Processing’, *International Journal of Remote Sensing*, 35.24: 8217–8251.

Stout, S., F. Kuester, and M. Seracini (2012), ‘XRAY Fluorescence Assisted: Multispectral Imaging of Historic Drawings’, *Denver X-ray Conference (DXC) on Applications of X-ray Analysis*, 56.

Zhang, L., B. Du (2012), ‘Recent Advances in Hyperspectral Image Processing’, *Geo-spatial Information Science*, 15.3: 143–156.

Zhenghao, S., L. He, K. Suzuki, T. Nahamura, and H. Itoh (2009), ‘Survey on Neural Networks used for Medical Image Processing’, *International Journal of Computational Science*, 3.1: 86–100.

van der Maaten, L. J. P. and G. E. Hinton (2008), ‘Visualizing High-Dimensional Data Using t-SNE’, *Journal of Machine Learning Research*, 9: 2579–2605.

Xu, R., L. du Plessis, S. Damelin, M. Sears, and D. Wunsch (2009), ‘Analysis of Hyperspectral Data with Diffusion Maps and Fuzzy ART’, *International Joint Conference in Neural Networks* (IJCNN).

Wang, L. and Z. Chunhui (2015), *Hyperspectral Image Processing* (Berlin, Heidelberg: Springer).

Walvoord, D. J. and R. L. Easton, Jr. (2008), ‘Digital Transcription of Archimedes Palimpsest’, *IEEE Signal Processing*, 25, 100–104.

Article

Three Complementary Non-invasive Methods Applied to Mediaeval Manuscripts

Bernadette Frühmann, Federica Cappa, Wilfried Vetter, and Manfred Schreiner | Vienna

1. Introduction

During the last decades, a particular collaboration between representatives of various philologies, art history and conservation/restoration, on the one hand, and physics, chemistry, and biology, on the other has been established, which was completed by a collaboration with computer vision specialists. At the same time, the booming development of analytical methods in the sciences has offered the possibility to use a great number of new instrumental micro-analytical techniques with non-sampling (without taking original sample material) and *in situ* applicability for the analysis of written heritage objects and works of art.

To give this collaboration a solid structure, at the beginning of 2014 the Centre of Image and Material Analysis in Cultural Heritage (CIMA)[1] was established with the aid of the Structural Fund for Austrian Higher Education Area of the Austrian Federal Ministry of Science and Research.[2] Within this framework, a series of mediaeval manuscripts from various Austrian libraries, especially the Austrian National Library (ÖNB), were examined. The selection comprises badly preserved or overwritten manuscripts (palimpsests), on the one hand, and manuscripts with a remarkable design, on the other, deriving from the ninth through the fourteenth century. The material investigation part aims to determine the composition of inks and pigments used for writing and illuminating, as well as to characterize the support. In addition to chemical analyses, multispectral imaging was carried out, which has already been presented.[3]

For manuscripts of this kind, the application of non-invasive techniques is obligatory. This implies the use of the aforementioned methods that are able to measure *in situ*.

The paper will give an overview of the work. It was carried out using three non-invasive methods for elemental as well as compound specific material analyses: X-ray Fluorescence (XRF), Fourier Transform Infrared spectroscopy in the reflection mode (rFTIR), and Raman spectroscopy. Out of all the manuscripts analyzed, the two following codices are selected as case studies: Codex Vindobonensis slavicus 8, a richly decorated manuscript with full-color miniature paintings, and Codex Vindobonensis theologicus graecus 209, with no color decorations but several palimpsested folia. Both investigations started with the XRF analysis in order to identify the elements present in the areas of interest. In a second step, rFTIR and Raman spectroscopies were applied[4] to combine the elemental information with compound-specific data and allow an interpretation of the gained spectra, as well as to improve the accuracy of the results. Similar equipment has been used to study manuscripts by other authors.[5]

2. Equipment

For the elemental identification of the inks used for the text and the pigments applied e.g. for illuminations in the manuscripts, two different portable XRF devices are available in ISTA.[6] The most important difference between the two devices is the spot size of the primary X-ray beam and therefore also of the area analyzed. One of the

[1] CIMA is an interuniversity research institution with an interdisciplinary approach to the investigation of cultural heritage, see https://hrsm.cvl.tu-wien.ac.at/ or https://hrsm.cima.or.

[2] I.e., the Hochschulraum Strukturmittel project 2013 'Erschließung und Erhaltung von Kulturgut – Moderne bildgebende und materialanalytische Verfahren zur Visualisierung, Dokumentation und Klassifikation von historischem Schriftgut (Handschriften)'.

[3] Cf., e.g., Camba et al. 2014.

[4] Chalmers, Edwards, and Hargreaves 2011; Derrick, Stulik and Landry 1999.

[5] Bruni et al. 2008; Doherty et al. 2013; Miliani et al. 2012; Pessanha, Manso, and Carvalho 2012; Hahn 2010.

[6] Institute of Science and Technology in Art, Academy of Fine Arts Vienna.

instruments works with a rather large spot size (7 mm in diameter), whereas the spot size of the other is relatively small (1 mm in diameter) and suited for measuring the fine lines of characters. As the X-ray radiation has a certain penetration depth, the element detection refers not only to the surface layer (e.g. ink), but is the result of all elements present in all layers, including the constituents of the parchment, sometimes even of the material on the verso side. To be sure to collect the information only of the investigated folio, a 5-mm-thick PMMA[7] plate is placed underneath the parchment. This synthetic material shows no signals in the XRF spectrum. If the spot size of the instrument is larger than the character lines, information on the surrounding area will be detected, too (this is most notable for the Spectro XSort system, presented in the following). Therefore, it is essential to carefully select the area of analysis in order to avoid possible interference caused by surrounding material. Furthermore, as the analyses are carried out in air, elements with an atomic number lower than silicon (Si) cannot be detected. The same applies to organic compounds, and even inorganic compounds such as ultramarine with sodium (Na) or silicon (Si) as their main constituents are not easy to register. Thus, the results gained by XRF are lists of elements present in particular areas, where the correlation to a specific pigment or ink is not always easy and is sometimes even impossible to achieve. To receive the elements of the ink, a comparison with the spectrum of the bare support material (in our cases parchment) has to be carried out.

The measurements of Cod. Vind. slav. 8 were carried out with a μ-XRF device[8] containing an X-ray beam 1 mm in diameter, able to identify the various pigments, e.g. in miniature paintings. Designed and developed at our institute especially for use in the field of art, it is equipped with an Rh X-ray tube with a maximum voltage of 50 kV together with a silicon drift chamber detector. To measure manuscripts, it is mounted on a tripod. The system is furthermore equipped with two laser pointers for positioning. For the analyses of the inks and pigments in Cod. Vind. slav. 8, a tube voltage of 35 kV and a tube current of 0.8 mA for 100 sec were chosen.

For the Cod. theol. gr. 209, the other system was used, namely a handheld XRF device made by Spectro Analytical Instruments, type xSORT,[9] designed primarily for commercial application. It can also be applied for non-invasive *in situ* analyses, as it offers the following advantages: light weight, fast measuring procedure, and the ability to detect light elements with an atomic number even below 20 (e.g. Mg, Al, Si, and P). This system is equipped with an Ag X-ray tube with a maximum voltage of 40 kV, a tube current between 7 and 35 μA, and an ultra-fast silicon drift chamber detector. It is mounted on a museum adapter on a tripod. In addition, two pointing lasers for alignment purposes and an integrated camera for positioning are assembled. As the spot size is rather large, measuring *c*. 7 mm in diameter, it is not suitable for fine decorations. The settings for the measurements were the following: 40 kV with 5 μA for 6 sec. and 15 kV and 7 μA for 30 sec for the detection of elements with lower atomic numbers.

For the compound-specific identification of pigments and inks, Raman spectroscopy was applied.[10] The measurements were carried out *in situ* with the Pro-Raman-L-Dual-G made by Enwave Optronics, USA, a fully integrated and transportable instrument. The excitation sources applied for the investigations were Diode Lasers at 785 nm (~350 mW) and 532 nm (~50 mW) with narrow line-widths of 2.0 cm^{-1} and 1.5 cm^{-1}, respectively. The instrument is based on a two-dimensional, temperature-regulated (-60°C) CCD array detector. The integrated microscope is equipped with a 1.3-Mpixel CMOS camera with in-line LED illumination. The measured spot size varies depending on the applied laser and on the objective lens of the microscope. Using an objective lens with 40x magnification, the spot size is about 50 μm in diameter for the 785 nm laser, whereas for the 532 nm laser the spot size reduces to 35 μm. The spectra were evaluated by comparing with an ISTA reference database.[11]

To gain information about the compounds or even some organic mixtures, FTIR spectroscopy is a useful tool. For these measurements, we have a portable Bruker ALPHA[12] FTIR spectrometer with a spot size of approximately 6 mm.

---

[7] PMMA – Polymethylmethacrylat $C_5H_8O_2$ – known as acrylic glass.

[8] Desnica and Schreiner 2006.

[9] Spectro Analytical Instruments GmbH, Boschstrasse 10, D-47533 Kleve. <www.spectro.com> (last accessed 15 April 2018).

[10] Lee, Otieno-Alego, and Creagh 2008.

[11] Database created by mockups of the pigment collection in the institute; cf. <http://www.fch.akbild.ac.at/index_e.html> (last accessed 15 April 2018).

[12] Bruker Optics, Ettlingen, Germany. <https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ft-ir-routine-spectrometers/alpha/overview.html> (last accessed 15 April 2018).

Total reflection spectra (specular and diffuse reflection) were collected *in situ* in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} over 64–128 scans. The background was acquired using a gold mirror as reference sample. The total reflection spectra were transformed to absorption index spectra by applying the Kramers-Kronig algorithm,[13] which is included in the software package OPUS, version 6.5, used to control the ALPHA instrument as well as the data acquisition and evaluation. After the transformation, a baseline correction was carried out on the absorption index spectra. The spectra were evaluated by comparison with the databases IRUG[14] and IR Hummel Industrial Polymers,[15] as well as with a database with spectra obtained from the materials collection of the ISTA.[16] Freshly prepared (approx. 2-year-old) parchment delivered by the Institute INCDTP[17] in Bucharest, Romania was used as a reference for the support.

3. Codex Vindobonensis slavicus 8, fol. 74^{v}

Cod. Vind. slav. 8, written in 1368 by Prince Novak of Krbava (Croatia), is one of the most beautiful Glagolitic manuscripts of the Austrian National Library.[18] In total, 27 folia of this missal were analyzed. The codex is richly illustrated with illuminations and decorations, while the script itself is written in black and red inks. The main aim of our analysis was to identify the illuminations' pigments, the binding media, and the inks used for the script.

For their identification, analytical measurements with XRF, rFTIR, and Raman spectroscopy were carried out. Fol. 74^{v} is presented as an example because of the wide variety of colors used on this page. Fig. 1 shows the folio with the analyzed points: the first twelve (P1–P12) were analyzed with all three methods, whereas the last seven (P13–P19) were examined only with Raman spectroscopy.

Fig. 1: Cod. Vind. slav. 8, fol. 74^{v} with the selected measurement points. Points shown in green were examined with all three analytical methods, whereas those in pink were studied only with Raman spectroscopy.

3.1 Analysis of parchment and inks

XRF of the parchment (P1) yielded elements such as phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), and small amounts of iron (Fe). Calcium carbonate was identified by rFTIR in every measurement point; it was most probably used to whiten the parchment or during the parchment's manufacture. Moreover, some silicates were identified by rFTIR; these could derive from the process of polishing with pumice.[19] In addition, indications of oxidative degradation were detected (broadening of the amide I band at *c*. 1720 cm^{-1} due to the formation of carbonyl compounds)[20]. XRF measurements of the black ink of the script (P12) yielded

[13] Griffiths and Haseth 2007.

[14] Infrared and Raman Users Group, database with spectra obtained mainly in the transmission mode. <www.irug.org> (last accessed 15 April 2018).

[15] IR Hummel Industrial Polymers, Wiley-VCH 2005.

[16] Institute of Science and Technology in Art, Academy of Fine Arts Vienna, database with spectra obtained in transmission and reflection mode. <http://www.fch.akbild.ac.at/index_e.html> (last accessed 15 April 2018).

[17] The National Research & Development Institute for Textiles and Leather, Bucharest, Romania.

[18] An edition of this remarkable manuscript is presently being prepared by a team of Slavists in Zagreb and Vienna with the aid of CIMA. For a description, see <http://www.enciklopedija.hr/natuknica.aspx?id=41178#top> (last accessed 15 April 2018).

[19] Fuchs, Meinert, and Schrempf 2001; Thompson 1956.

[20] Derrick 1991; Strlic et al. 2009; Socrates 2001.

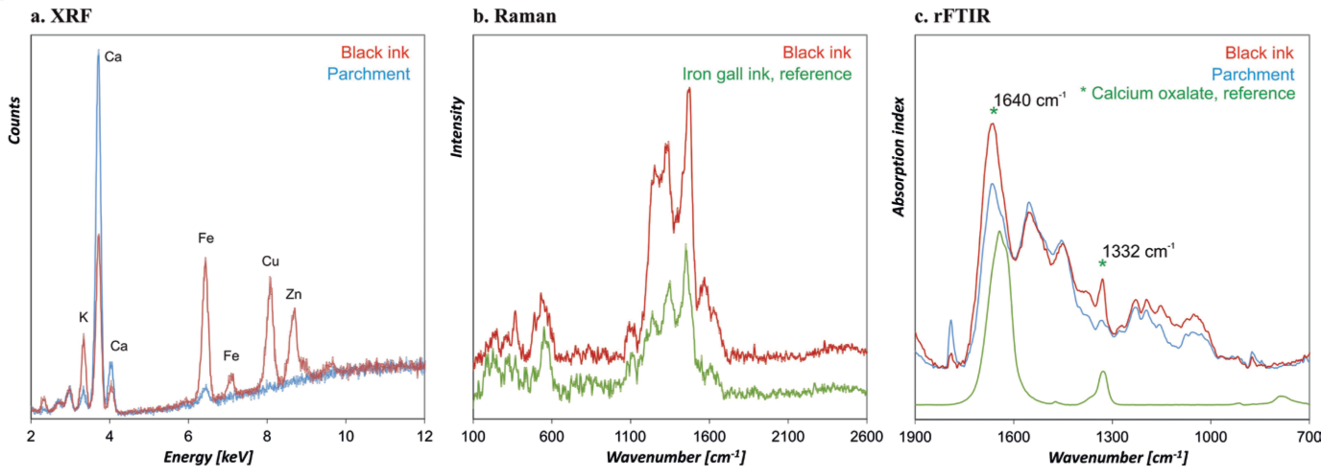


Fig. 2: Results of the measurements of the black ink in measurement point P12 on f. 74ᵛ of Cod. Vind. slav. 8 performed with all three analytical methods. a) XRF spectrum of the black ink (red) in comparison with the parchment P1 (blue), where K, Fe, Cu, and Zn were detected. b) Raman spectrum of the black ink (red) together with a reference spectrum of iron gall ink (green). c) rFTIR spectrum of black ink (red) in comparison with the spectrum of parchment P1 (blue) and pure calcium oxalate (green) as reference.

the presence of potassium (K), iron (Fe), copper (Cu), and zinc (Zn), which can be an indication of iron gall ink. This result was verified by Raman spectroscopy (the same for P18 and P19).[21] rFTIR spectroscopy could not contribute to the identification of the ink at all. However, calcium oxalate was detected, which is an indication of the degradation of ink components by mold fungi.[22] The spectra of XRF, rFTIR and Raman analyses are summarized in Fig. 2. In contrast to these results, only small amounts of copper (Cu) and gold (Au) were detected with XRF in the black margin line of the illumination (P10), which could originate from the paint layer underneath. In this point, no iron (Fe) – characteristic of iron gall ink – was registered. The use of carbon black for this line (similar to P14) was proven by Raman spectroscopy.

For the red ink (P16 and P17), Raman spectroscopy proved the use of vermilion (HgS). XRF was used to analyze similar regions on other folia, e.g. fol. 90ʳ P5 or fol. 104ʳ P3, where sulfur (S) and mercury (Hg) were detected (Fig. 3), whereas rFTIR found indications of the use of a proteinaceous binding medium for the red ink. The spectra obtained in the red ink show the characteristic bands for proteins, but with remarkable differences from the parchment support, particularly much stronger signals of the amide I band and amide II band at 1650 and 1550 cm^{-1}, the N–H and O–H stretching vibrations around 3300 cm^{-1}, and differing C–H stretching vibrations between 2950 and 2800 cm^{-1} (Fig. 4). A strong influence from the support was not to be expected, due to the relatively strong ink application. Vermilion does not absorb mid-infrared radiation, and therefore its spectra show no bands in the analyzed spectral range. According to the literature, the most important proteinaceous binding media were egg white and glues produced from the swim bladders of fish, as well as parchment.[23] However, rFTIR was unable to precisely determine the material, as the reference spectra of the proteinaceous materials are very similar.

3.2 Analysis of the pigments in the miniature painting

The identification of pigments used for miniature painting is limited by the fact that XRF detects not only the elements in the uppermost layer, but also those in the material underneath, e.g. the ground or support. The information gained is always a mixture of each material present in the area of analysis, including the ground layer beneath the painting and any overlap of different paint layers. This makes it difficult to classify the pigments used. However, as rFTIR and Raman spectroscopy detect mainly the materials present in the surface layer, the combination of all three methods helps to distinguish the data in the evaluation process.

[21] Lee, Otieno-Alego, and Creagh 2008; Bicchieri et al. 2009; Lee, Otieno-Alego, and Creagh 2005.

[22] Bicchieri et al. 2013.

[23] Roosen-Runge 1988; Thompson 1956.

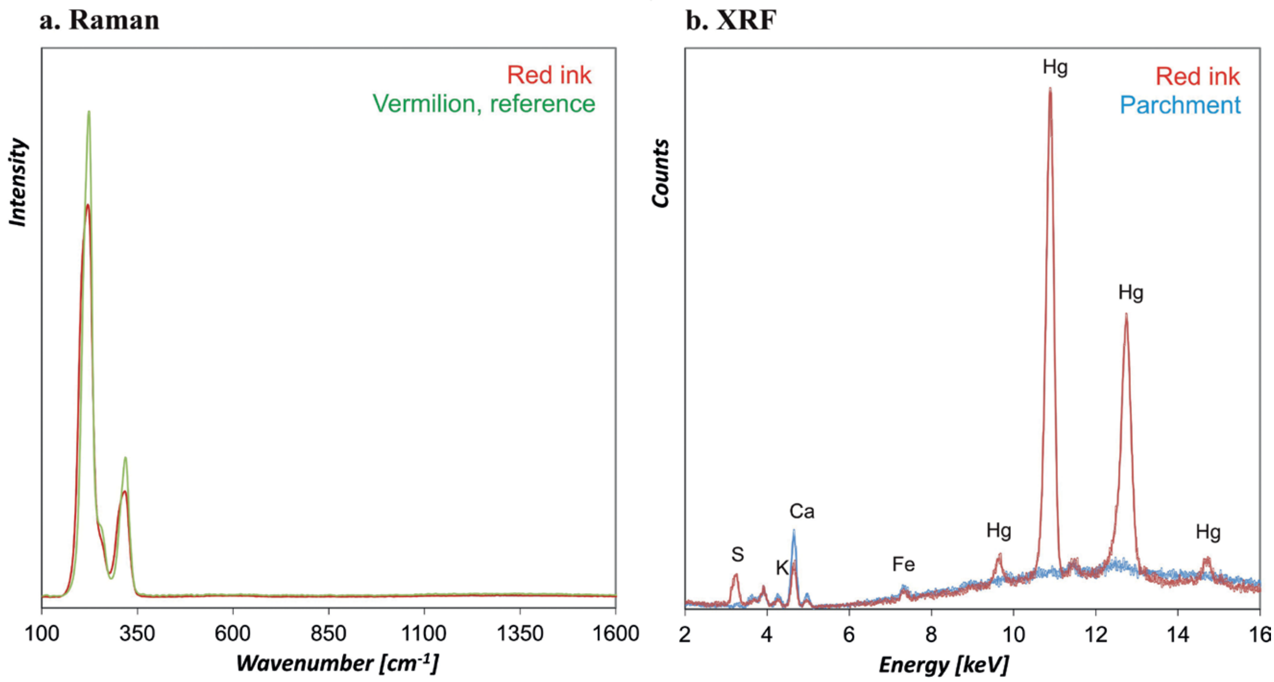


Fig. 3: Results of the measurements of the red ink of Cod. Vind. slav. 8. Vermilion was identified with two methods. a) Raman spectrum of P16/17 on fol. 74v for the red ink (red) together with the reference for vermilion (green); b) XRF spectrum of P3 on fol. 104r for the red ink (red) where S and Hg were detected, in comparison with the parchment P1.

A detail of the miniature painting of Cod. Vind. slav. 8 with the measured areas is depicted in Fig. 5. Lead (Pb) was detected with XRF in almost all measurement points of this miniature painting. rFTIR spectroscopy proved that lead white was used in several parts (e.g. P4 and P5) to brighten the color (Fig. 6). Fine white lines, such as in the grey or orange areas, were identified in P6 and P7 as lead white, as well. In addition, rFTIR revealed that a natural gum was used as binding medium. Particularly in P4, a strong signal from a natural gum was obtained (Fig. 6). The characteristic absorptions of the polysaccharides are around 3400 cm^{-1} (O–H stretching vibrations) and between 1160 and 1000 cm^{-1} (C–O stretching)[24] and match the reference spectrum of acacia gum in the IRUG database (ICB00084). Moreover, in most of the colored areas (P3-8), lime soaps (e.g. calcium stearate) were also detected. It remains unclear where these materials derive from; one explanation might be that soap was added as a wetting agent, which formed lime soaps with Ca^{2+} from water or calcium carbonate ($CaCO_3$) on the parchment. The bands for calcium stearate are clear, minor additives cannot be excluded.

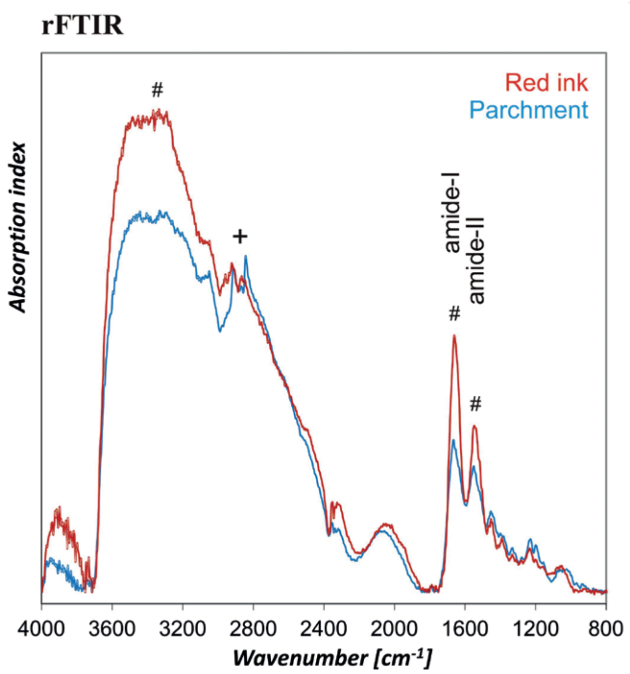


Fig. 4: Comparison of the rFTIR spectrum from the red ink in P5 on fol. 90r of Cod. Vind. slav. 8 with the corresponding parchment of P1. The proteinaceous compound in the red ink showed partially stronger bands (#) than the parchment and differing C-H vibrations were observed (+).

[24] Socrates 2001.

Fig. 5: Detail of the miniature painting on fol. 74v of the Cod. Vind. slav. 8.

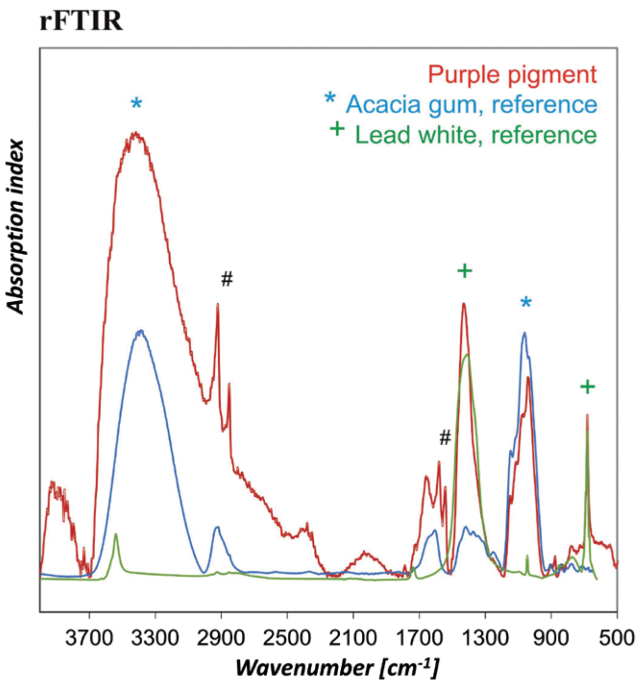


Fig. 6: rFTIR spectrum of P4 (red) in comparison with reference spectra of lead white (green) and acacia gum (blue). Additionally, bands of calcium stearate are labeled with #.

For the gilding in the miniature, XRF measurements proved the application of gold (Au) in P2 and P11. In areas where leaf gold was peeled off, rFTIR identified gypsum as a ground layer for gilding (a detail of such an area can be seen in Fig. 7). However, no binding medium for applying gold was detected.

For the measurement point (P3) in the blue area, the XRF analysis showed a large amount of copper (Cu) together with lead (Pb) and a low intensity of manganese (Mn) and iron (Fe). FTIR spectroscopy verified azurite, mixed with small amounts of calcium carbonate and calcium stearate. A spectrum of this area is presented in Fig. 8. The bands recorded for natural gum were much weaker than in P4 (Fig. 6).

Identification of the purple pigment (P4) turned out to be difficult, but during this measuring campaign it was not possible to use other methods than the mentioned. XRF detected low amounts of copper (Cu) and lead (Pb). rFTIR proved the application of lead white, whereas no azurite was registered (Fig. 6). However, calcium stearate and some calcium carbonate were detected. Raman spectroscopy did not identify any inorganic or organic pigment, either, but due to the results obtained by XRF and the technology used for purple colors,[25] a mixture of a red lake pigment (e.g. madder or kermes) with azurite can be assumed. A natural gum was used as binding medium, as shown in Fig. 6. For P9 in the dark purple area of the background, no FTIR reference for a pigment was found, either; the binding medium here was gum, as well.

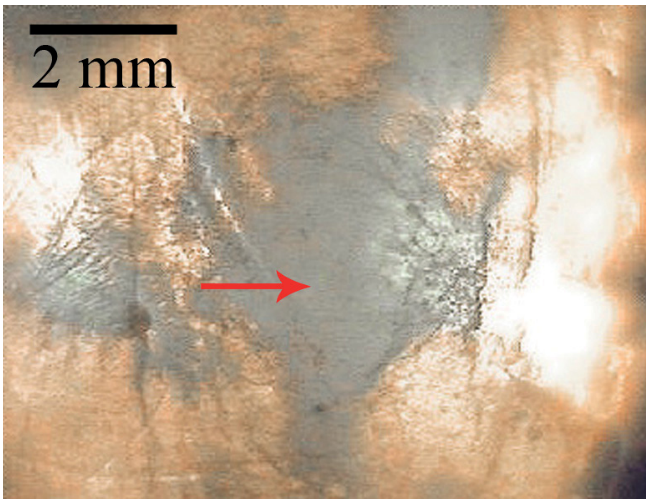


Fig. 7: Detail of the gilded area in P11 on fol. 74v of Cod. Vind. slav. 8. The red arrow marks the area where gypsum can be seen underneath the gold layer.

The green/blue pigment used for the cloak of the saint in P5 showed small amounts of iron (Fe), lead (Pb), and some copper (Cu). A mixture of green earth (iron silicate) with lead white and azurite or a copper-containing green pigment such as malachite or verdigris can be concluded from these results. However, these conclusions were not confirmed by rFTIR except for lead white. Additionally, calcium stearate, some calcium carbonate, and natural gum as binding medium

[25] Bicchieri 2014; Roosen-Runge 1988.

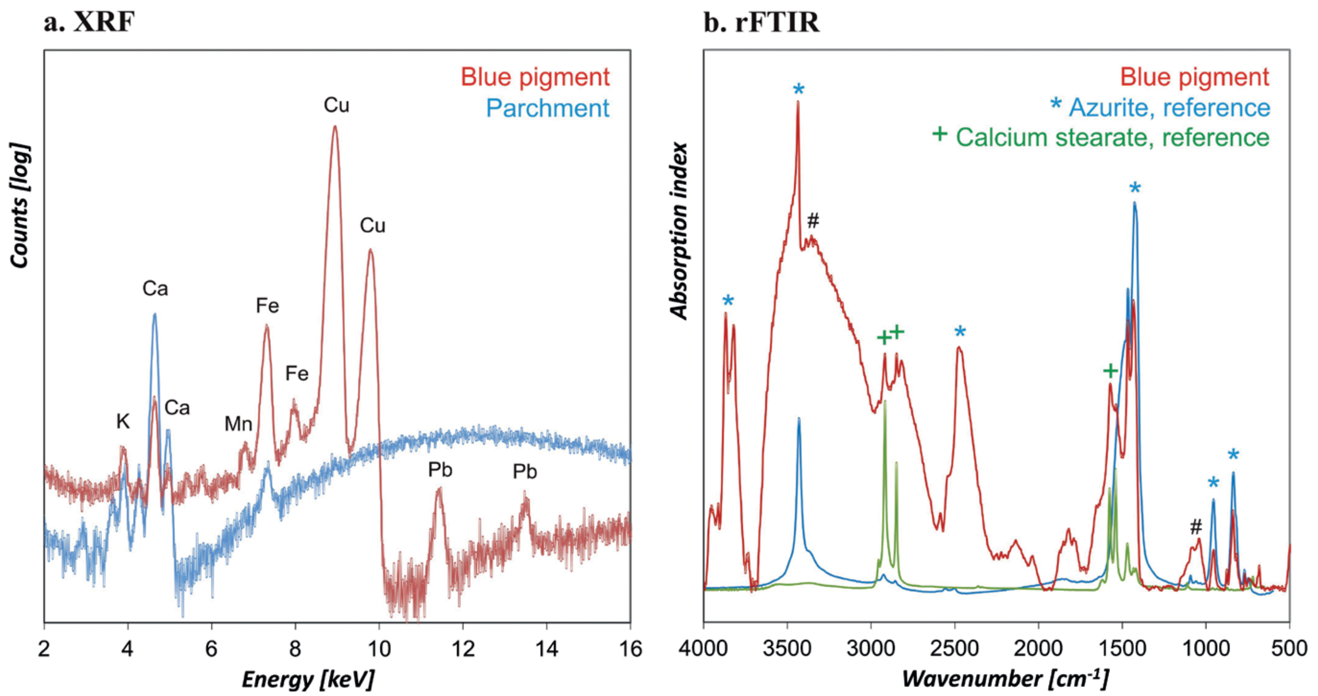


Fig. 8: Results of the measurements of the blue pigment in measurement point P3 on fol. 74v of Cod. Vind. slav. 8. a) XRF spectrum of the blue pigment (red) in comparison with the parchment P1 (blue), where Mn, Fe, and Cu were detected. b) rFTIR spectrum of P3 (red) together with the reference spectrum for azurite (blue) and calcium stearate (green). The characteristic bands for natural gums are labeled with #.

were detected. Raman spectroscopy could not identify any pigment.

The XRF results for the grey paint (P6) show small amounts of iron (Fe), copper (Cu), and lead (Pb). Lead can be associated with lead white, whereas the results of rFTIR do not correlate the copper with any specific compound. Calcium carbonate, calcium stearate, and natural gum as binding medium were identified by rFTIR. The Raman spectra of P6 and P15 did not match any reference in the grey area. Usually, grey paint is based on carbon black, which was not proven by Raman spectroscopy; possibly too little of it is present in this case.

The orange pigment in P7, P8, und P13 was identified with Raman analysis as minium (red lead), presented in Fig. 9. XRF measurements detected copper (Cu) and lead (Pb), whereas the copper most likely derives from a layer underneath. rFTIR spectroscopy proved the application of lead white, calcium carbonate, and calcium stearate. The binding medium was natural gum.

Summarizing the results obtained by XRF, rFTIR, and Raman spectroscopy measurements in the Cod.Vind. slav. 8, we can state that

- in general, only small amounts of calcium carbonate were identified; they were applied during the preparation of the parchment. Exceptions are the three folia: fol. 5r, fol. 6v, and fol. Ir*, where greater quantities were determined;
- for most of the areas measured with rFTIR in the parchment, a broader amide I than in the reference data was observed, which implies oxidative degradation of the parchment;
- different results for black inks were observed: for fols 1v up to 104r, the ink of the script contains iron (Fe) and copper (Cu), as well as small amounts of zinc (Zn). For fols 174r up to 270r, only iron (Fe) and copper (Cu) were identified in the text ink. For the text added in the margins of some pages (e.g. fol. 6v P3 or fol. 269v P2), an ink with iron (Fe) only was used. This leads to the conclusion that, for this codex, three different ink materials were used, which were clearly identified as iron gall ink by Raman spectroscopy;
- for the black color in the margins in the miniature painting, carbon black was applied, as confirmed by Raman spectroscopy;
- in the text ink areas, calcium oxalate was detected by rFTIR, probably indicating fungal degradation;

- the red ink of the script and the initials contains mercury (Hg) as well as sulfur (S) and was identified as vermilion, which was proven by Raman spectroscopy. A proteinaceous binding medium was detected by rFTIR;
- the orange pigment in the miniature painting is minium;
- yellow ink was identified as orpiment (fols 4r, 90r, 97v);
- lead white was applied mainly as an addition to brighten the colors;
- for the blue areas azurite was identified by XRF as well as rFTIR;
- kaolinite was used as an extender in brown and red pigments present in the miniature paintings on fol. 84r (brown in P2) and fol. 158v (brown in P7/8 and red in P6/10/12);
- for the green areas, probably a mixture of green earth and a pigment containing copper, such as malachite or verdigris, can be assumed from the XRF results, whereas the purple pigment in such areas could not be identified at all;
- natural gum was used as a binding medium for the pigments (paints).

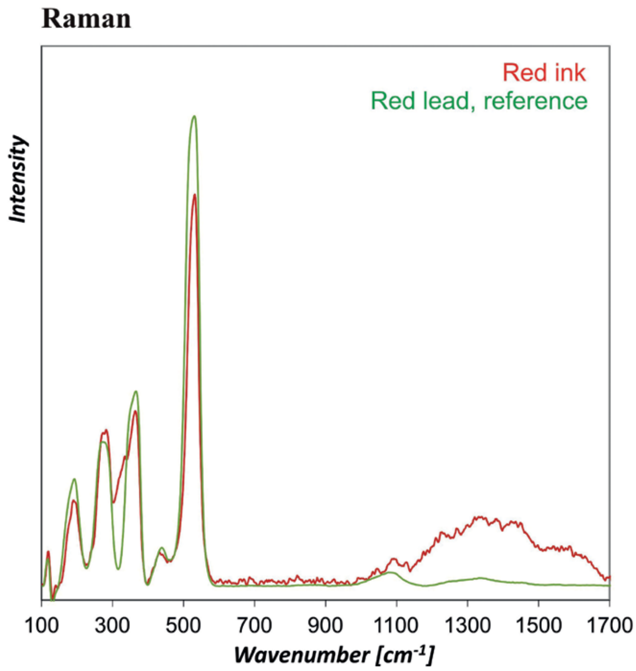


Fig. 9: Results of the Raman measurement performed on the red pigment in measurement point P7 on fol. 74v of Cod. Vind. slav. 8. The spectrum of P7 (red) shows a perfect match with the reference spectrum for red lead (green).

4. Codex Vindobonensis theologicus graecus 209, fol. 24v

Cod. theol. gr. 209 is a twelfth-century Greek manuscript in the Austrian National Library containing Greek palimpsests from the ninth and eleventh centuries.[26] From this manuscript, 15 folios were analyzed. Most of them are palimpsests, where a text underneath the upper script is visible. No colored illuminations can be found in this codex, and only a few decorations in black ink are present. But in a few cases, the underlying text shows small decorations carried out with red material.

Analytical measurements with XRF (by instrument Spectro xSort), Raman, and rFTIR were carried out to identify the ink used for the upper script and the undertexts. As an example, the results obtained for fol. 24v, shown in Fig. 10 with the analyzed points, are discussed: one point in the parchment, two in areas with black ink, two with red

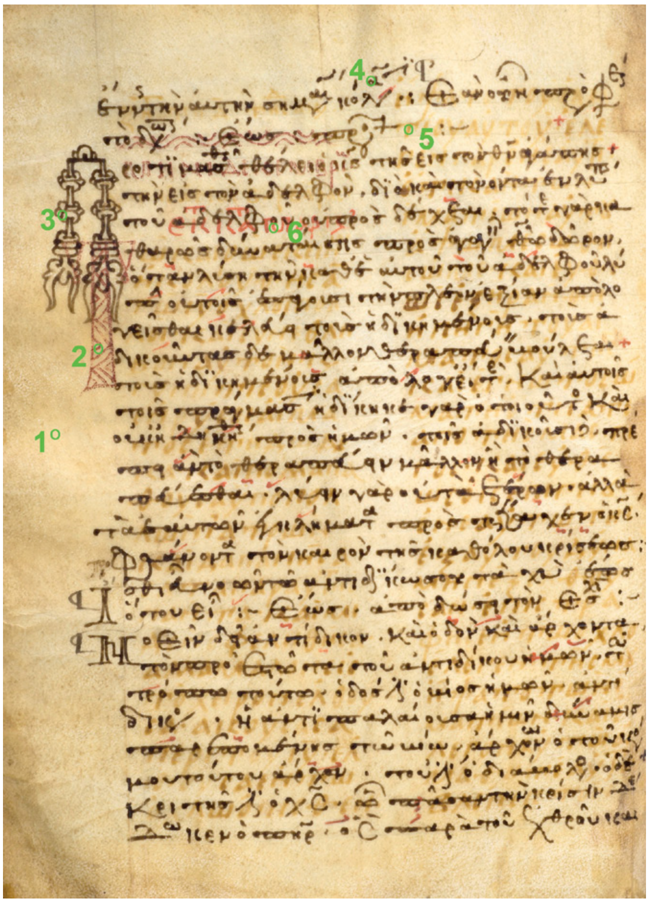


Fig. 10: Fol. 24v of the Cod. Vind. theol. gr. 209 with the selected measurement points.

[26] Analysed within the Austrian Academy palimpsest project, see <http://www.oeaw.ac.at/imafo/die-abteilungen/byzanzforschung/language-text-script/buchkultur/griechische-palimpseste/fruehere-palimpsestprojekte/> (last accessed 15 April 2018). Cf. also <http://hrsm.caa.tuwien.ac.at/links/ and the description on http://bilder.manuscripta-mediaevalia.de/hs//katalogseiten/HSK0785_b0033_jpg.htm> (last accessed 15 April 2018).

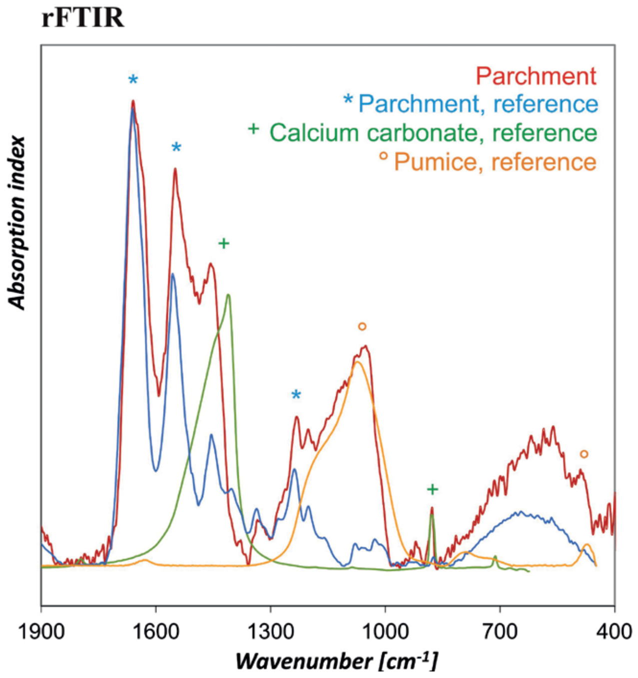


Fig. 11: rFTIR spectrum of the parchment (P1) in fol. 24[v] of Cod. Vind. theol. gr. 209. The spectrum of P1 (red) is shown in comparison with the reference spectra of freshly prepared parchment (blue), calcium carbonate (green), and pumice (orange).

inks, and one in the (major) palimpsest deriving from the ninth century.

The XRF measurement of the parchment (P1) yielded the elements phosphorus (P), sulfur (S), and chlorine (Cl), as well as potassium (K). These constituents were detected in all folios of this manuscript. Additionally, rFTIR identified calcium carbonate and silicate (pumice) on each folio (Fig. 11), while in some folios oxidative degradation of the parchment was also detected, as described already in chapter 3.

XRF analysis of the upper script ink (P3 and P4) revealed calcium (Ca) and iron (Fe), as shown in Fig. 12. This is an indication of iron gall ink, which was proven by Raman spectroscopy in other folios (fol. 2[r], fol. 3[r], and fol. 17[r]). The ink materials could not be identified by rFTIR, except for calcium oxalate (in a much greater amount in P3 than in P4).

The XRF analysis of the palimpsest ink (P2) did not yield any differences from the spectra obtained for the parchment. Similar results were observed with rFTIR spectroscopy. The IR spectrum is similar to those of the parchment. However, as already discussed in chapter 3, calcium oxalate was also detected in the ink of the undertext. Raman investigations clearly identified iron gall ink in the ink of the undertext of various folia.

In the undertext of fol. 24[v], also two different red ink materials can be seen, which can be easily distinguished by their hue. In the dark red area (P2), iron (Fe) and small amounts of lead (Pb) were detected by XRF. rFTIR provided indications of the use of an iron oxide pigment. The spectrum showed two bands with maxima at 570 and 480 cm^{-1} similar to the reference spectrum of iron(III) oxide-hydroxide in the Hummel database (HIP31376). Additionally, calcium carbonate and silicate were identified. In the bright red area (P6), mercury (Hg) and lead (Pb) were registered with a large amount of lead (Pb). As only small amounts of the lead white were identified by rFTIR, a mixture with red lead (minium) with vermilion must be assumed.

Table 1: Summary of all results for the points of interest on fol. 24[v] of Cod. Vind. theol. gr. 209.

P	Measurement point	XRF results*	Interpretation (XRF, rFTIR, Raman)
1	parchment in the middle	P, S, Cl, K	parchment with calcium carbonate and silicate (pumice)
2	red ink (dark) undertext	Fe, Pb	iron (III) oxide-hydroxide (weak rFTIR signal), calcium carbonate and silicate, calcium stearate, no lead white, but red lead mixed with vermilion
3	black ink decoration upper text	Ca, Fe	iron gall ink (fol. 17[v] P2), high amount of calcium oxalate, calcium carbonate and silicate
4	black ink, upper text	Ca, (Hg, Pb)	iron gall ink (fol. 17[v] P4), calcium oxalate, calcium carbonate and silicate
5	palimpsest right column	no difference	iron gall ink (fol. 17[v] P5), calcium oxalate
6	red ink (bright) undertext	Hg, Pb	vermilion, few lead white, minium (red lead), binding medium – could not be identified

* For XRF results only elements with higher amounts than in the parchment detected as well as additional elements are considered.

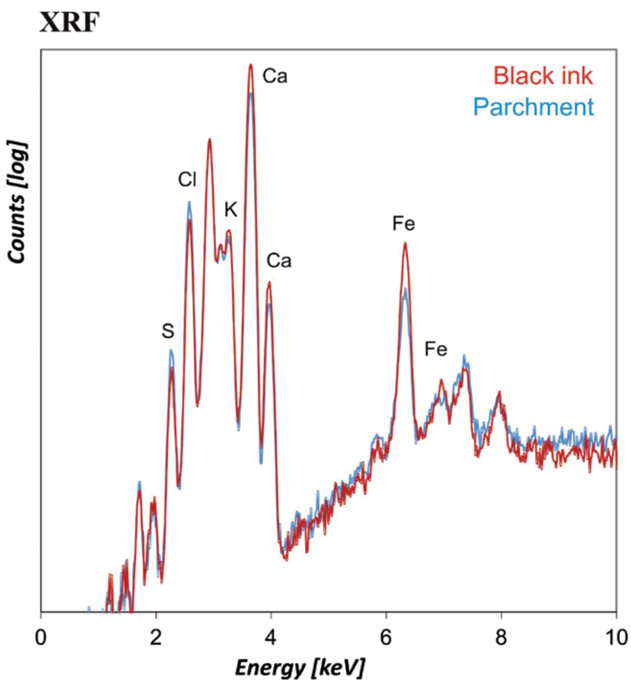


Fig. 12: Results of the XRF measurement of the black ink in measurement point P3 on fol. 24v of Cod. Vind. theol. gr. 209. The spectrum of ink (red) is shown in comparison to the parchment (blue), where Fe was also registered.

XRF, rFTIR, and Raman spectroscopy were used to analyze a representative number of folios of the Cod. theol. gr. 209 from the Austrian National Library. This codex shows no colored decorations, but an older palimpsest layer shows two different red ink materials used in addition to the black ink of the underlying text. Various black inks were used for the overtext, as the XRF measurements revealed small differences in the elemental composition. In general,

- in the parchment, calcium carbonate and silicate (pumice) were detected in varying amounts, depending on the folio;
- in some folia, rFTIR registered oxidative degradation of the parchment;
- the ink of the overtext contains calcium (Ca) and iron (Fe), in some points additionally potassium (K) and copper (Cu), and was identified as iron gall ink by Raman spectroscopy;
- in most areas of the ink, calcium oxalate was detected, probably indicating degradation by mold fungi;
- it should be mentioned that rFTIR detected no calcium oxalate in the ink containing iron (Fe) and small amounts of copper (Cu);
- the XRF spectra of the (brown) ink of the undertext reveal no significant differences from those of the parchment. In a few cases, small amounts of iron (Fe) and calcium (Ca) were detected, but more generally no clear indication of iron gall ink was found, except in P5 on fol. 17v, where iron gall ink was definitely identified by Raman;
- the dark red ink in the decoration of the undertext was proven to be iron(III) oxide-hydroxide in a mixture with minium (red lead), whereas
- vermilion mixed with lead white and minium was used for the bright red ink.

5. Conclusion

A variety of manuscripts from the Austrian National Library, dating from the ninth to the fourteenth century, were investigated non-invasively by XRF, rFTIR, and Raman spectroscopy; one Slavic and one Greek codex were chosen for this publication. The combined use of the three methods allowed the characterization of the parchment's different manufacturing qualities and degree of degradation, as well as of various black/brown text inks and red inks in the decorations. In the case of black/brown inks, oxalates were frequently detected, which indicate degradation by mold fungi. It was further possible to identify typical pigments in illuminations (lead white, azurite, orpiment, red lead, vermilion, red iron oxides, and carbon black), as well as extenders (kaolinite) and binding media (natural gums and proteinaceous material). Moreover, the confirmation of the material used underneath the metal coatings indicated a layer containing gypsum as a support for gilded areas.

Each method showed particular strengths and weaknesses, and only the joint evaluation of the data sets yielded comprehensive results. In particular, XRF provided important information about the elemental composition, which was important for the evaluation of rFTIR and Raman spectra and allowed us to identify several inorganic pigments. The main drawbacks of XRF are its lack of compound-specific information and its inability to identify organic materials. The verso side of analyzed folios also contributes to the signal. In contrast, the rFTIR signal derives mainly from the uppermost surface. Although rFTIR enabled the identification of various inorganic materials, the method does not permit the detection of important metal oxide and sulfide pigments, such as vermilion, red lead, and orpiment. Furthermore, no indication of iron gall ink components was found in the manuscripts, although it was found in mockup samples. This might be due to a low concentration of the colored materials in the ink, as a lack of sensitivity was also observed in measurement points with light color shades in illuminations. However, rFTIR was the only method able to identify binding media and compounds such as calcium oxalate and calcium stearate. It turned out that only Raman spectroscopy permits a clear identification of iron gall ink.[27] This method further provided compound-specific information in the case of orpiment and red lead, where XRF yielded only equivocal results. On the other hand, the experimental setting did not enable the detection of binding media.

ACKNOWLEDGEMENTS

This work was accomplished in the framework of CIMA, an interuniversity research institution with an interdisciplinary approach to the investigation of cultural heritage. The authors are grateful to their partners in the project, especially to Heinz Miklas, Robert Sablatnig, and Fabian Hollaus.

This research could not have been performed without the support of the colleagues in the Austrian National Library (ÖNB), especially Prof. Dr Ernst Gamillscheg and Dr Katharina Kaska, Department of Manuscripts and Rare Books.

[27] Vandenabeele, Edwards, and Moens 2007.

REFERENCES

Bicchieri, M. (2014), 'The purple Codex Rossanensis: Spectroscopic characterisation and first evidence of the use of the elderberry lake in a sixth century manuscript', *Environmental Science and Pollution Research International*, 21.24: 14146–57. <doi: 10.1007/s11356-014-3341-6>.

——, M. Monti, G. Piantanida, and A. Sodo (2009), 'All that is Iron-ink is not always Iron-gall!', *Raman Spectroscopy*, 39: 1074–1078.

——, ——, ——, and —— (2013), 'Non-destructive spectroscopic investigation on historic Yemenite scriptorial fragments: Evidence of different degradation and recipes for iron tannic inks', *Analytical and Bioanalytical Chemistry,* 405.8: 2713–21.

Bruni, S., S. Caglio, V. Guglielmi, and G. Poldi (2008), 'The joined use of n.i. spectroscopic analyses – FTIR, Raman, visible reflectance spectrometry and EDXRF – to study drawings and illuminated manuscripts', *Applied Physics*, A 92: 103–108.

Camba, A., M. Gau, F. Hollaus, S. Fiel, and R. Sablatnig (2014), 'Multispectral imaging, image enhancement, and automated writer identification in historical manuscripts', *Manuscript Cultures*, 7: 83–91.

Chalmers, J. M., H. G. M. Edwards, and M. D. Hargreaves (eds) (2012), *Infrared and Raman Spectroscopy in Forensic Science* (Oxford: Wiley Blackwell).

Derrick, M. (1991), 'Evaluation of the State of Degradation of Dead Sea Scroll Samples Using FT-IR Spectroscopy', *The Book and Paper Group Annual*, 10.

——, D. Stulik, and J. M. Landry (1999), *Infrared Spectroscopy* in *Conservation Science* (Los Angeles: The Getty Conservation Institute).

Desnica, V., and Schreiner, M. (2006), 'A LabVIEW-controlled portable x-ray fluorescence spectrometer for the analysis of art objects', *X-Ray Spectrometry*, 35: 280–286.

Doherty, B., A. Daveri, C. Clementi, A. Romani, S. Bioletti, B. Brunetti, A. Sgamellotti, and C. Miliani (2013), 'The Book of Kells: A non-invasive MOLAB investigation by complementary spectroscopic techniques', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 11.5: 330–336.

Fuchs, R., C. Meinert, and J. Schrempf (2001) (eds), *Pergament: Geschichte – Material – Konservierung – Restaurierung*, vol. 12 (Munich: Anton Siegl).

Griffiths, P. R., J. A. de Haseth (2007), *Fourier Transform Infrared Spectrometry*, edited by Winefordner, J. D., 2nd edition (Hoboken, NJ: John Wiley & Sons).

Hahn, O. (2010), 'Analyses of Iron Gall and Carbon Inks by Means of X-ray Fluorescence Analysis: A Non-Destructive Approach in the Field of Archaeometry and Conservation Science', *Restaurator*, 31.1: 41–64.

Lee, A. S., P. J. Mahon, and D. C. Creagh (2005), 'Raman Analysis of Iron gall Inks on Parchment', *Vibrational Spectroscopy*, 41: 170–175.

——, V. Otieno-Alego, and D. C. Creagh (2008), 'Identification of Iron-gall Inks with Near-Infrared Raman Microspectroscopy', *Raman Spectroscopy*, 39: 1079–1084.

Miliani, C., D. Domenici, C. Clementi, F. Presciutti, F. Rosi, D. Buti, A. Romani, L. Laurencich Minelli, and A. Sgamellotti (2012), 'Colouring materials of pre-Columbian codices: Non-invasive in situ spectroscopic analysis of the Codex Cospi', *Journal of Archaeological Science*, 39: 672–679.

Pessanha, S., M. Manso, and M. L. Carvalho (2012), 'Application of spectroscopic techniques to the study of illuminated manuscripts: A survey', *Spectrochimica Acta Part B*, 71–72: 54–61.

Roosen-Runge, H. (1988), *Reclams Handbuch der künstlerischen Techniken: Buchmalerei* (Stuttgart: Reclam).

Socrates, G. (2001), *Infrared and Raman Characteristic Group Frequencies* (Chichester: John Wiley & Sons), 122.

Strlic, M., I. Kralj Cicic, I. Rabin, B. Pihlar, and M. Cassar (2009), 'Autooxidation of Lipids in Parchment', *Polymer Degradation and Stability*, 94: 886–890.

Thompson, D. V. (1956), *The Material and Techniques of Medieval Painting* (New York: Dover Publications).

Vandenabeele, P., H. G. M. Edwards, and L. Moens (2007), 'A decade of Raman spectroscopy in art and archaeology', *Chemical Reviews*, 107: 675.

PICTURE CREDITS

Figs 1, 5, and 10: © Computer Vision Lab (CVL), Vienna University of Technology, DI Fabian Hollaus.

Article

Palaeography and X-Ray Fluorescence Spectroscopy: Manuscript Production and Censorship of the Fifteenth Century German Manuscript Cod. germ. 1 of the Staats- und Universitätsbibliothek Hamburg

Marco Heiles, Ira Rabin, and Oliver Hahn | Aachen, Hamburg, Berlin

Abstract

The manuscript Codex germanicus 1 (Cod. germ. 1) of the Staats- und Universitätsbibliothek (State and University Library) Hamburg[1] is a fifteenth-century German-language manuscript. It comprises two codicological units and has an especially complex developmental history. To trace this developmental history, neglected until now in the research literature,[2] the manuscript was investigated, for the first time not solely with classical codicological and palaeographical methods, but also with the aid of X-ray fluorescence spectroscopy, in order to determine the composition of the writing materials. These methods made it possible, first, to support and check palaeographic findings and, second, to gain information about the stratigraphy of the manuscript where palaeographic methods find their limits – in regard to short entries, rubrications, and non-alphabetical signs.

The Manuscript

Cod. germ. 1 of the State and University Library Hamburg is a 214-page, German-language manuscript in folio format (here 29 × 20 cm). It can be dated to the 1450s and 1460s based on scribe entries (fol. 98^{vb}: 'Deo gratias 1463', fol. 211^{r}: 'Anno etc. liiijdo jm mayen' [=1454]) and the analysis of watermarks.[3]

The codex consists of two codicological units. The first (fols 1–108) is the joint product of five primary hands (see Table 1 and Table 2). One after the other over several years around 1463, they entered medical texts (Hand I: fols 1^{ra}– $47^{rb,}$ 51^{ra}–51^{va}, 62^{rb}–64^{vb}), household and garden recipes (Hand I: fols 47^{rb}–50^{vb}), wonder drug recipies, joke recipes, and damage recipes (Hand I: fols 51^{va}–57^{rb}), a lapidary (Hand I: fols 57^{va}–62^{ra}), paint and ink recipes (Hand III and Hand V: fols 65^{ra}–75^{ra}), an encyclopaedia (Hand VIII: fols 75^{va}–98^{vb}), and clerical maxims and prayers (Hand IX: fols 99^{ra}–100^{vb}). The last pages of this part remained empty. The second part (fols 109–214) is an older transcription, completed by 1454, of the cycle of stories of the *Sieben weise Meister* (*Seven Wise Masters*, fols 109^{r}–211^{r}) by yet another scribe (Hand XII). But this part was clearly damaged, for which reason another scribe (Hand XI) replaced it with the outermost bifolio of the first quire (fols 109/120) and the first folio of the last quire of this part (fol. 205). Since the scribe used a kind of paper that had already been used for the rear quires of the first part, it must be assumed that he or she worked together with the first part's scribes and was able to use the same stock of paper. The codex was thus probably bound for the first time when the first part was produced, around 1463. This cannot be maintained with absolute certainty, because the original binding was not preserved. The comparatively large number of writing hands

---

[1] Images of this manuscript can be found in Wikimedia Commons: <https://commons.wikimedia.org/wiki/Category:Hamburg,_Staats-_und_Universitätsbibliothek,_Cod._germ._1>. All research data of this project including the images will be published in the upcoming *Hamburg Open Science Repository*.

[2] On Cod. germ. 1, cf. so far: *Handschriftencensus: Eine Bestandsaufnahme der handschriftlichen Überlieferung deutschsprachiger Texte des Mittelalters* <http://handschriftencensus.de/4859>; Heiles 2018a, 244; Heiles 2018b; Heiles 2014; Ulmschneider 2011, 124–127; Brévart 2008, 37, n. 116; Di Venosa 2005, 40; Gottschall and Steer 1994, 13* (No. 24); Gerdes 1992, 1186; Gottschall, 1992, 95–102; Weißer 1987, 916; Weißer 1982, 47, 125, 436; Fechter 1935, 97–98; Henrici 1911; Schorbach 1894, 42–43 (no. 23); Paschke 1891, 7–8; Lambel 1877, III; Lappenberg 1834, col. 99–100; Petersen *c.* 1830; *Catalogus Manuscriptorum Codicum Bibliothecae Uffenbachianae*, 1747, 218; *Bibliothecae Vffenbachianae Universalis, Tomus III*, 1730, 554, no. LXXXV.

[3] A detailed description of the manuscript Cod. germ. 1 by Marco Heiles will soon be publishes in *Manuscripta Medievalia* <http://www.manuscripta-mediaevalia.de/dokumente/html/obj31593540>.

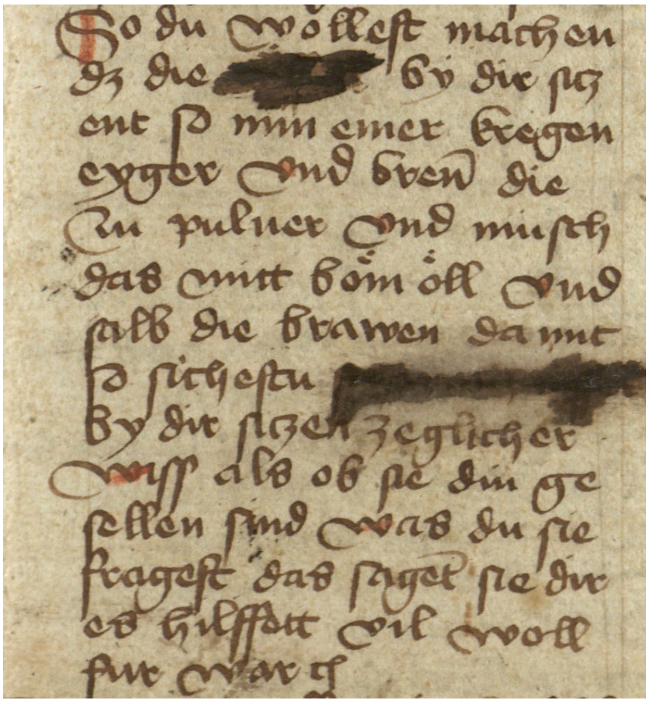


Fig. 1: Excerpt from fol. 57^{ra}.

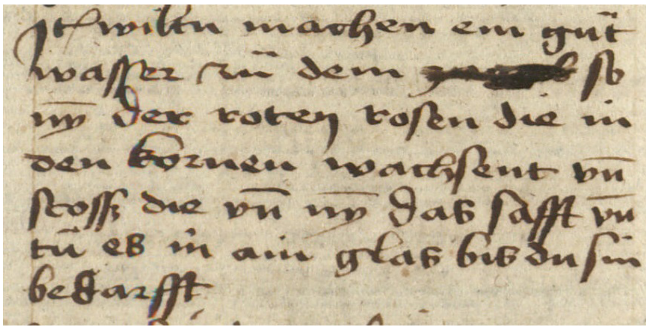


Fig. 2: Excerpt from fol. 64^{vb}.

acting rapidly one after the other, which are supplemented by text sections (fols 64^{v}, 75^{r}, 101^{r}, 211^{v}, 212^{r}) from six other hands, suggests that the manuscript comes from a cloister community. The dialectal character of the texts supports the assumption that the entire manuscript comes from the region of Swabia. Numerous subsequent supplements, remarks, and doodles in different handwritings in the margins and on empty pages show that the book was long (the date 1573 on fol. 1^{r}) and intensively used.

The thematic spectrum of the texts contained in the book makes it equally suited for religious instruction, as a reference work for medical problems, or as an entertaining reader. It includes a cookbook, instructions in caring for trees, and medical recipes; in the encyclopedia, it explains the Christian worldview and thereby touches upon both natural-scientific and especially pastoral questions; and it gathers prayers to the Virgin Mary in the collection of sayings. From the perspective of German philology, the manuscript deserves special attention because of the encyclopedia, extant only here. This is a compilation of the German *Lucidarius* with selected independent translation, found only in this manuscript, of the Latin *Elucidarium* of Honorius Augustodiensis.[4] Of media- and cultural-historical interest is the parallel transmission of the recipe collection of the first codicological unit in the manuscript Augsburg, Staats- und Stadtbibliothek, 2° Cod. 572. This text collection is substantially more extensive in the Augsburg manuscript. The scribe of the Cod. germ. 1 or the *Vorlage* he or she used consciously left out some recipes. This goes, on the one hand, for all the Latin texts, but also, on the other hand, for those in which magical signs (characters) and forms of blessings were used. Thus, not only characteristics of language but also and above all theological arguments played a role in the transmission.[5]

Question and method

Our primary interest in the Cod. germ. 1 was initially in two recipe texts in which individual words important in understanding the text were crossed out and thus censored.[6] The first text on fol. 57^{ra} – as the parallel transmission in Augsburg, Staats- und Stadtbibliothek, 2° Cod. 572 shows,[7] is a guide to summoning 'schwarcz tüfel' ('black devils') who can answer one's every question. Here, the words for 'devil' and 'black devil' (Fig. 1) were crossed out. The second censored text on fol. 64^{v} is a recipe for 'ein gut wasser czu dem zagel' that can be obtained from poppies.[8] Here, the word

[4] Ulmschneider 2011, 124–127; Gottschall 1992.

[5] A detailed examination remains to be performed. Examples are named by Heiles forthcoming.

[6] Cf. Heiles 2014.

[7] Augsburg, Staats- und Stadtbibliothek, 2° cod. 572, fols 94^{vb}–95^{ra}: '[S]o du wellest machen das die tewfel bey dir sitzen so nim einer kregen eyr vnd prene die zepulfer mit bång̊mol vnd salb die brawen da mit so sihest du schwarcz tüfel by dir siczen zu yglicher wis als ob es din gesellen sein vnd was du si fragest das selb sagent si dir.' Translation: 'If you want to make the devils sit with you, take the eggs of a crow and burn them to a powder and mix this with olive oil and anoint [your] brows with it. In this way, you will see black devils sitting with you, as if they were your friends. Whatever you ask them, they will tell you.'

[8] Hamburg, Staats- und Universitätsbibliothek, Cod. germ. 1, fol. 64^{v}: 'Item wiltu machen ein gut wasser czu dem [crossed out word: zagel], so nym der roten rosen, die in den kornen wachsent vnd stosß die vnd nym das safft

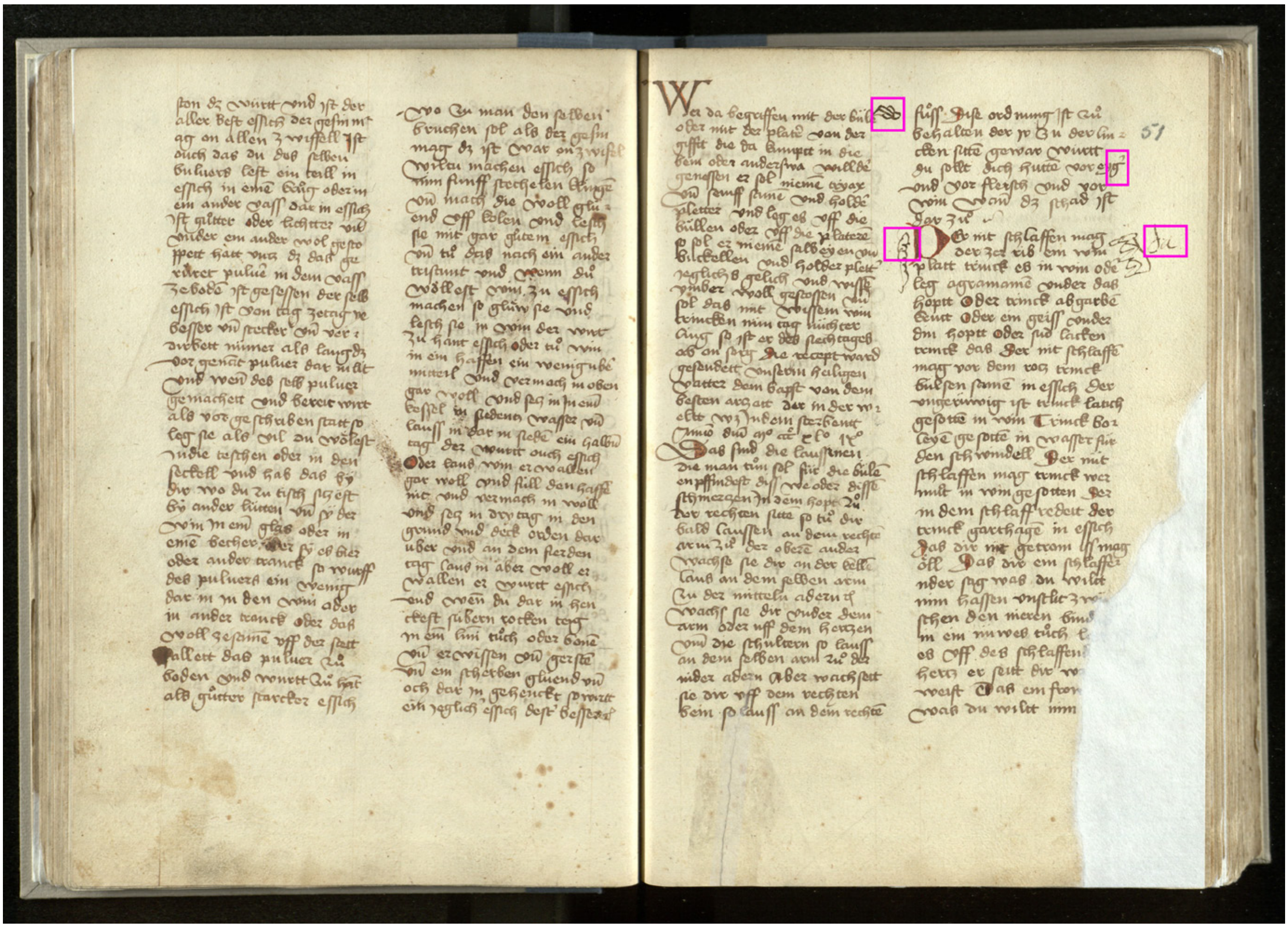


Fig. 3: Fols 50ᵛ–51ʳ with measuring points.

'zagel' was crossed out; it means tail, but also penis (Fig. 2). While the censorship in the first recipe aims to prevent sinful communication with the devil, which would be an infraction of the First Commandment, the second censorship aims at a speech taboo, possibly fueled by the feeling of shame. The aim of our materials-scientific investigation was to find out more about these processes of censorship. Who carried them out? Did the scribes of the texts correct themselves, or are the deletions by a later hand? Can the ink be attributed to the hand of another scribe or to a hand that made some of the additions and marginal entries? Or could this be a much more recent intervention in the text with a modern, industrially produced ink?

We wanted to answer these questions with the aid of an X-ray fluorescence spectroscopic examination of the inks and the red decorative inks. To this end, measurements had to be made of each of the palaeographically differentiated scribes' hands (Hands I–XIV) and of the most important entries in the margins. Of the latter, entries were chosen that permit dating or attribution to a specific person, for example the year date on fol. 1ʳ; the pen test on the same page, in which Duke Ulrich of Württemberg (1487–1550) is mentioned; and the entries of names on fols 20ʳ and 108ᵛ. In addition, we considered entries that supplemented or corrected the texts (fols 28ᵛ and 75ʳ) or that follow a recurrent pattern (pointing hand, cloud, 'da', double virgule (||) [Fig. 3]) (see Table 3). At the same time, we took the opportunity to conduct additional measurements of the red and green inks used, as well of as the inks that mark the writing space and the quire numbering, which should further illuminate the developmental history of the manuscript. A total of 48 measurement points were selected, whereby on each page one additional measurement point on unwritten paper had to be examined as a reference for the substrate. In taking the measurements, we had to make sure that the reverse side of the page was not written on at the point of measurement, because otherwise the inks

vnd tu es in ain glas bis du sin bedarfft.' Translation: 'If you want to make a good water for the [crossed out word: tail/penis], take red roses that grow in the grain and pestle them. And take the juice and put it in a glass until you need it.'

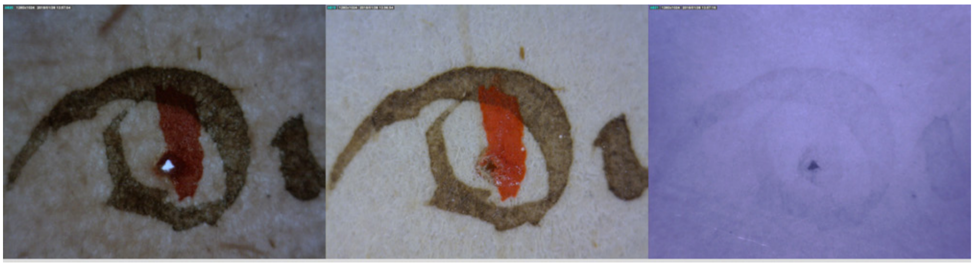


Fig. 4: Microphotographs of fol. 58va with transmitted, visible and near infrared light.

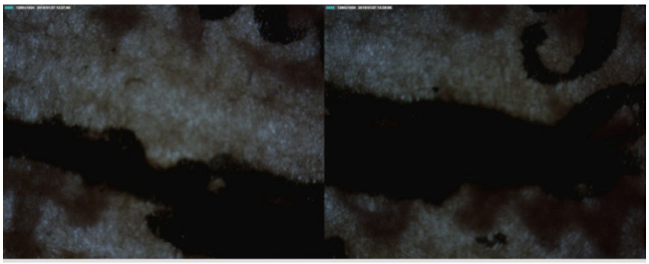


Fig. 5: Microphotographs of the censorship on fol. 64vb with transmitted light.

on the reverse side would contribute to the measurement result, thereby falsifying it. To ensure this, microphotographs of each measuring point were taken with transmitted light (Fig. 4). In the case of the second censored area on fol. 64vb, it thereby became clear that no reliable measurement could be made here, because the reverse side of the page, too, bears text in precisely this place (Fig. 5). The microphotographs and the X-ray fluorescence spectroscopic measurements were carried out on two working days in the manuscript laboratory of the Centre for the Study of Manuscript Cultures.[9]

The text of the Cod. Germ. 1 was written with iron gall inks. The red decorative inks contain mineral pigments like red lead and cinnabar. As also presented in the paper by Bosch et al. in this issue and confirmed by numerous contemporary recipes,[10] iron gall ink is produced by mixing iron vitriol (iron sulfate) with gallic acid and adding a binding medium (usually gum arabic) and a solvent (water).[11] The resulting ink is applied to the writing surface with a pen.

The iron vitriol was not produced artificially produced, but could have been quarried as a mineral in mines and purified. Despite this purification and depending on the deposit, it contains various impurities of other salts that contain, for example, copper (Cu), zinc (Zn), or manganese (Mn)[12]. Beyond that, sometimes other salts are mixed in to alter the characteristics of the ink.

A method that permits the determination of these traces or minor constituents and thereby to differentiate among iron gall inks is X-ray fluorescence analysis (XRF), which characterizes the elemental composition primarily of inorganic compounds. The examination consists of exposing the sample to X-rays, which interact with the material; the atoms thereby excited release their own characteristic radiation. With a suitable detector, the X-ray fluorescence is detected, providing information about the composition, since the energy of the X-rays emitted by each element is characteristic. The signal intensity permits conclusions about the amount of the element present. The method of 'fingerprints'[13] can be applied to the mineral components of the red decorative inks.

The black inks

Hands I, II, III, and IV, Addendum 01–13

We have presented the results of the examination of the black iron gall inks in a diagram showing the relative concentrations of zinc (Zn), copper (Cu), manganese (Mn), and potassium (K) in relation to iron (Fe) (Figs 6a–c). The first five measuring points already show that the selected method is suitable for our purposes. Not only do the values for the two subsequent entries on fol. 1r differ markedly from the ink used by Hand I, which has a very similar composition on fol. 2vb as a few pages later on fol. 15rb; the inks of the two subsequent hands also differ

[9] We thank the State and University Library Hamburg and the former head of the Manuscript Division Hans-Walter Stork (currently Director of the Erzbischöfliche Akademische Bibliothek Paderborn) for providing access to the manuscript.

[10] No such recipe is found in the collection of paint and ink recipes in the Cod. germ. 1, but it is found in several other fifteenth-century manuscripts. Christoph Krekel offers an overview of the 32 different recipes for iron gall ink in the *Liber illuministarum* (Munich, Bavarian State Library, Cgm 821) 2005, 631–636. Three different recipes for iron gall ink are transmitted in the recipe collection 'Was du verwen wilt von sîden oder zendel' in the manuscripts Salzburg, Universitätsbibl., Cod. M III 3 and Codex Berleburg, cf. with Edition: <https://www.arteslitteratur.de/wiki/Kategorie:Eisengallustinte>.

[11] Cf. Krekel 1999, 25–36, and Fuchs 1999.

[12] Hickel 1963.

[13] For further literature on determining the fingerprints of iron gall inks, see Malzer, Hahn, and Kanngießer 2004, and Hahn 2010.

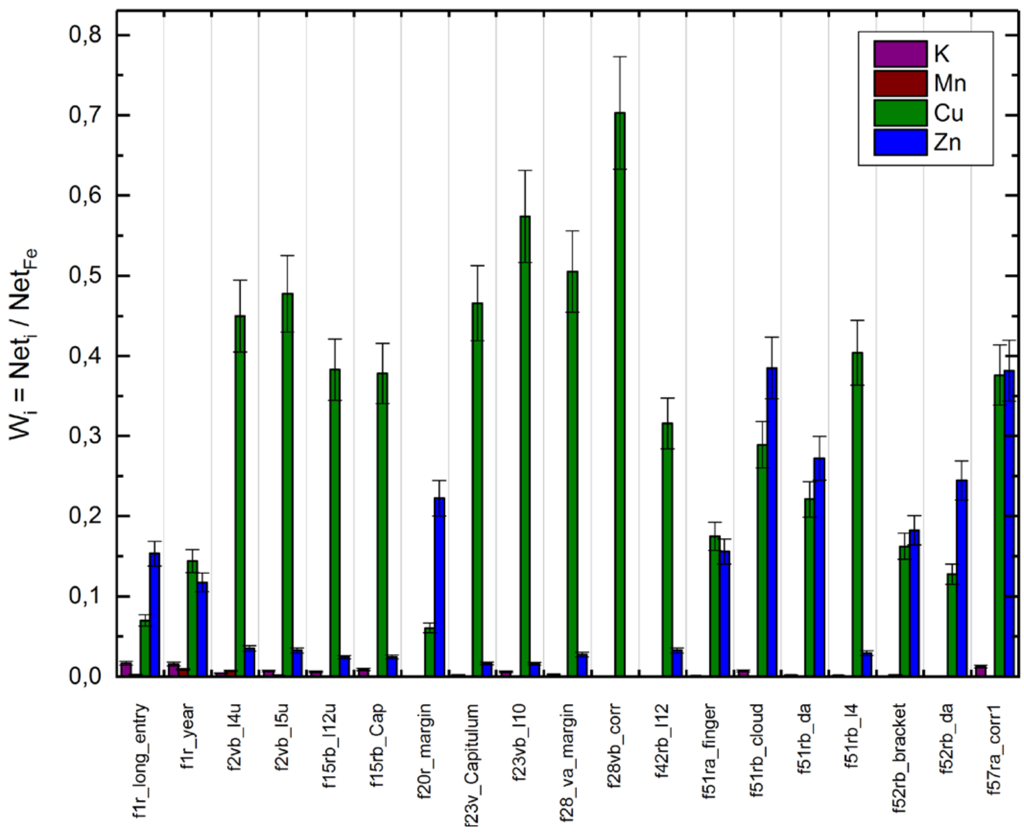


Fig. 6a: XRF investigation of the black inks. Fingerprint values W_i of different elements normalised to iron.

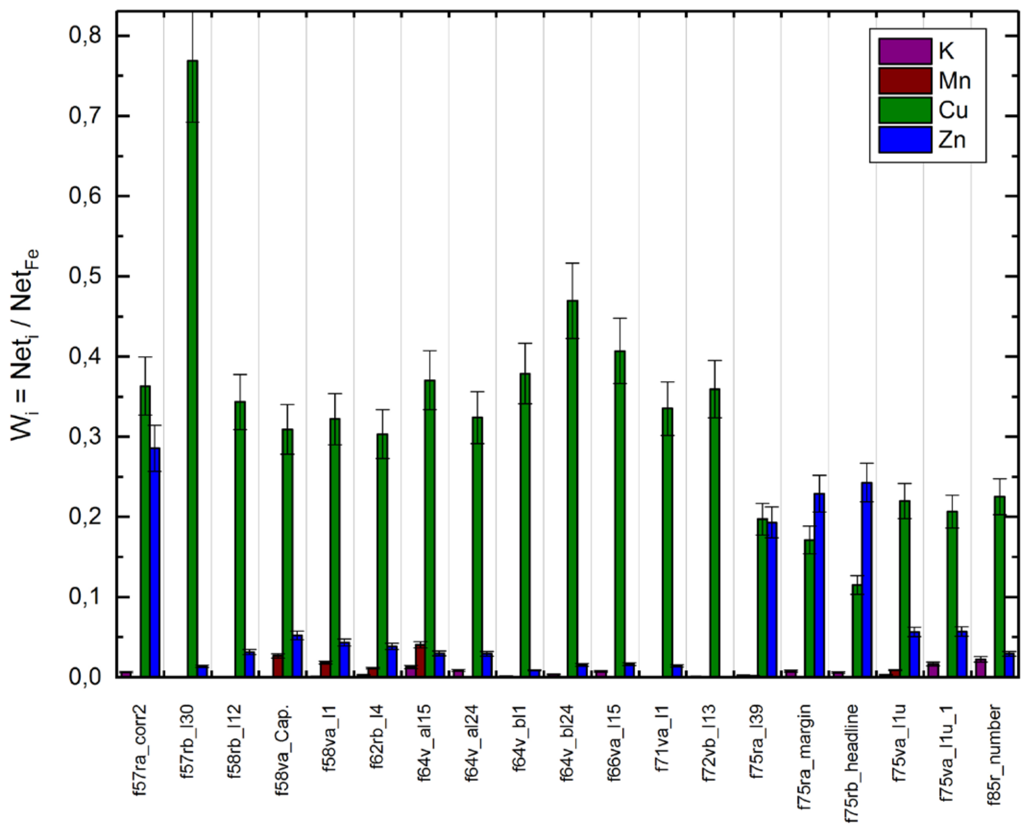


Fig. 6b: XRF investigation of the black inks. Fingerprint values W_i of different elements normalised to iron.

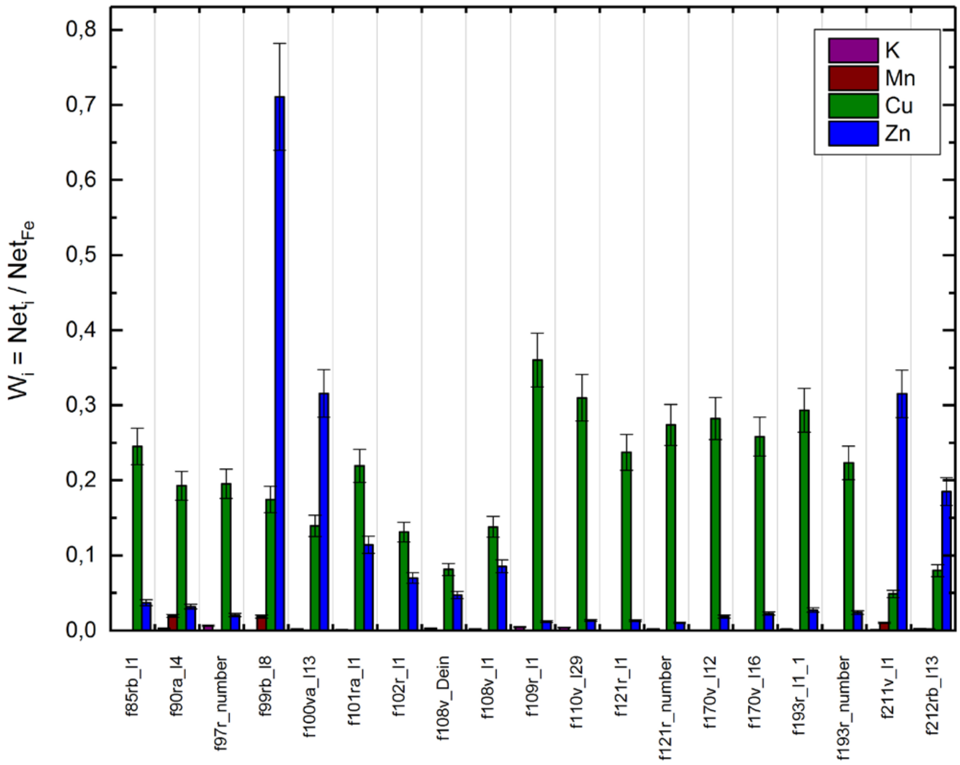


Fig. 6c: XRF investigation of the black inks. Fingerprint values W_i of different elements normalised to iron.

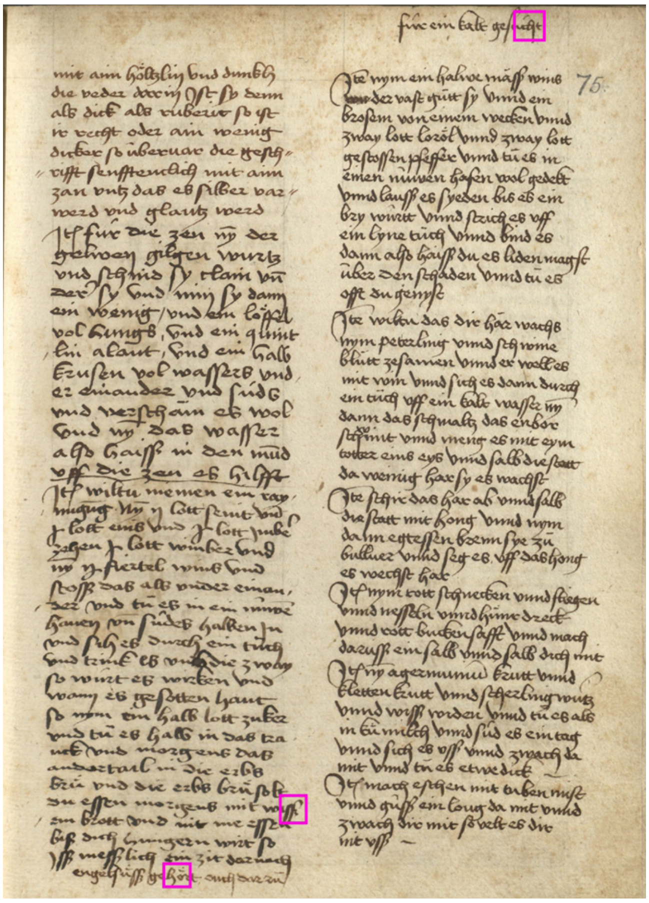


Fig. 7: Fol. 75ʳ with measuring points marked.

quite markedly from each other. The ink that Hand I used on the first pages is characterized by a quite high proportion of copper and a smaller but marked proportion of zinc. Hand I used this ink up to fol. 58ʳᵇ.[14] The double virgule (||) in the margin on fol. 23ᵛᵇ and the supplements in the margin on fol. 28ᵛᵃ were written with the same ink and are thus very probably from the same Hand I. This finding is interesting especially for the double virgule, which appears frequently in the manuscript and provides the occasion for a closer examination of this kind of paratext. The marginal name entry 'Johann' on fol. 20ʳ, the corrected strikeout on fol. 28ᵛᵇ, the index finger, the cloud, the note 'da' (there) on fol. 51ʳ (Fig. 3), and the bracket and 'da' on fol. 52ʳ, in contrast, were certainly not written or drawn with the ink that Hand I used, but by other, possibly as many as six different hands.[15] From fol. 58ᵛᵃ to fol. 64ᵛᵃ, we measured a different ink for Hand I, one that also contains a little manganese.[16] During the inscription of Volmar's *Steinbuch* ('lapidary'), the scribe apparently shifted inks with the turn of

[14] Cf. in Fig. 6a: f2vb_5u, f2vb_4u, f15rb_12u, f23vb_l10, f51rb_l4. Cf. in Fig. 6b: f57rb_l30.

[15] Cf. in Fig. 6a: f20r_margin, f28vb_corr, f51ra_finger, f51rb_cloud, 51rb_da, 52rb_bracket, f52rb_da.

[16] Cf. in Fig. 6b: f58va_l1, f62rb_l4, f64va_l15.

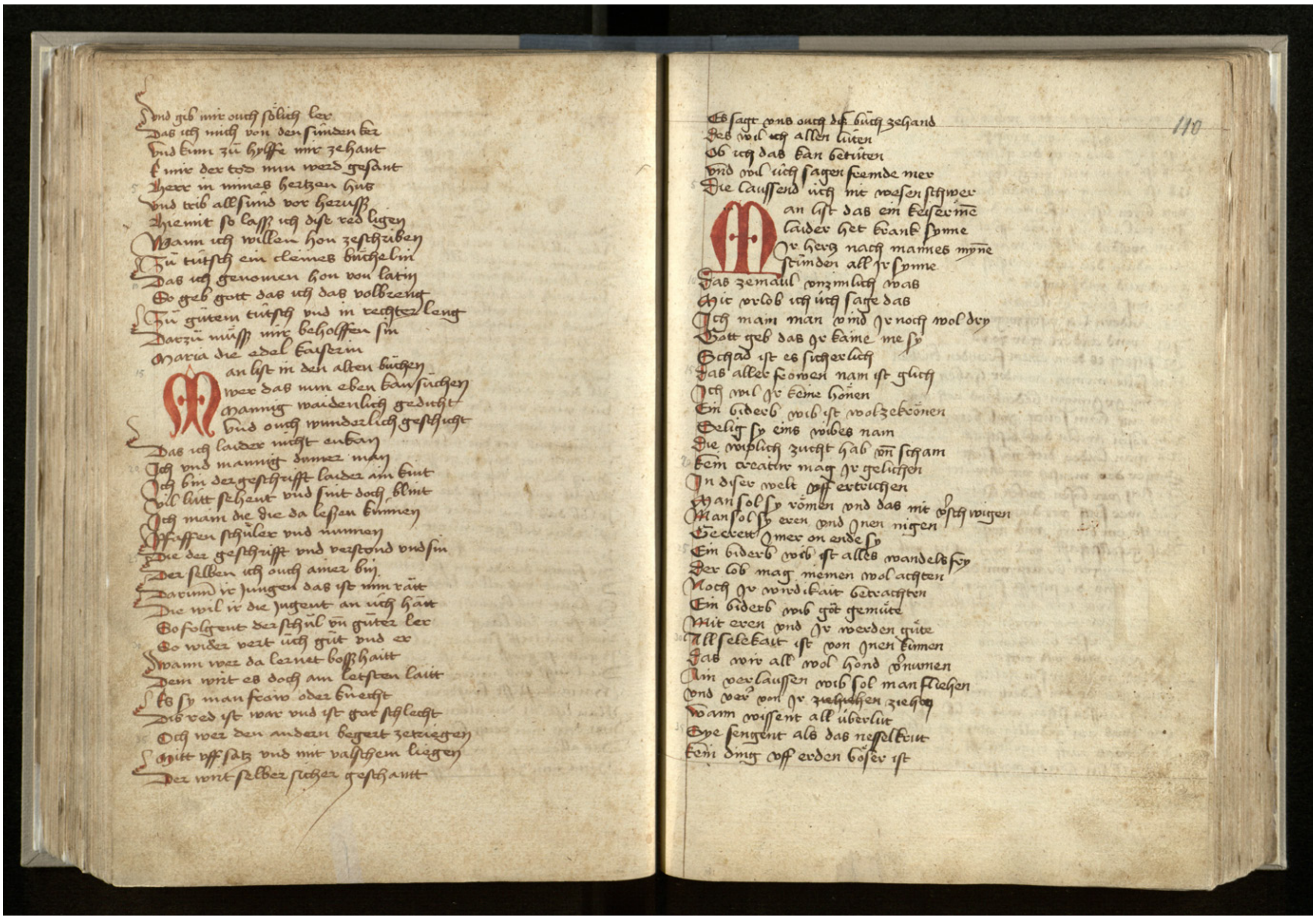


Fig. 8: Fols 109^{v}–110^{r}.

the page from fol. 58^{r} to fol. 58^{v}. This is not recognizable with the naked eye; nor are there palaeographic signs of a possible change in scribes. The *capitulum* sign placed next to the text on fol. 58^{v} was written with this ink containing manganese and thus very probably comes from Hand I like the preceding double virgule. On fol. 66^{va}, we measure for Hand I once again an ink resembling one of the first inks without manganese. Such an ink was also used for the subsequent entries by Hands II, III, and IV on fol. 64^{v}, and Hand III also writes the paint recipe on fol. 71^{va} with a comparable ink. It is possible that they all took recourse to the same stock of ink or the same raw materials to produce the ink.

Hand III and Hand V

The collection of paint and ink recipes of the Cod. germ. 1 extends across fols 71^{ra}–75^{ra} and can now be ascribed to two scribal hands. Hand III wrote the first part of the paint and ink recipes with an ink similar to that used by Hands I, II, and IV. The second part of the paint and ink recipes following fol. 72^{v}, in contrast, was written by Hand V with another ink containing only copper, but no zinc, manganese, or potassium. These clear differences in the composition of the inks helped specify the palaeographic distinctions between the hands. Hand III and Hand V have a very similar writing ductus and they form most letters in the same way. In addition, the change in scribes from fol. 72^{r} to fol. 72^{v} shows no difference in the text's content or in the layout. Only the few empty lines at the lower edge of the column fol. 72^{rb} initially indicate that a production step ended here; this was the reason for choosing the two measuring points f71va_l1 and f72vb_l13. When the results of the X-ray fluorescence spectroscopy indicated a possible change of scribes, it was possible to palaeographically determine this unambiguously. Hand V shows a broader and more right-leaning ductus than Hand III and fits fewer lines (35–38 as opposed to 41–45 lines) into the same writing space. The clearest differentiating trait, however, is the writing of the ſʒ ligatures: Hand III writes while Hand V writes (see also Table 1). There are also clear differences in the writing of the <d>: while Hand III writes twelve (of 47) <d> with a loop in column 71^{rb} alone; in more than ten

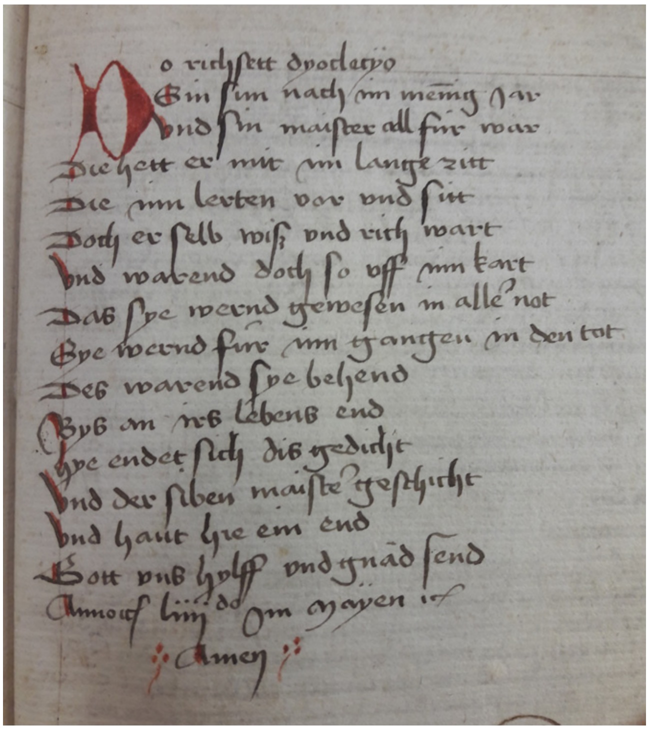


Fig. 9: Excerpt from fol. 211^{r}.

columns, we counted only eleven forms with a loop for Hand V.

Hand VI, VII, VIII, IX, X, and Addendum 14–17

On fol. 75, after the eight lines of Hand V's last ink recipe, Hands VI and VII used the rest of the space to enter more recipes, but this time medical ones. On this page, too, the composition of the inks clearly differs, and the marginal entry supplementing the content under the left column was written with a different ink (Fig. 7).[17] On the following page begins the text of the *Lucidarius-Elucidarius* compilation written by Hand VIII. The measured values of the ink or inks Hand VIII used on fols 75va, 85^{rb}, and 90ra all show comparably high proportions of zinc and copper.[18] In terms of the presence of small amounts of potassium and manganese, however, they differ. Here it is unclear where the intermittently appearing manganese and potassium impurities come from. A greater density of measuring points might make it possible to recognize a pattern. The quire numbers on fols 85^{r} and 97^{r} show a ratio between zinc and copper similar to that in Hand VIII's inks surrounding them as well as a small amount of potassium, so that they cannot be attributed to Hand VIII with certainty.[19] Behind that, on fol. 99^{r}, not only does a recognizably different hand begin in a markedly darker ink (Hand IX); the measured values on fol. 99^{rb} also display a marked difference from the other inks and a very high proportion of zinc. On fol. 100va, as well, Hand IX's writing shows even higher proportions of zinc and copper.[20] The last pages of the first codicological unit have only subsequent entries. On fol. 101^{r}, Hand X entered some recipes in a sixteenth-century *Kurrent* script. Other recipes from this hand are found also on the last page of the second codicological unit. There, on fol. 212^{r}, however, the ink has a different composition.[21] The scribe probably did not write the two pages immediately one after the other, but possibly after some time. Additional subsequent entries from the sixteenth century in the form of pen tests are found on fol. 102^{r} (in *Fraktur* and *Kurrent*) and 108^{v} (*Kurrent*), where the name entry 'angnes kellerin' is also found in what seems to be a fifteenth-century cursive script. All three entries were written in ink with a similar composition containing high proportions of copper and zinc.[22]

Hand XI, XII, and XIII

The second codicological unit of the manuscript contains the collection of exemplars, the *Sieben weise Meister*, to which several recipes were subsequently added. The codicological finding of the manuscript showed that here a probably defective codicological unit dating from 1454 was repaired around 1463 by someone who had recourse to the same supply of paper as used in the first codicological unit.[23] The first double sheet of the first quire was replaced, just like the first sheet of the last quire. These pages (fols 109$^{r/v}$, 120$^{r/v}$, 205$^{r/v}$) were written by Hand XI, the rest of the text of the *Sieben weise Meister* by Hand XII. But the results of the X-ray fluorescence spectroscopy depicted in Fig. 6 do not show this yet. Very similar values were measured on fol. 109^{r}, as on fols 110^{v}, 121^{r}, 170^{v}, and 193^{r}. Only the recipes

[17] Cf. in Fig. 6b: f75ra_l39, f75ra_margin, f75rb_headline.

[18] Cf. in Fig. 6b: f75va_l1u, f75va_l1u_1. Cf. in Fig. 6c: f85rb_l1, f90ra_l4.

[19] Cf. in Fig. 6b: f85r_number. Cf. in Fig. 6c: f97r_number.

[20] Cf. in Fig. 6c: f99rb_l8, f100va_l13.

[21] Cf. in Fig. 6c: f101ra_l1 and f212rb_l13.

[22] Cf. in Fig. 6c: f102r_l1, f108v_Dein, f108v_l1.

[23] Precise information on the dating and distribution of watermarks and on the structure of layers is offered by the manuscript description by Marco Heiles, which will be published in *Manuscripta Medievalia* <http://www.manuscripta-mediaevalia.de/dokumente/html/obj31593540>.

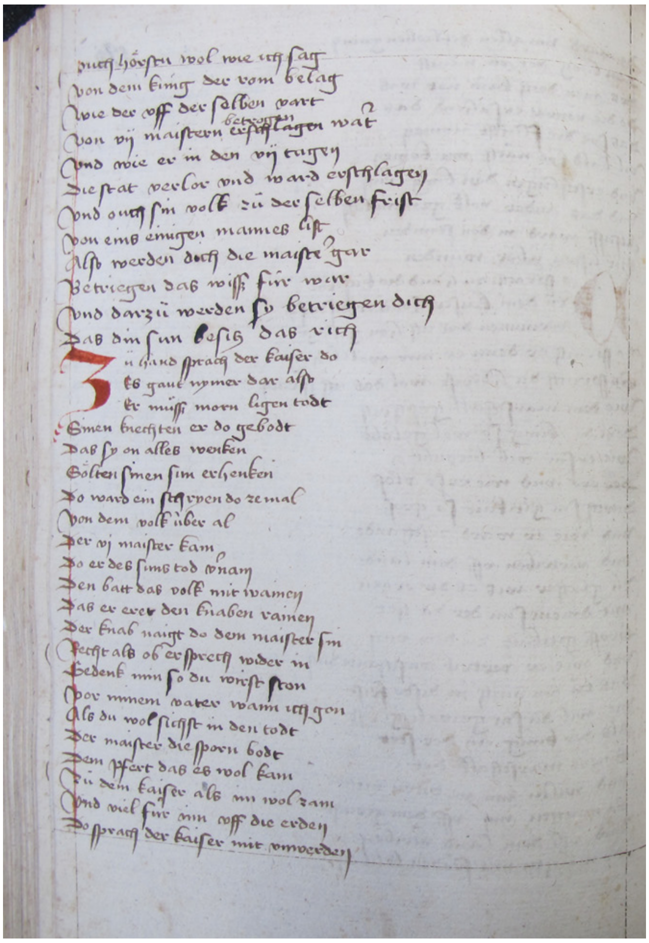


Fig. 10: Fol. 170^{v}.

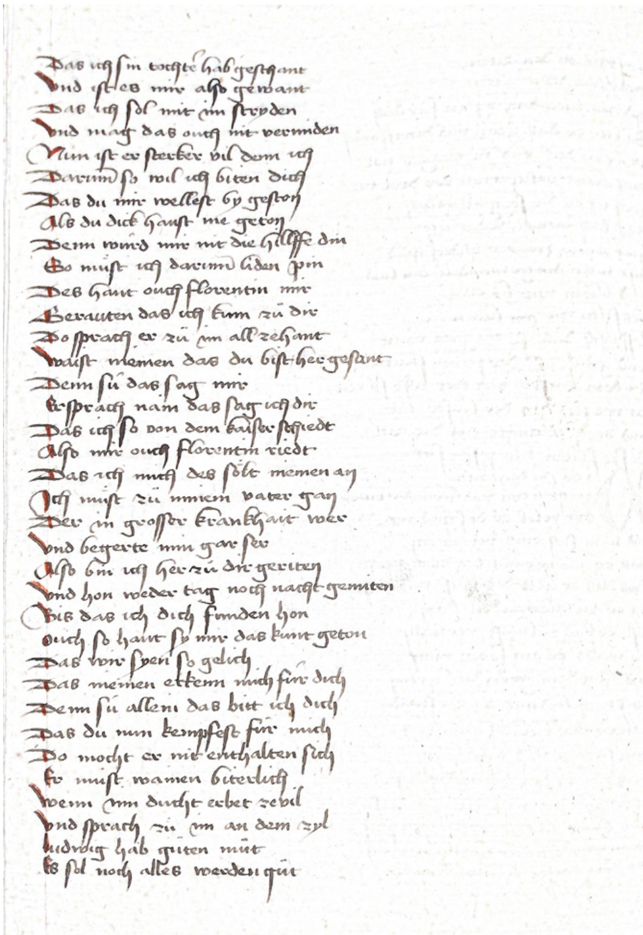


Fig. 11: Fol. 201^{v}.

subsequently entered by Hands XIII and X show once again a markedly different ink composition. Palaeographically, the distinction between Hands XI and XII is unambiguous and is also supported codicologically. On the double page fols 109^{v}/110^{r}, this is clearly recognizable (Fig. 8). On the left side (Hand XI, fol. 109^{v}), the versals <v> and <d> are always written with characteristic adornments – which research calls 'elephant trunks'[24] – that are not found on the right side (Hand XII, fol. 110^{r}). The two hands clearly differ also in the formation of the ſʒ ligatures (compare Table 1). Particularly palaeographically fascinating is the handwriting of Hand XII, namely because if the first page written by this hand, fol. 110^{r} (Fig. 8), is compared with the last, fol. 211^{r} (Fig. 9), it is easy to gain the impression that these are two different handwritings. On fol. 110^{r}, the hand writes a *Bastarda* with open loops – i.e. b, h, k, and l with loops at the right of their ascenders – and the same hand writes a *Bastarda* on fol. 211^{r} without loops – b, h, k, and l (compare also Table 1). In Lieftinck's terminology – which, however, was not developed based on southern German, but on Dutch scripts – this would even lead to a differing categorization of the two handwritings: the first would be a cursiva libraria, the latter a hybrida libraria.[25] There are additional differences. Thus, the <d> at the beginnings of verses on fol. 110^{r} always shows a closed loop, while those on fol. 211^{r} never show a loop. But no point can be pinned down where the one hand stops and the other begins. There is a point on fol. 170^{v} where the writer once skipped down and began again more concentratedly and cleanly (Fig. 10). But the form of the letters changes here as little as does the composition of the ink (Table 4).[26] Instead, the appearance of Hand XII's writing changes gradually. While Hand XII on fols 110^{r} and 110^{v} still writes all <d> at the beginnings of verses with a loop, starting on fol. 111^{v} a few individual <d> without loops appear, which, starting with fol. 112^{r},

[24] Cf. Schneider 2014, 77–79.

[25] Cf. Derolez 2006, 130, 163.

[26] Cf. in Fig. 6c: f170v_112, f170v_116.

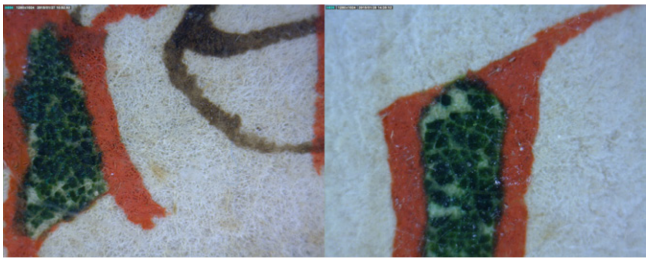


Fig. 12: Microphotographs of lombards with cinnabar and copper green on fols 2^{r} and 62^{r}.

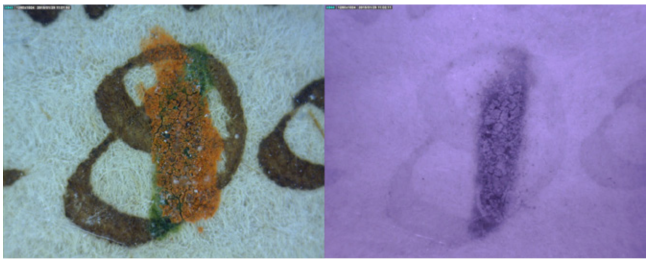


Fig. 13: Microphotographs of a dotted<d>with cinnabar and copper green on fol. 54^{va} under visible and near infrared light.

provide most of the versal <d>. By fol. 113^{v}, only a few <d> show loops at the beginnings of verses, and on the following folios there are none whatsoever. The shift from a *Bastarda* with loops to one without loops proceeds more quickly and can be observed on fol. 201^{v} (Fig. 11), where initially forms without loops appear intermittently from line 24 on and finally only these are used. In this case, X-ray fluorescence analysis supports the palaeographic finding, but without the palaeographic examination would not be unequivocal, like the similar measured values of the inks from Hand XI and Hand XII show.

The red and green inks

In the Cod. germ. 1, red and green color was used along with black iron gall ink. The texts entered by Hand I were adorned with black, red, and green lombards (decorative initials) (see Fig. 3); capital letters and the beginnings of verses were furnished with red and green strokes (see Figs 1, 3, and 4); and in some cases titles were underlined in red. A red hatching is also found in Hand IX's entry, and Hands XI and XII also display red lombards and strokes (see Figs 8, 9, 10, and 11), whereby here several pages were skipped – as with Hand I.[27]

The green pigment used is copper green. The production of such copper green inks with verdigris, vinegar, and saffron (Recipe 5) and optional with the addition of winestone (potassium bitartrate), gum arabic, egg yolk, and honey (Recipe 18) is described in the collection of paint and ink recipes of Cod. germ. 1.[28] This kind of ink is recognizable with the naked eye and is especially marked under the microscope (Fig. 12) due to its metallic luster and its characteristic structure. It is also still visible under infrared light (NIR, Near Infrared, 940 nm) (Fig. 13). For this reason, to confirm this finding, we measured this ink only on fols 3^{r} and 62^{r}.

Two fundamentally different kinds of red ink were used for rubrication in Cod. germ. 1: inks containing cinnabar and inks containing red lead. Both kinds of 'ruberic' were also mentioned in the recipe collection, whereby in Recipes 16 and 26 there only the act of mixing the inks made of 'zinober' (cinnabar) or 'myni' (minium/red lead) were described and not their production.[29] Cinnabar is β-mercuric(II) sulfide (HgS) and in the Middle Ages was either mined as a mineral or artificially produced.[30] Minium or red lead, is lead (II,IV) oxide, which was mostly produced artificially[31]. Fig. 14a depicts for 18 measuring spots the amount of mercury (Hg), copper (Cu), iron (Fe), and manganese (Mn) in relation to lead (Pb). The red inks with a very high mercury content used on fols 2^{r}, 3^{v}, 58^{v}, 59^{r}, and 62^{r} are thus clearly cinnabar inks, the others red lead inks. The sometimes high measured values for copper and iron can probably be attributed to impurities deriving from the copper green and iron gall inks used in the same place. They show that the measuring points should have been selected more carefully.

These two kinds of red inks can be distinguished with the naked eye in Cod. germ. 1. The cinnabar is characterized by its intense, bright red color, while red lead appears more brownish. Cinnabar inks were accordingly used on fols 2^{r}–7^{r}, 8^{v}, 53^{r}–54^{r}, 58^{v}–59^{r}, and 61^{r}–62^{v}. All other rubrications were carried out with red lead. The data gathered do not permit a more distinction among individual ink batches; only the red lead ink used on fol. 100v stands out for its high mercury content. But we can distinguish two groups of red lead inks. There are red inks without mercury on fols 58^{r},

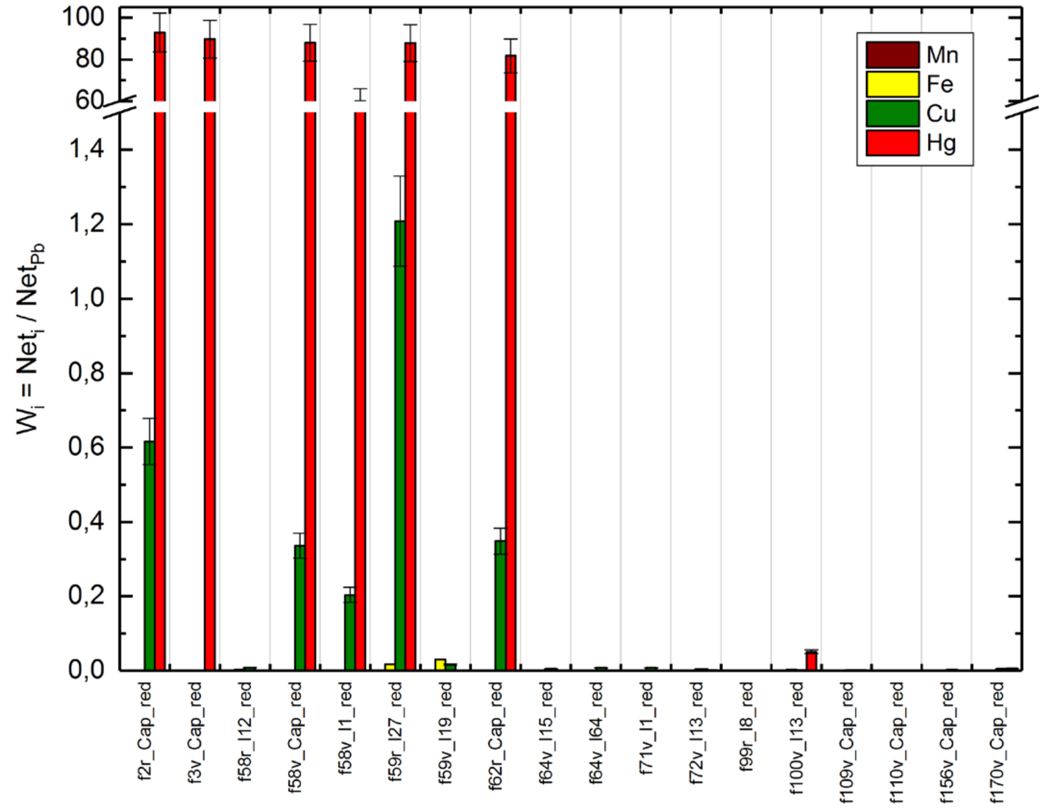
[27] Precise information on the way rubrication was carried out is found in the manuscript description by Marco Heiles, in *Manuscripta Medievalia* <http://www.manuscripta-mediaevalia.de/dokumente/html/obj31593540>.

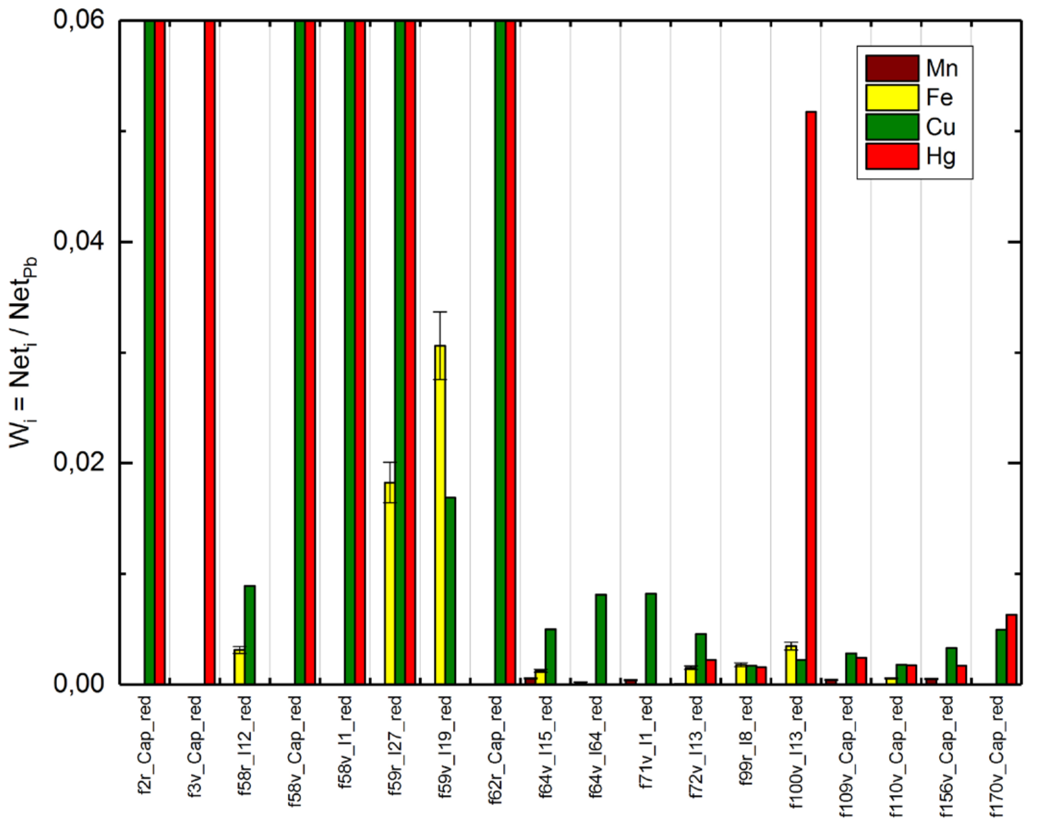
[28] Cf. Heiles 2018b, 13–61.

[29] Cf. Heiles 2018b, 13–61.

[30] On this, cf. Bartl, Krekel, Lautenschlager, and Oltrogge, 2005, 542–544.

[31] Arnold, Ullrich, Dobianer, and Grunz 2009, 20–24.





Figs 14a and b: XRF investigation of the red inks. Fingerprint values W_i of different elements normalised to lead.

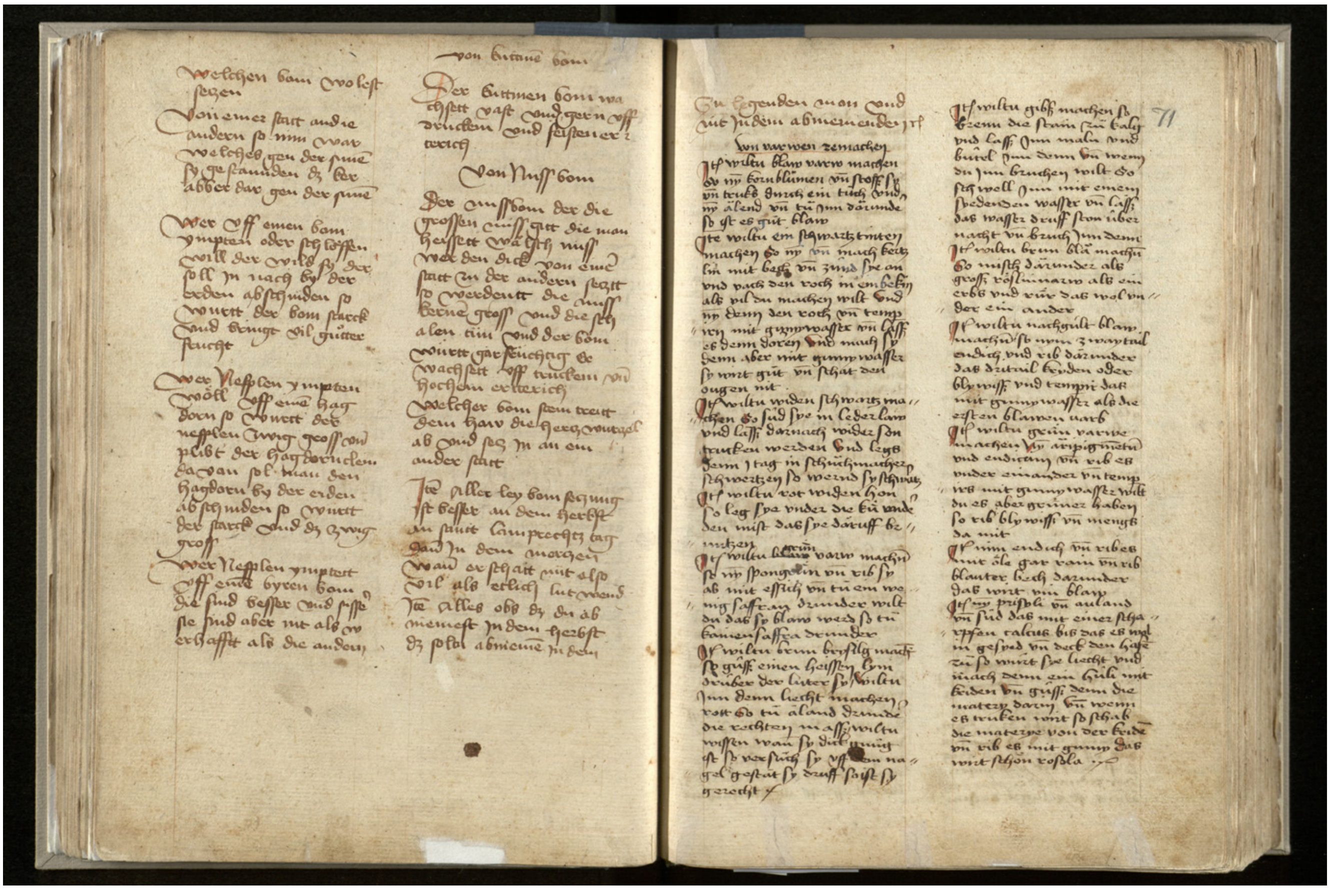


Fig. 15: Fols 70^{v}–71^{r}.

59^{v}, 64^{v} and 71^{v} and red inks with very little mercury on fols 72^{v}, 99^{r}, 109^{v}, 110^{v}, 156^{v} und 170^{v} (Fig. 14b). Codicological evidence shows, that these entries were not made by only two rubricators, but it is remarkable, that there is a change of ink between fols 71^{v} and 72^{v}, where scribal hands are changing too (Hand III and Hand V).

Conspicuous is that copper green was used only where cinnabar was also used. There is no combination of red lead and copper green. Additionally, copper green and cinnabar are found together only in entries by Hand I. These entries are thus very probably the work of a single rubricator, either Hand I or someone who worked together with Hand I. But it is not clear why only certain sections of Hand I texts were rubricated by this rubricator.

The censorship on fol. 57ra

X-ray fluorescence analysis did not help us with the strikeout of the 'zagel' on fol. 64^{vb}, but it did with the 'schwarcz tüfel' on fol. 57ra. The two measurements f57ra_corr1 and f57ra_corr2 that were made there show that the text here was censored with an iron gall ink (Fig. 6). That means that, with very probability, this was not done in very recent times. The ink shows a high tin and copper content, with the copper content higher than the tin in the second measurement, and there are traces of potassium. The censorship was thus definitely not done immediately during Hand I's writing, since the ink Hand I used differs markedly from that of the censorship. But we were unable to find anywhere in the entire manuscript other inks that have a similar composition. That does not mean that none of the other persons participating in the manuscript could have been the censor. But he or she did not do it with the same ink as used to write other texts. The gain in knowledge from the specific censored passages on fol. 57ra and fol. 64^{vb}, taken by itself, does not have a favorable relationship with the effort of the examination. But on the production process of the manuscript itself and the attribution of marginal entries that could not be palaeographically attributed to specific writing hands, definitely valuable new knowledge was gained that can also encourage new studies. It seems to us that here, in the examination of marginalia, lays a particular potential of X-ray fluorescence analysis. Another untapped potential for revealing the work processes in a scriptorium seems to lie in examining the ruling of the writing space by means of microscopy and X-ray fluorescence analysis.

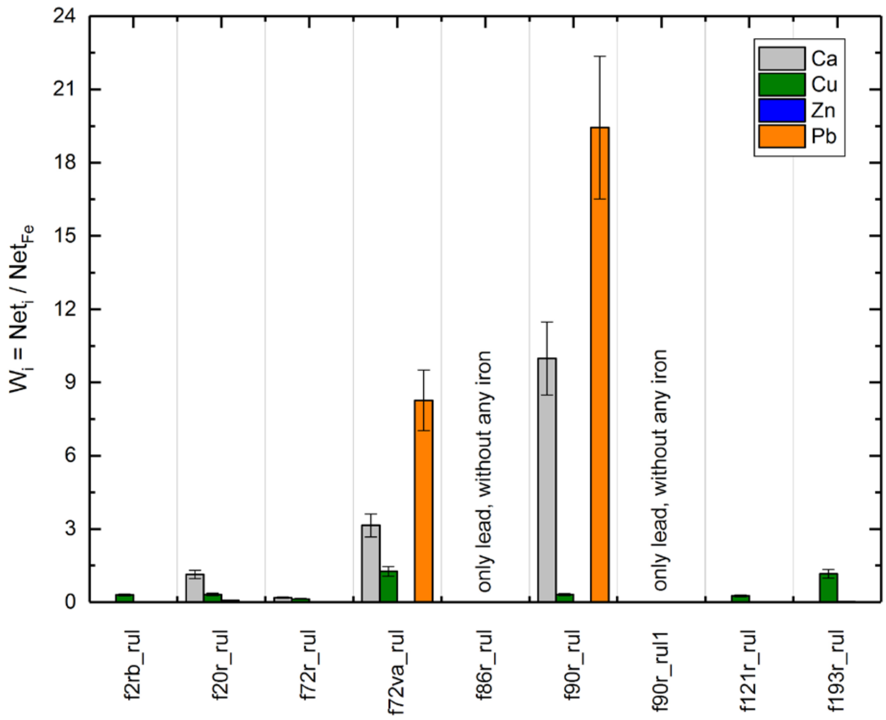


Fig. 16: XRF investigation of the rulings. Fingerprint values W_i of different elements normalised to iron.

The lines marking the writing space in the first codicological unit, which are also on the unwritten last pages of the unit, offer a consistent image visually and also under the ruler, but our data show that they certainly were not made in a unified work process. Among the sole four values measured in this codicological unit that showed iron gall inks, at least three different inks could be made out. Added to this are two lines actually drawn with a lead stylus. It thus appears that only a few pages were ruled at a time, for which ink or lead were used optionally. The change in ink from fol. 72ʳ to fol. 72ᵛ also indicates that this working step was not undertaken for a whole quire, but was connected with a change of scribe and rubricator, which we can observe at precisely this point.

Here, a more precise examination with a much greater number of measuring points would certainly provide deeper insight into the collaboration of the many people who contributed to this manuscript. Since the lead lines, unlike the iron gall inks, are visible also under infrared light (Fig. 17) and can therefore be easily distinguished from them, here preliminary examinations are also possible without great technological effort.

Outlook: ruling and writing space boundaries

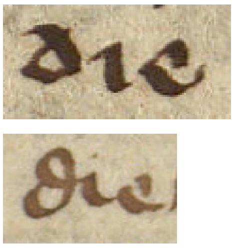
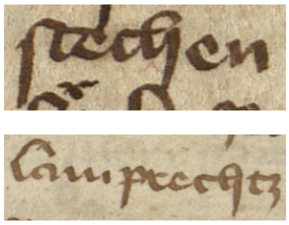
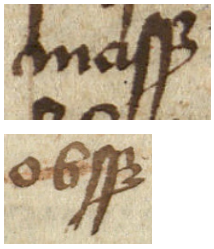
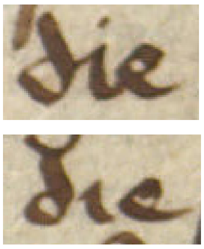
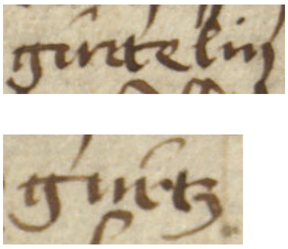
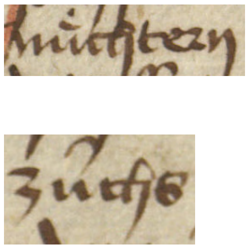
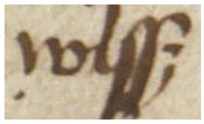
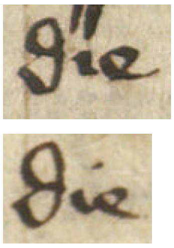
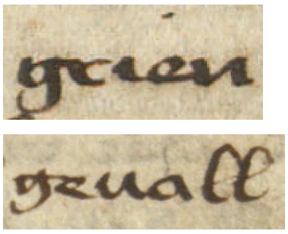
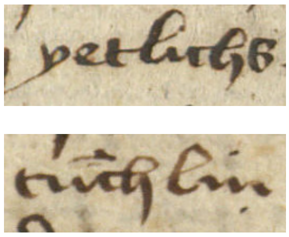
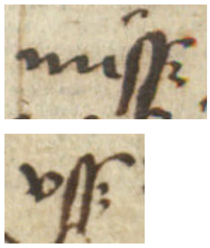
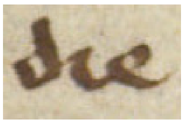
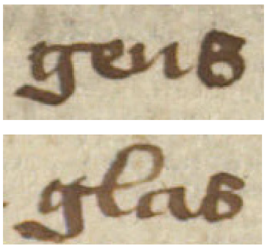
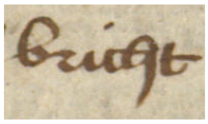
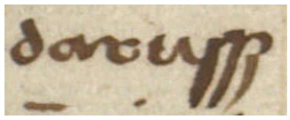
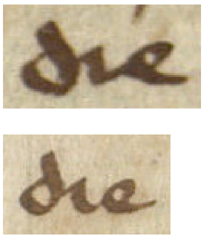
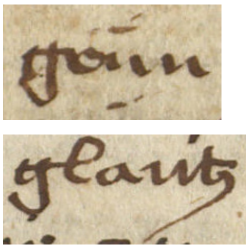
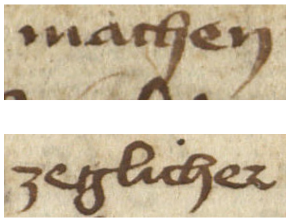
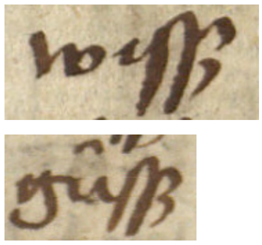
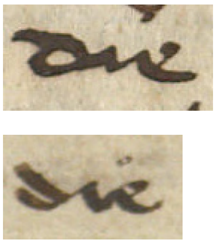
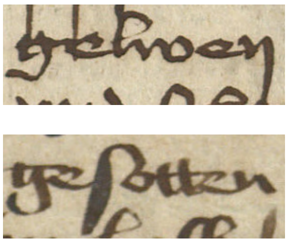
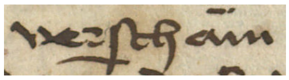
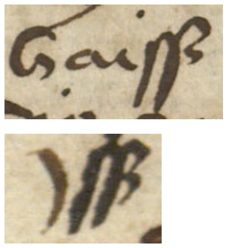
The writing space of Cod. germ. 1 is consistently arranged in both codicological units. The first codicological unit was set up throughout with a two-column frame always ca. 14.5 cm wide. On fols 2ʳ–70ᵛ, these were always inscribed by Hand I with ca. 35–37 lines that, taken together, are ca. 21 cm high. On fols 71ʳ–108ᵛ, the primary Hands III, V, VIII, and IV used more space (Fig. 15). The text is now ca. 25 cm high and contains up to 45 lines, whereby this value differs for each hand. The primary text of the second codicological unit, the verse processing of the *Sieben weise Meister*, is written in one column. These pages all have an upper, a lower, and a left-hand frame line. The writing space measures *c*. 23 × 16 cm and holds 36–38 lines (see Fig. 8).

To examine the inks, we needed measuring points whose reverse side had not been written on, so we often chose letters on the edge of the writing space, which thus often lay very close to the ruling lines bounding the writing space. So, we used the favorable opportunity to gather data about these rulings without great effort. The measured values of these very arbitrarily chosen eight measuring points are presented in Fig. 16, where the amounts of lead (Pb), zinc (Zn), copper (Cu), and calcium (Ca) are set in relation to the amount of iron (Fe).

Fig. 17: Microphotographs of the iron gall ink and lead lines on fol. 75ʳ (above) and fol. 193ʳ (below) with visible and near infrared light.

Tabelle 1: Differentiation of hands in Codex germanicus 1.

Hand	Folio	Type of script	Characteristics
Hand I	2^{r}–71^{ra}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops at the right of their ascenders d with and without loop w with and without loop in some cases r with vertical hairline (e.g. fol. 2^{rb}, l. 24 *rott*)
Hand II	64^{va}	*Bastarda/Semihybrida libraria*	single-compartment a f and ſ descending below the baseline b and l with and without loops h and k with loops d without loop w without loop
Hand III	64^{vb}, 71^{ra}–72^{rb}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d with and without loop w without loop
Hand IV	64^{vb}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d without loop w without loop
Hand V	72^{va}–75^{ra}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d with and without loop w without loop
Hand VI	75^{ra}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d without loop w without loop

First and last instance of			
⟨die⟩	⟨g-⟩	⟨-ch-⟩	⟨-ß⟩
			
			
			
			
			
			

Hand	**Folio**	**Type of script**	**Characteristics**
Hand VIII	75^{v}–98^{vb}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d with and without loop w without loop
Hand IX	99^{ra}–100^{vb}	*Bastarda/Semihybrida libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with and without loops d with and without loop w without loop
Hand X	101^{r}, 212^{r}	*Kurrentschrift*	single-compartment a, f and ſ descending below the baseline b, h , k, and l with loops d with loop, w without loop
Hand XI	$109^{r/v}$, $120^{r/v}$, $205^{r/v}$	*Bastarda/Cursiva libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops d without loop w without loop
Hand XII	110^{r}–119^{v}, 121^{r}–204^{v}, 206^{r}–211^{r}	*Bastarda/Cursiva libraria* and *Hybrida libraria*	single-compartment a f and ſ descending below the baseline b, h , k, and l with loops (until 201^{v}), without loops (201^{v}–211^{r}) d without loop w without loop
Hand XIII	211^{v}	*Bastarda/Cursiva libraria*	single-compartment a f and ſ decending below the baseline b, h , k, and l with loops d without loop w without loop

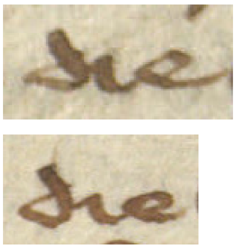
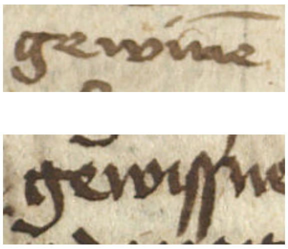
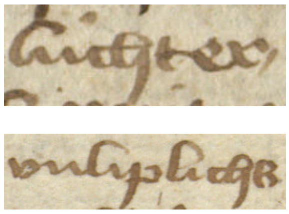
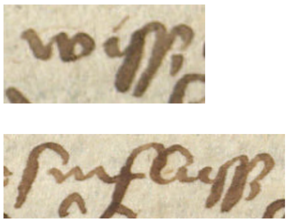
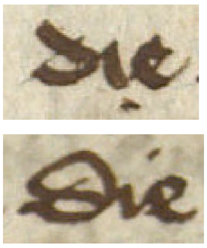
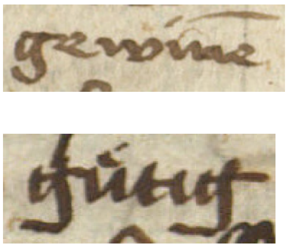
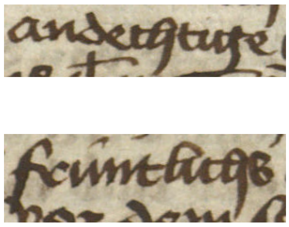
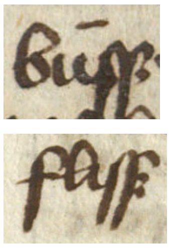
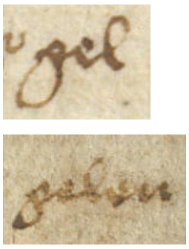
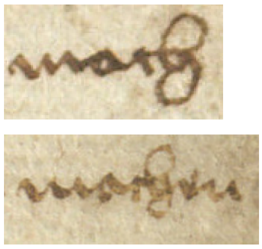
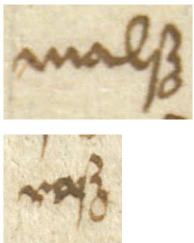
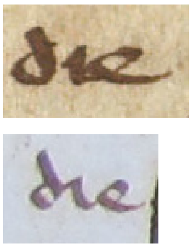
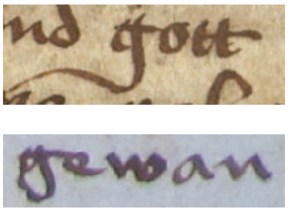
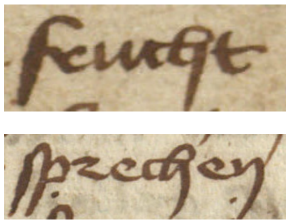
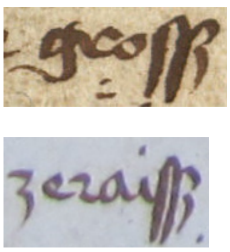
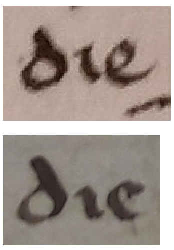
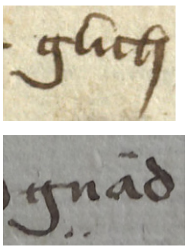
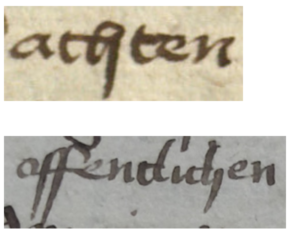
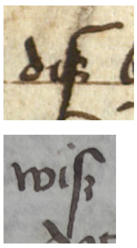
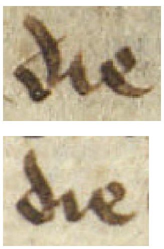
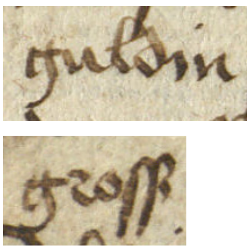
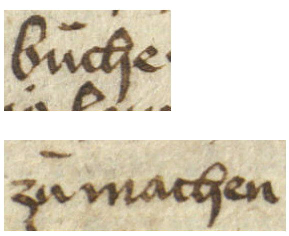
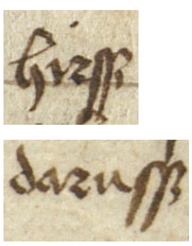
First and last instance of			
⟨die⟩	⟨g-⟩	⟨-ch-⟩	⟨-ß⟩
			
			
			
			
			
			

Table 2: Content of Codex germanicus 1.

Folio	**Texts**	**Hand**
fol. 1^{r}	Pen tests	
fols $5^{r/v}$, 1^{ra}	Bloodletting times and rules	Hand I
fols 1^{ra}–3^{ra}	Suitable bloodletting sites	Hand I
fols 3^{ra}–3^{va}	Unlucky Days (*Verworfene Tage*)	Hand I
fols 3^{va}–4^{ra}	The German *Macer* (Vulgate version), prose foreword (shortened and heavily redacted)	Hand I
fols 4^{ra}–4^{va}, 6^{ra}–11^{vb}	Herbal book compilation, based partly on the German *Macer* (Vulgate version)	Hand I
fols 11^{vb}–47^{rb}	Medical recipes: treatment of various body parts (*A capite ad calcem*), women's medicine, wounds and poisonings, urine test, and veterinary medicine	Hand I
fols 47^{rb}–50^{ra}	Recipes for preparing wine	Hand I
fols 50^{ra}–50^{vb}	Vinegar recipes	Hand I
fols 51^{ra}–51^{rb}	Plague recipes: *Der Sinn der höchsten Meister von Paris* ('The opinion of the greatest masters from Paris') and *Sendbrief-Aderlaßanhang* ('epistle – bloodletting annex')	Hand I
fols 51^{rb}–51^{va}	Sleep recipes	Hand I
fols 51^{va}–52^{rb}	Instructions on obtaining and using stones with supernatural qualities, illusion tricks, recipes against vermin	Hand I
fols 52^{va}–54^{va}	Technological, joke, and damage recipes	Hand I
fols 54^{va}–55^{ra}	Ps.-Albertus Magnus: *De virtutibus herbarum*, German (translated excerpts)	Hand I
fols 55^{ra}–56^{rb}	Ps.-Albertus Magnus: *De virtutibus lapidum*, German (translated excerpts) and a recipe	Hand I
fols 56^{rb}–57^{rb}	Drug monograph, Ps.-Albertus Magnus: *De virtutibus animalium*, German (translated excerpts) and trick recipes	Hand I
fols 57^{va}–62^{ra}	Volmar: *Steinbuch* (H)	Hand I
fols 62^{rb}–62^{vb}, $63^{va\text{-}b}$, $63^{ra\text{-}b}$	Lunar prognostic: *Krankheitslunar* (HaD)	Hand I

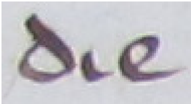
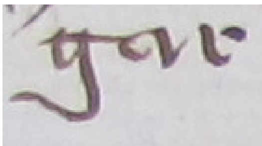
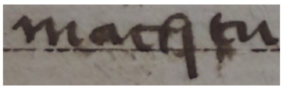
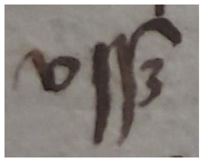
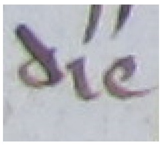
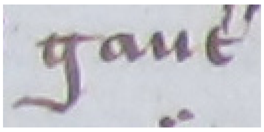
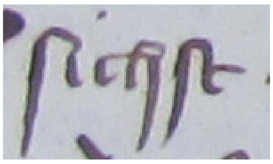
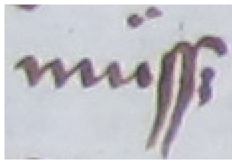
fol. 64ra	New Year's prognosis	Hand I
fols 64ra–64va	Medical and other recipes	Hand I
fol. 64va	Recipe against lice	Hand II
fol. 64^{vb}	3 medical recipes	Hand III
fol. 64^{vb}	Medical recipe	Hand IV
fols 65ra–69va	32 cooking recipes	Hand I
fols 69va–71ra	Recipes for caring for trees from Gotfried von Franken's *Pelzbuch*	Hand I
fols 71ra–75ra	41 paint and ink recipes	Hand III and Hand V
fol. 75ra	2 medical recipes	Hand VI
fol. 75^{r}	1 medical recipe and 5 recipes against hair loss (dirt pharmacy)	Hand VII
fols 75va–98^{vb}	*Lucidarius* / translation of *Elucidarius*	Hand VIII
fols 99ra–100^{vb}	Johannes von Indersdorf (?): Maxims and prayers	Hand IX
fol. 101$^{ra\text{-}rb}$	(Cooking) recipes	Hand X
fol. 101^{v}	– *empty* –	
fol. 102^{r}	Broken-off entry	
fols 102^{r}–108^{r}	– *empty* –	
fol. 108v	Name entry *angnes kellerin* and pen tests from the 16th century	
fols 109^{r}–117^{r}, 118^{v}–211^{r}	*Sieben weise Meister (The Seven Wise Masters)*, German, verse version	Hand XI and Hand XII
fols 117^{v}–118^{r}	– *empty* –	
fol. 211^{v}	6 medical recipes	Hand XIII
fol. 212$^{ra/rb}$	5 cooking recipes	Hand X
fols 212^{v}–214^{v}	– *empty* –	

Table 3: Measuring points of black ink

Folio	**Type of the ink**	**ID No.**
001^{r}	Addendum 01 Year	f1r_year
001^{r}	Addendum 02 *probatio pennae*	f1r_longEntry
002^{v}	Hand I 01	f2vb_5u
002^{v}	Hand I 02	f2vb_4u
015^{r}	Hand I 03	f15rb_12u
020^{r}	Addendum 03 margin (Johann)	f20r_Marg
023^{v}	Addendum 04 margin (double virgule)	f23vb_capitulum
023^{v}	Hand I 04	f23vb_l10
028^{v}	Addendum 05 margin (text)	f28va_margin
028^{v}	Addendum 06 correction	f28vb_corr
051^{r}	Hand I 05	f51rb_l4
051^{r}	Addendum 07 margin (finger)	f51ra_finger
051^{r}	Addendum 08 margin (cloud)	f51rb_cloud
051^{r}	Addendum 09 margin (da)	f51rb_da
052^{r}	Addendum 10 margin (bracket)	f52rb_bracket
052^{r}	Addendum 11 margin (da)	f52rb_da
057^{r}	Addendum 12 strike through	f57ra_corr1, f57ra_corr1
057^{r}	Hand I 06	f57rb_l30
058^{r}	Hand I 07	f58rb_l12
058^{v}	Hand I 08	f58va_l1
058^{v}	Addendum 13 margin (*capitulum* with red stroke)	f58va_Capitulum
062^{r}	Hand I 09	f62rb_l4
064^{v}	Hand I 10	f64va_l15
064^{v}	Hand II 01	f64va_l24T,Vis, IR
064^{v}	Hand III 01	f64vb_l1
064^{v}	Hand IV 01	f64vb_l24

066v	Hand I 11	f66va_l15
071v	Hand III 02	f71va_l1
072v	Hand V 01	f72vb_l13
075r	Hand VI 01	f75ra_l39
075r	Addendum 18 margin (text)	f75ra_margin
075r	Hand VII 01	f75rb_headline
075v	Hand VIII 01	f75va_l1u, f75va_l1u_1
085r	Quire number 01 "9"	f85r_number
085r	Hand VIII 02	f8rrb_l1
090r	Hand VIII 03	f90ra_l4
097r	Quire number 02 "10"	f97r_number
099r	Hand IX 01	f99rb_l8
100v	Hand IX 02	f100va_l13
101r	Hand X 01	f101ra_l1
102r	Addendum 19 headline	f102ra_l1
108v	Addendum 20 *agnes kellerin*	f108v_l1
108v	Addendum 21 *probatio pennae*	f108v_Dein
109r	Hand XI 01	f109r_l1
110v	Hand XII 01	f110v_l29
121r	Hand XII 02	f121r_l1
121r	Quire number 03 "2"	f121r_number
170v	Hand XII 03	f170v_l12
170v	Hand XII 04	f170v_l16
193r	Hand XII 05	f193r_l1_1
193r	Quire number 04 "8"	f193r_number
211v	Hand XIII 01	f211v_l1
212r	Hand X 02	f212rb_l3

Table 4: Forms of letters on fol. 170v.

Ink	⟨die⟩	⟨g-⟩	⟨-ch-⟩	⟨-ß⟩
Ink #1				
Ink #2				

REFERENCES

Arnold, Bärbel, Detlef Ullrich, Borris Dobianer, and Rico Grunz (2009), 'Historische Herstellung von Kupfer- und Bleipigmenten', in Brandenburgisches Landesamt für Denkmalpflege und Archäologisches Landesmuseum (ed.), *Umweltbedingte Pigmentveränderungen an mittelalterlichen Wandmalereien: Beiträge des 3. Konservierungswissenschaftlichen Kolloquiums in Berlin/Brandenburg am 13. und 14. November in Potsdam und Ziesar* (Worms: Werner), 20–24.

Bartl, Anna, Christoph Krekel, Manfred Lautenschlager, and Doris Oltrogge (2005), *Der 'Liber illuministarum' aus Kloster Tegernsee: Edition, Übersetzung und Kommentar der kunsttechnologischen Rezepte* (Publication of the Institut für Kunsttechnik und Konservierung im Germanischen Nationalmuseum, 8) (Stuttgart: Steiner).

Bibliothecae Vffenbachianae Universalis (1730), Tomus III, [...] (Frankfurt am Main). <http://nbn-resolving.de/urn:nbn:de:gbv:3:3-18817> (last accessed 15 May 2018).

Brévart, Francis B. (2008), 'Between Medicine, Magic and Religion: Wonder Drugs in German Medico-Pharmaceutical Treatises of the Thirteenth to the Sixteenth Centuries', *Speculum,* 83: 1–57.

Catalogus Manuscriptorum Codicum Bibliothecae Uffenbachianae (1747) (Frankfurt am Main). <https://hdl.handle.net/2027/hvd.32044080348816> (last accessed 15 May 2018).

Derolez, Albert (2006), *The Paleography of Gothic Manuscript Books: From the Twelfth to the Early Sixteenth Century* (Cambridge Studies in Palaeography and Codicology, 9) (Cambridge: Cambridge University Press).

Di Venosa, Elena (2005), *Die deutschen Steinbücher des Mittelalters: Magische und medizinische Einblicke in die Welt der Steine* (Göppinger Arbeiten zur Germanistik, 714) (Göppingen: Kümmerle).

Fechter, Werner (1935), *Das Publikum der mittelhochdeutschen Dichtung* (Deutsche Forschungen, 28) (Frankfurt am Main: Diesterweg).

Fuchs, Robert (1999), 'Der Tintenfraß historischer Tinten und Tuschen – ein komplexes nie enden wollendes Problem', in Gerhard Banik and Hartmut Weber (ed.), *Tintenfraßschäden und ihre Behandlung* (Werkhefte der staatlichen Archivverwaltung Baden-Württemberg. Serie A: Landesarchivdirektion, Serie A, 10) (Stuttgart: Kohlhammer), 37–76.

Gerdes, Udo (1992), 'Sieben weise Meister', in Wolfgang Stammler et al. (eds), *Die deutsche Literatur des Mittelalters: Verfasserlexikon*, 2nd edition, vol. 8, 1174–1189.

—— (2004), 'Sieben weise Meister', in Wolfgang Stammler et al. (eds), *Die deutsche Literatur des Mittelalters: Verfasserlexikon*, 2nd edition, vol. 11, 1430.

Gottschall, Dagmar (1992), *Das 'Elucidarium' des Honorius Augustodunensis: Untersuchungen zu seiner Überlieferungs- und Rezeptionsgeschichte im deutschsprachigen Raum mit Ausgabe der niederdeutschen Übersetzung* (Texte und Textgeschichte, 33) (Tübingen: Niemeyer).

—— and Georg Steer (eds) (1994), *Der deutsche 'Lucidarius'*, vol. 1: *Kritischer Text nach den Handschriften* (Texte und Textgeschichte, 35) (Tübingen: Niemeyer).

Hahn, Oliver (2010), 'Analyses of Iron Gall and Carbon Inks by Means of X-ray Fluorescence Analysis: A Non-destructive Approach in the Field of Archaeometry and Conservation Science', *Restaurator: International Journal for the Preservation of Library and Archival Material,* 31.1: 41–64.

Handschriftencensus: Eine Bestandsaufnahme der handschriftlichen Überlieferung deutschsprachiger Texte des Mittelalters, <http://handschriftencensus.de/4859> (last accessed 15 April 2018).

Heiles, Marco (2014), 'Seelenheil und Prüderie: Zensur in einer deutschen Sammelhandschrift des 15. Jahrhunderts', *Manuskript des Monats* 12/2014. <http://www.manuscript-cultures.uni-hamburg.de/mom/2014_12_mom.html>; 'Salvation of the soul and prudery: Censoring a 15th-century German-language manuscript', Manuscript of the Month 12/2014. <http://www.manuscript-cultures.uni-hamburg.de/mom/2014_12_mom_e.html> (last accessed 15 May 2018).

—— (2018a), 'Das Wunderbare in der deutschsprachigen Rezeptliteratur des 15. Jahrhunderts', in Stefanie Kreuzer and Uwe Durst (eds), *Das Wunderbare: Dimensionen eines Phänomens in Kunst und Kultur* (Traum – Wissen – Erzählen, 3) (Paderborn: Fink), 233–250.

—— (2018b), 'Die Farb- und Tintenrezepte des Cod. germ. 1 der Staats- und Universitätsbibliothek Hamburg und ihre Vorlagen', *Mittelalter: Interdisziplinäre Forschung und Rezeptionsgeschichte,* 1: 13–61. <https://mittelalter.hypotheses.org/11576> (last accessed 15 May 2018).

—— (forthcoming), 'Gesicherte Geheimnisse? Über Buchschlösser und das, was sie verbergen', in *Proceedings des 17. Symposium des Mediävistenverbandes 'Geheimnis und Verborgenes im Mittelalter'*.

Henrici, Emil (1911), Handschriftliche Archivbeschreibung für die Königlich-Preußische Akademie der Wissenschaften zu Berlin, 19 and 21 Oct. 1911 (Berlin), in Berlin-Brandenburgische Akademie der Wissenschaften (ed.), *Deutsche Texte des Mittelalters: Handschriftenarchiv*, <http://www.bbaw.de/forschung/dtm/HSA/startseite-hsa.html> (last accessed 15 May 2018).

Hickel, Erika (1963), *Chemikalien im Arzneischatz deutscher Apotheken des 16. Jahrhunderts unter besonderer Berücksichtigung der Metalle* (Brunswick: Pharmaziegeschichtliches Seminar der Technischen Hochschule; Dissertation, Technical University Brunswick).

Kanngießer, Birgit (2004), 'A Fingerprint Model for Inhomogeneous Ink Paper Layer Systems Measured with Micro X-ray Fluorescence Analysis', *X-Ray Spectrometry,* 33: 229–233.

Krekel, Christoph (1999), 'Chemische Struktur historischer Eisengallustinten', in Gerhard Banik and Hartmut Weber (ed.), *Tintenfraßschäden und ihre Behandlung* (Werkhefte der staatlichen Archivverwaltung Baden-Württemberg. Serie A: Landesarchivdirektion, Serie A, 10) (Stuttgart: Kohlhammer), 25–36.

Lambel, Hans (ed.) (1877), *Das Steinbuch: Ein altdeutsches Gedicht von Volmar* (Heilbronn: Henninger). <http://www.archive.org/details/dassteinbuchein00heingoog> (last accessed 15 May 2018).

Lappenberg, Johann Martin (1834), 'Inhalt einer Handschrift in der Hamburger Stadtbibliothek', *Anzeiger für Kunde des deutschen Mittelalters,* 3: 99–100.

Paschke, Paul (1891), *Über das anonyme mittelhochdeutsche Gedicht von den sieben weisen Meistern* (Breslau: Breslauer Genossenschafts-Buchdruckerei; Dissertation, Royal University Breslau – Universitas litterarum Vratislaviensis). <http://www.archive.org/details/berdasanonymemh00pascgoog> (last accessed 15 May 2018).

Petersen, Christian (ca. 1830), *Handschriftliches Verzeichnis der Codices germanici der Stadtbibliothek Hamburg* (manuscript, available in the Manuscripts Reading Room of the State and University Library Hamburg).

Schneider, Karin (2014), *Paläographie und Handschriftenkunde für Germanisten*, 3rd revised edition (Berlin: de Gruyter).

Schorbach, Karl (1894), *Studien über das deutsche Volksbuch Lucidarius und seine Bearbeitungen in fremden Sprachen* (Quellen und Forschungen zur Sprach- und Culturgeschichte der germanischen Völker, 74) (Strasbourg: Trübner). <http://www.archive.org/stream/quellenundforsc03unkngoog#page/n163/mode/2up> (last accessed 15 May 2018).

Ulmschneider, Helgard (2011), *Der deutsche 'Lucidarius'*, vol. 4, *Die mittelalterliche Überlieferungsgeschichte* (Texte und Textgeschichte, 38) (Berlin/New York: de Gruyter).

Weißer, Christoph (1982), *Studien zum mittelalterlichen Krankheitslunar: Ein Beitrag zur Geschichte laienastrologischer Fachprosa* (Würzburger medizinhistorische Forschungen, 21) (Pattensen/Hanover: Wellm) .

—— (1987), 'Neujahrsprognosen', in *Die deutsche Literatur des Mittelalters: Verfasserlexikon*, 2nd edition, vol. 6, 915–918.

—— (2004), 'Neujahrsprognosen', in *Die deutsche Literatur des Mittelalters: Verfasserlexikon*, 2nd edition, vol. 11, 1049.

Artesliteratur.de, 'Kategorie: Eisengallustinte', <https://www.artesliteratur.de/w/index.php?title=Kategorie:Eisengallustinte&oldid=1450> (last accessed 15 May 2018).

Wikimedia Commons, 'Hamburg, Staats- und Universitätsbibliothek, Cod. germ. 1', <https://commons.wikimedia.org/wiki/Category:Hamburg,_Staats-_und_Universit%C3%A4tsbibliothek,_Cod._germ._1> (last accessed 15 May 2018).

PICTURE CREDITS

Figs 1–3: State and University Library Hamburg (State and University Library Hamburg); CC BY 4.0.

Figs 4–5: Marco Heiles; CC BY 4.0.

Figs 6a, b, c: © Oliver Hahn and Ira Rabin.

Figs 7–11: State and University Library Hamburg (State and University Library Hamburg); CC BY 4.0.

Figs 12–13: Marco Heiles; CC BY 4.0.

Figs 14a and b: © Oliver Hahn and Ira Rabin.

Fig. 15: State and University Library Hamburg (State and University Library Hamburg); CC BY 4.0.

Fig. 16: © Oliver Hahn and Ira Rabin.

Fig. 17: Marco Heiles; CC BY 4.0.

Article

Advanced Codicological Studies of Cod. germ. 6 (Hamburg, Staats- und Universitätsbibliothek): Part 2

Mirjam Geissbühler, Georg Dietz, Oliver Hahn, and Ira Rabin | Bern, Dresden, Berlin, Hamburg

Abstract

The work presented here follows the article *Combining Codicology and X-Ray Spectrometry to Unveil the History of Production of Codex germanicus 6 (Staats- und Universitätsbibliothek Hamburg)*, published in 2014.[1] It confirms the main result of the previous article: the *Artusnotiz*, the fourth text in the bound manuscript, must have been introduced as the last one. This paper offers further details of the codex production, based on the composition of the black and red inks collected in four measurement campaigns. Furthermore, using imaging μ-XRF, we succeeded in understanding the strong variation of the composition of the red inks in the initials of all the texts except for *Parzival* and *Jeanne d'Arc*.

1. Introduction

Codex germanicus 6 (Cod. germ. 6) was created by a private person named Jordan around 1450 in the Rhenish-Franconian area. The 614-page manuscript contains eleven texts written in Middle High German and one in Latin. It is a simple manuscript (texts written with black ink, rubricated), but it has a complex history. The texts' order in the bound manuscript does not correspond to the sequence in which they were originally copied. We have added ink and paper analysis to the classical codicological methods that could not clarify this order.[2]

Since our previous study in 2013, we have continued the work on Cod. germ. 6 using μ-X-ray fluorescence in line scan modus. Adding some 100 measurements of black inks and 140 measurements of red inks enabled us to divide the texts into distinct units based on ink similarity and suggesting that the writing was conducted in various stages.

Table 1 shows the structure of Cod. germ. 6 in the bound manuscript.[3] Pages 7, 366 and 588 were left blank and indicate a gap between the *Meisterlieder* (*Horn* and *Mantel*) and *Parzival*, *Artusnotiz* and *Wigalois*, as well as between *Friedrich* and *Jeanne*. The study of the watermarks shows that there must be another gap between *Wigalois* and *Abul Nasr*.[4] We found five types of watermarks in the shape of the heads of oxen in the manuscript, though not a single one could be identified with certainty.[5] The numerous similar examples of the five watermarks we examined all date to between 1448 and 1452.[6] The paper exhibiting watermarks 1 and 2

[1] Rabin et al. 2014.

[2] Christine Putzo employed classical codicological methods to determine the production process of the Cod. germ. 6 in her description of the manuscript. Cf. Putzo 2002.

[3] For simplicity, we use short forms for some texts in the following: *König Artus' Horn* = *Horn*, *Luneten Mantel* = *Mantel*, *Sultansbrief Abul Nasr* = *Abul Nasr*, *Sultansbrief Almansor* = *Almansor*, *Der König im Bad* = *König*, *Jeanne d'Arc* = *Jeanne*.

[4] While *Abul Nasr* begins on quire 23, it ends on quire 24, which shows other watermarks.

[5] The examinations of the watermarks were carried out in the period from January to April 2017 using the Bernstein meta-portal <www.memoryofpaper.eu> (last accessed 15 April 2018). To assess the meta-portal, 35 watermark databanks containing more than 240,000 examples of watermarks are included.

[6] Watermark 1 resembles WZIS_DE2910-PO-75104 (Freiburg, Breisgau, 1448) and WZIS_DE3285-PO-75109 (n.p., 1448); Watermark 2 resembles WZIS_DE2910-PO-75122 (Freiburg, Breisgau, 1449); Watermark 3 greatly resembles WZIS_DE1185-S306_272 (period of use: 1420/1430 by Jacobus de Voragine for ManuMed); Watermark 4 resembles: WZIS_CH0780-PO-76559 (???, 1452), WZIS_CH0780-PO-76562 (Lucerne, 1452) and WZIS_DE2910-PO-76565 (Freiburg/Breisgau, 1452); Watermark 5 resembles WZIS_CH0780-PO-76556 (Basel, 1451), WZIS_CH0780-PO-76571 (Neuenburg, 1452), WZIS_CH0780-PO-76572 (???, 1452), WZIS_CH0780-PO-76573 (???, 1452), WZIS_CH0780-PO-76574 (Lucerne, 1452), WZIS_DE1695-PO-76569 (Lichtenberg, 1452), WZIS_DE2730-PO-76576 (Friedberg, 1453), WZIS_DE2910-PO-76570 (Freiburg/Breisgau, 1452), WZIS_DE4200-PO-76595 (???, 1451), WZIS_DE4200-Lichtental66_999a (???, ???), WZIS_DE4620-PO-76577 (Danzig, 1454), WZIS_DE4620-PO-76578 (Stargard, 1455) and WZIS_DE8085-PO-76580 (Kirchheim / Teck, 1452). Watermarks 1 and 2 greatly resemble each other. These could be the watermarks of a paperwright mould-and-deckle pair. Unlike watermarks 1 and 2, watermark 3

Table 1: Structure of Codex germanicus 6

Page(s)	Content	Position in writing process[7]	Quire	Watermark(s)
flyleaf	index[8]		-	-
1	left blank		1	1
2a–4a	1 *König Artus' Horn*	B: 2, 4 / A: 3, 5, 6, 7, 8, 9, 10 / ?: 11, 12	1	1
4a–6b	2 *Luneten Mantel*	B: 4 / A: 1, 3, 5, 6, 7, 8, 9, 10 / ?: 11, 12	1	1
7	left blank		1	1
8a–365a	3 *Parzival*	B: 1, 2, 4, 5, 6, 7, 8, 9 / ?: 10, 11, 12	1–15	1, 2
365a	colophone (*Parzival*)		15	1
365a	4 *Artusnotiz*	A: 1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12	15	1
366	left blank		15	1
367a–560a	5 *Wigalois*	B: 1, 2, 4, 6, 7, 8, 9 / A: 3 / ?: 10, 11, 12	16–23	1, 2, 3
560a	colophone (*Wigalois*)		23	1
560a–567a	6 *Sultansbrief Abul Nasr*	B: 1, 2, 4, 7, 8, 9 / A: 3, 5, 10 / ?: 11, 12	23, 24[9]	2, 4, 5
567a–569a	7 *Sultansbrief Almansor*	B: 1, 2, 4, 8, 9 / A: 3, 5, 6, 10 / ?: 11, 12	24	4, 5
569a–575b	8 *Der König im Bad*	B: 1, 2, 4, 9 / A: 3, 5, 6, 7, 10 / ?: 11, 12	24	4, 5
576–587a	9 *Friedrich*	B: 1, 2, 4 / A: 3, 5, 6, 7, 8, 10 / ?: 11, 12	24, 25	4, 5
588	left blank		25	4
589a–610b	10 *Jeanne d'Arc*	B: 1, 2, 4, 6, 7, 8, 9, 11, 12 / ?: 3, 5	25	1, 2
611a–612b	11 *Lüttich*	B: 4, 12 / A: 10 / ?: 1, 2, 3, 5, 6, 7, 8, 9	25	1, 2
612b	12 *Notabile*	B: 4 / A: 10, 11 / ?: 1, 2, 3, 5, 6, 7, 8, 9	25	1, 2
613–614	left blank[10]		25	4

(quires 1-23 and 25) is probably older than the one showing watermarks 4 and 5 (quire 24 and the outermost double sheet of quire 25[11]). In addition, it should be considered that the only double sheet in the Cod. germ. 6, which has watermark 3, is the oldest. This is the innermost double sheet of quire 23. All the sheets of the manuscript contain vertical and horizontal lines drawn in lead (Pb) to circumscribe the writing area; the only exception is the double sheet with the watermark 3, where such lines are missing. It is noteworthy that the quality of the lines is not constant throughout the manuscript. They are fine and hardly discernable with the naked eye on the sheets with watermarks 1 and 2, but become thick and easily seen on the sheets with watermarks 4 and 5.

shows an additional circle in the forehead area and should be regarded as an independent watermark. Watermarks 4 and 5 resemble each other, but are not identical. The markedly different intervals between the catenary lines make a direct connection in the paper doubtful.

[7] Each number refers to the text number in the column on the left. 'B' stands for 'before', 'A' for 'after' and '?' for 'not yet clarified'.

[8] The index, also written by Jordan, mentions texts 3, 5, 6, 8, 9, 10, 11.

[9] Quire 24 begins on page 563.

[10] This page was pasted on the flyleaf of the inside of the back cover until the restoration of Cod. germ. 6 in 1967.

[11] As discussed in the previous article, this double sheet must have been added later. Cf. Rabin 2014 et al., 128. Cf. also Putzo 2002, 136–137, n. 134.

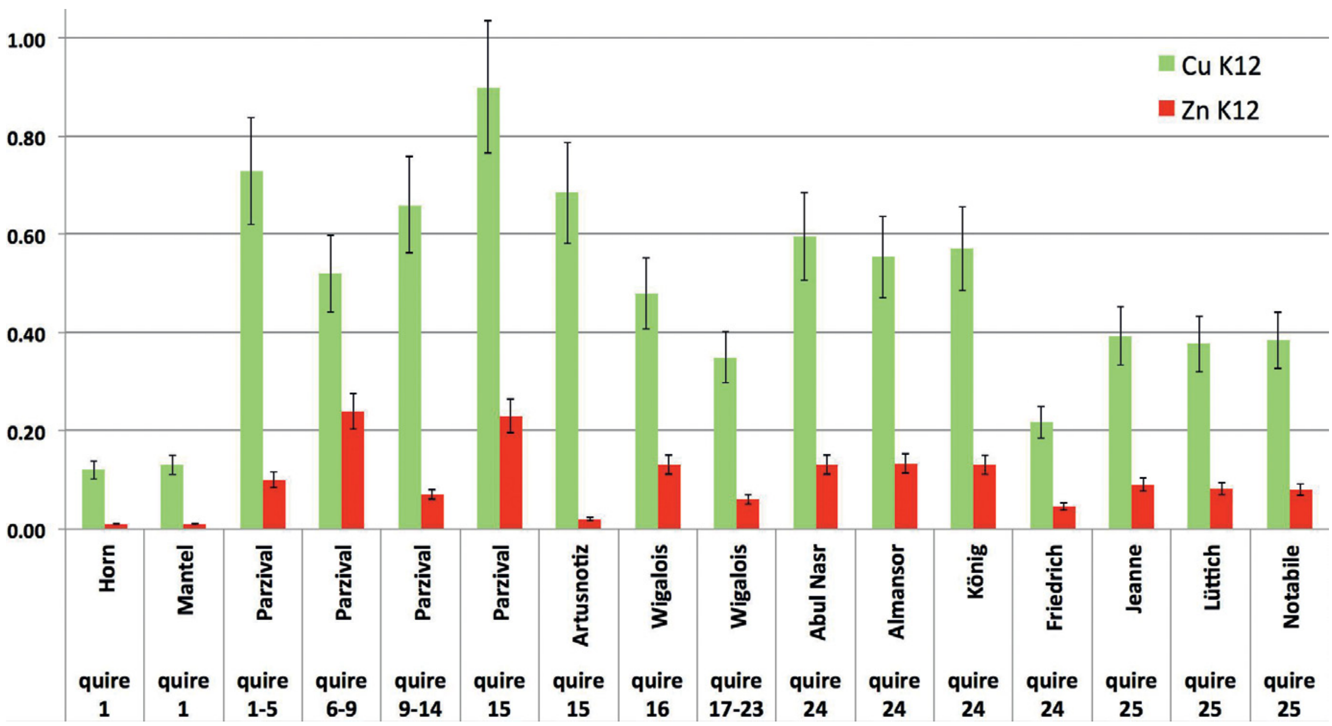


Fig. 1: Summary of the relative composition of the black ink in the texts of Cod. germ. 6.

The double sheet with the singular watermark 3 was most probably inserted to obtain sufficient paper to copy the *Wigalois* text. The lack of lines on this sheet may indicate that Jordan did not rule the paper himself. Moreover, the fact that the sheets with the *Parzival* and *Wigalois* texts (with the exception of the double sheet discussed above) and quire 25 possess the same watermarks may suggest that Jordan penned *Wigalois* after *Parzival* and the texts of quire 25.

Furthermore, inspection of Jordan's characteristic style reveals that he copied the *Meisterlieder* and *Friedrich* into the bound manuscript.[12] From the previous study of Cod. germ. 6, we also know that there is a gap between *Parzival* and *Artusnotiz*, meaning that the latter was added at the end of the writing process.

The arguments above suggest seven separate stages in the writing process of Cod. germ. 6: *Meisterlieder* / *Parzival*, / *Artusnotiz*, / *Wigalois*, / *Abul Nasr*, *Almansor*, *König* / *Friedrich* / *Jeanne*, *Lüttich* and *Notabile* (= quire 25). But one should keep in mind that each *Meisterlied* and each text of the twenty-fourth and twenty-fifth quire could be a single unit – and especially the short texts *Lüttich* and *Notabile* at the end of the bound manuscript could have been added later.[13] In the following, we demonstrate the extent to which the new material study supports or necessitates a revision of the grouping of the texts.

2. Results of the analysis of the black ink

Fig. 1 shows the amounts of copper and zinc in relation to iron, the main element of the iron gall ink. This fingerprint distribution summarizes the results for the black inks we measured. The green columns represent the values for copper, the red ones those for zinc.

In Cod. germ. 6, we measured eleven different sorts of black ink in total, with six inks used for the Arthurian romances, *Parzival* and *Wigalois*. The first of these, with its 350 pages, displays four different compositions of black ink, whereas the 200 pages of the second romance show two different inks. Therefore, it seems that Jordan had to acquire new ink after writing four to six quires, i.e. for approximately 100 to 150 pages. Furthermore, the change in the black ink at the end of the first romance and the beginning of the second indicates that the Arthurian romances in Cod. germ. 6 can be considered two separate units. The rest of the Codex consists of 10 short texts that were penned in 5 different inks, whereby no ink change ever occurred within one text. If every single ink composition corresponds to a single unit in the writing process, the texts can be grouped accordingly: *Horn*, *Mantel* / *Artusnotiz* / *Abul Nasr*, *Almansor*, *König* / *Friedrich* / *Jeanne*, *Lüttich*,

[12] The characteristic style of the *Artusnotiz* written on the right-hand column of page 365 provides no insight into this aspect.

[13] Rabin et al. 2014, 12.

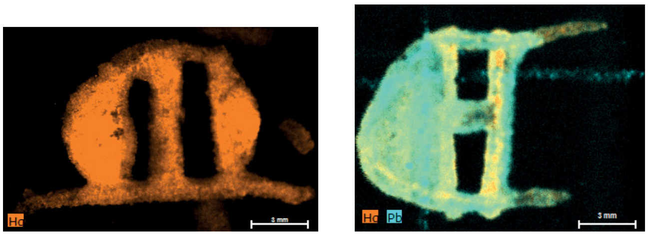


Fig. 2: Distribution of the element mercury (Hg) in the initial from the page 353 (*Parzival*, left) and in that of the mercury (Hg) and lead (Pb) on page 2 (*König Artus' Horn*, right).

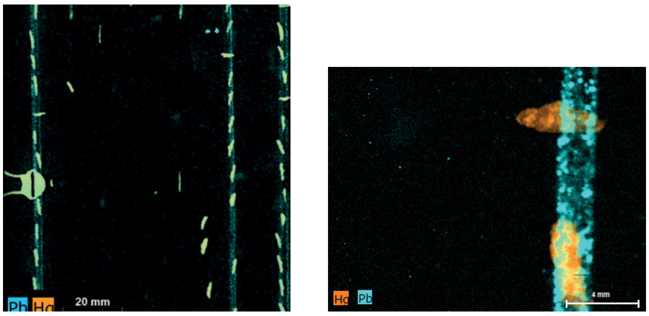


Fig. 3: Distributions of the elements mercury (Hg) and lead (Pb) on pages 558 (*Wigalois,* left) and 196 (*Parzival*, right), respectively.

Notabile. Thus, the measurements confirm the codicological suggestion that the two *Meisterlieder Horn* and *Mantel* form a single unit. They also corroborate our earlier finding, based on the composition of the red ink, that *Artusnotiz* presents a separate unit. The measurements of the black ink suggest two units in the twenty-fourth quire: the first three texts, *Abul Nasr*, *Almansor* and *König*, appear in one ink, forming one unit, while *Friedrich*, which was penned in another ink, would correspond to a separate unit. Finally, the measurements of the black ink in quire 25 indicate that *Lüttich* and *Notabile* at the end of the manuscript were not added later. They have the same black ink as *Jeanne*, the text placed at the beginning of the twenty-fifth quire.

The analysis of the black inks strongly supports the text units suggested on the basis of purely codicological study. Moreover, it reveals that the texts *Abul Nasr*, *Almansor* and *König* in quire 24 formed a single unit, while the texts *Lüttich* and *Notabile* in quire 25 were not added later.

If we assume that each unit corresponds to a copying stage from a certain exemplar, we suggest that the twelve texts in Cod. germ. 6 were copied from seven different exemplars.

3. Results of the analysis of the red inks

Unlike the black inks, the red inks of the codex present a rather complicated picture. Roughly speaking, the composition of the inks changes from pure cinnabar in *Parzival* to cinnabar adulterated with minium in other texts, whereby the content of minium progressively grows and even exceeds that of cinnabar in *Artusnotiz*. It is noteworthy that only the texts *Parzival*, *Artusnotiz* and those from quire 25 display a constant ink composition throughout the text and therefore can be used in conjunction with the conclusions based on the analysis of the black inks.

Jordan seems to have copied the *Parzival* text for his own use.[14] This view is offered by codicological quire analysis and is consistent with the composition of black and red inks. Similarly, *Artusnotiz* consistently presents a separate unit with its distinct, minium-rich red and black inks, which appear only in this text. The same arguments apply to the texts of quire 25. Their black inks indicate a single unit, while the red inks with less than 10% minium could suggest that the writing occurred between that of *Parzival* and that of *Wigalois*. The latter suggestion is, however, contradicted by their appearance on the separate quire, albeit written on paper identical to that of the *Parzival*. Therefore, we tentatively suggest that the texts of the twenty-fifth quire were penned first and later attached to the end of the manuscript when it was bound.

The remaining seven texts contain multiple rubrications, initials, titles and subtitles, a colophone (in *Wigalois*) and decorations executed in red inks whose composition doesn't seem to be well defined throughout the texts.

Two examples in Fig. 2 illustrate how the initials in *Parzival* and in *König Artus' Horn*, the first of the *Meisterlieder*, were executed. The distribution of mercury in the initials tracks the pigment cinnabar, whereas the element lead (Pb) corresponds to the pigment minium used to adulterate the very expensive cinnabar ink. In the left-hand picture, an example from the *Parzival* text, we see no traces of lead. However, one clearly sees that the pigment was added to the initial in more than one step. In the picture on the right, the initial from *König Artus' Horn* was also coloured in multiple steps. However, this time red inks with different degrees of adulteration were used, resulting in a composition with a

[14] The further explanations support Christine Putzo's thesis that Cod. germ. 6's compilation of texts was not planned from the outset. Cf. Putzo 2002, 65f.

Table 2: Summary of the red inks used to rubricate the texts.

Parzival	*Wigalois*	*Abul Nasr*	*Almansor*	*König*	*Artusnotiz*	*Friedrich*	*Meisterlieder*	quire 25
0	~0.2	~ 0.3	~0,4	~0.45	>1	~0.2	~0.2	~0.1

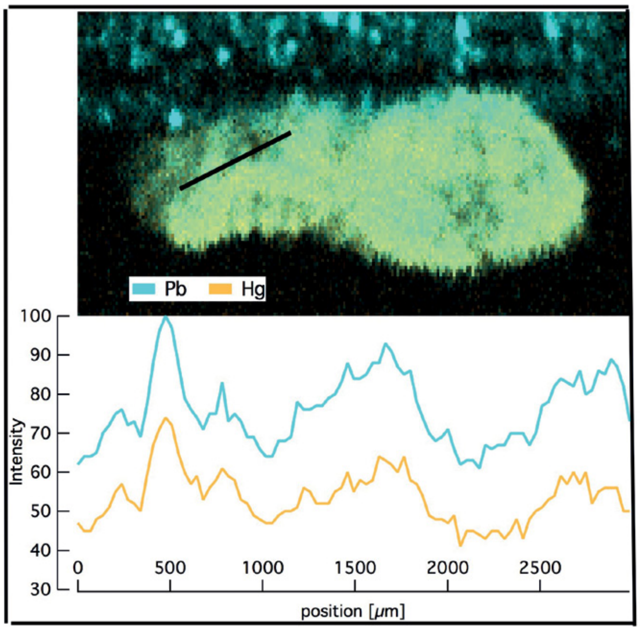
heterogeneous Pb/Hg ratio. We found this behaviour in the initials of every text studied except *Parzival* and the texts of the twenty-fifth quire.

The unequivocal determination of the red ink composition is further complicated because a larger number of rubrications fall on the first letters in the verses, which invariably coincides with the text area guiding line executed in lead. Fig. 3 demonstrates the distributions of the elements mercury and lead on pages 558 (*Wigalois*) and 196 (*Parzival*), respectively.

In the left-hand image, a fast overview scan of a large area displays the basic distribution of the red inks encountered throughout the manuscript. Two outer thin lead lines (in turquoise) belong to the layout of page 558, whereas the inner line corresponds to page 557. Its appearance reflects the fact that a paper sheet does not present the barrier to X-rays resulting from the element lead (Pb) that we detect in our analysis. Thick short lines in green result from the superposition of the orange colour we assigned to the element mercury (Hg) and correspond to the rubrications. We clearly see from this picture that only a small number of rubrications fail to coincide with the lead guideline. Moreover, initials are also at least partly drawn onto the existing lead lines. A more detailed scan on the right shows a portion of the guideline and the rubrications from the *Parzival* text on page 196. Here we see with greater clarity that the vertical rubrication coincides with the guideline, whereas the horizontal one crosses it. In the first case, no determination of the ink used for rubrication is possible, whereas in the second one we were able to use only a small portion of it.

For a quantitative evaluation of the Pb/Hg ratios, we extracted regions of interest and compared the spectra pixel by pixel using imaging XRF or, alternatively, used a line scanner to collect spectra from a virtual line across a region of interest. Fig. 4 illustrates the method and shows different typical ink profiles found in the manuscript under study. The composition of the black inks was determined in the same fashion.

In the first case, we present the data analysis for a rubrication from *Artusnotiz* on page 365 (Fig. 3 left). The profiles of the elements mercury and lead show a perfect match, reflecting that it was drawn with a single ink containing constant amounts of mercury and lead. In the second example, namely an initial from the text *Wigalois* (Fig. 3 right), the profiles of the elements Hg and Pb run



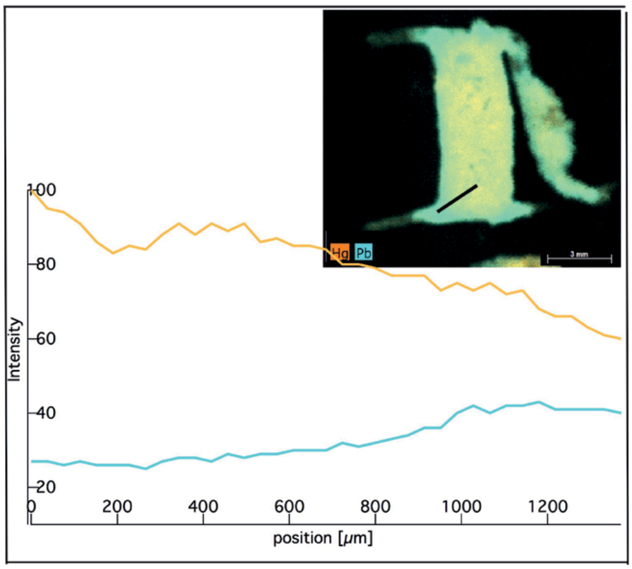


Fig. 4: Distributions of the elements mercury (Hg) and lead (Pb) extracted from the regions of interest for the rubrication on page 365 (*Artusnotiz*, left) and the initial on page 550 (*Wigalois*, right). The regions of interest or so-called line scans are indicated in the inserts showing the corresponding XRF images.

apart, clearly showing that inks of different compositions were involved in colouring this initial. In the latter case, we cannot determine unequivocally either the composition of the inks used or the sequence of their application.

Since neither initials nor first-letter rubrications can help reconstruct the production process, we are left with the in-text rubrications. Here of course, we cannot be sure that Jordan was adding all the rubrications in one go immediately after a text was penned. On the contrary, the analysis of the initials indicates that the red ink at hand was used during each correction cycle of the manuscript, producing random Pb/Hg ratios. Taking all the limitations into account, we have succeeded in estimating the composition of the red inks of the individual texts. In Table 2, the six texts are arranged in increasing order of minium content. The texts of the twenty-fifth quire, *Meisterlieder* and *Friedrich*, fall out of the scheme and are placed separately.

The values of the red inks not only place *Artusnotiz* outside of the main production process, they also indicate the singularity of *Friedrich*, *Meisterlieder* and the texts from quire 25. Interestingly, the similarity in the composition of the red inks found in *Friedrich* and *Meisterlieder* coincides with the result of the style study, namely that all three texts were written into the bound manuscript. Though the composition of the black inks speaks against grouping these texts together, the composition of the red inks could indicate that their completion was not separated by a large interval of time. On the other hand, the fact that the text of *Wigalois* was rubricated with similar inks should serve as a caution against using ink composition as the sole factor in the reconstruction of the manuscripts' production. In contrast, the composition of the red and black inks supports the codicological thesis that the texts of quire 25, i.e. *Jeanne*, *Lüttich* and *Notabile* constitute a single unit copied independently from the rest of the manuscript.

4. Note on the correction process

We observed many traces of multiple corrections. These include text cancelling performed in white lead or just crossing out in the red inks as opposed to direct overwriting in black and red inks. We interpret the overpainting of initials as a correction of the latter type. It seems that corrections of this type served to enhance the colour of the inks and were performed during multiple inspections of the manuscript. In principle, it might even be possible to reconstruct the correction cycles by comparing the composition of the correction ink with that of the original ink. However, such painstaking work would require a great deal more effort than what we have invested so far.

5. Conclusion

The analysis of the black inks confirms six 'gaps' in the writing process, which were already suggested codicologically. In addition, black and red ink analysis indicate that *Abul Nasr*, *Almansor* and *König* in the twenty-fourth quire, on the one hand, and the texts *Jeanne*, *Lüttich* and *Notabile* in the twenty-fifth quire, on the other, form two independent units, each probably copied within a relatively short time period. Combining the results of classic codicological examination with those obtained by materials analysis, we suggest the following seven stages in the writing of the texts in the Cod. germ. 6.: [I: *Parzival*], [II: *Jeanne*, *Lüttich*, *Notabile*] [III: *Wigalois*], [IV: *Abul Nasr*, *Almansor*, *König*], [V: *Friedrich*] [VI: *Horn*, *Mantel*] and [VII: *Artusnotiz*]. The importance of these findings for the collection's concept of Cod. germ. 6 will be presented in detail in Mirjam Geissbühler's dissertation (publication expected for 2018).

ACKNOWLEDGEMENTS

The Swiss National Science Foundation (SNF) and the Zeno Karl Schindler Foundation (Geneva), which enabled the advanced studies of Cod. germ. 6 by providing a scholarship.

The funding support provided by the German Research Foundation (DFG) for the SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa' / Centre for the Study of Manuscript Cultures (CSMC), University of Hamburg.

BAM Bundesanstalt für Materialforschung and -prüfung for the use of its instruments.

Irina Wandrey from the CSMC and Hans-Walter Stork and Jürgen Neubacher from the State and University Library Hamburg for their support of the material analysis.

AMENDMENTS TO THE PREVIOUS PUBLICATION

a. The quire formula of Cod. germ. 6 on page 127 can be elaborated to (VI+1)13 + 13 VI169 + VII183 + 7 VI267 + VI293 + (VI+2)307.

b. The statement on page 128 ('There is no indication that the remaining texts in the two last quires of the codex were penned before the two Arthurian romances, *Parzival* and *Wigalois*. It is therefore most likely that the two longer texts in the codex were the first to be transcribed.') has to be revised in view of this study and the evaluation of the watermarks. We find that the texts in the twenty-fifth quire might have been copied before *Wigalois* or even before *Parzival*.[15]

c. Two values in table 2 on page 129 have to be modified. Control measurements have shown that the second value in the table (Rubrication in *Parzival*) is below 0.01.

d. Page 130 states that the *Meisterlied Luneten Mantel* and *Notabile* show the same red ink (0.07 Pb/Hg). The re-investigation of the red inks proved this sentence to be wrong.

[15] This modification has also effects on table 1 on page 127 in the article. The improvements are not listed here, but they are considered in the first table of the present article.

REFERENCES

Bernstein – The Memory of Paper, The Bernstein Consortium, Institute for Medieval Research, Austrian Academy of Sciences. <http://www.memoryofpaper.eu/BernsteinPortal/appl_start.disp#> (last accessed 15 April 2018).

Putzo, Christine (2002), 'Cod. germ. 6', in Eva Horváth and Hans-Walter Stork (eds), *Von Rittern, Bürgern und von Gottes Wort: Volkssprachige Literatur in Handschriften und Drucken aus dem Besitz der Staats- und Universitätsbibliothek Hamburg* (Keil: Ludwig), 64–67 and 136–141.

Rabin, Ira, Oliver Hahn, and Mirjam Geissbühler (2014), 'Combining codicology and X-ray spectrometry to unveil the history of production of the Codex germanicus 6', *manuscript cultures*, 7: 126–31.

Article

The *Atri Fragment* Revisited I: Multispectral Imaging and Ink Identification*

Sebastian Bosch, Claudia Colini, Oliver Hahn, Andreas Janke, and Ivan Shevchuk | Hamburg

Abstract

This paper reports the outcome of an interdisciplinary team's application of multispectral imaging techniques and material analysis to a music fragment from the first decades of the fifteenth century: Atri, Archivio Capitolare, Museo della Basilica Cattedrale, Biblioteca del Capitolo della Cattedrale, Frammento 17. This important parchment leaf has rarely been investigated since its discovery 45 years ago. Thanks to the applied techniques and methods (such as the evaluation of the data using the fingerprint model), it is now possible to discuss new evidence supporting conclusions regarding the fragment's origin and afterlife.

The *Atri Fragment*

In 1973, Agostino Ziino reported the discovery of a music fragment from the first decades of the fifteenth century containing a copy of the well-known *Gloria Micinella* (Fig. 1) by the papal scribe and composer Antonio Zacara da Teramo (ca. 1360–1416).[1] This *Atri Fragment*[2] contains on its verso side the *ballata Be'llo sa Dio*, which recently could be attributed to the same Antonio (Fig. 2).[3] The secular text and the music of this *ballata* were (partially) transmitted and reworked in different contexts from the first decades of the fifteenth century until the end of the fifteenth century and even into the sixteenth century.[4] Unfortunately, not much more is known about this version of *Be'llo sa Dio*, since the verso side of the fragment suffered badly because bookbinders reused the parchment leaf at least two times.[5]

In this paper, a team consisting of scholars, scientists, conservators, and technicians revisits the *Atri Fragment*, applying state-of-the-art technology to recover the lost writing and to identify the inks used. This will lead to new insights on this important manuscript source from the beginning of the fifteenth century and allow further investigations.[6] This endeavour was made possible by the director of the Museum and Chapter Archive in Atri (Italy), Don Filippo Lanci, who gave permission to Francesco Zimei to carry this valuable object to the Centre for the Study of Manuscript Cultures in Hamburg for multispectral imaging and ink measurements during a two-day conference on *Liturgical Books and Music Manuscripts with Polyphonic Settings of the Mass in Medieval Europe*.[7] We thank Filippo Lanci and Francesco Zimei for the kind support that made this paper possible.

The fragment measures 24 × 30 cm and seems to already have been detached from its host volume by the time of its discovery.[8] Unfortunately, the host volume has yet to be found. There are not enough indicators that could help

* The research for this article was carried out in the context of the SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa' funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC).

[1] Ziino 1973. The *Gloria* is not complete, since the conjoint parchment leaf and the rest of the fascicle are missing.

[2] Atri, Archivio Capitolare, Museo della Basilica Cattedrale, Biblioteca del Capitolo della Cattedrale, Frammento 17; *olim* Archivio Capitolare, Sala Innocenzo IV, Cartella A, frammento n. 5.

[3] Janke and Nádas 2015.

[4] Ziino 1973, 237–239; Fallows 1999, 504–505, 2010a, 15, and 2010b; Wilson 2009, 41–55; Janke and Nádas 2015, 209–211.

[5] One concordance is found in the *San Lorenzo Palimpsest* (Florence, Archivio del Capitolo di San Lorenzo, MS 2211), fol. CXXXV^r, but without the text, see No. 151 in Janke and Nádas 2016.

[6] A second article on this fragment is in preparation by Andreas Janke and Francesco Zimei: 'The *Atri Fragment* Revisited II', forthcoming in the series *Musica Mensurabilis*, 9.

[7] Organised by Oliver Huck and Andreas Janke.

[8] See Ziino 1973, 235.

determine with certainty the recto and verso side, but the margins are wider on the right of the hair side and on the left of the flesh side, thus supporting Ziino's interpretation. Therefore, the legible part, the hair side, is referred to as the recto side (Fig. 1) and the mostly illegible flesh side as the verso side (Fig. 2).

After removing it from its original codicological structure, the fragment was surely reused to protect a fascicle, as were the fragments that today are referred to as the *Lucca Codex* (Lucca, Archivio di Stato, Ms. 184; Perugia, Biblioteca Comunale 'Augusta', Ms. 3065).[9] The *Atri* parchment leaf was folded in half: the fold is still visible, although the fragment is now perfectly flat, since it was particularly damaged by water or humidity. There are traces of mechanical damage, although some of the holes are compatible with archival sewing.[10]

The flesh side is much more damaged than the hair side, indicating that the latter was probably in contact with the fascicle while the former was the external part of the protection. The thickness of the fold, the place and number of the sewing holes and the different levels of damage to the parchment suggest that the fragment was used to protect a small fascicle, possibly containing the index of an independent volume or of an archival series. The fact that the right portion of the flesh side is more damaged than the left portion reinforces the hypothesis of an independently bound fascicle, unlike some of the *Lucca Codex* fragments, which were also reused as fascicle protections but stored or even sewn inside the host volumes. The level of damage seen in *Atri* indicates that the fragment was kept in this state for a considerable amount of time.

It is likely that in a second stage the fragment was reused again, this time as a paste-down of a different volume. The fragment was unfolded, and the now more damaged side was glued to the new board, using a water-soluble paste, gelatine, or starch-based adhesive. During this procedure, the fragment was damp: this may have caused a transfer of some parts and particles of the inks to the board (on the side in contact with the new binding), but also the washout of the more mobile ions from the ink strokes and their dispersion through the parchment's surface (on both sides). This reuse hypothesis is supported by the presence of a small round green stain in the margin of the verso, at the end of the 5th system (Fig. 2), possibly caused by the corrosion of a nail used to attach a fastening component. Another round mark, although larger and characterised only by a darker shade of the parchment, can be seen in the bottom corner of the same margin – it might also have been caused by a nail, in this case attaching a studded corner. Moreover, a group of woodworm holes is visible on the same margin (at the end of the 4th system), but none of the holes is present on the left margin. This indicates that they were most likely created when the fragment was unfolded. Since the majority of woodworm species prefer cellulosic material, it is unlikely that this damage was done while the fragment was part of its original parchment manuscript, but it is probable that the infestation was in the paper leaves or the wooden board of the second host volume.

More recently, the fragment underwent a conservation treatment. The detachment was probably done by humidifying the parchment so that the moistened glue softened, making the removal of the parchment more effective and less harmful to the support. It is possible that what was not damaged during the positioning of the paste-down was damaged during the removal, causing the partial transfer of the inks to the board, the abrasions on the parchment and the displacement of some of the movable ions from the inks to the support. The wet parchment was probably flattened after detachment while drying, since no wrinkle or wave can be seen, not even in the location of the middle fold.

Multispectral Imaging

Although Multispectral Imaging (MSI) is an established method for the recovery of lost writing, it is only in recent years that MSI has been applied successfully to different kinds of damaged music manuscripts, among them the *San Lorenzo Palimpsest*[11] and the *Rostocker Liederbuch*[12] – all work carried out by scholars and scientists connected to or collaborating with the Hamburg Centre for the Study of Manuscript Cultures.

[9] See the description of the 'vacchette' in Nádas and Ziino 1990, 15–16.

[10] See in particular in Fig. 1 the four small holes visible in the middle of the fold: first, above the 1st system; second, on the 4th stave line below the minima of the 2nd system; third, below the 5th system, but above the text (letter 'l' of 'altissimus'); fourth, on the 5th stave line of the 7th system. On the term 'archival sewing', see Szirmai 1999, 301, and 303, Fig. 10.15.a.

[11] Florence, Archivio del Capitolo di San Lorenzo, Ms. 2211, see Janke and MacDonald 2014, and more recently Janke and Nadas 2016.

[12] Rostock, Universitätsbibliothek, Mss. philol. 100/2. See *Digitales Archiv zum Rostocker Liederbuch (DARL)* <http://www.rostocker-liederbuch.de>. Ivan Shevchuk and Franz-Joseph Holznagel are preparing an article about the imaging process.

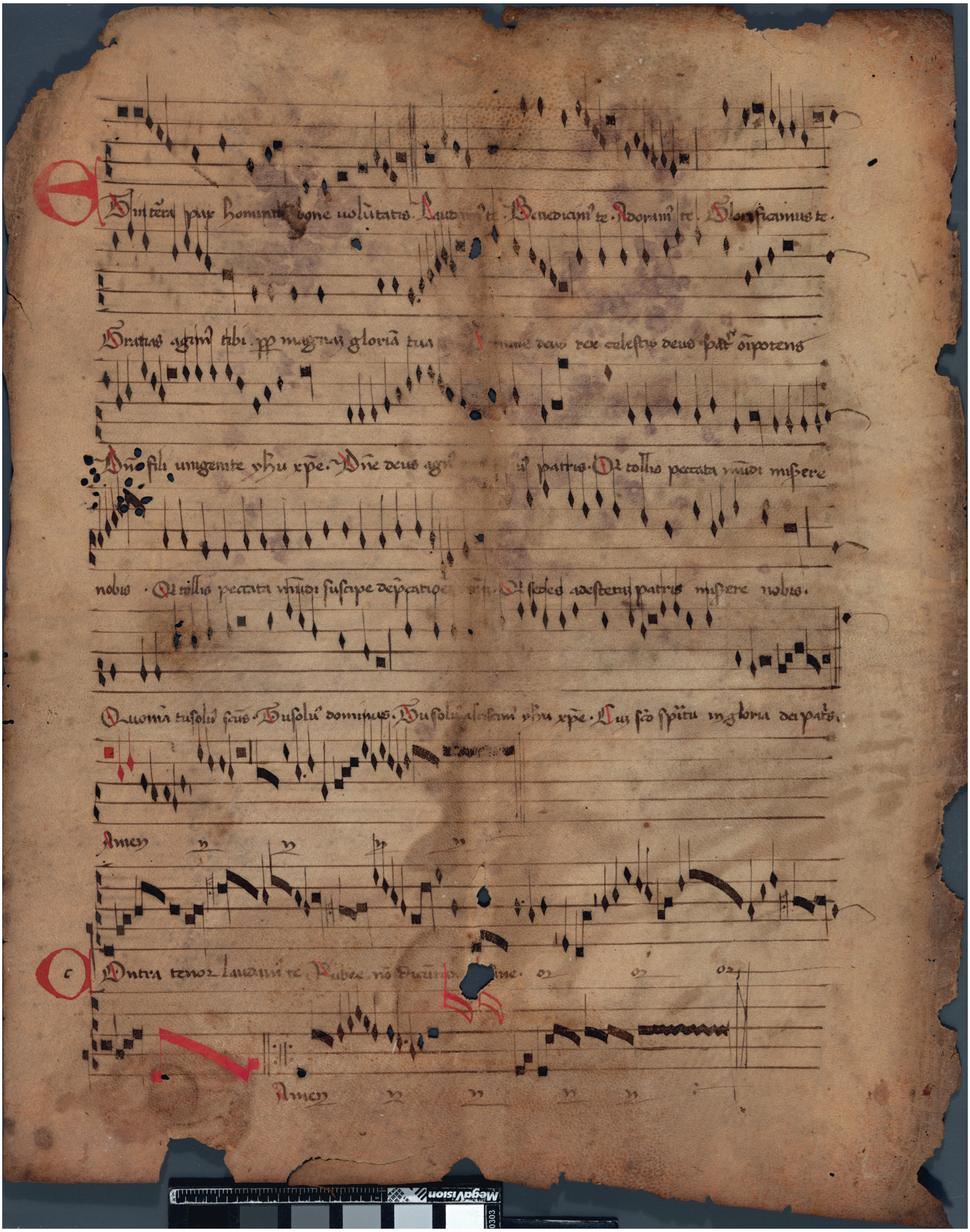



Fig. 1: *Atri Fragment*, recto.

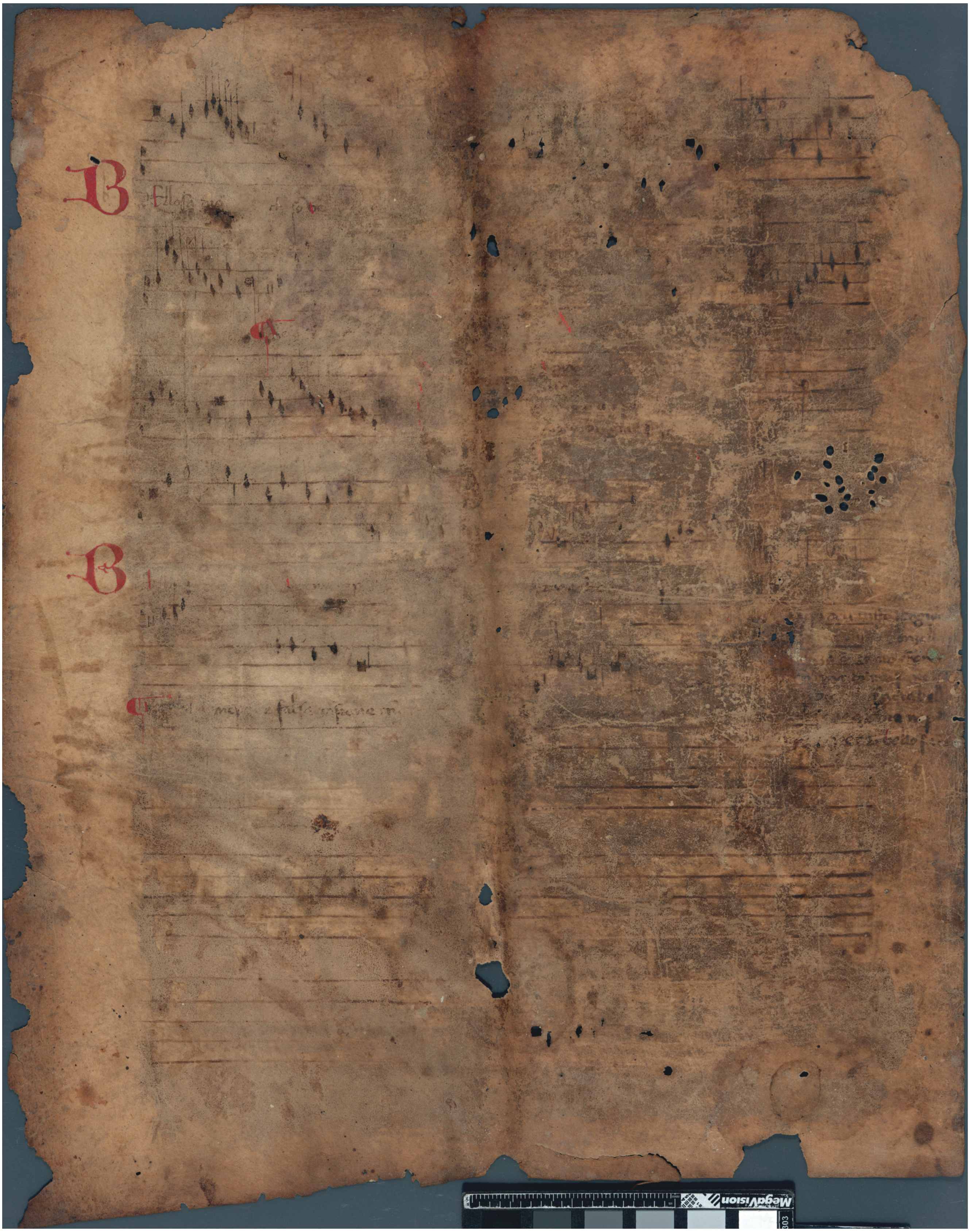


Fig. 2: *Atri Fragment*, verso.

Fig. 3: *Atri Fragment*, verso, processed image.

The general camera setup and processing methods have already been described in detail,[13] but in 2016 our MSI camera system was upgraded. Key hardware improvements include the use of more powerful LED light sources, with additional wavelengths in the ultraviolet and visible range, and a transmissive light sheet. In total, the number of images taken during a single sequence was increased from around 24 to 50 images. The illumination range of the imaging setup (365–1050 nm) has not been changed. A new Orange filter[14] was added to the filter wheel; it supresses shorter wavelengths below 550 nm and lets the longer wavelengths through. This filter has proven to be especially useful for the recovery of iron gall inks. Fluorescence images taken with the Orange and Red filter[15] using short wavelengths in the region of 365–450 nm provided most of the useful information for the recovery of *Be'llo sa Dio*.

The image processing was performed in two steps: First, feature extraction, using statistical analysis techniques, was performed in ENVI 5.3 Classic by extracting independent and principal components of the fragment. Second, the contrast between the writing, extracted during statistical processing, and the background was increased to further improve overall legibility and appearance in GIMP 2.8.22. For statistical processing, the 50 greyscale images were divided into four different types: reflectance (20), fluorescence (22), raking (4) and transmissive (4), and each was statistically processed separately. Images of each type were combined into 3D Arrays (cubes). Standard image-processing algorithms, such as Independent Component Analysis (ICA) and Principal Component Analysis (PCA), were applied to the pre-processed image cubes. After statistical processing, a pseudocolour image was created from the bands that held the best information. The result can be seen in Fig. 3.

Compared with the verso side seen with the naked eye (Fig. 2), the pseudocolour image reveals significantly more of the music and text. This is especially true for the void notational signs, which by their nature disappear quickly when the surface of a manuscript is damaged. Further, we can now recognize two text *residua*,[16] which allow us to understand the text and its transmission in a much clearer way.[17] Particularly interesting is the *custos*[18] at the end of system one. In the pseudocolour image, it is rendered more legible; moreover, we can also see *custodes* in systems two and four. All three of them resemble the *custodes* used on the recto side. This is usually an indication that both musical settings were written by the same scribe. However, a closer look reveals slight differences in the shapes of the note signs between the recto and verso side, which could contradict the hypothesis of a single scribe. We will return to this question after having discussed the ink measurements.

On the recto side, remnants of red ink can barely be seen in the top margin (Fig. 1).[19] In music manuscripts from the beginning of the fifteenth century, this is usually the space used for providing composer attributions (if intended by the compiler). In this case, the name of the composer of the *Gloria* – Antonio Zacara da Teramo – is already known due to concordances of the *Gloria* that appear in other manuscript sources.[20] One of these provides an attribution: 'Z. Micinella', which refers to Antonio Zacara da Teramo. Since the residue red ink does not block the underlying parchment from fluorescing, as there are no fluorescence blockers such as tannins, it is difficult to recover the text using the fluorescence images. However, the outline of what had been the attribution can be partially recovered using ICA on reflectance images and appears in black in Fig. 4.

Unfortunately, due to the properties of the red ink and the damage to the fragment, the composer's name could not be recovered in a way that allows one to read at least parts of it. However, it is now possible to understand that originally a quite extensive attribution (ca. 66 mm) was entered on the

---

13 Janke and MacDonald 2014; Janke and Nádas 2016, vol. I, 9–15.

14 Wratten O22 Deep Orange Longpass filter.

15 Wratten R25.

16 Usually the refrain and the first stanza are written below the musical notation. A text *residuum* contains additional stanzas of the poem and is written down in a single text block wherever on the page or the opening space was available.

17 The text will be discussed in Janke and Zimei (forthcoming).

18 The sign placed at the end of a system to denote the pitch of the first note in the following system.

19 The verso side also shows some remnants of red, but not in the correct position for an attribution.

20 The *Gloria* is found in five other sources: Bologna, Civico Museo bibliografico musicale, Ms. Q 1, recto; Bologna, Civico Museo bibliografico musicale, Ms. Q 15, fols 16v–17r; Bologna, Biblioteca Universitaria, Ms. 2216, fol. 4v; Grottaferrata, Biblioteca dell'Abbazia di S. Nilo, Ms. segn. provv. Kript. Lat. 224, fol. 4v; London, British Library, Add, Ms. 82959, verso.

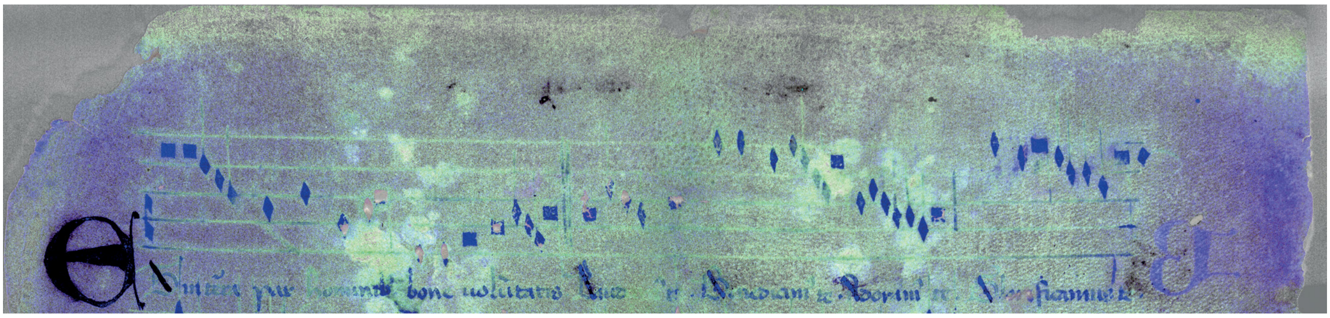


Fig. 4: *Atri Fragment*, recto, processed detail.

recto folio. It is quite possible that the attribution included not only a name, but also toponymic information such as ‘Teramo’ or other descriptors like ‘Micinella’.[21]

Ink measurements

In the field of manuscript studies, the application of analytical techniques can provide valuable information about the material composition of artifacts and is thus capable of answering still unresolved questions about the history of manuscripts. However, dealing with such precious objects requires careful handling and non-invasive methods. In combining fast, precise and non-destructive data acquisition, X-ray Fluorescence Spectroscopy (XRF) has been established as a powerful tool in identifying inorganic compounds in inks and colourants used for writing and decorating manuscripts.[22] Here, we can demonstrate the potential of XRF analysis applied to the determination of the inks (black[23] and red) used in the *Atri Fragment*. The XRF results of the red ink are further supported by additional measurements with visible spectrophotometry – another non-destructive method for the identification of colourants based on their properties in reflecting visible light. Additionally, we will point out some limitations of the applied analytical methods and comment on the exact analytical protocol, which had to be adapted in a specific way in order to collect reliable data in a limited period of time.[24]

The XRF analysis was carried out with the energy dispersive micro-X-ray spectrometer ELIO,[25] which consists of an air-cooled, low-power rhodium tube (40 kV, 20 µA) as excitation source, a large-area silicon drift detector (SDD, 25 mm^2) and a microscope camera for easy object positioning. The excitation X-ray beam is collimated to a 1.2 mm spot diameter on the sample surface, which also offers the possibility of precisely analysing very small ink areas. Recorded XRF spectra were evaluated with the ArtTAX software[26] and finally presented here, making use of the fingerprint model.[27]

The red ink in the *Atri Fragment* was further examined with the colour spectrometer eXact[28] in order to measure the reflection of visible light (380–730 nm) from coloured materials such as dyes and pigments. The measuring spot is 1 mm in diameter and illuminates the object at an angle of 45° for less than a second using a small 2 W light bulb. The reflected light from the object’s surface is recorded in a resulting reflectance spectrum, which can be compared with a reference in order to identify the specific colourant.[29]

---

[21] There are around forty known attributions that refer to Antonio Zacara da Teramo. These are discussed and listed in Nádas 1986, 172–174. See also the catalogue of works by this composer in Zimei 2004, 391–419: 400–401 and Janke and Nádas 2015, 201–202. One cannot rule out the possibility that the missing verso side of this opening, which once contained all voices of Antonio’s *Gloria*, also contained parts of the attribution. On another erased (and this time overwritten) attribution by Antonio Zacara da Teramo, on fol. 55^r in the *Lucca Codex*, see Calvia 2017, 46–52.

[22] See for example Hahn et al. 2005.

[23] This refers also to inks that today appear to be brown.

[24] The fragment had to be imaged and measured within only two days.

[25] XGLab S. R. L., Italy.

[26] Bruker Nano GmbH, Germany.

[27] Hahn 2010.

[28] X-rite GmbH, Germany.

[29] Fuchs and Oltrogge 1994.

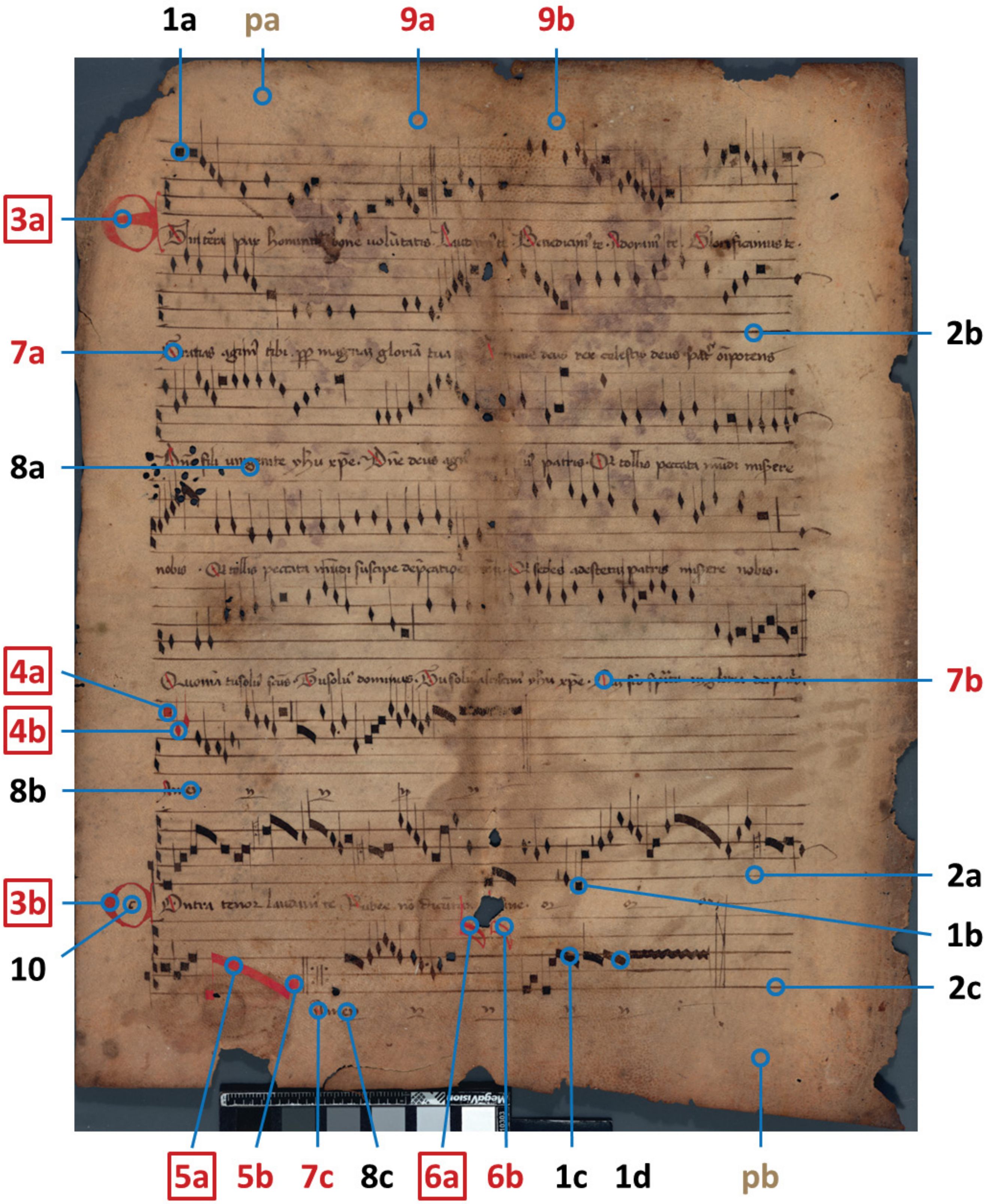


Fig. 5: Measured spots on the recto side of *Atri Fragment*. The black, brown and red numbering corresponds to XRF measurements. Numbers with a red frame indicate additional reflectance measurements by spectrophotometry.

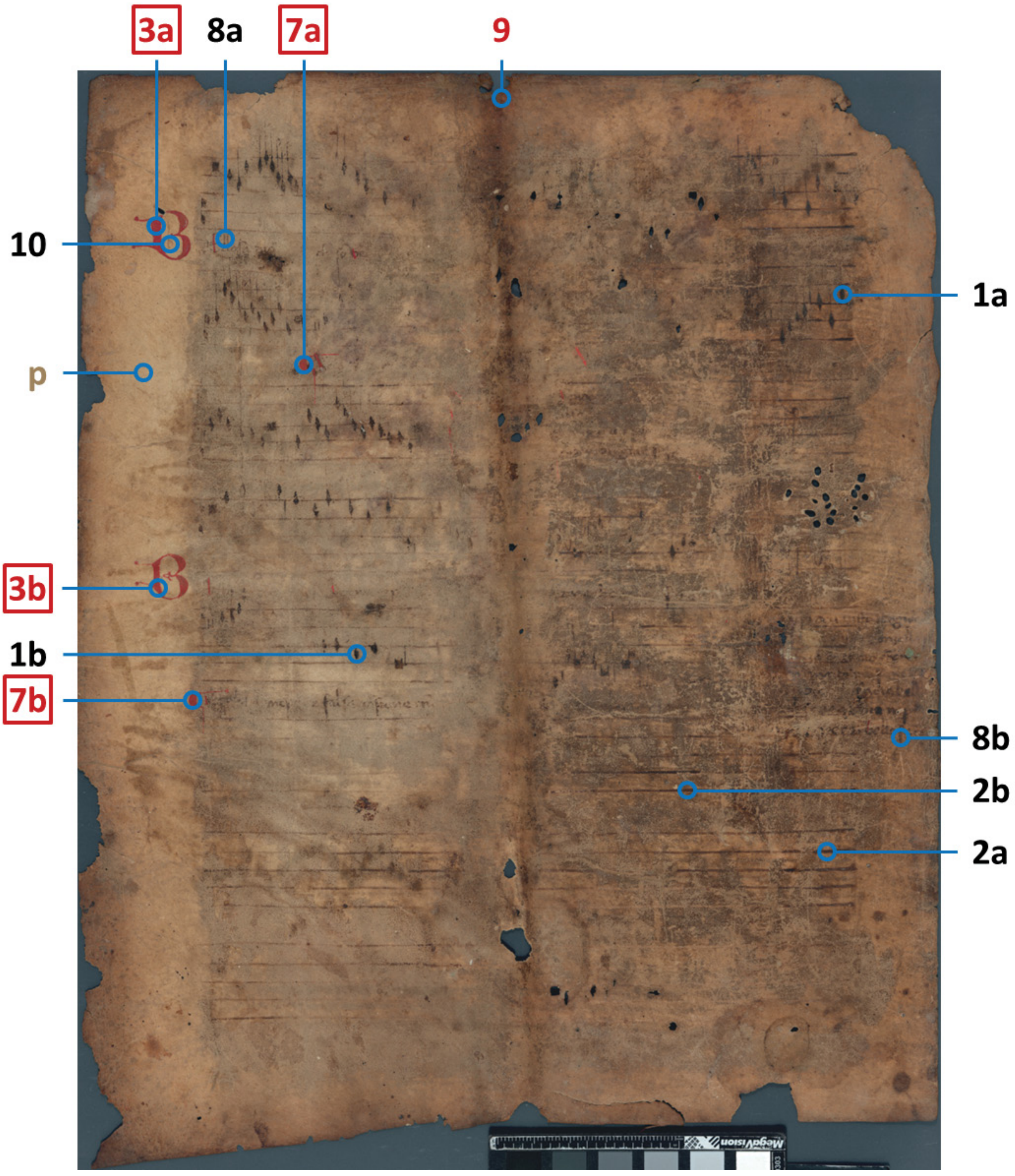


Fig. 6: Measured spots on the verso side of *Atri Fragment*. The black, brown and red numbering corresponds to XRF measurements. Numbers with a red frame indicate additional reflectance measurements by spectrophotometry.

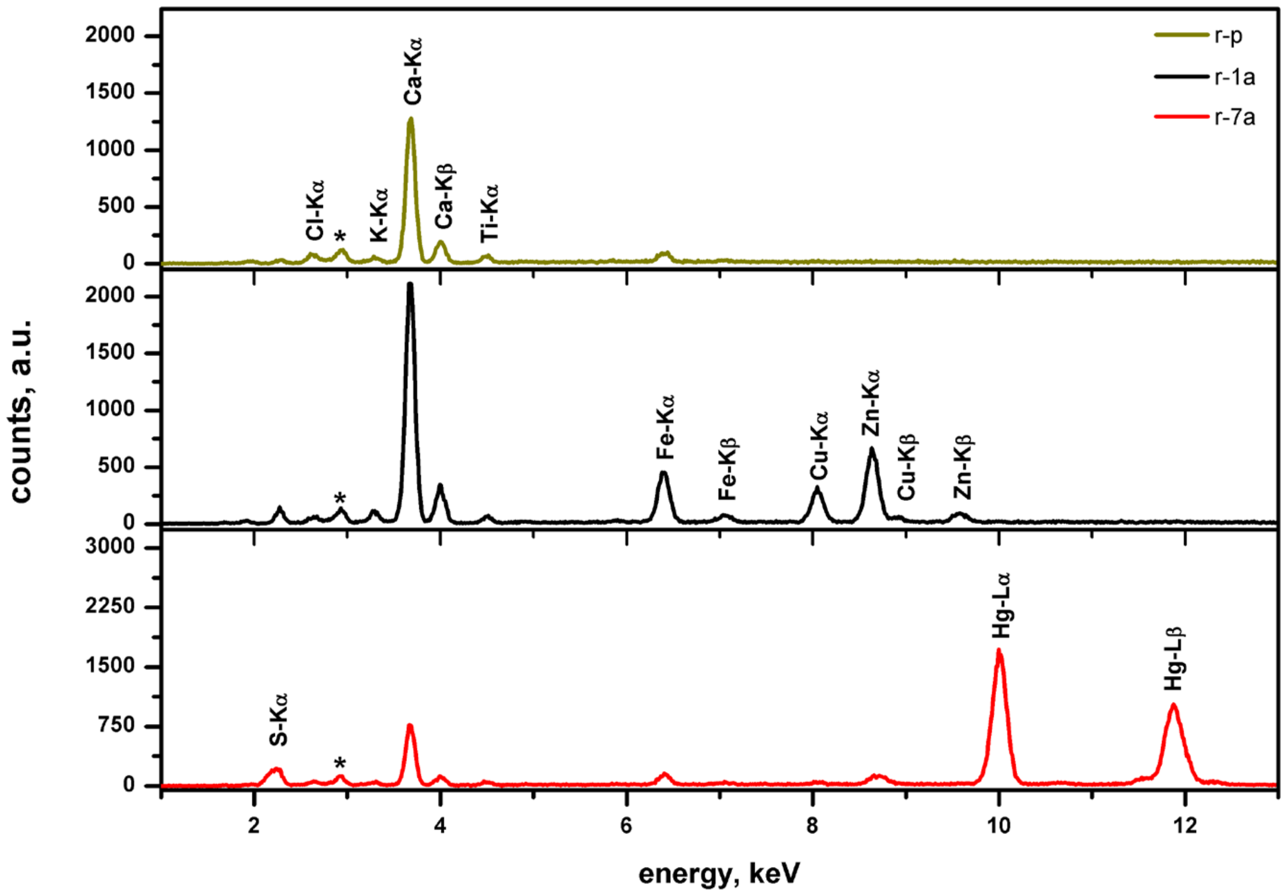


Fig. 7: Raw XRF spectra of parchment (r-p), iron gall ink (r-1a) and cinnabar (r-7a). The asterisk (*) labels the Kα peak of Argon (Ar-Kα) present in the air.

Figures 5 and 6 show the measuring points on both sides of the *Atri* leaf, where we recorded reliable data via XRF (black, brown and red numbering) and spectrophotometry (red frame).[30] The areas of interest for black inks are thereby:

- musical notation: r-1a, r-1b, r-1c, r-1d, v-1a, v-1b
- stave lines: r-2a, r-2b, r-2c, v-2a, v-2b
- text underlay[31] and text *residuum*: r-8a, r-8b, r-8c, v-8a, v-8b
- guide letters: r-10, v-10

The areas of interest for red inks are:

- initials: r-3a, r-3b, v-3a, v-3b
- red notation: r-4a, r-4b, r-5a, r-5b, r-6a, r-6b
- highlights: r-7a, r-7b, r-7c, v-7a, v-7b
- residues on top of page: r-9a, r-9b, v-9

And, finally, we measured some reference spots from the parchment (r-pa, r-pb, v-p). It is important to point out some limitations in the XRF analysis of manuscripts, especially when using the semi-quantitative fingerprint model.[32] Due to the high penetration depth of X-rays, detected signals are always the sums of emitted X-rays from the surface materials of interest and all underlying parts, such as the writing support and the materials from the rear side of the folio. For that reason, it is necessary to exclude these interfering signals by selecting the right analytical protocol, which will be described in the following.

Rear-side effects can be minimised by predefining the most promising measuring points prior to the actual measurements. These areas are certainly limited in the case of parchment leaves, which have writing on both sides. Suitable spots must be identified by shining white light through the folio in order to discern the writing from the rear side. This was particularly challenging in the case of the *Atri Fragment*,

[30] The letters 'r' and 'v' stand for recto and verso.

[31] This term denotes the poem's text written below the musical notation.

[32] The fingerprint model is described in detail below.

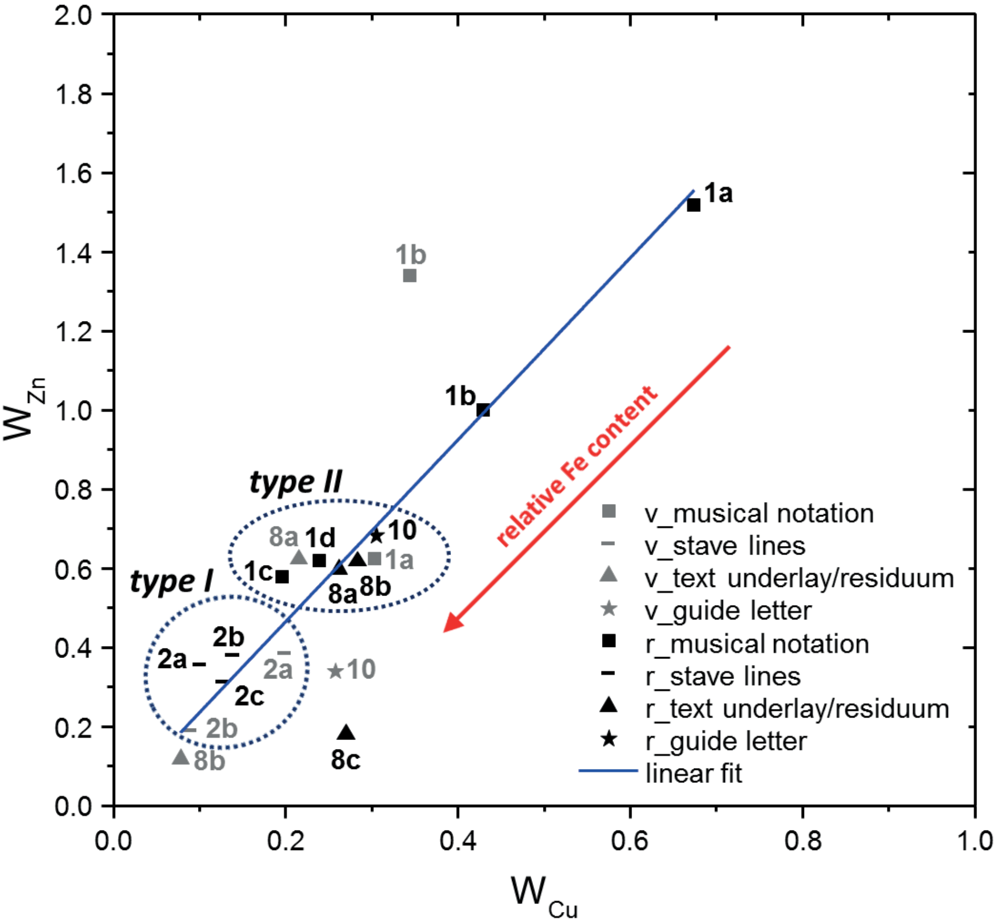


Fig. 8: Evaluated XRF data for all measured black spots without the subtraction of parchment using the fingerprint model. The composition fingerprint of zinc (W_{Zn}) as a function of the fingerprint of copper (W_{Cu}) leads to the clustering of two different ink types determined for the *Atri Fragment*.

due to its poor physical condition. Nonetheless, we managed to collect XRF data of 39 spots in total (Figs 5 and 6).

Some measurements were also taken from the parchment itself, since this data is usually used as a reference to exclude the influence of the writing support by simply subtracting integrated XRF signal intensities. However, in the present case we were faced with some difficulties in applying this procedure for the differentiation of the black iron gall inks (Fig. 7). These inks are mainly composed of iron (Fe), which could be also detected in reasonable amounts in the reference spectra of the pure parchment. Indeed, iron might be part of the parchment itself, but it is very likely that the possible water damage flushed out a class of ions from the inks, which then were randomly distributed throughout the fragment. Furthermore, at some measuring points only small amounts of ink material remained, causing rather low signal intensities and thus resulting in higher error rates when subtracting the parchment signals. Despite all these limitations, we were able to identify two types of iron gall ink (types I and II) by applying the fingerprint model to the raw data without parchment subtraction (Fig. 8).

Inorganic contaminants, such as copper (Cu) and zinc (Zn), that are present in the iron gall inks provide a basis for the characterization. Further discrimination is possible with the 'fingerprint'. For a certain minor constituent 'i' (such as Cu and Zn), a characteristic value, 'W_i' can be specified. The fingerprint method relies on the determination of specific elemental compositions in samples. These kinds of investigations are well-established methods for provenance and dating studies of glass objects,[33] as well as for the chronological classification of alloys.[34] The present XRF measurements for the iron gall inks were quantified using the composition fingerprint model, which is based on fundamental parameter procedures leading to the value W_i

[33] Hoffmann et al. 2000.

[34] Rye 1993.

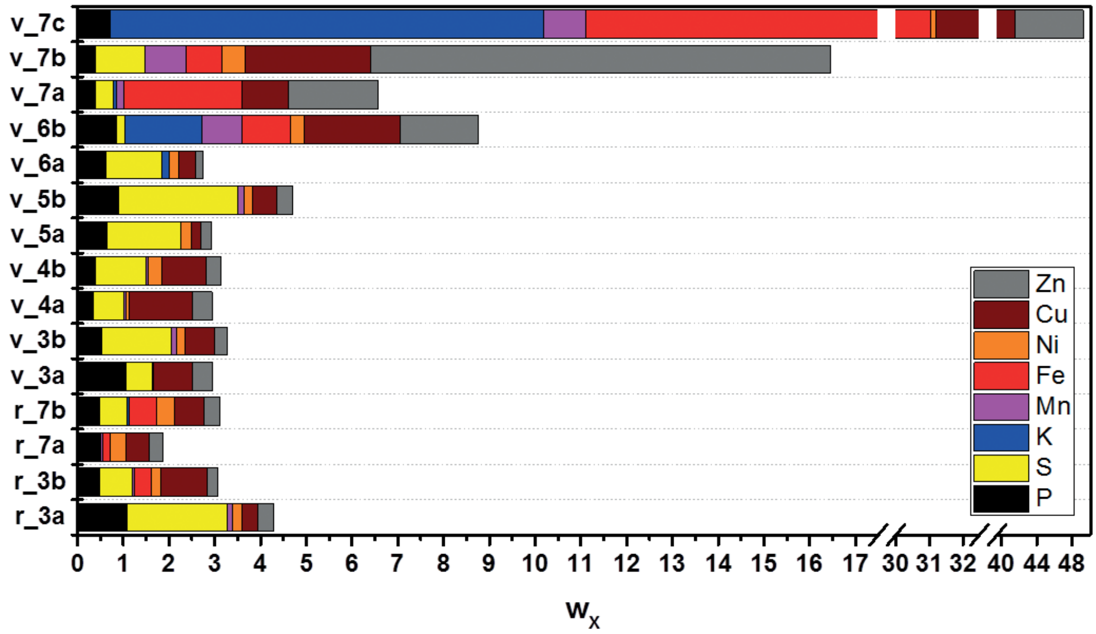


Fig. 9: Evaluated XRF data for all measured red spots depicted in a bar graph representation of trace elements (W_X in percentage) relative to mercury (Hg). Here, the amount of these trace elements is shown as a percentage of the amount of Hg, which is the main element in cinnabar (see Fig. 7).

(relative amount of weight concentration of the element i relative to Fe). The composition fingerprint value W_i involves mainly three different parameters: the experimentally determined transmittance of the entire layered system, the penetration depth of the writing material into the writing support and a normalized absorption coefficient taking into account the matrix composition. The respective calculations are based on a model ink containing a certain amount of iron sulphate as a constant parameter. Small variations of any other parameters do not crucially affect the value of W_i. Determination of such a 'fingerprint' – i.e. the amount of a minor metal component relative to the main compound iron – allows the characterization of different inks even in the absence of absolute quantification.[35]

The evaluated results of the examination of iron gall inks used in the *Atri Fragment* clearly demonstrate a clustering effect of different composition fingerprint values (W_i) for the trace elements copper (W_{Cu}) and zinc (W_{Zn}). Whereas the lines of the staves (ink type I) contain low amounts of copper and zinc, the musical notation and text underlay/ *residuum* (ink type II) display a significantly higher amount of these trace elements. This compositional difference finally revealed the presence of two different ink types used for the production of this manuscript. Besides this clear result, some measured spots do not belong to these ink clusters, which can be explained by effects such as the random distribution of washed-out ions and/or the small amount of ink material remaining in these specific positions. However, considering the relatively large number of analysed spots, these outliers can be neglected in the present case.

As depicted by the fitting line in Fig. 8, another interesting result – the constant ratio of the copper and zinc fingerprint values ($2W_{Zn} = W_{Cu}$) – indicates that both ink types were produced with the same sort of vitriol. As one of the main ingredients in historical iron gall inks, the vitriol (mostly a mixture of $FeSO_4$, $CuSO_4$ and $ZnSO_4$) predefines an ink's elemental ratio between iron and trace metals such as copper and zinc. Thus, the two ink types determined in the *Atri Fragment* differ mainly in their relative amount of iron. Since the same vitriol was used for both ink types, we conclude that the manuscript's severe exposure to water lowered the iron content in ink type II. This can be explained by the different amounts of formerly used gallic acids in the ink recipes. The low amount of gallic acid in ink type II thereby led to the formation of fewer ferrous gallate complexes that afterwards were oxidised to the hardly water-soluble ferric pyrogallate

[35] Hahn et al. 2004; Malzer et al. 2004

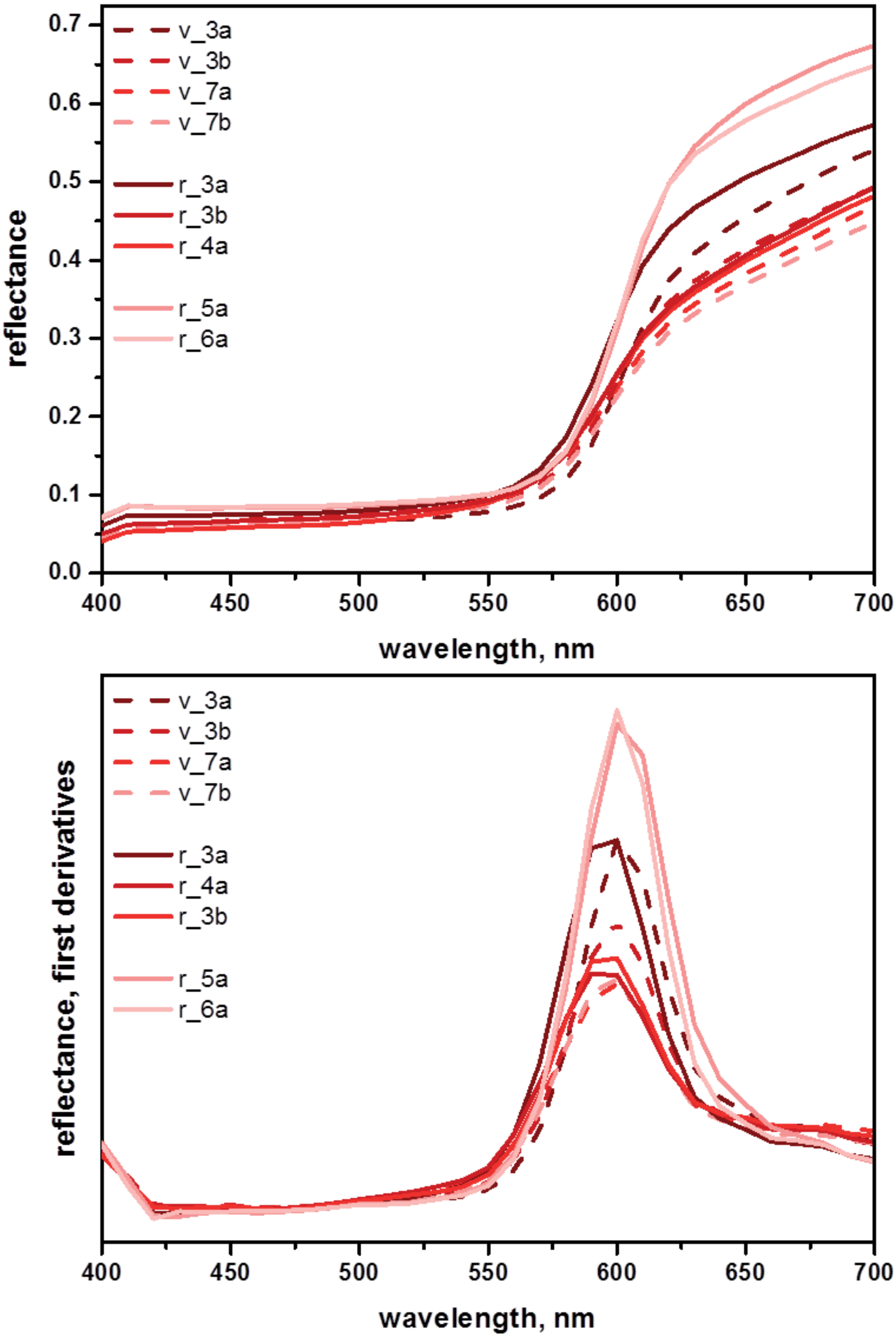


Fig. 10: Reflectance spectra of the red spots and their corresponding first derivatives, showing all inflection points at 600 nm, which is characteristic for cinnabar.

complexes.[36] The remaining iron ions not complexed by the gallic acid display a general higher solubility and thus would be washed out more easily in contact with water. This finally leads to the lower amount of iron in ink type II. Ironically, this distinction between ink types by XRF measurements could not have been detected without the severe water damage to the analysed manuscript, since only the washing out of metal ions led to the different final ink compositions.[37] Interestingly, this effect caused the same elemental changes

[36] Krekel 1998.

[37] We assume that free iron ions, being not complexed by the gallic acid, were washed out of the ink material, and thus conclude that different ink batches with varying amounts of gallic acid were used in this case.

on both sides of the folio, which leads to the assumption that the stave lines (ink type I) and the black notation and text underlay/*residuum* (ink type II) are the same on both the recto and verso sides.

Regarding the measurements of red ink, no significant changes in the different measured spots could be detected, since they all showed a typical XRF spectrum of mercury sulphide (HgS), the main compound in the pigment vermillion made from the mineral cinnabar (Fig. 7). Therefore, it can be assumed that only one type of red ink was used for the *Atri Fragment*. Only minor changes in trace elements could be identified for most of the spots (Fig. 9). As in the case of the black inks, some outliers (r-6b, r-7a, r-7b, r-7c) can be explained by the low amount of ink in these positions and the resulting higher influence of surrounding materials and parchment constituents. The spots at the top of each side (r-9a, r-9b and v-9) present the same problem and are therefore not shown in Fig. 9. However, the presence of a residual trace of mercury was detected. Such data is consistent with the MSI results depicted in Fig. 4 (r-9a and r-9b).

The XRF results of the red ink are further confirmed by the recorded reflectance spectra shown in Fig. 10. The analysed spots show similar spectral behaviour and the same inflection points at 600 nm, which is characteristic for cinnabar.[38]

Results and conclusion

The *Atri Fragment* is the remnant of a collection of polyphonic music, be it a larger volume or a smaller unit[39]. Due to its afterlife use, the surface of the verso side in particular was rendered mostly illegible, but thanks to the MSI techniques applied we were able to make most of the original writing visible, allowing further investigation, which would not be possible with simpler methods such as the sole use of ultraviolet light.[40] One important outcome is that the text of the *ballata* can now be clearly recognised as being concordant with the version of the much later *Chansonnier Cordiforme*. While in this codex the text is incomplete, we find the full text in the *Atri Fragment*.[41]

Not surprisingly, the *Atri Fragment* was produced with iron gall inks and a red cinnabar ink, as was common practice. From the limited surviving contents, it is difficult to say what the main repertorial interest of the compiler was. The only evidence at this point is the extensive attribution on the recto side, which leads to the assumption that the *Gloria* belonged to the main repertory of the original manuscript. It is very likely that the verso side never contained a composer attribution; at least there is no clear trace of it to be found by applying MSI or ink measurements. Further, the *ballata Be'llo sa Dio* differs in visual appearance from the *Gloria*, especially regarding the notational signs. These observations allow us to assume that *Be'llo sa Dio* was added to the manuscript at a different time than the *Gloria*. One could speculate that the surviving fragment might have been the final leaf of a fascicle, which was originally blank on its verso side (except for the stave lines). *Be'llo sa Dio* would be a typical piece, small enough to be added later to a manuscript wherever space was left free.[42] The fact, however, that only one type of *custos* is used on both sides and that the same ink was used for the music and text (ink type II), leads to the conclusion that both musical pieces were written by the same scribe. Therefore, any difference in the shape of the note signs between the recto and verso side probably derives from using differently sized pen nibs. The possibility of differentiating two ink types was – in this case – detectable only due to the severe water exposure of this fragment.

Ink type I was used beforehand in a preparatory step to draw all stave lines. It cannot be determined whether the same person was involved using a different ink or if someone else prepared the folios before the music scribe started his work. Due to the same relative elemental composition of trace elements, however, we can conclude that both inks were prepared in the same region with the same sort of vitriol.

38 Aceto et al. 2004.

39 E. g. a fascicle manuscript. This term was coined by Charles Hamm, see Hamm 1962.

40 Agostino Ziino reported this to be unsuccessful in the case of the *Atri Fragment*, see Ziino 1973, 237.

41 Paris, Bibliothèque nationale de France, Rothschild 2973 (I.5.13), fols 1^v–2^r. The two text versions and the variants will be discussed in Janke and Zimei (forthcoming).

42 See the discussion on 'space filler' pieces in the *San Lorenzo Palimpsest*, and specifically No. 151 in the Inventory in Janke and Nádas 2016.

REFERENCES

Aceto, Maurizio, Angelo Agostino, Gaia Fenoglio, Ambra Idone, Monica Gulmini, Marcello Picollo, Paola Ricciardi, and John K. Delaney (2014), 'Characterization of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry', *Analytical Methods*, 6: 1488–1500.

Calvia, Antonio (2017), 'Nuove osservazioni su "Donna, posso io sperare?" e sulla ballata dialogata polifonica nel Trecento italiano', *Philomusica on-line*, 16. <http://dx.doi.org/10.13132/1826-9001/17.1895>.

Fallows, David (1999), *A Catalogue of Polyphonic Songs, 1415–1480* (Oxford: Oxford University Press).

—— (2010a), 'Catalogue Appendix', <http://personalpages.manchester.ac.uk/staff/david.fallows/appendix.pdf>.

—— (2010b), *Chansonnier de Jean de Montchenu (ca. 1475). Kommentar zum Faksmile der Handschrift Rothschild 2973 (I.5.13) in der Bibliothèque Nationale de France*, German transl. by Susan M. Weinert (Münster and Valencia: Verl. Biblioteca Rara and Vicent García).

Fuchs, Robert and Doris Oltrogge (1994), 'Painting Materials and Painting Technique in the Book of Kells' in Felicity O'Mahony (ed.), *The Book of Kells*: *Proceedings of a Conference at Trinity College Dublin 09/1992* (Aldershot et al.: Scolar Press et al.), 133–171.

Hahn, Oliver, Wolfgang Malzer, Birgit Kanngießer, and Burghard Beckhoff (2004), 'Characterization of Iron-Gall Inks in Historical Manuscripts and Music Compositions using X-Ray Fluorescence Spectrometry', *X-Ray Spectrometry*, 33: 234–239.

——, Birgit Kanngießer and Wolfgang Malzer (2005), 'X-Ray Fluorescence Analysis of Iron Gall Inks, Pencils, and Colored Crayons', *Studies in Conservation*, 50: 23–32.

—— (2010), 'Analysis of Iron Gall and Carbon Inks by Means of X-Ray Fluorescence Analysis: A Non-Destructive Approach in the Field of Archaeometry and Conservation Science', *Restaurator*, 31: 41–64.

Hamm, Charles (1962), 'Manuscript Structure in the Dufay Era', *Acta Musicologica*, 34: 166–184.

Hoffmann, Peter, Stefan Bichlmeier, Martin Heck, Claudia Theune, and Johan Callmer (2000), 'Chemical Composition of Glass Beads of the Merovingian Period from Graveyards in the Black Forest, Germany', *X-Ray Spectrometry*, 29: 92–100.

Janke, Andreas and Claire R. MacDonald (2014), 'Multispectral Imaging of the San Lorenzo Palimpsest (Florence, Archivio del Capitolo di San Lorenzo, Ms. 2211)', *Manuscript Cultures*, 7: 113–124.

—— and John Nádas (2015), 'New Insights into the Florentine Transmission of the Songs of Antonio Zacara da Teramo', *Studi Musicali*, Nuova Serie, 2: 197–214. Reprint in 2017: Janke, Andreas and Francesco Zimei (eds), *Arte Psallentes: John Nádas, Studies in Music of the Tre- and Quattrocento* (Studi e Saggi, 9) (Lucca: Libreria Musicale Italiana), 201–215.

—— and —— (2016), *The San Lorenzo Palimpsest: Archivio del Captiolo di San Lorenzo Ms. 2211*, *Introductory Study and Multispectral Images* (Ars Nova, Nuova Serie, 4) (Lucca: Libreria Musicale Italiana).

—— and Francesco Zimei (forthcoming), 'The Atri Fragment Revisited II' (Musica Mensurabilis, 9) (Hildesheim: Olms).

Krekel, Christoph (1999), 'Chemische Struktur historischer Eisengallustinten', in Gerhard Banik and Hartmut Weber (eds), *Tintenfraßschäden und ihre Behandlung* (Werkhefte der staatlichen Archivverwaltung Baden-Württemberg, Serie A, Landesarchivdirektion, 10) (Stuttgart: Kohlhammer), 25–36.

Malzer, Wolfgang, Oliver Hahn and Birgit Kanngießer (2004), 'A Fingerprint Model for Inhomogeneous Ink-Paper Layer Systems Measured with Micro X-Ray Fluorescence Analysis', *X-Ray Spectrometry*, 33: 229–233.

Nádas, John (1986), 'Further Notes on Magister Antonius dictus Zacharias de Teramo', *Studi Musicali*, XV: 167–182 (*errata corrige* XVI:175-6). Reprint in 2017: Janke, Andreas and Francesco Zimei (eds), *Arte Psallentes: John Nádas, Studies in Music of the Tre- and Quattrocento* (Studi e Saggi, 9) (Lucca: Libreria Musicale Italiana), 187–199.

—— and Agostino Ziino (eds) (1990), *The Lucca Codex: Codice Mancini; Lucca, Archivio di Stato, MS 184; Perugia, Biblioteca Comunale 'Augusta', MS 3065*, Introductory Study and Facsimile Edition (Ars Nova, 1) (Lucca: Libreria Musicale Italiana).

Rye, Owen (1993), 'Anagama: The Art of Uncertainty', *Ceramics, Art and Perception*, 10: 39–42.

Szirmai, János A. (1999), *The Archaeology of Medieval Bookbinding* (Aldershot: Ashgate).

Wilson, Blake (2009), *Singing Poetry in Renaissance Florence: The 'Cantasi Come' Tradition (1375–1550),* (Italian Medieval and Renaissance Studies, 9) (Florence: Olschki).

Ziino, Agostino (1973), 'Nuove fonti di polifonia italiana dell'Ars nova', *Studi Musicali*, 2: 235–248.

Zimei, Francesco (ed.) (2004), *Antonio Zacara da Teramo e il suo tempo* (Lucca: Libreria Musicale Italiana).

PICTURE CREDITS

Figs 1–2: © Courtesy of the Museum and Chapter Archive, Atri, Italy. Photos taken by the CSMC.

Figs 3–10: © CSMC.

Article

An Attempt at a Systematic Study of Inks from Coptic Manuscripts

Tea Ghigo, Olivier Bonnerot, Paola Buzi, Myriam Krutzsch, Oliver Hahn, and Ira Rabin | Rome, Berlin, Hamburg

Introduction

When it comes to Egyptian writing and drawing materials, it is surprising to realize how much information we have on pigments compared with the little we know about inks.

It is well documented that throughout Antiquity, ancient Egyptians used mostly carbon inks as a writing material.[1] In Late Antiquity, some metals started to be added to carbon-based inks. We have records of five manuscripts from the Dead Sea Scrolls collection whose carbon inks were found to contain copper.[2] Also, lead was recently found as an additive in carbon inks on a charred fragment from Herculaneum.[3] Furthermore, the earliest evidence of iron-gall ink was found in the Book of Proverbs (Codex Ms. Berol. orient. oct. 987) dating to the third fourth centuries CE.[4] It has been suggested that along with carbon and iron-gall inks, there is no reason to think that purely tannin inks were not also in use in Egypt.[5] However, so far, we just have evidence of a copper-tannin ink identified in a number of documents from Egypt in the first third centuries BCE.[6]

In an attempt to fill this gap in this extremely fragmented scenario during our studies of the socio-geographic history of inks, we arrived at the conclusion that the continuous production of Coptic manuscripts from Late Antiquity to the Middle Ages offers a unique opportunity for the historical study of inks across a large geographic area. Few analyses with specific reference to Coptic Egypt have been conducted so far. Among them, we can list the study of a fragment of parchment purchased in Cairo in the mid-1970s. This revealed that the two sides of the document had been inscribed with iron-gall inks that differ in their metal salts composition, suggesting that the same manuscript may have been inscribed by more than one person or by the same person but at different times.[7] A previous study of Coptic inks and pigments laid on a variety of supports dating from the sixth to the eighth centuries, pointed out that carbon ink was used on pottery while iron-gall inks were used on parchment.[8]

Aim of the project

The studies presented so far are just sporadic pieces of investigation into the history of writing materials in Egypt. For this reason, thanks to the collaboration with the ERC project 'PAThs' (www.paths.uniroma1.it) based at the Sapienza University of Rome and within the activities of a PhD research dedicated to this topic, we created a new project focused entirely on the analysis of Coptic inks. Pigments and dyes, if present in the manuscripts, will also be investigated.

This study of Coptic codices will address primarily the history of the development of inks. As stated above, we have record of different kinds of inks used in Coptic fragments, but we still do not know if this difference is due to an evolution of materials and methods during the Coptic period or to a regional arrangement of the writing materials, which seems to be very possible considering that the Coptic language experienced a regional fragmentation into various dialects throughout its history.[9] We hope that systematic study will be able to unequivocally address the validity of MacArthur's suggestion that the choice of ink type might

[1] e.g. Lucas 1962.

[2] Nir-El and Broshi 1996.

[3] Brun et al. 2016.

[4] Rabin and Krutzsch 2016 (unpublished lecture).

[5] Buzi and Emmel 2015.

[6] Delange et al. 1990.

[7] Rabin et al. 2012.

[8] MacArthur 1995.

[9] Buzi 2015.

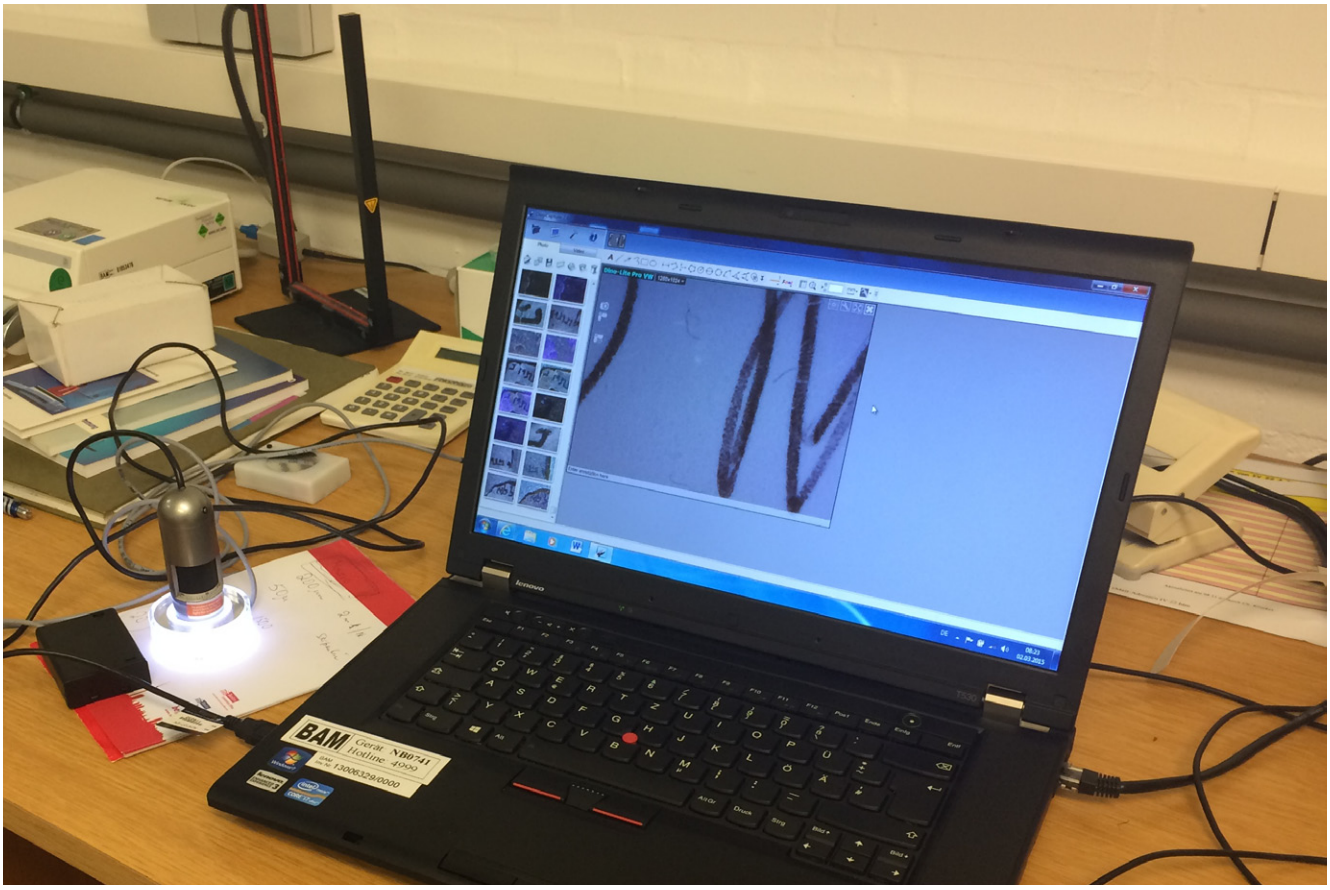


Fig. 1: DinoLite microscope, AD413T-12V.

have depended on the writing surface.[10] Therefore, the study will include the detailed description and characterization of the writing surfaces parchment and papyrus. Of course, it is also possible that more than one of the conditions presented above coexisted in the same temporal and spatial context, thus making the results of this study even more important.

Aside from the study of the history of writing materials, this investigation may make a valuable contribution to Coptic paleography and codicology. As already demonstrated in a previous study,[11] a correct scientific approach to the study of writing materials makes it possible not only to distinguish among different types of inks, but also, in the case of iron-gall inks, to distinguish among different types of materials used in the preparation of the inks. This information, if complemented by additional paleographical and codicological expertise, might lead to some interesting considerations regarding the persons and phases involved in the production of a specific codex.

Finally, the ink production recipe revealed by scientific methods can be used as a geochronological marker, making it possible to lay a first foundation stone for an inks database. This could help to date, localize, or provide new elements for understanding the typology and dating of some other Coptic scripts, thus completing dating results obtained so far from paleographic and textual methods.

Corpus

The full corpus of the documents covering a broad time span is still to be defined and adjusted in accordance with the results obtained in the course of work. In any case, we are going to work with the texts whose codicological and paleographical aspects have been properly studied in the frame of the PAThs project.

Our first analysis deals with the manuscripts that very likely originate in the cathedral of Thi(ni)s, nowadays Girga, located not far from Abydos. The library of Thi(ni)s is indeed a crucial and transitional instance in the history of Coptic manuscripts, which saw the creation of new codicological and palaeographical features, on the one hand, and the

[10] MacArthur 1995.

[11] Rabin et al. 2012; Buzi 2016.

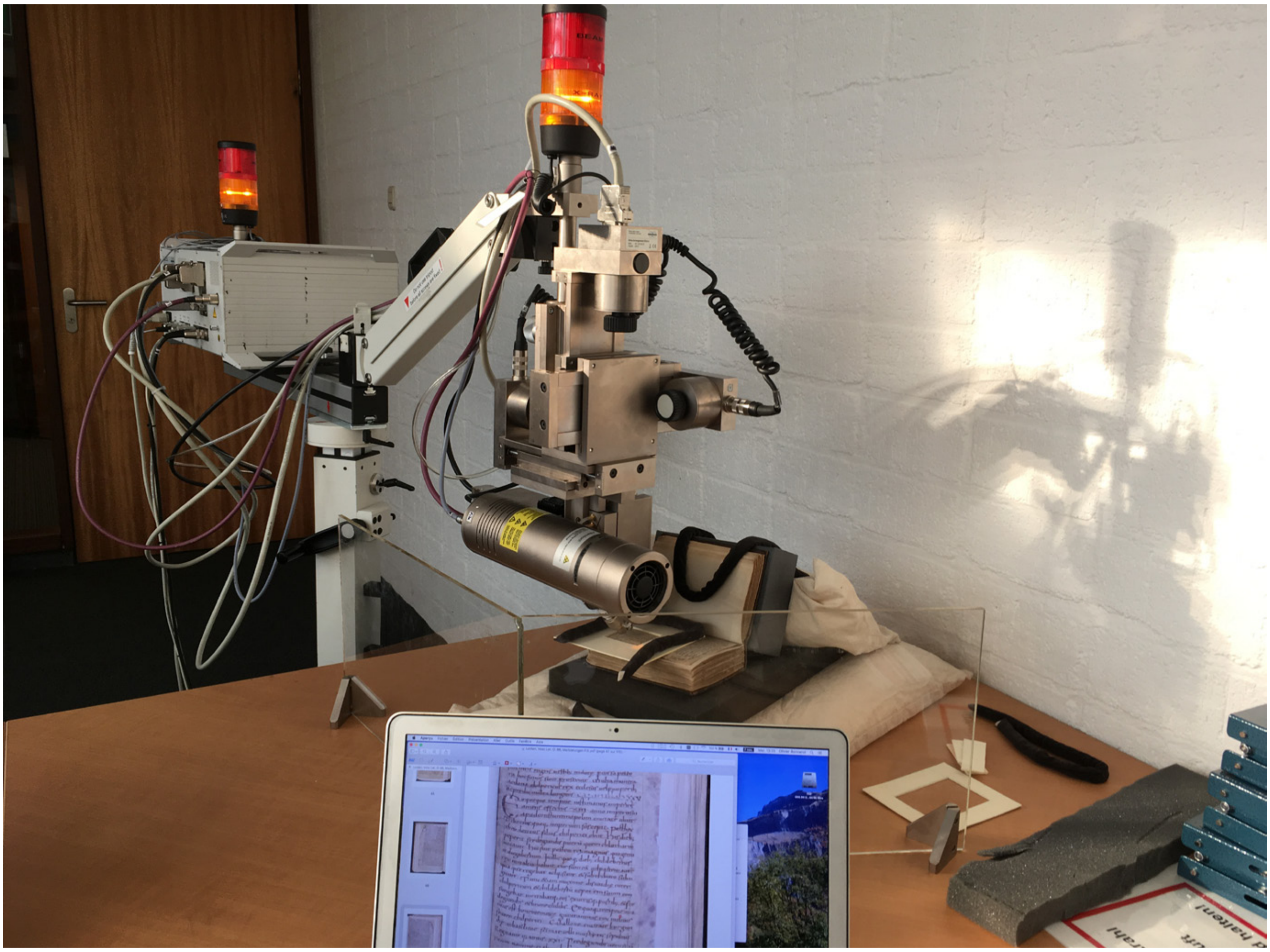


Fig. 2: ARTAX Bruker Nano GmbH.

progressive emergence of multiple-text codices, on the other. This explains the great importance of acquiring information concerning the material aspects of these codices. Besides, the fact that the manuscripts in question were very likely manufactured in a limited span of time and were written by a limited number of copyists made the study of the library of Thi(ni)s the first choice in our corpus.

The other collection to be analyzed includes fragments from the White Monastery in Sohag (Upper Egypt). Under the leadership of Shenoute (approximately 348–465/66 CE), the confederation of monasteries coordinated by the White Monastery became one of the most important centers of Coptic literary production. Its library (dating back to the ninth–eleventh centuries) is nowadays preserved in several collections all over the world, because the codices were dismembered and ended up in different places[12] such as the Staatsbibliothek zu Berlin (State Library Berlin)and the Bibliothèque nationale de France (National Library of France) in Paris.

Furthermore, we will work also on some manuscripts from the Michaelides collection. George Michaelides, a Greek collector who died in 1873, possessed a fine collection of manuscripts. The Cambridge University Library acquired part of this collection between 1976 and 1979, including some texts in Coptic. According to Michaelides, the texts date to the period between the sixth and ninth centuries and originate in the Fayyum region.[13]

Growing recognition of the importance of the material studies of the manuscripts, coupled with the development of the non-invasive protocols, encouraged many renowned institutions to give us access to their collections. We have already carried out analysis at the Egyptian Museum in Turin, at the State Library Berlin, and at the Cambridge University Library. During the first year of the project, we

[12] Buzi 2016.

[13] Clackson 1993.

plan on performing the analysis also at the Apostolic Vatican Library in Rome and at the National Library in Paris. Finally, the Bodmer Library in Cologne has also expressed its interest in cooperating with the project.

Experimental protocol and equipment

Our standard protocol for ink analysis consists of a primary screening to determine the type of the ink and a subsequent in-depth analysis using several spectroscopic techniques: XRF, FTIR, and Raman .[14]

The primary screening is carried out by means of NIR reflectography. Strictly speaking, optical differences between carbon, plant, and iron-gall inks are best recognized by comparing their response to the infrared light: carbon ink has a deep black colour, iron-gall ink becomes transparent above 1200 nm, and plant ink disappears at about 750 nm. We have simplified the analysis using a small USB microscope (with the built-in NIR (940 nm) and UV (390 nm) LED in addition to an external white light source. Working at 940 nm, we determine the ink typology by observing the changes in the opacity of the ink. Here, carbon-based inks show no change in their opacity when illuminated with NIR wavelengths, while the opacity of iron-gall inks changes considerably, and plant inks become transparent.[15] The in-depth investigation includes micro-XRF analysis to obtain the contribution of the inorganic components of the ink. In the case of iron-gall inks, we establish the fingerprints, i. e., the characteristic ratios of the vitriolic components of the ink.[16] Finally, in specific cases that may require more insight and further investigation, we perform FTIR spectroscopy to collect information on the chemical composition of the binders and Raman spectroscopy to determine the co-presence of carbon and iron-gall ink.

First results

The evidence of the earliest iron-gall ink we have ever measured comes from the Book of Proverbs kept at the Staatsbibliothek in Berlin (Ms. Berol. orient. oct. 987).

The single-layer Book of Proverbs codex consists of forty bifolia and three single folios that were cut to shape from three papyrus rolls. As Hugo Ibscher[17] has already determined, the rolls were previously halved in height. The dimensions of the folios are about 13 cm (height) × 29 cm (width), while the inner double folios are up to 4 cm narrower because this was the only way the form of the book block could be shaped in a unified way. If the double folios, detached from the codex, are laid beside each other individually in the sequence of the pages in the codex, the work method of cutting the sheets to shape from the roll becomes recognizable. The course of the fibers on the recto side shows that the double sheets were cut from the roll from right to left.

It is difficult to examine the material quality and technical details of the papyrus, because the codex was embedded in chiffon silk in 1958 and 1959. It is nonetheless possible to determine that the papyrus material is of low quality and poor structure. The quality difference between the recto and the verso is obvious. Thus, many verso sides display conspicuously dark, very coarse fiber strands. Six double folios (fols 2, 4, 12, 21, 30, and 40) have patches; here, too, these are on the verso side.

An examination of the codex showed that two-thirds of the double sheets display two sheet glue bonds each; one-third have only one-sheet glue bond; and one double sheet has no glue bond. The sheet glue bonds are manufactory glue bonds[18] of the common Type II. As could be expected, the left sheets lie over the right sheets. The sequence of the sheets thus corresponds with the direction of the script. The width of the glue bonds varies between 2 and 3 cm; it reaches 3.5 cm in three cases and even 4 cm in one case. Precisely the width of the sheet glue bonds can indicate the time of the production of the papyrus material placing it in in Roman or even Byzantine times.

Figures 3a and 3b show the reflectographic images and the XRF spectra. The observed loss of opacity when the illumination is changed from the white (Fig. 3a left) to the NIR light (Fig. 3a right) indicates that the ink belongs to the iron-gall type. In Fig. 3b, we observe that the peaks corresponding to iron (Fe), copper (Cu), and potassium (K) grow considerably in the spectrum of the inks as compared with that of the underlying writing surface papyrus. A constant ratio between copper and iron, found throughout the ink of the manuscript, delivers a decisive proof that we are dealing with iron-gall ink.

[14] Rabin et al. 2012.

[15] Mrusek et al. 1995.

[16] Hahn 2010; Rabin 2012.

[17] Ibscher 1958.

[18] Krutzsch 2017.

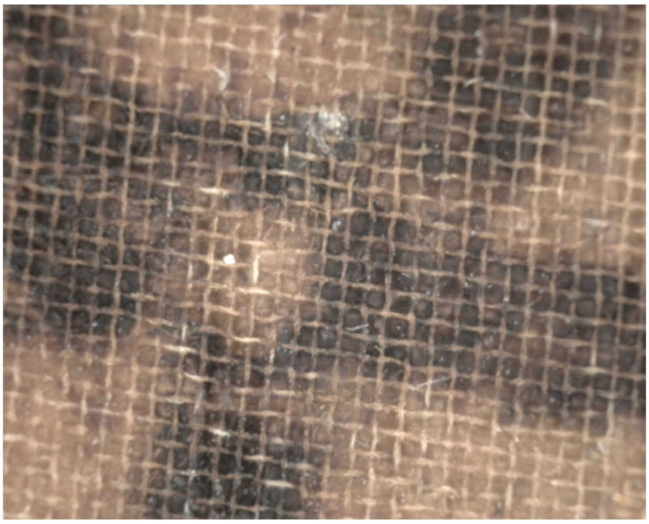


Fig. 3a: VIS images of a black ink from the Book of Proverbs.

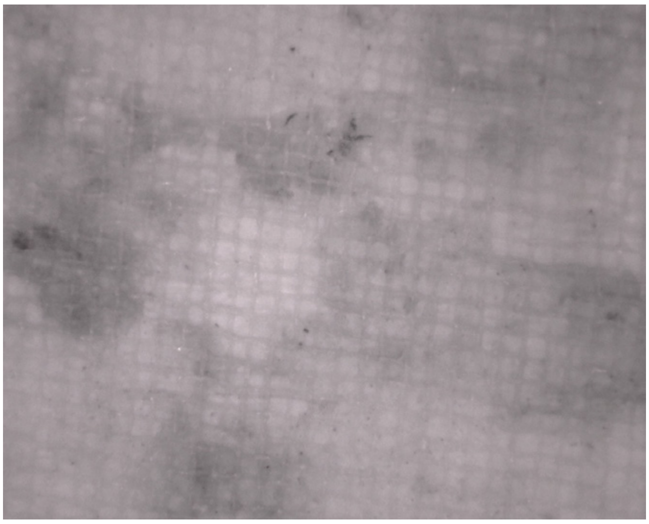


Fig. 3b: NIR images of a black ink from the Book of Proverbs.

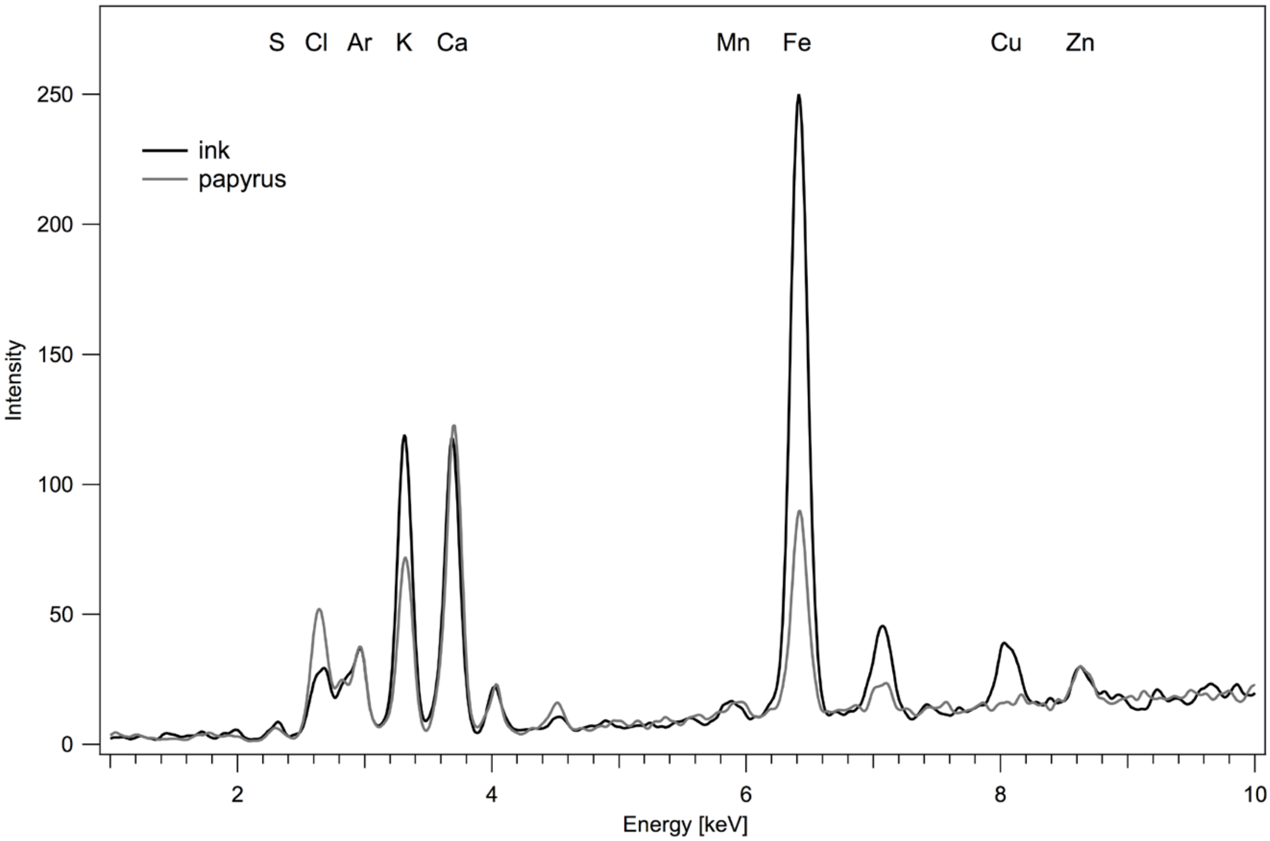


Fig. 3c: XRF spectra of the papyrus and the ink (grey and black curves, respectively).

Fig. 4a: VIS images of a black ink from Codex II preserved at the Egyptian Museum in Turin.

Fig. 4b: NIR images of a black ink from Codex II preserved at the Egyptian Museum in Turin.

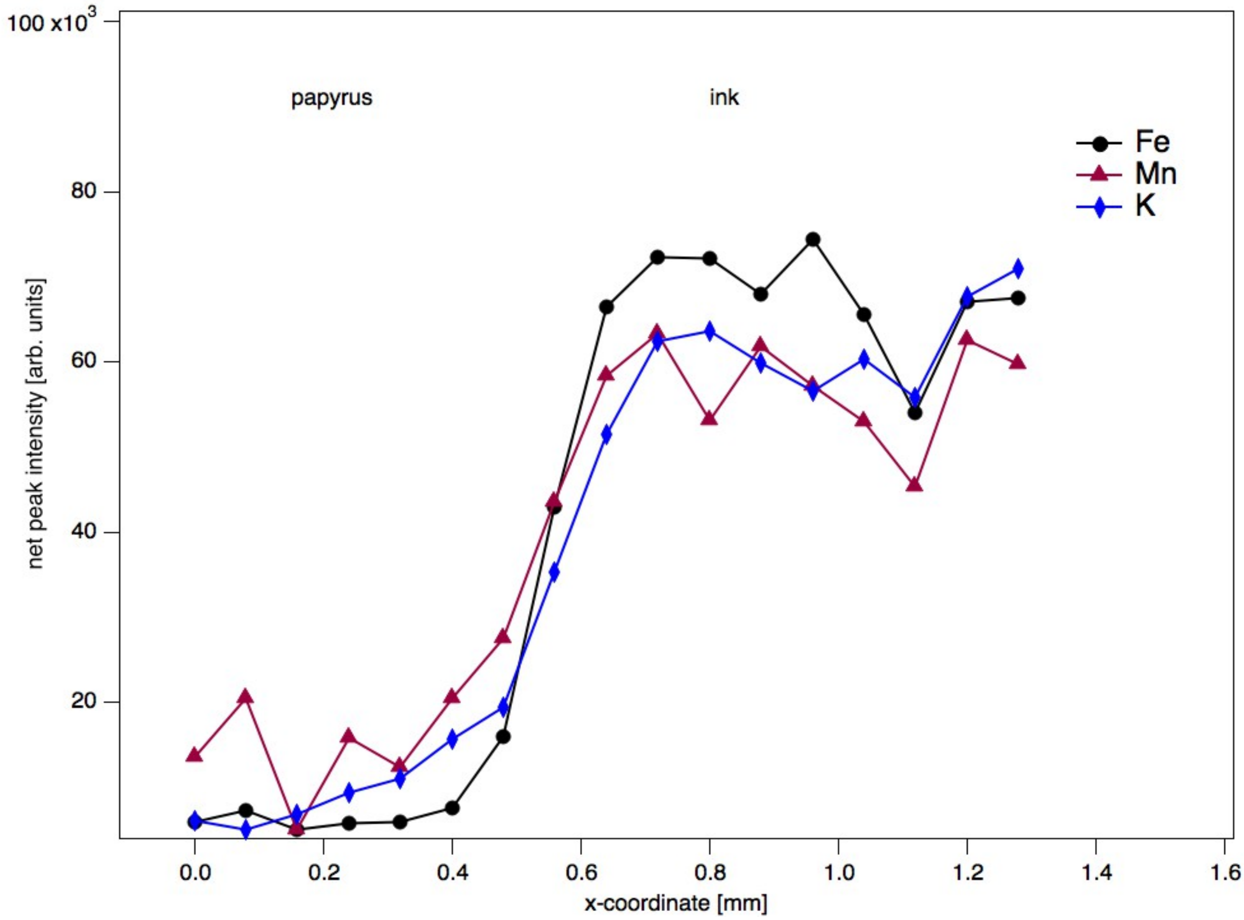


Fig. 4c: Intensity profiles of the characteristic ink from Codex II preserved at the Egyptian Museum in Turin.

Our next surprising finding was that a deep black colour of the ink from the Thi(ni)s fragments corresponded to iron-gall rather than carbon ink, as we instinctively believed. As in the previous case, the change in opacity observed in reflectographic analysis indicated the iron-gall nature of the ink. The composition study by means of XRF analysis confirmed a considerable growth of the iron signal in the ink. Figure 4b shows the intensity profiles of the elements iron, potassium, and manganese extracted from the measurements taken along the line connecting non-inked and inked areas, called the line scan. From the similarity of the profiles, we conclude that all three elements belong to the ink composition. Potassium is usually present in plant inks, but its increased abundance most probably indicates that gum arabic was used here as a binder in accordance with many recipes for iron-gall inks. The element manganese could be an indication of the use of a specific form of vitriol that lacked copper and zinc. On the other hand, it could be an indication that the ink was produced using a source of iron other than vitriolic salts. We plan to address this question in our future experiments.

Our third preliminary result that we would like to mention here is connected with the Michaelides collection preserved at the Cambridge University Library. Here we find carbon and iron-gall ink in different fragments that allegedly originated in the same region and within a relatively short time span, thus confirming the coexistence of different kinds of ink in Coptic Egypt.

Conclusion

The number and reputation of the institutions involved indicate that the study attracts the attention not only of the community of scholars working on Coptic manuscript tradition, but also of all professionals dealing directly or indirectly with the history of inks and writing materials. In fact, this pioneering study aims not only at a better understanding of the complex Coptic multicultural and plurilingual society, but also and mainly at clarifying the links among the Coptic and other societies in the ancient and medieval eras. Finally, it will cast light on the history of the technological development of inks in the Eastern world, from Antiquity to the Middle Ages.

ACKNOWLEDGEMENTS

The research presented in this article was carried out at the SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa', funded by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) and within the scope of the Centre for the Study of Manuscript Cultures (CSMC), in collaboration with the ERC advanced project PAThs (Tracking papyrus and parchment) of Sapienza University of Rome.

We would like to acknowledge the help of the personnel of the museums, archives and libraries who permitted our access and supported our work. Our special thanks go to the staff of Fondazione Museo delle Antichitá Egizie di Torino, in particular to Susanne Töpfer, Thomas Christiansen, and Sara Aicardi, who allowed and supported every step of our analytical campaign. Warm thanks are also due to the staff of the Staatsbibliothek zu Berlin, especially to Christoph Rauch, Melitta Multani, and Nicole Fürtig.

REFERENCES

Brun, E., M. Cotte, J. M. R. Wright, P. Tack, and C. M. Vincze (2016), 'Revealing Metallic Ink in Herculaneum Papyri', *Proceedings of the National Academy of Sciences*, 113.14: 3751–3754.

Buzi, P. (2015), 'Coptic Paleography', in Bausi, A. et al. (eds), *Comparative Oriental Manuscript Studies: An Introduction* (Hamburg: CoMSt; Tredition), 283–286.

—— (2016), 'From Single-Text to Multiple-Text Manuscripts: Transmission Changes in the Coptic Literary Tradition, Some Case-Studies from the White Monastery Library', in Friedrich, M., and C. Schwarke (eds), *One-Volume Libraries: Composite and Multiple-Text Manuscripts* (Berlin: De Gruyter), 93–110

——, and Emmel, S. (2015), 'Coptic Codicology', in Bausi, A. et al. (eds), *Comparative Oriental Manuscript Studies: An Introduction* (Hamburg: CoMSt; Tredition), 137–140.

Clackson, S. (1993). 'The Michaelides Coptic Collection in the Cambridge University Library and British Library', in Johnson, D. W. and T. Orlandi (eds), *Acts of the 5th international Congress on Coptic Studies* (Rome: Centro Italiano), 123–138.

Delange, E., Grange, M., Kusco, B., and Eve, M. (1990), 'Apparition de l'encre metallogallique en Egypte a partir de la collection de papyrus du Louvre', *Revue d'égyptologie*, 41: 213–217.

Hahn, O. (2010), ‘Analyses of iron gall and carbon inks by means of X-ray fluorescence analysis: A non-destructive approach in the field of archaeometry and conservation science’, *Restaurator* 31.1: 41–64.

Ibscher, H. (1958), ‘Beschreibung der Handschrift’, in Böhling, A., *Der achmimische Proverbientext nach Ms. Berol. orient. oct. 987*, part 1: *Text und Rekonstruktion der sahidischen Vorlage* (Studien zur Erforschung des christlichen Ägyptens, 3) (Munich: Lerche), XXI–XXVII.

Lucas, A. (1962), *Ancient Egyptian Materials and Industries* (London: Edward Arnold Publishers).

Krutzsch, M. (2016) ‘Reading Papyrus as Writing Material’, *British Museum Studies in Ancient Egypt and Sudan*, 23: 57–69 <http://www.britishmuseum.org/pdf/Krutzsch_23.pdf> (last accessed 15 April 2018).

—— (2017), ‘Einzelblatt und Rolle’, in Feder, F., G. Sperveslage and F. Steinborn (eds), *Ägypten begreifen: Erika Endesfelder in memoriam* (Internet-Beiträge zur Ägyptologie und Sudanarchäologie, IBAES, 19) (Berlin/London: Golden House Publications), 217. <http://www2.rz.hu-berlin.de/nilus/net-publications/ibaes19> (last accessed 15 April 2018).

MacArthur, D. (1995), ‘AGLAE et l’étude des encres et des colorants de manuscrits’, *Techne: la science au service de l’historie de l’art et des civilisations*, 2: 68–75.

Mrusek, R., Fuchs, R., and Oltrogge, D. (1995), ‘Spektrale Fenster zur Vergangenheit – Ein neues Reflektographieverfahren zur Untersuchung von Buchmalerei und historischem Schriftgut’, *Naturwissenschaften*, 82: 68–79.

Nir-El, Y., and Broshi, M. (1996), ‘The Black Ink of the Qumran Scrolls’, *Dead Sea Discoveries*, 3.2: 158–167.

Rabin, I. (2015), ‘Instrumental Analysis in Manuscript Studies’, in Bausi, Alessandro et al. (eds), *Comparative Oriental Manuscript Studies: An Introduction* (Hamburg: CoMSt; Tredition), 27–30.

Rabin, I., and M. Krutzsch (2016), ‘The writing surface papyrus and its materials’, 28th International Congress on Papyrology, Barcelona (not yet published paper).

Rabin, I., R. Schütz, A. Kohl, T. Wolff, R. Tagle, S. Pentzien, O. Hahn, and S. Emmel (2012), ‘Identification and Classification of historical writing Inks in Spectroscopy: a Methodological Overview’, *Comparative Oriental Manuscript Studies Newsletter*, 3: 26–30.

Contributors

Corneliu T. C. Arsene
University of Manchester
School of Arts, Languages and Cultures /
School of Mathematics
Oxford Road
Manchester, M13 9PL, UK

eMail: arsenecorneliu@yahoo.co.uk

Marina Bicchieri
Istituto Centrale Restauro e Conservazione del Patrimonio Archivistico e Librario (Icrcpal)
Chemistry Department
Via Milano 76
00184 Rome, Italy

eMail: marina.bicchieri@beniculturali.it

Paola Biocca
Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario (Icrcpal)
Via Milano, 76
00184 Rome, Italy

eMail: paola.biocca@gmail.com

Olivier Bonnerot
BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Division 4.5
Unter den Eichen 44-46
D-12203 Berlin, Germany

University of Hamburg
Centre for the Study of Manuscript Cultures CSMC
Warburgstraße 26
20354 Hamburg, Germany

eMail: olivier.bonnerot@bam.de

Sebastian Bosch
University of Hamburg
Centre for the Study of Manuscript Cultures CSMC
Warburgstraße 26
20354 Hamburg, Germany

eMail: sebastian.bosch@uni-hamburg.de

Maddalena Bronzato
University of Padova
Department of Chemical Sciences
Via Francesco Marzolo, 1
35131 Padova PD, Italy

eMail: maddalena.bronzato@gmail.com

Paola Buzi
Sapienza University of Rome
Facoltà di Lettere e Filosofia
ERC advanced project PAThs (project n. 687567)
Piazzale Aldo Moro 5
00185 Roma

eMail: paola.buzi@uniroma1.it

Federica Cappa
Academy of Fine Arts Vienna
Institute for Natural Sciences and Technology in the Arts
Augasse 2–6, D1.17.2–17
1090 Wien, Austria

eMail: f.cappa@akbild.ac.at

Thomas Christiansen
Fondazione Museo delle Antichità Egizie di Torino
Via Accademia delle Scienze 6
10123, Turin, Italy

eMail: thomas.christiansen@museoegizio.it

Stephen Church
University of Manchester
School of Physics and Astronomy
Oxford Road
Manchester, M13 9PL, UK

eMail: stephen.church@manchester.ac.uk

Zina Cohen
EPHE Ecole Pratique des Hautes Etudes
Equipe SAPRAT
45-47 rue des Ecoles
75005 Paris, France

BAM Federal Institute for Materials Research and Testing
Unter den Eichen 44-46
D-12203 Berlin, Germany

eMail: zina.cohen@outlook.fr

Claudia Colini
University of Hamburg
Centre for the Study of Manuscript Cultures
Warburgstraße 26
20354 Hamburg

eMail: claudia.sirim@gmail.com

Mark Dickinson
University of Manchester
School of Physics and Astronomy
Oxford Road
Manchester, M13 9PL, UK

eMail: mark.dickinson@manchester.ac.uk

Georg Dietz
Papierstruktur: datieren von kunst & dokumenten auf papier
Kreuzstr. 3
01067 Dresden, Germany

eMail: georg.dietz@papierstruktur.de

Bernadette Frühmann
Academy of Fine Arts Vienna
Institute for Natural Sciences and Technology in the Arts
Augasse 2–6, D1.17.2–17
1090 Wien, Austria

eMail: b.fruehmann@akbild.ac.at

Mirjam Geissbühler
University of Bern
Institute of Germanic Languages and Literatures
Länggassstrasse 49
3012 Bern, Switzerland

eMail: mirjam.geissbuehler@germ.unibe.ch

Tea Ghigo
University of Rome La Sapienza
Department of History Cultures Religions
Piazzale Aldo Moro 5
00185 Rome, Italy

BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Division 4.5
Unter den Eichen 44-46
12203 Berlin, Germany

eMail: tea.ghigo@bam.de

Oliver Hahn
BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Division 4.5
Unter den Eichen 44-46
D-12203 Berlin, Germany

University of Hamburg
Centre for the Study of Manuscript Cultures CSMC
Project Z02 - Material Analysis: Material-Scientific Methods for Reconstructing the History of Manuscripts
Warburgstraße 26
20354 Hamburg, Germany

eMail: oliver.hahn@bam.de

Marco Heiles
RWTH Aachen University
Germanistisches Institut
Templergraben 55
52056 Aachen, Germany

eMail: m.heiles@germlit.rwth-aachen.de

Andreas Janke
University of Hamburg
SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa'
Centre for the Study of Manuscript Cultures
Warburgstraße 26
20354 Hamburg

eMail: andreas.janke@uni-hamburg.de

Keith Knox
Early Manuscripts Electronic Library
<www.emel-library.org>
2739 Puu Hoolai Street
Kihei, Hawaii 96753, USA

eMail: knox@cis.rit.edu

Myriam Krutzsch
Egyptian Museum and Papyrus Collection SMB
Geschwister-Scholl-Str. 6
10117 Berlin, Germany

eMail: aemp@smb.spk-berlin.de

Ana S. Leal
CNR-IMM – National Research Council of Italy, Institute for Microelectronics and Microsystems
Naples Unit
via P. Castellino 111
80131 Naples, Italy

eMail: ana@na.imm.cnr.it

Vito Mocella
CNR-IMM – National Research Council of Italy, Institute for Microelectronics and Microsystems
Naples Unit
via P. Castellino 111
80131 Naples, Italy

eMail: vito.mocella@na.imm.cnr.it

Luca Nodari
University of Padova
Department of Chemical Sciences
Via Francesco Marzolo, 1
35131 Padova PD, Italy

eMail: Luca.nodari@unipd.it

Ira Rabin
University of Hamburg
SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa'
Project Z02 – Material Analysis: Material-Scientific Methods for Reconstructing the History of Manuscripts
Centre for the Study of Manuscript Cultures CSMC
Warburgstraße 26
20354 Hamburg, Germany

BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Division 4.5
Unter den Eichen 44-46
D-12203 Berlin, Germany

eMail: ira.rabin@bam.de

Silvia Romano
CNR-IMM – National Research Council of Italy, Institute for Microelectronics and Microsystems
Naples Unit
via P. Castellino 111
80131 Naples, Italy

eMail: silvia.romano@na.imm.cnr.it

Manfred Schreiner
Academy of Fine Arts Vienna
Institute for Natural Sciences and Technology in the Arts
Augasse 2–6, D1.17.2–17
1090 Wien, Austria

eMail: m.schreiner@akbild.ac.at

Ivan Shevchuk
University of Hamburg
SFB 950 'Manuskriptkulturen in Asien, Afrika und Europa'
Project Z01 - Manuscript Analysis to Recover Lost Writing
Centre for the Study of Manuscript Cultures CSMC
20354 Hamburg, Germany
Warburgstraße 26
D-20354 Hamburg, Germany

eMail: ivan.shevchuk@uni-hamburg.de

Simon Steger
BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Unter den Eichen 44-46
D-12203 Berlin, Germany

eMail: simon.steger@bam.de

Marina Toumpouri
Aristotle University of Thessaloniki
"Athoniki Psifiaki Kivotos"
54124 Thessaloniki, Greece

eMail: marina.toumpouri@gmail.com

Wilfried Vetter
Academy of Fine Arts Vienna
Institute for Natural Sciences and Technology in the Arts
Augasse 2–6, D1.17.2–17
1090 Wien, Austria

eMail: w.vetter@akbild.ac.at

Melania Zanetti
University of Venice Ca' Foscari
Department of Humanistic Studies
Dorsoduro 3484/D
30123 Venezia, Italy

eMail: melania.zanetti@unive.it

Alfonso Zoleo
University of Padova
Department of Chemical Sciences
Via Francesco Marzolo, 1
35131 Padova PD, Italy

eMail: alfonso.zoleo@unipd.it

Studies in Manuscript Cultures (SMC)

Ed. by Michael Friedrich, Harunaga Isaacson, and Jörg B. Quenzer

Writing is one of the most important cultural techniques, and writing has been handwriting throughout the greater part of human history, in some places even until very recently. Manuscripts are usually studied primarily for their contents, that is, for the texts, images and notation they carry, but they are also unique artefacts, the study of which can reveal how they were produced and used. The social and cultural history of manuscripts allows for 'grounding' the history of human knowledge and knowledge practices in material evidence in ways largely unexplored by traditional scholarship.

With very few exceptions, the history of the handwritten book is usually taken to be the prehistory of the (printed Western) book, thus not only denying manuscripts their distinct status as carrier medium, but also neglecting the rich heritage of Asian and African manuscript cultures from which, according to conservative estimates, more than ten million specimens survive until today.

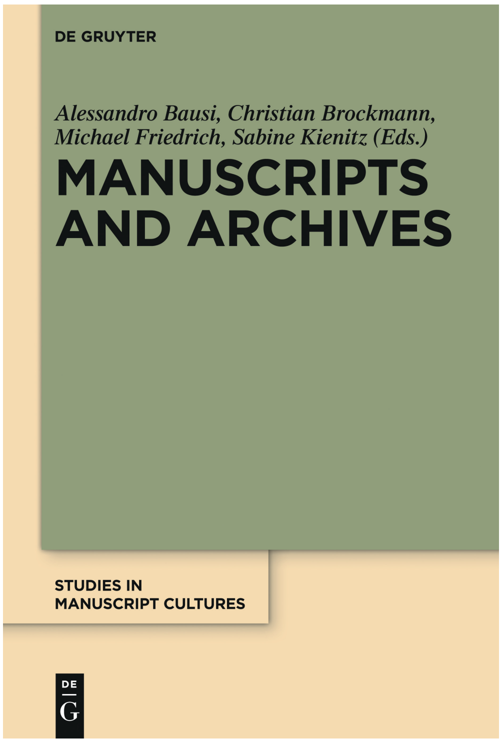
The series *Studies in Manuscript Cultures (SMC)* is designed to publish monographs and collective volumes contributing to the emerging field of manuscript studies (or manuscriptology) including disciplines such as philology, palaeography, codicology, art history, and material analysis. SMC encourages comparative study and contributes to a historical and systematic survey of manuscript cultures.

Publisher: de Gruyter, Berlin

DE GRUYTER

From volume 4 onwards all volumes are available as open access books on the De Gruyter website:
https://www.degruyter.com/view/serial/43546
http://www.manuscript-cultures.uni-hamburg.de/Studies_e.html

Just published



11 - *Manuscripts and Archives: Comparative Views on Record-Keeping* edited by Alessandro Bausi, Christian Brockmann, Michael Friedrich, and Sabine Kienitz

Archives are considered to be collections of administrative, legal, commercial and other records or the actual place where they are located. They have become ubiquitous in the modern world, but emerged not much later than the invention of writing. Following Foucault, who first used the word archive in a metaphorical sense as 'the general system of the formation and transformation of statements' in his 'Archaeology of Knowledge' (1969), postmodern theorists have tried to exploit the potential of this concept and initiated the 'archival turn'. In recent years, however, archives have attracted the attention of anthropologists and historians of different denominations regarding them as historical objects and 'grounding' them again in real institutions. The papers in this volume explore the complex topic of the archive in a historical, systematic and comparative context and view it in the broader context of manuscript cultures by addressing questions like how, by whom and for which purpose were archival records produced, and if they differ from literary manuscripts regarding materials, formats, and producers (scribes).

ISSN 1867–9617

'Manuskriptkulturen in Asien, Afrika und Europa'
Universität Hamburg
Warburgstraße 26
D-20354 Hamburg

www.manuscript-cultures.uni-hamburg.de