

Article

Three Complementary Non-invasive Methods Applied to Mediaeval Manuscripts

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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

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.

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 applied⁴ 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

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

⁵ Bruni et al. 2008; Doherty et al. 2013; Miliiani 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 PMMA⁷ 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 device⁸ 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 μ A, 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 μ A for 6 sec. and 15 kV and 7 μ A 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 ALPHA¹² FTIR spectrometer with a spot size of approximately 6 mm.

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).

⁷ PMMA – Polymethylmethacrylat $\text{C}_5\text{H}_8\text{O}_2$ – known as acrylic glass.

⁸ Desnica and Schreiner 2006.

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 IRUG¹⁴ 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 INCDTP¹⁷ 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



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.

with all three methods, whereas the last seven (P13–P19) were examined 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.

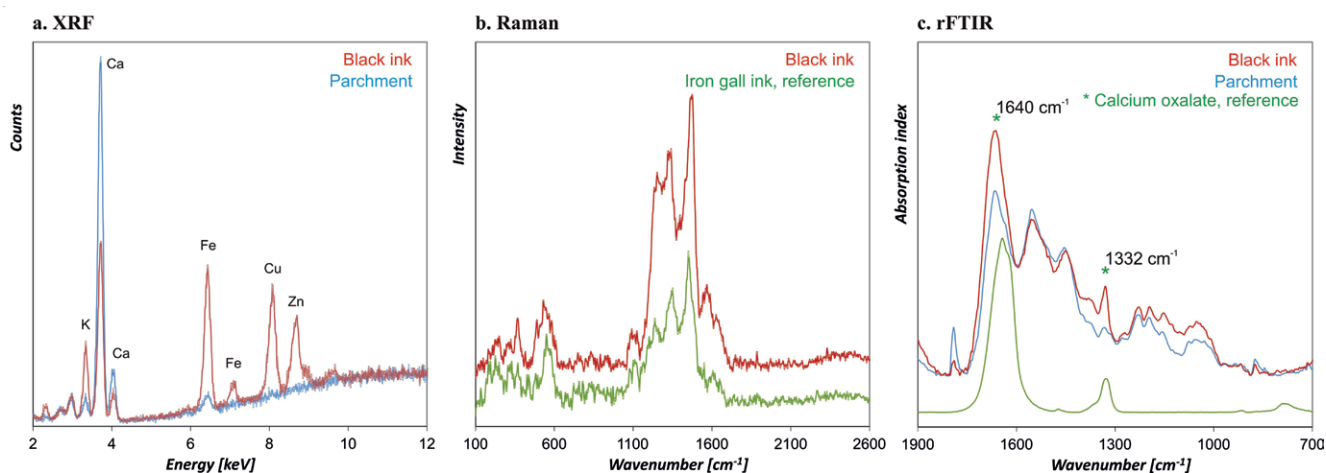


Fig. 2: Results of the measurements of the black ink in measurement point P12 on f. 74^v of Cod. Vind. slav. 8 performed with all three analytical methods. a) XRF spectrum of the black ink (red) in comparison with the parchment P1 (blue), where K, Fe, Cu, and Zn were detected. b) Raman spectrum of the 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. 90^r P5 or fol. 104^r 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.

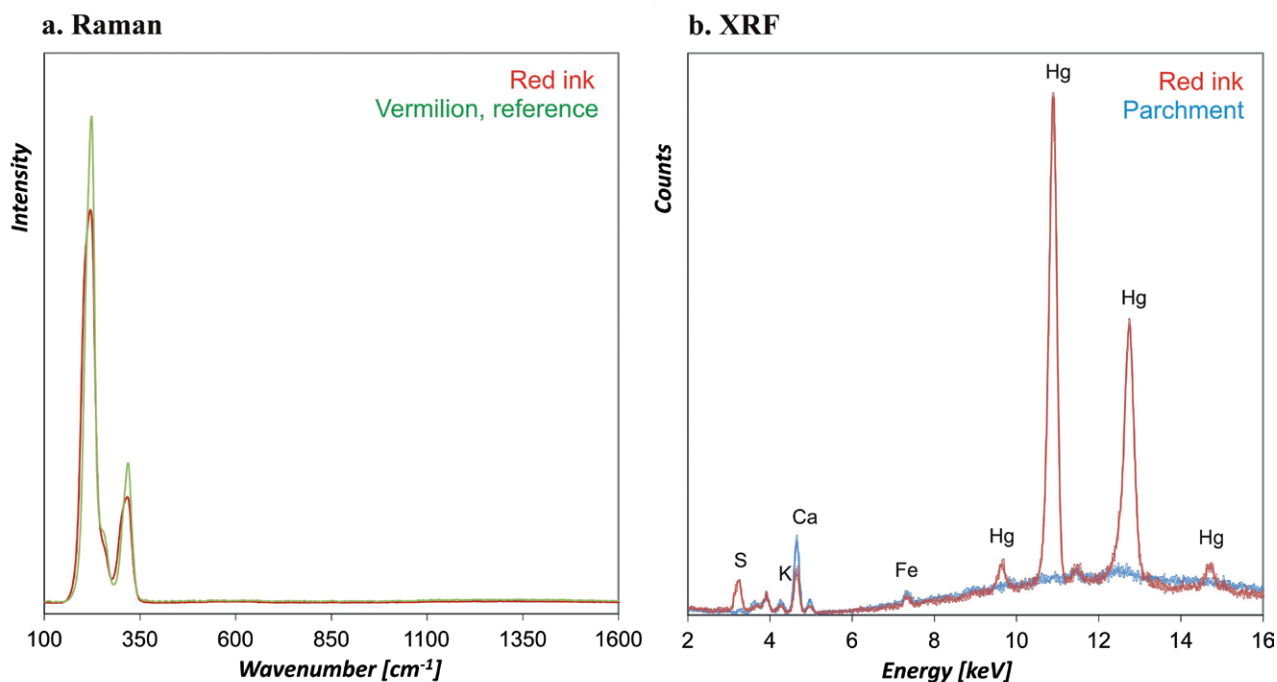


Fig. 3: Results of the measurements of the red ink of Cod. Vind. slav. 8. Vermilion was identified with two methods. a) Raman spectrum of P16/17 on fol. 74^r for the red ink (red) together with the reference for vermilion (green); b) XRF spectrum of P3 on fol. 104^r for the red ink (red) where S and 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 Ca²⁺ from water or calcium carbonate (CaCO₃) on the parchment. The bands for calcium stearate are clear, minor additives cannot be excluded.

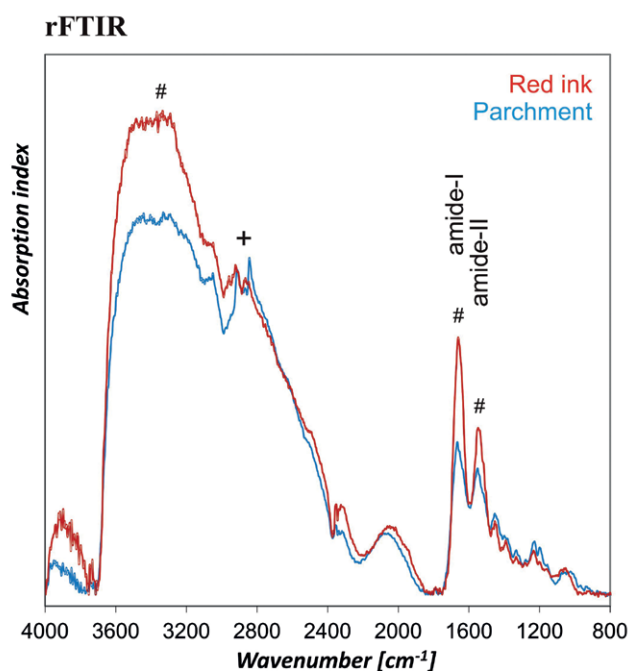


Fig. 4: Comparison of the rFTIR spectrum from the red ink in P5 on fol. 90^r of Cod. Vind. slav. 8 with the corresponding parchment of P1. The proteinaceous compound in the red ink showed partially stronger bands (#) than the parchment and differing C–H vibrations were observed (+).

²⁴ Socrates 2001.



Fig. 5: Detail of the miniature painting on fol. 74^v of the Cod. Vind. slav. 8.

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.

²⁵ Bicchieri 2014; Roosen-Runge 1988.

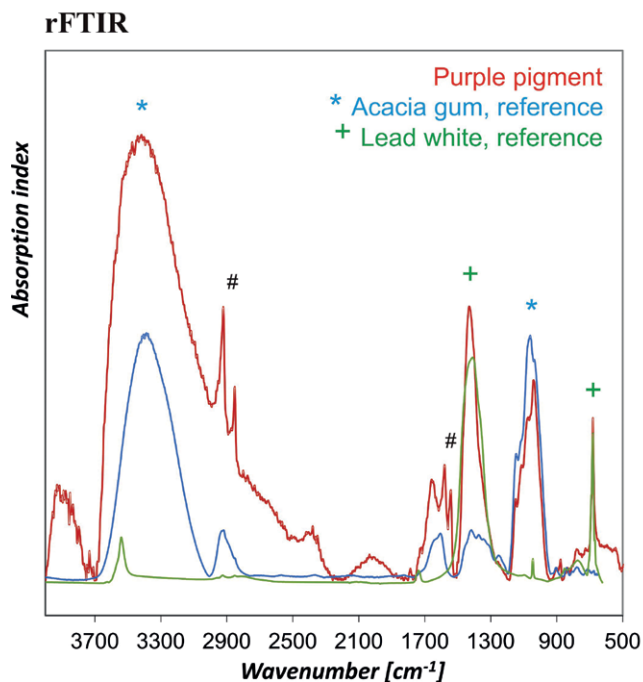


Fig. 6: rFTIR spectrum of P4 (red) in comparison with reference spectra of lead white (green) and acacia gum (blue). Additionally, bands of calcium stearate are labeled with #.

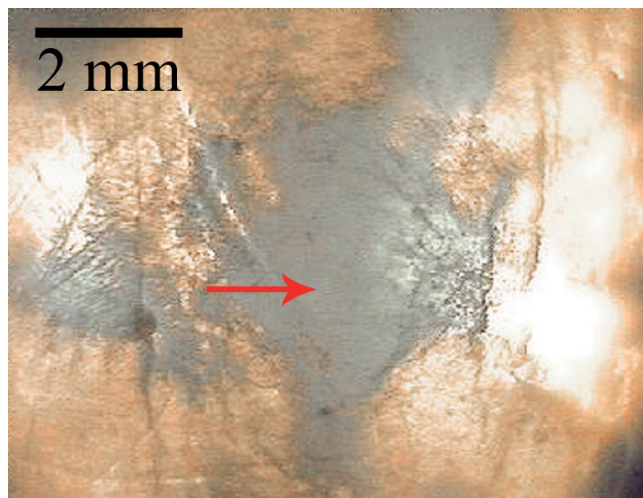


Fig. 7: Detail of the gilded area in P11 on fol. 74^v of Cod. Vind. slav. 8. The red arrow marks the area where gypsum can be seen underneath the gold layer.

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

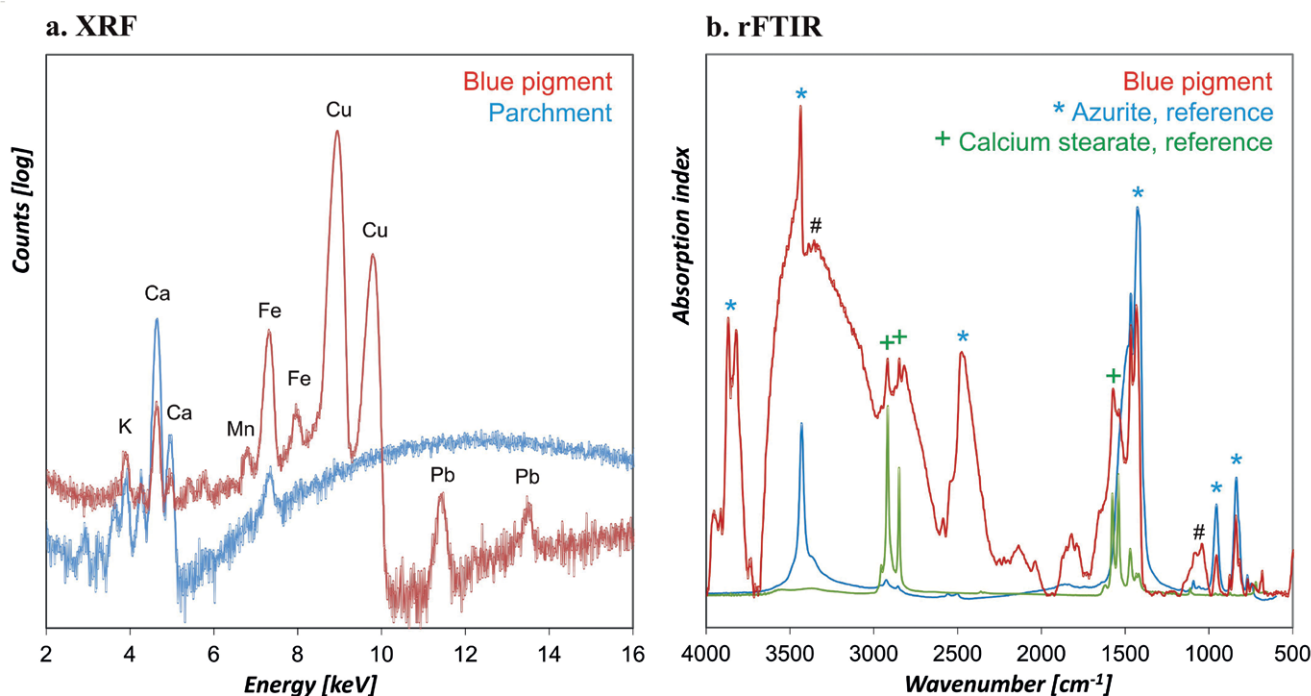


Fig. 8: Results of the measurements of the blue pigment in measurement point P3 on fol. 74^v of Cod. Vind. slav. 8. a) XRF spectrum of the blue pigment (red) in comparison with the parchment P1 (blue), where Mn, Fe, and Cu were detected. b) rFTIR spectrum of P3 (red) together with the reference spectrum 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. 5^r, fol. 6^v, and fol. 1^{r*}, 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 1^v up to 104^r, the ink of the script contains iron (Fe) and copper (Cu), as well as small amounts of zinc (Zn). For fols 174^r up to 270^r, 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. 6^v P3 or fol. 269^v 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 4^r, 90^r, 97^v);
- 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. 84^r (brown in P2) and fol. 158^v (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).

4. Codex Vindobonensis theologicus graecus 209, fol. 24^v

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. 24^v, shown in Fig. 10 with the analyzed points, are discussed: one point in the parchment, two in areas with black ink, two with red

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).

Raman

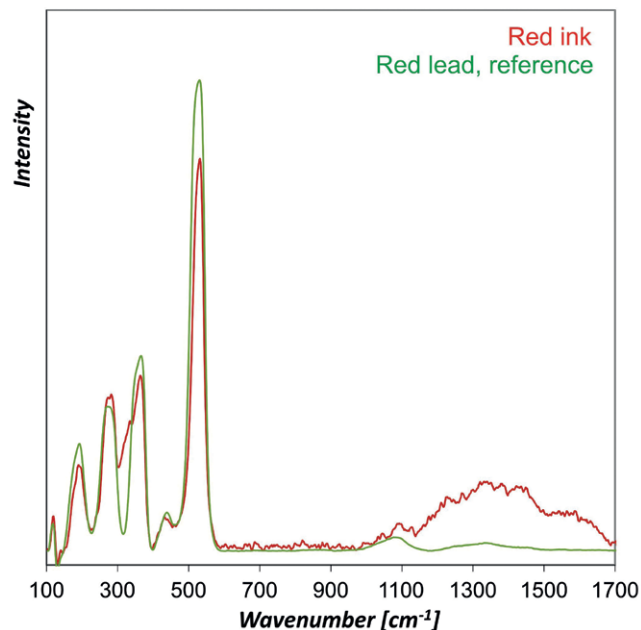


Fig. 9: Results of the Raman measurement performed on the red pigment in measurement point P7 on fol. 74^v of Cod. Vind. slav. 8. The spectrum of P7 (red) shows a perfect match with the reference spectrum for red lead (green).



Fig. 10: Fol. 24^v of the Cod. Vind. theol. gr. 209 with the selected measurement points.

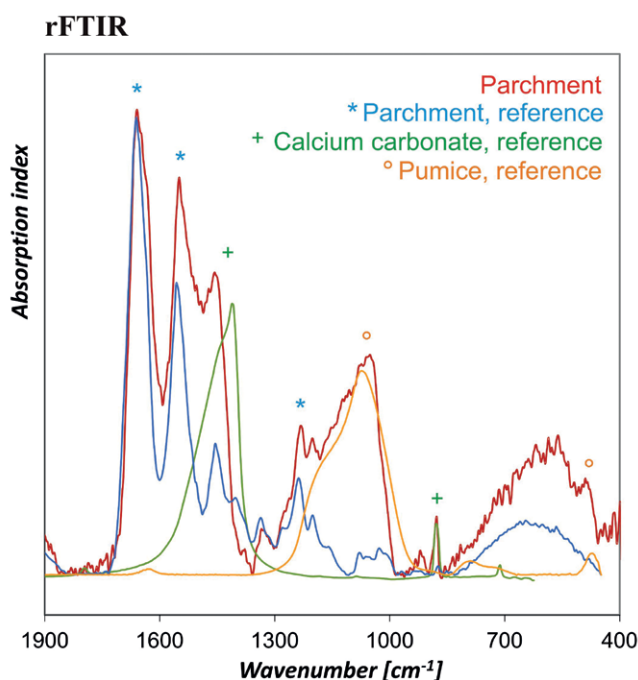


Fig. 11: rFTIR spectrum of the parchment (P1) in fol. 24^v of Cod. Vind. theol. gr. 209. The spectrum of P1 (red) is shown in comparison with the reference spectra of freshly prepared parchment (blue), calcium carbonate (green), and pumice (orange).

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.

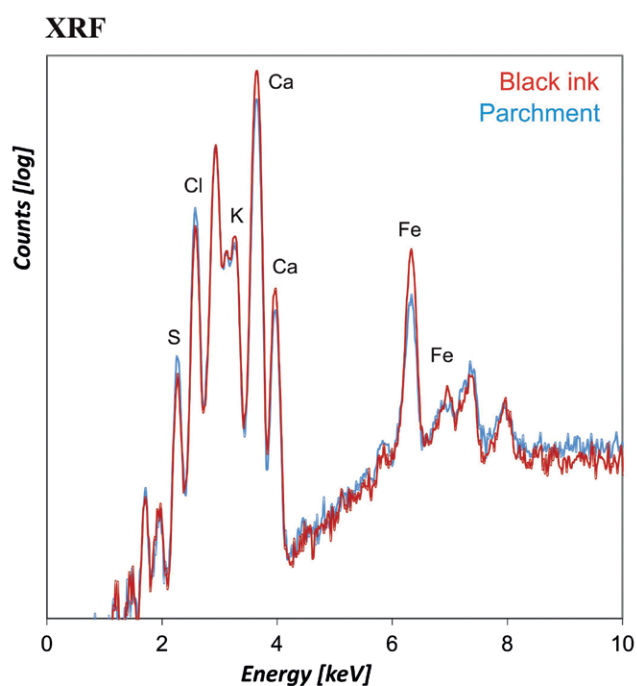


Fig. 12: Results of the XRF measurement of the black ink in measurement point P3 on fol. 24^v of Cod. Vind. theol. gr. 209. The spectrum of ink (red) is shown in comparison to the parchment (blue), where Fe was also registered.

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. 17^v, 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.

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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. Schrepf (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

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