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Analytical investigations on the *Coronation Gospels* manuscript

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ABSTRACT

The *Coronation Gospels* or *Krönungsevangeliar* is a manuscript kept in Vienna at the Kunsthistorisches Museum Wien, datable to the end of VIII century A.D. and produced at Charlemagne court. It is an example of a purple codex, i.e. its parchment is coloured in purple. It has to be considered as one of the most important medieval codices, according to its use to take oath in the coronation ceremony of kings and emperors of the Holy Roman Empire up to 1792. In order to gather information of the manufacture of the manuscript and its present conservation state, a diagnostic investigation campaign has been carried out in situ with totally non-invasive techniques. X-ray Fluorescence Spectrometry (XRF), UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS), spectrofluorimetry, optical microscopy and multispectral analysis have been applied in order to identify the colourants used in the decoration of the manuscript, with the main concern to the dye used to impart the purple hue to the parchment. The information collected was useful in order to address some of the questions raised by art historians concerning its history.

1. Introduction

The manuscript called *Coronation Gospels* or *Krönungsevangeliar*, kept in Vienna at the Kunsthistorisches Museum Wien (KHM, Secular Treasury, inv. no. XIII 18), has to be regarded as one of the most important codices preserved from medieval times [1,2]. The book consists of 236 parchment pages comprising the four Gospels plus 16 canon plates, prologues and short descriptions of the life of the Evangelists [3,4]. The beginning of each Gospel is decorated with an image of the respective Evangelist as the author of the following text (Fig. S1). The text is written in gold and silver inks, using types which are following the model of late antique scripture: *capitalis rustica*, *capitalis quadrata* and *uncialis*. The parchment is coloured throughout in purple colour, showing many different shades from lilac to deep purple or brown and, in one case (the quire containing ff. 77 and 84) nearly black. Because of the colouring many traces remained visible on the pages that can be linked to the process of preparing the parchment [5].

The Vienna *Coronation Gospels* is the principal work within a small group of manuscripts that were written and decorated at the court of the Frankish king Charlemagne (reigned 768–814) at Aix-la-Chapelle [6]. In the context of the intense work that was pursued by theologians and scholars to provide Charlemagne's court with new and revised editions of biblical and ecclesiastical texts, it is possible to date the manuscript of the *Coronation Gospels* around 795/800. During these years, Charlemagne pursued his aim of reviving the former Roman Empire (*renovatio Romani imperii*) and to become the first emperor in the Latin West after antiquity. More than any other manuscript from his court, the Vienna *Coronation Gospels* with its specific features – the choice of a purple dye as a colourant for all of the pages, the use of late antique models for both the scripture and the images of the Evangelists – demonstrate Charlemagne's ambition to represent his reign in the tradition of the late Roman emperors. The images of the four Evangelists come as close to classical Hellenistic models as no other work of medieval art known today. It has been assumed that foreign artists – either from Byzantium or from Italy – had come to Aix-la-Chapelle around 795 to create this outstanding book for Charlemagne. Not a single work of art, however, has survived, neither from Constantinople nor from Italy, that would show a similar level of understanding and reviving classical art at that time.

A tradition that dates back at least to the 12th century links the *Coronation Gospels* with a book that was said to have been found in the

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tomb of Charlemagne when this was opened in the year 1000 by emperor Otto III [7]. Due to the fact that the images of the Evangelists from the actual manuscript have been used as a model by illuminators already in the 9th century, it is clear that the burial of the book in Charlemagne's tomb is a legend [8]. This context, however, provided the Gospel book with a special status as a relic linked to Charlemagne, who got canonised as a saint in 1165. Subsequently the book was used for the coronation ceremony of kings and emperors of the Holy Roman Empire to take their oath, up to 1792 [9]. In 1794, the manuscript was retrieved from Aix-la-Chapelle together with other parts of the insignia of the Holy Roman Empire and brought to Vienna subsequently.

Due to the high symbolic value of this manuscript, an analytical investigation has been carried out, mainly with spectroscopic techniques, in order to have information useful for its thorough knowledge and its conservation. In particular, some issues were raised by art historians and conservators who inspected it:

1) identifying the palette of pigments used in its decoration, with main concern to the miniatures (the images of the four Evangelists and the initials), in order to appreciate the value of the materials used;
2) identifying the colourants used to impart the purple hue to parchment, verifying the peculiar appearance of the parchment of folios 77r, 77v, 84r and 84v, whose hue is dark blue rather than purple; understanding the occurrence of pale zones on selected parchments (e.g. at folio 190v).
3) assessing the purity of gold and silver used for the inks and comparing the composition of the gold alloy of the inks and in the golden details; comparing the composition of the golden ink used for the main text and that used for the writing "Demetrius Presbyter" at folio 118r (this name could represent the scribe of the manuscript);
4) verifying the hypothesis that some of the Evangelists' features had been retouched;
5) understanding the phenomenon of poor adhesion of the painted areas to the parchment, which is apparent in all the four large miniatures.

In consideration of the high value of the artwork and of its fragility, only non-invasive measurements were used for investigating the manuscript. Analyses on the manuscript were performed in situ with X-ray Fluorescence Spectrometry (XRF), UV-visible diffuse reflectance spectrophotometry with optical fibres (FORS), spectrofluorimetry and optical microscopy. Multispectral analysis was also performed in order to add further information on the pictorial materials used. The results were compared with those previously obtained in other analytical studies [10,11].

2. Material and methods

2.1. XRF instrumentation

XRF measurements were performed with a handheld EDXRF Thermo (Waltham, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with a Ag tube (max. 50 kV, 100 μA, 2 W), large area SDD detector, energy resolution of about 136 eV at 5.9 keV. The analysed spot had a diameter of 3 or 8 mm and was focused by a CCD camera, with a working distance of 2 mm. The total time of analysis was 240 s and the instrument was held in position with a moving stage allowing millimetric shifts, in order to reach the desired probe-to-sample distance; the stage was laid on a tripod. The obtained spectra were processed with the commercial software WinAxil, derived by the academic software QXAS from IAEA. The quantitative analysis was supported by the calibration of the portable instrumentation by using reference standard materials, able to determine the instrumental parameters and to define the correlation coefficients by means of the De Jongh algorithm. Successively, a wider approach was used, applying the fundamental parameter method (Rousseau algorithm) to take into account different real situations during the analytical in situ operations.

Additional measurements on reference samples dyed with different organic colourants as well as on the *Coronation Gospels* were performed using the portable μ-XRF instrument PART II (Portable Art Analyzer II) [12,13] of the KHM applying the following measurement parameters: X-ray tube: molybdenum; excitation voltage: 40 kV, current: 0.6 mA; polycapillary lens focusing the exciting beam to a spot size of 145 μm at 5.41 keV (Cr K_α); measurement time for each spot: 100 s; Si-drift detector.

For clarifying the detection of Br on the parchment of the *Coronation Gospels* by the handheld instrument described above, a few comparative measurements were done by the staff of the International Atomic Energy Agency, Seibersdorf Laboratories, also using a NITON XL3T-900 GOLDD analyser.

2.2. FORS instrumentation

FORS analysis was performed with an Avantes (Apeldoorn, The Netherlands) AvaSpec-ULS2048XL-USB2 model spectrophotometer and an AvaLight-HAL-S-IND tungsten halogen light source; detector and light source were connected with fibre optic cables to an FCR-7UV200-2-1,5x100 probe. In this configuration, both the incident and detecting angles were 45° from the surface normal, in order not to include specular reflectance. The spectral range of the detector was 200–1160 nm; depending on the features of the monochromator (slit width 50 μm, grating of UA type with 300 lines/mm) and of the detector (2048 pixels), the best spectra resolution was 2.4 nm calculated as FWHM. Diffuse reflectance spectra of the samples were referenced against the WS-2 reference tile provided by Avantes and guaranteed to be reflective at 98% or more in the spectral range investigated. The investigated area on the sample had a diameter of 1 mm. In all measurements the distance between probe and sample was kept constant to 1 mm. To visualise the investigated area on the sample, the probe contained an USB endoscope equipped with a set of LEDs to illuminate the area. The instrumental parameters were as follows: 10 ms integration time, 100 scans for a total acquisition time of 1 s for each spectrum. The whole system was managed by means of AvaSoft v.8 dedicated software, running under Windows 7.

For sake of comparison, a further FORS portable instrument was used. It was composed of a quartz tungsten halogen light source, a Y assembly of a set of diametral 100 μm optical fibres for the source and receptor, and a field plan Oriel spectrograph with a 400 T/mm edged grating and mirrors in Czerny-Turner assembly, equipped with an entrance slit of 25 μm in width. A 1024 photodiodes Oriel detector received the reflected diffuse light from the coloured surface. An MgO white surface served as reference white, and an Er_2O_3 surface for the wavelength calibration; the absorption spectra obtained by Oriel had a 0.6 nm resolution and were evaluated with self-produced visual basic software implemented in Excel [14].

2.3. Spectrofluorimetry instrumentation

An Ocean Optics (Dunedin, Florida) Jaz model spectrophotometer was employed to measure molecular fluorescence spectra. The instrument is equipped with a 365 nm Jaz-LED internal light source; a QF600-8-VIS/NIR fibre fluorescence probe is used to drive excitation light on the sample and to recover emitted light. The spectrophotometer is working in the range 191–886 nm; according to the features of monochromator (200 μm slit width) and detector (2048 elements), the spectral resolution available is 7.6 nm calculated as FWHM. The investigated area on the sample is 1 mm in diameter. In all measurements the sample-to-probe distance was kept constant to 1 mm (corresponding to the focal length) with the aid of a small black cylinder inserted on top of the probe, in order also to exclude contributions from external light. Instrumental parameters were as follows: 2 s integration time, 3 scans for a total acquisition time of 6 s for every spectrum. The system is managed with SpectraSuite software running under Windows 7.

2.4. Multispectral analysis

For the folios showing miniatures, visible light and UV fluorescence photographic images were taken as well as X-ray radiography and infrared reflectography (IRR) studies performed at the KHM. The following instruments and parameters were used:

- X-ray radiography: Seifert Isovolt 160T industrial X-ray tube; Agfa Structurix DW ETE 4 film; 12.5 kV; 4 mA; 2 min exposure time; distance to X-ray tube 1.1 m;
- Infrared reflectography: Indigo Apha NIR camera with indium-gallium-arsenide detector; sensitivity range: 900–1700 nm;
- UV fluorescence images were taken using common UV fluorescence lamps.

3. Results and discussion

During all the measurements, the manuscript was laid on a soft cradle; the analysed folios were held in place with cloth covered weights made of lead (Fig. 1a). The book was kept open at no more than 120°, in order to avoid mechanical stress to the binding (Fig. 1b).

3.1. Characterisation of the palette used in the decoration of the manuscript

The palette used in the decoration of the full-page miniatures is characteristic for the early medieval painting technique. According to the information yielded by non-invasive measurements and to data from the literature [15], the following materials were identified:

- black: a carbon-based pigment was used for all the black details;
- blue: the precious lapis lazuli was used for the backgrounds of the full-page miniatures; also indigo was used for some paler blue areas in the skies;
- brown: an iron oxide pigment was used to depict the hair of the Evangelists and architectural details;
- green: a copper-based green pigment is present, most probably verdigris according to the spectral features shown by FORS analysis (a maximum band centred at ca. 720 nm in apparent absorbance coordinates);
- gray: pure silver was used in a way similar to gold, i.e. in inks and as a pigment for depicting some features such as frames in the miniatures;
- red: minium was the primary red pigment, used mainly to depict the pillows on the Evangelists' thrones, on which some highlights were obtained with cinnabar;
- white: lead white was largely used as white pigment, sometimes mixed with other pigments;
- yellow: the only yellow pigment present was gold, which was widely used as shell gold to depict different details, such as the Evangelists' halos but also frames, columns and, of course, the text.

Fig. 1. (a) Handheld XRF and (b) FORS analysis on the *Coronation Gospels*.

3.2. Painting technique of the miniatures

Concerning the miniatures, additional details barely appreciable under visible light could be observed especially in the UV and X-ray radiographic images, e.g. ornaments in the part of the gildings or different characters as well as additional lines in the books and scrolls of the Evangelists, as shown in Fig. 2a to d for the Evangelist Matthew as an example. The X-ray images also clearly show the texture of a highly fluid and opaque paint and the use of a comparatively broad brush for its application: In Fig. 2c this can be seen for the areas of the sky and the halo, in the pillar of the desk and at the inner edge of the painted frame of the miniature.

As for the painting sequence, the halo was applied first leaving a small gap for the head of the Evangelist, than filled in later on. Also the posture of the head was changed from an originally profile to a three-quarter profile view. The figure of Matthew was laid out with a line following his contour starting at the right shoulder and leading to the right thigh, as can be seen in the IRR in Fig. 2d. The X-ray image also shows the naked right leg underlying the folds of the cloak. Normally the incarnate was brightly underpainted followed by the application of half shadows and subsequent precise graphic contours on top.

A firm vertical line in the pillar of the desk can be interpreted as a sketch for its outer limit, whereas the modelling of the pillar of the desk and the legs of the stool was reached by the application of a thicker X-ray absorbing paint in the highlighted areas (Fig. 2c). An area of higher X-ray absorbance can also be detected in the lowermost quarter of the book leading to the interpretation of a change in the size of the book during the paint process. No signs for outlines of the painted frames and the construction of the haloes could be seen for all the four miniatures. Generally the haloes seem to be applied first and the elements in the rear of the miniatures were painted before the ones in the front.

The UV- and X-ray images also lead to some further information on the conservation state of the miniatures: the gilded areas and the ones blended with lead white show the best adhesion to the parchment. Severe losses of paint are mainly restricted to the green and red areas. In contrast to the halo of Matthew, which is in good conservation state, the halos of the other Evangelists are noticeably rubbed and, therefore, appear darker in the corresponding X-ray images.

Fig. 2. Evangelist Matthew, *Coronation Gospels*, folio 15r: (a) visible light image; (b) UV fluorescence image; (c) X-ray radiography; (d) IR reflectogram (©: KHM-Museumsverband).

3.3. The different parchment hues: identification of colourants and alteration phenomena

3.3.1. The purple hue

Among the most relevant features of the *Coronation Gospels* is the fact that its parchment is coloured in purple, which characterises it as an example of a *purple codex*. The meaning of the purple colour has been thoroughly discussed and recognised and its symbolic value cannot be underestimated. Nevertheless there seems to be some inconsistency between the great importance of purple codices, which were usually made upon commitment by kings or emperors, and the actual materials used to obtain this colour. In fact, the firm belief that the highly prised Tyrian purple dye was generally applied has been overruled by the results of recent diagnostic investigations performed on several purple codices. In systematically all instances the manuscripts investigated revealed the presence of lesser noble alternatives to Tyrian purple, such as folium, the dye extracted from *Chrozophora tinctoria* plant [10,11,16–19] or, most usually, lichen dyes [10,11,20–24]. In the case of the *Coronation Gospels* there is one additional feature that renders the presence of Tyrian purple unlikely: in several folios, the purple hue of the parchment has turned to paler tones. This behaviour is not in compliance with the well-known lightfastness of Tyrian purple [25,26]. Finally, one quire inside the manuscript, the one containing folios 77r, 77v, 84r and 84v, shows a dark blue, rather than purple, hue, more consistent with indigo than with Tyrian purple or any other purple colourants.

The identification of the colourants present on the parchment of the *Coronation Gospels* has been started with elemental analysis, in order to look for bromine. This element has been frequently considered as a marker for Tyrian purple according to its presence in the structure of 6,6′-dibromoindigotine, but a recent publication [27] showed that bromine is also contained both in coastal-sourced lichens and in *Chrozophora tinctoria*. A small peak for bromine was identified on the parchments of the manuscript by means of portable handheld XRF analysis (Fig. 3) with both the instruments used, while portable μ-XRF analysis applying the PART II instrument did not highlight its presence. The latter instrument shows a detection limit for arsenic of 6 ppm [12], indicating that the detection limit for Br can be assumed approximately the same. The Br K-lines, therefore, lie in a very sensitive region of the spectrum. Measurements performed with this μ-XRF instrument on a selected set of reference samples indicated a clear detectability of bromine whenever Tyrian purple was used for dyeing the samples – this is also true for the blue hues (Fig. 4) sometimes gained by genuine purple dyeing. Therefore, if Tyrian purple had been used for dyeing the parchment of the *Coronation Gospels*, it should be possible to detect a clear bromine peak using the PART II instrument. By analysing the purple dye on the folios 1v, 5v, 15v, 50v, 235r and 233r by portable μ-XRF, no bromine

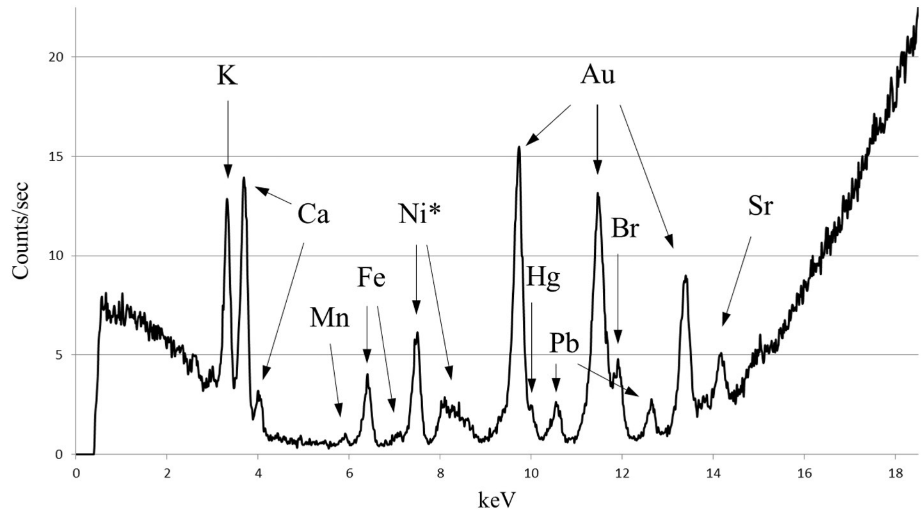

Fig. 3. Handheld XRF spectrum from the parchment of the *Coronation Gospels* (f. 50r); Ni, indicated with an asterisk, is due to instrumental noise.

as well as no lead could be found (Fig. 5), indicating that these components are present in quantities below the detection limits of PART II. In addition, gold could also only be observed as a minor trace in some spectra collected with the portable μ-XRF instrument. The Pb, Hg and Au signals detected using the handheld instruments are on one side connected to the dislocation of inks and pigments used in the texts, decorations and miniatures, possibly by abrasion over the centuries. On the other side they are detectable only by handheld XRF due to a different measurement geometry and beam diameter exciting a larger sample volume (and therefore several pages in depth with all its abrasions, decorations and scripture) compared to the PART II instrument.

To further clarify the colourants used on the parchment, molecular techniques were applied. FORS analysis suggested the presence of lichen dyes such as orchil, according to apparent absorbance maxima occurring at 548 and 593 nm (Fig. 6) that fit well with the spectral features indicated by the literature [27]. This is confirmed also by the spectra obtained with the second FORS set-up (Fig. 7) on the folios 2r, 5r, 22r,45r, 50r, 67r, 78r, 99r, 109r, 118v, 204v, and 224v, where the absorbance maxima can be detected around 547–548 nm and 596-597 nm. For these studies other absorptions observed around 485–490 nm and 570–575 nm, more visible on folios 2r, 5r, 22r, 45r 78r and 224v, suggest the presence of an additional anthraquinonic red dye from insects like e.g. cochineal or kermes.

The inflexion points of the FORS spectra vary in the range 620–650 nm, partially explaining the different hues of the parchment that goes from pure purple to brown. Analysis with spectrofluorimetry confirmed the presence of orchil: the fluorescence peak occurring at ca. 628 nm fits well with literature data [27,28]. As the small quantities of Br detected with handheld XRF can be explained as impurities of orchil (as mentioned before), the use of Tyrian purple to dye the parchment of the *Coronation Gospels* can be excluded.

With concern to the application of dyes to parchment, visual inspection of folios suggests that the dye had been applied by painting rather than by dyeing. A clue for this procedure is the occurrence of apparent transverse signs across the parchment surface, which could be caused by rubbing a dye solution with a clothlet.

3.3.2. Parchment folios with dark blue hue

The quire of parchment containing folios 77r, 77v, 84r and 84v, which appears dark blue, shows a different behaviour when analysed with FORS (Fig. 6). The spectra revealed clearly that indigo was used

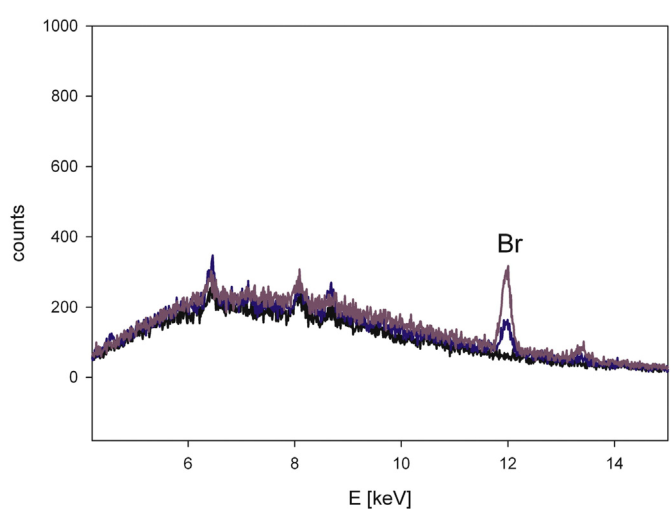

Fig. 4. PART II μ-XRF spectra of reference samples: wool (black line), wool dyed violet with Tyrian purple (violet line), wool dyed blue with Tyrian purple (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

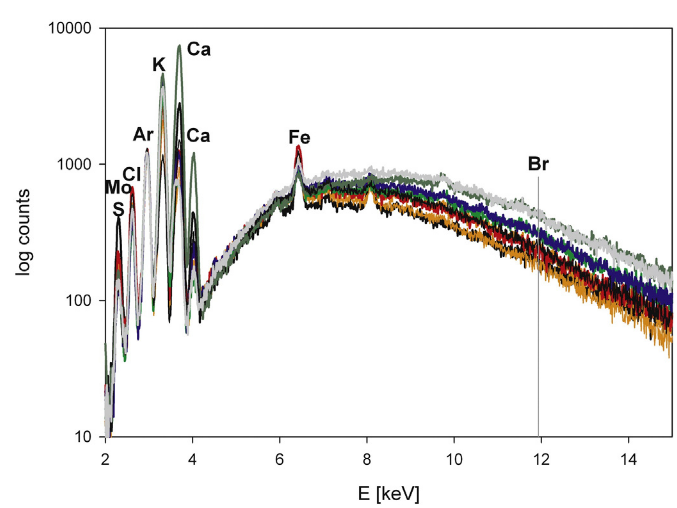

Fig. 5. PART II μ-XRF spectra of purple folios of the Coronation Gospels: f. 1v (orange), f. 5v (red), f. 15v (light green), f. 50v (blue), f. 235r (dark green), f. 233r (gray), reference: empty sheet (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

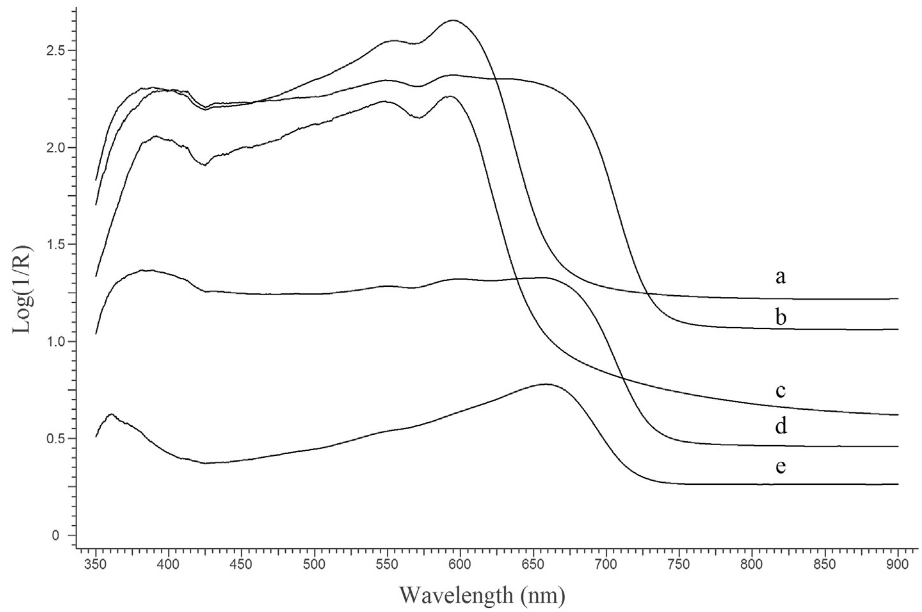

Fig. 6. FORS spectra in Log(1/R) coordinates from the parchment of *Coronation Gospels*: a) f. 50r; b) f. 77r, blue area; c) std. orchil; d) f. 77r, green area; e) std. indigo. Spectra are offset for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in addition to orchil to impart colour to these folios, according to the additional absorbance maximum occurring at 660 nm and to the inflexion point at 720 nm. In addition, analysis with spectrofluorimetry in these folios showed a much lower fluorescence peak than in the purple folios, indirectly confirming the presence of indigo: the emission due to orchil, in fact, most probably is absorbed by indigo since it falls inside the indigo absorption band centred at 660 nm. Another confirmation of an additional dyeing or painting of this quire with indigo is given by the fact that some areas show a green hue, even if not as apparent as the overall blue. In the corresponding FORS spectrum (Fig. 6) the reflection maximum, i.e. the wavelength representing the macroscopic colour of the analysed area, is located at 515 nm in the green region of the visible spectrum; nevertheless, the molecules present are similar to indigotine, as confirmed by the apparent absorption band at 660 nm. This behaviour is to be linked to the different concentration of the dye in the different areas of the quire.

It can be assumed that in the case of this quire, the first application of colour with orchil did not yield the desired hue on the parchment and it was decided to have a second passage with indigo to correct the hue. The apparent lowering of fluorimetry emission suggests a double application using firstly orchil and secondly indigo.

Indeed, it must be also considered that ff. 77r and 84v, which belong to the same side of the sheet, show vertical lines that are, as stated before, apparent signs of rubbing (see Fig. S2 showing a comparison of f. 77r with 78r): this allows hypothesising a painting, rather than dyeing, application of colourant, possibly of indigo over orchil.

From the historical point of view, the use of orchil both alone and in sequence with indigo appears reasonable. Ancient dyers most probably knew how to obtain a final colour similar to purple using plant dyes. The III century A.D. demotic Greek manuscript known as *Papyrus Holmiensis* contains, among others, fraudulent lichen-based recipes to imitate the expensive mollusc-based purple colour [29].

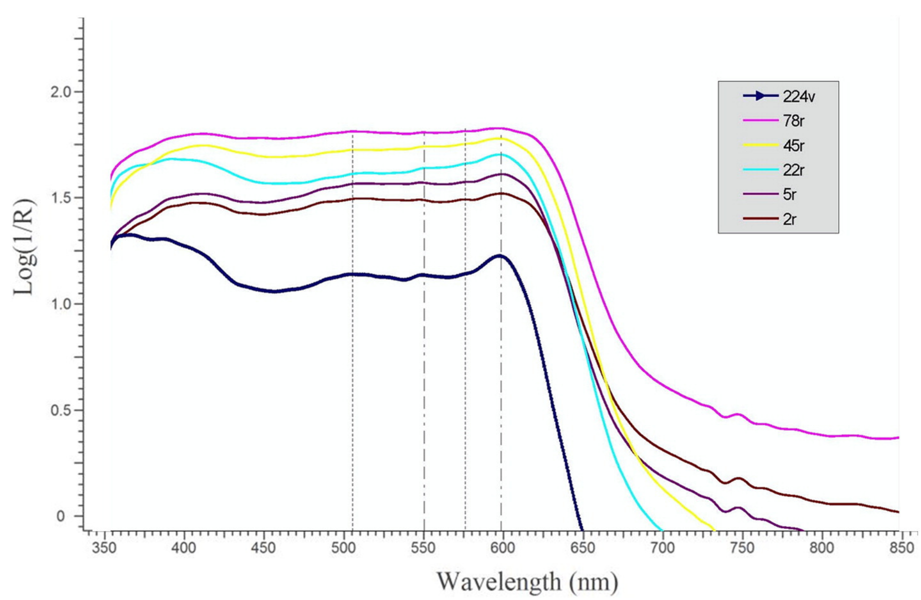

Fig. 7. FORS spectra in Log(1/R) coordinates obtained with the second setup from ff. 2r, 5r, 22r, 45r, 78r and 224v. Spectra are offset for clarity.

3.3.3. Paler areas of parchment

In several folios of the *Coronation Gospels*, paler purple zones are present on the parchment. This phenomenon is particularly noticeable at folio 190v. A comparison of FORS spectra evidences a higher reflectance level in the paler zones (Fig. 8a) but the absorption features are exactly the same (Fig. 8b, spectra in apparent absorbance coordinates), i.e. orchil is present in equal amounts in both normal and paler zones. This result points towards a chemical alteration rather than a difference in dye mass. Causes for this phenomenon could be contacts with chemical solvents; acid substances (such as wine or vinegar), alkaline substances (lye); oxidising or reducing agents seem unlikely since they would change orchil to a different hue.

3.4. Noble metals used for inks and miniatures

A major question raised by art historians concerned the purity of gold and silver used in the inks, in the decorated initials and in some other artistic details. Analysis by means of handheld XRF allowed obtaining some information useful to evaluate this feature.

All values were obtained by means of an algorithm taking into account the influence of secondary fluorescence and were then normalised. The normalisation process increases, as it is known, the error associated to the values. Detection limits for the metals reported in the table are averaging around 100 part per million (ppm) or 0.01%. The detection limit is equal to three times the standard counting error of the background intensity and it depends on the reliability of the measurement data.

In the calculation of the alloy composition it was defined arbitrarily which elements to include, excluding iron (always present in parchment) and lead whenever it was apparently due to a white lead preparation. In the light of this assumption, it is difficult to define the *real* composition of metal alloys, due to the arbitrary constraints chosen. Nevertheless, some considerations can be expressed on the compositions of the precious metals present in the *Coronation Gospels*. In nearly all cases binary alloys of gold/silver were used; only in a few cases copper is also intentionally present.

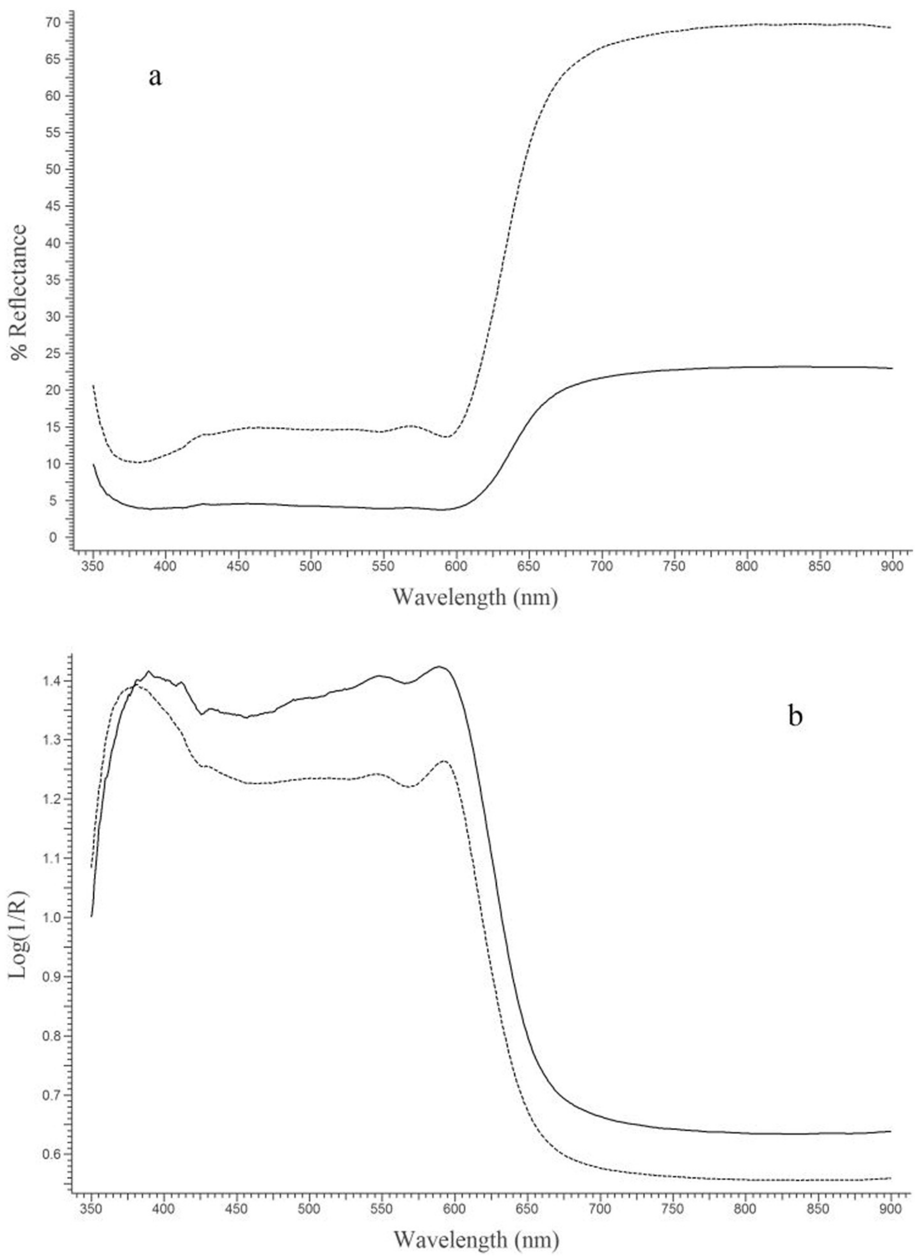

Fig. 8. FORS spectra (solid line: darker area; dotted line: paler area) from f. 190v of the parchment of *Coronation Gospels*: a) reflectance; b) apparent absorbance.

Table 1 summarises the results of the XRF semi-quantitative analysis of the metal inks used for writing and the golden areas in the miniatures.

3.4.1. Comparison of gold used in the miniatures and in the inks

Two different alloys had been used in the *Coronation Gospels*. The gold used in the miniatures (e.g. in the golden halos of the Evangelists) seems to be purer, reaching up to 92% in the arbitrary definition of the alloy. It appears to be applied as shell gold, i.e. as a mixture of gold glitter with an organic binding medium. A lower percentage of gold is instead present in the metal inks. All the inks contain gold and silver; those macroscopically appearing golden are richer in gold (e.g. the one present at f. 178v) while those showing a more greyish hue have a higher content of silver (e.g. the one present at f. 1r). The differences in composition among the gold inks and the silver inks, surprisingly, are lower than expected.

3.4.2. Comparison of gold used in the text and in the inscription at folio 118r

On the top part of folio 118r, an inscription made in golden ink reports the name *Demetrius Presbyter*. It has been hypothesised that this could be the name of the scribe of the *Coronation Gospels*. The results from the XRF analysis show that the ink used for this inscription is purer than the other gold inks present in the manuscript, whereas it is more similar to the gold used for the miniatures. Therefore, it is possible that *Demetrius Presbyter* has been the name of the miniaturist rather than the one of the scribe.

3.5. Evidence of retouches

It has been assumed that the miniatures representing the four Evangelists (ff. 15r, 76v, 117v and 178v) had been retouched, in particular for what concerns the details of the faces and the hands. On the basis of FORS and XRF analysis, though, it was not possible to confirm this hypothesis, since no evidence of deviant pigments was found in these features with respect to the general palette.

3.6. Poor adhesion of the painted areas to the parchment

It has been noted that all along the *Coronation Gospels*, and in particular in the four miniatures depicting the Evangelists, the paint layers are partly in bad condition. In several places the paints suffered from detachment, up to the point that the underlying parchment comes into evidence. This behaviour has been frequently noted in Byzantine miniature paintings on parchment [30]. The reason for this must be looked for in the preparation of the paints and the parchment. First of all, it is highly probable that a scarcely effective binding medium had been chosen by the artists working on the *Coronation Gospels*. The role of the medium is to impart both adhesive and cohesive properties to the paints; in this case, the adhesive properties seem to be so poor that the pictorial layer peels off in certain areas. Unfortunately, by means of non-invasive analysis only it is not possible to gain any further information on the binding medium used. Secondly, the paints had probably been applied at exaggerate thickness and density, with poor cohesion and homogeneity. Finally, parchment is usually characterised by a glossy and smooth surface that is probably unsuitable for a perfect and long-lasting adhesion of thick paints.

Table 1
Concentration values (wt%) for the different metal alloys detected.

Samples		Au	Ag	Cu	Pb	Hg[a]
Inks	KE 1r-gold text	68.0%	30.6%	0.27%	0.6%	0.6%
	KE 1r-silver text	63.7%	35.2%	0.31%	0.7%	[b]
	KE 5r-silver text	12.7%	55.0%	13.2%	16.0%	3.1%
	KE 5r-gold text	69.4%	27.3%	2.7%	[b]	[b]
	KE 77r-silver	72.0%	27.5%	0.7%	0.30%	[b]
	KE 77r-gold	92.0%	7.2%	0.7%	0.04%	[b]
	KE 118r-side text	91.0%	6.2%	1.4%	1.3%	[b]
Miniatures	KE 15r-golden halo	92.0%	6.0%	1.4%	0.18%	[b]
	KE 178v- golden halo	92.0%	7.4%	[b]	[c]	[b]

[a] Hg presence could be originated by contamination from pigments.
[b] Below detection limit.
[c] Pb concentration not expressed as considered due to the underlying white lead pigment.

4. Conclusions

The combination of non-destructive molecular (FORS, spectrofluorimetry), elemental (XRF) and optical (multispectral analysis) techniques yielded a large amount of information concerning the manufacturing techniques of the *Coronation Gospels* and its present state of conservation. The palette used by the artist/s for the decoration of the manuscript has been fully characterised as well as the organic colourants used to gain the purple hue of the parchment. In addition, some relevant issues raised by art historians have been addressed by means of analytical evidence.

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