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The use of mobile Raman spectroscopy to compare three full-page miniatures from the breviary of Arnold of Egmond

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ABSTRACT

The Breviary of Arnold of Egmond is one of the most wealthily illuminated fifteenth century manuscripts in the Northern Netherlands. The manuscript originally contained a number of full-page miniatures, which were all removed at an unknown date before 1902. The three remaining miniatures studied here, are today part of different collections, but they were brought together for an exhibition. Although several historical and art historical details of this breviary have extensively been studied, no examination of the materials used was undertaken before. Analytical techniques, such as mobile Raman spectroscopy, can be used to characterise and identify these materials in a non-invasive way. This paper presents the results of the in situ Raman analysis of three full-page miniatures of the Breviary of Arnold of Egmond. During this study, different pigments could be identified, such as lead white ($2PbCO_3{\cdot}Pb(OH)_2$), lead–tin yellow type I (Pb_2SnO_4), ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), massicot (PbO), vermilion (HgS) and red lead (Pb_3O_4). Next to identification of the pigments, visual analysis was used to detect differences and similarities between the stylistic elements of the three analysed folios.

1. Introduction

For art historians, it is important to have knowledge of the materials (pigments, binding media, substrates, etc.) and their provenance; to understand the ancient techniques; to locate and attribute the manuscript to a particular artist or workshop; or to date a manuscript. Although several historical details of mediaeval manuscripts have been studied extensively, the examination of the materials used is still in its infancy. The investigation of manuscripts by spectroscopic techniques is important to check their conservation state, to understand the causes of degradation and to plan an accurate conservation or restoration.

In comparison with other spectroscopic techniques, Raman spectroscopy has a number of advantages: the technique is non-invasive, no pre-treatment of the sample is necessary and mixtures can be investigated. Due to these advantages Raman spectroscopy was proven to be an interesting tool for the examination of works of art [1], in particular manuscripts. The Raman spectroscopic analysis of manuscripts has been mainly concerned with pigment identification, gathering information about the pigment palette [2,3] used for the illuminations or a pigment palette of a specific artist [4]. As a result of the identification of the pigments, also anachronisms can be traced [5] and information on the evolution of the pigment use [6] can be gathered. Next to the identification of the pigments, a lot of spectroscopic researches focus on the identification of the degradation products found on the manuscript, in order to protect the manuscript against further degradation. Some of these degradation processes result in a colour change of the pigment: the light-induced degradation of realgar (red) into pararealgar (yellow) [7], the degradation of red lead into galena (grey) and degradation of an alloy of copper, lead and zinc (gold) into a copper carboxylate (green) [8,9]. Next to the spectroscopic analysis of the pigments, also analysis of the ink [10,11] can be performed.

In this study, a mobile Raman spectrometer was used to analyse the three different folios. In spite of a strong fluorescence background, different pigments were identified, obtaining important information on the pigment palette used for the illumination of the different folios. The identification of the pigments was used as an additional argument to detect differences and similarities between the three analysed folios.

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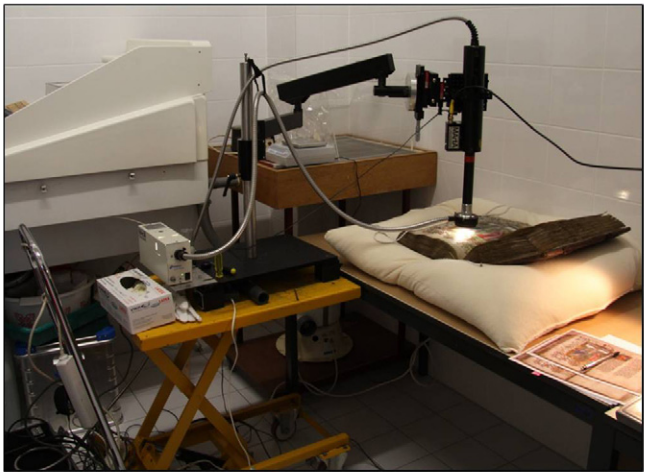

Fig. 1. Picture of the experimental set-up of the Mobile Art Analyser (MArtA) in the conservation department of the Museum Het Valkhof.

1.1. *The Breviary Arnold of Egmond*

The Breviary of Arnold of Egmond is one of the most wealthily illuminated fifteenth century manuscripts in the Northern Netherlands. The manuscript consists, in its present state, of 433 folios; containing beautifully decorated margins, consisting of thin bars, inhabited by many small flowers, animals, monsters, human figures, hybrid creatures and lush acanthus leaves [12] (Fig. 1). Illuminating this large manuscript was too much for one artist or even for a single workshop to handle, therefore the illuminations were executed by at least two different workshops: one group of artists working in the style of the Master of Zweder van Culemborg and the other group working in the style of the Masters of Otto van Moerdrecht. On folio 324r in the breviary, the male commissioner of the manuscript is depicted kneeling in front of St. Nicholas. For a long time nobody could identify the patron of the manuscript, except that he was a Guelders duke, because of the arms of Guelders and Jülich, implemented in the manuscript. In older literature [12], the manuscript has been dated to the period between 1420 and 1430. Considering this period, the patron could be: Reginald IV Duke of Guelders († 1423), Rupert von Berg († 1433) and Arnold of Egmond († 1471), the husband of Catherine of Cleves [13]. However, when looking at the miniatures made by the Zweder Masters (Fig. 2(b)), well developed landscapes and masterfully applied fine brush strokes suggest a matured style. Furthermore, influences of the Flemish painting technique of the early 1430s can be detected, making a date around 1435 more likely [13].

The manuscript originally contained a number of full-page miniatures, which were all removed at an unknown date before 1902. Three of them remained and are the subject of this study.

2. Experimental

2.1. *The analysed folios*

The three analysed folios belong to different institutions (the Fitzwilliam Museum in Cambridge (UK) (Fig. 2(a)), the University Library of Utrecht (The Netherlands) (Fig. 2(b)) and the London British Library (UK) (Fig. 2(c))) and were brought together for the exhibition 'The hours of Catherine of Cleves: devotions, demons and daily life in the fifteenth century' (Museum Het Valkhof, Nijmegen, The Netherlands, 10/10/2009–4/01/2010). The examinations were performed in the conservation department of the museum, during or shortly after the dismantling of the exhibition (Fig. 1).

The first analysed folio (318), originally forming f.318 in the breviary, depicts King Salomon in the Temple (Fitzwilliam Museum), the second analysed folio (104), shows The Stoning of Saint Stephen (British Library) and the last analysed folio (202), presents The Resurrection of Christ (University Library of Utrecht).

2.2. *Mobile Raman spectroscopy*

In situ Raman spectroscopy was performed on the three selected miniatures. The positions of the analysed points were conscientiously marked on prints of the miniatures. Sampling was not allowed. Analysis was performed in a darkened room in the conservation department of the museum.

Raman spectra were obtained using the Mobile Art Analyser (MArtA) [14]. This spectrometer contains a portable Raman imaging microscope (Spectracode, West Lafayette, IN, United States) and a SpectraPro 150i f.15 spectrometer (Roper scientific, Princeton Instruments). More detailed information of the instrument has been described elsewhere.

The measurements were executed using a 600-grooves/mm dispersion grating and a 785 nm diode laser. Spectra were obtained in the spectral region between 100 and 2500 cm^{-1}. A 6× objective lens was used, giving a clearance of approximately 5 mm above the manuscript surface. The selected measurement point of the manuscript could be observed through a digitally controlled colour camera incorporated in the probe head. Micro-positioning and focussing was achieved using the flexible arm and the manually controlled micro-positioners. Using the 6× objective lens, a spot size of approximately 50 μm was achieved. Extreme care was taken to avoid damaging the illumination with the laser beam: by adjusting the laser current, every measurement started with a very low laser power. When necessary, the power was carefully increased in order to improve the signal-to-noise ratio.

3. Results and discussion

3.1. *Visual examination based on style*

As mentioned before the illuminations in the Breviary of Arnold of Egmond were executed by at least two different workshops [12] the Masters of Zweder van Culemborg and the Masters of Otto van Moerdrecht. Both groups have the same idea, but the illuminations of the Moerdrecht Masters are more primitive and rigid. They also make use of uniform colour fields, which makes the figures look like puppets (Fig. 3(a)). In contrary, the Masters of Zweder van Culemborg use different paint layers to create depth and contrast. As a result of this, the figures look more natural and human (Fig. 3(b)). [12]

Since the full-page miniatures were removed from the manuscript a long time ago, the condition of these folios is different from the illuminations in the Breviary of Arnold of Egmond itself. The paint layers of the loose folios have suffered some damage, where the surfaces are worn. Therefore the classification based only on the stylistic examination of the faces is difficult.

Based on the stylistic study, the folios with The Resurrection of Christ (Fig. 2(b)) and The Stoning of Saint Stephen (Fig. 2(c)), belong to the same workshop, as the same background is used for both miniatures and as the painting style of the plants and the build-up of the faces is similar. They are painted in the style of the Masters of Zweder van Culemborg.

Opposite to this, folio 318 with King Salomon in the Temple (Fig. 2(a)), shows somewhat a different style: the figures at the side are rather shapeless, the from and build-up of the faces is different and there is almost no shadow in the figure.

Although this miniature is also painted in the style of the Masters of Zweder van Culemborg, it could have been executed by a different hand than the two other folios [15].

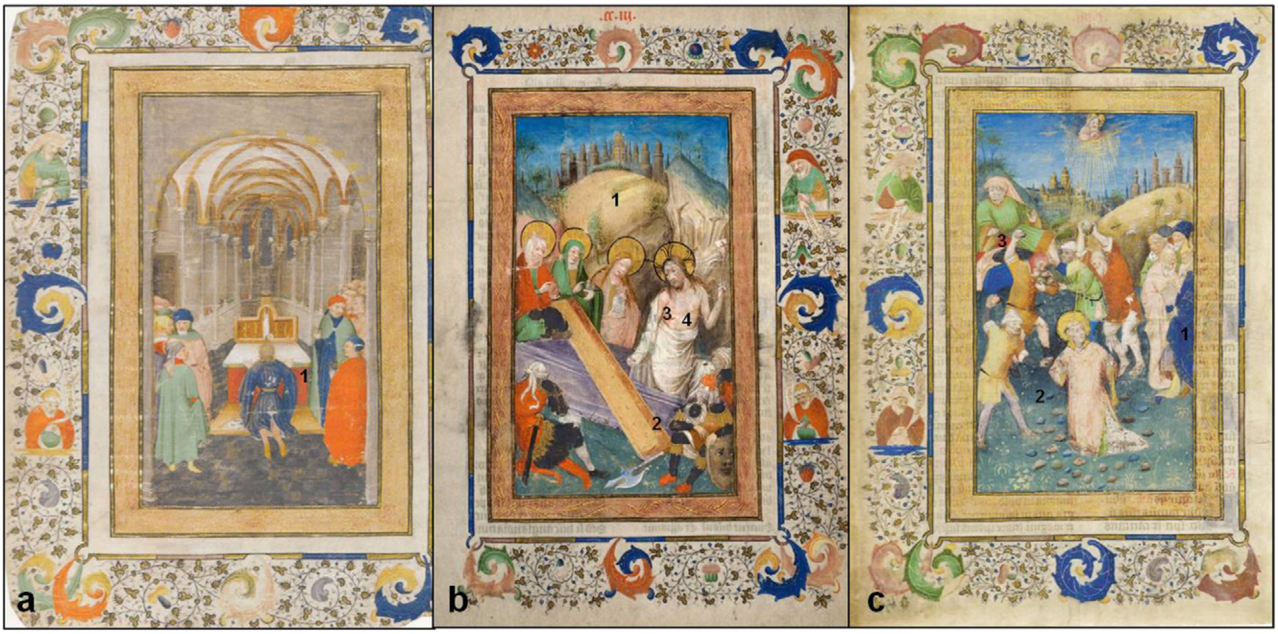

Fig. 2. Pictures of the three analysed miniatures: (a) King Salomon in the Temple (Fitzwilliam Museum), (b) The Resurrection of the Christ (University Library of Utrecht); and (c) The Stoning of Saint Stephen (British Library).

Fig. 3. Pictures of two folios painted by two different styles: (a) the style of the Masters of Otto van Moerdrecht; and (b) the style of the Masters of Zweder van Culemborg.

3.2. Analysis with mobile Raman spectroscopy

Table 1 gives an overview of the identified pigment on the three analysed folios.

3.2.1. White colour

The white pigment used for the three folios could be identified as lead white ($2PbCO_3{\cdot}Pb(OH)_2$). Fig. 4(a) shows the Raman spectrum of lead white, with the characteristic Raman band of the symmetric stretch vibration of CO_3^- at 1050 cm^{-1}. Lead white has been by far the most important of the white pigments used in Europe from the Roman period till the 19th century, when it was replaced by less toxic pigments such as zinc white. Basic lead carbonate is the chemical equivalent of the natural hydrocerrusite. However, hydrocerrusite is extremely rare and consequently barely used as pigment source, which implements that already since the Roman period the synthetic equivalent was used as pigment [16].

3.2.2. Yellow colour

Lead–tin yellow type I (Pb_2SnO_4) could be identified as the yellow pigment used in the three different folios. Fig. 4(b) shows the Raman spectrum of lead–tin yellow type I, with the characteristic Raman bands at: 527, 457, 378, 337, 293, 279, 201 and 136 cm^{-1}. Lead tin yellow type I is found widely in paintings throughout

Table 1
Overview of the identified pigments of the three analysed folios: The Stoning of Saint Stephen, The Resurrection of Christ and King Salomon in the temple.

Colour	f.104	f.202	f.318
White	Lead white	Lead white	Lead white
Yellow	Lead tin yellow type I	Lead tin yellow type I	Lead tin yellow type I
Blue	Lapis lazuli	/	/
Green	Lead tin yellow type I + ultramarine	Lead tin yellow type I	/
Grey	/	Lead white + lead tin yellow type I	/
Brown	/	Massicot	/
Red	Red lead, vermilion	Red lead, vermilion	Red lead, vermilion

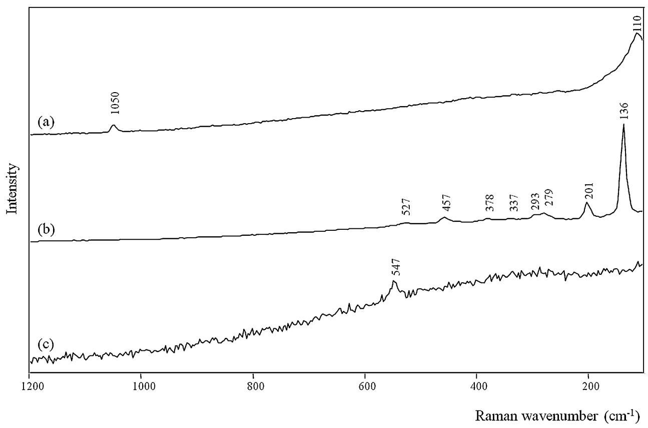

Fig. 4. Raman spectra (6× objective, 1 × 60 s, 10% laser power) of: (a) the white pigment lead white ($2PbCO_3{\cdot}Pb(OH)_2$), (b) the yellow pigment lead-tin yellow type I (Pb_2SnO_4); and (c) the blue pigment ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

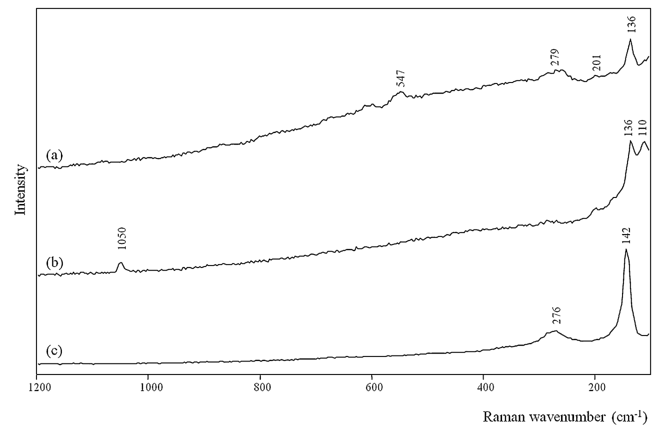

Fig. 5. Raman spectra (6× objective, 1 × 60 s, 10% laser power) of: (a) the green colour, which is a mixture of ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) and lead–tin yellow type I (Pb_2SnO_4); (b) the grey colour, which is a mixture of lead–tin yellow type I (Pb_2SnO_4) and lead white ($2PbCO_3{\cdot}Pb(OH)_2$); and (c) the brown colour, for which massicot (PbO) was used. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Europe from the 14th century until the first half of the 18th century. It does not appear to have been used in other places or cultures unless specific trade with Europe took place [16].

3.2.3. Blue colour

Only for The Stoning of Saint Stephen, the precious pigment lapis lazuli ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) could be identified. This pigment was found on the garment of the male figure depicted on the right side of the folio (Fig. 2(c) point 1). This male figure could be identified as King Saul [15]. The importance of this male figure is also confirmed by the presence of lapis lazuli, which was a very expensive pigment in the 15th century and was only used for important or holy figures. For all the other blue colours on the three folios we were not able to identify the blue pigment with Raman spectroscopy. Probably the pigment used for these blue areas is azurite ($2CuCO_3{\cdot}Cu(OH)_2$). Azurite has a similar colour as lapis lazuli, but was much cheaper during the 15th century. Unfortunately azurite is a very weak Raman scatter and is therefore difficult to detect with Raman spectroscopy, especially during in situ measurements.

Fig. 4(c) shows the Raman spectrum of lapis lazuli, with the characteristic Raman band at 547 cm^{-1}. This Raman band is caused by the $\nu(S{-}S)^{2-}$ symmetric stretching mode. The pigment lapis lazuli is sometimes also named ultramarine, a term of historical importance used since Antiquity. Additionally, this term is also used for artificially prepared pigments of similar composition. Consequently, the qualifications 'natural' and 'synthetic' are frequently used to differentiate between the two types. The pigment used for this miniature is most likely natural ultramarine, as the first commercial production of synthetic ultramarine dates from 1828. Raman spectroscopy is not able to distinguish between natural and synthetic ultramarine in paint layers [16].

3.2.4. Green and grey colour

The green colour used on The Stoning of Saint Stephen (Fig. 2(c) point 2), could be identified as a mixture of lapis lazuli and lead–tin yellow type I. The Raman spectrum (Fig. 5(a)) shows the characteristic Raman band at 547 cm^{-1} of ultramarine and the Raman bands of lead–tin yellow type I: 279, 201 and 136 cm^{-1}.

For the grey colour on The Resurrection of Christ (Fig. 2(b) point 1), a mixture of lead–tin yellow type I and lead white could be identified. The Raman spectrum (Fig. 5(b)) shows a combination of the most intense Raman band of lead–tin yellow type I (136 cm^{-1}) and the characteristic Raman bands of lead white (1050 and 110 cm^{-1}).

3.2.5. Brown colour

The pigment used for the brown colour on The Resurrection of Christ (Fig. 2(b) point 2), could be identified as the yellow pigment massicot (PbO). The red pigment used in the mixture to get the brown colour hue could not been identified. Massicot has characteristic Raman bands at 276 and 142 cm^{-1} (Fig. 5(c)). It occurs as soft yellow earthy masses in association with lead ore deposits worldwide [16]. Massicot is currently used to refer to the orthorhombic lead(II) oxide mineral with composition PbO. In contrary, litharge [16] is used to refer the tetragonal lead(II)oxide mineral with composition PbO. Litharge has also a yellow colour, but is in the context of painting technique, it is mentioned as driers added to oil. Traces of litharge were also found as impurities in red lead [17]. Red lead refers to the red lead(II,IV) oxide mineral with composition Pb_3O_4 (minium) [16].

3.2.6. Red colour and incarnation

For the red colour two pigments could be identified: red lead (Pb_3O_4) (Fig. 6(a)) and vermilion (HgS) (Fig. 6(b)). Vermilion was perhaps the Romans' most valuable pigment, it was used in ambitious works and proved great wealth [16]. During the Middle

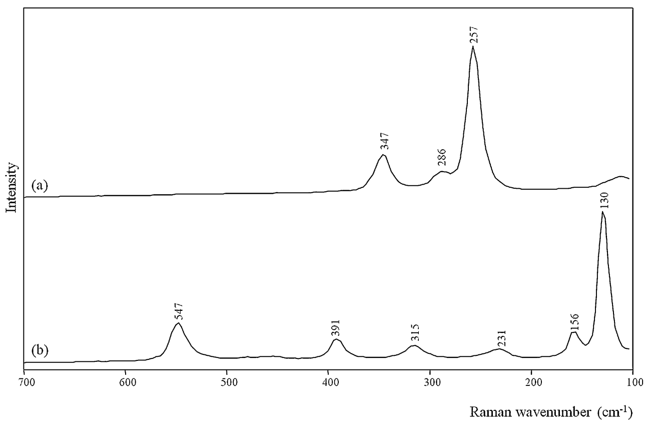

Fig. 6. Raman spectra (6× objective, 1 × 60 s, 10% laser power) of two identified red pigments: (a) vermilion (HgS) and (b) red lead (Pb_3O_4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Ages the expensive pigment vermilion was therefore sometimes replaced by a cheaper pigment, namely red lead. Red lead commonly occurs in small amounts as a bright red or orange powder or crust formed as a secondary mineral in the weathering zone around lead ore deposits. The mineral may have been used as a pigment in ancient times although the synthetic analogue was one of the first pigments to be manufactured [16]. The preparation of the synthetic red lead from lead white was already known in the Greek and Roman times. In the 15th century red lead was derived from lead metal in a two stage process of which litharge was the intermediate product [18].

On King Salomon in the Temple, vermilion was only found on the altar (Fig. 1(a) point 1). For all the other red parts of the folio, red lead was identified as red pigment. These results lead to the assumption that the more expensive vermilion was only used for the holy objects, such as the altar. On The Resurrection, the same assumption could be made: the more expensive vermilion was found in the wounds of Christ (mixed with lead white) (Fig. 2(b) point 3 and 4).

Based on this information we assumed that on The Stoning of Saint Stephen (Fig. 2(c)) no traces of vermilion would be identified, because no red colour was used for the Holy figures King Saul (depicted on the left) and Saint Stephen (depicted in the middle). Nevertheless, vermilion was found for the colouring of the garment laying on the ground, which is depicted in the back of the miniature (Fig. 2(c) point 3). For all the other red parts red lead was identified as pigment.

The hierarchical colour use can only be found on the first two folios, while for the 3rd folio a garment laying in the back of the folio was painted with the more expensive vermilion. This information about the identification of the red pigments, may point in the direction that only King Salomon in the Temple and The Resurrection of Christ, were made by the same workshop and that folio 104, The Stoning of Saint Stephen, was eventually made by another hand.

3.3. Interpretation of the results

Based on stylistic examination The Resurrection of Christ and The Stoning of Saint Stephen, were assigned to the same hand in the workshop, while King Salomon in the Temple probably was made by a different hand, working in the style of the Masters of Zweder van Culemborg. However, based on the identification of the red pigments by Raman spectroscopy, King Salomon in the Temple and The Resurrection of Christ were made by the same hand, while The Stoning of Saint Stephen, might be made in another hand. Next to the hierarchal colour use of the red pigments, also hierarchical colour use of the blue pigments can be retrieved. For The Stoning of Saint Stephen, the blue pigment used for the garment of the King Saul is the more expensive ultramarine. This results in contradiction in the classification based on the identification of the red pigments and, even more important, different of the classification based on stylistic comparisons.

The possible explanation for this difference in classification could be found in a passage on the stoning of Saint Stephen in the Bible: *58 Then they cast him out of the city and stoned him.* ***And the witnesses laid down their garments at the feet of a young man named Saul****. 59 And as they were stoning Stephen, he called out, "Lord Jesus, receive my spirit." 60 And falling to his knees he cried out with a loud voice, "Lord, do not hold this sin against him." And when he had said this, he fell asleep [Acts 7:54].*

In this passage, only the witnesses laid down their garment, but it could be that the garment in the back visualises the garment of the Holy Stephen, and therefore the more expensive vermilion was used.

Combining all these results lead to the following conclusion: the three folios are probably made in the same workshop, following the style of the Masters of Zweder van Culemborg, where the artists respected the hierarchal colour use. King Salomon in the Temple, shows significant stylistic differences with the two other folios. Raman spectroscopic analysis was not able to identify differences between the different hands. Further research on the pigment use in workshops has to be performed.

4. Conclusions

In this work, in situ Raman spectroscopy was used to investigate the colour palette of three different full-page miniatures from the Breviary of Arnold of Egmond. Although it is clear that once these miniatures were part of the same manuscript, at some point in the past they were separated and today, they belong to the three different collections. By performing in situ Raman spectroscopy measurements in the darkened room in the conservation department, it was possible to identify the pigments lead white, lead tin yellow type I, lapis lazuli, massicot, red lead and vermilion. When studying the blue and red pigments hierarchical pigment use could be demonstrated.

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