# A TXRF and Micro-Raman Spectrometric Reconstruction of Palettes for Distinguishing Between Scriptoria of Related Medieval Manuscripts

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Assigning related medieval manuscripts to different workshops on the basis of codicological characteristics, is not straightforward. We present the first attempt to distinguish between scriptoria by means of a large-scale total reflection X-ray fluorescence (TXRF) analysis of pigment elements and an identification of pigment molecules with micro-Raman spectroscopy. We analyzed 324 colored items in 10 medieval manuscripts, of which 7 are folio-sized illuminated manuscripts, all ordered by Raphael de Mercatellis in the late 15th and early 16th century. Palettes in miniatures were not yet examined. Blue palettes are exclusively azurite-based and are easily differentiated by means of the respective amounts of Ti, Ba, and As. Differences for green palettes are also pronounced. The green Cu-based pigment was not yet identified, but it certainly is not malachite or verdigris. Red pigments used are HgS, vermilion, and $Pb_3O_4$, red lead. The Flemish gold-leaf technique is used. The 7 Mercatellis manuscripts show two different palettes, both different from the non-Mercatellis manuscripts. The grouping of the Mercatellis manuscripts according to date and to palettes is, in general, consistent with a grouping on the basis of a classical codicological analysis, although some conflicting results are obtained. A quantitative and qualitative reconstruction of palettes by means of TXRF- and Raman-spectra, provides with a complimentary and objective tool for distinguishing between scriptoria.

## Introduction

Confronting conclusions of (art-)historians about important artifacts from the past with those obtained by scientific experimental techniques, remains an intellectual challenge[1]. Well-known examples are the proton milliprobe analysis of Gutenberg's bible[2] and the debate that arose about the Shroud of Turin[3][4][5].

The late Middle Ages and the early Renaissance are crucial periods for the transfer of knowledge, since exactly then a large manuscript-production was confronted with the in(ter)vention of printing. Many medieval manuscripts are illuminated and decorated. The quality of their miniatures not seldom compares well with that of paintings by illustrious contemporary artists[6]. But, whereas today almost everything is known about the contents of these manuscripts, in some intriguing cases little is known, until today, about the workshops (scriptoria) involved. Using a codicological approach, *distinguishing* between workshops producing *similar* manuscripts is very difficult, when no alternative historical sources are available, e.g. archives in abbeys or monasteries regarding their scriptoria or other identification means, sometimes left in the manuscript by scribes or illuminators[6].

Only recently, progress has been made in *identifying* pigment *elements* used in paintings and in medieval manuscripts[7][8] by TXRF (total reflection X-ray fluorescence) spectrometry, a technique conceived already in 1971[9][10]. The use of micro-Raman spectroscopy in manuscripts for identifying *molecules* started in 1984[11]. This technique was also recently applied by Clark et al.[12][13][14].

Sampling in manuscripts for these analyses is non-destructive and a large number of samples can be taken without damaging the manuscript. One sample provides enough material for both TXRF and Raman analyses. Despite all these possibilities, no large scale study has yet been reported on a *quantitative* reconstruction of palettes in a series of *related* medieval manuscripts. The 80 manuscripts, ordered by *Raphael de Mercatellis*[15], an illegitimate son of Philip the Good, Duke of Burgundy, represent such a series. A codicological analysis of the 60 remaining Mercatellis manuscripts, now held by libraries all over the world, has been carried out[16][17][18] and led to a classification of all

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  1434−1948/98/0505−0639 $ 17.50+.50/0 

Table 1. Manuscripts and samples

| Ms | **Short description** (Date[a]) | Codicological group[b] | Parts or hands[c] | TXRF-samples | Blue | Green | Gold | Red | UL[d] |
|---|---|---|---|---|---|---|---|---|---|
| M1 | Georgius Reisch, Margarita Philosophica (1505 ?) | **3(3)** | 2 | 56 | 19 | 7 | 8 | 22 | Ms 7 |
| M2 | Richardus de Bury et al., several works (1492/4) | **3(2)** | 3 | 27 | 9 | 1 | 3 | 14 | Ms 67 |
| M3 | Plutarchus, De Viris Clarissimis (1492) | **2(1)** | ≥1 | 25 | 6 | 5 | 4 | 10 | Ms 109 |
| M4 | Decretum Gratiani (1505?) | **3(6)** | 3 | 70 | 21 | 4 | 9 | 36 | Ms 3 |
| M5 | Auctoritates Aristotelis (?) | **3(8)** | 3 | 30 | 11 | 3 | 4 | 12 | Ms 13 |
| M6 | Plato, Opera (?) | **3(8)** | 3 | 37 | 10 | 4 | 5 | 18 | Ms 1 |
| M7 | Petrus de Abano, Expositio problematum Aristotelis (1479) | **2(1)** | 3 | 47 | 17 | 4 | 5 | 21 | Ms 72 |
| nM1 | Hagiologicum Slavicum (?) | (Bulgaria) | 1? | 5 | – | 1 | – | 4 | Ms 408 |
| nM2 | Thomas Aquinas (1280–1400 ?) | (Paris) | 1? | 19 | 9 | – | – | 10 | Ms 117 |
| nM3 | Exercitiones (?) | (Cologne) | 1? | 8 | – | – | – | 8 | Ms 211 |
| | | Total | ≥18[e] | **324** | *102* | *29* | *38* | *155* | |

[a] Probable date of production or acquisition from indications in the Ms. – [b] Classical codicological group(sub-group)[16]. – [c] If the number of hands >1, different hands or workshops *might* have been involved in the manufacturing of the manuscript[16]. – [d] Ghent University Library holding. – [e] M1–M7.

Mercatellis manuscripts in function of their codicological characteristics.

Given the technical and artistic skills required and the financial implications for producing manuscripts[6], the actual number of Mercatellis workshops must have been rather small, since these manuscripts were all made in the region Ghent-Bruges, where there was a tradition of manuscript-manufacturing in the late Middle Ages and early Renaissance. Scriptoria, working in this very typical and famous *Ghent-Bruges style*, however, did not make Mercatellis manuscripts[17]. Who exactly produced these 80 Mercatellis manuscripts remains an open and still intriguing question, although several suggestions have been made[16][17][18].

Therefore, we decided to use two analytical techniques to reconstruct both qualitatively (with Raman) and quantitatively (with TXRF) some Mercatellis palettes. The initials, the paragraph marks, the rubrication, and especially the very typical colored decorations *in margine* provide with an excellent basis for pigment analysis and palette reconstruction. This study is a first step in a larger project, aiming at an inventory of palettes of scriptoria, to be used for the identification of other historically important manuscripts of unknown or uncertain origin.

## Manuscripts

Table 1 gives a short description (with date), the codicological group, determined by a number of visible characteristics, and the number of parts of the 7 Mercatellis manuscripts (M1–M7) studied. Three non-Mercatellis manuscripts (nM1–nM3) were also analyzed.

## Results and Discussion

*Elements Detected by TXRF:* Table 1 also shows the distribution of the 324 samples, taken by rubbing a dry and clean cotton-wool swab (Q-tip) over the not-varnished colored surfaces (initial, paragraph-mark, rubrication, ...). With a Mo-tube, 12 elements were detected: Ca, Fe, Zn, Cu, Hg, Au, Pb, Ti, As, Mn, Ni, and Sr. With a W-tube Ba, Ag, Sn, and Sb could be retraced. Since nanogram samples can not be weighted, concentrations must be estimated by normalizing the sum of the elements detected to 100. This is by no means exact, since elements with atom number < 11 can not be detected.

*Element Classification and Pigment Identification by Micro-Raman Spectra:* Ca, Fe, and Zn are considered as *non-pigment elements.* Their presence in the majority of samples is due to the preparation of the parchment and to the presence of (traces of) ink. Although ink is not considered here as a pigment, samples taken from the inks predominantly contain Ca, Fe, and Zn and the latter two elements are highly correlated. Raman spectra of white grains show that Ca is mainly present as $CaSO_4$ (gypsum) and $CaCO_3$ (chalk).

The only *pigment key-element for blue and green* is Cu. The blue pigment used is azurite, easily identified by Raman. The green pigment, usually believed to be malachite or verdigris, must be another still unidentified but certainly Cu-based pigment (malachite and verdigris were not yet detected by Raman).

Two *pigment key-elements were found for red*: Hg in the pigment vermilion (HgS) and Pb in the pigment red lead ($Pb_3O_4$), both identified by Raman.

Two *precious elements* were detected Ag and Au (mainly in 38 gold initials).

Finally, 8 (to 11) *minor elements* were found: Ti, Ba, As, Sn, Ni, Mn, Sr, and Sb (to be combined with Cu, Hg, and Pb when *not* present as a main pigment element). The white pigment $BaSO_4$ was identified by Raman. All Raman spectra will be presented elsewhere[19].

*Blue, Green, and Red Palettes:* Figure 1 shows the experimental TXRF-results (percentages of elements found) for each of the 9 blue samples in nM2, without the main pigment element Cu and the non-pigment elements Ca, Fe, and Zn. For 7 samples, the overall constitution is very similar and amounts to an average of about 6% of the sample total. In the samples on pages 1 and 2, Ba is *not* detected.

This is not surprising, since Ba in this manuscript is the key-element in the whitener $BaSO_4$.

Figure 1. All 9 blue samples for nM2, without Cu and non-pigment elements (8% level)

The consistent reproduction of nearly the same percentages for each of the minor elements in the samples must result from the fact that a large number of basic manuscript elements (parchment, parchment preparation, pigment, pigment composition, granular structure, adhesion, resistance to rubbing, ...) remains invariant throughout the complete manuscript.

These observations lead to the conclusion that this 800-page *pecia* manuscript, made in Paris in the 14$^{th}$ century, was made in a single workshop, whereby the same technique and material (azurite) was used for blue initials and paragraph-marks. A specific whitener, $BaSO_4$, was used in the larger part of the manuscript (except in the first pages).

Conversely, these results demonstrate the consistency of the sampling and of the TXRF-analysis.

In Figure 2 on the other hand, the *average* composition for blue and green samples is given for all manuscripts.

Two very different *blue palettes* appear: one for the group M1-M4-M5 and another one for M2-M3-M6-M7, although the same pigment azurite is used in both cases. But, although within each group the palettes are very similar, the *averaged totals* of the element percentages differ significantly, in contrast with the results in Figure 1. For blue, the palette of nM2 resembles that found for M1, but the "absolute" amounts of material vary from 2.5% for M1 to over 5% for nM2 (a difference of a factor of 2).

In the hypothesis that the same, yet unidentified, Cu-based green pigment is used in all Mercatellis manuscripts M1−7, the *green palettes* confirm the group M1-M4-M5 but the pair M6-M7 emerges. Green for M2-M3 is intermediate. For green, the nM1 palette compares with those found for M2 and M3.

This grouping is further confirmed by the *red palettes* (not shown)[19]: two red pigments are identified by Raman (HgS, vermilion and $Pb_3O_4$ , red lead).

The 7 Mercatellis manuscripts can therefore be divided in 2 distinct palette-groups:

*Palette-group I:* **M1**, *1505?*; **M4**, *1505?*, and **M5**, *date?*.

*Palette-group II:* (**M2**, *1492/94*))*?*; **M3**, *1492*; **M6**, *date?*, and **M7**, *1479*.

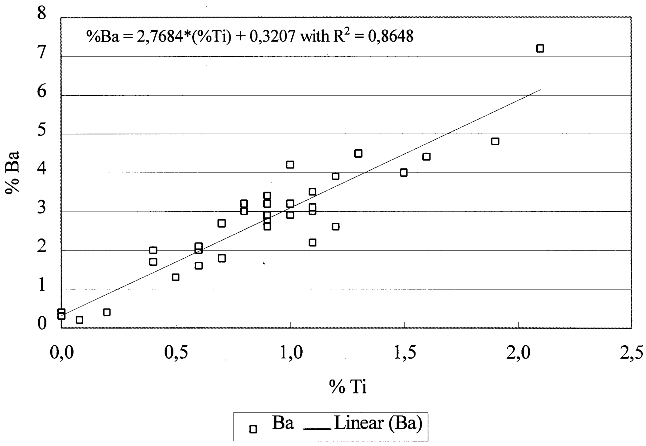
The detailed confrontation of this result with a codicological analysis is given below. A first conclusion is that the yet undated manuscript M5 can be situated around *1505* and the other one M6 in the period 1479−94 (with a preference for *1479*).

*Group II* is the oldest, as it goes back to pigments used from 1479 onwards, and remained active at least for some 15 years, using the same style and the same coloring technique.

*Ba/Ti-Ratio in Blue Samples:* Another detail on palettes revealed by TXRF spectrometry is shown in Figure 3, where %Ba is plotted against %Ti for 34 *blue* samples, in which Ba is detected. The average Ba/Ti ratio equals 2.8, with a correlation $R^2$ better than 0.86. The observed fluctuations in this ratio (not shown) remain between ± 40%, a result to be expected in the case of element ratio's on account of the accuracy of TXRF analyses. The origin of this ratio is not yet clear.

Figure 2. Average palettes for blue and green (without Cu and Ca) for all manuscripts

Figure 3. %Ba versus %Ti for 34 blue data points




Raman spectra show that Ba is present as $BaSO_4$, a whitener (see also Figure 1). The molecule containing Ti remains a problem. Normally it would be $FeTiO_3$, but an Fe-Ti correlation was not (yet) found. $TiO_2$, a modern whitener, must be excluded, since it is generally accepted that this pigment was not known in the Middle Ages (although the mineral rutile, found in the Alps, is known as a gem from Antiquity). Raman did not reveal any traces of $TiO_2$. No correlation was found for Ti or Ba with any of the 14 other elements. Their presence as a pair is mainly restricted to blue samples in *group I* manuscripts *and in nM2*.

Almost no As is found in the blue samples of *Group I* manuscripts, where large amounts of Ti and Ba are found. The opposite situation applies for *Group II* (see Figure 2).

*Gold:* The two classical types of illuminations are present in Mercatellis manuscripts: *shell* (or liquid) *gold* is used mainly in *decorations in margine*, whereas *gold leaf* is reserved for *initials*. Shell gold was detected in 25 leaves and ranks out of 60 rubbed, although just rubbing of a colored surface was intended.

Gold initials continue to be real eye-catchers of medieval manuscripts, as intended 500 years ago. Gold is not always used for the initial itself but also for its *background*. Gold-leaf techniques can vary locally[6]: in Flanders and Germany, the parchment is first covered with a *brownish gesso* where an illumination is wanted, on which the gold leaf is fixed when the gesso was dry. In many Mercatellis manuscripts, this brownish gesso shows through the parchment at the back of the initial.

In most of the 38 gold initials, silver is detected and the Ag/Au ratio varies from 0.01 to 0.15. In one M2-initial 37% Ag was found, exactly as much as Au. Another initial (first page in M2) contains 4,4% Sn, which *could* indicate that mosaic or synthetic gold ($SnS_2$) was used, but this is highly improbable*. In *group II*, three initials are found with Pb/Au ratios between 6 and 1, whereas usually only a few percent Pb is found. In all three, gold leaf is used in the background. Here, lead is probably originating from white decorations in the initial (internal contamination, see also below).

In Figure 4, a logarithmic scale is used to plot the Cu/Au ratios for 37 gold initials (for one initial Cu/Au = 0). The majority of initials shows a low Cu "palette" (Ag, Cu, Hg, Pb, and Ni contribute 10 to 15% to the sample-total). However, for 10 initials in the two *palette-groups* (i.e. the 10 data points in Figure 4 with black background), the slope of the line connecting the data points almost vanishes and a plateau emerges at an average Cu/Au ratio of about 1:75. This *might* indicate that, irrespective of the palette-group, orders for gold (or gold leaves) were invariantly placed with the same merchant or that the same kind of coin was used for making gold leaves[6]. However, further work remains to be done on this point.

The first 12 gold initials in Figure 4 have a relatively high Cu/Au ratio (>0.1). High Cu/Au- and Pb/Au-ratios for gold initials must be explained by internal and/or external contamination. Sampling small decorated gold initials can easily lead to contamination by pigment elements in the initial's decorations (internal contamination). But, samples were also taken from large initials, where internal contamination can be avoided. Even then, as much as 30% Ca can be found, indicating that "external" contamination is substantial. This contamination is due to the intense contact between *facing pages* in a manuscript, kept closed almost constantly for about 500 years by means of straps. This kind of contamination is even clearly visible in M1: the white lower margin on f. 263r almost shows a "color-copy" of a decoration *in margine* on folio 262v.

### *TXRF and Raman Results versus Classical Codicological Results*

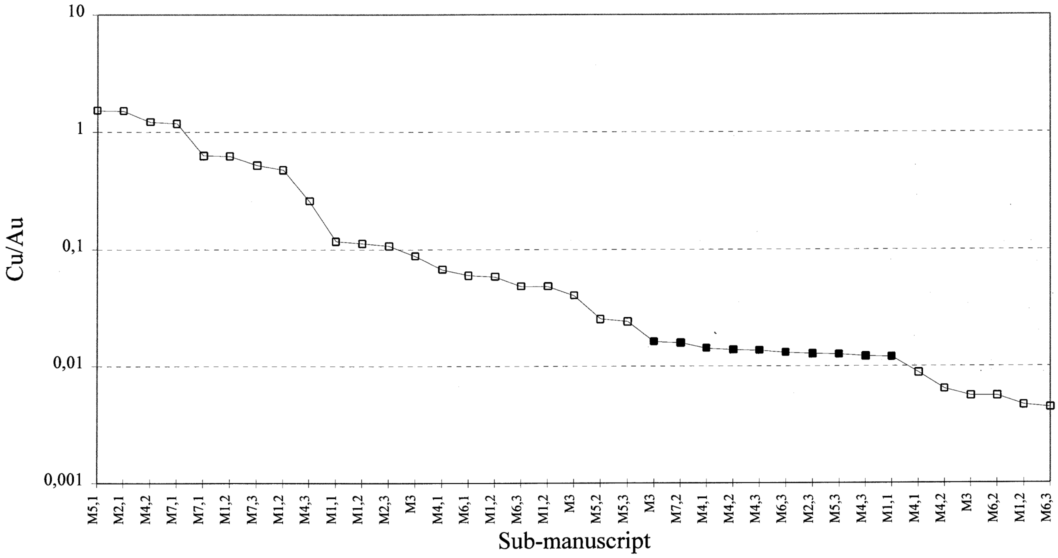
Only the identification of pigments used in manuscripts by means of Raman spectroscopy allows one to reconstruct palettes on the basis of TXRF results. In this work, Raman spectra provided with conclusive evidence concerning the presence of some important (pigment-)molecules, such as $BaSO_4$, HgS, $Pb_3O_4$, $CaSO_4$, $CaCO_3$, $2CuCO_3 \cdot Cu(OH)_2$. Attempts to identify Ti molecules and lapis lazuli were not yet successful (miniatures were not yet analyzed in this work). Given the importance attached to blue pigments in the making of medieval manuscripts[1][6](see also below), it is a pity that *lapis lazuli* can not be detected by TXRF. So far, we did not yet find Raman evidence for lapis lazuli in any of the 93 blue samples but the Raman analysis shows that the blue pigment used in all manuscripts, studied here, is azurite. This observation allows us to confront the results of the palette reconstruction for blue illustrations, obtained in this work, with the results of codicological analyses on the same Mercatellis manuscripts. This confrontation is done on two levels: the complete manuscript and the sub-manuscripts (see Table 1).

### *The Complete Manuscripts*

A classical codicological analysis is based upon a comparison of the visible characteristics of 60 Mercatellis

* Sn is found in only 7 of 324 samples (1 gold initial and *6 blue ranks*), and is highly correlated with Pb (%Pb = 5.456 × %Sn − 5.88 with $R^2$ = 0.9647). Here Pb, with Sn, is probably used as white lead (to be confirmed by Raman spectra).

Figure 4. Ratios Cu/Au for gold initials, descending order




manuscripts still in existence[16][17][18]. Applying TXRF and Raman makes some invisible characteristics also visible.

The different codicological groups for the 7 Mercatellis manuscripts are given in Table 1. The result of the confrontation of the codicological with the analytical studies is given in Table 2.

Table 2. Confrontation of a codicological classification (CC) with palette-groups for 7 Mercatellis manuscripts

| *CC*[a]*/Palette-group*[b] | **2(1)** | **3(2)** | **3(3)** | **3(6)** | **3(8)** |
|---|---|---|---|---|---|
| Palette-group I | | | M1 | M4 | M5 |
| Palette-group II | M3, M7 | M2 | | | ***M6*** |

[a] Taken from Table 1. – [b] This work.

For 6 out of 7 Mercatellis manuscripts, an acceptable result is obtained. However, the palette reconstruction suggests that the dividing line for the codicological classification should not be drawn between the major codicological groups **2** and **3** but between the codicological subgroups **3(2)** and **3(3)**, if the palette classification for M2 is valid (see above). In addition, M6 and M7 have similar palettes, whereas the codicological analysis reveals differences. This result for M6 is intriguing, so we further quantified and refined the palette reconstruction for blue decorations, which have always been important in manuscripts and since azurite is the only blue pigment found.

### *Correlation Between Sub-Manuscripts on the Basis of Blue Palettes*

In Table 1, the 4th column gives the number of *parts* distinguished codicologically in the 7 Mercatellis manuscripts, giving a total of 18 sub-manuscripts (see bottom line in Table 1). Correspondingly, sub-manuscripts are distinguished as follows: the 2 different parts in M1 will be designated as $M_{1,1}$ and $M_{1,2}$ and so on for all 7 Mercatellis manuscripts.

Table 3 gives a correlation matrix for these 18 Mercatellis sub-manuscripts, calculated on the basis of the average percentages found for 10 *minor* elements in blue samples: Hg, Au, Ti, Ba, Ag, As, Sn, Ni, S and Sb. The correlation matrix consists of the Pearson product-moment correlation coefficients for the variables. A positive correlation between 0.6 and 1, rounded off, is given in bold; the identity in the diagonal is given by *1*.

The first 8 sub-manuscripts of *palette-group I* are similar (except in part for $M_{5,3}$) and the 10 sub-manuscripts of *palette-group II* form an even more homogenous set (in each case a *positive* correlation is found). There is no or a slightly negative correlation between sub-manuscripts of the two different *groups I and II* (except in part for $M_{6,3}$).

Parts $M_{5,3}$ and $M_{6,3}$ are slightly different from the other parts in M5 and M6. But, Table 3 also shows that most parts distinguished codicologically are not only consistent with the complete manuscript but also with the Mercatellis palette-groups *I and II*, the manuscript belongs to. Removing one (sub-)manuscript from one palette-group to the other, as suggested codicologically (see Table 2), would distort the symmetry of Table 3.

The blue palette of nM2 is correlated with *group I* and less with *group II* (see also Figure 1 and Figure 2). This is remarkable, since the *pecia* nM2 originates from Paris. The fact that a similar technique was used by geographically separated scriptoria in the 14th century for a completely different kind of manuscript, is an extra argument for distinguishing between two local Mercatellis workshops, which used different blues.

The refined analysis in Table 3 confirms that both M2 and M6 are members of *palette-group II*, which is in support of their position in Table 2. An extra codicological argument for the position of M6 is that the size and the ruling of this manuscript are the same as for Mercatellis manuscripts in group **2(3)**[16].

Table 3. Correlation matrix for blue data-points by palette-group and by sub-manuscripts on the basis of 10 minor elements

| Sub-ms | $M_{1,1}$ | $M_{1,2}$ | $M_{4,1}$ | $M_{4,2}$ | $M_{4,3}$ | $M_{5,1}$ | $M_{5,2}$ | $M_{5,3}$ | $M_{2,1}$ | $M_{2,2}$ | $M_{2,3}$ | $M_3$ | $M_{6,1}$ | $M_{6,2}$ | $M_{6,3}$ | $M_{7,1}$ | $M_{7,2}$ | $M_{7,3}$ | $nM_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Palette Group I* | | | | | | | | | | | | | | | | | | | |
| $M_{1,1}$ | *1* | | | | | | | | | | | | | | | | | | |
| $M_{1,2}$ | **0.9** | *1* | | | | | | | | | | | | | | | | | |
| $M_{4,1}$ | **0.9** | **0.9** | *1* | | | | | | | | | | | | | | | | |
| $M_{4,2}$ | 0.4 | **0.7** | **0.6** | *1* | | | | | | | | | | | | | | | |
| $M_{4,3}$ | 0.5 | **0.8** | **0.8** | **1** | *1* | | | | | | | | | | | | | | |
| $M_{5,1}$ | **1** | **0.9** | **0.8** | 0.5 | **0.6** | *1* | | | | | | | | | | | | | |
| $M_{5,2}$ | **0.6** | **0.8** | **0.7** | **0.9** | **0.9** | **0.7** | *1* | | | | | | | | | | | | |
| $M_{5,3}$ | 0.0 | 0.4 | 0.4 | **0.8** | **0.8** | 0.0 | **0.6** | *1* | | | | | | | | | | | |
| *Palette Group II* | | | | | | | | | | | | | | | | | | | |
| $M_{2,1}$ | 0.1 | 0.2 | 0.0 | −0.1 | −0.1 | 0.1 | 0.0 | 0.1 | *1* | | | | | | | | | | |
| $M_{2,2}$ | −0.1 | 0.2 | 0.0 | 0.1 | 0.1 | −0.1 | 0.1 | 0.5 | **0.9** | *1* | | | | | | | | | |
| $M_{2,3}$ | −0.2 | 0.1 | −0.1 | 0.0 | −0.1 | −0.2 | −0.1 | 0.4 | **0.9** | **1** | *1* | | | | | | | | |
| $M_3$ | 0.0 | 0.1 | 0.2 | −0.2 | 0.0 | −0.1 | −0.2 | 0.3 | **0.6** | **0.6** | **0.6** | *1* | | | | | | | |
| $M_{6,1}$ | −0.1 | 0.0 | −0.1 | −0.2 | −0.2 | −0.2 | −0.2 | 0.2 | **1** | **0.9** | **1** | **0.7** | *1* | | | | | | |
| $M_{6,2}$ | −0.1 | 0.0 | −0.1 | −0.2 | −0.2 | −0.2 | −0.2 | 0.2 | **1** | **0.9** | **1** | **0.7** | **1** | *1* | | | | | |
| $M_{6,3}$ | 0.4 | **0.6** | **0.6** | 0.4 | 0.5 | 0.4 | 0.4 | **0.6** | **0.7** | **0.7** | **0.7** | **0.7** | **0.6** | **0.6** | *1* | | | | |
| $M_{7,1}$ | −0.1 | 0.0 | −0.1 | −0.2 | −0.2 | −0.2 | −0.2 | 0.2 | **0.9** | **0.9** | **1** | **0.7** | **1** | **1** | **0.7** | *1* | | | |
| $M_{7,2}$ | −0.2 | 0.0 | −0.2 | −0.2 | −0.2 | −0.2 | −0.2 | 0.2 | **0.9** | **0.9** | **1** | **0.7** | **1** | **1** | **0.6** | **1** | *1* | | |
| $M_{7,3}$ | −0.2 | −0.1 | −0.2 | −0.2 | −0.2 | −0.2 | −0.2 | 0.2 | **0.9** | **0.9** | **1** | **0.7** | **1** | **1** | **0.6** | **1** | **1** | *1* | |
| *non-Mercatellis group* | | | | | | | | | | | | | | | | | | | |
| $nM_2$ | **0.9** | **0.8** | **0.7** | 0.3 | 0.3 | **0.9** | 0.5 | 0.0 | **0.6** | 0.4 | 0.3 | 0.2 | 0.3 | 0.4 | **0.7** | 0.4 | 0.3 | 0.3 | *1* |

## Conclusion

The 7 Mercatellis manuscripts analyzed were certainly made in Flanders using two different coloring techniques but also in two different periods, suggesting that also two different workshops were involved in their production. A large scale TXRF- and Raman-analysis can indeed lead to a quantitative reconstruction of palettes in medieval manuscripts and, even for related manuscripts, palette-differences can be detected. These differences must be attributed either to different hands or techniques, simultaneously available in the *same scriptorium*, to an evolution in manufacturing techniques in the *same scriptorium* or to *different scriptoria*.

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## Experimental Section

A description of the instrumentation used for TXRF and Raman is given elsewhere[7][8][19].

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