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μ-XRF/μ-RS vs. SR μ-XRD for pigment identification in illuminated manuscripts

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ABSTRACT For the non-destructive identification of pigments and colorants in works of art, in archaeological and in forensic materials, a wide range of analytical techniques can be used. Bearing in mind that every method holds particular limitations, two complementary spectroscopic techniques, namely confocal μ-Raman spectroscopy (μ-RS) and μ-X-ray fluorescence spectroscopy (μ-XRF), were joined in one instrument. The combined μ-XRF and μ-RS device, called PRAXIS unites both complementary techniques in one mobile setup, which allows μ- and in situ analysis. μ-XRF allows one to collect elemental and spatially-resolved information in a non-destructive way on major and minor constituents of a variety of materials. However, the main disadvantages of μ-XRF are the penetration depth of the X-rays and the fact that only elements and not specific molecular combinations of elements can be detected. As a result μ-XRF is often not specific enough to identify the pigments within complex mixtures. Confocal Raman microscopy (μ-RS) can offer a surplus as molecular information can be obtained from single pigment grains. However, in some cases the presence of a strong fluorescence background limits the applicability. In this paper, the concrete analytical possibilities of the combined PRAXIS device are evaluated by comparing the results on an illuminated sheet of parchment with the analytical information supplied by synchrotron radiation μ-X-ray diffraction (SR μ-XRD), a highly specific technique.

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1 Introduction

During the last decade, diagnostic techniques have become an essential tool for the conservation of works of art as they can provide decisive information for the selection of the appropriate conservation treatment. As a result, numerous analytical techniques have found a valuable application in the conservation of art. However, every single method has particular limitations. For this reason, in most cases it is necessary to employ a combination of several techniques in order to obtain a complete overview of the composition of a layer of paint.

XRF and μ-XRF are among the most cited analytical methods in literature dealing with the investigation of inorganic materials such as pigments, glasses, ceramics, etc. [1]. The popularity of XRF in art conservation can be explained by the fact that no other analytical technique can identify so many different elements in an efficient and non-destructive way. On the other hand, some drawbacks limit the applicability of XRF. For example, unless a confocal setup is being used, the identification might be hampered in case of a multilayered paint sample. When cross-sections are analysed, the spatial resolution is often too low to investigate the composition of separate layers, which sometimes are only a few μm of thickness. Alternatively, the incident beam can penetrate several layers of paint if the X-rays are directed perpendicular on to the surface of the paint. In this situation, it is often not clear to which layer the detected elements can be attributed. Also, being an element-specific technique that is insensitive to the chemical state, crystal phase or the molecular environment in which the elements are present, XRF is often not specific enough to identify the pigments with certainty. For instance, the detection of copper can indicate the presence of several pigments (azurite, malachite, etc.). In that case, other criteria, for instance the colour of the paint layer or the age of the painting, have to be considered in order to identify the pigment by deduction. Also the characterisation of mixtures of several pigments can be problematic. Moreover, light elements can be difficult to trace, depending on the instrumentation and measurement conditions. In this way the identification of organic pigments and dyestuffs and pigments composed of only light elements (e.g., the carbon-based pigment lamp black) are excluded.

μ-RS is a powerful and more specific technique for the identification of painting materials [2, 3]. It is a vibrational technique based on the fact that a small part of incident radiation is scattered inelastically by a material. The difference in energy between the incident beam (laser light) and the scattered light provides a unique spectral finger print by means of which the molecule can be identified. This method is in many ways complementary to μ-XRF, as it has already been demonstrated by Ricci, et al. [4]. Confocal Raman microscopes can achieve a high spatial and depth resolution, allowing the identification of single pigment grains without interference of surrounding materials. Nevertheless, a strong fluorescence background often caused by the organic medium can limit the applicability of μ-RS spectroscopy. Bearing in mind the complementarity of both techniques, a combined μ-XRF and μ-RS instrument, called PRAXIS, was built at the University of Antwerp, together

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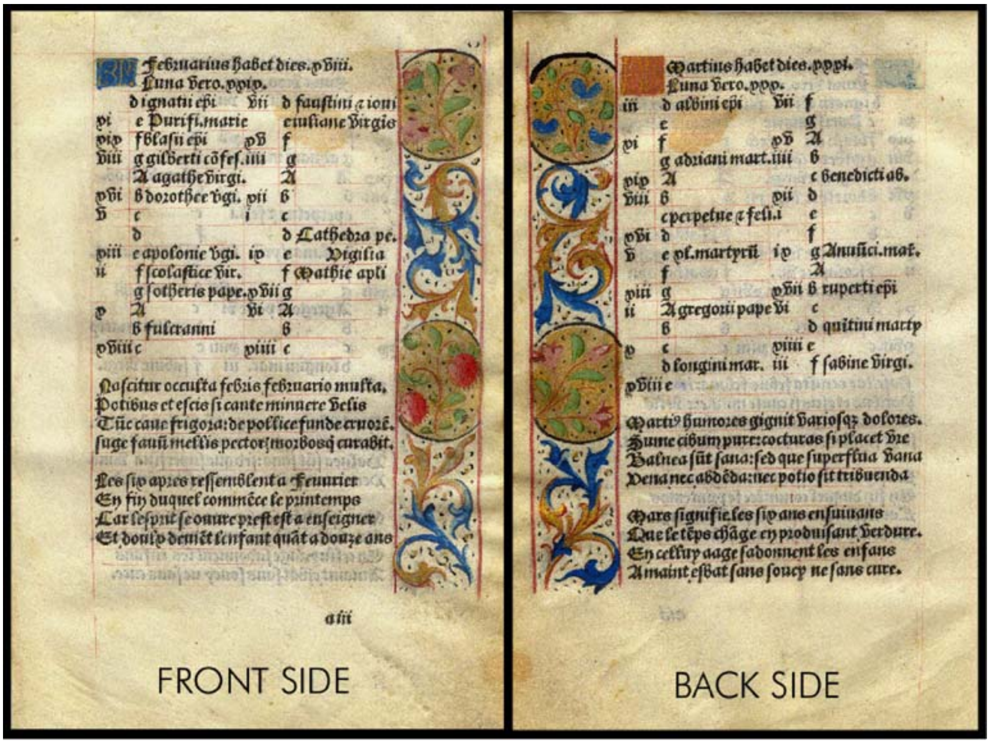

FIGURE 1 Front and back side view of the analysed sheet of parchment

with several other partners: European Laboratory for Non-Linear Physics, Firenze (I); Institut für Gerätebau, Berlin (D); Jobin-Yvon S.A., Longjumeau (F); Ormylia Arts Diagnostic Centre, Chalkidiki (Gr) [5]. In this way, PRAXIS links the elemental, 'bulk' information obtained by XRF to the molecular, surface-related data supplied by Raman. Both techniques were joined in one setup, allowing in situ and micro-analysis.

To evaluate the combined analysis possibilities of PRAXIS, an excerpt from an illuminated, fifteenth or sixteenth century book of tides was analysed (see Fig. 1). The sheet of parchment was written on and painted on both sides. A Latin text is present in black ink, accompanied by a French translation. Red-pink rulers were drawn on the parchment in order to facilitate the writing. In the right margin, various vegetal motives such as strawberries and flowers were applied in gilded cartouches with black borders. The cartouches are separated by decorative scrollwork in blue and gold. The fine trace lines of the figurative depiction were executed in a pink fluid material, which looks very similar to that of the rulers in the text.

2 Experimental

The PRAXIS device consists of an easily transportable base unit which holds the spectrometer, the laser source and a cold light source. A remote measuring head contains a computer controlled *x*–*y*–*z* sample stage, a μ-focus X-ray tube, a polycapillary X-ray lens, an X-ray detector and a Raman probe, as illustrated by Fig. 2.

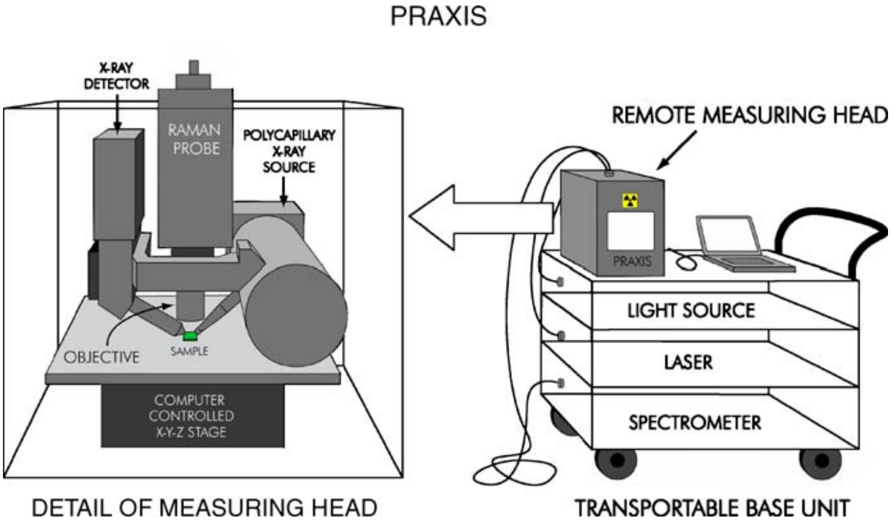

FIGURE 2 Schematic representation of PRAXIS, the combined μ-XRF and μ-RS instrument. On the *left* a detail of the remote measuring head. Dimensions of the transportable head are ca. 25 × 25 × 40 cm^3

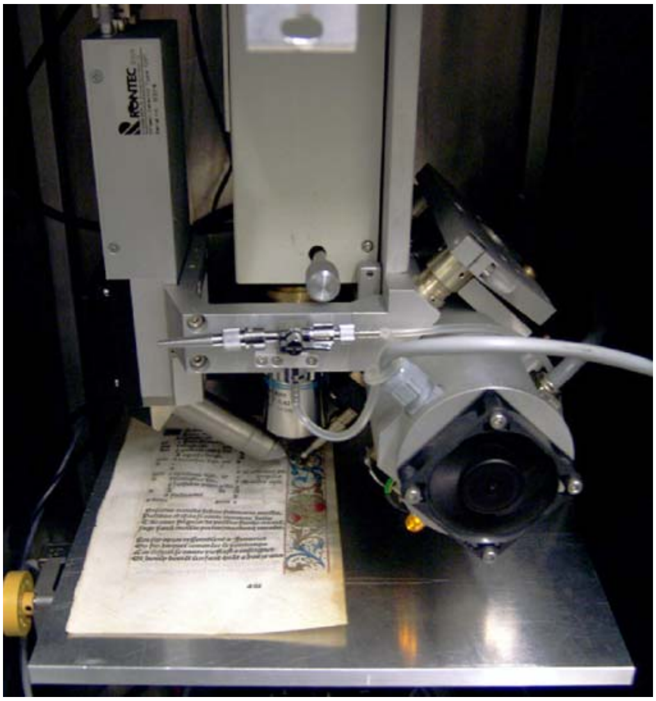

FIGURE 3 The sheet of parchment on the motorised *x–y–z* sample stage of the PRAXIS instrument

2.1 *μ-RS spectroscopy*

The Raman measurements were carried out directly on the sample which was placed on the translation stage. The analysed pigment particles were selected by moving the translation stage and viewing the image of the sample using the on-axis TV-camera that is incorporated in the Raman probe. Due to the current set-up, the sample size is limited to ca. 30 × 30 cm^2.

The laser excitation source was a diode laser (Sacher Lasertechnik, Lynx tunable Littrow external cavity diode Laser) consisting in a laser head and a laser driver (Pilot) to control the laser output power. The laser emitted at 785 nm (to minimize fluorescence of the organic medium). The laser light was transmitted to the Raman probe (Jobin Yvon Superhead) via a single mode optical fibre. The probe contained an on axis TV-camera, an interference filter to eliminate the scattered Raman radiation caused by the optics and an extra long working distance (ELWD) objective (Mitutoyo, 50 ×/0.42 with a working distance of 20.5 mm), which permitted to focus the laser beam on a spot with a diameter of ∼ 5 μm. The scattered light was collected through the same objective and directed to the spectrometer via a separate multimode optical fibre. The entrance to this fiber functions as a confocal pinhole, resulting in a depth resolution of ∼ 8 μm. A holographic notch filter was employed to separate the inelastic scattering from the Rayleigh scattering (see Fig. 3).

μ-Raman spectra were obtained using an Induram scanning spectrometer equipped with a cooled charge-coupled device detector (CCD, Andor, 1024 pixels × 256 pixels), thermoelectrically cooled at −60 °C. The spectrometer was equipped with two dispersive gratings mounted on the same axis (1200 lines/mm and 950 lines/mm). All Raman spectra were collected using the 950 l/mm grating. The spectral resolution achieved with this system is on average 1.5 cm^{-1}/pixel with a 1200 l/mm grating and 1.3 cm^{-1}/pixel with a 950 l/mm grating.

Calibration of the spectrometer was accomplished by using the Raman lines of a slab of metallic silicon. Measurements were carried out for each type of material. The pigments were identified by comparison of their raman spectra with those in a home made database of reference spectra. This extensive database consists of spectra collected from powdered pigments, supplied by several sources.

2.2 *μ-XRF (EDS)*

X-rays were generated with an air cooled, low-power Mo-tube with an acceleration voltage of maximal 50 kV. The primary X-rays were focussed by means of a polycapillary X-ray lens, resulting in a measuring spot size with a diameter of ca. 50 μm. All μ-XRF-spectra were collected using an electro-thermally cooled (−15 °C) silicon drift detector (Röntec Xflash detector Type 1207) with an active area

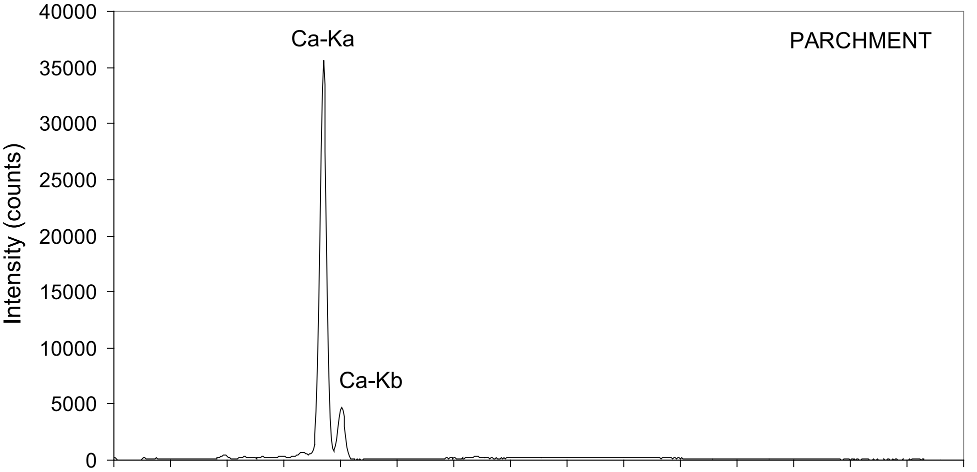

FIGURE 4 μ-XRF spectrum collected on the unpainted parchment, from the spot of analysis shown in Fig. 6

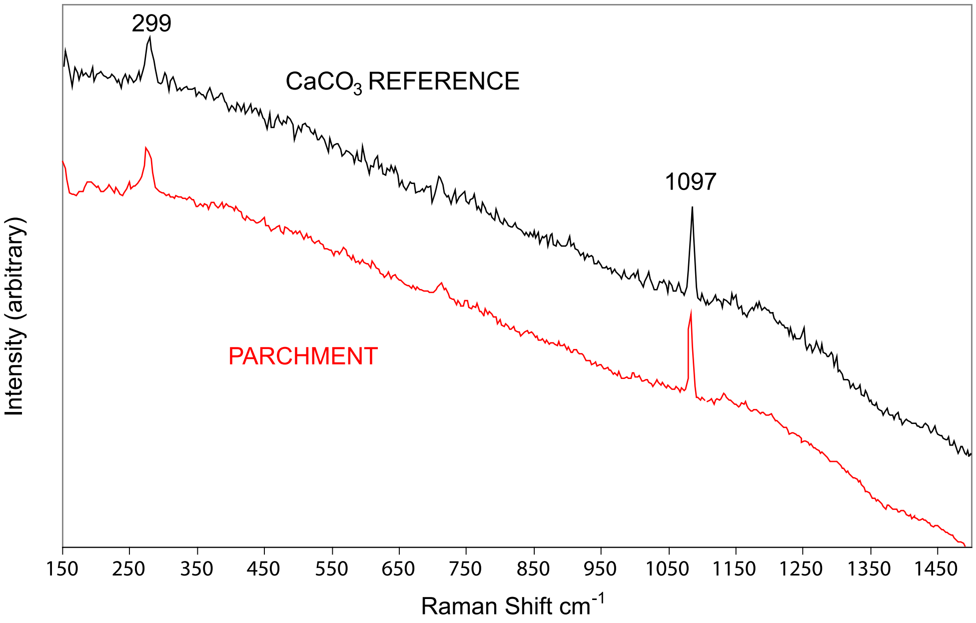

FIGURE 5 The reference μ-RS spectrum of calcite (*black*) vs. the μ-RS spectrum collected on the unpainted parchment (*red*), from the spot of analysis shown in Fig. 6

FIGURE 6 Detail of the area where the μ-XRF and μ-RS spectra of the unpainted parchment and the ink were collected. Data shown in Figs. 4 and 5 respectively

of 5 mm^2, an 8 μm thick beryllium window and a zirconium collimator with an aperture of 2.4 mm. Working under a Helium atmosphere is possible but this option was not exploited during these experiments. All measurements were performed at 35 kV, 500 μA, and with an acquisition time of 200 s (live time). The sample positioning was identical as for Raman spectroscopy.

2.3 *μ-XRD*

μ-XRD experiments were carried out at HASYLAB, Beam Line L. Monochromatic X-ray microbeams of 10–15 μm diameter of low divergence (< 4 mrad) were generated by means of a Si⟨111⟩ monochromator and a single-bounce elliptical capillary [6]. A Bruker 1000 X-ray diffraction camera, positioned in transmission geometry, together with a Si(Li) detector at 90°, allows one to simultaneous collect μ-XRF and XRD data on the irradiated part of the sample.

3 Results and discussion

Prior to the analysis on the parchment, a μ-RS and μ-XRF reference database was established by measuring raw pigments from several sources (Kremer, Winsor & Newton, etc.). The database also includes optimum measuring parameters and the damage thresholds of the pigments under the 785 nm laser light. This information facilitated the Raman analysis and also allowed to avoid damage or degradation to the paint layer by localized overheating.

As Figs. 6, 8 and 11 illustrate, several spots on the parchment, representing all present materials, were selected for analysis. It concerned measurement positions inside the red, green, blue, and pink painted areas and positions on the unpainted parchment, the gilding and the black ink. All spots were analysed both by means of μ-RS and μ-XRF.

3.1 *Parchment*

The μ-XRF spectrum shown in Fig. 4 revealed a substantial amount of Ca in the parchment. This was expected, as chalk was abundantly used during the preparation of parchment. At the same spot, Raman spectra were obtained which confirmed these results (see Fig. 5). The collected spectra matched the reference spectrum of calcite ($CaCO_3$), showing the characteristic carbonate stretch around 1097 cm^{-1}.

3.2 *Black ink*

Four types of black ink were known in the 15th–16th century: soot ink, bister, sepia and iron gall ink. Soot ink and bister are two carbon-based inks, prepared from wood-ashes, while sepia is an animal product obtained from squids. The main ingredients of the fourth type, namely iron gall ink, were vitriol ($FeSO_4$), tannic acid (from gall nuts), Arabic gum and water [7]. Bister and sepia have a brownish ink colour and were predominantly used for drawings, so it is not very likely that they were used as a writing material in this case. The fact that the μ-XRF-measurements did not reveal any Fe in the ink, allowed to exclude iron gall ink, leaving soot ink as the only ink compatible with these indications. Unfortunately, it was

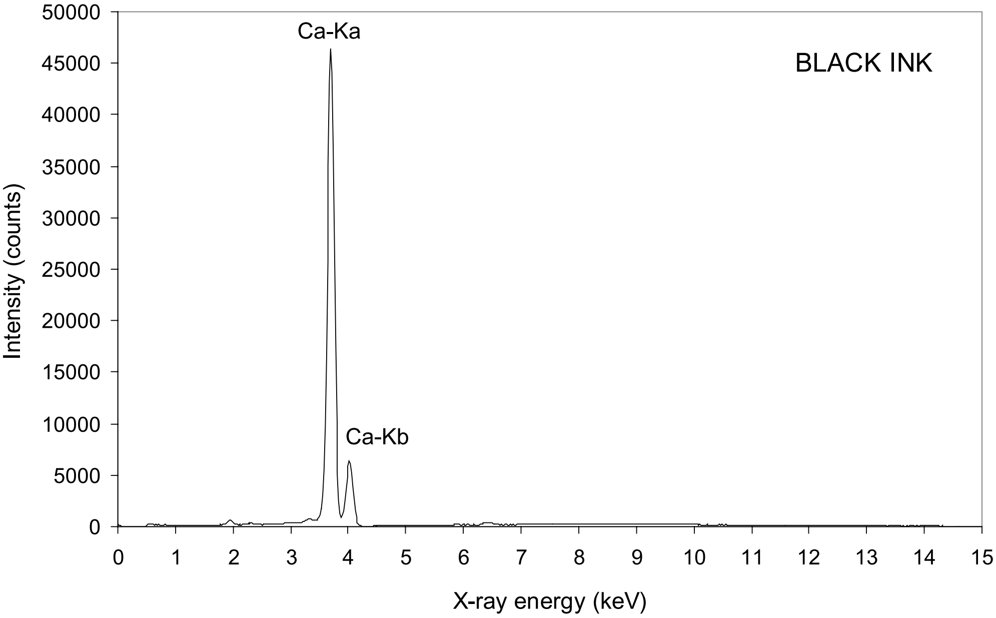

FIGURE 7 μ-XRF spectrum collected on the black ink

not possible to produce a clear Raman spectrum demonstrating the carbon vibration stretch to confirm this hypothesis. The characteristic broad bands at about 1350–1380 cm^{-1} and 1580–1600 cm^{-1} were not observed. The μ-XRF spectrum of the black ink (see Fig. 7) only showed the characteristic X-ray emission lines of Ca, which could be attributed to the underlying parchment.

3.3 *Paint and gilding*

The μ-XRF spectrum of the red paint (Fig. 9) showed intense Hg and S peaks, two elements which can be related to the red pigment vermilion (HgS). This mercury(II)sulphide is a red pigment that was frequently used by artists from antiquity until the 20th century. Both vermilion from mining sources (also called cinnabar) and from artificial production was used; however, neither X-ray fluorescence nor Raman spectroscopy allow to make a distinction between the natural and synthetic variants [8]. The presence of a small peak of Ca in the X-ray spectrum can be due either to chalk, which was often used as a filler in paint, or to the parchment itself (as explained above). The identification of the red pigment was confirmed by the result of the μ-RS analysis, as the collected spectrum correlated with the reference spectrum of cinnabar (Fig. 10). The Raman spectrum collected in the red paint yielded strong bands at 253 and 343 cm^{-1} and a weaker band at 282 cm^{-1}.

In Fig. 12, the μ-XRF spectrum of the gilded area shows, apart from the expected Au peaks, also significant Cu peaks. The copper is not related to the gilding but to the blue paint on the back of the parchment. This is an example of how the penetration depth of the X-rays can lead to interpretation problems, a problem which has been reported by other authors [1]. μ-RS analysis of the blue paint indicated that the copper containing pigment was azurite ($2CuCO_3 \cdot Cu(OH)_2$) with characteristic bands at 398, 763, 834, 931 and 1094 cm^{-1} (Fig. 13). Azurite is a basic copper(II) carbonate which was one of the important blue pigments in European painting until ca. the eighteenth century when it was largely replaced by Prussian blue, next to the more expensive lazurite ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$).

In this case, the interpretation of Raman data was substantially simplified by the results of μ-XRF, as this technique

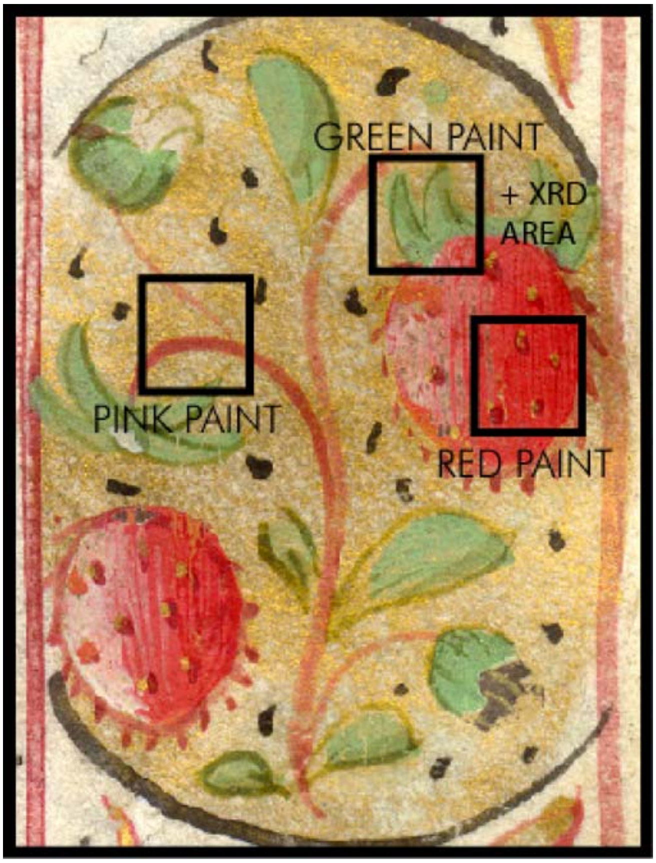

FIGURE 8 Detail of the *green*, *red* and *pink areas* where the μ-XRF and μ-RS spectra were collected. Data shown in Figs. 9 and 10 respectively. The XRD data presented in Figs. 18 and 19 were recorded in the *green paint area*

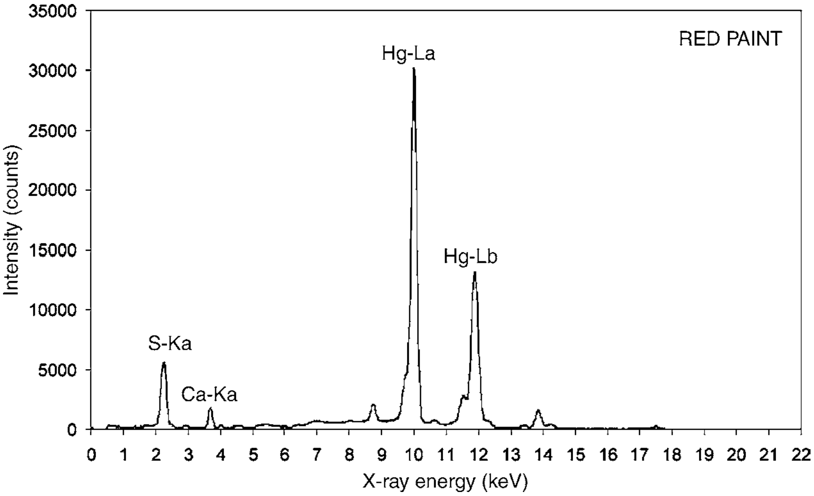

FIGURE 9 μ-XRF spectrum collected in the red paint, from the spot of analysis shown in Fig. 8

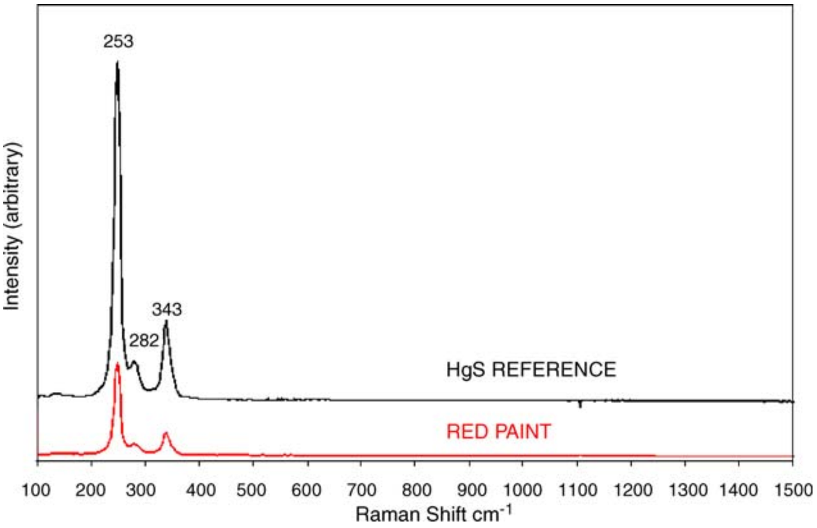

FIGURE 10 The reference μ-RS spectrum of vermilion (*black line*) matches the μ-RS spectrum collected in the red paint (*red line*), from the spot of analysis shown in Fig. 8

allowed to narrow down the number of possible pigments that are present. The identification by μ-RS of a completely unknown pigment can take a substantial amount of time, since all pigments not only require various optimal parameters but also show different damage thresholds toward laser light. As only one copper containing blue pigment was known at that time, the proper parameters could be selected quickly, by means of the reference database. The gold could not be identified by means of Raman spectroscopy, as most metals do not produce characteristic Raman bands [8].

According to the μ-XRF measurements (see Fig. 15), the green paint contains a substantial amount of both copper and lead. This last element could be ascribed to the presence of lead-tin yellow (Type I: Pb_2SnO_4 or type II: $PbSn_2 \cdot SiO_7$) and/or lead white ($2PbCO_3 \cdot Pb(OH_2)$). With regards to Cu, three green copper-based pigments were in use at the time, namely malachite ($CuCO_3 \cdot Cu(OH)_2$), verdigris ($Cu(CH_3COO)_2 \cdot nCu(OH)_2$) and copper resinate. Copper resinate is the general name for a group of organo-copper complexes and is in fact verdigris dissolved in oil and/or resin [10]. The image in Fig. 14 demonstrates that the green paint contains yellowish, greenish and blue grains. The Raman spectra of this area, shown in Fig. 17, revealed that the green grains are malachite. The characteristic peaks

FIGURE 11 *Left*: a detail of the gilded area where a μ-XRF spectrum was collected (data in Fig. 12). *Right*: the same area on the back side of the parchment with blue paint. Signals from the gilding and the blue pain appear in the μ-XRF spectrum

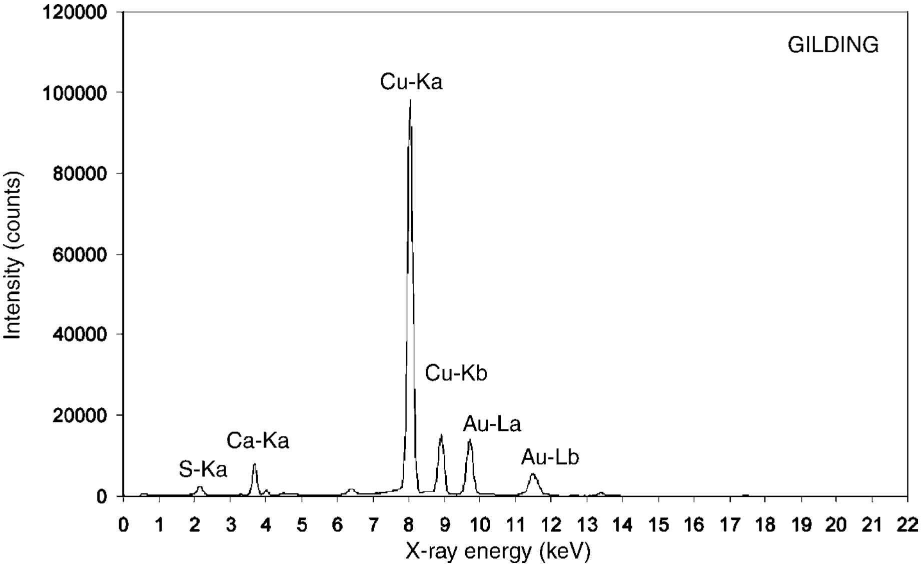

FIGURE 12 µ-XRF spectrum collected in the gilded area, from the spot of analysis in Fig. 11

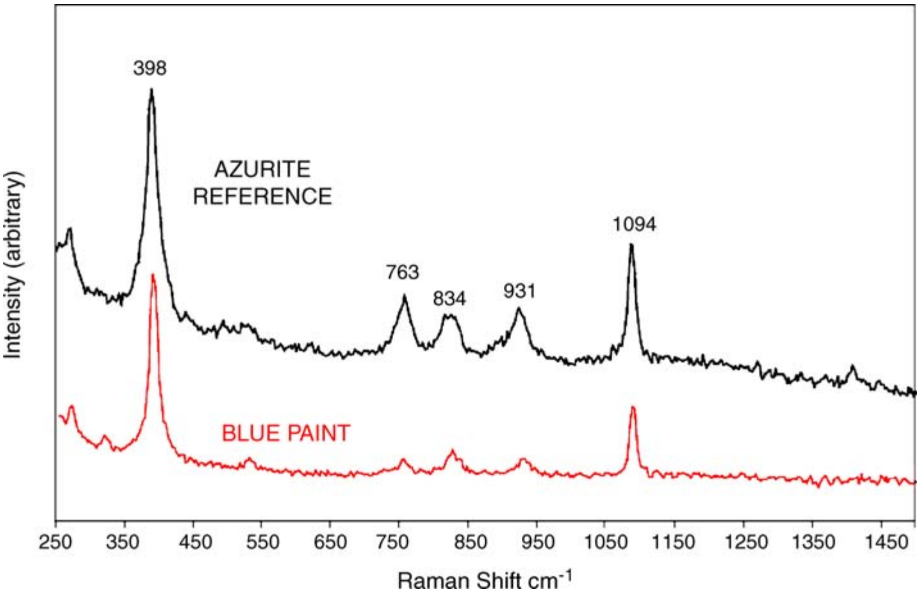

FIGURE 13 Reference µ-RS spectrum of azurite (*upper line*) vs. the µ-RS spectrum collected in the blue paint (*lower line*), from the spot of analysis shown in Fig. 11

around 217, 265, 350, 430, 531 and the carbonate stretch vibration around 1050–1110 cm^{-1} are present. Most Raman spectra only yielded a weak signal while the collection of a clear malachite spectrum required a considerable amount of time, probably due to the fact that the red laser light was strongly absorbed by the green pigment. The blue grains were identified as azurite ($2CuCO_3 \cdot Cu(OH)_2$), as demonstrated by Fig. 13. The distribution of the blue grains is not homogeneous and it is not clear whether the azurite was added intentionally by the artist or if it concerns a contamination of the green, copper containing pigment. Such a contamination is plausible since the azurite mineral is usually found in association with malachite [9]. Raman spectroscopy indicated that the yellowish grains are lead-tin yellow (Type I: Pb_2SnO_4) with bands at 198, 275, 293, 338 and 457 cm^{-1} (see Fig. 16). Burgio et al. also identified lead-tin yellow mixed with malachite to produce a green colour on a 15th century Latin manuscript. A combination of a green with a yellow pigment, was common practice at that time, according to the

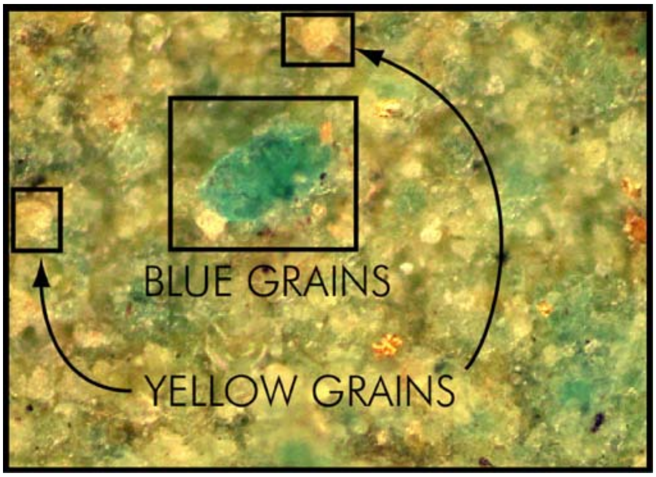

FIGURE 14 Detail of the green paint, shown in Fig. 8. Blue and yellow grains are present in the green paint. Optical microscope Olympus BC40, X50

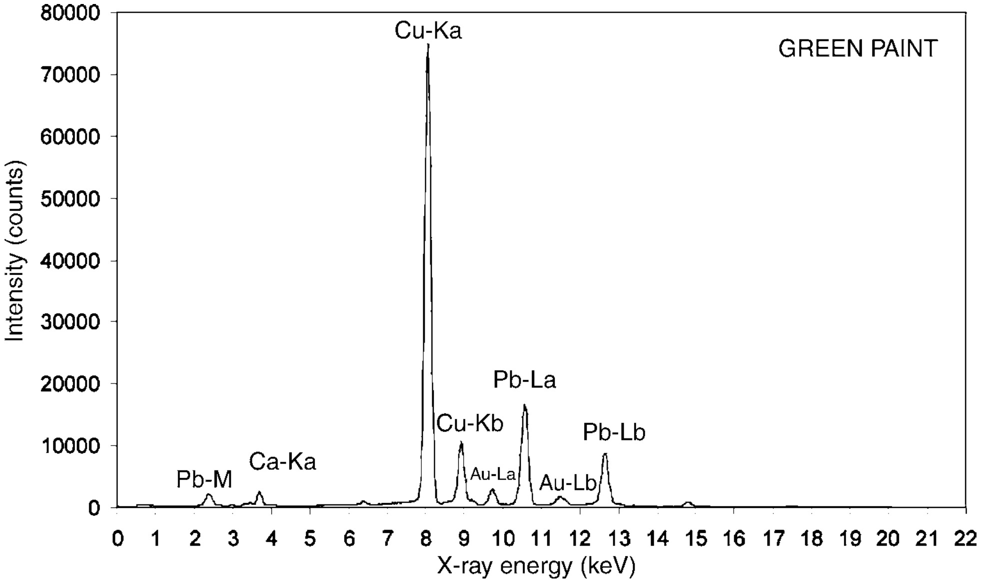

FIGURE 15 μ-XRF spectrum collected in the green painted area, from the spot of analysis shown in Fig. 8

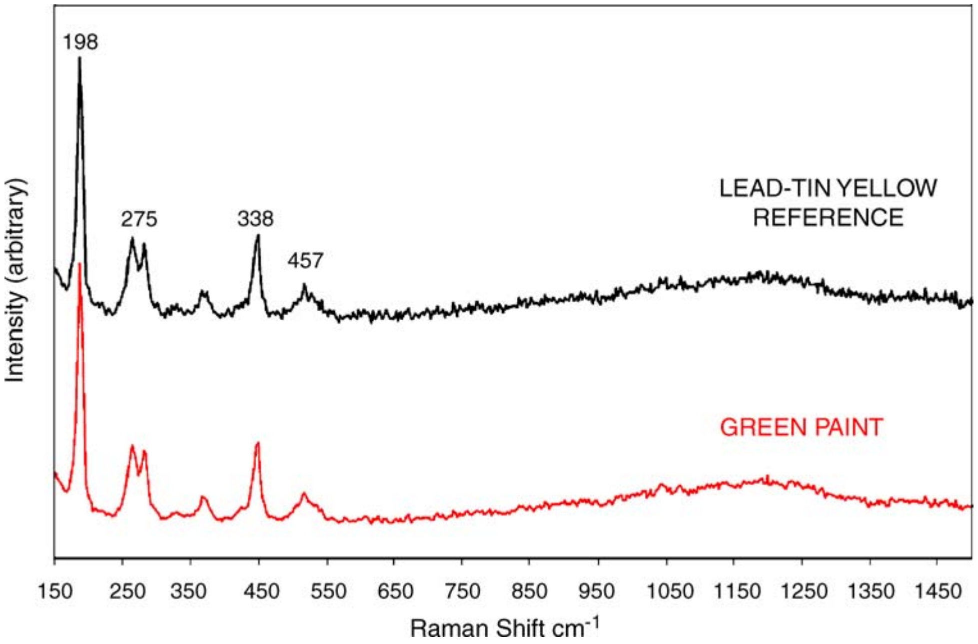

FIGURE 16 Reference μ-RS spectrum of lead-tin yellow type I (*black line*) vs. the μ-RS spectrum of the yellow grains in the green paint (*red line*), from the spot of analysis shown in Fig. 8

same authors [11, 12]. No lead white was found by means of μ-RS. This case highlights that μ-RS is a valuable tool for the characterisation of mixed pigments and contaminations. While μ-XRF gave an indication about the nature of the main green pigment (Cu), μ-RS identified it as malachite and established the presence of two other pigments (azurite and lead-tin yellow) which could not be identified by μ-XRF alone.

The pink pigment, used to draw the rules, could not be identified, as it was not possible to detect by means of μ-XRF any elements related to a red pigment. Furthermore, the collected Raman spectra showed only a fluorescence background and no bands of any known red pigment. This result could imply that some kind of organic dye was used, for example a red lake. Dyes and lakes are known to fluorescence in the visible region and the signal from this fluorescence can hide the characteristic Raman peaks of the organic material [13].

3.4 *SRμ-XRD*

In order to estimate the results of the above-discussed pigment identification by means of the PRAXIS instrument, measurements with SR μ-XRD, a highly specific method of phase identification, were carried out at the Synchrotron facility in Hamburg (Hasylab, Beam Line L). These analyses confirmed the presence of calcite in the parchment, azurite in the blue coloured area, malachite and lead tin yellow in the green paint, vermilion in the red paint and gold in the gilded area. The XRD pattern in Fig. 18, recorded in an area with green paint and gilding, also demonstrates the presence of hydrocerussite (lead white), a material which was not traced by means of μ-XRF/μ-Raman. For each phase a reflection was chosen, which did not overlap with other lines: gold (111), calcite (104), lead-tin yellow (121), lead-white (110) and malachite (120).

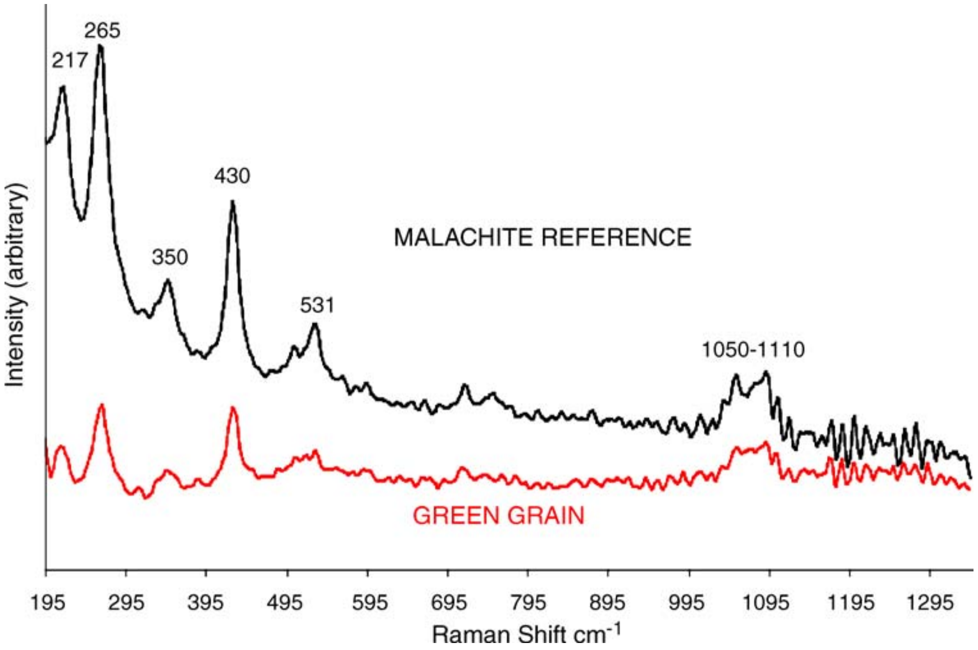

FIGURE 17 Reference μ-RS spectrum of malachite (*black line*) vs. the μ-RS spectrum of the green grains in the green paint (*red line*), from the spot of analysis shown in Fig. 8

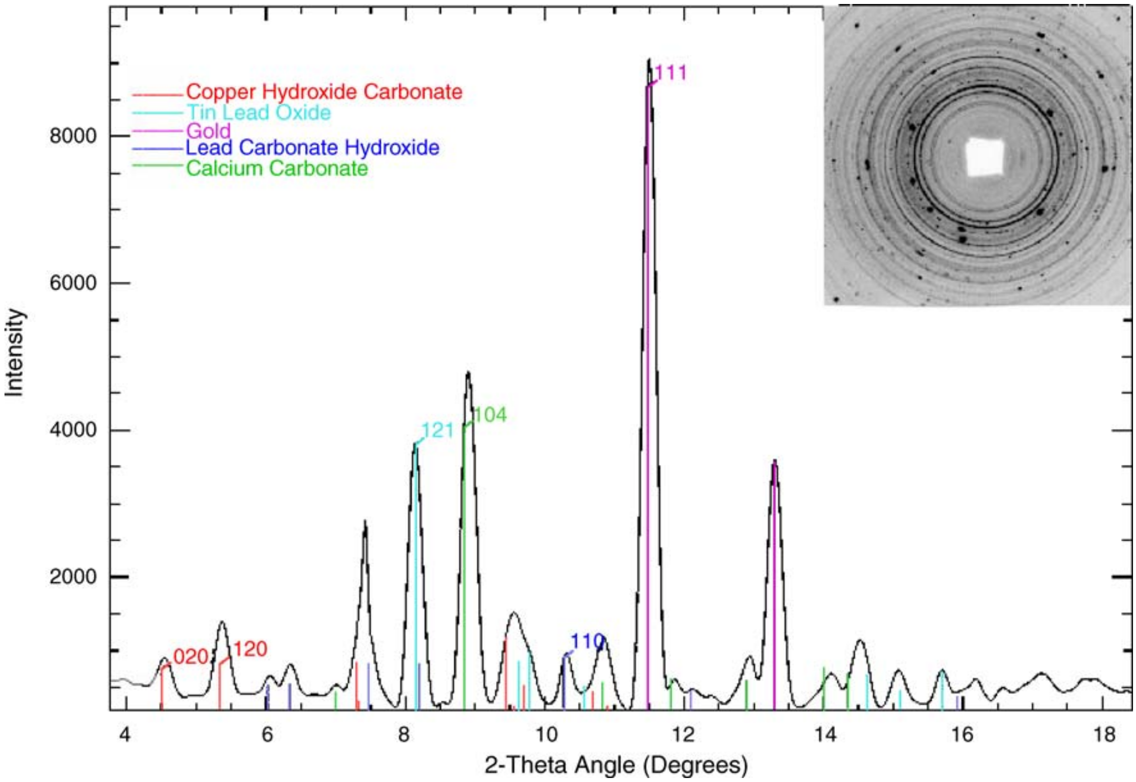

FIGURE 18 XRD patern recorded in the green and gilded area (shown in Fig. 8) confirming the presence of calcite and gold; also the presence of malachite and hydrocerussite (lead white) could be established

In addition, enough crystals were present in the beam to give a powder diffractogram, e.g., fully occupied Debye rings. Therefore the reflection intensity distributions represent the pigment composition in the area. Figure 19 clearly demonstrates that the presence of hydrocerussite is limited to the green paint. Indeed, based on the outcome of the PRAXIS μ-XRF analyses, the presence of lead white in the green area could not be excluded (see Fig. 15). The fact that μ-RS did not detect any lead white could be related to the location of the pigment. Since it is not certain that the lead white was mixed with the green paint, it cannot be excluded that the green paint was superimposed on a locally applied layer of lead white. This hypothesis could not be confirmed, but could explain why the penetrating synchrotron radiation traced crystals of lead white, while the laser beam of μ-RS did not encounter any lead white at the surface. On the other hand, μ-RS clearly identified the blue grains in the green paint as being azurite, this pigment was not detected by SR μ-XRD. This

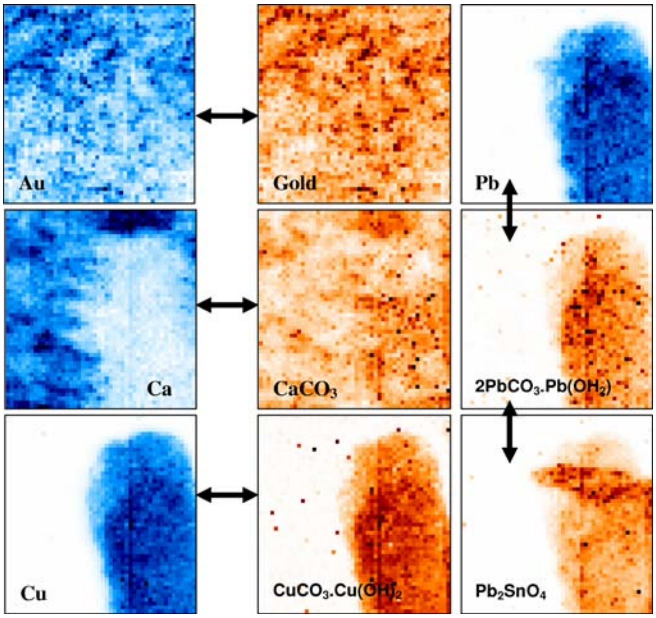

FIGURE 19 Phase composition and corresponding elemental distribution maps obtained by combined μm-XRD-XRF, are shown for the 'green paint'-area displayed in Fig. 8. This $2 \times 2\,\mathrm{mm}^2$ region was mapped with $40 \times 40\,\mu\mathrm{m}$ steps

might be due to the inhomogeneous distribution of the grains (see above) and the fact that probably only a few grains were present in the analysed area.

4 Conclusion

The combination of μ-XRF and μ-RS in the PRAXIS-device has proven itself to be very useful for the identification of pigments. A more complete and definite image of the composition of the samples could be established by linking the bulk-representative, elemental information supplied by μ-XRF to the surface-related, molecular data offered by μ-RS. The complementarity of both analytical techniques became in particular clear during the study of the copper containing green and blue paint layers. It has been demonstrated that μ-XRF can narrow down the number of probable pigments and in that way can facilitate and render the pigment identification more rapid with μ-RS analysis. Also, it was shown how μ-XRF alone, in some cases only allows one to establish uncertain hypotheses. (e.g., about the green pigment used for the vegetal leafs). Nevertheless, these could be ascertained by μ-RS spectroscopy. The spatial resolution (~ 50 μm) of μ-XRF was beneficial for the analysis of the monochrome areas on the parchment, but appeared insufficient to investigate mixtures or multilayered paint layers, whereas μ-RS offered the possibility to identify single pigment grains. In this way, the problems with μ-XRF that originated from the penetration depth of the X-rays, could be counteracted by the depth resolution (~ 8 μm) of the confocal μ-RS setup. Also, the evaluation of these results by means of SR μ-XRD highlighted the fact that this additional technique was necessary to show the presence of lead white with certainty. In spite of this culmination of analytical techniques still a number of organic or non-crystalline pigments (e.g., black and pink ink) could not be identified. This leads to the conclusion that a supplementary method like for example FT-Raman (Nd:YAG laser emitting at 1064 nm) or FT-IR is desirable to enable the identification of organic substances, in order to obtain a complete overview of the composition of all applied materials.

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