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RESEARCH ARTICLE

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Raman mapping of the S_3^- chromophore in degraded ultramarine blue paints

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Abstract A specific case of degradation was observed in synthetic ultramarine paint within 3 paintings from the early 20th century, manifesting as an intricate pattern of white lines criss-crossing the blue paint surface. Raman spectroscopy can be performed directly on untreated sample surfaces and is sensitive to the colour components in ultramarine (S_3^- and S_2^- chromophores). This method was chosen to map the chromophore intensity distribution and to relate it to the surface degradation pattern. Raman signal intensity, however, decreases when the laser is out of focus, providing a challenge when mapping signal intensity across rough or undulating surfaces. To account for this, a series of experiments was conducted to determine the laser and objective combination least sensitive to changes in surface topography. The optimal settings were found to be the 785nm excitation wavelength with the 50× long working distance objective (numerical aperture 0.50). This combination gave the smallest focus-dependent signal decrease on test samples: When shifted 5 µm out of focus above or below the sample surface, the signal from the same spot showed a decrease of 7% only. Maps of the blue (S_3^-) chromophore signal at 548 cm^{-1} taken from 3 samples showed a clear decrease in intensity on the degraded white lines. Patterns of signal intensity distribution matched well with the optical degradation pattern. From this observation, in conjunction with previous surface characterisation reported elsewhere, it was concluded that the surface phenomenon was indeed a discolouration of the ultramarine pigment, caused by a reduction in the concentration of the chromophore.

KEYWORDS chromophore, degradation, Raman mapping, ultramarine

Ultramarine blue - The pigment occurs naturally as the mineral lazurite and has been used as an artist's pigment since the 6th century. The mineral form was largely supplanted by its synthetic equivalent, ultramarine, when a manufacturing process was developed in the first half of the 19th century. Like the natural form, synthetic ultramarine $Na_8Al_6Si_6O_{24}S_2$ comprises a sodium aluminosilicate framework with AlO_4 and SiO_4 tetrahedral units linked by shared oxygen atoms. Colour giving chromophores (S_2^- yellow, S_3^- blue, S_4^- red) are encapsulated in the cavities. These radical sulphur anions are extremely reactive but are stabilised by the pigment framework structure, which prevents reaction with other species.
Ultramarine is generally considered to be a very stable pigment in terms of light exposure and mixing with other pigments. Both natural and synthetic forms are also resistant to ammonia and caustic alkalis.

The degradation observation - the pigment is known to discolour rapidly in the presence of mineral and organic acids, with several reported instances of colour change of natural ultramarine in canvas paintings. These alterations are referred to 'ultramarine sickness', typically observed as a greyish discolouration of the paint surface. The phenomenon discussed here is optically different, expressed as discoloured white lines propagating according to a yet undisclosed mechanism (Fig. 1).

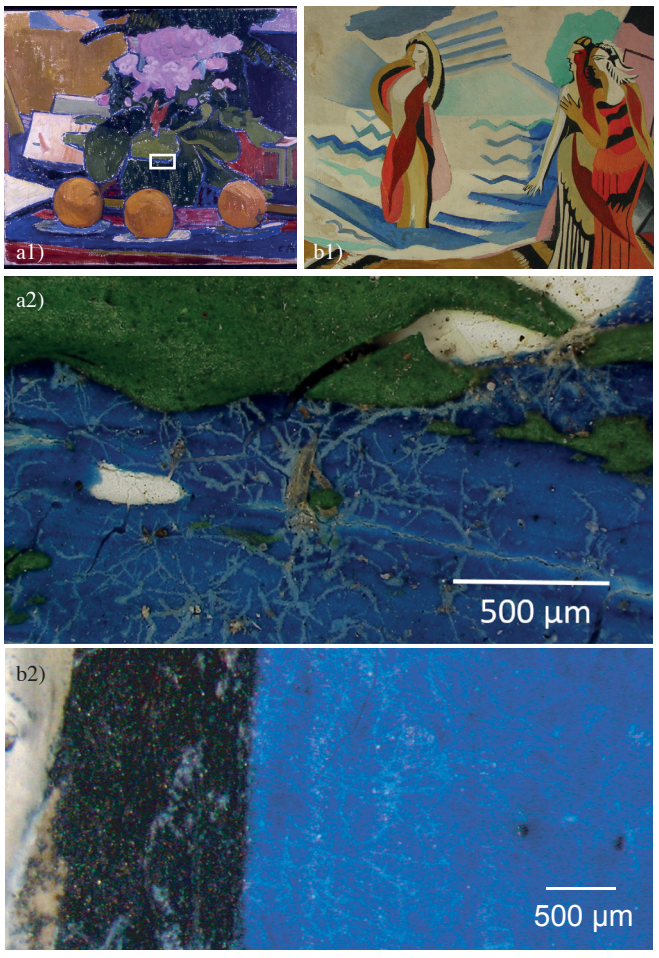

Fig. 1 Paintings showing specific patterns of ultramarine degradation. a1) „Still life with three oranges", painted in 1907/08 by Cuno Amiet with a2) pattern of white lines criss-crossing the surface. b1) „Nausikaa", painted in 1928 by Alexandra Exter. b2) The systematics of the pattern propagation remains yet to be explained.

The analytical challenge - the line discolouration is a surface phenomenon, i.e. it does not propagate into depth and as such cannot or is difficult to be studied in crosssection. Raman spectroscopy does not require sample preparation, is responsive to the S_3^- band (blue chromophore), but is highly sensitive to variable focus (topography). A non-varnished paint surface is 'rough' and thus poorly reflecting the laser beam to make use of the autofocus feature. Comparing relative Raman intensities across an area, based on a single Raman band is thus a tricky task, requiring a setup that minimises the influence of slightly variable focus (Figs. 2 & 3, Tab. 1).

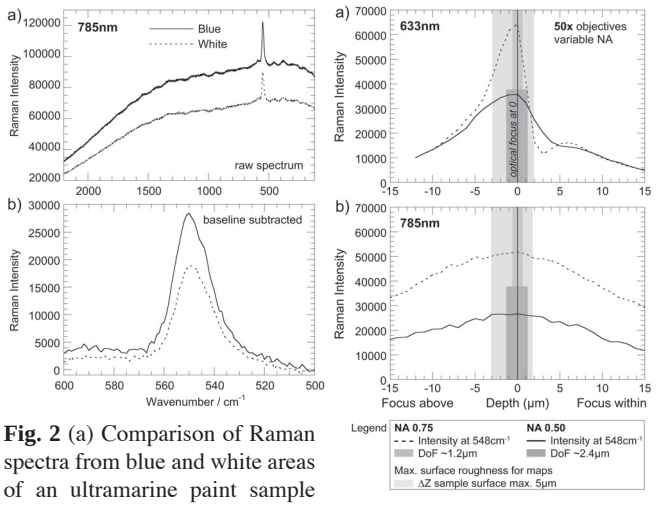

Fig. 2 (a) Comparison of Raman spectra from blue and white areas of an ultramarine paint sample surface. The symmetric stretching vibration of the blue chromophore is visible at 548 cm^{-1} in both spectra; however, no other signals were observed. (b) Comparison of the net intensities at 548 cm^{-1} of the spectra presented in (a) on a blue versus white area after a linear baseline correction in the region of interest.

Fig. 3 Graph of the 548 cm^{-1} chromophore signal intensity on an ultramarine paint film using (a) 633 nm and (b) 785 nm excitation, starting at –15 µm above the sample and ending at +15 µm within the sample. Comparison was made between the standard 50× objective with a higher counting efficiency (NA 0.75), but lower depth of focus (DoF approx. 1.2 µm) versus the 50× long working distance objective (NA 0.50, DoF 2.4 µm). The flatter the intensity distribution, the lower the sensitivity to defocusing

Off focus	1µm	1µm	5µm	5µm
NA	0.50	0.75	0.50	0.75
Laser λ	intensity loss			
633 nm	2-3%	7-30%	35-60%	55-75%
785 nm	1%	1-4 %	7%	8-15%

Tab. 1 Quantification of signal intensity loss when the laser is shifted out of focus.

How we solved it - Performing depth profiles on a single spot with different laser wavelengths reveals the sensitivity to focusing on the surface. In the case of the ultramarine S_3^- band within a paint surface, the combination of the lower the numerial aperture (NA) objective (i.e. greater field of depth) and the higher laser wavelength delivers a setup that is tolerant to within ~5μm of surface roughness (Fig. 4). Thus, by monitoring and selecting an area of interest on the sample surface with less than 5μm topography, the difference in intensity due to variable focus within 5 microns is far less than between original blue and degraded white lines. Mapping the intensity of the S_3^- band at 548cm^{-1} across these white lines therefore documents the degradation of the blue chromophore in ultramarin (Figs. 5-7).

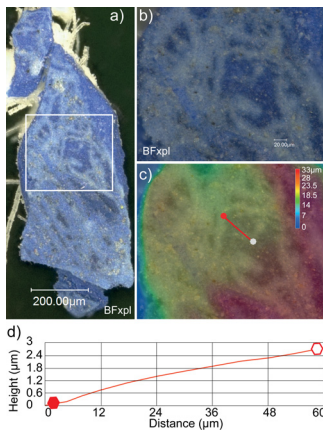

Fig. 4 Light microscopy images of (a) Sample B1, (b) the area selected for analysis based on (c) the topography profile, which indicated a 2.5 µm change in height across the boxed area (d).

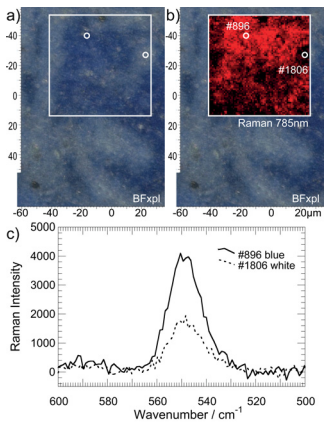

Fig. 5 Sample B1, mapping of the 548 cm^{-1} blue chromophore signal intensity across an area containing both blue and white (degraded) paint showing (a) the light microscopy image of the ultramarine sample surface, (b) the intensity distribution of the chromophore signal with red being high intensity and (c) comparison of two spectra, one taken from a blue area and one from a white. Spectra acquired using 10% laser power (Psample ~ 1.2 mW), 6 s exposure time, and one accumulation.

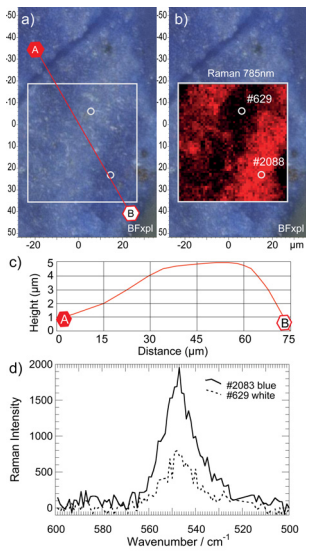

Fig. 6 Sample B2, mapping of the blue chromophore signal intensity distribution across an area containing healthy blue ultramarine and a degraded white line. (a) Light microscope image of the ultramarine paint surface, (b) the 548-cm^{-1} signal intensity distribution of the blue chromophore, where red is high intensity, (c) the topography of the mapped area, (d) comparison of chromophore signal intensity taken from two points, one from a blue area and the other from a white area. Spectra were acquired with 1% laser power (P_{sample} ~ 0.12 mW), 2 s exposure time, and five accumulations.

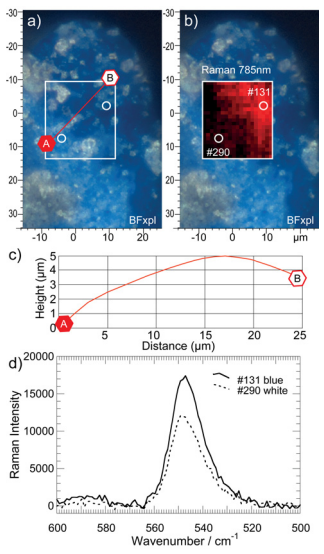

Fig. 7 Sample B3, mapping (a) distribution of the blue chromophore 548 cm^{-1} signal intensity, (b) light microscope image of the mapped surface, (c) the topography of the mapped area, (d) comparison of two points from the mapped region, one degraded white spot and one unaltered blue spot. Spectra were recorded with 10% laser power (P_{sample} ~ 1.2 mW), 10 s exposure time, and one accumulation.

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