Paintings in the laboratory: scientific examination for art history and conservation

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More than thirty five years have passed since the preliminary paper, on the use of the electron microscope on samples from problematic brown discoloured green areas in paintings, was presented at the ICOM Conference in Venice in 1975. In the ‘Discussion’ at the end of this paper a firm statement as to the authenticity of the brown surface layer(s) was not presented. Since then, similar investigations have been made by L. Kockaert at IRPA in Brussels and Joyce Plesters at the National Gallery in London. Summarising this particular conservation problem: green areas in paintings often appear brown. The question then posed by the restorer treating the picture is: is this an original copper resinate (or oleate) type glaze turned brown? or is it a darkened oil varnish or a darkened, varnish applied at a later date? Solving these types of

Fig. 1 Lucas van Leyden, *The Last Judgement*, Museum De Lakenhal, Leiden.


problems is only possible by interpretation of the magnified image of the paint surface together with the observation and analysis of a paint cross-section of the same area. Even in the paint cross-section, when translucent brown layers, including darkened varnishes, are present it is sometimes difficult to judge how far the layers are indeed originally applied green (or yellow?) glazes turned brown, or original oil varnishes or later additions. It is clear that there are several reasons for the brown appearance of green areas, as stated in the 1975 ICOM paper. Copper glazes partially turned brown pose less of a problem as far as originality is concerned, as will be shown below. For this revision of the early paper some of the same cross-sections, described in the paper, were examined and analysed again. For clarity, there are colour illustrations, - colour photography was not allowed for the ICOM paper at the time. Some additional samples from similar problematic areas will be referred to.

The 1975 ICOM paper treats the analyses of three samples from green areas appearing brown in Lucas van Leyden’s *The Last Judgement*, 1526/7, Museum De Lakenhal in Leiden (figs. 1 and 2).

Samples were removed during the restoration (restoration by P.F.J.M. Hermesdorf)³. *The Last Judgement* was

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covered, at the time, by several thick layers of easily soluble varnishes (fig. 3), whose solubility was quite distinct from other deep brown layers, present in green areas below the obviously later applied layers of varnish.

4a and 4b micro photograph of a brown area in the trees, top right, outer right hand side panel of St. Paul, after taking sample 14. 4c thin section of the cross-section of sample 14. 4d cross-section 14 after the micro-destructive scan in 1975, idem 4e, and 4f in blue-uv. Bottom layer: chalk ground; then azurite with a lighter layer of azurite, basic copper sulphate, lead-tin yellow and lead white on top; then a slightly fluorescing dark brown layer and several dark brown varnish layers, showing little fluorescence (oil varnish?).
On the painting surface, in the green areas, the visual effects vary from a slight browning - in drapery -, to a thin layer - at the edge of trees -, to a thick brown crust.

Fig. 5
- Above: electron microprobe analyse sample 14 from 1975 publication;
- middle: SEM-EDX line scan for Cu, S and Fe, ICN 2010;
- below: electron micrograph of sample 14, ICN 2010.
Sample 14 is from the dark green centre of the trees of the outer right hand side panel of St. Paul, where the brown is like a thick brown crust, as shown in figs. 4a and 4b. The sample was analysed again now, using scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX) (fig. 5, middle and bottom). The instrument was a Jeol 5910, used at low vacuum of 32 Pa and 20kV. The 1975 XRD identification of azurite, basic copper sulphate, lead-tin yellow and lead white in the green layers was confirmed as far as the chemical elements present is concerned: SEM-EDX scan confirmed the XRD result of there being comparatively more basic copper sulphate mixed with the azurite in the top layer than in the bottom layer of the two opaque green payers: the ratio Cu/S is clearly lower in the top one (c.1:1) than in the bottom one (c. 4:1). The line scan in fig. 5-middle also shows that the brown top of the leaves is not due to a brown ochre pigment: iron is absent. The browning does not seem to be a case of painting autumn. Instead, there is Cu, and S, distributed though the brown glaze. The varnish layers contain no copper. This means that there is a green glaze turned brown between the opaque bluish green paint layers and the dark varnishes. Sample 117, also from the green of a tree of the outer left-hand panel of St. Peter, was not analysed again using SEM-EDX (fig. 6). However, renewed microscopic examination of the fluorescence of the top layers helped to re-interpret the result described in the 1975 paper: the orange-brown translucent layer, showing a whitish fluorescence and therefore not a copper resinate, is a later addition (copper resinates and oleates do now fluoresce).

With the, compared to 1975, much improved illumination in the research microscope, both in normal light and in blue/ultraviolet, examination of the paint cross-sections and their interpretation has become easier and more secure. It is at least possible to distinguish between glazes and later applied varnishes. In some cases, detecting copper in the thin dark top layers is a problem; the observation under the optical microscope, together with the experienced eye of the restorer, has to suffice. Figs. 7 - 9 illustrate this point.

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4 Object nr 672. Paint cross-sections and micro photographs are being kept at ICN.

5 With thanks to Dr. Ineke Joosten at the ICN in Amsterdam.
Fig. 6 sample 117, brown-green from a tree on the outer panel on the left, depicting St. Peter. The whitish fluorescence at the top at the right hand side of the cross-section in 6b, orange-brown in normal light in 6a, indicates non-original material. 6c see fig. 3, p. 124.

Fig. 7a Cross-section from sample 122, from the top of the tree on the right-hand side of the right outer panel of St. Paul (the same tree as in detail in fig. 8). The brown layer overlaps the blue paint of the water (lead white, finely ground azurite). On the right cross-section from sample 123, both from the tree on the outer panel right hand side, St Paul. The thin section in 7b and the blue-uv photograph 7c show that the green pigment particles are embedded in a non-fluorescing, oil medium. Varnish is absent here, but there is a thin superficial dark brown layer over the original darkened oil medium containing particles of a green copper pigment.
Brown passages in landscapes are not exclusive to Northern painting. As an example the small panel, circle of Giovanni Bellini. In areas, where no green or blue pigment could be detected with the naked eye or the stereomicroscope, the cross-section showed that the brown paint was original, containing azurite in a dark(ened) medium (figs. 9a and b).

Fig. 8 Micro photograph of a detail of the tree at the top of the right hand outer panel of St. Paul. The brown of the trees overlap the water. After removal of sample 15. Right sample 15 in normal light (top) and blue-uv (bottom). At the top of the sample the fluorescing varnish is visible. The - in normal light - translucent orange layer shows only slight fluorescence and is original.

9a Circle of Giovanni Bellin (c.1431/6-1516), St Jerome reading in a landscape, panel, 26.6 x 21.7 cm, Ashmolean Museum, Oxford, A302.

9b Paint cross-section from a sample from the brown-green landscape in 5a. Particles of azurite in a brown oil medium on top of opaque paint containing lead white and azurite.
Fig. 10 sample 119 Green drapery St. Peter, left outer wing. Above and left the 1975 micro-destructive scan.

The top most layer, whitish fluorescence, contains chalk. The darkened copper resinate has an orange colour in normal light and shows no or hardly any fluorescence.
The discolouration of parts of St Peter’s green drapery - on the left outer wing in Lucas van Leyden’s triptych - is due to the darkening of copper resinate (or oleate) in the top of the translucent green paint. The thin sections made from the cross-section of sample 119 (figs. 10 and 11) show the there is a translucent green layer that has darkened to an orange colour at the top. Already the 1975 scan showed there to be copper in the orange brown. This find was confirmed by the SEM-EDX analyses, done at ICN 2010 (figs 12a and b). Iron was absent. Additional finds were that the lead white under the green glaze contains copper as well and therefore its purpose must have been to serve as an underpaint for the green glaze. Also, the top layer, now dark, was shown to contain mostly chalk: perhaps another, originally yellow? glaze. Organic yellows, for instance aloe, were mentioned in early written sources in connection with green glazes.6

The green drapery of the angel on the left-hand inner panel showed a slight browning, which is copper resinate/oleate turned brown (figs. 13a-13d). At the time of sampling, there were also thick varnish layers, that, in the cross-section, can be clearly distinguished from the green-brown glaze. This type of discolouration from green to brown is due to the influence of light. Proof of the pudding is the observation that when, on canvas paintings the green is covered by the frame, or by another paint layer, there is no discolouration.

Fig. 13, sample 52 from a light area in the drapery of the angel in the left-hand inner panel of Lucas van Leyden’s Last Judgement. Fig. 13b, on the right, is a thin section made from the same cross-section.

Fig. 13c and 13d, cross-section and thin section from sample 53, from a shadow in the green drapery of the angel in the left-hand inner panel of Lucas van Leyden’s Last Judgement.
Conclusion

At the time of writing the ICOM paper, in 1975, on the brown appearance of green areas in paintings, a firm statement was not made. Now, 35 years later, it is easier to draw conclusions from the magnified image on the paintings and from samples from the particular areas in the paintings. Besides experience, improvements of visual means, especially the illumination of the optical microscope in both normal and long wavelength uv, make interpretation of the paint samples easier. The results obtained by the use of the electron microscope now did not improve the results it selves obtained with the electron microscope in 1975; however, the instrumentation is now, much more user friendly, due to the existence of computers and the results can be more easily and clearly visually presented.

Original green copper containing glazes, wholly or partially turned brown, are indeed present in the trees and draperies in Lucas van Leyden’s Last Judgement in the Lakenhal in Leiden and in many other paintings, Northern and Southern and from different periods.