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XRF and Infrared Analysis of an 18th Century Portrait

An unsigned portrait painting from the 1700's, (Oil on canvas, 13" x 16") from an estate sale (shown in Fig. 1), was examined by the RevealScan™-M multispectral infrared system as well with an M6 X-ray Fluorescence Imaging device (Manufactured by Bruker Nano Systems of Berlin, Germany)[1]. As the painting's artist is unknown, the examination was aimed at details to exploring the materials used and any possible hidden details like underpaintings or underdrawings that might be useful in identifying the painter. The work was named Philosopher and was approximately dated to the 18th century at the time of purchase based on the type and appearance of the clothing of the painting's subject. The painting has a very dark background and had yellowed old varnish. The back of the painting showed water damage which does not seem to have affected the front of the painting. The damaged canvas was removed and replaced along with the decayed wood stretches.

Fig 1 (a) Photo of the portrait designated as the "Philosopher". Unknown painter, oil on canvas, 13" x 16", (b) Verso of the painting, without any identifiable marking and only showing possible water damage.The old frame also had a line suggesting the water damage extended to the frame.

The RevealScan™-M system scanned visible, VNIR, and NIR regions. The main difference from the visible outer image is a long area of drops starting on the forehead and ending in a larger spot in front of the left eye of the subject on the painting. This "defect", and several other small spots that are not visible, may be spots and spills on the original canvas and possibly painted over with the dark background and do not seem to be part of an earlier underpainting.

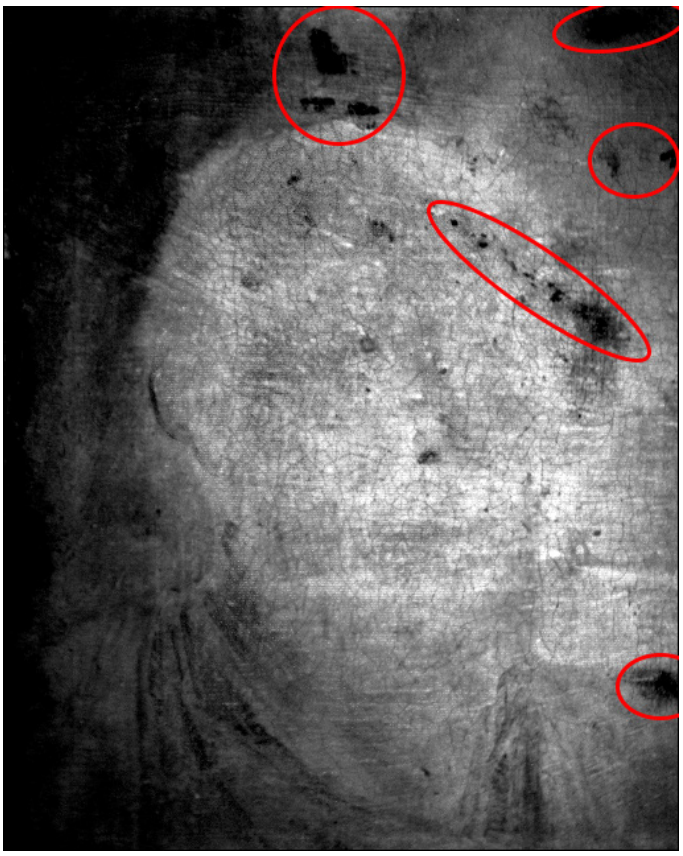

Fig 2. Combination of infrared reflectance images of the Philosopher painting with the man's face removed, highlighting dark droplets scattered across the right side of the painting, circled in red for clarity.

Using RevealScan™ Analysis software to combine the 1000 nm and 1650 nm wavelength images, the man's face is deemphasized in favor of the dark "defects" making the extent of the defects stand out in comparison to the rest of the painting, see Fig. 2. In this case, the spectral imaging did not reveal a complete underpainting, only a possible paint spill on the original canvas. The painting was probably done by a sure hand, as no detailed underdrawing was shown either. Since the RevealScan™-M's series capture takes only a few minutes to collect, using this system was a great way to quickly identfy an interesting feature in this painting that warrants further analysis with other time consuming methods.

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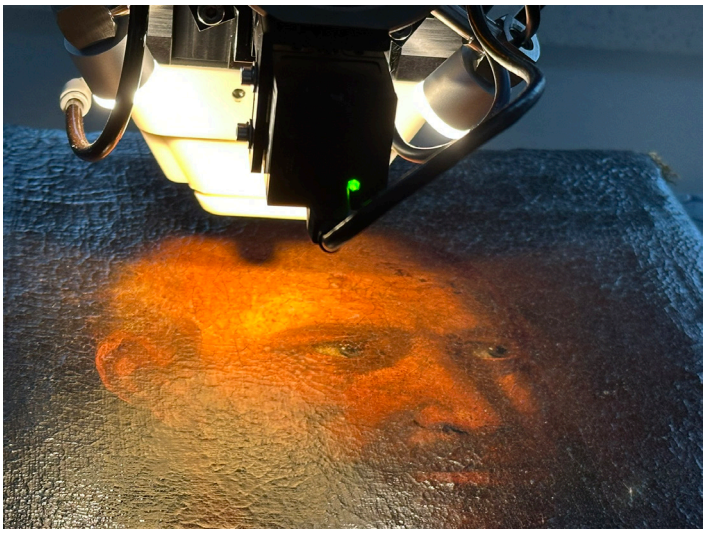

Fig 3. M6 XRF Imager scanning the Philosopher painting

In order to further investigate the defect found with infrared imaging and characterize the paints and other features, an M6 high resolution X-ray fluorescence imager was used to image the entire painting. The system has an Aperture Management System, a polycapillary focusing system that improves the data quality for rough 3D sample surfaces. The M6 utilizes a 50 kV, 600 µA Rh source with 145 eV resolution, and with the optional helium purge, the M6 can detect elements as light as sodium. The step size for the scan was 500 µm for about 4 hours of overall scan time. Integration time was set to 100 ms, see Fig. 3.

The ESPRIT software can automatically select which elements are detected based on the resulting spectrum of each pixel and also allows for manual adjustment of the included elements to further refine the results. A concentration map for each element or combinations of elements can also be created in the software. In the scan of Philosopher, the most evenly distributed higher level element seemed to be lead (Pb), see Fig.4. It is obvious that lead, likely in the form of PbO white paint is used as a diluent, in the face to adjust for darkness and was in high levels in the collar area.

In the 1700's Zn-oxide (ZnO) was not available for painters, so it is surprising that in the collar area, Zn shows up in clearly detectable quantities. It seems that it is mostly in the centerline of the clothing as highlights of the brightest part of the entire painting (Fig. 5). ZnO was discovered in the 1780's by the French chemists Jean-Baptiste Courtois and Louis-Bernard Guyton de Morveau. As a material in oil paint that could be acquired by painters the white paint only became available in the 1860s and marketed as Chinese White[2].

Fig 4. Pb distribution in the painting.

Fig 5. Zn distribution in the painting.

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Based on the lack of availability of ZnO paint in an 18th century painting, it must have been restored or changed at a much later date after its initial completion. Given that zinc is much more localized than lead and that zinc only appears in areas that also have high lead, it is more likely that ZnO white was added on top of the painting at a later date in areas that had faded. Additional support for the painting being restored at a later date is that the canvas seen from the back turned out to be a second layer adhered to the original canvas that had the paint on it, suggesting other modifications were made in addition to the new layer of white paint. It is also interesting that the water damage seems to be confined to the back lining, with the original canvas remaining free from water damage. A reasonable choice for the future conservation of Philosopher based on the XRF results would be to remove the ZnO layer, which has since grayed and does not appear to be part of the original materials used.

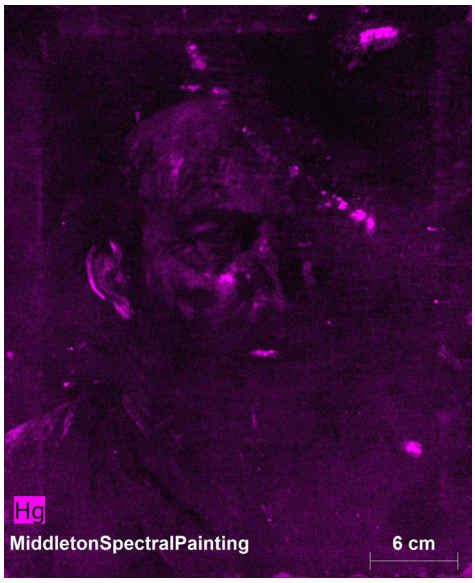

Fig 6. Hg distribution in the painting. Mercury is known in old oil paintings only to be contained in high quantities in the red pigment Vermillion.

Among other images of elements, it was interesting to find that mercury (Hg) was found in the same area that was highlighted in the infrared image as well (Fig. 6). Vermilion is the only pigment that contains mercury in substantial quantities and it was extensively used in old paintings as a red paint. The “spill”, which is not an integral part of the painting, thus was identified as vermillion. Looking at the Hg elemental image it seems that red was used to highlight the reddish color of the ear and the lip of the gentleman on the painting. Other small spots are possibly spills or earlier contaminants on the canvas under the paint of the portrait. For better comparison of the main elements, a combined element map of zinc, lead, and mercury is shown in Fig. 7.

Fig 7. Element distribution of lead (yellow), zinc (blue) and mercury (violet) overlaid

In summary, in the case of this painting XRF imaging was not only complementary to the infrared study but quite revealing on the possible later changes to the painting, identifying the materials, even the color of the paint spill partially invisible under the dark background.

References:
1. M6 Product materials – Bruker Nano Systems, Berlin, Germany
2. Sarah Sands (2018), in www.Justpaint.org/zinc-oxide-warnings-cautions-and-best-practices and www.Justpaint.org/zinc-oxide-faq/
3. Paints and Their Main Compositional Elements, Application Table (2024) available from Middleton Spectral Vision, Middleton WI, USA