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Supplementary Information for

Uncovering modern paint forgeries by radiocarbon dating

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Paint sample characterization

As described in a pilot study, sample characterization is of high importance to ensure reliable dating of the organic binder. Preliminary XRF measurement conducted by Smith et al.(1) allowed to narrow down the sample selection to the white painted building as indicated in Figure 1. Indeed titanium revealed the most intense signal, hereby indicating that titanium dioxide was used as main white pigment. Traces of lead were also observed and may be linked to the residual lead white ground from the stripped re-used canvas. Molecular structure information were provided by additional Fourier transform infrared (FTIR) and Raman spectroscopy. The collected FTIR spectrum (see figure S1) displays clear spectral features of the binding media; CH_2 stretching bands are visible at 2926 and 2854 cm^{-1} typical for saturated hydrocarbons along with the respective bending vibrations at 1463 and 1380 cm^{-1}, a prominent C=O peak typical for triglyceride esters at 1733 cm^{-1}, which all point to a partially hydrolyzed drying oil binder. Additionally, the presence of amide bands I and II at 1654 and 1535 cm-1, imply the presence of proteinaceous materials, i.e. egg or hide glue. This is supported by findings from Smith et al., who noted the presence of both oil and protein using FTIR and PYGCMS on several paint location of the investigated Trotter painting. It is to be noted that the spectrum is relatively complex with many overlaying peaks, which renders a clear attribution non-trivial. For instance, the broad band at 1070 cm^{-1}, the shoulder at 983 cm^{-1} and two small signals at 1180 and 607 cm^{-1}, indicate the presence of barium sulfate. This information in combination with the trace of zinc observed in the XRF may infer the use of lithopone ($ZnS + BaSO_4$) as previously presumed by Smith et al. (1), which is an inexpensive filler used in paints. Also to be noted, is the omnipresence of PY3 in the green areas of the painting, which was not observed in the cracks of the white building. Although no green layer was visually observable, weak PY3 absorption bands are visible in the FTIR spectra, maybe from a brush not properly cleaned.

Raman spectra (figure S2) provides clear evidence for anatase as white pigment due to the strong peak at 142 cm^{-1} and weak one at 516 cm^{-1} (2), therefore confirming XRF findings of titanium dioxide as main white pigment used for the white house.

During his trial, Trotter mentioned using Copal as varnish agent for his forgeries, however Smith et al. demonstrated that his modus operandi is not constant and that in this case, a shellac coating layer was identified. This was further confirmed by derivatization of the varnish layer with SF_4 (3-5).

Sample suitability assessment for ^{14}C analysis

From the spectroscopic analysis, it was concluded that the white paint sample is composed of anatase as main white pigment in combination with barium sulfate and lithophone, i.e all inorganic compounds, and thus is a viable candidate for ^{14}C analysis. The binder is a mixed medium of oil and proteinaceous materials, i.e. egg or hide glue. Owing that both must be fresh for application, it is reasonable to assume a similar ^{14}C signature for both components. Nevertheless, the presence of an additional varnish and minor PY3 contaminants were to be removed as these additional carbon sources may complicate the dating of the organic binder. To prevent any mixed radiocarbon age results, the shellac was removed from the sample by multiple ethanol washes and checked for any residues by FTIR. The washing procedure hereby also allowed to eliminate the PY3 contaminants, as it is fairly well known that PY3 is well soluble in a wide range of solvents (6). In consequence, all extraneous carbon source other than the binder were removed from the sample and this one was further prepared for ^{14}C analysis. The evolved carbon dioxide following sample combustion was directly linked to the organic binder and no negative effect from the varnish nor PY3 on the ^{14}C-analysis were observed.

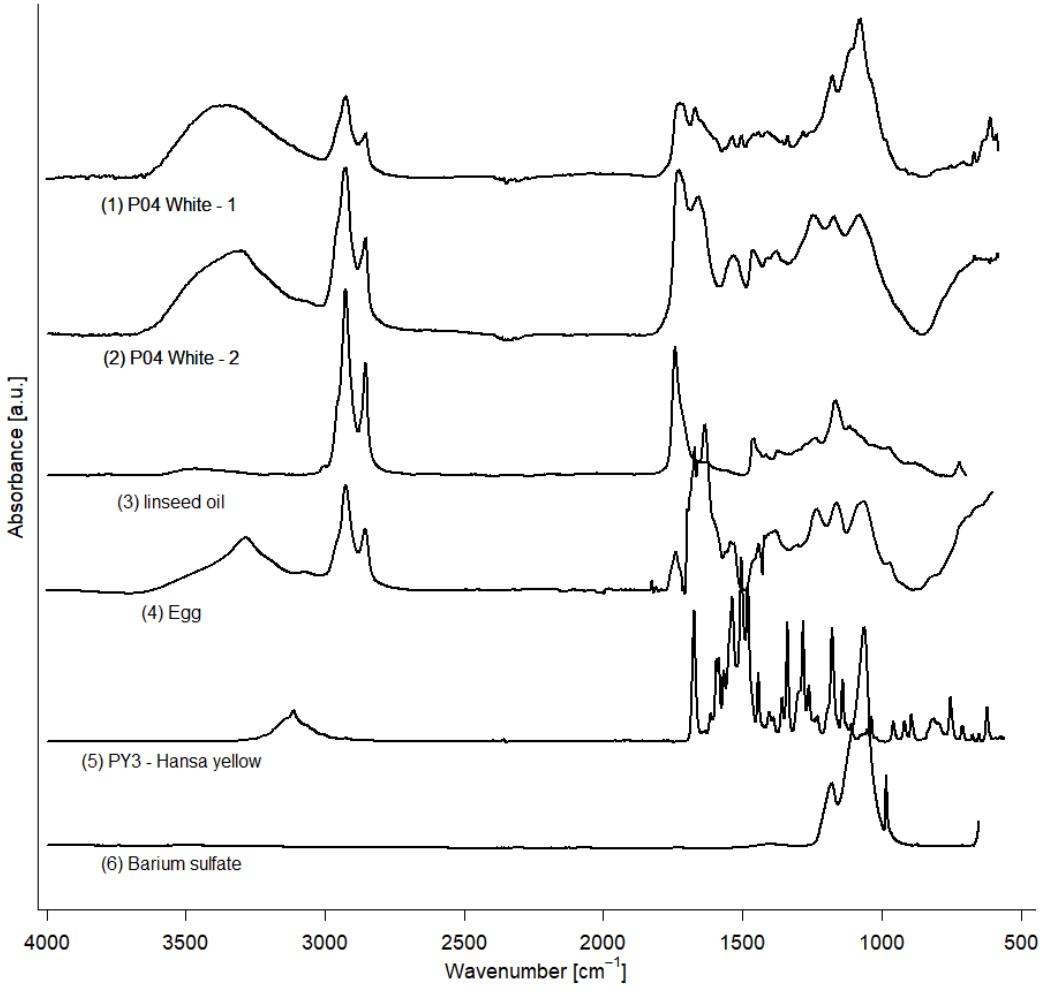

Fig. S1. FTIR spectrum of the collected paint sample from the white building (1) and (2) in comparison with reference spectra of linseed oil (3), egg (4), PY3 – Hansa yellow (5) and barium sulfate (6).

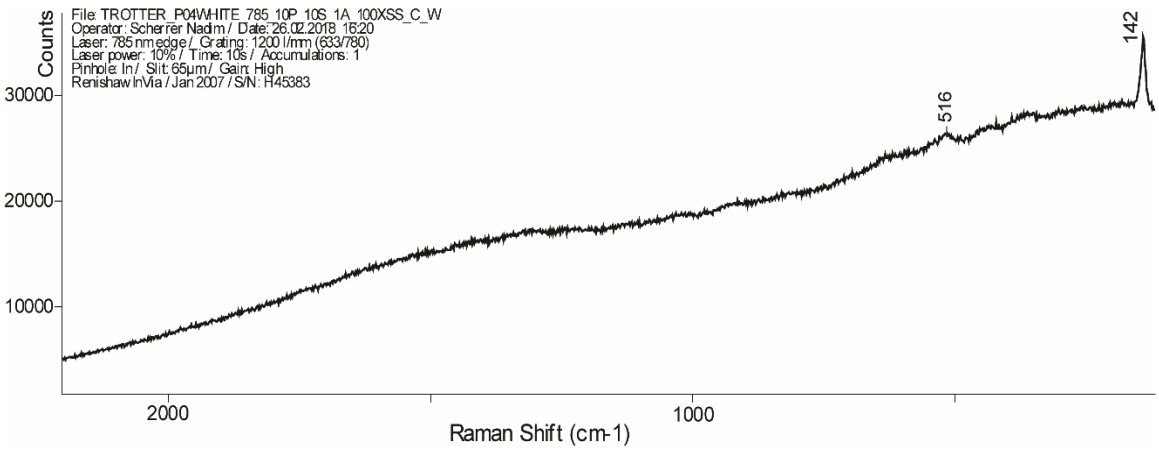

Fig. S2. Raman spectra of the collected paint sample from the white building. The distinct peak at 142 cm-1 is characteristic of anatase.

References

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