Non-traditional materials in the ground layer of paintings from the Danish Golden Age identified via MS-based proteomics

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The application of palaeoproteomics to artistic materials enables the retrieval of a level of information almost unachievable with other analytical techniques. Tandem MS-based sequencing can lead to the confident and untargeted identification of all proteins present in a sample, including any non-traditional and undocumented materials. This study reports the protein characterisation of the ground layers of ten paintings by Christoffer Eckersberg and Christen Købke, dating back to the Danish Golden Age. Micro-samples removed from the tacking edge of the paintings were processed using a guanidine hydrochloride solution, followed by enzymatic digestion, peptide purification on Stage-Tips, and nano-LC-MS/MS analysis. Data analysis was performed with the MaxQuant software.

Collagen from bovine and/or ovicaprine species was identified in 8 of the 10 paintings, showing the presence of animal glue, the most traditional binder for canvas ground layers. However, fermentation-related proteins from baker's yeast and seed-specific proteins from multiple species of cereals (primarily barley, wheat, and buckwheat) were also identified. Also considering mechanical and preservation factors, these proteins suggest the use of a brewing product (probably beer or a brewing by-product) in the ground layers. The acquired proteomic data were further processed with a metabolomics data analysis workflow, matching MS/MS spectra against GNPS reference libraries, and peptidic *in silico* predicted structures through DEREPLICATOR. This approach suggested the use of a drying oil in one of the paintings. In turn, this suggests that the adopted proteomics protocol might be optimised to achieve the characterisation of more than just proteinaceous materials. The chronology and provenance of the paintings showing this unusual recipe suggests that this binder formulation was used for the preparation of canvases at the workshops of the Royal Danish Academy of Fine Arts, which provided artistic materials to students and professors. These results provide a new platform for studying degradation phenomena in these and contemporary paintings.