Names and affiliations of applicants (* indicates experimentalists):

Dr. Geert Silversmit*, Prof. Laszlo Vincze; Ghent University, Analytical Chemistry, Krijgslaan 281 S12, B-9000 Ghent.

SAMAIN Louise, STRIVAY David; Universite de Liege CEA INPAS, Allée du 6 Août Bât, B5a 4000 Liège BELGIUM.

Report:

Scientific background and aim of the proposal

Prussian blue was invented in Berlin in 1704 and is a hydrated iron(III) hexacyanoferrate(II) complex that can contain ammonium, potassium or sodium ions. Because of its low cost the pigment enjoyed immediate popularity and was widely used by artists until 1970. However, the permanence of Prussian blue was already questioned by the mid-18th century, as the pigment shows a tendency to fade in the light. The degradation processes of Prussian blue in paintings are not completely understood, although the comprehension of these mechanisms can help for preventive conservation and restoration of paintings.

The blue colour is due to an intervalence charge transfer between the two oxidation states of iron at 680 nm A loss or shift of colour means thus a disruption in the Fe^{III}-N-C-Fe^{II} moiety. The aim of the proposal was to identify the changes in the local electronic and structural configuration of the iron ions in aged Prussian blue painted samples by Fe K X-ray absorption spectroscopy.

Experimental method

Commercial soluble and insoluble Prussian blues were purchased both from Sigma-Aldrich and from Winsor & Newton, London, England, a supplier of artists' materials. Soluble Prussian blue, KFe^{III}[Fe^{II}(CN)$_6$]·xH$_2$O, was synthesized according to the so-called indirect method, which consists in a precipitation reaction between aqueous solutions of 0.1 M FeCl$_2$·4H$_2$O and 0.1 M K$_4$Fe(CN)$_6$·3H$_2$O. These powders were painted on canvas in boiled linseed oil, gum arabic or paraloid B72, as pure pigments and mixed with lead white, (PbCO$_3$)$_2$Pb(OH)$_2$, zinc white, ZnO, or titanium white, TiO$_2$, pigments. The samples were subjected to accelared ageing up to 800 hours by using a SUNTEST CPS+ weathering chamber equipped with a xenon lamp. Half of the surface area of the paint layers on canvas were covered with aluminium to serve as reference after ageing.

Because of the low amount of iron in the diluted painted layers, the spectra were recorded in fluorescence mode. The EXAFS data reduction and analysis were performed with the XDAP software. The phase shifts and backscattering amplitudes used in the EXAFS analysis were obtained from FEFF8.0 calculations on the soluble Prussian blue crystal structure.

Results obtained

Fe K XANES analysis

The FeK XANES spectra obtained on pure, unaged and aged laboratory-synthesized soluble Prussian blue, $KFe^{III}[Fe^{II}(CN)_6]$, mixed with lead white, $(PbCO_3)_2Pb(OH)_2$, at a 1:100 dilution ratio are shown in **Fout! Verwijzingsbron niet gevonden.**. The spectrum of the pure Prussian blue was recorded in transmission mode while the spectra of the paint layers were recorded in fluorescence mode. Differences in absorption intensity are due to self-absorption effects. A shift in the absorption edge towards lower energy is observed upon ageing. This shift suggests a decrease in the average oxidation state in the Prussian blue or an increase in the density of states. Because the centroid of the pre-edge peak does not show a significant shift towards lower x-ray energy, see the inset to Figure 1, a decrease in the average iron oxidation state is not likely.
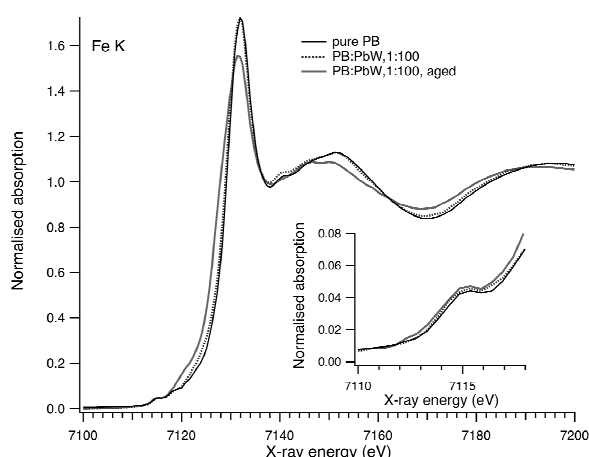

Figure 1: Normalised Fe K XANES spectra for pure soluble Prussian blue in powder and mixed with lead white, PbW, in 1:100 dilution ratio. The darker coloured curve corresponds to the aged sample. Inset: An expansion of the pre-edge peak spectral region.

Fe K EXAFS analysis

The k^2 weighted EXAFS spectra for the pure laboratory-synthesized soluble Prussian blue measured in transmission is compared in Figure 2 with the fluorescence detection spectra for the unaged and aged pigment mixed with lead white in a 1:100 ratio. The Fe K EXAFS spectra recorded in fluorescence mode resulted in lower EXAFS data quality compared to the transmission reference sample.

EXAFS spectra for the pure powder compound and the unaged painted layer were fitted with the phase and backscattering functions based on the $K_4[Fe(CN)_6]$ and $KFe^{III}[Fe^{II}(CN)_6]\cdot xH_2O$ powder references. For the EXAFS fit on the aged painted layers, the fit model on the corresponding non-aged paint layer was used as starting model and the bond distances, inner potential corrections and coordination numbers were optimised. In general there was no change in bond distances, but a decrease in coordination number for the third shell, *i.e.* Fe(II)-Fe(III), was observed in all discoloured Prussian blue samples, see Figure 2, right. The aged laboratory-synthesized soluble Prussian blue paint layer mixed with lead white in a 1:100 dilution ratio, which exhibits the strongest fading, shows also a decrease in coordination number for the second shell, *i.e.* Fe(II)-N and Fe(III)-C.

This decrease in Fe-Fe coordination number upon ageing will necessarily lead to a weakening of the intervalent charge transfer and can therefore explain the fading of Prussian blue. This assumption seems to disagree with the common hypothesis for fading proposed in the literature, *i.e.* the reduction of Prussian blue into ferrous ferrocyanide. However, the underlying mechanism of the change in the intervalent charge pathway is not yet clearly identified. The decrease in the coordination number can also be explained by the presence of smaller crystals in the paint layer. The final interpretation is still ungoing.
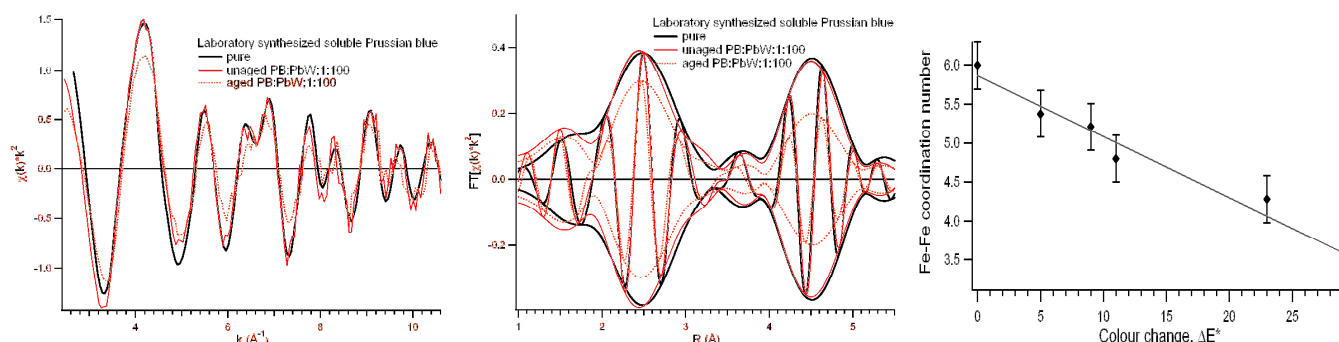

Figure 2: $k^2*\chi(k)$ (left) and $FT[k^2*\chi(k)]$ spectra (middle) (Δk = ~5.3 - ~10.5 Å^{-1}) for laboratory-synthesized soluble Prussian blue, in pure form and as unaged and aged painted layer mixed with lead white in a 1:100 ratio; Fe-Fe coordination number as function of colour change (right).