APPLICATION NOTE

PHOTO-PHYSICAL PROPERTIES OF ANCIENT AND MODERN ARTWORK PIGMNETS

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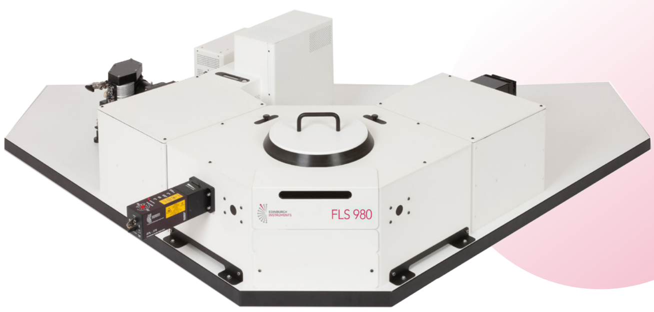
INTRODUCTION

The interest in non-invasive investigations for the study and identification of painting materials has greatly increased during the past two decades.[1] The nature of museum objects is such that sampling is always kept to a minimum, thus, a spectroscopic approach is ideal for this purpose. In this respect, an ancient and a modern pigment, cuprorivaite,



FLS980 Fluorescence Spectrometer

$CaCuSi_4O_{10}$ (Egyptian blue)[2] and barium manganate (VI) sulphate compound (manganese blue)[3] respectively, have been photo-physically investigated. The investigation includes qualitative information, i.e. emission and excitation spectra, as well as quantitative that is the photoluminescence quantum yields (PLQY) that have been obtained in the near-infrared (NIR) region.

METHODS & MATERIALS

Excitation and emission spectra were measured using an FLS980 Fluorescence Spectrometer equipped with a 450 W Xe lamp with double excitation and emission monochromators. Near-infrared detectors (Hamamatsu) were used for the detection of both samples. PLQY have been calculated by corrected emission spectra obtained by using a barium sulphate coated integrating sphere, following the procedure described by De Mello et al.[4] Experimental uncertainties were estimated to be ±20% for emission quantum yields, ±2 nm

RESULTS - DISCUSSION

and ±5 nm for absorption and emission peaks, respectively.

Figure 1 reports the excitation and luminescence spectra of the two samples.Egyptian blue shows two different electronic transitions ($^2B_{1g}$-^2E_g and $^2B_{1g}$-$^2A_{1g}$) that can be assigned to Cu^{2+} ions, which are expected to be the only luminescent components of cuprorivaite.[1] On the other hand, those of Manganese Blue can be attributed to ligand-field (LF) transitions (^2E-$^2T_2$, c.a 800 nm - 900 nm) and to ligand-to-metal charge-transfer bands (between 600 nm and 800 nm) of the MnO_4^{2-}-unit.[5]

The luminescence profiles have peaks at 920 nm and 1300 nm for Egyptian blue and manganese blue, respectively. Consequently, the corresponding PLQYs have been obtained.

Manganese blue showed a quantum yield of Φ=0.5%[6] attributed to luminescence quenching factors that occur at lower energy. By contrast, Egyptian blue revealed to be a very strong NIR emitter (Φ=10.5%)[1] that, to the best of our knowledge, has the highest quantum efficiency for a molecule-level chromophore in the 800 nm – 1100 nm range.

CONCLUSION

The photo-physical properties of an ancient and a modern art pigment were investigated by means of fluorescence spectroscopy. In addition, the PLQY of the pigments has been measured, as a quantitative means of their photoluminescence properties and demonstrate the effectiveness of this method as a minimally invasive means of measuring samples of cultural significance.

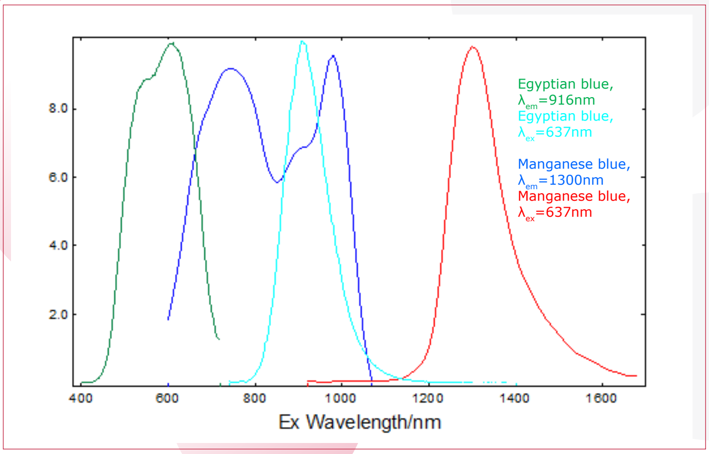


Figure 1: Excitation and emission spectra of ancient, Egyptian blue, and modern, manganese blue, pigments. The energy levels corresponding to each transition are also displayed.

FLS Spectrometer Integrating Spheres

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