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, CaCuSi₄O₁₀ (Egyptian blue) and barium manganate (VI) sulphate compound (manganese blue) respectively, have been photo-physically investigated. ²,³ The investigation includes qualitative information, i.e. emission and excitation spectra, as well as quantitative that is the phosphololuminescence quantum yields (PLQY) that have been obtained in the near-infrared (NIR) region.

Methods and Materials
Excitation and emission spectra were measured using an FL5980 Fluorescence Spectrometer equipped with a 450 W Xe lamp with double excitation and emission monochromators. Near-infrared detectors were used for the detection of both samples. PLOY 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, ±2nm and ±5nm for absorption and emission peaks, respectively.

Results - Discussion
Figure 1 reports the excitation and luminescence spectra of ancient, Egyptian blue, and modern, manganese blue, pigments. The energy levels corresponding to each transition are also displayed.

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

Conclusions
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.

References

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