Photo-physical Properties of Ancient and Modern Artwork Pigments

Gianluca Accorsi[1], Giovanni Verri[2], Georgios Arnaoutakis[3]

[1] Italian National Research Council, CNR NANO, Lecce, Italy,

[2] The Courtauld Institute of Art, London, UK, [3] Edinburgh Instruments Ltd, Livingston, UK

AN_P23 v.2

DATE 7 Dec. 15

Edinburgh Instruments Ltd
2 Bain Square,
Kirkton Campus,
Livingston, United Kingdom
EH54 7DQ

Telephone (UK)
+44(0) 1506 425 300
Telephone (North America)
1-800-323-6115

Email
enquiries@edinst.com
Website
www.edinst.com

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, $CaCuSi_4O_{10}$ (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, ±2nm and ±5nm for absorption and emission peaks, respectively.

Results - Discussion

Figure 1 reports the excitation and luminescence spectra of the two samples.

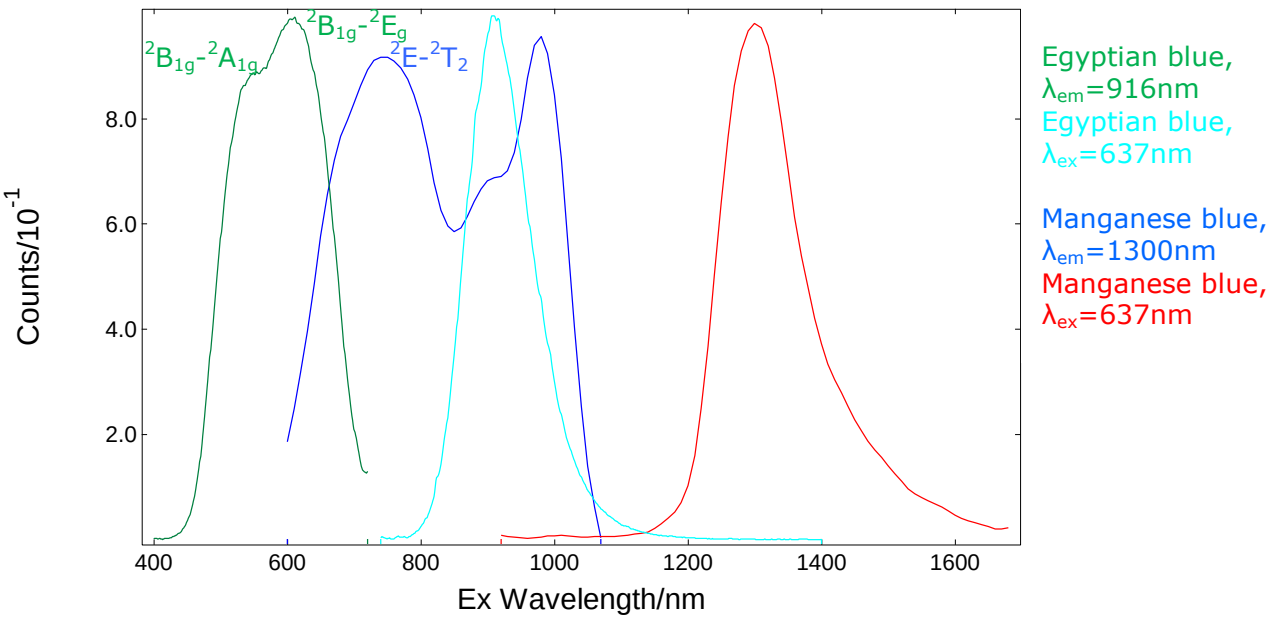

Figure 1: Excitation and emission spectra of ancient, Egyptian blue, and modern, manganese blue, pigments. The energy levels corresponding to each transition are also displayed.

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.

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

1. Accorsi, G.; Verri, G.; Bolognesi, M.; Armaroli, N.; Clementi, C.; Miliani, C.; Romani, A. The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue). *Chem. Commun.* 2009, (**23**), 3392-3394.
2. *(a) Artist's Pigments – A Handbook of Their History and Characteristics*. Elisabeth West Fitzhugh editor: 1997; Vol. 3; (b) Berke, H. The invention of blue and purple pigments in ancient times. *Chem. Soc. Rev.* 2007, ***36*** **(1)**, 15-30.
3. Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *Barium Manganate(IV) Sulfate*. Butterworth-Heinemann: Oxford (UK), 2008.
4. De Mello, J. C.; Wittmann, H. F.; Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency. *Adv. Mater.* 1997, ***9*** **(3)**, 230-236.
5. Chen, Z. L.; Schmalle, H. W.; Fox, T.; Blacque, O.; Berke, H. NH-functionalized tungsten complexes of 2-(dimethylphosphino)imidazole. *J. Organomet. Chem.* 2007, ***692*** **(22)**, 4875-4885.
6. Accorsi, G.; Verri, G.; Acocella, A.; Zerbetto, F.; Lerario, G.; Gigli, G.; Saunders, D.; Billinge, R. Imaging, photophysical properties and DFT calculations of manganese blue (barium manganate(VI) sulphate) - a modern pigment. *Chem. Commun.* 2014, ***50*** **(97)**, 15297-15300.

Proprietary notice

Confidentiality status

This document is Open Access. This document has no restriction on distribution.

Feedback on this Application Note

If you have any comments on this Application Note, please send email to sales@edinst.com giving:

- the document title
- the document number
- the page number(s) to which your comments refer
- an explanation of your comments.

General suggestions for additions and improvements are also welcome.