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# NIR Luminescence and Composition of Egyptian Blue as Markers in Archaeometric Evaluations

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The unique NIR luminescence of the ancient pigments Egyptian Blue, Han Blue and Han Purple [1] has recently attracted significant interest because its existence allows fast identification these pigments even when present in minimal amounts and using non-destructive tools [2]. A more comprehensive study of this feature associated also to micro-imaging and compositional evaluations can be used as a mean to improve archaeometric studies about production technologies [3], giving also useful data to hint the provenance of the pigments and their trade routes. The three pigments, and especially Egyptian Blue (EB) were widely used in a large span of years and places. Indeed, EB was invented during the 4th millennium BCE [4] and until Middle Ages has been by far the most used blue pigment in all the Mediterranean Basin and the Near East. It was first produced probably in Egypt from where it has been heavily traded to many Mediterranean countries. However the technology of production evolved in time and spread in different places such as Mesopotamia and Italy [5]. EB invention is related to the development of close related materials such as pottery, bronze and especially glass and Egyptian faience.

A large part of Egyptian faience is light blue (LBEF) and its color is due to copper ions [6–8]. LBEF glaze and other Cu-rich glassy materials are so intimately linked to EB that they can show almost the same color and share a very similar elemental composition. The differences between EB and the outer layer of LBEF may relay mainly on the production technology used. However, from a chemical stand point the main difference is that EB has a structure made of CaCuSi4O10 (cuprorivaite) crystals embedded in an amorphous matrix rich in Na or K, while LBEF glaze and Cu-rich glasses are a glassy phase made of Si, Ca and O, rich in Na and/or K from the flux, and Cu from the coloring agent. Although EB surface is generally darker and dull in comparison to LBEF and Cu-rich glasses, sometimes it is very difficult to distinguish these materials from each other. The first of the two case-studies that we present in this paper we performed in the Museo Egizio of Turin (see Figure 1). As shown the use of portable and non-destructive techniques such as Visible Induced Luminescence Imaging (VIL) can immediately show the difference between EB and LBEF since the NIR luminescence of EB is linked to cuprorivaite crystalline structure. Thus LBEF and Cu-rich glasses lacking cuprorivaite have no luminescence. They look instead dark in VIL Images due to the NIR absorbing properties of Cu-rich glass.

As shown, even the simple use of VIL allows a clear differentiation between the technologies used to produce the blue materials. The images unveiled the kind of productions technology and outstanding ancient decorative patterns no more detectable with the naked eye due to the slight chromatic alteration and the patinas onto the ancient objects. To best of our knowledge this is the first time that VIL has been used to study mummy nets and other objects traditionally considered blue Egyptian faience.

Reliably the technique to produce and use EB can vary place by place from a single workshop to another. For this reason, a more in-depth comparison between a group of archaeological objects can be done using the NIR luminescence and compositional features of EB as markers of the different workshops. This approach is the focus of the second case study that we present in this paper. It consists in the study of a group of 54 shabti statuettes of the New Kingdom currently hosted in the Museo Egizio of Turin and found in different locations in the village of Deir el-Medina in Egypt (Luxor, West Bank). The shabtis were firstly studied non-destructively using X-Ray Fluorescence (XRF) and VIL then on 10 representative statuettes samples have been collected and studied using correlative Scanning Electron Microscopy (SEM-EDS) and Raman confocal micro-spectroscopy.

Although the final aim has been the development of a non-destructive way to correlatively study composition and luminescence of EB, the observation and correlation of the data collected on the micro-samples turned to be very precious. It allowed to correlate the photoluminescence and the chemical composition of the ancient samples and introduce Raman spectroscopic imaging as a mean to capture simultaneously VIL and Raman signals. Through this approach we were able to identify two classes of silicate phases in the pigment (VIL active and inactive) that may be connected to production technologies.

Gaussian mixture modeling was employed to observe subtle differences in composition within each sample; however, we found that grains that appeared similar in EDS in some cases had distinct Raman spectra. Furthermore, we observed the characteristic luminescence of cuprorivarite despite the varied elemental compositions in the pigments identified using EDS. This indicates that the characteristic luminescent property used to identify EB relies on the crystalline structure that forms during its production.

High-resolution chemical characterization provides unique insights into the structure and composition of EB. The multi-modal approach applied here revealed the variation in EB composition across the 10 micro-samples taken from shabti statuettes of similar period and origin. Ternary diagram representations of quantitative EDS data show the varied composition both between samples and within individual samples. These differences might be related to different production parameters and, possibly, to different production workshops. Using a Raman spectrometer, we have shown that interestingly, the luminescence does not correlate to a specific elemental composition detectable by the methods employed herein and instead relies overall on the crystallinity of the pigment itself.

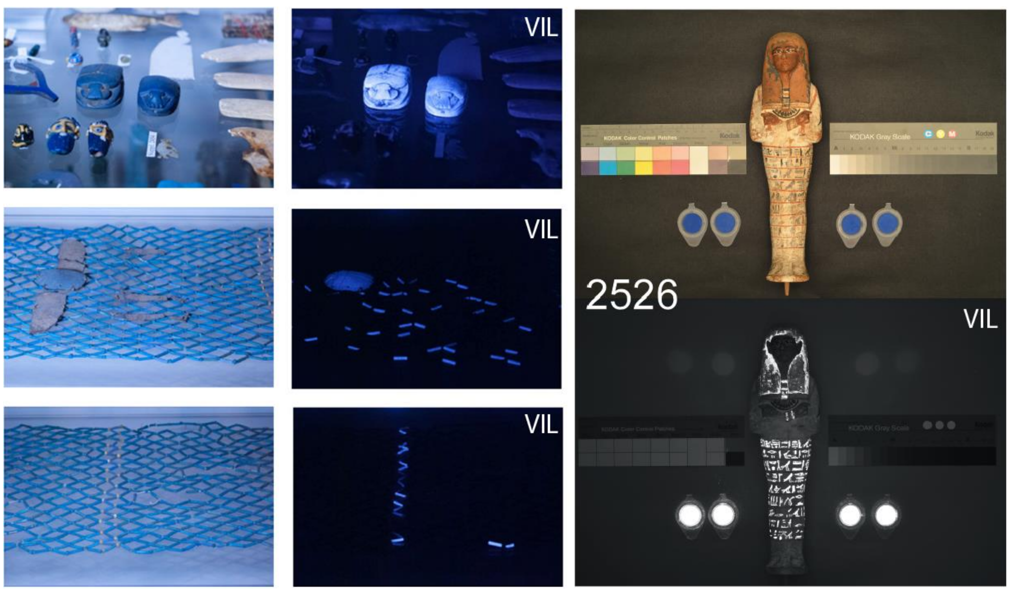


**Figure 1.** NIR luminescence imaging of Egyptian blue-based artifacts at the Museo Egizio in Turin (Italy).

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