Dyes and Pigments 136 (2017) 104–115

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Application of forensic photography for the detection and mapping of Egyptian blue and madder lake in Hellenistic polychrome terracottas based on their photophysical properties

Ioanna Kakoulli [a, b, c, *], Roxanne Radpour [a, c], Yuan Lin [a, c], Marie Svoboda [d], Christian Fischer [b, c]

[a] University of California Los Angeles, Department of Materials Science and Engineering, HSSEAS School of Engineering and Applied Science, 420 Westwood Plaza, 3111 Engineering V, Los Angeles, CA 90095-1595, USA
[b] University of California Los Angeles, UCLA/Getty Conservation Program, Cotsen Institute of Archaeology, A210 Fowler Building, Los Angeles, CA 90095-1510, USA
[c] University of California Los Angeles, Molecular and Nano Archaeology Laboratory, HSSEAS School of Engineering and Applied Science, 420 Westwood Plaza, 3111 Engineering V, Los Angeles, CA 90095-1595, USA
[d] J. Paul Getty Museum Antiquities Conservation, 1200 Getty Center Drive, Los Angeles, CA 90049-1679, USA

ARTICLE INFO

Article history:
Received 2 July 2016
Received in revised form
9 August 2016
Accepted 11 August 2016
Available online 18 August 2016

Keywords:
Photoluminescence
Imaging
Vitreous pigments
Natural dyes
Metal complexes
Archaeometry/archeological forensics

ABSTRACT

Two of the oldest synthetically produced and most widespread pigments employed in the decoration of ancient polychrome artifacts are Egyptian blue, a vitreous blue compound, and madder lake, a hybrid organic-inorganic composite. Both of these pigments are known to be photoluminescent after electronic excitation by photons in the visible and re-emission of photons in the near infrared (NIR) and visible (Vis) respectively. The emissions of Egyptian blue are typically due to d-d electronic bands and for madder lake generally due to π-π^* type transitions. In this research, the photophysical properties of these two pigments were examined by means of forensic photography. The usefulness of this type of imaging is based on the properties of Egyptian blue and madder lake in exhibiting characteristic near infrared and visible emissions when excited by red and green light respectively providing reliable fingerprint markers for their identification and mapping. To probe and capture the characteristic excitation and emission photon energies of Egyptian blue and madder lake an alternate light source (ALS) and a modified digital single-lens reflex (DSLR) camera with suitable optical filters were employed in the examination and analysis of two Canosa polychrome terracotta vases from the J. Paul Getty Museum collection dated to the third century BCE. Reference materials and supplementary analysis by fiber optic reflectance spectroscopy (FORS) and X-ray fluorescence (XRF) spectroscopy were used for verification.

1. Introduction

Photographic techniques to record (roughly between 350 and 1100 nm) the reflectance and luminescence properties of materials in works of art and map their spatial distribution are well established in the fields of conservation and archaeometry [1–19]. These are often used to aid to the legibility of the surface and subsurface and to help identify features not visible to the naked eye providing useful information in the attribution and classification of artifacts and informing analytical and conservation protocols. In recent years, visible-induced near infrared (NIR) luminescence photography [20,21] has become a standard technique in the examination of ancient paintings and sculptures to identify and map the presence of Egyptian blue, a ceramic blue pigment that has found extensive use in the Old World [22–41]. In contrast, the high photoluminescence yield in the visible (red region) with visible (λ_{ex} ~500–550 nm) photoexcitation of madder lake [42,43], a 'luxury' red colorant from the plant of the family of Rubiaceae, which also predominated the Old World [44–52], has not been fully exploited. Most commonly, ultraviolet (UV)-induced visible fluorescence is

* Corresponding author. University of California Los Angeles, Department of Materials Science and Engineering, HSSEAS School of Engineering and Applied Science, 420 Westwood Plaza, 3111 Engineering V, Los Angeles, CA 90095-1595, USA.
E-mail address: kakoulli@ucla.edu (I. Kakoulli).

http://dx.doi.org/10.1016/j.dyepig.2016.08.030
0143-7208/

performed in the examination of paintings and objects to reveal the presence and spatial distribution of madder lake. However, while this photographic technique is able to capture the photoluminescence of this colorant with a characteristic orange color [53,54], the strong absorption of ultraviolet radiation and emission of light in the visible by many other organic compounds, such as binding media and other colorants often present in a paint film, or certain colored coatings and conservation materials applied at the surface and subsurface can obscure its discrimination.

In this paper we present a field application for the detection and mapping of Egyptian blue and madder lake on ancient polychromy using visible-induced visible and NIR luminescence photography. This technique is adapted from forensic applications to support non-invasive on site investigations in art and archaeology necessitating unbiased characterization arising from concerns of authenticity and cultural context of archaeological polychrome artifacts without having to move the objects or take any samples. As proof of concept, this research examines two polychrome south Italian third century BCE Canosa vases (accession numbers 81.AE.156 and 81.AE.157) from the J. Paul Getty Collection (Fig. 1) painted with Egyptian blue and madder lake. To our knowledge, this is the first time that the characteristic visible excitation and visible emission photon energies of madder lake are exploited using forensic photography in archaeometry and archaeological forensics.

1.1. Photoluminescence photography

Photoluminescence is a form of luminescence (emission of light) following photoexcitation (excitation by photons) of shorter wavelength than that of the emission. In this paper, the phenomenon of photoluminescence based on radiation emitted by matter in the visible (~400–700 nm) when excited by radiation in the ultraviolet (UV) will be referred to as 'UV-induced visible fluorescence' (to use well-established terminology); 'visible-induced (Vis-) visible (Vis) luminescence' when excited by visible radiation of shorter wavelength (i.e. green) and captured in the visible, however of a longer wavelength (i.e. red), and 'visible-induced (Vis-) near infrared (NIR) luminescence', when emission of radiation in the near infrared occurs with excitation by electromagnetic radiation in the visible.

Fig. 1. Canosa Vases 81.AE.156 (a) and 81.AE.157 (b) from the J. Paul Getty Museum collection in front, side and back views with surviving visible polychromy mainly in the frontal part and sides.