# A Comparison of the Organic Dyes Used in Icons and Textiles of the Mediterranean Area in the Byzantine and Post Byzantine Period

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*Figure 1: "Christ Pantokrator Enthroned", (1350-1400 AC). St. Nicolas church, Polygyros. Sample was extracted from Christ's tunic.*

## Introduction

The colours are the necessary tools to transform a drawing to an icon or painting. Although the message of an icon that a spectator perceives is the result of the combination of the drawing and the colours, the latter constitute an independent "entity" as they convey their own messages/meanings. Although people respond to different colours in different ways, there is usually a symbolism that it is hidden behind the use of a particular colour. In the religious Byzantine iconography the "colour language" uses its own rules of communication and symbolizes its own meanings. For example, the purple colour represents (usually) "power" while the use of a reddish hue is many times chosen to represent "divine love". White usually stands for "purity".

The above attempt to clarify the symbolic meanings of the colours is based on the Byzantine iconographic tradition. However, further decryption of the "colour language" requires the identification of the colouring materials used to provide the desired hues. Furthermore, the analysis of the colouring components of an icon, or more general of an art object of the cultural heritage, contributes to the optimization of the

applied conservation strategies and reveals valuable historical data associated with the provenance of the art work and the relevant pigment technologies, dyeing procedures and painting techniques. Although several analytical techniques, such as FTIR and Raman spectroscopy, have been successfully employed to identify inorganic pigments, they have provided limited results in the case of the organic dyes. Chromatographic methods and primarily High Performance Liquid Chromatography (HPLC) has been proved to be more powerful than the spectroscopic techniques for natural organic dyestuff identification. However, HPLC has been mostly used to analyze textile samples rather than samples extracted from icons or paintings [1-3]. Furthermore, the organic colouring materials of Byzantine icons have been rarely studied [4]. The present investigation aims to apply HPLC for the identification of organic dyes in samples extracted from icons which are dated in the Byzantine and post Byzantine period. The presented results are based on the examination of fifteen (15) Byzantine and post Byzantine icons, which belong to entities (monasteries, churches) of the area of Chalkidiki, including Mount Athos (figure 1). Also, the famous artwork “The Baptism” of El Greco, shown in figure 2 is included [5]. Samples from this important historical object were provided by S. Stassinopoulos. The conclusions drawn from the icons are discussed in the light of relevant results achieved by the examination of Byzantine ecclesiastical garments of the Mount Athos. Samples from the garments were provided by C. Karydis.

**Experimental**

Microsamples extracted from the icons, were mounted in polyesteric transparent resins which were grinded and polished, using a Struers Planopol-V machine. Cross section were studied with reflected light

and UV-fluorescence using a Zeiss Axiotech 100 HD polarized microscope, equipped with a quartz halogen and an UV excitation light source (100W). In most of the extracted samples inorganic pigments were found. In some cases, however, red and blue organic dyes were found to have been used by three different ways: (i) in mixtures with inorganic pigments, (ii) as exclusive colouring matters (no inorganic pigments) and (iii) as glazes applied on top of layers contained inorganic pigments. In the cases in which organic dyes were found, more microsamples (around 1 mg) were extracted and submitted to HPLC.

*Figure 2: El Greco, "The Baptism" (1567/68). Municipality of Heraklion. Sample was extracted from Angel's cloak.*

Reversed phase liquid chromatography (RPLD) was carried out using Thermoquest (Manchester, UK) HPLC system consisted of P4000 quaternary HPLC pump, SCM 3000 vacuum degasser, AS3000 auto sampler with column oven, Reodyne 7725i Injector with 20μl sample loop and Diode Array Detector UV 6000LP. The HPLC separation was carried out on an Alltima HP C18 5μm column with dimensions 250mm x 3.0mm (Alltech Associates, Inc., USA) by a gradient elution program that utilizes two solvents: solvent A: $H_2O$-0.1%TFA and solvent B: $CH_3CN$-0.1%TFA. Prior to HPLC analysis microsamples were treated with a solution mixture of $H_2O$:MeOH:37% HCl (1:1:2, v/v) to remove any mordant metal. After filtering, the solutions were evaporated (50-60$^oC$) under gentle nitrogen flow. The dry residues were dissolved in $H_2O$:MeOH (1:2, v/v) and submitted for HPLC analysis.

**Results and discussion**

Figure 3 shows the chromatogram acquired in the case of a reference cochineal sample (*Dactylopius coccus* Costa) and the identification of the colouring compounds. Cochineal appeared to be the major (i.e. most common) colouring organic material found in the tested icons. Cochineal was also identified in several ecclesiastical garments of the Mount Athos leading thus to the conclusion that it played a central role in the dyeing technology of the Byzantine art. We note that cochineal was also found in the artwork of El Greco ("The Baptism"). A similar conclusion can be drawn for redwoods (*Caesalpinia* trees) which were also found in many samples extracted from both collections, icons and garments. The two reddish dyestuffs, mentioned above, are of different origin: cochineal is of insect origin, while redwoods are plants. In a few samples the two dyes were found in mixtures. Another reddish

organic dye that has been detected was madder (*Rubia* species). It was found only in one icon (in mixture with cochineal and redwood) and in only one garment as exclusive colouring material. To close the presentation of the results with respect to red organic dyes, we note that lac dye (*Kerria lacca*) was detected in samples extracted from the garments but not in the samples of the icons.

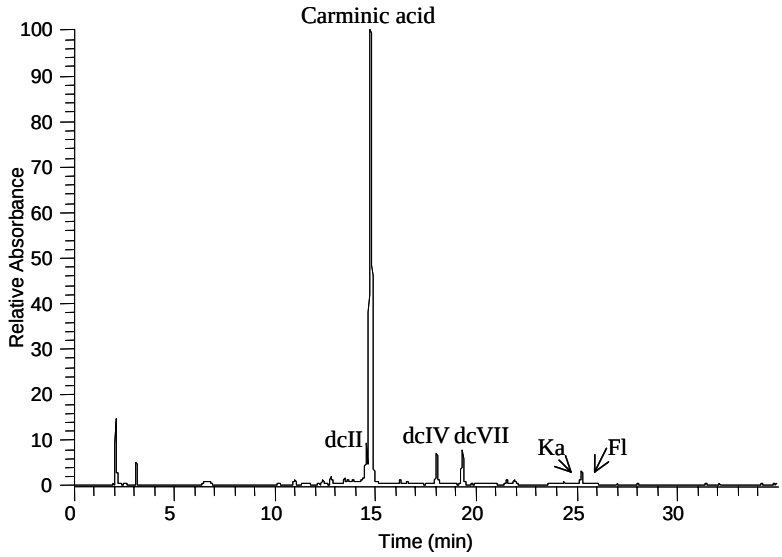


*Figure 3: Chromatogram of cochineal (Dactylopius coccus Costa) at 275nm. Carminic acid, the major colouring component, and the secondary Kermesic (Ka) and Flavokermesic (Fl) acid are shown. Other minor components of cochineal marked as dCII, dCIV and dCVII are indicated.*

Figure 4 shows schematically the frequency at which the three red organic dyes, cochineal, redwood, and madder, were found in the tested art objects. Cochineal was found in 14 artworks (including "The Baptism"), redwood in 6 and madder only in 1 icon. Figure 4 suggests that cochineal was the most usual organic dye that has been used in the iconography of the Mediterranean area in the Byzantine and post

Byzantine period. On the contrary, madder, has not been used extensively in the dyeing technology, compared to the other two red dyes, cochineal and redwood. Apparently, the above statements are based on the examination of a relatively small collection of icons (only 16). Consequently, they have to be considered rather as indications than conclusions. To determine the frequency by which species of

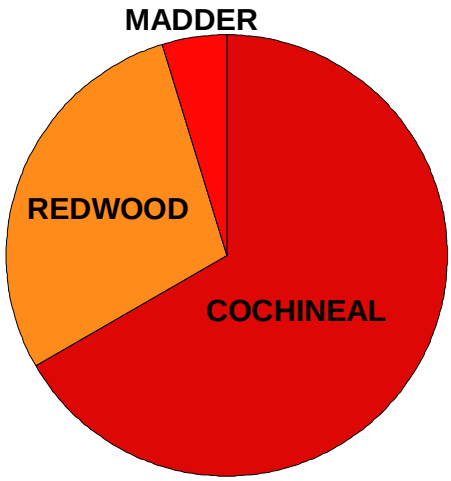


*Figure 4: This figure illustrates the frequency at which the three identified reddish dyes were found in 16 icons.*

organic dyes appear in Byzantine iconography several more icons and paintings have to be investigated. However, figure 4 is an interesting observation because madder is generally considered to be the most abundant organic mater that has been used since antiquity. This may not be true for the dyeing technology developed in the Mediterranean area in the Byzantine and post Byzantine period, according to the indications presented in this paper.

Indigo (*Indigofera tinctoria* L.) and/or woad (*Isatis tinctoria* L.) were found to be the main organic dyes, used to produce the blue colour either in icons or in textiles. Despite the large progress of the

analytical techniques it is still not possible to distinguish/separate these two species and therefore we cannot determine which of the two has been detected. Both dyestuffs contain the same major colouring compounds: indigotin and indirubin.

No yellow organic dyes have been detected in any of the tested icons, in contrast to the garments in which young fustic (*Cotinus coggygria* Scop.) and dyer's broom (*Genista tinctoria* L.) were identified. In Byzantine iconography the yellow shades were produced with sheets of gold or by the application of inorganic pigments such as yellow ochre.

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