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Maya Pigments

From Maya Blue to “Maya Yellow”: A Connection between Ancient Nanostructured Materials from the Voltammetry of Microparticles[**]

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Maya Blue is a famous pigment that was widely used in wall painting, pottery, sculptures, and luxury art in Mesoamerica and even as therapeutic agent in pre-Columbian times.[1] This pigment has claimed considerable attention because of its peculiar hue, ranging from a bright turquoise to a dark greenish blue, characteristic brightness, and extraordinary stability to chemical and biochemical attack.[2]

First described by Merwin in 1931 in the archaeological site of Chichén Itzá,[3] Gettens and Stout further coined the term Maya Blue for designing the pigment.[4] In the 60s, Shepard proposed the idea of Maya Blue being an unusual material consisting of a dye attached to certain Yucatán clays.[5] Arnold identified palygorskite in Yucatán clays and recognized the use of this clay in Mesoamerican ceramicware,[6] identifying sites for its extraction,[7] while Van Olphen prepared synthetic specimens analogous to Maya Blue from both palygorskite and sepiolite, a related phyllosilicate, and indigo.[8]

Maya Blue (MB) can be described as a hybrid organic–inorganic material[2] resulting from the attachment of indigo, a blue dye extracted from leaves of añil or xiuquitlitl (*Indigofera suffruticosa* and other species) to the clay matrix of palygorskite, a fibrous phyllosilicate of ideal composition $(Mg,Al)_4Si_8(O,OH,H_2O)_{24}\cdot n\,H_2O$. The location of indigo molecules in the palygorskite framework, the nature of the indigo–palygorskite association in Maya Blue, and the reasons for its peculiar hue still remain controversial.[9] In the absence of ethnographic sources describing its preparation recipe(s), Van Olphen’s basic “dry” and “wet” methods, both involving a thermal treatment between 120 and 180 °C of indigo plus palygorskite mixtures, have been used in recent literature.[8,9g] The ancient Mayas could also prepare MB by burning copal incense in the context of ritual ceremonies.[10]

Most of recent research on Maya Blue appears to be implicitly (and often explicitly) based on “uniqueness”, with three hypotheses: 1) there is an unique organic component in MB; 2) there is an unique type of attachment between indigo and palygorskite; and 3) there was an unique preparation recipe used by the ancient Maya people. In previous reports, we provided a series of reasons for questioning these hypotheses. First, dehydroindigo, the oxidized form of indigo, accompanies this dye in the palygorskite, so that the hue of the pigment can be determined by the dehydroindigo/indigo ratio, in turn depending on the extent and type of thermal treatment,[11] while different palygroskite-associated indigo and dehydroindigo topological isomers could be formed.[11d,e] Secondly, the appearance of different types of spectral and electrochemical responses permits to conjecture that different types of preparations were used along the historical Maya times, since late pre-classic times (ca. 300 BC–300 AD) to the post-classic period (ca. 950 AD-17th century).[12] In particular, it is conceivable that the Mayas could prepare yellow and green from indigo-based dyes using procedures directly related with that used and well-documented for the preparation of indigo[13] and attach it to clays to obtain Maya Blue-type pigments.

This would be consistent, on first examination, with the study from Vandenabeele et al.,[14] which involved Raman spectroscopy of a series of yellow, green, and blue Maya Blue samples from the site of Ek’ Balam (Yucatán, Mexico). The Raman spectra of all of the samples were indistinguishable, which suggests that possibly leucoindigo, the reduced form of indigo, accompanied this last component in yellow samples.

The above hypotheses can be viewed within a more general context where the Mayas, as well as other pre-Columbian peoples, like the Aztecs, could use a variety of natural dyes for preparing pigments. In this sense, in the *Florentine Codex*, Bernardino de Sahagún mentions only two yellow vegetal pigments used by the Aztecs: zacatlaxcalli (*Cuscuta sp.*) and xochipalli (*Cosmos sp.*; sunflower).[15] Recent literature on pre-Hispanic cultures in Mesoamerica, however, mention, apart from inorganic yellow ochre (goethite and/or limonite minerals), a series of yellow dye-based pigments (Table 1).[15,16]

The voltammetry of microparticles (VMP) method, an electrochemical technique developed by Scholz et al. for analyzing sparingly soluble solids,[17] provides a powerful

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Table 1: Characteristics of the yellow dyes cited as possible coloring agents in the Yucatán area in pre-Columbian times.[15,16]

Plant	Colorant	Chemical family
Cuscuta americana, *Cuscuta tinctoria*, fam. *Convolvulaceae* (zacatlaxcalli, devil's guts, goldthread)	several	carotenoids and xantophiles
Cosmos sulphurous, fam. *Asteraceae* (xochipalli, girasol Amarillo, mirasol amarillo)	corepsin, quercitin, luteolin	flavonoids
Diphysa robinoides, fam. *Fabaceae* (guachupín)	lapachol	naphthoquinonics
Chlorophora tinctoria, fam. *Moraceae* (fustic, fustete, mora amarilla, palo amarillo)	morin	flavonoids
Gliricidia sepium, fam. *Fabaceae* (mata raton, rabo de ratón; cacao de nance)	several	flavonoids
Tagetes erecta, fam. *Asteraceae* (el cempasúchil, cempaxóchitl, cempoal or zempoal, flor de muertos or clavel chino)	lutein	carotenoids

technique for identifying dyes in micro- and nanosamples from works of art.[18] Complemented with spectral (FTIR, UV/Vis, Raman, NMR) and microscopy (SEM/EDX, TEM, AFM) techniques, VMP has offered significant information for the study of Maya Blue.[11,12] The application of such techniques to the series of yellow samples from Yucatán (Mexico), whose description and dating is shown in Table 2, reveals interesting features. First, SEM and TEM images of archaeological samples show the presence of typical elongated crystals of palygorskite (Figure 1). Remarkably, no gross pores associated with the loss of zeolitic water, a feature observed in genuine Maya Blue samples,[12] were observed. These features suggest that such "Maya Yellow" samples consist of a palygorskite-based pigment in whose preparation no treatment or smooth thermal treatment was used.

Table 2: Samples used in this study.

Site	Period
Acanceh, remainings of wall paintings	early classic (ca. 450 AD)
Chacmultún, building of paintings	late classic (ca. 700 AD)
D'zula, structure I	late classic (ca. 700 AD)
Chihén Itzá, substructure of the temple in the initial series	terminal classic (ca. 880 AD)
Mayapán, El Pescador temple	post classic (ca. 1200 AD)
Mayapán, Solar Symbols temple	post classic (ca. 1200 AD)

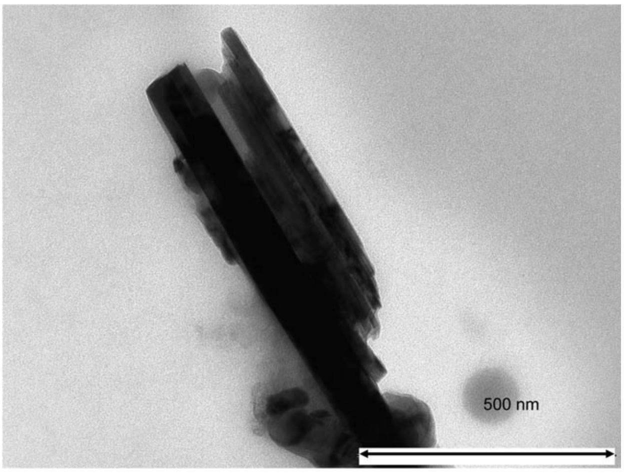

Figure 1. Micrograph obtained by TEM for a "Maya Yellow" sample from Acanceh (15 000× magnification).

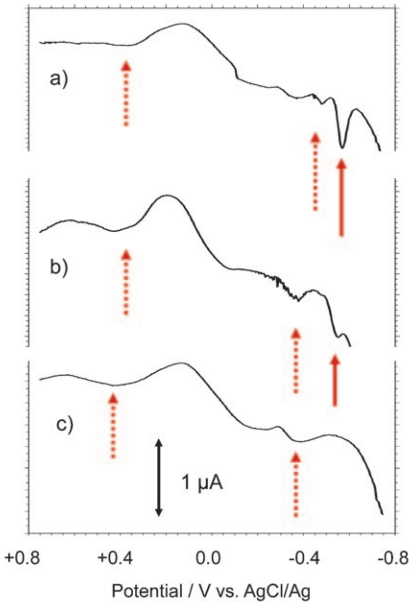

Figure 2. Square-wave voltammograms for samples from a) Acanceh, b) D'zula, and c) Mayapán attached to paraffin-impregnated graphite electrodes immersed into 0.50 M acetic acid/sodium acetate aqueous buffer, pH 4.75. Potential scan initiated at -0.75 V in the positive direction. Potential-step increment 4 mV; square-wave amplitude 25 mV; frequency 5 Hz. Peaks for isatin (solid arrows) and the dehydroindigo/indigo/leucoindigo system (dotted arrows) are marked.

The voltammetric response of the "Maya Yellow" samples studied yields peaks at $+0.45$, -0.30, and -0.55 V versus AgCl/Ag in contact with aqueous acetate buffer (Figure 2). The last peak is particularly prominent for samples from Acanceh and Chacmultún, which are all dated to the early classic and late classic periods, respectively, whereas becomes weaker for the D'zula sample (late classic period) and is absent in Chichén Itzá and Mayapán samples, which are both dated to the post classic phase. The two first peaks correspond to those obtained in the dehydroindigo/indigo/leucoindigo system, whereas the peak at -0.55 V differs from those recorded under identical conditions for other yellow dyes in the Mesoamerican area (fustic, lapachol). This peak is also absent in the voltammograms for indoxyl, the main indigo precursor in plants,[11c] indirubin, and both genuine Maya Blue samples and synthetic specimens prepared as dye (1% w/w) together with palygorskite complexes. Other possible yellow dyes, such as carotenoids and xantophiles, remain electrochemically silent. The unique coincidence was obtained for the case of the isatin (indole-2,3-dione) plus palygorskite complex (see the Supporting Information), which displays a reduction signal at −0.55 V that is attributable to a two-proton, two-electron reduction of the carbonyl group at position 3.[19]

These results suggest that isatin, possibly accompanied by other indigoids, would be responsible of the yellow hue in "Maya Yellow" samples extracted from several of the studied mural paintings. Analysis of spectral data is complicated, however, by the close similarity between the infrared and Raman spectra of the different indigoids,[14] and the frequent use of ochre by the Mayas painters.[12b] The presence of ochre, appearing as yellow nodulae upon light microscopy analysis of stratigraphic cross-sections of paint layers, is confirmed by SEM/EDX analysis and its characteristic spectral signature in the visible region. Not surprisingly, the visible spectrum of most yellow samples becomes quite similar to that of ochre, as can be seen in Figure 3. Remarkably, subtraction of the ochre spectrum from that of "Maya Yellow" samples leads to a difference spectrum that corresponds to that recently reported[20] for dehydroindigo associated with palygorskite, with two overlapping bands at λ_{max} of 550 nm and 440 nm, whereas the spectral signature for leucoindigo (λ_{max} 417 nm) appears to be absent. The analysis of the ultraviolet region where isatin absorbs (λ_{max} 302 nm) is not conclusive because indigo, dehydroindigo, and leucoindigo, and also indoxyl and the other indigo precursors in plants, indican and the isatans, absorb in this region.[19d,20] Experiments on aerobic ageing of mixtures of indoxyl (1% w/w) plus palygorskite confirmed the presence of small amounts of dehydroindigo, not only in Maya Blue but also in "Maya Yellow" (see the Supporting Information).

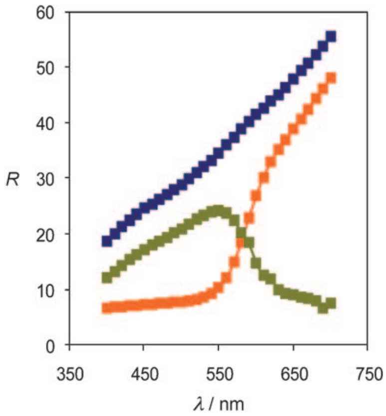

Figure 3. Visible absorption spectra for a "Maya Yellow" sample from Mayapán (blue), ochre (orange), and the subtracted spectrum (green).

Additionally, cluster analysis of peak potential data for "Maya Yellow" from the different sites permits their location into a ramified, evolutionary scheme consistent with that independently proposed for the preparation of Maya Blue[12] (see the Supporting Information).

All these results suggest that, at least, several yellow pigments in Maya wall paintings consist of indigoids attached to palygorskite. The preparation of such "Maya Yellow" pigments could be carried out as an intermediate step during the preparation of indigo and Maya Blue. Using the traditional procedures previously described in Yucatán,[11e,f] leaves and twigs of *Indigofera* plants would be soaked overnight in a suspension of slaked lime in water. Then, the coarse material could be removed by filtration and a portion of the yellow suspension separated to add palygorskite and prepare the "Maya Yellow" pigment. To prepare indigo and Maya Blue, the remaining suspension could then be subjected to intensive ventilation by means of a prolonged stirring ("batido") so that the suspension becomes greenish and finally blue. Here, the resulting suspension could be filtered and further dried to separate the indigo to be used for dyeing purposes and/or to prepare the Maya Blue after crushing with palygorskite.

In summary, synergic combination of SEM/EDX, TEM, VIS/UV, and VMP techniques was used to identify the presence of indigoid compounds as pigmenting agents in yellow samples from Maya wall paintings from different archaeological sites in Yucatan. The data indicate that: 1) the ancient Mayas used not only blue–green Maya Blue but also yellow pigments with comparable indigo and palygorskite association; 2) the presence of isatin, dehydroindigo, and/or ochre and possibly other minor organic compounds would be responsible for the yellow hue exhibited by the samples; and 3) local workshops produced characteristic varieties of the pigment able to be correlated with the corresponding varieties of Maya Blue. From the ethnohistoric point of view, these results indicate that the Mayas developed a preparative technology not circumscribed to Maya Blue which, in fact, anticipates contemporary synthesis of organic–inorganic hybrid materials.

Experimental Section

Synthetic indigo (Fluka), isatin, (Aldrich), indoxyl beta-D-glucoside (Sigma), indirubin (RG Chromadex), lapachol (Extrasynthèse), morin (Aldrich) and palygorskite, collected from the Sak lu'um classical site in Yucatan,[11] were used as reference materials. Voltammetry experiments on microparticles were performed at sample-modified paraffin-impregnated graphite electrodes using equipment and procedures already described.[11,12] SEM/EDX and TEM examination of samples was carried out as described in detail elsewhere.[11,12] Visible spectra were obtained with a Minolta CM-503i spectrophotometer using a Xe arc lamp and a Si photodiode detector. Statistical analyses were performed with the Minitab 14 software package.

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