



# Identification of indigoid compounds present in archaeological Maya blue by pyrolysis–silylation–gas chromatography–mass spectrometry

María Teresa Doménech-Carbó<sup>a,\*</sup>, Laura Osete-Cortina<sup>a</sup>, Antonio Doménech-Carbó<sup>b</sup>,  
María Luisa Vázquez de Agredos-Pascual<sup>c</sup>, Cristina Vidal-Lorenzo<sup>c</sup>

<sup>a</sup> Institut de Restauració del Patrimoni, Universitat Politècnica de València, Camí de Vera 14, 46022 València, Spain

<sup>b</sup> Departament de Química Analítica, Universitat de València, Dr. Moliner, 50, 46100 Burjassot, València, Spain

<sup>c</sup> Departament de Història de l'Art, Universitat de València, Passeig al Mar, València, Spain

## ARTICLE INFO

### Article history:

Received 18 October 2013

Accepted 28 November 2013

Available online 7 December 2013

### Keywords:

Py-GC–MS

Maya blue

Indigo

Dehydroindigo

Hierarchical cluster analysis

Archaeometry

## ABSTRACT

A study based on the use of pyrolysis–silylation–gas chromatography–mass spectrometry (Py-GC–MS), which aimed to identify indigoid compounds and to clarify the multicomponent composition of Maya blue (MB) pigment, has been carried out. A series of reference compounds and synthetic MB specimens prepared in the laboratory have been analysed by this technique. An analysis of archaeological MB samples from 14 Maya archaeological sites from Mexico and Guatemala has also been performed. The obtained results demonstrate that, in addition to indigo, oxidised species such as dehydroindigo, which is formed as a result of redox processes taking place while preparing the pigment, are present in archaeological MB samples. Remarkably, the results of the chemometric analysis carried out with the set of obtained Py-GC–MS data agree with the notion that the pigment preparation procedure varied locally and evolved in time during the Maya civilization.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Maya blue (MB) is a particular pigment discovered by Merwin (1931), subsequently termed by Gettens and Stout (1946), which was widely used by ancient Mayas and other Mesoamerican people in mural paintings, pottery, sculptures and luxury art. Studying the composition and structure of such historic materials has attracted the scientific community's interest for not only their high archaeological and ethnohistoric value, but also their implications for modern synthesis as this pigment has been extensively considered a precursor of contemporary hybrid organic–inorganic materials [1].

MB is generally described as a nanostructured material obtained upon the attachment of indigo dye to fibrous clays. The raw materials used in the preparation of MB are palygorskite, a phyllosilicate clay with an ideal composition,  $\text{Si}_8(\text{Mg}_2\text{Al}_2)\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ , and indigotin or indigo (3H-indol-3-one-2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro, extracted from the leaves of *añil* or *xiuhquilitl* (*Indigofera suffruticosa*). Preparation of the historical

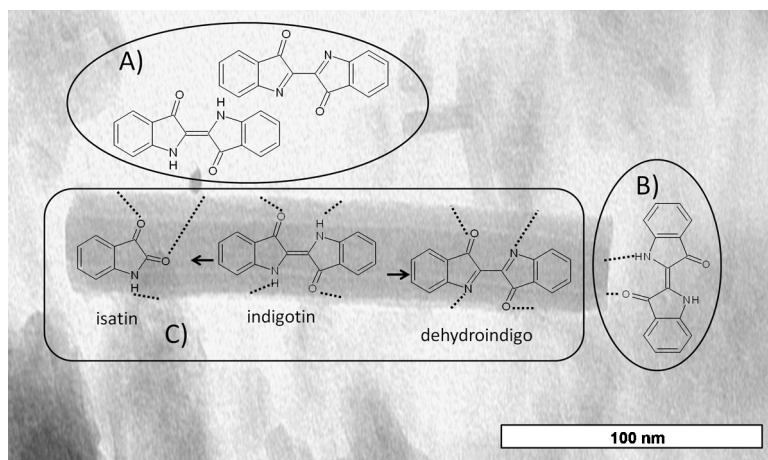
pigment remains unknown as historical sources are lacking [2]. Despite this fact, different preparation recipes are available [3,4] and, among them, the 'dry' preparation of MB-type materials by grinding a mixture of solid dye and clay, followed by subsequent heating at temperatures between 100 °C and 200 °C, was more commonly used [3–7].

Despite numerous studies having been conducted, controversy persists about the nature of MB, particularly, the type of clay–dye association and the location of dye molecules within the clay framework [3,5–9]. The most extended view considers MB to be constituted exclusively by molecules of the parent dye (indigotin), which are distributed externally and/or in the pores and channels of clay [3,5–9]. In addition to this view, and based on an analysis of real MB samples by solid-state electrochemical techniques, we proposed that dehydroindigo, the oxidised form of indigo, accompanies this dye as a minority, but in a significant proportion – component of MB. Thus, dehydroindigo contributes to the peculiar variability in the pigment hue, which ranges from blue to turquoise greenish blue [10–13]. To a greater or lesser extent, this compound is formed during the heating process, where it is subjected to the dye–clay system during its preparation [10–13]. This hypothesis has been supported by recent archaeological discoveries in which have been detected other associations between clays and indigoid dyes in the Maya area, suggesting that 'Maya chemistry' existed which was not only limited to MB [14,15]. Fig. 1 illustrates the redox processes that take place during MB preparation. However,

\* Corresponding author. Tel.: +34 963877835; fax: +34 963877836.

E-mail addresses: [tdomenec@crbc.upv.es](mailto:tdomenec@crbc.upv.es) (M.T. Doménech-Carbó),

[losete@crbc.upv.es](mailto:losete@crbc.upv.es) (L. Osete-Cortina), [antonio.domenech@uv.es](mailto:antonio.domenech@uv.es) (A. Doménech-Carbó), [M.Luisa.Vazquez@uv.es](mailto:M.Luisa.Vazquez@uv.es) (M.L. Vázquez de Agredos-Pascual), [Cristina.Vidal@uv.es](mailto:Cristina.Vidal@uv.es) (C. Vidal-Lorenzo).



**Fig. 1.** Scheme of the different placements and redox processes taking place after heating the indigo–palygorskite system according to traditional MB preparations. The scheme has been depicted over a photograph of a Maya blue sample obtained by transmission electron microscopy, and shows a Maya blue fibrous particle surrounded by grains of chalk and other Maya blue fibrous particles. (a) Molecules of indigo and dehydroindigo, not attached to palygorskite fibres. (b) A molecule of indigo anchored at the entrance of the palygorskite internal channels. (c) Molecules of indigo inside the palygorskite channels: anchorage to the internal walls combined with heating promotes redox processes, which result in the formation of oxidised indigoid species such as dehydroindigo and/or isatin.

recent literature does not unanimously recognise the occurrence of redox processes in such hybrid materials [16–20]. In this sense, it is relevant to note that preparation type and dye loading play a crucial role; in fact, most recently prepared MB-type materials [16–20] involve indigo loadings that are greater (up to 20 wt%) than the theoretical maximum channel occupation in palygorskite (ca. 4 wt%) [21], which is considered a typical value for ‘historical’ MB (ca. 1 wt%) [2,22]. In such circumstances, it appears that the majority of dye remains as ‘external’ microparticulate deposits [20].

It should also be emphasised that most of the studies carried out to elucidate the structure of MB have been based on the data obtained from spectrometric (XRD), spectroscopic (MNR, Raman, FTIR and UV–vis spectroscopy) and microscopy techniques (AFM, TEM and SEM–EDX). Nevertheless, no indigoid species other than indigotin have been identified. This obeys the elusive nature of other involved species (i.e., dehydroindigo, isatin), which are possibly formed under very definite conditions when indigo attaches to palygorskite clay. As they are minority components in the MB system, their spectral features remain obscured by those of the main component, indigo. In former works, we presented extensive studies in which these techniques were combined with solid-state electrochemistry techniques to provide relevant data on the redox processes taking place in MB preparation [10–15].

Despite the interest shown by many scientists in studying the MB structure, studies based on chromatographic techniques are scarcely found given the difficulty of extracting the indigoid compounds that are strongly anchored to palygorskite clay in MB. In these cases, the chromatographic approach is based on high performance liquid chromatography (HPLC) [23,24] and ultra pressure liquid chromatography (UPLC) [24].

Pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) has been proposed to be an efficient instrumental technique for analysing the organic dyes present in artworks, especially indigo. Accordingly, the works by Fabbri et al. [25] and Chiavari et al. [26] can be considered pioneering in that they demonstrate the capability of this instrumental technique to reveal the presence of natural organic pigments which, in turn, produce volatile thermal degradation products, in pictorial samples from artworks. Two derivatisation reagents have been used for this purpose in combination with pyrolysis: tetramethylammonium hydroxide (TMAH) [25] and hexamethyldisilazane (HMDS) [26,27].

This paper presents a study based on pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) using HMDS as the derivatisation reagent, in order to identify indigoid compounds in MB archaeological samples. It also presents data from archaeological MB samples from 14 Maya archaeological sites in Mexico and Guatemala, which were obtained and compared with others from a series of synthetic MB specimens prepared in the laboratory. The results obtained from the set of analysed archaeological samples are consistent with those which previously introduced dehydroindigo as an essential component of MB [10,24] and which described it as a polyfunctional hybrid inorganic–organic material where different dye molecules can be located in different clay sites, which helps define different topological redox isomers [28–30]. Remarkably, the results of the chemometric analysis carried out with the Py–GC–MS data agree with the notion that the pigment preparation procedure varied locally and evolved in time during the Maya civilization [12,13,31].

## 2. Experimental

### 2.1. Instrumentation

Pyrolysis–silylation gas chromatography–mass spectrometry (Py–GC–MS) experiments were carried out with an integrated system composed of a CDS Pyroprobe 1000 heated filament pyrolyser (Analytical Inc., NY, USA), and a gas chromatograph Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA) coupled to an Agilent 5973N mass spectrometer (Agilent Technologies) and equipped with a pyrolysis injection system. A capillary column HP-5MS (5% phenyl–95% methylpolysiloxane, 30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness, Agilent Technologies) was used to achieve the adequate components separation. Pyrolysis was performed at 600 °C for 10 s using a precalibrated Pt coil type pyrolyser (CDS pyroprobe). The pyrolyser interface and inlet were set at 250 °C. Samples were injected in the split mode (split ratio 1:40).

The chromatographic conditions were as follows: initial temperature of 50 °C held for 10 min. to be then increased at 5 °C  $\text{min}^{-1}$  up to 300 °C and held for 8 min. The helium gas flow was set at 1.5  $\text{ml min}^{-1}$ . The electronic pressure control was set to the constant flow mode with vacuum compensation. Ions were generated by electron ionisation (70 eV). The mass spectrometer was scanned from  $m/z$  20 to  $m/z$  800, with a 1-s cycle time. An Agilent

Download English Version:

<https://daneshyari.com/en/article/1198388>

Download Persian Version:

<https://daneshyari.com/article/1198388>

[Daneshyari.com](https://daneshyari.com)