

Available online at www.sciencedirect.com



thermochimica acta

Thermochimica Acta 456 (2007) 56-63

www.elsevier.com/locate/tca

# Thermal and Raman-spectroscopic analysis of Maya Blue carrying artefacts, especially fragment IV of the Codex Huamantla

Hans G. Wiedemann<sup>a</sup>, Klaus-Werner Brzezinka<sup>b</sup>, Klaus Witke<sup>b</sup>, Ingolf Lamprecht<sup>c,\*</sup>

<sup>a</sup> Tränkebachstraße 17, CH-8712 Stäfa, Switzerland

<sup>b</sup> BAM, Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, D-12489 Berlin, Germany

<sup>c</sup> Institute for Biology, Department of Biology, Chemistry, Pharmacy, Free University of Berlin, Grunewaldstraße 34, D-12165 Berlin, Germany

Received 18 October 2006; received in revised form 22 January 2007; accepted 4 February 2007

Available online 13 February 2007

Paper dedicated to Dr. Antonius Jammers, former Generaldirektor der Staatsbibliothek, Preußischer Kulturbesitz zu Berlin who made these investigations possible.

#### Abstract

Maya Blue, a pigment composed of very low concentrations of natural indigo and the clay mineral palygorskite, is one of the most brilliant blue dyes, intensively used for more than 2000 years in Mesoamerica. It is extremely stable against environmental attacks and was applied by the Indians for inside and outside mural paintings, ceramics, textiles and for colouring their famous codices. In the present paper it was studied as a powder (compared with modern synthetic indigo) and as colour on tissues, a Maya clay head, and fragment IV of the famous Codex Huamantla. Investigations using Raman spectroscopy in the visible and near-infrared range showed a high degree of correspondence among all Maya Bluecarrying samples and a good agreement with synthetic indigo. Additional spectral lines may be explained by a transformation of the planar indigo molecule when binding to the palygorskite lattice. Thermal investigations of the original "amatl" paper of the codex and of recent paper from fig-trees showed a high similarity and thus proved that this tree was chosen for paper making by Mayas, Aztecs and other Indian tribes. This was also true for the codex.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Art; Codices; Differential scanning calorimetry; Mesoamerica; Raman spectroscopy; Thermogravimetry

### 1. Introduction

#### 1.1. Codex Huamantla, fragment IV

At the end of his American research expedition Alexander von Humboldt lived nearly a year (1803/1804) in Mexico City and used this opportunity to visit ruins in the area and to inspect archaeological treasures of the past cultures. He looked at quite a number of the old pictured manuscripts, which lay unnoticed by Mexican scholars in governmental archives and private collections. Humboldt bought some of these documents assuming that they originated from the "Museo Indiano" of the Italian historian and archaeologist Boturini who collected Mesoamerican documents in the middle of the 18th Century [1,2]. He ded-

0040-6031/\$ – see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2007.02.002

icated a collection of 13 fragments of historical hieroglyphic writings of the Aztecs to the Royal Library to Berlin, nowadays the State Library to Berlin (Staatsbibliothek zu Berlin, Stiftung Preußischer Kulturbesitz; "SBB"). Among them are two fragments (designated as III and IV) which were part of a much larger map of about  $8 \text{ m}^2$ , the "Codex Huamantla" which was written in the end of the 16th or in the 17th Century and found in the State of Tlaxcala, about 100 km southeast of Mexico City. One has to be careful not to confuse them with fragments III and IV kept in the Museo Nacional de Antropologia, Instituto Nacional de Antropologia and Historia, Mexico City (MNA) that preserves six other fragments of this codex.

The two Berlin fragments III and IV measuring  $102.5 \text{ cm} \times 71.5 \text{ cm}$  (H × B) and  $43.5 \text{ cm} \times 64.0 \text{ cm}$ , respectively, were described, explained and – if necessary – translated by Seler [3]. Fragment IV shows a peaceful situation with blue water flowing to the right and four persons sitting on blue-painted chairs in front of their thatched-roof houses

<sup>\*</sup> Corresponding author. Tel.: +49 30 833 54367; fax: +49 30 814 99144. *E-mail address:* biophys@zedat.fu-berlin.de (I. Lamprecht).





Fig. 1. (a) Fragment IV of the Codex Huamantla. The bad state of the fragment is clearly seen; also that it is only a part of a larger piece. Spectra were taken from the blue chair of the second person from left, from the upright standing club of the soldier, and the right end of the blue river (indicated by the red arrows). (b) Total view of fragment IV of the Codex Huamantla on the freely movable Perspex table in front of the Olympus microscope. By courtesy of Staatsbibliothek zu Berlin, Stiftung Preußischer Kulturbesitz, Berlin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

(Fig. 1a). A soldier above the water stream carries a shield and blue-painted club. A line of footprints crosses the scene up to the houses. It may indicate an often used common trail or symbolize the migration of the Aztecs that led to their settlement in the valley of Mexico in the 12th Century [3]. A larger part of this paper is missing, underlining the often used description of "muy maltrado" (very maltreated) in connection with this fragment. It was a great chance for the authors to be allowed to investigate this invaluable piece of human cultural heritage. It had to leave its climatized treasure for quite a number of hours, to be transported straight across Berlin to the research institute and to be subjected to the spectroscopic investigations. All precautions were observed to avoid too intensive irradiation and heating of the precious codex. Fig. 1b shows the specially developed transport table to move the paper without touching it.

(a)

## 1.2. Maya clay sculpture

To compare Maya Blue from different origins and periods, original Maya Blue from the MNA and several Latin-American human artefacts were included in the investigation. Their authenticity and age were guaranteed by the donors. By courtesy of the Ethnological Museum in Berlin (Staatliche Museen zu Berlin, Stiftung Preußischer Kulturbesitz, Ethnologisches Museum) we got a 10 cm fragment of a Maya clay sculpture from the classical period (300–900 A.D.): the head of a bearded man, partly decorated with Maya Blue (Catalog No. IVCa 21166) (see Fig. 3). Spots of Maya Blue in several parts of the head and its decoration served as control for a true Maya Blue.

## 1.3. Blue coloured threads

Five blue-coloured threads from tissues used in the last 2000 years were investigated. Four of them were friendly gifts of the same Ethnological Museum as with the Maya head: (i) a headband (Ocucaje) made from camelid wool in the period between 0 and 200 A.D. (No. VA 44827); (ii) a cotton cloth, originating from Chiribote/Peru and the time from 1200 to 1400 A.D. (VA 51292); (iii) a cotton cloth from Barrio de San Paulo/Mexico, 1889 (IVCa 7980); (iv) a cotton children's huipil (girl's shirt) from Santo Thomas Chicicastenango/Guatemala, 1964 (IVCa 45153). In addition, a cotton thread from a modern blue-jeans (Wrangler, 1999) coloured with synthetical indigo was included in the research.

#### 1.4. Pre-Columbian paper

Pre-Columbian Mesoamerican people knew two kinds of paper, "metl" made from agave (*Agave americana*) and "amatl" from the inner bark of different fig-trees, in the majority of cases *Ficus padifolia* [4–7]. It could be shown that the bark was beaten with stone implements to produce pulp, which was held together by natural gums. The raw paper was set and polished by hot, flat iron-shaped planches, giving the product a non-blotting surface [7].

This paper, called "huun" by the Mayas, was far superior to the Egyptian papyrus products concerning texture and durability [7]. The Maya technique survived the centuries and is still used by the Otomi Indians of Mexico who sell such papers under the name "amates" to tourists. Both Mayas and Aztecs used the trees of their immediate surrounding, the Mayas the fast-growing *F. padifolia* from the warm lowlands ("terra caliente"), the Aztecs from the cold high plateau ("terra fria") and the hill sides. Thus, differences in Maya and Aztec papers can be readily explained.

Thermal investigations were carried out with milligramsamples from fragment VI of the Codex Huamantla preserved at the MNA, Mexico City. These were supplemented by coupled thermogravimetry (TG)/mass spectrometry (MS) investigations, scanning electron microscopy (SEM) studies for visible effects of bark beating and fungal contaminations, and by energy dispersive X-ray analysis for metals in the paper.

#### 1.5. Maya Blue colour

A prominent role in decorating the codex is played by Maya Blue, a colorant composed of indigo and some clay components, most prominent among these being palygorskite (synonym: attapulgite [8]). It was a widely used blue colour in Pre-Columbian Mesoamerica for about 2000 years and introduced in a paper by José-Yacamán et al. [9] with the sentence "Magnificent blue colour with a turquoise tone similar to that of the Caribbean ocean, on the shores of the Maya homeland". Maya Blue is not always blue but may change to turquois or greenish hues. It became clear in the 19th Century that Maya Blue was not a copper mineral and had no relations to natural ultramarine, ground Lapis Lazuli or Lazurite. Its unprecedented stability which kept it brilliant over 12 centuries is astonishing. While palygorskite was found in the soils of the Mayan kingdom, specially in Northern Yucatan ("Saklu'um") [10,11], indigo originated from the local plant "Xinquilit" (Indigofera suffructicosa, sometimes also suffruticosa) [12]. Due to a lack of heavy metals and the use of natural products Maya Blue was an environmentally friendly dye. Intensive research on Maya Blue and its indigo component was carried out in the last decades, applying spectroscopic as well as microscopic and other physico-chemical methods [9–15].

In an early paper, when the composition of Maya Blue was still unknown, van Olphen produced a synthetic indigo–attapulgite complex with a colour very similar to Maya Blue [16]. He could show that the essential point for a stable pigment was a thermal treatment for several days at temperatures between 75 and 150 °C. Because of the very low dye content in the final product he assumed that indigo was absorbed at the external palygorskite surfaces only and not inside its channels. These observations were confirmed for natural Maya Blue. Later on it was shown in an X-ray investigation that indigo also inserted into the palygorskite channels [10].

# 1.6. Palygorskite

Palygorskite, the inorganic component of Maya Blue, is a clay mineral with the chemical formula (Mg, Al)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>4H<sub>2</sub>O and the empirical formula Mg<sub>1.5</sub>Al<sub>0.5</sub>Si<sub>4</sub>O<sub>10</sub>4H<sub>2</sub>O [17]. Palygorskite (with priority to the name attapulgite) is yellowish, light brown to pure white and has a micro crystalline, finefibril, felt like structure (with a thickness of 30-60 nm) [18], giving its surface a fabric or leather looking character. Fernandez et al. showed that an orthorhombic model fits better to the palygorskite structure than a monoclinic one and helps to explain the properties of archaeological pigments in general and also of Maya Blue [19,20]. Its siloxyl group may produce covalent bonds with organic reagents and thus attach them firmly to the clay [19]. All experiments to separate the indigo of Maya Blue from its palygorskite component failed because of an intimate structural relationship [9].

DSC and DTG analyses of palygorskite indicated a loss of hygroscopic and zeolithic water up to  $200 \,^{\circ}$ C followed by a loss of bound water between 250 and 450  $^{\circ}$ C. At even higher temper-

atures hydroxylic units were given of, in total all endothermic processes [18].

In a recent paper [15] the narrow channels of palygorskite were compared with the modern nanotubes. The chemical bonds inside the fibre-like structures produce – in modern nomenclature – a hybrid organic–inorganic nanocomposite. Such functional hybrids are considered to be highly innovative materials, ready to enter a multitude of different applications. Guided by these results a synthetic dye named Mayacrom was produced on the basis of natural plants and clays, avoiding heavy metals and poisonous additives as they are found in many usual pigments.

## 2. Material and methods

#### 2.1. Thermal analysis

Different thermal analytical methods were carried out with Mettler instruments (Mettler-Toledo AG, Greifensee, Switzerland). The thermosystem TA 400 was used for TG and DTG determinations of ancient Aztec paper with a scanning rate of 1 K min<sup>-1</sup>, the samples being in closed aluminium crucibles having a 2 mm hole in the cover and at still air. The DSC scans were performed with a Mettler DSC 25 on 4 mm diameter samples in aluminium crucibles at still air and 1 K min<sup>-1</sup>. A Mettler TG 50 coupled with a Balzers mass spectrometer MS-Cube<sup>TM</sup> (MSC 200; Balzers AG, Liechtenstein) served for the thermogravimetric/mass spectroscopic investigations of the original codex paper. A specimen of a few milligram was obtained from the edge of fragment VI kept at the MNA. Only DSC and thermogravimetric curves are shown in this publication.

#### 2.2. Raman spectroscopy

The Raman spectroscopic investigations were carried out with (i) a FT-IR-spectrometer IFS 66v along with a Raman device FRA 106 (BRUKER, Ettlingen, Germany) with excitation by a Nd:YAG-laser (DPY 421, ADLAS, Lübeck, Germany) at 1064 nm, and (ii) with a DILOR XY Raman spectrometer (DILOR, Bensheim, Germany) equipped with a nitrogen cooled CCD-camera (charged coupled device) as detector coupled to a BH-2 microscope (OLYMPUS, Hamburg, Germany) in micro-mode technique (objective  $50 \times$  and  $50 \times$  ulwd (ultra long working distance)). The 514.5 nm excitation line of an Arion laser (ILA 120-1, Carl Zeiss, Jena, Germany) with a radiant power of 5 mW provided an irradiance of about 0.5 mW  $\mu$ m<sup>-2</sup> at a laser spot diameter of 2  $\mu$ m. Integration periods varied between 10 and 300 s and 2–250 accumulations at a spectral resolution of about 1 cm<sup>-1</sup>.

# 2.3. Colours

Synthetic indigo was obtained from FLUKA (No. 56980; Indigo blue; indigotin; Buchs, Switzerland) in the form of small spheres ( $\emptyset \sim 40-60 \,\mu$ m). They were used as such or smeared on a microscopic slide in a thin layer. Authentic Maya Blue was only available in traces of a few micrograms originating from

Fig. 2. Head of a bearded man, fragment of a Maya clay figure, classical period (300–900 A.D.) (spots of measuring indicated by letters). By courtesy of Staatliche Museen zu Berlin, Stiftung Preußischer Kulturbesitz, Ethnologisches Museum, Berlin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

the MNA and was preserved between glass slides or fixed on an adhesive tape. Further specimens of true Maya Blue were found on a Mexican head sculpture and on cloth threads from Latin America (see Section 1.3) and of course on fragment IV of the codex.

## 2.4. Artefacts

The main and very precious artefact (insurance value several million Euros) was fragment IV of the Codex Huamantla. Its size amounts to  $43.5 \text{ cm} \times 64 \text{ cm}$  with a large hole from one side well into the centre (Fig. 1). Because of the limited space on the microscope stage (less than 10 cm) only blue spots at the periphery of the fragment could be used. A transport table from polyacryl was specially constructed and firmly attached to the microscope stage. It could freely move on several ball-bearings on a second polyacryl table connected with the spectrometer. Thus, the fragment could be manoeuvred by the microscope stage control in both directions with an accuracy of a few micrometers and without touching it. Spectra were taken from the blue chair of the second person from left (upper right corner of the Codex in Fig. 1b), from the upright standing club of the soldier (lower right corner), and the right end of the blue river (lower left corner).

In preparation of the present paper a Mexican artefact from the classical period, 300–900 A.D. was lent by the Berlin Ethnological Museum (Catalogue No. IV Ca 21166, Acten No. 1141/97). It represented the head of a bearded man with several blue decorations on the forehead, the left eyebrow, the right ear and in the head ornaments (Fig. 2). These spots served as further control for authentic Maya Blue. To keep and adjust the head, a special support was constructed for a sensitive and reproducible 3D-movement under the ulwd objective of the microscope. Further information about true May Blue was collected from cloth threads from 4 different periods of the 2000 years of this



colour in Latin America (see above). All were dyed with blue colour.

## 3. Results and discussion

## 3.1. Investigations by Raman and IR spectroscopy

## 3.1.1. Indigo and authentic Maya Blue from the MNA

Synthetic indigo in form of small globules ( $\emptyset \sim 40-60 \,\mu$ m) with pale greenish and slightly red hues showed bands between 466 and 1690/1700 cm<sup>-1</sup>, corresponding to those determined experimentally and calculated by Tatsch and Schrader [21]. But, compared with their data, some additional bands or band shifts occurred and some bands were missing. These differences were not due to indirubin, an isomeric form of indigo. It might be that traces of contamination or varying syntheses were responsible for these deviations. This indigo spectrum is compared in Fig. 5 with the results from the threads, the clay head and fragment IV.

Two microgram specimens of original Maya Blue from the MNA could only be investigated with microsample technique and excitation in the visible. The obtained spectra were marked by a high, unstructured background with some lines of the adhesive tape to which the pigment was fixed to. Similar effects were published by Coupry et al. [22]. Unfortunately, the investigation on authentic Maya Blue powder could not be followed further because of insufficient quantities of material.

#### 3.1.2. Maya clay head

Due to the negative results mentioned above, investigations of the four chosen blue spots of the sculpture head were performed with FT Raman spectroscopy and excitation in the near-infrared  $(1064 \,\mu\text{m})$  with intensities between 50 and 500 mW. They generated two broad bands (200–2100 and  $2500-3500 \text{ cm}^{-1}$ ) similar to bands from the red sculpture surface without colour. These bands cannot be connected with indigo. The wide band around  $3000 \,\mathrm{cm}^{-1}$  is a so-called "warming band" due to overheating of the sample. These NIR excited spectra are not shown here. Investigations of a piece of Blue Jeans tissue under identical conditions brought a spectrum rich with lines equivalent to those of indigo, corresponding well in wave numbers and relative intensities. Additional lines originate from cotton. These results indicate that indigo can be detected at the chosen experimental settings. Presumably, the indigo concentration on the sculpture surface is very low and its signals are obscured by the broad underground of palygorskite.

Excitation in the visible range (514.5 nm) presented spectra rich of bands and identical for all 4 spots A to D (Fig. 3). It could be shown that the spectra did not originate from the clay material, but from Maya Blue itself. All lines were very small, a good sign that there was no heating-up by laser excitation and that the historical artefacts were treated with much care. The relative line intensities were equal to those from historical tissues (see below). Moreover, some additional lines (e.g. 1380 and  $1593 \text{ cm}^{-1}$ ) were present in all four spectra, but missing in the signals of synthetic indigo. They were similar to lines seen in IR excited indigo spectra. This points to the fact that the flat indigo molecule was transformed when bound to the



Fig. 3. Raman spectra from the 4 indicated blue spots of the Maya clay fragment (Fig. 2). All four spectra are identical, originating from Maya Blue and not from the red colour of the head.

palygorskite lattice and that the mutual exclusion rule, which predict the occurrence of additional lines either in the IR or in the Raman spectra, were no longer valid [14]. But as Maya Blue is a natural indigo dye, impurities might also be responsible.

#### 3.1.3. Blue coloured tissue and threads

The four blue-coloured camelid-wool threads spanning 2000 years of Mesoamerican and South American history were included in these Maya Blue investigations, together with a modern Blue Jeans tissue. The most intensive Raman bands for indigo on wool or cotton (~597, 1249, 1364, 1574 and  $1700 \text{ cm}^{-1}$ ) determined by Coupry et al. [22] could be detected on all threads—as well as on the clay head and the fragment IV. Some changes might have occurred during the fixation of the pigment to the tissue due to a change in the symmetry character of the dye. The spectra of the 3 most recent threads (Blue Jeans/1990; children's huipil/1964; cotton cloth from Mexico/1889) were very similar, although it is not clear if natural or synthetic indigo was used for the 1889-sample. The possibility for both dyes exists. The results were compared and found in good agreement with data published in the literature [22–24].

#### 3.1.4. Fragment IV of the Codex Huamantla

Fragment IV of the Codex Huamantla is an extremely precious object which was only allowed to leave the climatized safes of the State Library for a few hours, considerably insured and attended by two specialists of the library. A short pre-experiment with FT-Raman spectroscopy showed no results, neither for Maya Blue nor for the supporting fig-tree paper. Therefore, it was decided to concentrate on a region between 1000 and 1800 cm<sup>-1</sup> with laser excitation at 514.5 nm. The experimental set-up is discussed above and seen in Fig. 1b.

Bad signal-to-noise ratios (SNR) and a high fluorescence background with weak Raman bands were typical for the obtained spectra. Prolonging the duration of exposure by the exciting laser light to reduce the fluorescence prior to the Raman measurements and shortening the counting time at high numbers



Fig. 4. Raman spectra of the three chosen spots in the fragment IV of the Codex Huamantla. Spectra were normalized to the same intensity in the strongest band and shifted vertically for better legibility.

of accumulations, the SNR could be increased and evaluations became possible. Moreover, a combination of several consecutive spectra with a small spectral shift kept the Raman bands at a constant place, while disturbances were shifted and annealed themselves. A combination of these different techniques generated Fig. 4 for the 3 blue spots indicated in Fig. 1a. These spectra are more or less identical and show Maya Blue bands only and no contributions from palygorskite. Again, some lines additional to those of synthetic indigo appeared as discussed and explained above for blue tissues. Moreover, the relative line intensities were significantly increased at several wave numbers. A mean spectrum of fragment IV is compared in Fig. 5 with those found in the literature and with synthetic indigo, threads and clay head.

The spectra of fragment IV correspond to those of the Maya head, except for a weak additional line at  $1695 \text{ cm}^{-1}$ . Some fragment lines are broader than those of the head, a phenomenon well-known from spectra of amorphous substances or solute in contrast to those of well-crystallized samples. Such disturbances can be cured by thermal treatment. It might therefore be that the indigo in Maya Blue on the clay head obtained a stronger binding to palygorskite by mild firing and thus a more regular structure and narrower lines. Such treatment is of course not possible with paper as a substratum for Maya Blue. To facilitate the comparison of the two main artefacts with pure synthetic indigo, Fig. 6 depicts the three spectra separately.

## 3.2. Thermal investigations

#### 3.2.1. Paper of fragment IV

Unfortunately, it was not possible to obtain a paper sample from the Berlin fragments III or IV. Therefore, investigations on fragment VI paper from the MNA were included in this research. The results of the thermal analysis are shown in Figs. 7 and 8. Fig. 7 presents DSC curves for the original Huamantla paper from the MNA (top) and for recent fig-tree material (below). Two main exothermic peaks are prominent: oxidative decomposition of cellulose at still air ranges from 240 to 350 °C, that



Fig. 5. Raman spectra with the 20 most prominent lines for synthetic indigo, 5 tissue threads, the Mayan clay head and fragment IV of the Codex Huamantla.

of lignin between 350 and 500 °C. The characteristics of the two slopes are very similar. The two prominent peaks occur at 289 and 422 °C for the codex and 290 and 410 °C for the new paper, respectively. Additional shoulders are seen at 372 °C in the upper graph and 420 °C in the lower one, which shows a further one at 389 °C hidden in the steep ascent to the lignin



Fig. 6. Comparison of Raman spectra of pure synthetic indigo (bottom), the Mayan clay head (centre) and fragment IV of the Codex Huamantla (top).



Fig. 7. DSC curves of a 2-mg piece of paper from the Codex Huamantla (Museo Nacional de Mexico) (top) and of a recent paper made from the inner bark of *Ficus padifolia* (bottom). Please notice the small endothermic peak around 150 °C mentioned in the text (see also insert). For both samples: *Y*-axis in arbitrary units, heating rate  $1 \text{ Kmin}^{-1}$ , still air, exothermic effects upwards, endothermic downwards. Adapted from [6].

peak. There are as yet no explanations for these peaks. A well-known endothermic effect is clearly indicated at 153 °C in the lower track and weakly detectable at 147 °C in the upper one. It is usually seen in papers produced by breaking the raw bark material during the mechanical treatment. When the cell walls of the bark are destroyed calcium oxalate forms from oxalic acid in the cell liquid and calcium in the water used for paper production.

The thermogravimetric curves of recent Ficus-tree material heated at still air show three distinct steps of mass loss, better indicated in the first time-derivative of its original curve (Fig. 8). A first loss of about 7% up to  $180 \,^{\circ}$ C is due to dissipation of free water, the most prominent step with about 67% occurs at 265  $^{\circ}$ C and can be ascribed to the oxidative mass loss of cellulose, while the last one of 26% at 398  $^{\circ}$ C corresponds to an oxidative loss of lignin. The residual ash content is very small.



Fig. 8. Thermogravimetric curve (TG) of paper made from bast of *Ficus pad-ifolia* (3.760 mg). The three steps around 100, 270 and 390 °C correspond to a weight loss of 6.6, 67.3 and 26.0%, respectively. Heating rate 1 K min<sup>-1</sup>, still air. The derivative slope (DTG) makes the three steps better visible. Adapted from [6].

## 4. Conclusion

In recent years some interesting papers connected with the present topic appeared showing the common interest in this world heritage. Berke [25] published an excellent historical and scientific survey of the "Invention of blue and purple pigments in ancient times" including Maya Blue. Various techniques like thermal analysis, Raman spectroscopy and model calculations were applied. Two years earlier Maya wall paintings of the late classical period (~900 A.D.) were described, found in an acropolis in Yucatán/Mexico. The whole set of Mayan pigments from red and yellow over green and blue to black was investigated by Raman spectroscopy [26]. Powder synchrotron diffraction and crystal structure refinements were applied to correct the assumed structure of palygorskite and Maya Blue [17], recently extended by the same authors with computation, thermal analysis and Raman spectroscopy [27].

Not only the original codices preserved in the MNA in Mexico City are listed in J.B. Glass' catalogue [28], but also numerous copies from different centuries. The Codex Huamantla is mentioned in the catalogue with 8 fragments left over from Boturini's collection, 6 fragments in the MNA, 2 in the SBB in Berlin. As Boturini's activities lay more than half a century before Humboldt's visit to Mexico and as his collection was dispersed and went through several hands the question arose which fragments are original and which are copies. Figure 39 in Glass' catalogue shows a composition of the (Mexican) fragments III and IV and a copy of the Berlin fragment III. But this copy is done without much care in many details. Already Seler remarked [3] that the Berlin parts are written on original "amatl" fig-tree paper. The Raman spectra of the 3 points on fragment IV show a high degree of similarity with those of the certified ancient artefacts (head, threads) proving that original Maya Blue was used to illuminate the codex. Although it was not possible to investigate a paper sample of the Berlin fragments and thus to get a further certification about the age and the material of fragments III and IV, all hints from the literature together with our spectroscopic results point to the fact that the Berlin fragments bought by A. von Humboldt in Mexico are part of the original former Boturini Codex Huamantla and no copies.

### Acknowledgments

This paper would not have been possible without the help of several institutions and a number of friendly persons. We are grateful to the Ethnological Museum in Berlin-Dahlem for the opportunity to investigate the rather old Maya clay head, the gift of historical threads with authentic Maya Blue and the support by Mrs. Lena Bjerregaard, Dr. Maria Gaida and M.A. Andrea Nicklisch.

Our special thanks go to the Berlin State Library, its at that time Managing Director Dr. Antonius Jammers and the Head of the Manuscript Division Dr. Eef Overgaauw for their readiness to let the extremely precious codex fragment leave its climatized treasure and be transported to the research institute for performing the spectroscopic investigations. Mrs. Dorothea Barfknecht and Dr. Julia Bispinck helped to prepare the action and Mrs. Margit Hundertmark and Dr. Renate Schipke accompanied the journey and handled the codex. To all of them our gratitude is due.

#### References

- "Indianische Handschriften und Berliner Forscher". Handbuch zur Ausstellung. Universitätsbibliothek, Freie Universität Berlin, Berlin ("Indian manuscripts and Berlin scholars". Handbook to an exhibition. University Library, Free University of Berlin, Berlin), 1988, p. 70.
- [2] A. von Humboldt, Vue des Cordillières et monumens (sic) des peuples indigènes de l'Amérique, Paris, 1810.
- [3] E. Seler, Die Mexikanischen Bilderhandschriften Alexander von Humboldt's in der Königlichen Bibliothek zu Berlin (The Mexican manuscripts of Alexander von Humboldt in the Royal Library at Berlin), Berlin, 1895.
- [4] R. Schwede, Über das Papier der Maya Codices (About the paper of the Maya codices), Richard Bertling, Dresden, 1912.
- [5] W. von Hagen, The Aztec and Maya Papermakers, Hacker Art Books, New York, 1977.
- [6] H.G. Wiedemann, A. Boller, Thermal analysis of Codex Huamantla and other Mexican papers, J. Therm. Anal. 46 (1996) 1033–1045.
- [7] H.G. Wiedemann, Paper technology from Egyptian, Chinese, and Mayan cultures, in: Proc. of the Workshop on State-of-the-Art of Thermal Analysis held at NBS, Gaithersburg, MD, May 21–22, Nat. Bur. Stand. Spec. Publ. 580 (1979) 201–217 (Issued May 1980).
- [8] Römpp Online (www.roempp.com) version 2.10, Thieme Chemistry, 2006.
- [9] M. José-Yacamán, L. Rendón, J. Arenas, M.C.S. Puche, Maya Blue paint: an ancient nanostructured material, Science 273 (1996) 223–225.
- [10] L.A. Polette, G. Meitzner, M.J. Yacaman, R.R. Chianelli, Maya Blue: application of XAS and HRTEM to materials science in art and archaeology, Microchem. J. 71 (2002) 167–174.
- [11] L.Polette, N. Ugarte, R. Chianelli, In-situ identification of palygorskite in Maya Blue samples using synchrotron X-ray powder diffraction. http://www.srs.dl.ac.uk/arch/ssrl/maya-blue.html.
- [12] D. Reinen, P. Köhl, C. Müller, The nature of the colour centres in 'Maya Blue'—the incorporation of organic pigment molecules into the palygorskite lattice, Z. Anorg. Allg. Chem. 630 (2004) 97–103.
- [13] E. Stokstad, Quantum secrets of Maya Blue, New Sci. 151 (1996) 17.

- [14] K. Witke, K.-W. Brzezinka, I. Lamprecht, Is the indigo molecule perturbed in planarity by matrices? J. Mol. Struct. 661/662 (2003) 235–238.
- [15] N. Massetti, Mayan Blue—Nanotech pigment from the 8th Century. Mayan Blue pigment: Vegetable or mineral? Its nanostructure provides the long sought answer. http://www.nanovip.com/forums/showthread.php?t=742.
- [16] H. van Olphen, Maya Blue: a clay-organic pigment? Science 154 (1966) 645–646.
- [17] G. Chiari, R. Giustetto, G. Ricchiardi, Crystal structure refinements of palygorskite and Maya Blue from molecular modelling and powder synchrotron diffraction, Eur. J. Miner. 15 (2003) 21–33.
- [18] R.L. Frost, Z. Ding, Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites, Thermochim. Acta 397 (2003) 119–128.
- [19] M.E. Fernandez, J.A. Ascencio, D. Mendoza-Anaya, V. Rodriguez Lugo, M. Jose-Yacaman, Experimental and theoretical studies of palygorskite clays, J. Mater. Sci. 34 (1999) 5243–5255.
- [20] G. Strübel, H. Zimmer, Lexikon der Mineralogie, Thieme Stuttgart, 1982.
- [21] E. Tatsch, B. Schrader, Near-Infrared Fourier transform Raman spectroscopy of indigoids, J. Raman Spectr. 26 (1995) 467–473.
- [22] C. Coupry, G. Sagon, P. Gorguet-Ballesteros, Raman spectroscopic investigation of blue contemporary textiles, J. Raman Spectr. 28 (1997) 85–89.
- [23] H.G.M. Edwards, D.W. Farwell, A.C. Williams, FT-Raman spectrum of cotton: a polymeric biomolecular analysis, Spectrochim. Acta A 50 (1994) 807–811.
- [24] G.N. Andreev, B. Schrader, H. Schulz, R. Fuchs, S. Popov, N. Handjieva, Non-destructive NIR-FT-Raman analyses in practice. Part 1. Analyses of plants and historic textiles, Fresenius J. Anal. Chem. 371 (2001) 1009–1017.
- [25] H. Berke, The invention of blue and purple pigments in ancient times, Chem. Soc. Rev. 36 (2007) 15–30.
- [26] P. Vandenabeele, S. Bodé, A. Alonso, L. Moens, Raman spectroscopic analysis of the Maya wall paintings in Ek'Balam, Mexico Spectrochim. Acta A 61 (2005) 2349–2356.
- [27] R. Giustetto, F.X. Llabrés i Xamena, G. Ricchiardi, S. Bordiga, A. Damin, R. Gobetto, M.R. Chierotti, Maya Blue: a computational and spectroscopic study, J. Phys. Chem. B 109 (2005) 19360–19368.
- [28] J.B. Glass, Catalogo de la Coleccion de Codices. Museo Nacional de Antropologia, Instituto Nacional de Antropologia e Historia, Mexico, 1964.