BEYOND THE EYE-SIGHT: THE PUZZLE OF A JAPANESE MANCHIRA

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Abstract

In the framework of a collaboration between the Opificio delle Pietre Dure and the Stibbert Museum (both Florence, Italy), a Japanese armour from the Edo period (XVII-XIX cent.), called manchira, was subjected to a multi-analytical diagnostic campaign. Due to the multi-layered structure of the object, constituted by silk, linen or hemp, wool, leather, and metallic parts, the diagnostic campaign entailed both non-invasive and micro-destructive techniques, such as multi-spectral photography, FORS, FT-IR, XRF and HPLC-DAD analysis, prior and in parallel to restoration practice. The main goals of the study were assessing the state of conservation in order to plan a thorough cleaning and consolidation strategy; characterizing the assembly and the materials employed; dating the object and clarifying the context of its production (e.g. the social status of the owner, the quality of the constituting materials, etc.). Reference ex-novo of dyed textiles were prepared accordingly to traditional Japanese recipes, by using materials purchased in Japan. The results were interpreted with the help of Japanese costume and textile historians and allowed us to clarify the nature of the constituting materials and to characterize the object under study. In this paper, the main results obtained by micro-destructive techniques are presented. In particular, the analysis by HPLC-DAD led to the identification of a black shade obtained by superimposing an indigoid dye to an iron-mordanted flavonoid dye (Sophora japonica) for the dark damask and of murasaki dye for the kikkō. The influence of the dyeing technique, entailing the application of an iron mordant, was fundamental in assessing the state of conservation of the object.

1 Introduction

The physical-chemical investigation of the materials used for manufacturing historical objects under restoration processes is an invaluable tool for assessing their state of preservation in order to plan a thorough cleaning and consolidation and preventive conservation strategies. By merging analytical data and information obtained by the artistic and historical research, it is often possible to assess the type and the quality (in terms of price and rarity) of the constituting materials, their provenance and the quality of the technique employed in their production and handicraft. The comparison with known dyeing recipes and handicraft manuals may yield information on the social status of its owner, and help to reconstruct the story of the use of the object. In the field of study of textiles and fabrics, the characterization of dyeing materials has proved to be fundamental to gain these goals1,2,3. The most common methods for identifying organic colorants in textiles are based on liquid chromatography interfaced with photodiode array and mass spectrometric detection. These micro-destructive techniques require the extraction of the chromophore-containing molecular markers with a treatment based on hydrolysis in acidic methanol, extraction with complexing agents, or organic solvents depending on the stability of the target analytes4. The unambiguous identification of the dye source can only be achieved by detecting molecular markers that are typical of selected dyes and comparing the chromatographic profiles of historical samples with the ones of ref-

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The campaign entailed the use of several techniques, and was supported by a thoughtful study of traditional techniques with the help of a Japanese costume and textile historian, and the preparation of ex-novo reference specimens. Especially when non-European dyes are involved, the reference libraries available in the literature or collected in specialised laboratories and networks are still incomplete, and identifying the original dye source is extremely challenging.4,5,6

This paper deals with the study of peculiar characteristics of a Japanese manchira, which is a seldom described part of the outfit of a samurai warrior.7 In particular, manchiras appear as elegant doublets, but included an armoured layer, which is suited for the protection of the upper part of the body, including the neck and arm pits. They were to be worn under or over the dō (the classic Japanese chest armour), and may include chains, armour plates or brigandine armoured parts. In particular, the object under study (see Figure 1) belongs to the Japanese section of the Stibbert Museum, but no further information is currently available on its provenance or dating. Due to its poor state of preservation, it is currently undergoing conservation at the Opificio delle Pietre Dure.8,9 The manchira conservation project entailed a thoughtful diagnostic campaign, aimed at characterizing the materials employed and their assembly and assessing the state of conservation in order to plan a thorough cleaning and consolidation strategy. Moreover, the analytical data helped in dating the object and clarifying the context of its production, in order to confirm and better specify the information obtained by the study of its fashion and style, which refer to the Edo period (XVII-XIX cent.). Considering the multi-layered and multi-material structure of the manchira, different issues needed to be faced at the same time. The diagnostic campaign entailed the use of several techniques, and was supported by a thoughtful study of traditional techniques with the help of a Japanese costume and textile historian, and the preparation of ex-novo specimens to be used for comparison purposes. To obtain the complete characterisation of the manchira, several techniques and analytical procedures were exploited, in order to get data on both the organic and inorganic components of the materials. Non-invasive analytical techniques were exploited for a preliminary survey prior to sampling, followed by the application of micro-destructive techniques. In particular, visual inspection, false colour photography/multispectral imaging and X-ray radiography were first undertaken at the Opificio delle Pietre Dure. In order to characterise the dyestuffs employed, a set of non-destructive analyses by Fiber Optics Reflectance Spectroscopy (FORS) was conducted. When sampling was possible, micro-destructive HPLC-DAD analysis was applied.

This paper summarises the results obtained by non-destructive techniques8,9 and focuses on the analytical data obtained by micro-destructive analysis of dyed yarns, with particular attention to HPLC-DAD analyses of the organic dyes.

2 Materials and Methods

2.1 FORS

The analyses were undertaken at the IFAC-CNR (Florence) using a portable Zeiss mod. MCS601 UV-VIS-NIR spectro-analyser with quartz optical fibres with a CCD detector (1024 diodes) with 0.8 nm/pixel resolution and operating in the 200-1050 nm range, equipped with a stabilized halogen lamp (20 W, mod. CLH600) with heat temperature around 3000 K. A Zeiss mod. MCS611 NIR spectrophotometer with CCD detector (512 diodes) with 6 nm/pixel resolution and operating in the 900-2250 nm range was also used. The measuring heads are two hemispheric probes designed by IFAC characterized by 2 mm acquisition spot, with probe configuration 2x45°/0° and 1x8°/0° geometries, respectively.10

2.2 Optical Microscopy (OM)

All the samples (single threads or single fibrils) were placed on glass slides and observed under the optical microscope in visible and UV light (both reflected and transmitted) without any further treatment. Selected samples were also embedded in a polyester resin and observed under the microscope both in diffused and in UV light. The optical microscope used was a Zeiss Axioplan allowing magnification from 5x to 20x and equipped with different light sources such as halogen lamp for the visible and HBO mercury vapours lamp for the UV range.

2.3 Liquid Chromatography

HPLC-DAD analyses were performed on a PU-2089 Quaternary Gradient Pump with degasser (Jasco International Co., Japan), equipped with a Rhodyne Model 7125 injection valve and coupled to a spectrophotometric diode array detector MD-2010 (Jasco International Co., Japan) was used. The data were
processed by ChromNav® software. The chromato-
graphic separation was performed on an analytical
reverse phase C-18 column Synergi 4u Fusion-RP 80A
100 x 2 mm. The eluents were: A, water with 0.1% tri-
fluoroacetic acid; B, acetonitrile with 0.1% trifluo-
roacetic acid. The programme was: 85% A, 15% B for
1 minute; then to 50% A, 50% B in 7 minutes; then to 10%
A, 90% B in 5 minutes and hold for 10 minutes. The
flow rate was 0.3 mL/min. The detection wavelength
was set at 275 nm and the acquisition of DAD spectra
was achieved in the range 200-650 nm, 4 nm steps.
The injection volume was 2 μL.

2.4 Reference Materials

Ex-novo reference specimens were prepared in order
to obtain suitable comparison for indigo and murasaki
dyed textiles. In detail, two recipes, kindly provided by
“Yoshioka Textiles” (Kyoto) and dated back to Edo peri-
od (XVII cent.), were followed for dyeing in indigo and
in murasaki (purple) colours.

Indigo (紺) dyeing from indigo plant
(Polygonum tinctorum)

Ingredients: 23 L of water (soft water); 1 Kg of fer-
mented indigo leaves (sukumo), obtained after drying
from the Tade-ai plant (Polygonum tinctorum L.); 700
g of oak ashes (kungi-moku-ai, Quercus acutissima);
100 g of bran (husuma); 20 g of calcium hydroxide
(Ca(OH)2); 25 x 50 cm piece of linen fabric.

Recipe: Preparation of alkaline solutions of oak ashes

Mix the ashes with 7 L of boiling water. Let the solution
rest for 2 days in order to allow the leftover to precip-
itate, then filter to obtain alkaline solution #1. Mix the
ashes with 14 L of boiling water and let the solution
rest for 3 days. Filter to obtain alkaline solution #2,
then repeat the procedure with 21 L of water to obtain
alkaline solution #3.

Preparation of indigo dye bath

First day: mix 1 Kg of plant material with 5 L of solution
#2. Mix with a bamboo stick, keeping the temperature
of the solution around 20 °C.

Second day: add 5 L of solution #3 to the dye bath and
left it rest 7-10 days, stirring twice a day until a film
layer will form upon the solution.

7th-10th day: add to the dye bath a solution of 100 g of
bran in 2 L of water previously prepared by heating the
mixture for 20-30 minutes and then left cooling down.
The bran will catalyse the indigo fermentation.

9th-12th day: add 5 L of solution #1 to the dye bath and
let it rest for one day. Afterwards, the dyeing proce-
dure may start (the pH of the dye bath should be in the
range of 11-12, and can be adjusted by adding proper
quantities of Ca(OH)2).

Dyeing:

Rinse the fabric in hot water (40-50 °C), then dip it in
the dye bath for 5 minutes at room temperature, stir-
ring. The fabric is then pulled out of the dye bath: the
dye readily oxidises in the air. The fabric is then rinsed
in cool, clean water to remove the excess of the dye.
The dyed fabric is then left drying in a cool, dark place.
In order to obtain a darker shade of blue, the whole
procedure may be repeated.

Murasaki (紫) dyeing

Ingredients: 10 L of water (soft water); 400 g of
murasaki (shikon, roots of Lithospermum purpuro-
caeruleum); 40 g of camellia ashes (tsubaki, Camelia
japonica); 100 g of textile.

Recipe: Preparation of the ash solution and of the fab-
ric

Admix 40 g of ashes with 2 L of boiling water, and let
the ashes precipitate for 2 days. Then filter. Rinse the
fabric in hot water (40-50 °C).

Extraction of the dyestuff

Wash 200 g of shikon and then soak the root chips in
hot water (50 °C). Then, smash the roots in a wooden
mortar and put them in a linen bag. The dye is extract-
ed in 3 L of hot water (40-50 °C). The final solution is
filtered and stored. The roots are again smashed and
subjected to hot water extraction two more times, and
the obtained solutions are admixed with the first one
and diluted to obtain 9 L of the final dye bath.

Dyeing:

Dip the textile into the obtained dye bath and let it rest
for 1 hour. Then slowly heat the dye bath up to 40 °C
and stir. Rinse the dyed textile in cool water to remove
the excess of the dye. Add 200 mL of the ashes solu-
tion in the dye bath, and slowly heat it up to 40 °C.
Then, dip the fabric in the dye bath again and stir for 20
minutes. Rinse again the fabric in fresh water. Repeat
the whole procedure twice (including the addition of
ashes to the dye bath). Rinse the fabric and let it dry in
a dark cool place. Repeat the procedure to obtain
darker shades, if needed.
The first layer from the inside is made up of a light blue linen fabric; the second one is an interlining made of undyed hemp. The typology of fibers was identified on the basis of the SEM observation and on the evaluation of their average diameter9,12. For the first layer, the average diameter of the fibers was 12.97 μm (compatible with linen, whose diameter ranges from 10 to 40 μm); for the second layer, the average diameter of the fibers was 34.54 μm (compatible with hemp, whose diameter ranges from 15 to 50 μm)12. The third layer, which is not detectable by visual inspection of the object, was previously characterized by X-ray radiography8 and consists in a metal armour formed by small iron (possibly steel) rings linked with hexagonal plates of treated leather and probably covered in lacquer. The fourth layer, which is visible under the thorns on the surface, is made of a cellulose fibre and is dyed in a dark blue shade. The top layer consists in a silk damask. The bottom of the collar and straps are lined in wool, while the braids are made of blue dyed silk. The whole structure is assembled by a beautiful, dyed leather border.

Once the assembly of the manchira and the source of the fibres were characterised, open questions still remained about the dyestuffs employed to yield the dark colour of the outer layer and the purple and green details of the collar and straps. In particular, the study aimed at understanding the reason for the poor state of conservation of the dark damask for restoration purposes, and at identifying the nature of the purple colour on the collar and straps, which may yield information on the recipes used for dyeing, and thus on the dating and price of the object. The results obtained by the inspection under the optical microscope, the study of cross sections of the threads embedded in suitable resins under UV and visible light and the interpretation of HPLC-DAD chromatograms will be discussed in the following paragraphs depending on the different investigated areas of the manchira.

### 3 Results and discussion

The preliminary results obtained by applying non-destructive techniques allowed for assessing the stratigraphy of the manchira and identifying the five layers used to build up its structure, as depicted in Figure 3.

#### 3.1 The damask (top layer)

The OM observation of the warp showed a bad conservation condition of the thread (see Figure 4 B), which appeared crystalline and coarse (see Figures 4 C, D and E), and the blue colour appeared evenly dis-
tributed on the surface of the threads. The OM observation of the weft showed an advanced degradation of the fibrils, which appeared crystallized and characterized by micro-fractures (see Figures 4 F, G and H). The dark colour appeared oddly distributed, and the surface was covered by a significant amount of particulate.

Two samples were collected from the weft and the warp of the silk damask, and were subjected to HPLC-DAD analysis. The chromatograms obtained from the two extracts gave different results: for the warp, indigotin was the detected dyeing molecule (Figure 5), and the chromatographic profile matched with the one obtained by analysing the indigo dyed ex-novo. In the chromatogram obtained for the weft, quercetin-glycosides were detected along with indigotin (Figure 6). We may conclude that the warp was dyed with an indigoid plant, such as *Indigofera tinctoria* or *Polygonum tinctorium*, also used for the preparation of the ex-novo. The presence of quercetin-glycosides suggested the presence of a flavonoid dye, such as *Sophora japonica*, a yellow Japanese dye. It is interesting to note that SEM analyses showed the presence of a relevant amount of iron in the weft threads (data not shown). These analytical data, merged with the study of Japanese historical recipes used for dyeing in black, suggest the hypothesis that the weft was double dyed, with an indigoid vat dye an then with *Sophora japonica* on an iron mordant. In particular, such recipe is mentioned for obtaining black shades for precious textiles, reserved for the Emperor and his court. Moreover, the presence of iron as a mordant may explain the bad state of conservation of the dark damask, with respect to the other threads in the *manchira*.

The puzzle of a Japanese Manchira, e-PS, 2013, 10, 19-26

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Figure 4: Pattern of the silk damask (A) and degraded area on the right shoulder (B). Images under the stereomicroscope of the warp (C) and the weft (F). Vis light; D, G: longitudinal sections of the warp and weft, respectively, acquired under the optical microscope in transmission, 20x; E, H: cross sections of the warp and the weft, respectively, acquired under the optical microscope, UV light, 50x.

Figure 5: HPLC-DAD chromatogram of the DMSO extract of the warp of the silk damask, at 620 nm (sample D2).

Figure 6: HPLC-DAD chromatograms of the extracts of the weft of the silk damask (sample D5): DMSO extract, at 620 nm (blue line) and extract after mild methanolysis, at 370 nm (black line).
3.2 The blue linings and the blue braids

Two samples from the inner pale blue lining and the top blue lining (Fa1 and Fb1, respectively) were analyzed by HPLC-DAD and, as expected, revealed the presence of indigotin, thus supporting the hypothesis that they were dyed with indigo. One sample collected from one blue braid (Ob2) was also analyzed by HPLC-DAD and revealed the presence of indigotin, thus suggesting also in this case the presence of an indigo dye.

3.3 The kikkō

The analysis of the kikkō entailed the characterization of the green watch chain along the hexagonal borders, of the purple braids in their centre, and of the background wool. Due to the excellent state of conservation of the green threads, no sample was taken from the watch chain, and only OM observation and FORS analyses were undertaken. It was possible to sample some fibres from the purplish silk in the centre of the hexagons and from the blue wool, and to observe them under the OM (see Figures 7 C, D and E for the purple silk, and F, G and H for the blue wool). The state of conservation of the sample threads appeared generally poor, with wide crystalline areas and diffuse particulate. A small sample of the blue wool constituting the background of the fabric on the shoulders and collar (Ml1) was also collected.

The results of FORS analysis applied to the green yarn are shown in Figure 8 A, and the reflectance minima are listed in Table 2. The comparison between the acquired spectrum and the database of the reference spectra allowed us to reference silk threads dyed with safflower yellow and indigo (see Figure 8 A). The application of complimentary non destructive techniques, such as multispectral imaging, are in progress in order to confirm this hypothesis.20

Figure 7: A: one of the kikkō; B: X-Ray radiography of one of the kikkō; C: sample collected from the blue wool (Ml1); D: longitudinal section: optical microscope, transmission, 20x; E: sample collected from the purplish area of the kikkō (Oa1); F: longitudinal section: optical microscope, transmission, 20x; G: cross section: optical microscope, UV, 50x.

Figure 8: A: FORS analysis of the green border of the kikkō (blue line), compared to the one obtained by the analysis of a reference silk thread dyed with indigo + yellow safflower (green dotted line); B: FORS analysis of the purplish inner part of the kikkō (blue line), compared to the one obtained by the analysis of a reference silk thread dyed with alkanet (green dotted line).

Figure 9: HPLC-DAD chromatograms at 490 nm of the DMSO extract of the purplish thread in the kikkō (sample Oa1) and of the DMSO extract of the ex-novo fabric dyed with murasaki (M).
Lithospermum purpurocaeruleum), respectively 13,14. Sieb. & Zucc.) or murasaki alkanet and gromwell (Lithospermum erythrorhizon naphthoquinones responsible for the purple colour of already mentioned, are two optical isomeric hydroxy-alkannin and shikonnin (see Figure 10), which, as whose UV-Vis spectrum matches with the one of matogram highlighted the presence of molecules shown in Figure 9 (purple line, matogram obtained by the analysis of the purple silk is of an indigoid dye source. The HPLC-DAD chro-
matter allowed us to detect indigotin, thus suggesting the use of an indigoid dye to an iron-mordanted flavonoid dye (Sophora japonica) for the dark damask and of murasaki-ki dye for the kikkō was crucial for linking the context of production of the manchira to high class purchasers18. The analytical results allowed to confirm the hypothesis based on the study of the iconography and the fashion of the manchira performed with the aid of a Japanese historian, and to date the production of the manchira to the first part of the XVII century22.

Moreover, the identification of the dyestuff used in the black threads allowed the restorers to understand the reason for their poor conservation state21, thus helping in planning their cleaning, consolidation and preventive conservation.

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