Journal of Cultural Heritage 18 (2016) 355–361

Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Case study

# Scientific analysis of Japanese ornamental adhesives found in Shosoin treasures stored since the mid-eighth century

Rikiya Nakamura*, Masakazu Naruse

*Office of the Shosoin Treasure House, Imperial Household Agency, Nara, Japan*

ARTICLE INFO

*Article history:*
Received 21 February 2015
Accepted 13 August 2015
Available online 12 September 2015

*Keywords:*
Shosoin treasures
Ornamental adhesive
Marquetry
Animal glue
Frankincense
Attenuated total reflectance
Fourier-transform infrared spectrometry
X-ray fluorescence spectrometry
X-ray diffraction
Orpiment
Nondestructive analysis

ABSTRACT

Shosoin treasures, stored in Japan continuously since the mid-eighth century, represent an important collection of beautifully decorated housing artworks made by gluing a variety of ornaments such as marquetry, metal, crystal, pearl, and amber. The ornamental adhesives used in the treasures were scientifically characterized by nondestructive methods such as attenuated total reflectance Fourier-transform infrared spectroscopy (ATR/FTIR) and X-ray analyses. FTIR spectroscopy was applied to the fragments of the following treasures: a red sandalwood armrest with marquetry decorations dedicated to Great Buddha of the Todaiji temple by Empress Komyo (701–760 AD), two *biwa* lutes with marquetry decoration, and the imperial ceremonial headdresses of Emperor Shomu (701–756 AD), Empress Komyo and Empress Koken (718–770 AD). Second-derivative transformation of the FTIR spectra identified the adhesives on the marquetry fragments as animal glue. The adhesives on the fragments of metal, crystal, pearl, and amber ornaments from the headdresses were identified as frankincense according to their IR absorbance and the second-derivative spectra. X-ray diffraction experiments and X-ray fluorescence spectrometry of the adhesives on the fragments of metal, crystal and pearl indicated that orpiment ($As_2S_3$) was mixed with the adhesives.



## 1. Research aims

The aim of this work is to perform scientific analysis of the ornamental adhesive materials found in an important Japanese collection of ancient artworks treasured in the Shosoin Treasure House since the mid-eighth century in Japan. The adhesives remained on the artworks were characterized by a noninvasive method as attenuated total reflectance Fourier-transform infrared spectrometry (ATR/FTIR). X-ray analyses were used to elucidate the inorganic mixture found in the adhesives. These results allow new information about the adhesive materials and techniques used for the ornaments in ancient Japan.

## 2. Introduction

The Shosoin is a famous treasure repository at the Todaiji temple in Nara, Japan, which was constructed in the mid-eighth century. The repository stores a variety of precious artworks such as Buddhist ritual objects, interior decorations, costumes, musical instruments, arms, stationery, ancient documents, drugs and incenses, which are known collectively as the "Shosoin Treasures." Almost all the treasures have an honorable historical origin. They have been handed down continuously since the mid-eighth century. A noteworthy character of the treasures is that they are worked out in rich materials and various excellent crafting techniques. Technically, they range over wood work, metal work, bamboo work, lacquer art, ceramics, glassware, textiles, paper and also sculpture, painting, marquetry, ivory carving (*bachiru*), mother-of-pearl and so on. The techniques and materials found in the Shosoin treasures have a rich international character because Japanese culture in the eighth century was enclosed in a cultural sphere centered on the cosmopolitan empire, namely the Chinese Tang Dynasty.

Adhesives have played a significant role for making artworks since ancient times [1]. Adhesive materials have been used as early as prehistoric times, 45,000 years ago [2]. Generally, the character of adhesive materials cannot be determined from visual observation, regardless of their state and degree of preservation; therefore, their study necessarily relies on their chemical characterization [3]. Although there is many reports about adhesive analysis in historic artefacts [4–10], the adhesive materials for ornaments such as marquetry, pearl, amber, crystal, and metal in ancient East Asia are still not understood based on scientific knowledge.

* Corresponding author. Tel.: +81 742 262811; fax: +81 742 240132.
*E-mail addresses:* rikiya.nakamura@kunaicho.go.jp (R. Nakamura), masakazu.naruse@kunaicho.go.jp (M. Naruse).

http://dx.doi.org/10.1016/j.culher.2015.08.001
1296-2074/

Analytical methods used for the characterization of adhesive and its related materials include gas chromatography (GC/MS), pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS) [11–18] and Fourier-transform infrared spectroscopy (FTIR) [19–23]. GC/MS and Py-GC/MS have been used to obtain the majority of results in the characterization of adhesive materials in art and archaeological samples by the identification of specific molecular markers. However, this approach requires taking samples from the precious artworks, which is not ideal because of the damage caused to the objects. In contrast, attenuated total reflectance FTIR (ATR/FTIR) is a very attractive method because it enables nondestructive analysis for the characterization of adhesive materials.

The present paper describes scientific analysis of the adhesive materials found in the Shosoin treasures by nondestructive methods such as ATR/FTIR and X-ray analyses. The aim of this study is to perform scientific analysis of the adhesives for making ornaments of the Shosoin treasures. Accordingly, Shosoin artworks from the eighth century (a red sandalwood armrest with marquetry decoration, two *biwa* lutes with marquetry decoration and the imperial ceremonial headdresses) were analyzed by ATR/FTIR. The adhesive materials were identified by comparison of the IR absorbance and the second-derivative spectra of the original adhesives with the references selected based on the knowledge from Japanese historic sources and the previous reports about the scientific identification of adhesive materials in the world. Furthermore, X-ray analysis identified an inorganic crystalline material mixed with the adhesives.

## 3. Materials and methods

### 3.1. Shosoin treasures analyzed in this study

The red sandalwood armrest with marquetry (Fig. 1a) belonged to Emperor Shomu and was dedicated to Great Buddha of the Todaiji temple in 756 AD. The corner edge of the armrest is decorated with marquetry of ivory, red sandalwood, boxwood, black persimmon, and green-colored antler. The remaining adhesive on the marquetry fragment shown on Fig. 1a was analyzed by ATR/FTIR for its chemical characterization. Adhesive residues in two *biwa* lutes (Fig. 1b and c) belonging to the Todaiji temple in the eighth century were analyzed as well. The *biwa* lute shown on the Fig. 1b has various flowers, leaves, and birds as decorative pattern of the marquetry made of ivory, boxwood, betel palm, black persimmon, and green-colored antler. The *biwa* lute shown on Fig. 1c has the body decorated with marquetry made of ivory and red sandalwood and describing three different kinds of lotus flower designs. The metal ornament (Fig. 1d), the hemispherical crystal fragment (Fig. 1e), the pearl fragment (Fig. 1f) and the spherical amber bead (Fig. 1g) are from the surviving parts of ornaments from imperial ceremonial headdresses belonging to Emperor Shomu, Empress Komyo and Emperor Koken. Adhesive residues are still present on the silver plates on the metal ornament, the crystal, the pearl, and the spherical amber bead fragments, which were analyzed in the present study. All these treasure fragments have been stored in the Shosoin Treasure House since the eighth century. The adhesives remained on the fragments are the original samples in the eighth century.

### 3.2. Materials

Animal glue reference from cow skin was supplied from *Amanosan bunnkaisan* research institute (Osaka, Japan). Soybean was obtained from a local supermarket (Nara, Japan). Frankincense references from *Boswellia sacra* and *Boswellia serrata* were purchased from Alba Co. (Sapporo, Japan). Frankincense from *Boswellia carteri*, and mastic from *Pistacia lentiscus* were purchased from Paret Co. (Kanagawa, Japan). Birch bark from *Betula platyphylla* was obtained from Hokkaido, Japan. Birch bark tar was prepared according to the previous study [5]. Pine resin from *Pinus* sp. was native in Nara, Japan. An orpiment reference was obtained from Osorezan (Aomori, Japan).

### 3.3. ATR/FTIR

ATR/FTIR measurements were performed on a BioRad FTIR microscope system (UMA 500) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector with a 15 × IR objective. The microscope was coupled to a BioRad FTS135 spectrometer. Interferograms were collected in side-reflectance mode on eight scans at a resolution of 8 $cm^{-1}$. ATR/FTIR spectra were collected using a Ge ATR accessory coupled to the microscope. In the Ge ATR accessory, the treasure fragments and the adhesive references were positioned in contact with the surface of the hemispherical Ge crystal that functions as the ATR element without damaging the samples. The measurements were conducted at a room temperature. Second-derivative FTIR spectra were calculated using the Savitzky–Golay algorithm with nine smoothing points after a manual correction applied to produce a flat baseline.

### 3.4. X-ray analysis

X-ray analytical measurements were performed directly on the samples using Philips X'pert Pro MRD PW2424 apparatus equipped with $CrK_{\alpha}$ radiation. X-ray diffractometry (XRD) was performed in the angular (2θ) range 10.0–90.0° at a step size of 0.10°. The scan rate was 2.4°/min, and the working voltage and current were 40 kV and 10 mA, respectively. The EDAX DSM962 detector for energy-dispersive X-ray fluorescence spectrometry (XRF) was equipped with the XRD diffractometer. Energy-dispersive XRF was measured under the following conditions: X-ray tube: Cr; working voltage: 40 kV; working current: 10 mA; working distance from spectrometer to sample: 25 mm; and measuring live time: 200 s.

## 4. Results and discussion

### 4.1. Adhesive references

Adhesive references were selected on the basis of knowledge of the specific materials known from ancient Japanese historic sources and the previous report about the adhesive analysis historically used in the world [4,5,13].

The ancient Japanese historic sources, that is, the Shosoin documents and the *Engishiki*, describe the following adhesives as used in artwork: animal glue, soybean glue, wheat and rice starch pastes, *mugiurushi* (Japanese lacquer mixed with wheat starch paste), and frankincense [8]. Animal glue is a proteinaceous glue, which is recorded as an adhesive for making artefacts such as desks, cabinets, boxes, and swords in ancient Japan. Animal glue has previously been described as structural adhesive in Shosoin wooden artworks (i.e. boxes, desks, a *wagon* zither, and a *gigaku* mask) [9]. Soybean glue, also a proteinaceous glue, is recorded as an adhesive used only in the case of pasting of sutra and ancient documents. Starch pastes mainly consist of polysaccharides, and are described as adhesives for gluing clothes and papers in furniture such as desks and folding screens. *Mugiurushi* is recorded as an adhesive for making canopy. Frankincense, also called olibanum, has been an important natural oleo-gum resin in ancient world, and is secreted by the genus *Boswellia*, which occurs only in the Horn of Africa, Arabia, and Northwestern India [24,25]. This resin includes more than 15 triterpenoid compounds such as amyrones, lupeorone, amyrins, lupeol, boswellic acids, lupeolic acid and their *O*-acetyl derivatives