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Original article

Characterization of membrane metal threads by proteomics and analysis of a 14th c. thread from an Italian textile

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ABSTRACT

Beginning in the 13th century, membrane metal threads – made out of animal skins (leather, parchment, and vellum) or membranous material (e.g., stomach, intestine) coated with metal – were the most popular variety of decorative metal threads used in European textiles. This work provides the proteomics groundwork for the identification of the species and the type of membrane used in the manufacture of a 14th century membrane gilded thread. A protocol for small sample extraction and nanoLC-Orbitrap MS/MS analysis was first tested on standards of pig peritoneum and cow intestine metal-coated with or without the presence of an egg adhesive. The proteomes of each membrane were characterized and compared by qualitative and quantitative bioinformatics; in addition to the predominant collagen proteins in each membrane type, minor tissue-specific proteins (e.g., smooth muscle proteins from intestine standards) were detected. Species-specific collagen peptides (i.e., from collagen I and collagen III) were confidently identified to determine the species of origin, regardless of the application of metal and egg-based adhesives. Likewise, the thin layer of egg adhesive was successfully characterized with the detection of egg white (ovalbumin, ovotransferrin, lysozyme) and egg yolk (vitellogenin I, II, III) proteins. When applied to the thread from a 14th century Italian textile, this comprehensive methodology resulted in the identification of seven collagen I and III peptides specific to cow, as well as other proteins suggesting that the ancient thread was made with intestine or stomach membrane without the use of an egg-based adhesive.

1. Introduction

Decorative metal threads have been extensively used for the embellishment of textiles since ancient times. Many examples of metal threads exist in artifacts of cultural importance, and even earlier references to lavish gold and silver textiles can be found in ancient texts, including a description of an ephod containing gold in the Old Testament of the Bible (Exodus 39:2–3 "They hammered out thin sheets of gold and cut strands (. . .)"). The popularity of textiles woven or embroidered with metal threads persisted, and their use is frequently associated with textiles intended to portray wealth or symbolic importance [1]. Metal threads were most often made of gold, silver, or their alloys, often gilt, with the fabrication method differing by region and changing over time [2]. Five categories describing the use of metals in textiles have been defined: I. Metal applied with adhesive to already woven fabrics, II. Metal wire or flattened strips used directly in weaving, III. Metal wire or strips wound around a fiber core, IV. Metallic surface applied to organic wrappings (cellulosic or proteinaceous) wound around a fiber core, and V. Metallic surface applied to organic strips (cellulosic or proteinaceous) without a fiber core [2–6].

Protein metal threads (Categories IV and V) were made from membranous tissues (e.g., stomach or intestinal walls of animals), although skin has also been used as a substrate [2,7]. Research at the end of the 19th century suggested that gilt membranes were made using the intestines from slaughtered animals [8]. Cow intestine was similarly used in the manufacture of gold foil, also called goldbeater's skin, during the same time period. Metal was applied to the membrane with metal leaves or by mottle gilding, using either the natural exudates of the organic membrane or an additional adhesive [7]. Reports have described the use of egg white, egg yolk, animal fat, animal and fish glues, gums, and clays as adhesives but to date, no scientific investigation has been carried to substantiate the presence and nature of the adhesives [4,7,9]. In category IV threads, also known as gilt membranes or Cyprus gold, the gilded membrane was cut into thin strips and wound around a silk or linen core [2]. No adhesive was used between the gilded organic wrapping and the

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fiber core; instead, the twist of the metal membrane thread around the core was sufficient to keep the material in place. Migration of adhesive and wrapping material into the core fiber has however been observed [5]. In category V threads the metal was applied to membrane strips and used in textiles without being wound [4].

Membrane metal threads were first used in the 11th century by Levantine traders in Cyprus [1]. Beginning in the 13th century, gilt membranes became the most common variety of metal threads used in European textiles, especially those from Italy and Spain, as well as Western Asia because they were flexible, lightweight, and inexpensive [7]. Substantial focus has been given to identifying the metals used in metal threads, as studies show that the composition of the metal and gold/silver ratios are suggestive of geographic origin of the metal thread [6,7,10]. Recently, a range of electron microscopy techniques and micro-Raman spectroscopy have been used to characterize cross-sections of metal threads revealing details of the production technology through study of the 3D texture [11]. Conversely, little attention has been given to identifying the membrane type or animal species used in organic metal threads, although the elucidation of this information would provide valuable insight into the origin, production technique, and use of membrane metal threads in the medieval period [1]. Identification of the membrane portion of the substrate poses difficulty, especially when a textile is in a deteriorated state. Using morphology on the microscopic scale, differences between leather, membranous material, parchment, and vellum have been made [1,2]; however, the appearance of the substrate can be drastically altered from its original state because of decomposition, embrittlement, wear, and treatment damage, making visual identification indefinite and oftentimes impossible. In contrast to morphological identification, DNA amplification and molecular biology techniques have been used to identify the animal species in organic metal threads found in textiles from the 11–15th centuries [9]. Unfortunately, this study could only narrow down the identification to a few candidate species. Here, we have adopted a bottom-up proteomics approach to analyze a 14th c. membrane thread: the entire membrane sample is characterized through a single extraction and digestion of the whole extract, including the membrane proteins and other binding proteins if present. The complex mixture is separated by liquid chromatography before analysis by an Orbitrap Velos mass spectrometer and the data obtained are searched against a public database. In the absence of historical information on the membrane's animal origin, any species can be targeted through a proteomics database search.

2. Research aims

To resolve the identification issue of the organic substrate of a metal thread several centuries old, a proteomics approach was devised. Proteomics has been used successfully to identify binders [12] and collagen-based substrates such as parchment [13], but has never been used to characterize membrane metal threads. The aim of this project is to show that a complex organic substrate, composed of a membrane base and protein binders, can be comprehensively characterized, including the type and species of the membrane and presence of proteinaceous adhesives. To test the applicability of proteomics to ancient samples, two series of standards (Table 1) were prepared at the University of Applied Arts Vienna (Austria) from the abdominal membrane of pig and from intestine of cow, then subjected to different treatments (heat fixation, egg white, or egg yolk used as adhesives for the metal coating). Pig and cow were chosen as species for their commonality and easy availability, and as probable source obtained in the past from butchered animals. The proteome of each membrane was determined by extracting proteins in samples of less than one milligram, thus revealing tissue-specific proteins, while peptides specific to the membrane species and the egg adhesive were characterized in untreated and treated samples. Finally, the developed protocol was applied to a membrane metal thread from a 14th century Italian textile (Fig. 1), thought to be made from an animal's internal organ and not skin.

Table 1
Reference standards.

Reference	Membrane	Adhesive	Fixation	Metal leaf type
Pig untreated	Peritoneum	None	None	None
Pig gilt	Peritoneum	None	None	Gilt silver
Pig gilt heat	Peritoneum	None	Heat	Gilt silver
Pig gilt egg white	Peritoneum	Egg white	None	Gilt silver
Pig gilt egg yolk	Peritoneum	Egg yolk	None	Gilt silver
Cow untreated	Gut	None	None	None
Cow silver	Gut	None	None	Silver
Cow silver heat	Gut	None	Heat	Silver
Cow silver egg white	Gut	Egg white	None	Silver

Fig. 1. 14th century Italian textile (#21714-1) from the History Museum in Graz, Austria, ©Universalmuseum Joanneum, Museum für Geschichte, Kulturhistorische Sammlung/Institute of Conservation, University of Applied Arts Vienna/Elisabeth Delvai 2017. The arrow points to where the thread was sampled. In the bottom right, the image of the thread was acquired with HIROX KH-8700 3D digital microscope (Hirox-USA, Inc., NJ), courtesy of Thomas Lam (Smithsonian's Museum Conservation Institute). Software: PowerPoint 2013.

3. Materials and methods

3.1. Standards

The gilt membrane reference standards were prepared at the Universität für angewandte Kunst (University of Applied Arts Vienna, Austria) based on what is known of traditional protocols [14,15]. Pig peritoneum, which is the membrane sack containing the abdominal organs, was obtained from the Veterinary University of Vienna (Vienna, Austria). Cattle gut was obtained from a local butcher. The fat was scraped off the membrane and the membrane washed and rinsed, then stretched and pinned. Gilt silver leaves or silver leaves were immediately applied on the damp membrane using egg yolk, egg white, or no adhesive (Fig. S1). The standards were allowed to dry overnight. Select standards were subjected to heat fixation with a heated spatula at approximately 80 °C. Reference standards are listed in Table 1.

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