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Case study

Revealing the binding medium of a Roman Egyptian painted mummy shroud

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A R T I C L E I N F O

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A B S T R A C T

Ancient Egyptian painted artworks are usually understudied from an analytical point of view, due to their extremely fragile nature. Attention typically focuses on pigments since identification is possible with non-invasive techniques, while limited information is available in the literature regarding the organic binding media. Here successful determination of the binder of a Roman Egyptian painted mummy shroud (2nd–3rd century A.D.) achieved through the application of enzymatic digestion followed by matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) is reported. The high specificity and sensitivity of this analytical strategy not only allowed the identification of the binding medium as a mixture of two different plant gums but also allowed the discrimination of the different species sources, even though the organic material was present in very small amounts and subject to degradation. The results of this study represent the first analytical identification of the earliest use of locust bean gum as a paint binder material as well as the use of gum arabic from an *Acacia* species different from the well-known *Acacia senegal*. The precise identification of the organic binder is a great step forward in the understanding of the painting materials and techniques used in Roman Egypt, of which little is known. The result of this research opens new avenues of art historical and conservation investigation into the specific plant sources and types selected by artists and it has implications for future conservation treatment options.

1. Introduction and research aim

Roman Egyptian funerary art combined two different artistic traditions: the Egyptian and the Hellenistic Greek. The Egyptian concept of the afterlife was translated into an artistic representation of the deceased that showed a connection with the life and social roles of the individual. This idea might have contributed to the funerary tradition during the Ptolemaic (323–30 B.C.) and Roman periods (30 B.C.–A.D. 641) to represent the dead with "everyday" details such as jewellery and clothing [1]. The object under consideration is a mummy shroud painted on linen and dating to the late 2nd–3rd century A.D. (The Metropolitan Museum of Art, X.390) (Fig. 1). The painting appears to be a fragment of a larger composition representing the portrait of a woman. The picture depicts a view of her hands: she wears an abundance of jewellery, including a ring on every finger of her left hand. The snake-ring on her right hand finds parallels in actual gold rings, which are usually dated to the first century A.D., but this shroud is probably later [2]. The uniqueness of this fragment is that painted textiles do not normally survive at any period and, notably, the shroud was never subjected to conservation treatments, thus ensuring that the original paint is not contaminated with contemporary materials.

Several natural products with adhesive properties could have been used as paint binders in ancient Egypt. Lucas [3] stated that on examination it is clear that ancient Egyptian painted artifacts are tempera painting, made with a water soluble binding medium such as protein- and polysaccharide-based materials, and not oil, excluding the group of artworks painted with a wax medium. Among the available materials, animal glue, egg and plant gums are the most likely organic binders used at that time. This assumption finds support through both observation by conservators of the sensitivity of the paints to water, and more recently by only a few analytical investigation of ancient Egyptian artifacts as reported below. To our knowledge, a surprisingly limited number of analytical studies of binding media have been conducted so far on these remarkable artifacts. In the literature, besides the investigation of the artist's pigments, only a few papers report the precise identification of the possible binding media of Egyptian paintings on linen, walls and wood, as reported below.

Animal glue is considered to be the most commonly used binder from a very early period, both in ground layers and in paints [3]. Glue was prepared by boiling animal bones, hides and connective tissues. The main sources of glue in ancient Egypt are not known,

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Fig. 1. Image of Fragment of a painted mummy shroud, The Metropolitan Museum of Art, Museum Accession (Accession Number: X.390) with the two sample sites (S1 and S2) indicated.

but could have included various animals and fish [4]. Protein-based glue has been identified as the medium of a Fayum-region mummy portrait from the 3rd century A.D. by simple solubility testing and biological staining [5]. However, these techniques are not able to discriminate among the different proteinaceous materials. Thin-layer chromatography (TLC) and gas chromatography-mass spectrometry (GC-MS) allowed the identification of animal glue in paint on a wooden Roman Egyptian sarcophagus [6] and GC-MS was used to analyze the organic binder of a Roman Egyptian mummy cartonnage. The presence of hydroxyproline among the amino acids detected was an indicator for the presence of collagen, thus suggesting that a gelatin-binding medium was used [7]. The same technique allowed the identification of animal glue as the binder used on a fabric painting from the 3rd–4th century A.D. [8]. A number of painted wooden artifacts from the Museum of Fine Arts, Boston (MFA) was investigated by high performance liquid chromatography (HPLC). Amino acid patterns were very close to those of collagen in some samples while in others, some other source or sources of amino acids was indicated and the profile could not be correlated to any reference binder [4]. In a recent paper, three Roman Egyptian panels from the collections of the J. Paul Getty Museum dating to A.D. 180–200 were found to contain animal glue in the ground layers by using a combination of enzyme-linked immunosorbent assay (ELISA) and GC-MS [9]. For the first time, the animal species used to make the glue was identified as cow (*Bos taurus*) by using nano-liquid chromatography-electrospray ionization-tandem MS (nanoLC-ESI-MS/MS).

Eggs from geese or ducks were available in Dynastic Egypt, while chicken eggs (*Gallus gallus*) were not common until classical times [3]. It has been stated that egg was a common binder in Roman Egyptian period mummy-portraits [10]. However, there are only two reliable identifications of egg used as binder at that time. The first is from a mummy portrait of the 4th century A.D. in the collection of the Petrie Museum. Egg yolk was identified by GC-MS analysis that showed a pattern of the lipid fraction characteristic of the non-drying oil in egg yolk [11]. The second is from a number of cartonnage fragments from the collections of the Petrie Museum at University College London that were examined both by ELISA and by GC-MS for the identification of the binding media. Results showed the presence of egg white, animal glue and plant gum, individually used or mixed together [12].

Plant gums are naturally occurring polysaccharides that are exuded or extracted from various sources as seeds, trees, shrubs and seaweed [13]. The ease of extracting and preparing plant gums, together with their sticky consistency, would have made them suitable for use as an adhesive and binding medium in ancient times. Chromatographic techniques enabled the identification of *Acacia* gum in a wall painting from the Nineteenth Dynasty tomb of Nefertari in Thebes [14,15], gum tragacanth was identified in a white filling material from a Twenty-first-Dynasty sarcophagus in Antwerp [16] and an unidentified gum was used as the binder in one Fayum-region mummy portrait [17]. Analyses of paint samples from a number of painted wooden objects and some stone objects in the Museum of Fine Arts, Boston showed the presence of gums as a common binder and, despite the limitations of GC-MS analysis in analyzing monosaccharides, the use of more gums and different *Acacia* species was suggested [18]. The same author identified possibly tragacanth gum and another polysaccharide as an additive by Fourier transform infrared spectroscopy (FTIR) and GC-MS in the red paint of a sarcophagus from the Eighteenth Dynasty [19]. It is possible to conclude that only a few analyses of the binding media have been performed on ancient Egyptian objects and, in most cases, results are not species specific and it is not possible to be certain of the nature of the binder (e.g. plant species, etc.).

The Roman Egyptian painted mummy shroud studied in this research has been described up to now as painted in tempera, but no analysis had been previously performed to identify specifically the nature of the binder (protein or polysaccharide-based). The aim of this study is to reveal the painting technique of this painted shroud in order to possibly shed light on and scientifically prove the nature of the organic binders used at that time. This paper presents a successful attempt to determine the nature and species of the binding media through the use of MALDI MS after enzymatic digestion of the sample [20,21]. This analytical strategy allowed us to obtain interesting information on the painting technique despite the age and limited amount of sample available. The knowledge of the painting technique of this unique and fragile art object is of high relevance both in terms of a historic-artistic point of view and for planning future conservation treatments.

2. Material and methods

2.1. Chemicals and samples

Exo-β-1,3-galactanase (EC 3.2.1.145) and endo-1,4-β-mannanases (EC 3.2.1.78) were purchased from NZYtech. Maltotetraose, maltohexaose and maltoheptaose were obtained by Carbosynth. Standard gum arabic from *A. senegal* in powder form was obtained from Zecchi (Florence, Italy). Two samples from the shroud fragment, both from a white paint area, were analyzed; the samples were not weighed, but estimated to be a few tens of micrograms. All other chemicals were purchased from Sigma Aldrich.

2.2. Apparatus

2.2.1. Samples

Two samples, named S1 and S2, taken from two different areas of white paint, weighed approximately one hundred micrograms each. The sampling spots are reported in Fig. 1. It is important to stress that no conservation treatment occurred on this artwork, so