

Characterization of two vases from Centuripe

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Abstract – This study presents the analysis of two Centuripe lekanides currently held in two northern Italian museum collections, both lacking a documented archaeological context. The investigation, planned in the frame of the exhibition “Color and Mystery” at the Archaeological Museum of Milan, aimed to verify the authenticity of the artifacts through the integration of non-invasive diagnostic techniques, particularly X-ray fluorescence (XRF) and multispectral imaging. XRF analysis enabled the identification of chemical elements in the decorative pigments, allowing hypotheses on the nature of some materials, such as Egyptian blue, red and yellow ochre, lead white and gypsum, as well as revealing traces of restoration and possible modern retouching. Digital microscope observations provided enhanced visualization of pigment distribution and surface details. The combined use of these techniques allowed for a more in-depth characterization of the painted surfaces, contributing to the historical and artistic understanding of the artifacts and providing useful data for broader reflections on authenticity and Centuripe ceramic production.

KEYWORDS: Centuripe lekanis; XRF; multispectral imaging; non-destructive analysis; cultural heritage diagnostics; archaeometry

I. INTRODUCTION

The aim of this study is the pigment characterization of two Centuripe-style vases through the combined use of XRF analysis and multispectral imaging.

The first vase is part of the collection of the Civic Archaeological Museum of Milan, while the second - complete with its lid - belongs to the Civic Archaeological Museum of Legnano and was temporarily exhibited at the museum of Milan from January 16 to June 8, 2025.

The investigations were initiated at the request of the Milan Archaeological Museum, with the main goal of verifying the authenticity of the artifacts. Both objects are

Centuripe lekanides donated to the museums from private collections, lacking any known archaeological context, which made necessary a thorough diagnostic investigation.

For this reason, the pigments were analysed using multiple techniques, to achieve the most comprehensive characterization possible, valuable for the historical, archaeological and artistic interpretation of the two items.

II. CENTURIFE LEKANIDES

The expression “Centuripe ware” indicates a group of figured and usually oversized vases, which were manufactured in the ancient homonymous city of Sicily between 250 and 100 BC. The “Centuripe vases”, which were intended for burial, are decorated with polychrome scenes mostly composed of female figures on a pink or black background and usually have a relief gilded secondary decoration of baroque taste. Style, technique and palette indicate that the scenes were often painted by professional painters and not by ceramists. The figures, in fact, are not simple coloured drawings, but often have shadings and highlighting effects, which give them a plastic effect typical of Hellenistic painting. Consequently, the Centuripe ware represents a direct testimony of the Hellenistic panel and wall painting.

The pigments are unfired and therefore the painted figures tend to fade away. This has led, since the beginning of the last century, to frequent cases of forgeries, often carried out by repainting on the same ancient vases polychrome scenes imitating the ancient ones. Consequently, a thorough diagnostic investigation on pigments of polychrome vases not coming from regular archaeological excavation is essential.

The two vases examined belong to the lekanis form, a container characterised by a large basin, a distinct foot, ribbon handles and a truncated cone-shaped lid.

Both vases feature separately moulded and applied plastic decoration consisting of acanthus leaves forming a corolla from which the lekanis seems to blossom. A sinuous raceme filled with small flowers winds its way around the

vase: in the centre is the head of Medusa with wings on her head and snakes knotted around her neck. In the Milan vase, the branch is decorated with amorini flying around it. The colour scheme of the two vases is different: blue is the colour chosen for the background of the Milan vase, together with red in the lower part. The entire composition was embellished with gold leaf covering the entire branch, Medusa's hair and the astragalus motif. The plant motifs expressed the hope of rebirth after death in a blissful afterlife, while the presence of Medusa had a positive and protective function.

The Legnano vase has a lid, which is not preserved in the Milan specimen, decorated along the rim with an astragal motif and below with five lion protomes, imitating an architectural frieze. The lid is painted with a scene, on a pink background, showing a girl with her back turned, dipping her hand into a louterion (a basin for lustral baths).

The same gesture is performed by another woman standing in front of her with her head in profile, holding a tympanon in her other arm. Both are wearing long blue dresses and white cloaks, with their hair gathered and encircled by a crown of ivy. A third woman wrapped in a cloak with a badly damaged three-quarter profile also participates in the scene.

The meaning of the depiction can be traced back to wedding preparation rites that involved consecration to Dionysus.

The vase is placed on a high support, like the lekanis in Milan, and ends with a decorative pinnacle

Both lekanides exhibit strongly irregular shapes and plastic decorations, features that influenced the measurement approach. Several points with clearly visible and easily accessible pigments were selected on both vessels and the lid for analysis. Selection criteria considered areas with distinct colour variations or decorative features, as well as regions sufficiently preserved to allow reliable measurements. However, the irregular geometry of the objects often made it difficult to maintain an optimal distance, making it necessary, in some cases, to subsequently normalize the spectra.

For the lekanis from the Civic Archeological Museum of Milan, six measurement points were identified (fig 1): one on the bare clay, one on a red area, two on red/gold zones, one on white and one on blue.

On the lekanis from the Civic Archeological Museum of Legnano, five points were analysed (fig. 2): one on red, one on yellow, one on brown zones, one on white and one on the bare clay. Here too the comparison with the clay spectrum allowed for clearer identification of pigment signals.

Finally, for the Legnano vessel's lid, eight points were analysed (fig. 3): one on the clay, two on pink areas (one flash-coloured and one bright), two on white, one on blue, one on brown and one on dark brown.



Fig. 1. Centuripe lekanis from the Civic Archaeological Museum of Milan, with measurement points marked in green



Fig. 2. Centuripe lekanis from the Civic Archaeological Museum of Legnano, with measurement points marked in green



Fig. 3. Lid of the Centuripe lekanis from the Civic Archaeological Museum of Legnano, with measurement points marked in green

III. METHODS

A. XRF Analysis

X-Ray Fluorescence is a widely used elemental analysis

technique in cultural heritage studies, valued for being non-invasive and enabling in situ measurements without moving or risking damages to the artifact. The principle is based on the emission of secondary X-rays from atoms in a material when excited by a primary X-ray beam: an electron from an inner shell is ejected and replaced by an electron from a higher energy level, releasing characteristic photons whose energies are specific to each chemical element, allowing their identification.

In this study, a portable energy-dispersive XRF (ED-XRF) spectrometer was used, which requires no sample preparation and allows fast data acquisition. These features are advantageous for diagnostics on artworks and historical artifacts where preserving the physical integrity is essential.

The qualitative analysis is based on the interpretation of the XRF spectrum, where each peak corresponds to the emission of an element present in the sample. However, the technique has intrinsic limitations related to the sensitivity of the detectors: it is not possible to detect light elements, which prevents the identification of organic material or compounds containing low atomic number elements. Furthermore, the analysis is surface-sensitive, with a penetration depth of the order of tens of micrometres. For these reasons, it is essential to integrate the information obtained from XRF with data from other analytical methods to achieve a comprehensive understanding of the sample.

The instrument employed is the FUXYA2020 spectrometer, equipped with a MINI-X2 X-ray tube (Amptek) with a rhodium anode operating in transmission mode, and an XGL-SPCM-DANTE-25 detector (XGLAB Bruker Nano Analytics, Milan, Italy).

Measurement conditions were set at 40 kV and 0.06 mA, with an irradiated area of approximately 8 mm² on the object's surface. Acquisition times were 160 seconds for the Milano Museum vase, 120 seconds for the Legnano museum vase and 60 seconds for the Legnano vase lid.

B. Digital Microscopy

To complement the elemental data, a Dino Lite digital microscope with a 5Mpx resolution was employed. Images were captured using the dedicated DinoCapture software at magnifications of 50x and 200x.

C. Visible Induced Luminescence

Visible Induced Luminescence (VIL) is a non-invasive imaging technique used primarily in art and archaeology to detect and map the presence of luminescent materials, such as Egyptian blue, by exciting them with visible light and capturing their infrared emission. The VIL examination was carried out using a modified Nikon D70 digital camera for infrared, equipped with a 950 nm IR cut filter and a red-light source (Visible Red Light. Red Source) at 630 nm with 6 watts of emission, featuring high spectral purity, from Madatec s.r.l.. While VIL provides a clear visual indication of Egyptian blue through the characteristic bright luminescence halo, it cannot always

distinguish between Egyptian blue and other luminescent compounds; therefore, the identification was confirmed through hyperspectral imaging, spectral comparison with the Kremer pigment reference library, and further supported by the detection of copper in XRF analysis. In addition to the first multispectral mapping (VIL), a second hyperspectral mapping was carried out for an initial verification of the blue pigment composition compared to the Kremer pigment archive. Hyperspectral imaging with a Specim IQ camera confirmed these findings and provided detailed spatial and spectral data (400–1000 nm, 204 bands). The hyperspectral imaging confirmed the initial findings from the VIL mapping and enabled the collection of both spatial and spectral data through a sequence of hundreds of images in the visible (400–750 nm) and near-infrared (750–1000 nm) regions. Each pixel in the hyperspectral image is associated with a reflectance spectrum.

IV. RESULTS

The characteristic elements of the pigments were identified by comparing each measurement with the bare clay spectrum. This comparison allowed us to hypothesize the pigments used and evaluate consistency with published literature. All the pigments detected were compatible with the historical period, except for one measuring point showing not negligible zinc content. It is worth noting that zinc, an element associated with modern pigments, has been detected near a reassembled break, clearly indicating a later restoration intervention.

More in detail, for the vase from Milan Museum (measurements points listed in section II and shown in Fig. 1), the analysis of the white area suggests the presence of a calcium-based pigment, such as calcite or gypsum, while the absence of lead excludes the use of lead white. In the gilded areas there is a clear superimposition of gold over the red (fig. 4); indeed, the spectra, supported by microscopic images, suggest that the red pigment is iron based, coherently with the use of red bole for the preparatory layer for the application of gold leaf [1],[2]. It should be stressed that the identification of the stratigraphy (red pigment beneath the gold) relies on digital microscopy observations; this visual evidence is consistent with the archaeological-artistic context and provides the basis to correctly interpret the spectroscopic data. As for the blue pigment, the presence of copper is consistent with the use of Egyptian blue; this hypothesis is confirmed by multispectral imaging. Reds, yellows, and browns: iron oxides, possibly diluted with white, with varying percentages of potassium oxide or manganese oxide, which alter the colour of the pigment.

These last pigments are also present on the Legnano museum vase (measurements points listed in section II and shown in Fig.2). As for its preparation layer, a significant presence of lead was found overall, possibly due to lead white [3], which may have been used as a preparatory

ground or to lighten other colours. The red and yellow areas, showing signals of both iron and lead, were attributed respectively to red and yellow ochres. The brown/purple areas showed no significant peaks, suggesting the use of organic pigments, which cannot be detected by XRF.

Concerning the lid of the Legnano vase (measurement points listed in section II and shown in Fig. 3), the results confirm the same materials as the corresponding vase, that is a widespread presence of lead, suggesting once again the use of lead white as a preparatory layer. In the white and pale pink areas titanium and potassium were also detected: the former may point to modern retouching, while the latter could be related to a restoration binder. The white pigment shows calcium and sulphur, compatible with gypsum (calcite sulphate). The blue pigment appears stratified over the white layer, as also documented by microscopic images, and is characterised by copper,



Fig. 4. Red and gold pigments on the rim of the vase from the Milan Museum. 50x magnification.

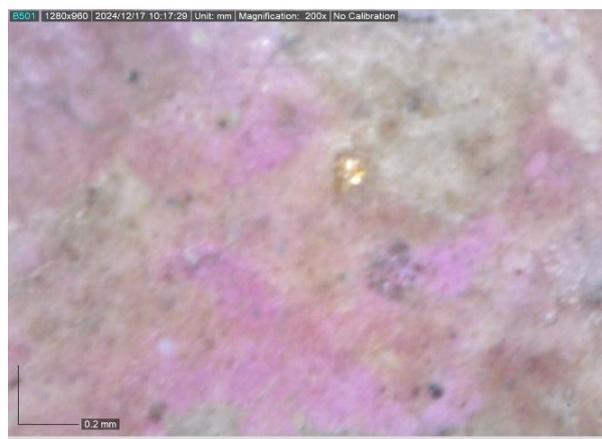


Fig. 5. Pigments from the pink area of the vase lid from the Legnano museum, with gold pigments. 200x magnification.

consistent with Egyptian blue. The bright pink area was likely created using organic pigments [1],[2],[3],[4], which are not detectable by XRF. Iron was not detected in the bright pink area; however, it was found in the brown and dark brown tones, suggesting the use of iron oxides mixed in varying proportions with manganese oxide.

Microscopic observation further revealed the presence of a few fragments of gold leaf on the lid. These are not part of the object's original decoration and are more likely traces of gold leaf application carried out in the workshop during production or restoration of other artifacts (fig. 5).

The Visible Induced Luminescence (VIL) analysis of the Lekanis vase lid from the Archaeological Museum of Legnano revealed strong infrared luminescence in the blue-painted garments of the three female figures, confirming the use of Egyptian blue. This pigment was also found in decorative floral elements and possibly in skin tones, likely to create shading or reflections. Microscopy (50x) confirmed a consistent, though limited, use of Egyptian blue mixed with a white pigment, applied with fine brushstrokes for a translucent, delicate effect. The Egyptian blue also appears in the lion-head border and shading effects. In contrast, the bowl portion of the same vase showed the use of this pigment only on the handle.

A comparison with the Lekanis vase from the Archaeological Museum of Milan showed a much thicker application of Egyptian blue in the background and in decorative plumage.

V. CONCLUSIONS

The investigation campaign presented in this work and related to the temporary exhibition “Color and Mystery” held at the Archaeological Museum of Milan from January 16 to June 8, 2025, confirms the authenticity of the two Centuripe Lekanis. The two vases were painted after firing, using tempera-like pigments in pink, white, red, yellow, blue, and green. These colours were applied over a white slip, giving them a pastel, fresco-like appearance. By combining imaging techniques, digital microscopy, and XRF, this approach offers museums a practical and powerful tool for authenticating and characterizing ancient polychrome ceramics.

VI. ACKNOWLEDGEMENTS

The authors would like to thank the “Civico Museo Archeologico di Milano” and the “Museo Civico Archeologico di Legnano Guido Sutermeister”; in particular, we are grateful to dr. Anna Provenzali (head conservator at Milan Archaeological Museum), Anna Maria Volonté (conservator at Legnano Archaeological Museum) and Sara Loreto (conservator at Milan Archaeological Museum) who provided valuable suggestions and insights that contributed to the development of this work.

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