

Article



# Seventeenth-Century *Barniz de Pasto* Objects from the Collection of the Hispanic Society Museum & Library: Materiality and Technology

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Abstract: The Hispanic Society Museum & Library (HSML) holds a collection of nine viceregal barniz de Pasto objects, made by Indigenous artisans in the 17th and 18th centuries. Designed to imitate Asian lacquers and intended for European aesthetic tastes, barniz de Pasto is an example of Indigenous technique and knowledge that has survived to the present day. An in-depth analysis of five of these barniz de Pasto objects, dated to the first half and last quarter of the 17th century based on their iconography, was carried out through a combination of non-invasive and micro-invasive techniques, including portable X-ray fluorescence (pXRF) spectroscopy to investigate the possible presence of inorganic pigments, and fiber-optics reflectance spectroscopy (FORS) and reflectance imaging spectroscopy (RIS) to provide molecular information on colorants and their distributions across the objects. Dyes and pigments were also identified using Raman spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and liquid chromatography/mass spectrometry (LC/MS). The nature of the resin was determined by FTIR and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), while the decoration stratigraphy and composition were analyzed by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). This paper confirms the use of mopa mopa, the resin used in the barniz de Pasto technique, in two objects not previously analyzed, and identifies indigo, insect-based red, calomel, lead white, and an unknown flavonol-based yellow dye, and challenges the use of calomel as a temporal marker for these works. Taken together, these results expand our understanding of the material use and explorations undertaken by artists during this time period to create such elaborate and enduring objects.

**Keywords:** *barniz de Pasto; Elaeagia pastoensis; mopa mopa;* lacquer; Colombia; viceregal; Indigenous art; pXRF; mass spectrometry; reflectance imaging spectroscopy

# 1. Introduction

In the 17th and 18th centuries, artisans working in present-day Pasto, Colombia, using Indigenous techniques became recognized for creating lacquered objects known as *barniz de Pasto* [1,2]. These decorated wooden pieces were intended to mimic Asian lacquers, while incorporating both Indigenous and European decorative elements and forms [3], and they were destined for local grandees and members of the clergy [4]. The practice continues today, and in 2020 was placed on UNESCO's List of Intangible Cultural Heritage in Need of Urgent Safeguarding. The present study includes a group of five *barniz de Pasto* objects



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). from the Hispanic Society Museum & Library (HSML) collection in New York. Represented in this group of objects are two types of decorative techniques that emerged in the 17th century: *matte barniz*, which is created by using pigment-saturated resin to achieve a matte appearance, and *barniz brillante*, which involves layering colored, translucent resin sheets over silver leaf to create a glittering effect [3,5].

The resin, known as *mopa mopa*, is produced by harvesting small resinous leaf buds called stipules from *Elaeagia pastoensis*, a tree that grows in the Andean rainforest. A thorough description and analytical study of *E. pastoensis* and *E. utilis*, the other known resin-producing species of *Elaeagia*, is reported by Newman and coauthors [6,7]. While the term *mopa mopa* is generally used to refer to *Elaeagia* resin, in this article it is used exclusively to indicate *E. pastoensis*. The traditional preparation process required purifying the resin from plant debris by boiling it in water and chewing it to improve its elastic and plastic properties [8]. Once purified, the resin was colored by mixing in natural pigments and dyes, and was then stretched into very thin sheets which were layered over the surface of an object with silver leaf and/or inlay to create complex and sophisticated designs. The resin created a lustrous finish similar to that of Asian lacquer, and when layered with silver leaf sought to imitate Japanese *makie* lacquer, which was sprinkled with gold powder [9].

Recent papers have been welcome additions to the art historical evaluation of *barniz de Pasto* objects [10–16], and several scientific studies have been published following the research undertaken by Burgio and coauthors [17]. Principal amongst these was a 2020 Special Issue of Anales del Museo de America following a study day focused on barniz de Pasto objects in Spanish collections and at the Victoria and Albert Museum in London. In this issue, Romero and coauthors presented material analysis results of five *barniz de* Pasto-decorated boxes in Spanish collections [18]. The authors confirmed the presence of a ground layer of resin plus lead white on a *matte barniz* box, where the black background color was made of indigo mixed with other compounds; in two boxes decorated with the brillante technique, the authors discovered that the silver leaf was sealed and protected by a transparent finishing layer of oil-rich resin, possibly chia oil [18]. Similar results were found by Sanchez Ledesma [19] on five microsamples taken from a large *barniz de* Pasto casket in the collection of the Museo de America. Using high-performance liquid chromatography with diode-array detection (HPLC-DAD) and Fourier-transform infrared (FTIR) spectroscopy, Sanchez Ledesma confirmed that the resin was *E. pastoensis*. Calomel (mercury(I) chloride), also known as mercury white, was the matte white pigment identified using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS), and indigo was detected by HPLC-DAD in the greens and blacks. The organic vellow and red components remained unidentified [19].

Separately, Crippa and coauthors [20] identified calomel using a portable Raman spectrometer in two works of art at the Fitzwilliam Museum in Cambridge—an English Missal (MS34, ca. 1470) and a portrait by Isaac Oliver from England (FM 3868, 1595–1600)—opening the possibility of calomel being used as pigment more widely in works of art, and predating its occurrence in *barniz de Pasto* objects. In Gliozzo's article on mercury-based red and white pigments [21], the author posits the possibility that calomel was sourced as a degradation byproduct of cinnabar, widely used and found in the Viceroyalty of Peru before the 17th century.

The current work builds on the study of a *barniz brillante* gourd vase, also in the HSML collection, which was the subject of a comprehensive analytical study aiming to identify all the materials involved in its decoration to investigate the manufacturing technique, as well as date the object [22]. The study confirmed the resin as *E. pastoensis* and identified the use of indigotin-based dye for black and blue colors, cochineal for red, calomel for white, and a mixture of indigotin-based dye and an unidentified yellow colorant for green. The complex stratigraphy included one or two layers of silver leaf, each underneath a layer of tinted resin, creating a typical iridescent effect. The gourd body was radiocarbon-dated, supporting an initial iconographical study that had attributed a circa 1625 date to the vase. Using a similar approach and array of analytical techniques, this study examines five additional

*barniz de Pasto* objects in the HSML collection dated by iconography to the 17th century. The current study aimed to confirm *E. pastoensis* resin as the binder, identify pigments and colorants and look for evidence of material and technological changes throughout the 17th century, and compare pigments and colorants used for *matte barniz* and *barniz brillante*. This work adds valuable insights into the technology of such culturally and artistically important decorative processes and generates new questions about the yellow dyes used in the production of colored resins and the use of pigments as chronological markers in these works.

#### 2. Materials and Methods

# 2.1. The Objects

The following *barniz de Pasto* objects were included in the analytical study: *Casket* (LS2361, 1625–1650), *Portable Writing Desk* or *Escritorio* (LS2446, ca. 1643), *Tabletop* (LS2447, ca. 1643), *Coffer* (LS2067, ca. 1650), and *Portable Writing Desk* or *Escritorio* (LS2000, ca. 1684) (Figure 1 and Table S1, Supplementary Material S1).



**Figure 1.** Images of the five *barniz de Pasto* objects studied for this research. (**A**) *Casket*, LS2361. (**B**) *Coffer*, LS2067. (**C**) *Tabletop*, LS2447. (**D**) *Writing desk* (*Escritorio*), LS2446. (**E**) *Portable writing desk* (*Escritorio*), LS2000. Courtesy of The Hispanic Society of America. (Details about the objects are reported in Supplementary Material S1, Table S1.)

The five artworks were divided into two groups based on their form, relative size, and dating. The first group includes the *Casket* (LS2361) and the *Coffer* (LS2067) (Figure 1A,B), similar in terms of structure, size, and date, despite having been made with different decorative techniques. They show the same basic wooden structure with arched interior lid supports and a domed lid. Except for the bottom, which is unfinished, all surfaces, inside and outside, are covered with resin (Figure 2). Within the reddish translucent band that frames each of the exterior panels of the *Casket* (LS2361), larger figures of a cherub, a Spanish lady and a man on horseback, and animals—deer, lions, dogs—are surrounded by flora and fauna on a black background, and contain the following limited palette: several



shades of ocher, pink, pale and dark blue, light green, olive green, and gray. This technique inlays different colored lacquered shapes to create the design or, in the case of the grayish hare, cuts away resin to reveal black detailing (Figure 3).

Figure 2. Casket, LS2361. The image shows casket structure and extent of decorated surfaces.



Figure 3. Detail from proper left side of Casket, LS2361, showing pale blue-gray hare.

The *Coffer* (LS2067), a *brillante* box, retains its original silver hardware and, like the other objects examined here, has all visible surfaces covered with resin, except for the bottom. The imagery harks back to medieval books of hours with a unicorn and fantastical sea creatures (Figure 4) rendered in colored resin layered over silver leaf, and details picked out in saturated white and black resin. The more limited palette of this box has a dark background with designs that are colored orange, red, and cream, with quite unusual *matte barniz* hand motifs which interestingly have been noted before only in *barniz de Pasto* flasks belonging to the Victoria and Albert Museum (V&A) [23]. Most of the finer details on this box are obscured by the oxidization of the silver leaf (Figure 5).



**Figure 4.** Back of *Casket*, LS2067, showing a unicorn at the center surrounded by other fantastical creatures and flora.



Figure 5. Example of silver oxidation on upper body and head of a 'snailman'. Coffer, LS2067.

The second group of objects consists of two *Escritorios*, one decorated with the *matte barniz* technique (LS2446) and the other decorated with *barniz brillante* (LS2000) (Figure 1D,E). The *matte barniz Escritorio* (LS2446) is a fall-front writing box with three drawers decorated with a technique similar to that of the *Casket* (LS2361), with inlaid colored resin making up the design. The *Escritorio* has a black and dark-red background with decorative details in blue, green, yellow, red, and black. The inscription just above the drawers identifies the original owner: "*CAPSULA H(A)EC EST MARTINI DE TOLOSA*" (Figure 6), which means "this box belongs to Martin de Tolosa". The religious imagery on the inside of the lid contains clues about his occupation: archival research has identified Martin de Tolosa as chief sacristan and chapel master at the Cathedral of Popayán from at

least 1630 to 1643. Consequently, the box was given a ca. 1643 date. Amongst the foliate decorations, both European and South American animals are illustrated. These include an *amaruca*, a dragon from Andean mythology on the back panel, and figures, including possibly a portrait of the box's owner, Martin de Tolosa [24].



Figure 6. Detail showing owner's inscription on Escritorio, LS2446.

The *matte barniz Tabletop* (LS2447) (Figure 1C) is included with this group because it was acquired with the *matte barniz Escritorio* (LS2446) and is assumed to have been part of the *Escritorio*'s table stand. In fact, the two objects share a similar color palette, particularly in the wide exterior decorative border that lies between two red framing bands with repeating flower and scroll details. The reverse of the *Tabletop* is unfinished and shows evidence of missing trestle legs, which would be consistent with the ca. 1643 date. However, the *Tabletop* contains the least amount of obviously Indigenous imagery of all the HSML's *barniz de Pasto* pieces. The central design (Figure 7) has a more vibrant palette and includes blue and white decorations. The central cartouche, oriented sideways, has a lion at the center with two griffins at the sides. The birds are stylized but they could be peacocks and parrots, and there is a white monkey above the cartouche.



Figure 7. Detail showing central cartouche on Tabletop, LS2447.

The last object belonging to this group is the *barniz brillante Escritorio* (LS2000), also a fall front, but with four drawers (Figure 1E). This *Escritorio*, subject of a previous study focused on historical and technical aspects [16], has the largest variety of tonalities in color: translucent reds, oranges, and yellows to give the illusion of gold, greens, and blues, all layered over finely beaten silver leaf with details picked out in black. The exterior of the

box is decorated with a repeating relief design of passion fruit flower vines and monkeys on a cream background; the interior of the box lid and drop front reveal vibrantly colored flowers and fruit in a basket and the Quiros family crest flanked by parrots (Figure 8). The coat of arms indicates that the *Escritorio* was a gift from the Bishop of Popayán to his brother, appointed Marqués of Monreal in 1683 [3]. The hardware is not original, having been replaced with plain modern brass, but the footprint of the original is still visible in the form of an old *barniz de Pasto* repair. The box's shape, with its slightly bombé sides and lid, displays a more Asian look compared to the *matte barniz Escritorio*, although it has a matte white lacquer background, whereas Asian lacquers would typically be black or red. By the later 17th century, artisans in the Spanish Americas were incorporating many different design influences. While there is no direct documentary evidence confirming the objects' manufacture, dates for the two writing boxes were supported by details in their design and iconographical study. Visual comparison with the HSML gourd (LS2400) [22], which has a verified date range, was also informative.



Figure 8. Lid interior of Escritorio, LS2000.

Like the vast majority of extant *barniz de Pasto* objects, the forms of these two groups are all European-style types of furniture, unknown in the Americas before Spanish colonization. The resin on all five objects displays a similar aging pattern, with minimal craquelure and typically, where they occur, losses on exposed corners, edges, and construction joins. The resin itself has unusual physical properties that contribute to its preservation in art objects [25].

#### 2.2. Analytical Approach

A first campaign of non-invasive analyses including portable X-ray fluorescence (pXRF) spectroscopy, fiber-optics reflectance spectroscopy (FORS), and reflectance imaging spectroscopy (RIS) was then followed by the collection of 7 representative microsamples (Table 1). Samples were removed from two of the five objects (LS2447 and LS2000) with a

surgical scalpel, with careful examination and location selection under a stereomicroscope. Cross sections and scrapings of representative-colored areas were both produced. Cross sections were first inspected by polarized and ultraviolet (UV) light optical microscopy, then by scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS). Loose samples were analyzed by Raman spectroscopy, FTIR spectroscopy, pyrolysis/gas chromatography/mass spectrometry (py-GC/MS), and liquid chromatography/mass spectrometry (LC/MS).

Sample	Object	Description Location	
S1		Cross section of a light blue area	Area of a light blue petal from a flower to the left of the peacock
S2		Scraping of orange decoration	Area of orange leaf at the bottom of the <i>Tabletop</i> view
S3	LS2447	Scraping of olive-green decoration	Area of olive-green flower decoration on top of the griffin to the left of the lion
S4		Scraping of white decoration	Area of white flower decoration next to the top-left corner of the
S5		Scraping of resin	Area of resin (possibly not colored) from a fractured area at the left-bottom edge of the <i>Tabletop</i>
S6		Scraping of black decoration	Area of black background from the top-left corner of the <i>Tabletop</i>
S1	LS2000	Cross section of a yellow area	Area of yellow petal from a fractured flower at the bottom at the outer-left side

Table 1. List of microsamples removed from LS2447 and LS2000.

#### 2.2.1. Cross Section Preparation

Cross sections were prepared by embedding each sample within a double layer of methyl methacrylate resin (Technovit<sup>®</sup> 2000 LC, Kulzer Technik, Hanau, Germany). Each layer of resin was cured under UV light for 20 min. Excess resin was ground off and the surface was finely polished using CarbiMet 2 and Micro-mesh abrasive paper of various grits to expose the samples' stratigraphy.

#### 2.2.2. Raman Spectroscopy

Micro-invasive analysis was performed using a Bruker Senterra Raman spectrometer equipped with an Olympus  $50 \times 1000$  working-distance microscope objective and a charge-coupled device (CCD) detector. A Spectra Physics Cyan solid-state laser and a continuous wave diode laser emitting at 488 and 785 nm, respectively, were used as the excitation sources, and two holographic gratings (1800 and 1200 rulings/mm) provided a spectral resolution of 3-5 cm<sup>-1</sup>. The output laser power, number of scans, and integration time were adjusted according to the Raman responses of the different samples. Spectra were interpreted by comparison with The Metropolitan Museum of Art's library databases and with the published literature, as discussed below.

#### 2.2.3. pXRF

Single-spot pXRF spectroscopic measurements were collected with a Bruker Elio XGLab energy-dispersive portable XRF spectrometer with a high-resolution large-area silicon drift detector (SDD), with 130 eV for manganese (Mn) K $\alpha$  with a 10 kcps input photon rate (high-resolution mode) and 170 eV for Mn K $\alpha$  with a 200 kcps input photon rate (fast mode). The system is equipped with changeable filters and a rhodium (Rh) transmission target with 50 kV maximum voltage and 4 W maximum power. The parameters employed for the scans were 40 kV voltage, 80  $\mu$ A current, a 60 s live time, with spot size of 1 mm.

Analyses of cross sections were performed with a Zeiss Σigma HD FE-SEM, equipped with an Oxford Instrument X-MaxN 80 SDD detector. Backscattered electron (BSE) images, EDS analysis, and X-ray elemental mapping were carried out with an accelerating voltage of 20 kV in high vacuum.

# 2.2.5. FORS

Diffuse reflectance spectroscopy from 400 to 1000 nm was performed using an Ocean Optics QE65 spectrometer equipped with a linear silicon CCD array. The spot selected for analysis was illuminated by a fiber-optic cable coupled to a halogen lamp. Diffusely reflected light was collected by a co-axial fiber and dispersed by the spectrometer. Spectra were recorded with an integration time of 10 ms, and averaged over 4 acquisitions.

#### 2.2.6. FTIR

All of the samples collected from *Tabletop* (LS2447) were analyzed with FTIR as an initial step in the analysis workflow. Analysis was performed with a Hyperion 3000 FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector. The sample was crushed in a diamond micro-compression cell (Spectra Tech, Thermo Fisher Scientific, Madison, WI, USA) and all materials contained in it were analyzed in bulk in transmission mode through a  $15 \times$  objective. Spectra were collected in the 4000–600 cm<sup>-1</sup> range at a resolution of 4 cm<sup>-1</sup>. Each spectrum was obtained as the sum of 64 scans. Spectra were interpreted by comparison with library databases (MMA and IRUG Edition 2000 and 2007) and the published literature, as discussed below.

# 2.2.7. Py-GC/MS

GC/MS mass spectral data were collected on an Agilent 5977B Series GC/MSD (Agilent Technologies, Santa Clara, CA, USA) equipped with a vent-free adapter. The mass spectrometer was configured with an auto sampler and a single quadrupole 8890 network mass selective detector. This system is equipped with a multi-shot pyrolyzer 3030D (Frontier Laboratories Ltd. Saikon, Japan) held at 550 °C and an interface temperature of 320 °C using a single-shot method.

Two samples from the *Tabletop* (LS2447) reflecting the resin binder (sample S5) and a clear layer applied over an orange resin (Sample S2) were analyzed with py-GC/MS. Approximately 20–30  $\mu$ g of each sample was placed directly into a clean, stainless-steel Eco-cup and analyzed with and without the use of a derivatizing agent. The derivatization method used herein has been described extensively elsewhere. Briefly, in the thermally assisted methylation experiment, 2–3  $\mu$ L of tetramethylammonium hydroxide (TMAH, 25% in methanol) was added directly to the sample and allowed to sit for 3–5 min before analysis.

Chromatographic separation was carried out on a non-polar phenyl arylene polymer J&W-DB-5MS (Agilent Technologies, Santa Clara, CA, USA) column (40 m effective column length, 250  $\mu$ m inner diameter, and 0.25  $\mu$ m film thickness). The samples were run with a 20:1 split ratio. The GC oven temperature program was as follows: 40 °C initial temperature held for one minute. The temperature was increased by 10 °C/min up to 320 °C with a hold time of fifteen minutes. Helium was used as the carrier gas. Agilent Chemstation (version F.01.03.2357) and OpenChrom (version 1.5.0) [26] were used for data processing, including peak identification and integration, taking advantage of the collection of mass spectra available through the National Institute for Standards and Technology (NIST) Chemistry WebBook [27], NIST 2005 spectral libraries, and the related literature.

## 2.2.8. LC/MS

Two samples (S2 and S3) from the *Tabletop* (LS2447) were extracted using 6  $\mu$ L of a 4% BF3 in methanol solution, which was added directly to a clean vial containing the sample. After the addition of the BF3 solution, the sample was sonicated for 5 min and then left overnight at room temperature. Subsequently, 50  $\mu$ L (two aliquots of 25  $\mu$ L) of methanol

were added and the solution was transferred to a small glass test tube. The extract in the glass tube was dried in a vacuum concentrator (Genevac EZ4P). Additionally, the vial with the sample was rinsed with 50  $\mu$ L of methanol and dried in the vacuum concentrator (Genevac EZ4P).

The residues were reconstituted with 20  $\mu$ L of a mixture of LC/MS or analytical-grade dimethylformamide and methanol/acetonitrile (1/1, v/v) (1:4:5) (the MeOH/ACN mixture also contained 0.1% aqueous formic acid) and transferred to a PTFE centrifugal filter tube before being centrifuged at 12,000 × g for 10 min. The filtered and centrifuged solution was transferred to a deactivated sample insert seated in a clean autosampler vial. From the total volume, 7  $\mu$ L of the extracted sample solution was injected into the LC/MS system. This process was repeated in analyses where both negative and positive ionization modes were employed.

LC/MS analysis was carried out on an Impact II quadrupole time-of-flight mass spectrometer (Bruker, Billerica, MA, USA) coupled with a NexeraXR HPLC consisting of two LC-20ADxr HPLC pumps with an HPLC gradient mixer, SPDM30A diode array detector, CTO-20AC column oven, DGU-20A5R degassing unit, SIL-20ACxr autosampler, and CBS-20A communications bus module (Shimadzu, Columbia, MD, USA). The electrospray ionization interface was used, and detection was carried out in both negative and positive ionization modes. Compass otofControl (ver. 6.3) and Compass Hystar (ver. 6.2) were used for the MS and LC operation, respectively, and data analysis was performed using the DataAnalysis software (ver.6.1).

A Zorbax SB-C18 reversed-phase column (3.5  $\mu$ m particle, 2.1 mm I.D.  $\times$  150.0 mm, Agilent Technologies, Santa Clara, CA, USA) was used with a guard column (Zorbax SB-C18, 3.5  $\mu$ m particle, 2.0 mm I.D.  $\times$  15.0 mm, Agilent Technologies, Santa Clara, CA, USA) with a flow rate of 0.2 mL/min. The column pre-filter (Upchurch ultra-low-volume pre-column filter with 0.5  $\mu$ m stainless-steel frit, Sigma-Aldrich, St. Louis, MO, USA) was attached before the guard column. The column temperature was held at 40 °C.

The mobile phase was eluted in a gradient mode of 0.1% formic acid in high-purity water (v/v) (A) and 0.1% formic acid in a mixture of methanol and acetonitrile (1/1, v/v) (v/v) (B). The gradient system was 90% (A) for 1 min  $\rightarrow$  to 60% (A) in 6 min in a linear slope  $\rightarrow$  to 1% (A) in 23 min in a linear slope, held at 1% (A) for 3 min, and then to 90% (A) in 1 min, and held at 90% (A) for 18 min.

#### 2.2.9. RIS

RIS was carried out with a visible-to-near-infrared (VNIR) (400 to 1000 nm) hyperspectral camera (SOC710-E Surface Optics Corporation) equipped with a scientific Complementary Metal-Oxide Semiconductor (sCMOS) image sensor. The image cubes produced are  $2048 \times 2048$  pixels with 1024 spectral channels.

The surfaces of the objects were illuminated with four SoLux halogen bulbs (EiKO BB18003, 50 W, 4700 K) housed in swivel yoke track heads (WAC lighting, HHT-809) and mounted onto two lighting tracks. The two light stands were positioned at 45 degrees, respective to the decorated surface's normal angle. Image cubes were collected of the decorative scenes and of a Spectralon<sup>®</sup> diffuse white reflectance panel (99% reflective, LabSphere, Inc., North Sutton, NH, USA) under the same illumination and data collection configuration; to convert the objects' data to apparent reflectance, the image cube of the white panel was divided out from the object image cube. Dark noise (the inherent electrical noise of the detector and baseline sensor signal) was measured and subtracted automatically for each acquisition.

Subsequent image processing was conducted in ENVI Classic version 5.6.3 (Exelis Visual Information Solutions, Boulder, CO, USA). The data processing used herein has been described extensively elsewhere [28]. Normalized apparent reflectance was calculated from the raw data, briefly described above and further detailed in [29]. The built-in Spectral Hourglass Wizard tool in ENVI was used to identify unique spectral signatures and endmembers, and to visualize the distribution of these endmembers across the imaged

scene using a spectral angle mapper (SAM) classification method. Endmember maps were visualized in FIJI (ImageJ version 1.53q) and related spectra were analyzed in Igor Pro 8 (WaveMetrics, Portland, OR, USA) [30]. Inflection points were determined by fitting a Gaussian function to peaks in the first-derivative calculated spectra and extracting the peak maximum from the Gaussian fit, while absorptions were identified by negative-to-positive value changes in the first-derivative spectrum (i.e., zero-crossings in the plots).

#### 3. Results and Discussion

In this research, a multi-analytical approach was taken to identify the nature of the resin and the organic and inorganic colorants used to confer specific colorations to resins. In the discussion below, the term "colored resin" is used to indicate the intentional mixture of the *mopa mopa* resin with pigments and colorants. Conversely, the term uncolored resin refers to the use of resin without the addition of these colorants.

# 3.1. Analysis of Binding Media and Organic Surface Coatings 3.1.1. Resin

For the identification of the resin, analyses by FTIR, Py-GC/MS, and LC/MS were performed on the resin binder (S5) collected from the surface of the 17th-century Tabletop (LS2447), as well as on reference samples of unprocessed and boiled E. pastoensis, as already described in [22]. The FTIR analysis of sample S5 presents spectral features corresponding to the methylene symmetric ( $2854 \text{ cm}^{-1}$ ) and asymmetric ( $2927 \text{ cm}^{-1}$ ) stretching modes and a broad OH envelope (Figure 9A, red trace). Additional features associated with aliphatic compounds are present at 1458, 1414, 1375, and 725 cm<sup>-1</sup>, with the peak at 1414 cm<sup>-1</sup> being related to methylene groups adjacent to esters or carboxylic acids. Oxygencontaining moieties are also indicated by a strong spectral feature at 1716 cm<sup>-1</sup> (carbonyl stretching), with a shoulder at approximately 1730  $\text{cm}^{-1}$  accompanied by bands at 1246, 1176, and 1100 cm<sup>-1</sup>. Similar spectral features are identified in the unprocessed *mopa mopa* reference sample (Figure 9A, black trace), as well as in reported analyses of mopa mopa resin [7,17,19]. Prior FTIR analysis of Colombian [7,22] and Peruvian [17,31] lacquerwares have also identified *mopa mopa* in a number of objects dated to the colonial era. No resin samples were collected from LS2000 or LS2361, and as such, no insights are possible on the composition of the resin on these objects.

Further analysis of the resin (S5) collected from the *Tabletop* (LS2447) and the unprocessed *mopa mopa* reference sample with py-GC/MS (Figure 9B) was largely consistent with the published results on *mopa mopa* resin [7,22,31].

Specifically, the chromatogram is dominated by the presence of an unidentified compound previously reported by Newman and coauthors [7] with mass fragments at 215, 173, 141, 81, and 87 m/z (by intensity in descending order) (Figure 9B, red trace).

Likewise, methyl p-methoxycinnamate (20.31 min) and methyl 3,4-dimethoxycinnamate (22.27 min), along with a homologue series of dicarboxylic acids and fatty acid methyl esters of azelaic (18.7 min), palmitic (22.64 min), and stearic acids (24.44 min), a series of glycerol derivatives (9.3–9.7 min), and dimethyl and trimethyl ethers of apigenin are characteristic of *mopa mopa* resins [7,22]. The later-eluting compounds identified here, primarily consisting of pentacyclic triterpenoids (30-40 min), are also reported in [22]. The differences in the peak ratios between the eluted compounds could reflect the manipulation (heating and aging) of the colored resin versus the unprocessed resin. The LC/MS analysis of the resin binder (Figure 9C) indicates the presence of several previously identified compounds, including ellagic acid, luteolin, apigenin, and diosmetin, a derivative of luteolin (Table 2) [7]. Based on the respective ratios of these compounds, the resin binder more closely resembles *E. pastoensis* than *E. utilis*. Although the resin binder has a reddish appearance itself, there was no red colorant identified by LC/MS. While py-GC/MS allows for the identification of some non-volatile compounds and can be useful for some dye analysis, LC/MS does not require that a compound be volatile, only soluble in a suitable mobile phase, making it more amenable to dye analysis. Fundamentally, the

two approaches rely on similar principles—the ionization of a compound in a gas or liquid mobile phase and then the chromatographic separation of the charged species—and the two techniques provide complementary and supplementary information. Moreover, liquid chromatography–tandem mass spectrometry, as employed here, has a higher sensitivity and selectivity than traditional LC/MS. The LC/MS analysis of the boiled resin sample indicates a similar presence of luteolin, apigenin, and diosmetin, all of which have been reported in the analysis of *mopa mopa* resins [6,22]. A Py-GC/MS analysis of the same boiled resin sample analyzed herein has previously been reported by Pozzi and coauthors [22]. For a tabulated summary of the compounds identified by the py-GC/MS analysis of the uncolored resin, see Supplementary Material S1, Table S2.



**Figure 9.** (**A**) Baseline-corrected FTIR spectra and (**B**) Py-GC/MS chromatograms of sample S5 from the *Tabletop* (LS2447, red) and the unprocessed *mopa mopa* resin (black), indicating the presence of (1) dimethyl azelate, (2) methyl p-methoxycinnamate, (3) methyl-3,4-dimethoxycinnamate, (4) methyl palmitate, and (5 and 6) compounds with similar fragmentation patterns to peaks 7 and 9 reported by Newman and coauthors [6]. (**C**) LC/MS analysis, in negative ionization mode, of the resin binder containing ellagic acid (E), luteolin (L), apigenin (A), and diosmetin (D).

Object and Sample	Retention Time [min]	UV Signals [nm]	Detected Compound	Suggested Material
LS2447 S2	7.2	215, 243, 323	1-O-Caffeoylglycerol C12H14O6	
Orange	12.2	219, 208, 253, 368	Quercetin C <sub>15</sub> H <sub>14</sub> O <sub>6</sub>	Unknown yellow colorant
	14.3	264, 357	Kaempferol C <sub>15</sub> H <sub>10</sub> O <sub>6</sub>	
	14.9	201, 255, 348	Isorhamnetin (quercetin derivative) $C_{16}H_{11}O_7$	
	22.7	N/A	Unknown C <sub>15</sub> H <sub>10</sub> O <sub>8</sub>	
	17.5	195, 229, 283, 462		Unknown red colorant
	19	196, 238, 283, 607	Possible indigo contamination (visible under microscope)	Indigo <sup>†</sup>
	9.1	252, 366	Ellagic acid C <sub>14</sub> H <sub>6</sub> O <sub>8</sub>	Mona mona (tentatively
	12.3	208, 347	Luteolin C <sub>15</sub> H <sub>10</sub> O <sub>6</sub>	E. pastoensis)
	14.2	199, 266, 336	Apigenin C <sub>15</sub> H <sub>10</sub> O <sub>5</sub>	
	14.8	204, 250, 344	Diosmetin (luteolin derivative) $C_{16}H_{11}O_6$	
LS2447 S3	7.2	215, 243, 323	1-O-Caffeoylglycerol C <sub>12</sub> H <sub>14</sub> O <sub>6</sub>	
Green	12.2	219, 208, 253, 368	Quercetin $C_{15}H_{14}O_6$	Unknown yellow colorant
	14.3	264, 357	Kaempferol $C_{15}H_{10}O_6$	
	14.9	201, 255, 348	(quercetin derivative)	
	22.7	N/A	$\frac{Unknown}{C_{15}H_{10}O_8}$	
	19	196, 240, 283, 617	Possible indigo traces (low extraction rate)	Indigo <sup>+</sup>
	9.1	252, 366	Ellagic acid C <sub>14</sub> H <sub>6</sub> O <sub>8</sub>	Mona mona (tentatively
	12.3	208, 347	Luteolin C15H10O6	E. pastoensis)
	14.2	199, 266, 336	Apigenin $C_{15}H_{10}O_5$	
	14.8	204, 250, 344	Diosmetin (luteolin derivative) $C_{16}H_{11}O_6$	
LS2447 S5	9.1	252, 366	Ellagic acid C <sub>14</sub> H <sub>6</sub> O <sub>8</sub>	Mona mona (tentatively
Resin binder	12.3	208, 347	Luteolin C15H10O4	E. pastoensis)
	14.2	199, 266, 336	Apigenin C <sub>15</sub> H <sub>10</sub> O <sub>5</sub>	
	14.8	204, 250, 344	Diosmetin (luteolin derivative) $C_{16}H_{11}O_6$	

Table 2. Summary of compounds identified by LC/MS analysis.

<sup>+</sup> The term indigo refers to indigotin-containing compounds and not to a specific indigo source.

# 3.1.2. Surface Coating

Spectral signatures indicative of wax were identified in the clear surface coating on sample S2 collected from the *Tabletop* (LS2447). Specifically, the FTIR spectrum displays a sharp peak at 1736 cm<sup>-1</sup> related to the C=O stretching of ester groups (Figure 10A) and the splitting of peaks at 1470 and 720 cm<sup>-1</sup> that are characteristic features of a number of plant and animal waxes. There were no discernable spectral features related to the *mopa mopa* resin identifiable in this material. In some cases, calcium sulfate was also identified

based on the occurrence of spectral features at 1620, 1100, and 660 cm<sup>-1</sup>. The analysis of a painted gero, thought to predate the colonial period, suggested that waxes might have been used as pigment binders in addition to mopa mopa resin [31], although later analyses only report the use of *mopa mopa* resin [6,7,17,19,22]. Wax has also been reportedly used in the repair of barniz de Pasto objects [22]. In the present study, however, it is unclear if these materials are original or if they are related to later routine maintenance or a conservation intervention. The wax does not appear to be used as a binder here, as it does not appear to be directly related to the colored materials, and instead is present in a layer atop the colored resin layer. To understand whether this waxy material was native to the object or a result of an unknown intervention, py-GC/MS was also employed. The most abundant features in the chromatogram of the clear coating were N,N-Dimethylglycine methyl ester, followed by an unknown compound eluting at 5.5 min (Figure 10B). This unknown compound has a base peak at m/z 72 and an apparent mass of 131 amu, which is similar to the reported fragmentation pattern for N-N-dimethylalanine methyl ester [32]. As neither pyrrole nor indole are identified here, it is likely that these compounds are instead related to TMAH itself. This clear coating material is also associated with a C24-C34 n-alkane series, with no even–odd preference, and  $C_{26}$  being the most abundant of the *n*-alkanes. In addition to n-alkanes, even-ordered fatty acid methyl esters between C<sub>12</sub> and C<sub>18</sub> were identified, with palmitic acid ( $C_{16}$ ) being the most abundant. The methyl ester of tetracosanoic acid  $(C_{24})$  could also be identified. The absence of di-acids suggests that no oil is present in the matrix. At present, the identification of this material is unclear.



**Figure 10.** (**A**) Baseline-corrected FTIR spectrum and (**B**) Py-GC/MS chromatogram of the clear coating isolated from the orange-colored resin sample (S2) collected from the *Tabletop* (LS2447). (Inset) Zoom-in of chromatogram spanning retention times between 6 and 32 min.

# 3.2. Analysis of Pigments and Colorants

# 3.2.1. White and Cream

The earliest object (*Casket*, LS2361), decorated with *matte barniz*, is characterized by a limited color palette dominated by cream-colored areas that showed the ubiquitous presence of mercury (Hg), accompanied by less intense peaks of chlorine (Cl) (Figure 11A) in its pink, lilac, gray, green, and blue-green areas. The simultaneous presence of these two elements indicates the use of the pigment calomel, whose use in works of art, including in other 17th-century *barniz de Pasto* objects, has been widely documented in the past few years [17–20,22,33]. Calomel is extensively used to draw fine lines and cream-colored designs, and is mixed with colored resins as a matting and lightening component. In the second *Coffer* (LS2067) belonging to the first group, decorated with *barniz brillante*, the use of calomel is limited to matte cream-colored areas (mostly fine outlines), as the detection of Hg and traces of Cl suggests (Figure 11B). As commonly found in *barniz brillante* objects, the detection of silver all over the object aligns with the presence of a silver leaf underneath the resin sheets.



**Figure 11.** Representative XRF spectra acquired from cream-colored and white areas on (**A**) *Casket* (LS2361) (red spectrum collected from a cream-colored area); (**B**) *Coffer* (LS2067) (green and dark green spectra show different contents of mercury measured in different areas); (**C**) *Tabletop* (LS2447) (orange spectrum) and *Escritorio* (LS2446) (blue spectrum); and (**D**) *Escritorio* (LS2000) (light blue and black spectra show the presence of lead white and possibly calomel from different areas, respectively).

Although grouped together for this study, the contemporary *Escritorio* and *Tabletop* (LS2446 and LS2447, respectively), both made with *matte barniz*, had some key compositional differences. None of the cream-colored areas of the *Escritorio* displayed the presence of chromophore elements, suggesting the sole use of organic colorants in combination with the resin (Figure 11C, blue spectrum). Surprisingly, pXRF measurements detected lead (Pb) in all white areas of the *Tabletop* (Figure 11C, orange spectrum). This finding infers the use of lead white as opposed to calomel in this object to obtain the white color. The second and more modern *Escritorio* (LS2000), made with *barniz brillante*, displays an extensive use of Pb (Figure 11D, light blue spectrum), likely in the form of lead white, in most of the colors, with sporadic areas where Hg was detected, supposedly related to the use of calomel (Figure 11D, black spectrum). To date, this *barniz de Pasto* object and the Gourd in the collection of the HSML have been the only evidence of the simultaneous use of lead white and calomel. In his accounts, Alexander von Humboldt, who described the colorants

employed in the manufacture of *barniz de Pasto* objects in 1801 [34], identified lead white as the source for white. The identification of calomel [20] poses the possibility of this unusual pigment as an Indigenous marker predating the introduction of lead white.

#### 3.2.2. Blue and Black

As anticipated, indigo appeared in all blue- and black-colored resins. Indigotin-rich dyes can be sourced from plants such as woad (*Isatis tinctoria*), which was principally available in Europe and parts of North America at this time, or *Indigofera tinctoria* and *Indigofera suffruticosa*, which occur widely in Central and South America. In the text below, the term indigo is used to refer to all indigotin-based compounds, without specific identification of the source. Given the large scale of the *Tabletop* (LS2447), the reflectance spectroscopy of this object was limited to point measurements (Figure 12).



**Figure 12.** (Left) Approximate FORS acquisition areas on *Tabletop* (LS2447) indicated by yellow enumerated open circles. (**Right**) FORS reflectance spectra shown with corresponding spot numbers at right of plot.

FORS analysis of a light-blue, arabesque-like illustration exhibits an absorbance maximum at 648 nm and an accompanying inflection point at 714 nm, which is consistent with the presence of indigo (Figure 12, spot 7). Indigo is also present in the nearly black medallion surrounding the central lion (Figure 12, spot 9), which is associated with an inflection point significantly red-shifted to 737 nm, although the characteristic apparent absorbance maximum is no longer evident. The reflectance properties of indigo include an absorbance maximum at approximately 660 nm and an inflection point between 690 and 730 nm [35]. This is significantly modulated by the binder, chemical environment, addition of other colorants, and concentration of indigo [36,37]. As suggested by Humboldt's accounts, indigo was used in both blue- and black-colored resins with the intensity of the color being modulated by the dilution of the pigment. Indigo was previously identified in both black and blue *mopa mopa*-based resins used to decorate a 17th-century gourd [22], a 17th-century wooden chest [19], and Peruvian painted qero cups dated to the Inka colonial period [31,38]. FORS, FTIR, and imaging analyses of four Peruvian textiles dated to earlier periods reveal the use of indigo in blue and black pigments [39].

The FTIR analysis of sample S6 (Figure 13A), a visually black resin collected from the *Tabletop* (LS2447), shows only minor differences in the spectral signatures compared

to the resin binder. In the carbonyl stretching region, the peak at  $1726 \text{ cm}^{-1}$  is more pronounced (Figure 13B), which may indicate the presence of an oil. Indeed, oils have also been identified in both colored and uncolored *mopa mopa* resins [7]. Other authors have suggested that oil slurries may have been used to facilitate the incorporation of colorants into the resin [40]. Additional weak features at 1627, 1614, and a shoulder at approximately  $1480 \text{ cm}^{-1}$  may be related to the use of indigo, which has been identified previously in blue-and black-colored resins in Colombian lacquerwares [7,22]. Raman analysis of the same sample confirms the identification of an indigotin-based colorant based on the presence of a characteristic Raman shift at 1576 cm<sup>-1</sup> (Figure 13C) [22,36,41].



**Figure 13.** (**A**) Baseline-corrected FTIR spectrum of sample S6, removed from a black area of *Tabletop*, LS2447, with the carbonyl stretching region highlighted, and (**B**) zoomed-in results of the same region with the black resin shown in black and the uncolored resin shown in red (offset and scaled by a factor of 2). The dashed line at 1726 cm<sup>-1</sup> may be indicative of an added oil. (**C**) Baseline-corrected Raman spectrum of sample S6, which contains indigo (main peak at 1576 cm<sup>-1</sup>) as the principal colorant.

The additional spectral features appearing at 868/860 cm<sup>-1</sup>, 811, and 783 nm are possibly related to the presence of unidentified oxalate compounds. It cannot be ruled out that an additional black colorant (i.e., bone or carbon-based black) was added to achieve the nearly black resins used in the background of the *Tabletop* (LS2447). The pXRF analysis of this area did not indicate the presence of phosphorus, nor did the FTIR analysis of this sample exhibit a characteristic peak at 2012 cm<sup>-1</sup>, which might indicate the presence of bone or ivory black. Moreover, broad features centered around 1325 and 1580 cm<sup>-1</sup> are absent from the Raman spectrum, indicating no detectable carbon-based black either. In the analysis of 150 Peruvian qeros, carbon black was identified on nearly every object [31]. Tentatively, the visually black color of this resin is solely attributable to indigo, which is consistent with the historical and scientific literature indicating the use of calcined or concentrated indigo to obtain black shades in *barniz de Pasto* objects [5,19,22,34].

Though the high curvature of the lid of the *Casket* (LS2361) precluded RIS analysis, the relatively flat face and short sides of the *Casket* could be surveyed. Each side of the *Casket* bears a visually black background that is associated with a uniform absorbance between



400 and 700 nm, a rise in reflectance at ca. 700 nm, and an inflection point at approximately 750 nm that is tentatively identified as indigo (Figure 14).

**Figure 14.** Area of **(A)** *Coffer* (LS2067) and **(D)** the front face of the *Casket* (LS2361) analyzed by RIS and endmember rule images (distribution maps) for **(B)** LS2067 and **(E)** LS2361 showing the distribution of a near-black, indigo-containing compound. Reflectance spectra corresponding to the endmembers for **(C)** LS2067 and **(F)** LS2361 with relevant reflectance properties indicated.

As discussed by other authors, in areas of concentrated indigo, the absorbance maximum typically observed at ca. 660 nm is absent [42]. Similar conclusions are reported by Alvarez-White and coauthors [5], who note that dark backgrounds on a selection of *barniz de Pasto* objects are possibly associated with densely saturated or calcined indigo. The pXRF analysis of the black background surrounding the lock on the front of the *Casket* detected only very weak signals of Cl and Hg, suggesting that no inorganic colorants are present in this area. However, their presence, even though in traces, might be either due to contamination or to a deeper layer possibly containing calomel.

Pale blue-gray decoration, including one of the central birds on LS2000, the lighter blue tail of the bird on the front of the *Casket* (LS2361), and the central hare on one side of the same *Casket*, are consistent with the presence of indigo, which presents an absorbance maximum at around 640–650 nm and an inflection point at ca. 700 nm (Figure 15).



**Figure 15.** Area analyzed by RIS for (**A**) *Escritorio* (LS2000) and (**B**) RIS endmember distribution map of the same area illustrating the distribution of a pale blue-gray-colored resin and (**C**) corresponding endmember spectrum. In a second example, the area analyzed by RIS for (**D**) side panel of the *Casket* (LS2361) with an illustration of a pale blue-gray hare. (**E**) Related RIS endmember distribution map and (**F**) related RIS endmember spectrum.

The pXRF analysis of the light-blue tail of the bird on the front of the *Casket* indicated the presence of mercury, presumably in the form of calomel, though no other colorant-related elements were identified, while the light blues on the *Escritorio* (LS2000) display a strong signal of Pb, consistent with the presence of lead white possibly used in combination with indigo. Mixtures of calomel and indigo were observed previously in the analysis of a comparable 17th-century table cabinet in the collection of the V&A [17].

Blue-green hues are found across all objects, particularly in the illustration of vine-like and floral details. The endmember spectra from the RIS analyses corresponding to these areas feature inflection points at 700–710 nm and absorbance maxima at ca. 645–650 nm. Together, these spectral features suggest the use of an indigo-based matrix. FORS analyses of indigo-based green pigments incorporating yellow colorants often retain the characteristic absorbance maximum of indigo along with a red shift in the inflection point to ca. 715 nm [43].

To avoid redundancy, for the remaining objects, only RIS results are reported and discussed herein. A full summary of the reflectance spectroscopy analyses for all ob-

jects is provided in the accompanying Supplementary Material S1 in Tables S3–S8 and Figures S1–S11.

#### 3.2.3. Red, Pink, and Purple

In the pre-Hispanic era, the most commonly used red dyes included insect dyes, such as cochineal (*Dactylopius coccus*), and plant dyes derived from *Galium* and *Relbunium*, all of which are anthraquinone dyes [42,44–46]. Humboldt's accounts, however, suggest that the colorant used in the production of red-colored resins in *barniz de Pasto* objects was achiote (*Bixa orellana*) [34], a carotenoid dye derived from the outer layer of the seed inside the shrub's fruit [46].

Except for the Escritorio (LS2446), which bears no red-colored resins, and the Tabletop (LS2447), areas of red- and pink-colored resins appear in varying shades across all the objects and the principal red dye identified is insect-based. For example, insect-based red colorants are also used across the Escritorio (LS2000) to produce varying shades of red, pink, and brown (Figure 16). Characteristically, these resins are associated with absorption features at ca. 520 and 560 nm with inflection points ca. 590–595 nm. Lake pigments derived from anthraquinones, such as cochineal or madder, typically exhibit structured double absorption bands between 500 and 580 nm; insect-based red lake pigments can be distinguished from plant sources based on shifts in the position of these structured absorptions, with insect reds' absorbance maxima typically appearing at ca. 520–535 and 560–565 nm and plant-derived anthraquinone dyes presenting absorbance bands at ca. 500–515 and 535–545 nm [43,47,48]. A peach-colored resin, used in the illustration of the bib of the central figure on the long face of the small *Casket*, and some of the fruits and animal illustrations on the sides, presents two absorbance bands at 520 and 560 nm, likely indicating the use of an insect-based red. One bright, magenta-colored resin used in the decoration of the head and front legs of a small unicorn on the front face of the small Casket (LS2361) lacks the characteristic absorbance of many insect resins (Supplementary Material S1, Figures S6 and S7). Instead, this resin presents only inflection points at ca. 585 nm. The hind and rear legs, however, exhibit classic, though weak, spectral signatures of an insect-red-based resin with absorbance maxima at 524 and 564 nm. Fonseca and coauthors have shown that in sufficiently thick applications of cochineal-containing paints, the absorbance features at 520 and 560 nm, typically used in the identification of insect-based reds, disappear [47].

A vibrant, red-colored resin appears on the *Coffer* (LS2067) and largely lacks any clear absorption features corresponding to an insect red. Instead, the red resin uniformly absorbs below ca. 580 nm before rising in reflectance. In some red areas, though, there are discernable, albeit weak, absorption bands corresponding to cochineal (Supplementary Material S1, Figure S1). pXRF measurements of details bearing this red-colored resin indicated the presence of mercury, although it is possibly related to the use of calomel, also identified elsewhere on this object, rather than a mercury-based red like vermilion. It is worth noting that, to date, there have only been limited references to the use of vermilion in objects containing *mopa* mopa resins [31,40,49,50]. Even with the added insights offered by pXRF analysis, it is not possible to identify the nature of these red-colored resins unequivocally.

Indigo is used in combination with insect-based reds to produce mauve- and purplecolored resins. For example, the FORS analysis of a floral detail on the lid of the small *Casket* (LS2361) yielded signatures of indigo, with an inflection point at 700 nm, and two characteristic absorption bands at 519 and 560 nm corresponding to an insect-based red colorant. Additional RIS data of the front and side panels of the *Casket* indicate the use of insect-based red colorants throughout a number of different illustrative elements. Similar to the influence of yellow colorants on the reflectance properties of indigo discussed above, mixtures of red colorants and indigo also often retain the individual properties of indigo. However, unlike the masking behavior of indigo in the identification of yellow dyes, the absorbance properties of the red colorant are occasionally still observable [43,51]. For example, a maroon-colored resin appears in some details on the *Escritorio* (LS2000) and presents three absorbance bands at 520, 560, and 655 nm, as well as two inflection points at 580 and 700 nm (Figure 16, red and yellow traces). These spectral features are possibly indicative of the admixture of indigo and an insect-based red in the resin.



**Figure 16.** (**A**) Area analyzed by RIS for *Escritorio* (LS2000). (**B**) Composite image for the same area illustrating the distribution of several red-, pink-, and brown-colored resins with each endmember shown in a different color, and (**C**) corresponding endmember spectra shown in the same colors (i.e. red-colored regions in (**B**) correspond to red-colored curve in (**C**)). Spectra offset for clarity. All of these colorants appear to be similarly prepared with an insect red dye, presumably cochineal.

#### 3.2.4. Yellow and Orange

Yellow colorants are notoriously difficult to analyze, and those challenges are only compounded here by the dearth of written information about the materials used in precolonial Colombia. Humboldt reported that the powdered flower root of *Escobedia scabrifolia* was used in the production of yellow-colored resins [34]. A prior HPLC-DAD analysis of a yellow inlay on a Colombian gourd was not consistent with *E. scabrifolia* [22]; however, to date, analytical evidence of dyes sourced from *E. scabrifolia* have yet to be reported in Colombian lacquerwares. Historical references also suggest that the colorant was used extensively as a food colorant [52].

Though not explicitly discussed in Humboldt's accounts, the production of orangecolored resin might be achieved through the mixture of red and yellow colorants. However, as discussed above, there is no evidence of an animal-based red here, as has been observed in the other objects. Instead, FORS spectra collected from the central griffin and one of the bearded figures on the surface of the *Tabletop* (LS2447) are associated with broad inflection points ca. 660 nm. Similarly, orange-colored resins on the *Escritorio* (LS2000) and small *Casket* (LS2361) lack any clear evidence of an animal-based red and often present similar absorbances to yellow-colored resins (Supplementary Material S1, Figures S2–S9).

The FTIR spectrum of sample S2, an orange-colored resin collected from the surface of the *Tabletop* (LS2447), is largely dominated by spectral signatures corresponding to the resin binder (Figure 17A). However, new spectral features, not present in the resin binder, are apparent and are tentatively assigned to a yellow-colored resin. Peaks at 3405,

1660, 1610, 1521, 1320, 1260, 1198, 1014, 840, and 825 cm<sup>-1</sup>, and increased intensity of the bands at 1170 and 1454 cm<sup>-1</sup>, are consistent with quercitrin [53,54] or a colorant similar to quercitron, such as yellow dye derived from the inner bark of North American black oak trees (Supplementary Material S1, Figure S13) [55–57]. Quercitron bark, however, was introduced and patented as natural dyestuff in 1775 and first exported from North America at the end of the 18th century [56,58], although there are earlier documented uses of the same oak by North American Indigenous groups such as the Ojibwe peoples, for example [59]. While quercitron bark derived from the North American black oak (Quercus velutina) itself is unlikely given its known geographical distribution, there is one oak endemic to Colombia, Colombian oak (Quercus humboldtii), that may or may not have similar dye properties. Studies of plant materials derived from Quercus species often present similar compositional profiles, including the flavonols quercetin, isorhamnetin, and kaempferol, and as such [60], it is possible that dyes prepared from these species may be compositionally similar as well. The chromophores responsible for the yellow color of quercitron dye, quercetin, and quercitrin [61], however, are the most commonly identified chromophores in flavonol-type dyes [62], and as a result the number of yellow dyes possibly used remains extensive.



**Figure 17.** (**A**) Baseline-corrected FTIR spectrum of sample S2, removed from an orange area of *Tabletop*, LS2447. (**B**) Baseline-corrected Raman spectrum of sample S2 (see text for discussion). (**C**) LC/MS base peak chromatogram (negative ionization mode) of extract from sample S2 containing 1-O-caffeoylglycerol (C), quercetin (Q), luteolin (L), apigenin (A), kaempferol (K), and diosmetin (D).

The Raman analysis of the orange-colored resin (sample S2) presented peaks at 1633(sh), 1606, 1590(sh), 1549, 1440, 1329, 1179, 1114, 943, 785, 640, 605, 579, and 522 cm<sup>-1</sup> (Figure 17B). Similar spectral features are observed in reported Raman analyses of quercitrin [53] and quercetin [63–65]. The subsequent analysis of the orange-colored resin by LC/MS in negative mode revealed detectable amounts of 1-*O*-caffeoylglycerol (7.2 min), quercetin (12.2 min), kaempferol (14.3 min), and an O-methylated quercetin derivative, isorhamnetin (14.9 min), none of which were observed in the resin binder (S5) (Figure 17C). Indigo is also identified here, based on the presence of indigotin (19 min), but it is expected to be related to the blue-colored resin adjacent to the orange-colored resin. An unknown red compound was also apparent at a retention time of 17.5 min, presenting several absorbance maxima at 195, 229, 283, and 462 nm. As discussed in another study by Newman and coauthors, quercetin and kaempferol may also be present in *E. utilis* and, to a lesser extent, in *E. pastoensis* [7].

Thus, distinguishing between colorant-related compounds, particularly in the case of yellow colorants, can become quite challenging. However, here, the peaks attributed to quercetin and kaempferol are significantly more intense than in the resin binder, suggesting that these compounds are either associated with the yellow dye or indicative of the use of *E. utilis* instead of *E. pastoensis*. Quercetin and kaempferol have been reportedly identified in the yellow component of green-colored resins by Newman and Derrick, although the analytical evidence for this identification remains unpublished [5]. Analyses of Francisco Pizarro's *Banner of Arms*, used in the 1532 conquest of the Inka empire, have also identified quercetin-O-rutinoside in yellow, orange, and green dyes [66]. These results exemplify how widely compositionally similar colorants occur both globally and temporally, appearing in both pre-Hispanic and colonial-era contexts alike, which complicates our understanding of the evolution of this artistic practice.

While the FTIR, Raman, and LC/MS analyses did not allow for the exact identification of the source of the yellow dye, it is possible to infer that the yellow dye can be classified as a flavonoid and more specifically as a flavonol. It is further possible to exclude some colorants such as weld, *E. scabrifolia*, quercitron bark, and marigold, all of which present significantly different spectral and chromatographic responses to that of the sample collected from the *Tabletop*. No bixin was detected, suggesting that achiote was not used in this instance. Likewise, the absence of quercitrin eliminates the possibility that the yellow dye, aside from the isolation of the dye from the resin, is a common challenge and is only compounded by a dearth of analyses of similar materials and historical documentation regarding this cultural practice.

For comparison, LC/MS analysis was also carried out on a reference sample of ground *E. scabrifolia* root. One challenge encountered here during the LC/MS analysis of yellow dye components during extraction with BF<sub>3</sub> was the degradation of some of the colorant-related carotenoid compounds. Carotenoids such as azafrin, which is the principal color-related component of E. scabrifolia [67], tend to degrade with heat, light, or acidic conditions. As such, it is possible that heating of a resin containing this pigment during the manufacturing process, or compounded effects of exposure to BF<sub>3</sub>, a Lewis acid, and the extended duration of the extraction procedure, may compromise or degrade azafrin [68] and preclude the identification of this important colorant-related compound in our sample. An additional extraction of *E. scabrifolia* roots was carried out by adding 40 µL of methanol and sonicating for 5 min at room temperature. Azafrin and aeginetin, markers of E. scabrifolia, were detected and results from both extraction methods were compared with samples from the Tabletop (LS2447) (Supplementary Material S1, Table S9). Compounds related to flavonoids, anthocyanins, carotenoids, and other unknowns were detected in the E. scabrifolia references, but only ferulic acid, a ubiquitous hydrocinnamic acid, was also present in the orange and green samples. These results confirm that *E. scabrifolia* was not the yellow dye used on this object.

# 3.2.5. Green

While green-colored resins in the *barniz de Pasto* artform are speculated to be a mixture of indigo and *E. scabrifolia* [33], there is also no evidence that *E. scabrifolia* was used here. The FORS analysis of an olive-green saddle illustration on the rounded lid of the small *Casket* (LS2361) exhibited an absorbance maximum at 432 nm, possibly related to the presence of an organic yellow compound (Figure 18A,B). pXRF analysis in the same area suggested the use of organic colorants as well, as no elements related to inorganic pigments could be detected. The RIS analysis of a similar colorant used in the illustration of a woman on the front face of the *Casket* (LS2361) aided in visualizing the distribution of this colorant across the object (Figure 18C,E). The reflectance spectrum of a lighter-green petal-like illustration, thought to be in an area of restoration, revealed a reflection point at 500 nm with apparent absorbance maxima at 648, 730, and 783 nm, pointing towards a mixture containing indigo (Supplementary Material S1, Figure S12).



**Figure 18.** (**A**) Top lid of *Casket* (LS2361) with FORS acquisition point on the olive-green saddle indicated by a yellow, open circle, and (**B**) corresponding reflectance spectrum. (**C**) Subset of RIS analysis area on long front face of the *Casket* centering a figure in a similarly colored, olive-green textile, with (**D**) RIS endmember distribution of this olive-green color and (**E**) corresponding endmember spectrum.

The pXRF analysis of the green-colored resin from the *Tabletop* (LS2447) collected from a central olive-green floral element suggested the presence of an organic colorant, as no copper or iron was identified. Subsequent FTIR analysis of this resin (S3) was largely consistent with the orange-colored resin collected from the same object, suggesting a similar, presumably yellow, colorant is used in both areas (Figure 19A). The Raman analysis of the green-colored resins suffered strongly from background fluorescence and was largely featureless, aside from weak spectral features at ca. 1605, 1440, and 600 cm<sup>-1</sup>, which corresponded to the most intense peaks identified in the orange-colored resin discussed above (Figure 19B). Previous reports have indicated that the green colorants encountered in objects containing *mopa mopa* resins were occasionally inorganic, including copper resinate, other copper-based greens, and Prussian blue [31,69]. Yet, analyses of other objects



produced in the *barniz de Pasto* artform have reported a mixture of an indigotin-based blue and an unidentified organic yellow colorant to produce green-colored resins [5,22].

**Figure 19.** (**A**) Baseline-corrected FTIR spectrum of sample S3, removed from a green area of Tabletop, LS2447. (**B**) Baseline-corrected Raman spectrum of sample S3 (see text for discussion). (**C**) LC/MS base peak chromatogram (negative ionization mode) of extract from sample S3 containing 1-O-caffeoylglycerol (C), quercetin (Q), luteolin (L), apigenin (A), kaempferol (K), and diosmetin (D).

The LC/MS analysis of the green-colored resin confirmed the presence of indigotin, based on its characteristic UV–Vis profile, and a yellow component with similar composition to the yellow used to produce the orange-colored resin (S2) discussed above. Specifically, the LC/MS analysis of the green sample indicated the presence of 1-O-caffeoylglycerol, quercetin, kaempferol, and isorhamnetin in the yellow dye component (Figure 19C). An additional compound eluted at 19 min was consistent with indigotin, supporting the results of the FORS, Raman, and FTIR analyses.

As already demonstrated by previous studies on *barniz de Pasto* objects [5,22], manufacturing techniques cannot be unraveled without investigating the decoration stratigraphy. Two cross sections were hence removed from a *matte barniz* object (LS2447) and a *barniz brillante* object (LS2000) and examined by using optical and electron microscopy. Under polarized light, the sample from the *matte barniz* object (sample S1, Figure 20A), removed from the *Tabletop*'s light-blue flower next to the peacock on the left, revealed a stratigraphy composed of three layers: (1) a thin, dark red-brown layer, possibly a preparation layer; (2) a thick black-colored resin layer (about 250  $\mu$ m), corresponding to the background of the whole *Tabletop*, on top of which lies (3) a thin light-blue-colored resin layer (about 40  $\mu$ m) characterized by the presence of dispersed white particles of variable size, not exceeding 25  $\mu$ m (Figure 20A).



**Figure 20.** (**A**). Cross section of S1 removed from a light-blue flower on the *Tabletop* (LS2447) with (**B**) detail of the light-blue layer. The numbers in (**A**) refer to the layers, see text for discussion. (**C**) Cross section of S1 removed from a yellow flower on the *Escritorio* (LS2000) with (**D**) detail of the whole stratigraphic sequence.

The microchemical analysis conducted by SEM-EDS, specifically on layers 1 and 3, was crucial to understand the nature of the materials used in these two layers. From bottom-up, the BSE images revealed the presence of two preparation sub-layers forming layer 1 (1a and 1b, Figure 21), mostly composed of mineral particles. They differ in terms of composition and grain size, with layer 1a being mostly composed of a fine-grained matrix made of calcium sulfate, likely gypsum, possibly mixed in with a clay, as inferred by the detection of silicon (Si), aluminum (Al), magnesium (Mg), sodium (Na), potassium (K), and iron (Fe). Small particles of quartz, iron oxides/hydroxides, feldspars (possibly plagioclase), phyllosilicates, and calcium carbonate (likely calcite) were also identified in this layer, further supporting the use of natural clay. Frequent particles of barite, a barium sulfate typically associated with gypsum sources, were detected in layer 1a. Layer 1b shows abundant mineral particles ranging between 10 and 30  $\mu$ m in size, characterized by a sheet structure typical of phyllosilicate minerals. Their composition shows the presence of Si and Mg, which is consistent with talc (Figure 21). Preparation layers have not been documented before in *barniz de Pasto* objects: typically, the transparent or colored resin film is applied directly to the wooden substrate [5,22]. The thick layer of black-colored resin (layer 2) applied over the preparation layers has a thickness of about  $210-220 \ \mu m$  and does not show any chromophore elements, suggesting the use of an organic dye. Finally, the light-blue opaque layer (layer 3, Supplementary Material S1, Figure S14B), completing the stratigraphy of this sample, revealed the presence of quite abundant particles of a

lead-containing compound, likely lead white, whose distribution was measured by EDS mapping (Supplementary Material S1, Figure S14C). The practice of adding powdered lead white (*albayalde*) to colored resins to lighten shades and to obtain a matte effect has been proved in *barniz de Pasto* objects of the colonial Period [5,18,19].



**Figure 21.** (**A**) BSE image of cross section of S1 from the *Tabletop* (LS2447). The red rectangle indicates the ground layer; (**B**) zoomed BSE image of the ground layer, with two separate layers of different compositions and grain size clearly visible. The elemental distributions of magnesium, silicon, calcium, and sulfur are reported below, as well as EDS analyses of a magnesium silicate particle, likely talc, and of a calcium–silicon-rich area, possibly due to a mixture of calcium sulfate (likely gypsum) and a very-fine-grained clay.

Cross section S2 was removed from the left side of LS2000, the *Escritorio* dated to 1684, next to a loss in the yellow and silver flower. The stratigraphy examined under the optical microscope counted four layers: (1) a brown layer, (2) a 200  $\mu$ m thick green-colored resin sheet, (3) a 100  $\mu$ m thick orange-colored resin sheet, and (4) a 2  $\mu$ m thick silver leaf on top (Figure 20C,D). SEM-EDS was employed to investigate the nature of layer 1 and the composition of the silver leaf; layer 1 appears as an aggregate of particles, mostly composed of quartz, iron oxides/hydroxides, feldspars (possibly plagioclase), phyllosilicates, and calcium carbonate (likely calcite). Overall, the composition of this layer is very similar to the gypsum-clay-based layer 1a described for sample S1. The silver leaf (layer 4) is composed of almost pure silver, containing traces of mercury and a low quantity of chlorine, whose presence might be related to silver chlorides developed as degradation products. Previous examinations of this object [7,8] described a slightly different stratigraphy, which comprised three layers including a transparent, colorless layer adhering to the wooden substrate, a silver leaf on top of it, and a finishing layer usually made of a colored, transparent resin. However, cross sections were never analyzed before for this object.

#### 4. Conclusions

The study of these five *barniz de Pasto* objects in the collection of the HSML produced some unexpected results that merit further investigation. On the strength of previous work by these and other researchers, the expectation was to find calomel used in most of the cream-colored motifs of these objects, which are all dated to the 17th century. Calomel was assumed to be a local pigment since it has been so rarely found in European works of art. Lead white, the predominant white pigment in European works, was believed to have been introduced by the Spanish and therefore would appear in later objects or those made specifically for Spanish patrons. Instead, the results show an inconsistent use of both calomel and lead white. In some objects, only calomel is used, for example in the *Casket* (LS2361) and *Coffer* (LS2067); lead white alone was found in the *Tabletop* (LS2447); and in the *Escritorio* (LS2446) only contains organic pigments.

Despite the different white pigments used, it seems that the palette of organic colorants remained largely consistent throughout the 17th century. FTIR, Raman, and LC/MS analyses of the green- and orange-colored resins collected from the Tabletop (LS2447) presented similar spectral responses, suggesting the use of the same colorant in both instances, likely a yellow, flavonoid dye. Although the specific identification of this yellow dye remains an open question, LC/MS allows for the exclusion of certain colorants, such as marigold, *E. scabrifolia*, or old fustic, for example, representing an important step towards identifying the yellow colorants used in *barniz de Pasto* objects. Moreover, the red component of the orange-colored resin remains unknown, as it is not consistent with cochineal by LC/MS, supporting the evidence by FORS that indicates against the use of this colorant in redcolored areas of the Tabletop (LS2447). FORS and RIS analyses suggested that all the black-, blue-, and green-colored resins studied here contained indigo, which was subsequently confirmed by FTIR, Raman, and LC/MS analyses. RIS and FORS analyses were also useful for the indication of lake pigments produced from anthraquinone dyes—most likely the insect dye cochineal—across most of the red-colored resins. However, in some objects, signatures for this red colorant were weak or absent, possibly indicating a different recipe or the use of an entirely different colorant.

This work represents an important datapoint in exploring the evolution of artistic practices around the use of colored *mopa mopa* resins and, as discussed above, challenges the use of some specific pigments as temporal markers. The use of calomel in these objects does not seem to support the hypothesis that its use is a chronological marker for the 17th century, but this may reflect the limitations of the group of objects studied here. In conjunction with past research, the results confirm that the use of calomel was not limited to a specific workshop or technique. As the literature pertaining to *barniz de Pasto* continues to grow, it will be possible to interrogate and understand if and where Indigenous and colonial influences meet and overlap.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/heritage7050125/s1; The following supporting information is provided: Supplementary Material S1: Tables and images not included in the main text, with their Spanish translation; Supplementary Material S2: Spanish Translation of this paper.

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