

Article

Unveiling Polychrome Printing Methods on Textiles: Preliminary Results from the Mariano Fortuny y Madrazo Collection in Venice

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Abstract: At the beginning of the 20th century, the eclectic artist Mariano Fortuny y Madrazo patented two innovative methods for polychrome printing on fabrics and textiles, giving life to Fortuny fabric production in Venice. The first patent was related to colour application, while the second to a special machine that allows continuous printing using cylindrical rollers. Despite the descriptions, the methodology and materials used remain a secret. In collaboration with the Fortuny Museum in Venice, this research aimed at studying and identifying the different steps of Fortuny printing methodologies. Printing matrices, fabrics and raw materials found in the artist's studio were analysed in a multi-analytical campaign through digital microscopy, X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy in attenuated total reflectance (FTIR-ATR), μ -Raman spectroscopy and gas chromatography–mass spectrometry (GC–MS). Three main pigments were identified in paper samples: ivory black, a copper-based pigment, and a carbon black pigment with ultramarine for blues. The pigments were bound with linseed oil and colophony in varying proportions. Polychrome silk fabrics were dyed with a base colour, and then the coloured patterns were superimposed by continuous printing. Prussian blue was identified as one of the textile inks. Results provided a better understanding of printing methodology.

Keywords: continuous printing; resist printing; Mariano Fortuny y Madrazo; paper; fabric; 20th century industrial printing



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1. Introduction

In ancient times, printing on textiles was mainly done using wooden matrices (planches) with a technique known as pad printing or stamp printing. It consisted of creating the design in relief on stamps on which the colour was spread, which was then impressed on the textile by pressure, with mediocre results in terms of the accuracy of the design [1].

In 1600, the typical Indonesian batik arrived in Europe, a reserve technique that consisted of covering the parts of the fabric that were not to be dyed with wax [2,3]. Around the same time, a technique called *pochoir*, as well as screen printing [4], spread within the European market, mainly used to produce coloured postcards. It was not until 1834 that Louis Perrot in France invented the Perrotine, the first mechanical printing press that used planches, i.e., plates engraved in relief on wood, to print five different colours simultaneously. A second revolutionary innovation was the modern process for silk-screen printing, patented by Samuel Simon in 1907: a square of silk (called a *buratto*) is sprinkled with a photosensitive emulsion, placed in a darkroom and struck with a light image corresponding to the motif to be printed, then developed and washed to remove the paint from the surface not imprinted by light [5].

Between the 19th and 20th centuries, printing techniques became increasingly important, mainly thanks to the development and improvements in the textile sector brought about by the Industrial Revolution, as well as the well-known development of artistic products thanks to the synthesis and commercialisation of new pigments and dyes.

Mariano Fortuny y Madrazo (1871–1945) was an eclectic artist who is regarded as one of the greatest representatives of art and artistic craftsmanship between the end of the 19th century and the first half of the 20th century. Although he was a painter, engraver, sculptor, photographer, set designer, lighting technician, decorator and furniture designer, he is mainly remembered today for his fabrics and clothing. Regarding the production of clothes and textiles, his major innovations were the Delphos dress model, inspired by the oldest Greek sculptures [5], whose main feature was the pleating obtained with an innovative machine with heated ceramic cylindrical rollers [6], and the industrial production of coloured textiles with very complex patterns. Those textiles were obtained in a single production step, with a considerable reduction in production time and costs and excellent quality (Figure 1).



Figure 1. Artistic production of Mariano Fortuny exhibited in the Fortuny Museum in Venice: (a) clothes and textiles; (b) museum exhibition hall; (c) paper printed. credits @CristinaDaRoit, courtesy of Mariano Fortuny Museum.

The development of the Fortuny printing process undoubtedly stemmed from the study of contemporary techniques. The procedure is well described in his patents of 1909, *Procédé d'impression polychrome sur tissus, papiers, etc.* nr 419.269 [7], and 1910 *Procédé d'impression sur tissus, papiers, etc.* nr 427.307 [8], the former relating to ink application and the latter to a special machine that allows continuous printing using cylindrical rollers. However, to the best of our knowledge, the specific materials used and the printing steps were still completely unknown prior to this research. This study, thus, envisages the discovery of his accurate printing methods and the specific materials used, to acquire and disseminate knowledge of a successful printing technique at the beginning of the 20th century. The relevance of Mariano Fortuny's work in this historical period needs to be rediscovered and disseminated, especially considering that the diffusion of new textiles and designs and the availability of cheap decorated fabrics is strongly linked to the rise of the middle classes and the social development of wealthy Western society.

In this research, collaboration with the Fortuny Museum in Venice, located in the artist's home in Palazzo Pesaro-Orfei, was fundamental. Its collections consist of pieces and materials that well represent the different outcomes of the artist's research, sorted by major topics: painting, light, photography, textiles and large clothes [9]. The material collected for the analyses came entirely from the collection, and the investigations were carried out with as little invasiveness as possible. The use of portable digital microscopy, portable Raman and external reflectance and ATR-FT-IR spectroscopy instruments in situ, together

with macro-XRF mapping and a few selected gas-chromatography analyses, allowed the materials' characterisation.

Mariano Fortuny y Madrazo and His Patents

Mariano was born in Granada, Spain in May 1871 to his father Mariano Fortuny y Marsal and his mother Cecilia de Madrazo [10]. In 1889, he moved with his family from Paris to Venice. Here, the 18-year-old Fortuny began his real artistic career. The designs on velvets, brocades, silks and sacred vestments in his father's collection, which his mother enlarged, had captured his imagination many years before. In 1906, Mariano and his wife Henriette set up a small textile printing workshop in the Orfei Palace. In his workshop in Venice, Fortuny designed a series of silk veils inspired by Cretan art, which he called Knossos veils, and then discovered the iridescent properties of velvet, which he used for clothes, curtains, tablecloths and cushions [11]. In 1909 and 1910, Fortuny patented a system of polychrome printing on fabrics and a continuous printing process by using *pochoirs* (similar to stencils). The *pochoirs* were obtained photographically or by other means [7,8]. In 1922, on the recommendation of his friend Stucky, Fortuny set up a factory on the island of Giudecca (Venice), where he developed a printing technique for white cotton that perfectly reproduced silk brocades [12]. In Giudecca, Fortuny controlled the entire polychrome printing process using the new machines he had invented, while the production of clothing remained mainly linked to Palazzo Pesaro-Orfei. His textiles were soon a success.

Fortuny's personality, together with his friend, the miller and entrepreneur Gian Carlo Stucky, dominated the Venetian business scene at the beginning of the 20th century, giving the city a remarkable industrial boost at a time of political and social crisis in post-unification Venice.

Fortuny participated as a painter in the Venice Biennale continuously from 1924 to 1942. His clothes appeared in Vogue and other important fashion magazines. Mariano Fortuny died in Venice on 2 May 1949 with more than 20 patents registered [12]. The following year, some of his paintings were exhibited at the 25th Venice Biennale alongside those of his father and the Madrazos.

This research begins by studying the patents related to polychrome printing methods on textiles and paper briefly summarised below. The first, granted in 1909, is a patent for polychrome resist printing [7]. The process is based on a continuous printing method involving rolls or stencils, one for each colour. Its novelty is the ability to achieve accurate juxtaposition of many coloured patterns without having to align the stencils or rollers as required by the conventional process. A first impression (called the partition impression) was made using a non-permeable medium to print the contours that define the design partition (Figure 2A,(4)). Subsequent impressions were made using coarsely engraved plates or stencils (Figure 2B,C) that deposited the inks between the boundaries of the partition (Figure 2(5),(6)). This avoids the risk of blurring or overlapping of the different colours, even in the case of imperfect alignment. The dyes spread by capillarity, due to the porosity of the fabric or paper, until they are stopped by the barrier created in the first step (Figure 2(7)).

The second patent relates to a method of printing on fabrics, papers and other surfaces using a cut stencil, a plate engraved in relief or hollow, or employing cylinders (the diagram of the cylinder machine is shown in Figure 3) [8]. The cylinder printing process allows continuous rotary printing with a significant reduction in costs. The purpose of the invention is to increase the length of the obtainable pattern, in comparison with the engraved cylinders of the Perrotine machines, with a fast continuous printing process not allowed by the traditional silkscreen printing. In addition, the pattern complexity was increased thanks to new methods for obtaining the *pochoirs* and new pattern arrangements.

The text of the patent provides general instructions to produce the *pochoirs*. A suitable textile is: (i) covered with photosensitive gelatine made from an alkaline dichromate solution; (ii) covered with a design (e.g., a black pattern drawn on tracing paper or other translucent support); (iii) exposed to light; and (iv) washed to dissolve the soluble parts

of the gelatine. Once the *pochoir* is prepared in the form of a long continuous strip, it is placed on cylindrical rollers fitted with pegs at equal intervals. These are driven and run over strips of textiles, which move in the same way. The bottom roller of stencil strips a, b and c in Figure 3 can be perforated and used to distribute the dye or paint.

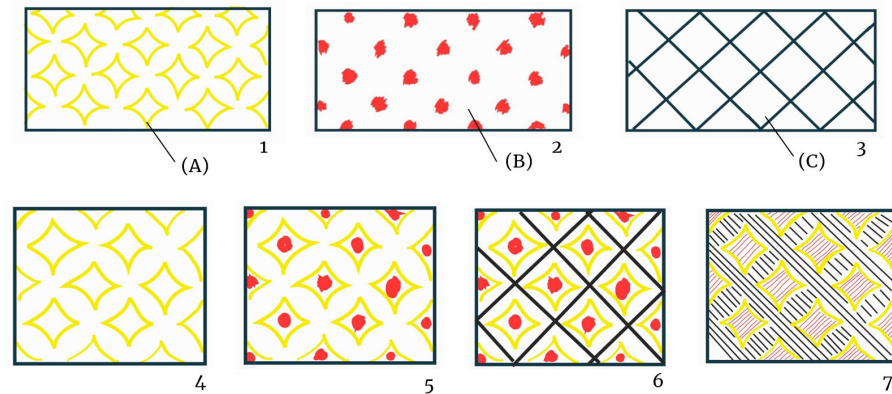


Figure 2. Process diagram of the reserve printing described by Fortuny (artwork by Virginia Farinelli based on the diagram published by Fortuny in its license) [7]. Frames 1, 2 and 3 depict the printing matrices, where (A–C) might be *pochoirs*, plates or stencils used for printing the textiles. Frames 4–7 depict the consequent printing phases on the textile: (4) print of partition; (5) deposition of the first colour within the partition; (5) print of the second colour within the partition; (7) diffusion of the colours to the partition boundaries and final result.

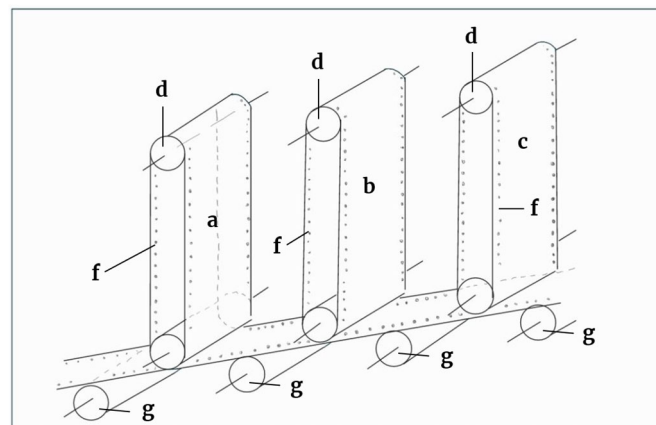


Figure 3. Diagram of the continuous rotary printing machine patented by Fortuny (artwork by Virginia Farinelli based on the diagram published by Fortuny in its license [8]; a, b, c = *pochoirs* for different colours; d = cylinders; f = equidistant holes; g = rolls for the advancement of textile or paper to be printed).

2. Materials and Methods

The materials analysed for this research come entirely from the collection of the Fortuny Museum in Venice. The collection is particularly rich in print matrices, papers depicting pattern designs for paper and textile printing, and printed textiles. Within the whole collection, preliminary observation and specific non-invasive in-situ analysis (such as observation, optical microscopy OM, ATR-FTIR spectroscopy and Raman spectroscopy) allowed the selection of representative materials and objects to further conduct the research.

After careful research into the materials and the artist, in-situ analyses were carried out using non-invasive portable instruments (observation, optical microscopy OM, ATR-FTIR spectroscopy and Raman spectroscopy), while non- and micro-invasive analyses (such as micro-Raman spectroscopy, X-Ray fluorescence imaging and gas chromatography–mass spectrometry (GC–MS)) were carried out in the laboratory on a few selected samples. The

choice of samples was based on representativeness and analytical significance. Materials that came loose during restoration were also taken into account to avoid damage to the collections.

The types of samples can be divided into two macro-categories: (1) designs or prints on paper and (2) polychrome textiles and fabrics. Table 1 and Figure 4 display a selection of significant investigated objects and depict the kind of materials involved in the Fortuny printing; the performed analysis will be described throughout the text.

Table 1. Materials were chosen for characterisation. Three different microscopes D (DINO), T (Olympus) and S (Zeiss) were used for optical microscope analysis. The symbol ‘*’ indicates the use of μ -Raman spectroscopy.

Object	Object Code	Description	Analyses				
			OM	XRF	ATR_FTIR	Raman	GCMS
Printed paper	234 D	Printed paper with floral festoon motif.	x ^S		x	x *	x
	462 D	Printed paper with a geometric floral motif, bordered by a square frame.	x ^S		x		x
	567 D	Paper printed with a geometric pattern of repeated triangles forming a circle.	x ^S		x	x *	x
	350 D	Glossy paper printed with a floral motif together with two mirrored deer in the centre of the design reminiscent of the style in Parisian Gothic churches.	x ^D	x	x		
	68 D	Printed paper with the coat of arms of the Franco regime in the 1938–1945 version according to the so-called ‘abbreviated’ model, which became very popular due to its wide circulation [13].	x ^S	x	x		x
	298 D	Fragment of paper printed with circular motifs and representations of small moons.	x ^D	x	x	x *	
	130 D	Paper printed with stylised roses in arabesques.		x	x	x	
Polychrome fabrics	215 T	Printed fabric with a floral pattern, whose main design appears to be a stylised representation of a pineapple.	x ^T		x	x	
	268 D	Fragment of blue textile with designs in red.	x ^T	x	x		x
	226 D	Orange-coloured fragment of fabric with a softer light-coloured part on the surface and a metallic grey corner.	x ^T	x	x		x

A digital contact optical microscope Dino-Light was used for in-situ preliminary observations in visible and UV light (390–400 nm) [14]. Sample observation by ZEISS SteREO Discovery (Jena, Germany), using a V8 benchtop microscope equipped with ZEISS Achromat S objectives and a 3.2 Mpx ZEISS Axiocam 208 colour camera, were carried out in the laboratory. Finally, textile and fibre samples were observed with a transmission Olympus (Tokyo, Japan) BX41 microscope under polarised light.

A portable Bruker ALPHA II Fourier-Transform IR Spectrometer was used in ATR-FTIR mode both on-field and in the laboratory. ATR-FTIR analysis was recorded in the spectral range from 4000 to 400 cm^{−1} at 4 cm^{−1} resolution, using a diamond crystal, with

48 scans for in-situ analysis and 128 scans for laboratory analysis, and the spectra were elaborated by OPUS software (Version 8-2-28).

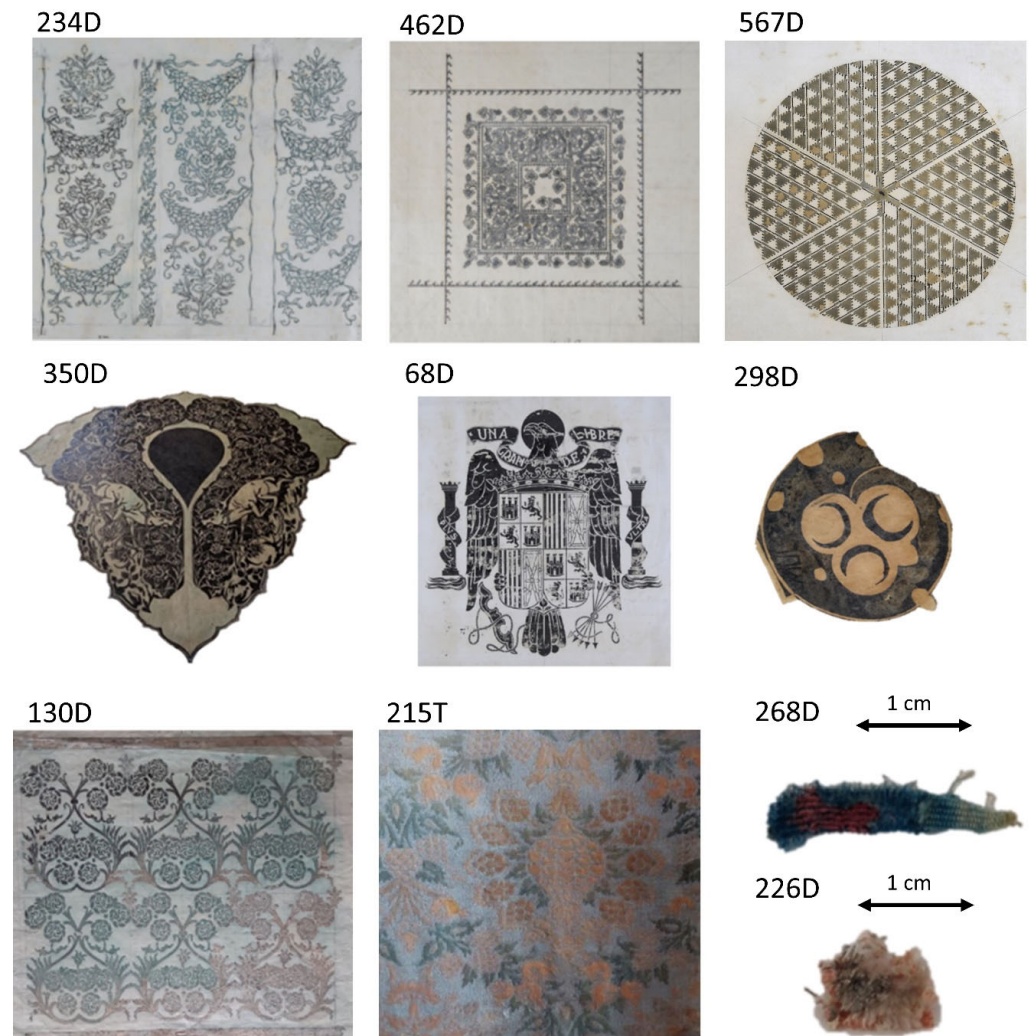


Figure 4. Images of the analysed objects, as described in Table 1.

The portable Raman instrument BRAVO by Bruker (Billerica, MA, USA) was used in situ. The DuoLaser™ excitation (785 nm and 852 nm) provides maximum sensitivity over a wide spectral range and thus guarantees maximum unambiguous verification. [12]. It is equipped with SSETM (Sequentially Shifted Excitation), a patented method of fluorescence attenuation based on controlled changes in laser temperature. The analysis spot size was 1 mm, with integration time between 2800 and 3200 ms (optimised for each spot), and five sample scans.

Micro-Raman measurements were carried out on collected samples with a Thermo Scientific Raman Microscope DXRTM3, a trinocular dispersive Raman microscope operating in reflected light at 10×, 50× at 532 nm and 750 nm, to better observe the Raman features [13]. Scans were collected from 100 to 3300 cm^{-1} at a resolution of 4 cm^{-1} , laser power 0.9 mW, aperture 50 μm pinhole, for two to four exposures with exposure time of 45 s. Naturally detached micro-samples from different paper prints were analysed. The same methodology was used on fragments of polychrome fabrics.

The X-ray fluorescence elemental spectrometry (XRF) was applied to spots on samples collected from the museum objects. On paper fragments and textiles, both analysis spots and elemental mapping were carried out. The CRONO Device SN01997 was used. Spots were acquired at 40 kV, 0.1 mA, 120 s and 1 mm spot size; mapping was performed at

40 kV, 0.15 mA, 10 ms/point, 1 mm spot size and 0.2 mm steps. Esprit software was used for data elaboration and semiquantitative evaluation of the spectra was carried out. The elemental maps were displayed, considering abundance of the corresponding oxides using the algorithms of the Esprit software. The evaluation is semi-quantitative and allows only the visualisation of elemental distributions of the studied objects.

GC–MS analysis was performed on small amounts (0.2 mg) of selected samples according to a procedure developed and tested on traditional and modern materials [15,16], among them Fortuny's tempera paints from the Fortuny Museum [17]. A Thermo Scientific (Waltham, MA, USA) Trace GC 1300 system equipped with a Thermo Scientific ISQ 7000 MS detector with a quadrupole analyzer was used for gas chromatographic–mass spectroscopy (GC–MS) analysis of selected samples. Helium was the carrier gas (1 mL/min flow rate), and the GC separation was carried out on a DB-5MS Column (30 m length, 0.25 mm, 0.25 μ m—5% phenyl methyl polysiloxane). The temperature was from 80 °C to 315 °C with a ramp of 10 °C, which was kept isothermally for 2 min. The MS ran in Full Scan mode (m/z 50–600) at the speed of 0.2 scans per second.

The samples were pre-treated with 30 μ L of MethPrepII (a methyl-esterifying agent consisting of a 5% solution of *m* (Trifluoromethyl)phenyltrimethylammonium hydroxide in methanol) and 10 μ L of the internal standard were added to each sample [16].

The qualitative analysis involved the preparation of standard solutions such as unsaturated fatty acid (UFA), saturated fatty acid (SFA), glycerol (Gly), and nonadecanoic acid as internal standard (C19). The compounds were identified as methyl ester (following a transesterification) by comparing their mass spectra to those in libraries created by the authors as well as those from NIST and MS Search 1.7. The Chromeleon 7 software was used for acquisition and identification. The molar ratios among the most important fatty acids considered were:

- A/P (azelaic to palmitic acid) to distinguish between egg paint ($A/P < 0.3$) and oil paint ($A/P > 1$) [16];
- P/S (palmitic to stearic acid) to identify the type of oil used, as SFA does not change during film formation processes;
- A/Sub (azelaic to suberic acid) to provide an assessment of any pre-heating processes that may have occurred in the preparation of the oil;
- D/P, the ratio of dicarboxylic acids (suberic, sebacic and azelaic) to palmitic acid, which gives a good estimate of the degree of drying of the oil over time, since the percentage of dicarboxylic acids increases as the fatty di-acids are formed during auto-oxidation.
- O/S (oleic to stearic acid), an index of oxidation used to define the maturity of a film (values around 0.1–0.2 are common for aged samples).

3. Results

3.1. Design, Pattern and Print Papers

Figure 5 shows images of paint layer samples collected from the investigated papers. Many of them were already detached due to low adhesion to the paper substrate, and the paint layer of 68D was collected by scalpel. Papers 298D and 350D were not sampled, but the entire objects were investigated by non-invasive analyses.

The paint sample from paper 234D appears green in colour; there are dark green and blackish particles in the darker areas, which makes them appear like a degradation-induced darkening of the original green hue. In the paint layer sample from paper 462D, there are no green particles, but mostly dark grains with jagged and irregular edges. White grains in the form of well-attached flakes are present, looking like small salt deposits formed on the surface of some grains. Possibly, that side of the sample was exposed to external degradation agents and deposition of marine aerosol. The paint layer of 68D appears to have grains with sharply fragmented, not fractured, regular edges. The surface of the grains appears shiny with intrusions of iridescent green-yellow grains. The paint layer of 130D is similar to that of 234D, but with a more brilliant appearance, with fragments of

colours detached easily from the thin translucent paper substrate. The colour has a shiny look, with a metal/glitter effect. Due to the presence of at least a double layer, the sample from paper 567D exhibits two distinct colours on the front and rear sides. The dark side looks like samples of 462D and 68D, without the presence of green intrusions. Observation of papers 298D and 350D highlighted that the colour is adherent to the substrate, unlike in the other samples. They look like traces of ink on paper, whereas the others show the use of a paint of greater thickness. On the surface of 298D, the presence of bright white grains, possibly salts, is visible.

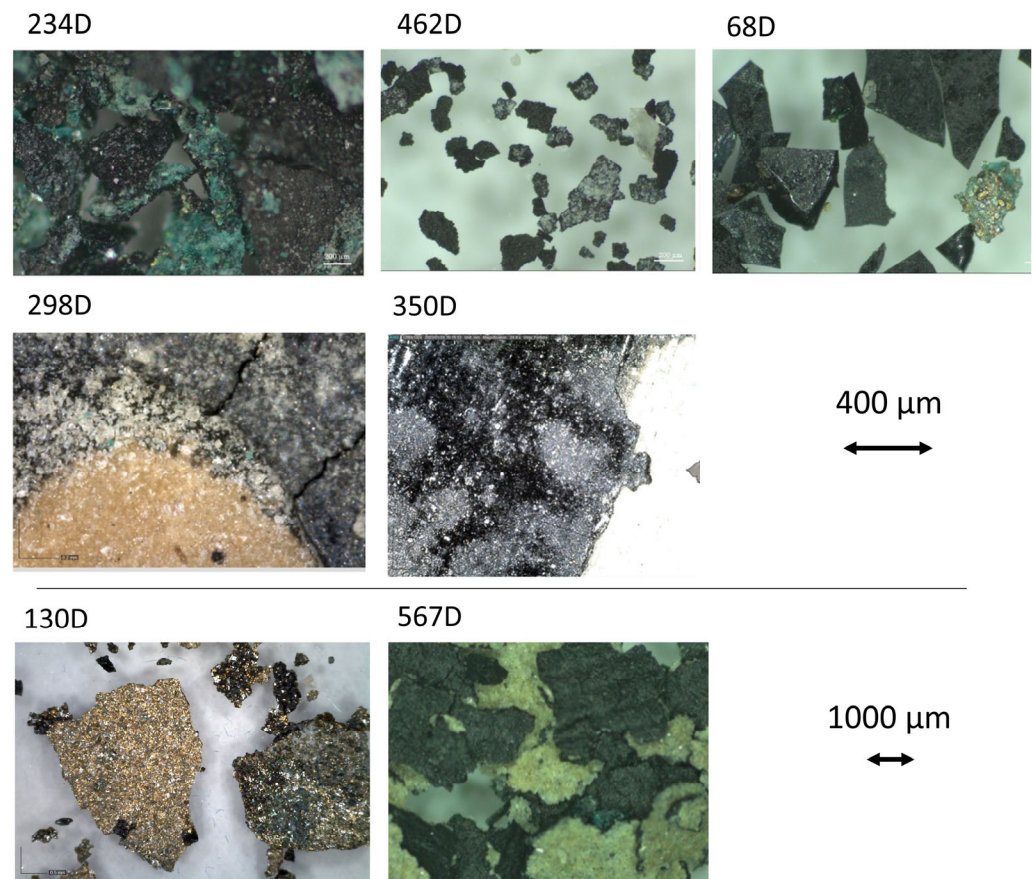


Figure 5. Optical images by dino-lite digital microscope (298D, 350D) or stereomicroscope (the others) of paint layers and paper samples. The written codes refer to the object code as listed in Table 1 and shown in Figure 4.

The observations of the papers stored in the museum pointed out the recurrent use of dark inks on papers (e.g., 298D and 350D) to obtain complex drawings. Many of them show pencil traces of pattern corrections and annotations. Moreover, the use of thick layers of paint on translucent papers, that exfoliate easily from the surface, were observed in many other collected items (e.g., samples 234, 462, 68, 130 and 567D). Possibly, the two kinds of paper were used in different phases of the printing process.

As shown in Table 1, the XRF elemental analysis was performed on four samples, collected from 68D, 130D and 350D (Figure 5), and on the entire object 298D, whose surface underwent XRF mapping.

The paint layer of 68D shows a high concentration of Ca, S and Si. They may be related to the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), silica or talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), often used as fillers and extenders in 20th-century paint/pigment production [18]. Mn is the metal present in the highest concentration, so it is conceivable that the main colour is manganese dioxide (MnO_2), used as a black pigment in European oil painting since the nineteenth century [19]. The paint layer of 130D shows a strong presence of Si, Ca and Cu. The high

concentration of Si and Ca could be associated with silicates and chalk/gypsum added as fillers. The Cu peak is visible, so the presence of a copper-based green pigment could be assumed. Technical literature describes how copper catalyses the oxidative degradation of pigments [20], increasing fragility and discolouration [21,22] due to its high catalytic activity even at a neutral pH. Its degrading effect is particularly amplified in alkaline conditions due to an increased production of hydroxyl radicals [23]. This process might explain the iridescent appearance of the design on the printed sheet. The presence of Fe may be due to the addition of black gall ink or FeSO_4 to create the shade of green desired by the artist [24].

In the small sample collected from 350D, the presence of Fe may be due to a small addition of iron oxide (Fe_3O_4) to the main pigment, or more probably FeSO_4 , given the strong covering power of this pigment. The presence of Pb and Zn could be related to compounds intentionally (e.g., paint admixtures providing specific nuances or metal soaps) or unintentionally (e.g., contaminants in the raw materials) added [23].

The elemental map of 298D is shown in Figure 6. Looking at the elemental distribution, Fe, P and Ca are present in black areas. The presence of Cu, Si and S was detected all over the surface, although a higher concentration was found in printed areas. The presence of Ca and P may suggest that the ink used is a bone black ($\text{Ca}_3\text{O}_8\text{P}_2$) mixed with iron- and copper-based pigments.

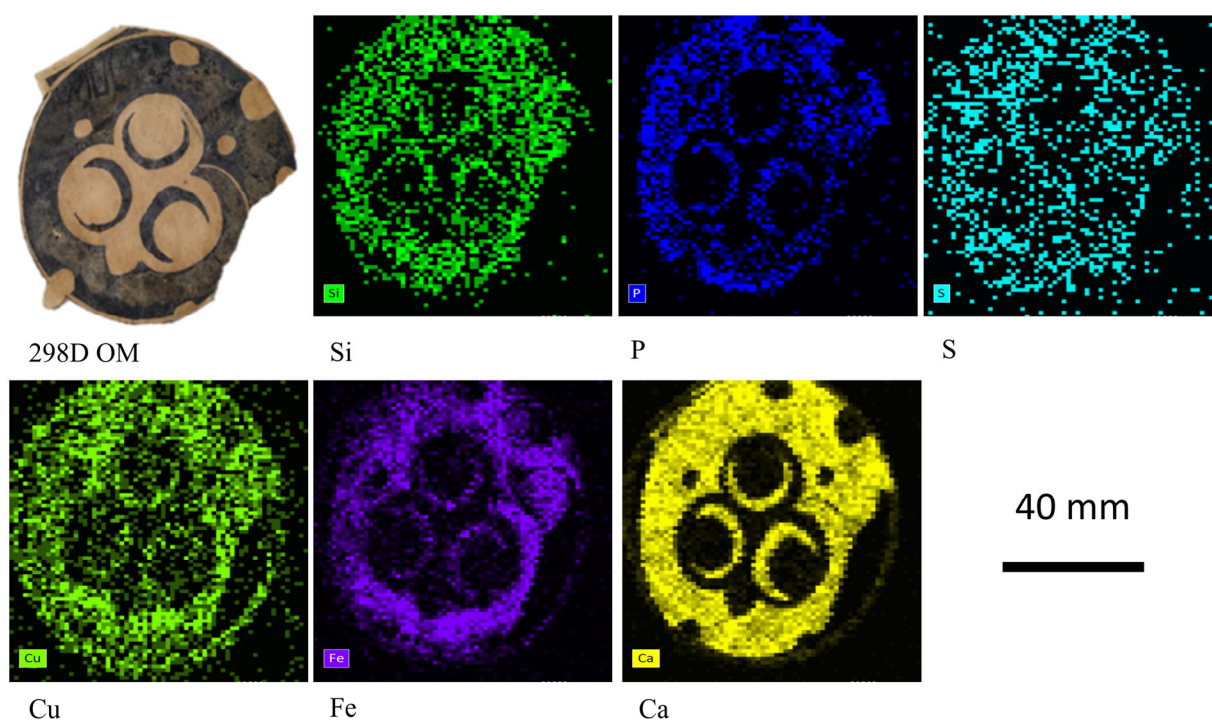


Figure 6. Visible image and XRF elemental maps of 298D. Starting from the first row: visible image; Si(green), P (blue), Cu (light green); Fe (violet); Ca (yellow); S (light blue).

Figure 7 displays some relevant FT-IR spectra. The strong band around 1010 cm^{-1} , present in all the spectra and the shoulder at 1086 cm^{-1} , together with the bands at 559 and 600 cm^{-1} of the phosphate group and the presence of P detected with XRF, coincide with a non-stoichiometric poorly crystalline apatite [25]. The presence of non-stoichiometric apatite peaks may indicate that some bone residues were not completely burnt. A fresh bone contains a non-stoichiometric, poorly crystallised apatite consisting of nanometric crystalline grains. As a result of natural diagenetic processes, or by thermal heating for the pigment creation, recrystallisation of apatite occurs, resulting in an ordering of the crystal structure and an increase in crystalline grains.

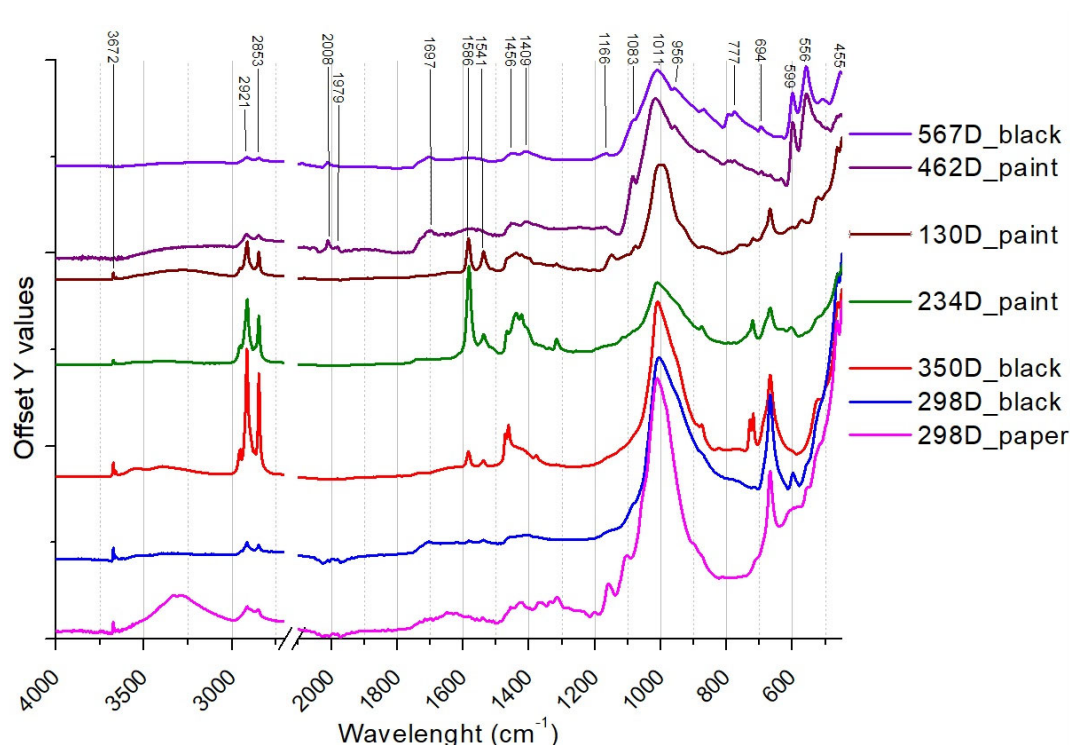


Figure 7. ATR-FTIR spectra of paint layers from 567D, 462D, 130D, 234D and on black-inked areas of 350D, 298D and paper of 298D.

Examples of spectra collected on clean paper of 298D and on black areas of 298D are shown. The typical features of cellulose are recognizable in paper 298D [26]: OH stretching at 3200–3400 cm^{-1} ; the CH stretching at 2850 and 2920 cm^{-1} ; the H_2O bending at 1635 cm^{-1} (in new papers this peak is often found around 1625 cm^{-1} , so here the displacement might be caused by the ageing of the paper); $\text{CH}_2\text{-COH}$ bending at 1420 cm^{-1} ; a small triplet at 1370, 1335 and 1316 cm^{-1} of CCH–COH bending; the COC stretching at 1150 cm^{-1} ; and a broad small peak at 896 cm^{-1} due to amorphous cellulose (this peak broadens with paper degradation) [26]. Small peaks attributable to calcium carbonate can be seen at 1420, 875 and 715 cm^{-1} , and the same peaks are more visible in 298D_black, 350D_black and in the paint layer of 234_D. The XRF results and the 298D_black FT-IR spectrum indicate the possible use of iron gall ink (peaks of FeSO_4 at 1093, a shoulder around 980, 525 cm^{-1}); the peaks are not present in 298D_paper, but are visible in 350D_black. In 350D_black the 1586 cm^{-1} peak is visible, possibly related to the presence of stearates in the binder. The coloured areas of 350D seem to be in between the inked paper and the paper covered by thicker layers. A broad band at around 1580 cm^{-1} was assigned to the C–O stretching of amides, and N–H 1538 cm^{-1} are indicative of the presence of gelatin or animal glue. The sharp band at 2008 cm^{-1} is characteristic of isocyanate (RNCO), thiocyanate (RSCN) and isothiocyanate (RNCS) groups bound to protein degradation products [27–29]. The presence of a proteinaceous substance could be related to the use of gelatine: the characteristic peaks were observed in spectra of the samples collected in papers 350D, 234D and 130D. These papers showed a glossy, translucent consistency.

The IR spectra of the thick paints had recurrent profiles, as can be seen for samples from 234D, 130D, 567D and 462D. In the spectra of the paint layers of 234D and 130D, the characteristic –CH stretching vibration bands at 2926 cm^{-1} (asymmetric stretching CH_2) and 2854 cm^{-1} (symmetric stretching CH_2) and the C=O stretching absorption of the triglyceride ester linkage that appears at ~ 1740 cm^{-1} are visible together with the band at 721 cm^{-1} corresponding to CH_2 rocking; they are related to the fatty acids and indicate the use of a lipidic material as the binding medium. The minor peaks around 1600 cm^{-1}

are attributed to the absorption of metallic soaps (1582 cm^{-1} corresponding to asymmetric carboxylate stretching eventually covered by amide peak when present, and at 1409 cm^{-1} corresponding to symmetric carboxylate stretching) [30], which were often used as a dispersing agent in oil-bound colours. The band at 1585 cm^{-1} might correspond to copper stearate, too [31]. A mixture of several green copper-based pigments in an oily binder could lead to fatty acid salts of metal cations due to a reaction with free fatty or dicarboxylic acids remaining after the ageing of the drying [30]. The dark colour and the presence of Cu in XRF analysis, together with the presence of a peak at 1580 cm^{-1} , lead to the hypothesis of the possible presence of degraded verdigris, which takes on a darker colour with age [32]. The literature attributes the chromatic alteration to the transient formation of Cu(I) in the copper complexes of the pigment/oil system, initiated by ambient light absorption through ligand-to-metal charge transfer, which favours the decarboxylation of the copper complexes leading to the reduction of Cu(II) into Cu(I). Dioxygen can react with partially decarboxylated dimers to form peroxy-Cu dimer complexes that can be responsible for the darkening [33]. The presence of talc is suggested by the peak at 3672 cm^{-1} due to -CH stretching, and the peaks of -CH bending at 1010 cm^{-1} (partially covered by residual signal of cellulose of the paper) and 667 cm^{-1} . Calcite is probably also present, given the peaks around 1400 cm^{-1} and 875 cm^{-1} of CO_3^{2-} stretching and bending.

For paint samples from 567D and 462D (Figure 7), the stretching vibrations of calcium carbonate CaCO_3 at 1456 , 1411 and 872 cm^{-1} are characteristic of carbonated hydroxyapatite, indicating the use of bone black [34]. The presence of the CH stretching peaks at 2916 and 2845 cm^{-1} and the C=O stretching at 1700 cm^{-1} are compatible with the use of siccativ oil as a binder.

Many of the specimens are strongly fluorescent and the μ -Raman analysis provides few readable spectra. Based on several spots collected on the surfaces of 298D and 567D (Figure 8), the characteristic spectrum of ivory black was registered on darker areas, confirming the assumptions made in the ATR-FTIR analysis. The ivory black has two broad peaks around 1580 and 1325 cm^{-1} [35] due to their amorphous carbon composition [28]. In the paint sample collected from 234D (Figure 5), small grains of an intense blue colour were observed under the microscope. The spectrum profile indicates the presence of the oil binder, given by the intense -CH stretching peaks observed in the region between 3000 cm^{-1} and 2800 cm^{-1} [36]. Two broad and overlapping bands possibly related to amorphous carbon, with intensity maxima at approximately 1580 cm^{-1} (G band) and 1350 cm^{-1} (D band), can be observed, corresponding to the black grains. The sharp single signal emerging at 1086 cm^{-1} indicates the presence of calcite [37]. The presence of gypsum is also probable, given the main peak around 1008 cm^{-1} related to the stretching of the SO_4^{2-} ion, and the fingerprint peak at 670 cm^{-1} . The peak at 546 cm^{-1} together with the weak one at 258 cm^{-1} might indicate the presence of ultramarine blue ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$) [38]; to confirm, another spectrum was collected in the same point with the 750 nm laser and the 1346 cm^{-1} , and 360 cm^{-1} peaks became visible [39,40]. The ultramarine was probably added to the main green copper-based pigment in order to obtain a bluish hue.

GC-MS chromatograms displayed in Figure 9 highlight the presence of saturated long-chain fatty acids, the presence of nonanoic (C9), myristic (C14), palmitic (C16) and stearic (C18) and unsaturated long-chain fatty acids such as oleic (C18:1), linoleic (C18:2), and linolenic (C18:3), characteristic of drying oils [16,41]. The presence of dicarboxylic acids such as suberic (2C8), azelaic (2C9) and sebacic (2C10) indicate that tertiary oxidation reactions of unsaturated oleic, linoleic and linolenic acids are taking place, related to the ageing process of drying oil-based binders. Oxidation products are detected, and in particular, oxidised octadecanoic acid is present in the form of oxy-, hydroxy- and epoxy-compounds. They are formed during propagation reactions and are produced by the oxidative cleavage of UFAs [42,43].

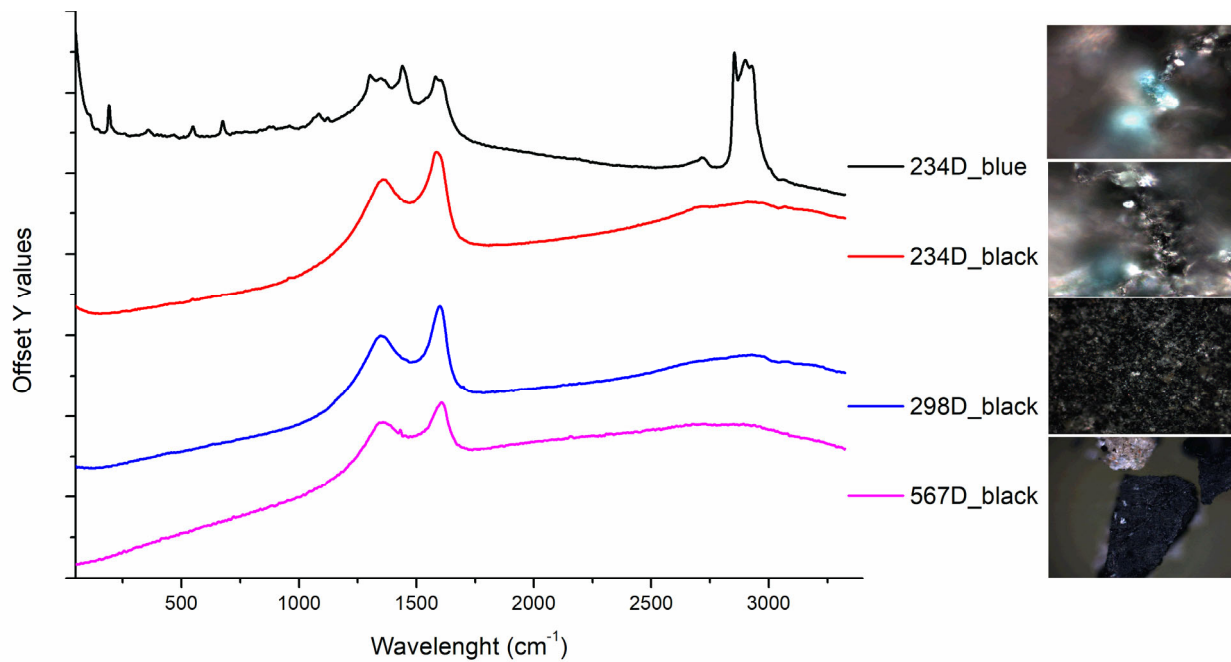


Figure 8. μ -Raman analysis of blue and black grains of sample 234D; black grains of 298D and 567D (10 $\times$).

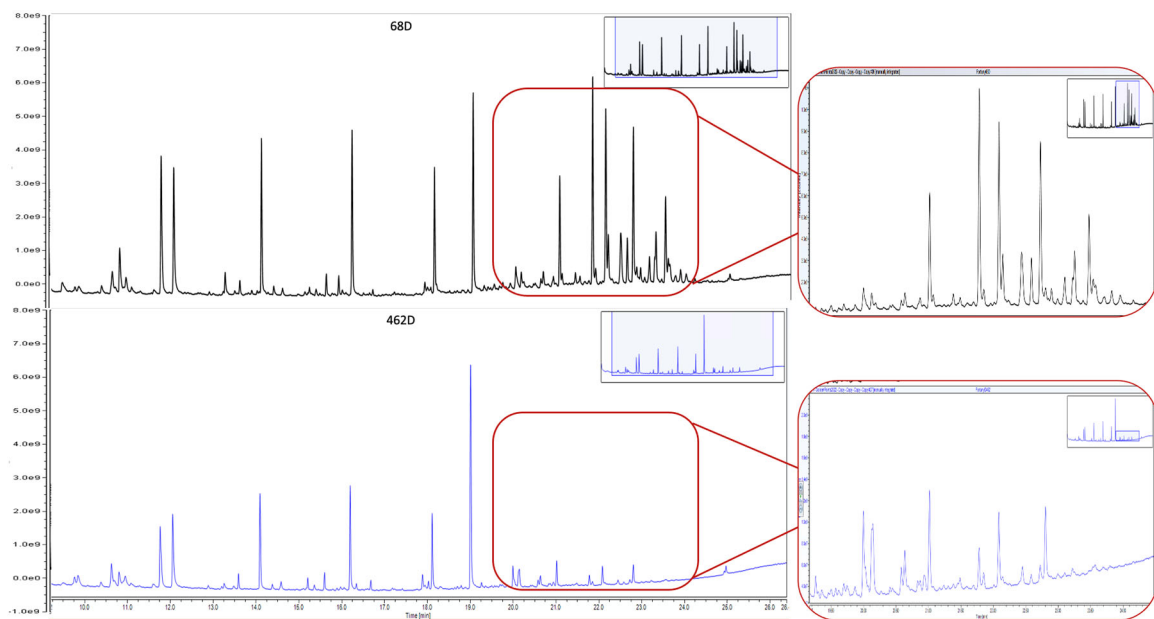


Figure 9. GC-MS chromatogram of samples 68D and 462D: analyses made it possible to observe the characteristic peaks corresponding to a terpenic fraction.

Besides the lipidic fraction, all samples had a terpenic fraction, indicated by the characteristic peaks of the diterpenes: pimaradienic (isopimaric and sandaracopimaric acids), abietadienic and trienic acids (abietic, dehydroabietic and 7-oxo-dehydroabietic acids). The occurrence of diterpenoid acids with abietane skeletons is indicative of a resin obtained from trees of the *Pinaceae* family [44]. The resin was identified as colophony (also known as rosin), used since ancient times in paper waterproofing, artistic varnishes and as a binding medium mixed with oils [45]. In particular, a sample from 68D showed an abundant terpenic fraction (Figure 10).

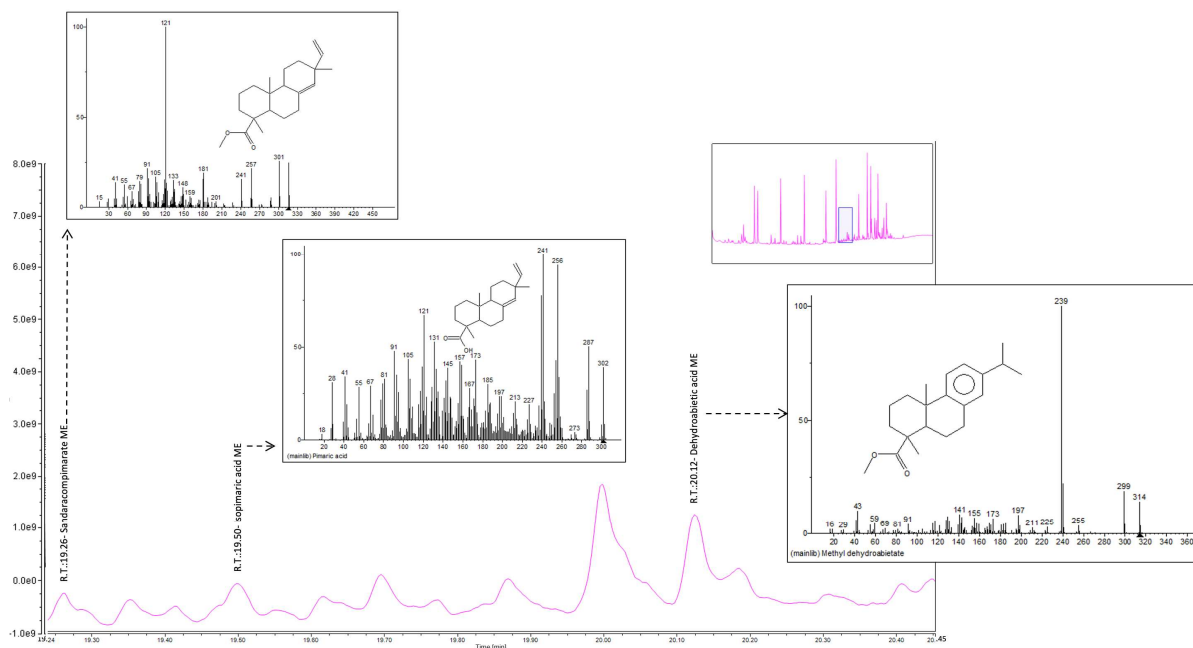


Figure 10. GC–MS chromatogram of sample 68D in which colophony was identified by its markers: mass spectrum and chemical structure of sandaracopimarite ME; mass spectrum and chemical structure of isopimaric acid ME; mass spectrum and chemical structure of dehydroabietic acid ME.

The calculated molar ratios and the concentration of the different components for all the samples are reported in Table 2. The molar ratio values have confirmed the presence of drying oil ($A/P > 1$), most likely linseed oil ($P/S = \sim 1.6 \pm 0.3$).

Table 2. List of compounds identified by GC–MS and their concentrations calculated in percentage. The reported results were calculated by the chromatograms of paint layer samples collected from the papers 567D, 462D, 68D and 234D. $\checkmark$ = present; - = not detected; A/P = (azelaic/palmitic); P/S = (palmitic/stearic); A/Sub = (azelaic/suberic); O/S = (oleic/stearic); D/P = (dicarboxylic/palmitic); $\%D$ = (sum of the percentages of the following dicarboxylic acids: suberic, azelaic and sebacic); ME = methyl ester; diME = dimethyl ester.

	Identified Compound	<i>m/z</i>	Paint Samples Collected from			
			567D	462D	68D	234D
Fatty acid and other compounds	Glycerol derivate	89	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Glycerol derivate	162	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Nonanoic acid, 9-oxo ME	172	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Glycerol derivate	75	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Suberic acid diME	202	6.91%	6.00%	9.57%	2.20%
	Phthalic acid diME	166	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Glycerol derivate	394	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Lauric acid ME	200	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	10-Oxodecanoic acid ME	200	-	-	$\checkmark$	-
	Azelaic acid diME	216	29.38%	25.54%	10.88%	9.13%
	Benzoic acid, 3,4-dimethoxy ME	182	-	$\checkmark$	$\checkmark$	-
	Caprylic acid ME	144	-	$\checkmark$	$\checkmark$	$\checkmark$
	Sebacic acid diME	230	3.64%	1.46%	3.46%	0.81%
	Myristic acid ME	242	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Aleuritic acid ME	304	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Palmitic acid ME	270	17.94%	25.54%	26.94%	44.99%
	Margaric acid ME	270	-	$\checkmark$	-	$\checkmark$
	Elaidic acid ME	296	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
	Linoleic acid ME	292	6.92%	3.50%	1.55%	1.89%

Table 2. Cont.

	Identified Compound	m/z	Paint Samples Collected from			
			567D	462D	68D	234D
Fatty acid and other compounds	Oleic acid ME	296	1.75%	0.55%	0.56%	14.53%
	Linolenic acid ME	294	0.05%	0.30%	0.27%	0.01%
	Stearic acid ME	298	20.94%	19.22%	20.90%	24.53%
	Nonadecanoic acid ME (IS)	312	✓	✓	✓	✓
	Sandaracopimarate ME	316	✓	✓	✓	✓
	Isopimaric acid methyl ester	316	✓	✓	✓	✓
	Oxiraneoctanoic acid, 3-octyl ME	312	✓	✓	✓	✓
	Eicosanoic acid ME	326	-	-	-	✓
	Glycerol	524	✓	✓	✓	✓
	Dehydroabietic acid ME	300	✓	✓	✓	✓
	Octadecanoic acid, 9,10-epoxy ME	312	✓	✓	✓	-
	Arachidic acid ME	312	✓	-	✓	-
	Methyl 6- dehydrodehydroabietate	306	✓	-	-	-
	Tetradhydroabietic acid, 7-methoxy ME	314	✓	✓	✓	-
	Octadecanoic acid, 9,10-dihydroxy ME	330	✓	✓	✓	✓
	10- Octadecanoic acid ME	354	✓	-	-	✓
	Behenic acid ME	340	✓	✓	✓	-
	7-Oxodehydroabietic acid ME	328	✓	✓	✓	-
	7,15-Dimethoxytetradhydroabietic acid ME	332	-	✓	✓	✓
	15-Hydroxy-7-oxodehydroabietic acid ME	330	-	-	✓	✓
Molar ratios among fatty acids	Octadecanoic acid, 9,10-oxo- ME	310	✓	-	✓	-
	A/P		1.64	1.01	0.92	0.20
	P/S		0.86	1.33	1.29	1.87
	A/Sub		4.25	4.30	2.58	4.16
	O/S		0.08	0.03	0.03	0.08
	D/P		2.23	1.30	1.40	0.27
	%D		39.93	33.24%	37.77%	12.14%

In particular, the A/P ratios in paint layer samples of 567D and 462D have values greater than 1, confirming the presence of drying oil, and the P/S value indicates a linseed oil. A/sub < 6 indicates that the drying oil was pre-heated (i.e., a pre-polymerisation of the binding material took place) [45], while the high D/P ratio confirms that the lipidic fraction underwent oxidation. The D/P ratio of 462D is lower than D/P in sample 567D, and consequently, so is the %D value. However, the paint layer of 462D shows an advanced state of oxidation. In the paint sample from 68D, the A/P ratio is slightly less than 1 since the rate of oxidation, degradation, polymerisation, the pre-heating treatments and the presence of pigments and driers have a significant impact on this ratio. The degree of oxidation is very similar to that of the sample from 462D, given the values of the D/P and O/S ratios, suggesting a similar ageing condition. The ratios for the paint layer of 234D are very different from the others, with an A/P < 1, probably influenced by the oxidation products of the pigment and by the pre-polymerisation of the oil. Previous investigations suggested that zinc stearate is present in 234D, and this is confirmed by the high amount of oleic acid (14.53%), as zinc tends to form a packed structure that can trap oleic acid, thus forming zinc soap [46,47].

3.2. Polychrome Textiles

Observation of 226D, 268D (Figure 11) and 215T (Figure 15) reveals tight-weave textiles (more than 8 thread/cm). In all samples, the differently coloured areas are juxtaposed and do not mix at the edges. The coloured areas of 268D appear impregnated with a dye. In the case of textiles 226D and 215T, the design of branches, flowers and pineapples appears to be printed with a full-bodied varnish on top of a coloured velvet, probably obtained from a previous dye bath. Where the paint is present, the hairs of the velvet appear crushed,

and the paint forms a crust on its surface. The layer is very cracked, having been applied on the flexible fabric. On the surface of 226D, traces of a glittery metallic paint can also be observed, similar to the one observed in paper 130D or 567D. Figure 11 shows the MO observation of the fibres of 226D and 268D, identifying them as silk fibres with smooth surfaces, structureless, triangular-shaped transparent rods [48].

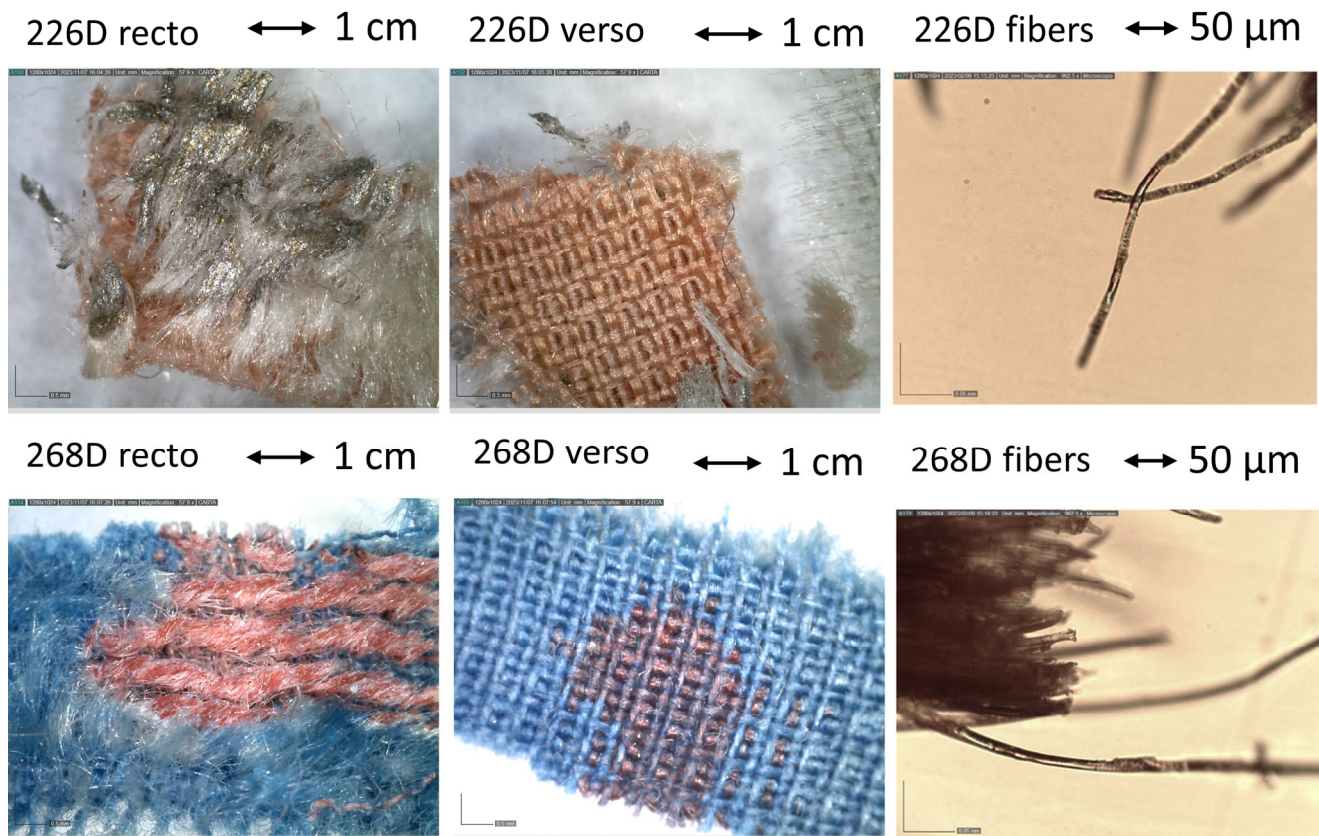


Figure 11. Transmitted light microscope images of polychrome fibres of 226D and 268D samples.

XRF imaging performed on textile fragments 226D and 268D are shown in Figures 12 and 13, respectively. Cu and Zn were detected in the light-red areas of 226D and 268D. Ca and S are distributed throughout the sample except in the dark, silver-coloured part, possibly related to the use of gypsum or chalk, often used in dyeing processes as a fixing agent [49]. Traces of Co were detected, too. The blue fabric of 268D shows a strong presence of Fe, with the exception of a red area, leading to the assumption that Prussian blue was used. The red area of 268D contains Cu and Zn.

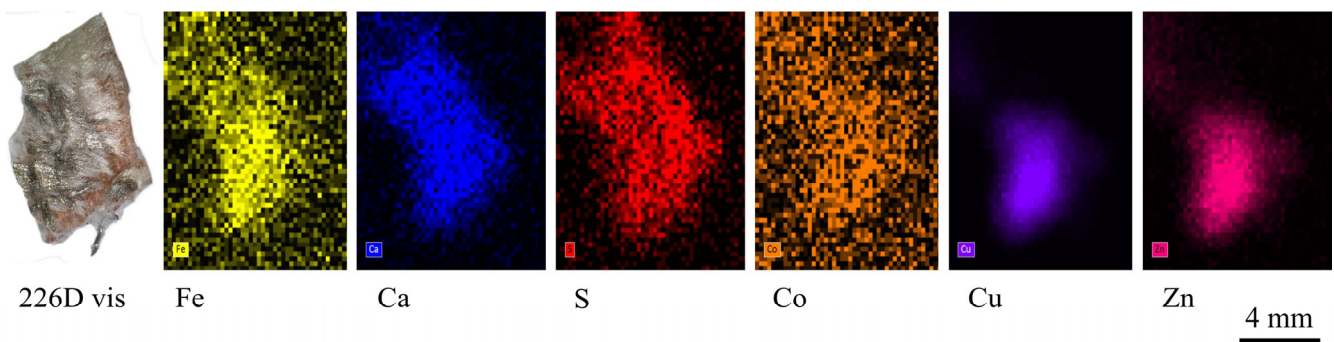


Figure 12. Visible light image of sample 226D and elemental maps. Fe (yellow), Ca (blue), S (red), Co (orange), Cu (violet), Zn (purple). Scale bars 4 mm.

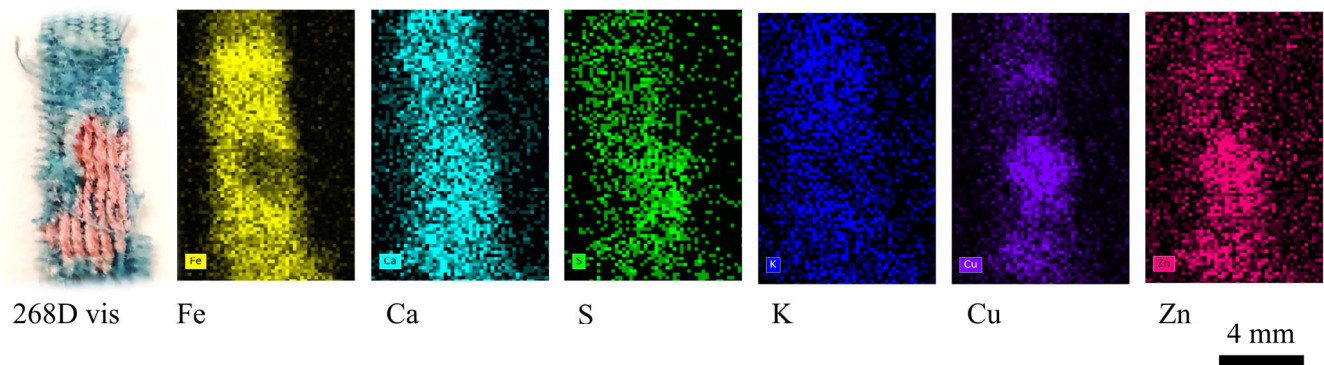


Figure 13. Visible light image of sample 268D and elemental maps. Fe (yellow), Ca (light blue), S (green), K (blue), Cu (violet), Zn (purple). Scale bars 4 mm.

The ATR-FTIR spectra of the analysed textiles (Figure 14) show the peaks typical of dyed silk. The characteristic bands of silk fibroin at 1622 cm^{-1} , 1508 cm^{-1} and 1225 cm^{-1} are respectively assigned to amide I, II and III [50]. The adsorption peaks at 996 and 976 cm^{-1} are typical of glycine and alanine sequences in silk fibroin [51,52]. In addition, there is a peak of -OH stretching at 3270 cm^{-1} , vibrational stretching and bending of -CH in the region $1470\text{--}1350\text{ cm}^{-1}$ and stretching of -CO in the region between 1200 cm^{-1} and 1000 cm^{-1} [53,54]. The peak at 2088 cm^{-1} is related to the $\text{C}\equiv\text{N}$ stretching mode and is characteristic of Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) [55,56], a result consistent with the large presence of Fe found with XRF. In this case, the employed GC-MS methodology enables us to identify only traces of fatty acids in samples collected from 226D and 268D fragments.

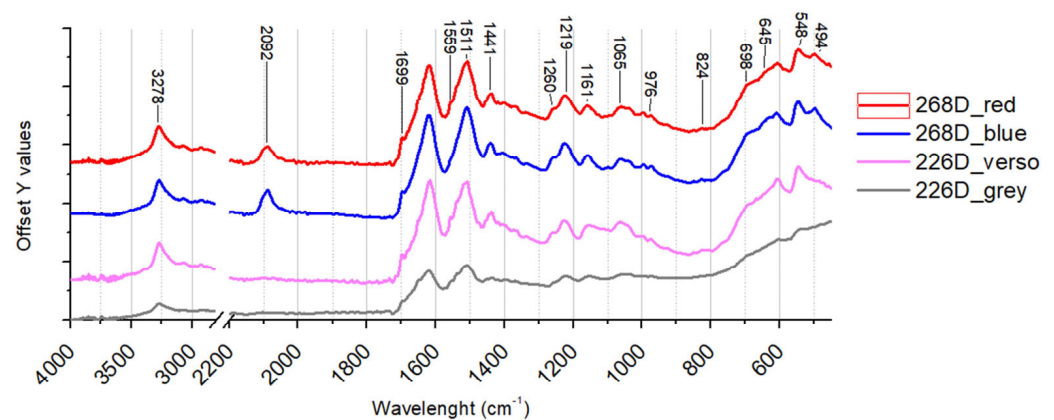


Figure 14. ATR-FTIR spectra of samples 226D and 268D exemplificative of the silk textiles.

The tablecloth 215T was analysed in the museum with a portable Raman and in-situ ATR-FTIR (Figure 15). The resulting Raman spectra, three of which are displayed in Figure 13 as significant examples, have a high similarity to the spectrum of a linseed oil reference, particularly concerning the CH bending vibrations at 1445 cm^{-1} and stretching vibrations around 2900 cm^{-1} , and the stretching of the $\text{C}=\text{C}$ bonds at 1603 cm^{-1} [57]. The peaks of amide (I) at 1664 cm^{-1} and amide (III) at 1223 cm^{-1} associated with silk are present. In addition, the presence of calcite is noted, given by the characteristic intense peak at 1082 cm^{-1} . This spectrum also shows the two characteristic peaks of Prussian blue at 2156 cm^{-1} and 2090 cm^{-1} , and at 538 cm^{-1} [35,40,58,59].

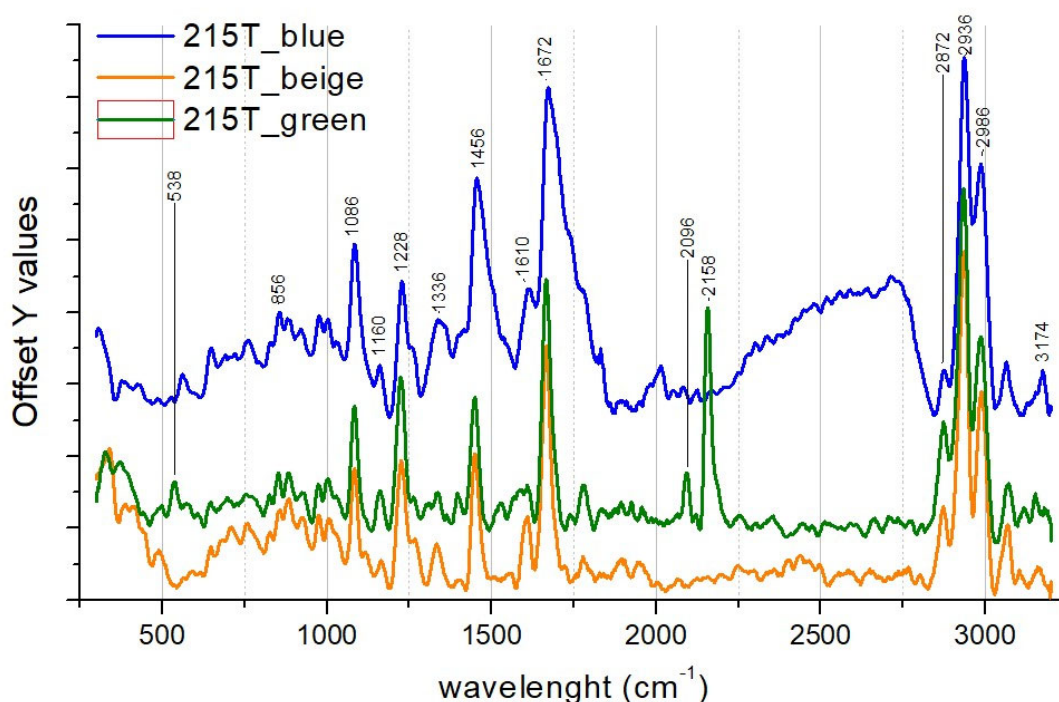


Figure 15. Raman spectra collected in different-coloured areas of the tablecloth 215T.

4. Discussion

Table 3 briefly summarises the results obtained from the analyses of the paper and textile samples.

Analyses show that almost all the colours are mixtures of pigments, probably mixed by Fortuny himself to create the colours he desired.

The morphology of the paint and the effect of the colour on the paper allow two types of samples to be distinguished: (i) papers printed with liquid inks that partly impregnated the substrate, and partly formed very thin layers on the surface; (ii) translucent papers on which a thick paint layer was printed, with a metallic effect, and easy to peel off. Sample 68D appears to be somewhere between the two, showing a coloured layer that is not well adhered, but it is very thin and of similar composition to inked papers (ivory black was identified in dark areas of samples 68D, 298D and 350D).

The inked papers (298D, 350D) display floral or geometric patterns and show pencil traces of revisions and corrections. It can be assumed that these are prints of original drawings by Fortuny, printed to see the design effect before creating the *pochoirs* and stored in portfolios. Nevertheless, these black drawings on thin or translucent paper could have been used to impress the *burattoes* coated with photosensitive gelatine, and to obtain the fabric strip *pochoirs*, too.

In the thicker paint layers of 462D and 567D, two main pigments were identified: ivory black and green copper-based pigments, probably verdigris which degraded to a darker brownish colour [33]. Samples 234D and 130D show similar compositions, with the presence of ivory black and small inclusions of blue grains. The presence of Si and S in XRF analyses suggests the use of ultramarine. Inorganic compounds such as calcite and talc were found in the sample, which were used as common fillers and extenders in commercial paint/pigment productions; their additions in the colours modify visual characteristics (e.g., lightening, deep hue) and adulterate pigment/dye formulations mixing cheap colours, and thus reduce manufacture costs [17]. GC–MS analysis made it possible to identify the binders present in the colours as a mixture of linseed oil with a diterpenic resin from the Pinaceae family. The ratio of the two binders varies from sample to sample, as evidenced by the large terpene fraction found mainly in sample 68D. The resin used was identified as colophony, often used also in paper waterproofing.

Table 3. Summary table of obtained results. n.d. = not detected.

Object Code	OM	XRF	ATR-FTIR & Raman Spectroscopy Raman	GC-MS
298D	White brilliant grains on the paper surface. Black areas.	Ca, Ti, Si, Fe, P, Cu	Bone Black (ivory), calcite, talc, zinc stearate, organic binder	n.d.
350D	Shiny areas on the surface. Presence of a black thin coloured layer. Easily detachable thin paint layer composed of grains with sharply regular edges. The surface of the grains appears shiny, with intrusion of iridescent green-yellow grains.	Si, Ca, Ti, Mn, Fe	Bone Black (ivory), calcite, talc, zinc stearate, organic binder	n.d.
68D	Easily detachable thick paint layer composed of green grains, in particular dark green particles in the dark areas.	n.d.	Bone Black (ivory), calcite, talc, zinc stearate, organic binder	Linseed oil, Colophony
234D	Easily detachable thick paint layer composed of dark grains with irregular edges. White flakes like salts deposit over some grains.	Si, Ca, Mn, Ti, S, Fe, Cu, Pb	Green copper pigments, linseed oil, calcite, talc, copper stearate, zinc stearate	Linseed oil, Colophony
462D	Easily detachable thick paint layer composed of distinct colours on the front (black) and back sides (light-brown) over a waxy paper.	n.d.	Bone Black (ivory), calcite, gypsum, linseed oil	Linseed oil, Colophony
567D	Layer of metallic paint, with iridescent and green grains that easily detach from the transparent paper. The paper has a waxy consistency.	n.d.	Bone Black (ivory), organic binder	Linseed oil, Colophony
130D	A thick layer of paint covers a dyed velvet fabric. The fabric looks shiny.	Si, Ca, Cu, Ti, Fe, Zn	Green copper pigments, linseed oil, calcite, talc, copper stearate, zinc stearate, carboxylates	n.d.
215T	Elongated smooth fibres.	n.d.	Silk, Linseed oil, Calcite, Prussian blue	n.d.
226D	Elongated smooth fibres.	Cu, Zn, Ca	Silk	Traces of fatty acids
268D	Elongated smooth fibres.	Fe, Ca	Silk, Prussian blue	Traces of fatty acids

The mixture of lipidic and terpenic fractions is one of the similarities between the composition of the colours used for paper prints and the composition of the tempera colours patented by Fortuny in 1933 and commercialised under the name of “Tempera Mariano Fortuny y Madrazo” [17]. Regarding the prints with thick paint, more than one hypothesis can be advanced: (i) paint layers to be transferred on textiles to obtain the embossed parts as partitions before reserve printing; (ii) print proofs of (i) on paper to be kept as portfolios; (iii) patterns to be used in the preparation of *pochoirs* by photographic impression. The absence of side perforations and the small size exclude the hypothesis that these were *pochoirs* themselves to be mounted on the continuous printing press.

The presence of white grains similar to salts and the lack of colour homogeneity, together with darkening of some areas, denotes a limited degradation of the paint layers. Marine aerosol, typical of the coastal areas, is an important damaging agent in Venice. It transports salts and atmospheric particles that can react with the objects in the museums and accelerate degradation. Moreover, a study of museum microclimatic agents conducted in historic Venetian palaces showed the presence of surface depositions of varying sizes, mostly consisting of Ca- and Ca-Si-rich particles, due to the degradation of the building material, i.e., the plaster on the walls [60]. Specific analyses on the Fortuny Museum microclimate are foreseen to better investigate this point.

Analyses on polychrome textiles were carried out on three silk textiles. Visual analysis of the samples showed that one colour has a very stiff appearance compared to the others. This probably corresponds to the paint layer used for partition on reserve printing. ATR-FTIR investigation did not produce any significant results for the identification of the dyes

used, as the silk peaks completely covered other absorptions related to the dye and colours. Nevertheless, Prussian blue was identified on sample 268D. Raman analysis on the 215T fabric suggests the presence of linseed oil on all three colours. Interestingly, the green hue of 215T also shows the characteristic peaks of Prussian pigments. It can be assumed that the fabric of 215T was first dyed with a brown colour, via a colour bath. Then, a blue pattern was printed using a *pochoir* with a thick paint to create a first design and the contours of the partition. The last colour, green, was probably obtained by capillary diffusion of Prussian blue, which, deposited on the leaves, coloured them up to the blue colour boundary. The dark greenish tint is obtained by the superimposition of Prussian blue over an orange base. Possibly, lightening due to the action of light and exposure to air occurs afterwards [61].

Fortuny's printing method and the steps involved can be deduced from the patents and the results. Fortuny firstly drew the patterns; some pencil drafts are conserved in the museum. The drawings were inked with ivory black-based inks, the formula of which he modified according to the desired characteristics. Prints were made from photographs and conserved as a reference, and photographs of patterns or photographic impressions of *burattoes* are present in the museum collection. The inked drawings were corrected and commented on with pencil. Both papers with semi-transparent paper coloured with a very opaque colour (ivory black) and others with non-transparent support are present in the collection. It can be assumed that the difference in the choice of paper was due to the subsequent use of the print: the transparent paper may have been used to make the *pochoir* / stencil, and the opaque paper as a sketch to see the drawings as a whole.

The second stage of the process involved the preparation of the *pochoir* (stencil) for printing on textiles. A thin, non-rigid, open-weave textile called *buratto* was selected and impregnated with a photosensitive gelatinous solution (probably created with potassium dichromate). Then, the drawing on transparent paper was placed over the gelatine-impregnated fabric and exposed to the action of sunlight: the drawing acted as a photographic matrix. The action of the sunrays hardened the gelatin areas not covered by the drawing. The *buratto* was washed and the non-exposed, water-soluble parts came off, thus obtaining the *pochoir*. Finally, the obtained *pochoir*, in the form of a strip perforated at both sides, was mounted on the continuous textile printing machine described by Fortuny in its patent, whose diagram is shown in Figure 3: the *pochoirs* were placed on rollers (d), while the textile to be printed was passed over rollers (g). The (d) rollers were probably perforated cylinders filled with colour paints. Most probably, the first rollers mounted *pochoirs* of broader weave. A thick paint, consisting of siccative oils and resins with inorganic pigments, copper-based pigments and, often, a metallic effect, poured through the stencil over the fabric to be printed, only where the design had been impressed. The paint layer created waterproof areas and boundaries needed for reserve printing on the following rollers. Further strips, made of tighter-weave *burattoes*, were mounted on the following rollers and were used to deposit liquid dyes within the boundaries of the thick paint print. The number of stencils prepared depended on the number of colours in the design. Unfortunately, neither the *pochoirs* nor the original machine has survived. Nevertheless, the museum holds prints of wide-weave fabrics that were probably used as a base for the creation of stencils, together with potassium dichromate powder and gelatine. The machine is well described in the patent pictures and, in the photographic documents of the museum, some machines similar to Perrotines for continuous printing are visible. Moreover, thick paint layers were observed both on textiles of the collection and with similar composition on papers (e.g., samples 234D, 462D, 567D, 68 D). Paper prints were probably used to evaluate the final products of the printed design and to keep them in portfolios.

5. Conclusions

Mariano Fortuny was one of the great innovators of the last century, combining different artistic disciplines to create new techniques and materials to use in his textiles. Even today, the details and materials used in his printing methods remain a secret.

Thanks to the characterisation of the materials used by Mariano Fortuny, it has been discovered that he probably used his paints for paper and textile printing. The desired hue was obtained by mixing different shades. Three main pigments were identified: ivory black, used in most of the samples as a base for the design, a copper-based pigment (probably verdigris) and a carbon-based black pigment mixed with ultramarine to create blue tones. GC–MS results revealed that the binder used for these paints was a mixture of linseed oil and colophony in varying proportions.

In the case of the polychrome silk fabrics, a basic colour obtained in a dyeing bath was used, while successive colours printed on the surface according to Fortuny's patents created the pattern. The analytical campaign identified Prussian blue as one of the dyes used. The research showed that the printing methods described in the two patents were probably used together, and that resist printing was used. Further research on other fabric types is needed for a more complete understanding, but this research has laid the foundations for a comprehensive knowledge of Fortuny's methodology. The precise reconstruction of the methodology and materials is important both for a better understanding of the artist's creative processes and the materials used in his works and for a better understanding of the processes of degradation, thus facilitating the correct conservation of these works of art. Moreover, thanks to this information, it is possible to better understand the history of industrialism in Venice in the 20th century, which saw the development of the artisan production sector.

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