

## Article

# Wall Drawing #736: Revealing Sol LeWitt's Ink Mural Technique Using a Multi-Analytical Approach

Adele Ferretti <sup>1</sup>, Iliara Degano <sup>1,2,\*</sup>, Marta Filomena <sup>1</sup>, Jacopo La Nasa <sup>1,2</sup>, Beatrice Campanella <sup>3</sup>, Stefano Legnaioli <sup>3</sup>, Sara Penoni <sup>4</sup>, Renata Pintus <sup>4</sup>, Cristiana Todaro <sup>4</sup> and Francesca Modugno <sup>1,2</sup>

<sup>1</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy; adele.ferretti@phd.unipi.it (A.F.); m.filomena2@studenti.unipi.it (M.F.); jacopo.lanasa@unipi.it (J.L.N.); francesca.modugno@unipi.it (F.M.)

<sup>2</sup> Center for Instrument Sharing of the University of Pisa (CISUP), University of Pisa, 56124 Pisa, Italy

<sup>3</sup> Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica dei Composti Organometallici, SS di Pisa, Via Moruzzi 1, 56124 Pisa, Italy; beatrice.campanella@pi.iccom.cnr.it (B.C.); stefano.legnaioli@pi.iccom.cnr.it (S.L.)

<sup>4</sup> Opificio delle Pietre Dure, 50122 Florence, Italy; sara.penoni@cultura.gov.it (S.P.); renata.pintus@cultura.gov.it (R.P.); cristiana.todaro@cultura.gov.it (C.T.)

\* Correspondence: ilia.degano@unipi.it

**Abstract:** Sol LeWitt, a pioneer of conceptual art, created during his career over 1350 wall drawings, including the Wall Drawing #736 (1993) at the Center for Contemporary Art Luigi Pecci in Prato (Prato, Italy). The painting, executed by Andrea Marescalchi and Antony Sansotta under LeWitt's instructions, features a grid of coloured rectangles obtained by overlapping different layers of inks. During a 2021 restoration by the Wall Paintings and Stuccoes Department of the Opificio delle Pietre Dure (Firenze, Italy), an in-depth investigation of the composition and the materials used by LeWitt's assistants in producing Wall Drawing #736 was performed. A multi-analytical approach entailing Raman spectroscopy, high-performance liquid chromatography coupled to diode array and high-resolution mass spectrometry, gas chromatography–mass spectrometry (GC–MS), and pyrolysis coupled with GC–MS was applied. Our results revealed the use of animal glue, shellac resin, paraffin wax, linseed oil, and various organic pigments. The binder in the preparation layer was identified as poly(vinyl acetate), while poly(n-butyl methacrylate) was determined as a fixative. This research provided valuable insights into LeWitt's techniques. The acquired knowledge on the paint technique is highly relevant in supporting conservators in restoration and consolidating the many wall drawings produced exploiting the same technique all over the world.

**Keywords:** Sol LeWitt; wall drawing; ink; GC–MS; Py–GC–MS; HPLC–DAD–ESI–Q–ToF



**Citation:** Ferretti, A.; Degano, I.; Filomena, M.; La Nasa, J.; Campanella, B.; Legnaioli, S.; Penoni, S.; Pintus, R.; Todaro, C.; Modugno, F. Wall Drawing #736: Revealing Sol LeWitt's Ink Mural Technique Using a Multi-Analytical Approach. *Heritage* **2024**, *7*, 4265–4281. <https://doi.org/10.3390/heritage7080201>

Academic Editor: Silvano Mignardi

Received: 11 July 2024

Revised: 1 August 2024

Accepted: 4 August 2024

Published: 10 August 2024



**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/>).

## 1. Introduction

The assessment of the material nature of works of art has become a standard procedure, essential for guiding conservation practices and enriching the historical and artistic understanding of artists' techniques. In this context, the characterisation of the materials employed in the creation of wall paintings by the American artist Sol LeWitt (1928–2007) stands as a unique case study.

Originating as faint graphite marks on the wall, Sol LeWitt's wall drawings transitioned into coloured pencils in 1969 at the Dwan Gallery in New York. Subsequently, in 1982, the introduction of coloured inks marked a pivotal evolution in Sol LeWitt's painting technique, yet these were supplanted by acrylic paints in the mid-1990s (signifying the artist's commitment to innovation and the evolution of materials within his practice).

Over the span of approximately 38 years, Sol LeWitt produced ca. 1350 wall drawings, adding up to 3500 when accounting for installations dispersed across over 1200 locations. Among this rich body of work, the series "Wall Drawings" stands out as one of the most

distinctive and emblematic of the artist, revered as one of the progenitors of the multifaceted movement within contemporary arts known as conceptual art.

Indeed, from the 1980s onward, a distinctive operative practice emerged, that we also observed in Wall Drawing #736, located in the Center for Contemporary Art Luigi Pecci in Prato (Italy). Since the late 1960s LeWitt began to delegate the execution of his wall drawings to trusted collaborators, who followed precise instructions that the artist himself provided. In particular, Anthony Sansotta and Andrea Marescalchi contributed to the production of most of the Italian artworks. This shift is crucial to understand the peculiar nature of LeWitt's wall drawings: these are therefore "institutionalized" art projects with legal and contract value, described in special "diagrams", certified as authentic and documented, including the names of the first performers and the place of the first installation. Using the same diagram, the work could be replicated and exist even in different places, even at the same time, so that the work consists both of a conceptual project created by the artist and of its physical execution by a performer. To define such a relationship between idea and execution, Sol LeWitt often used musical score as a metaphor: while the score written by the composer is unique and fixed, its executions on behalf of many performers is never the same.

At first, these creations were explicitly conceived as ephemeral, or, according to the artist, "permanent installations until they are destroyed" [1], essentially because they were initially intended for temporary exhibitions, and their "destruction" was somehow anticipated. When purchased by a collector, the owner could readily recreate the artwork if needed, for instance if relocating or repainting the walls, while remaining faithful to the project created by the artist and outlined in the accompanying diagram.

According to the artist, maintaining the exact correspondence of the appearance of the artwork to the primary idea is of paramount importance, as any "alteration" could betray the original intention. LeWitt articulated this concept in 1984, stating that "If a wall drawing is done and redone every certain amount of years, it'll be more exactly the same as when it was first done and conceived. It's a way for preserving the work... so you don't have deterioration" [2–4]. As a consequence, in many of LeWitt's works, including Wall Drawing #736, a disconnection occurs between two concepts traditionally related in conservation: authenticity and authorship of an artwork as materially created by the artist. At the same time, LeWitt introduces an innovative concept of artwork that can potentially be remade indefinitely without incurring a forgery.

Thus, to remain faithful to the artist's intentions, we found imperative to adopt a new approach in the conservation of Wall Drawing #736 and in the investigation of the materials. Here, the study of the technique and the materials was configured as a fundamental conservative action: in this case it was more imperative to preserve the process by which the artist had wanted Wall Drawing #736 to be created, than to safeguard the original materials. This entailed not only assessing of the characteristics of the inks, allowing for the peculiar chromatic effect planned by LeWitt, but also collecting the indications of the artist and all the documentation of the work to be able to re-enact it correctly in the future, using materials as similar as possible to the original ones. This is the current approach used for ephemeral or performative works like installations nowadays [5,6].

This approach follows the indications suggested by Yale University Art Gallery, where an archive and a study and conservation center dedicated exclusively to Sol LeWitt's wall drawings was set up in 2013 [7].

During the restoration of Wall Drawing #736, we had the opportunity to contact Andrea Marescalchi's heirs, who granted us access to the materials in his archive. Here, fundamental information was gathered for an unprecedented approach to conservation: LeWitt and Marescalchi methodology was indeed adopted by the *Opificio delle Pietre Dure's* restorers in the conservation intervention, and the original Pelikan inks conserved in the Marescalchi Archive were used to retouch the only lacuna.

In this framework, a full diagnostic campaign was carried out on selected samples collected from the wall painting and on the inks conserved in the Marescalchi archives.

Besides the application of non-invasive preliminary analyses and possibly portable XRF and in situ vibrational spectroscopies, non-destructive techniques as FTIR and Raman can be applied to obtain information on pigments and organic components of the inks and the paint samples [8,9]. Moreover, chromatographic techniques coupled with mass spectrometry (MS) are widely recognised as the most powerful micro-destructive techniques for characterizing the entire range of organic materials found in works of art and archaeological materials. Advanced gas chromatography–mass spectrometry-based techniques (GC–MS) and analytical pyrolysis–GC–MS allow the simultaneous screening of natural and synthetic binding media, additives and synthetic pigments [10–13]. Pyrolysis-based techniques are particularly useful when dealing with synthetic binders, commonly employed in the production of modern and contemporary wall paintings [14–16]. Additionally, detailed information can be obtained about individual classes of binding media and finishing materials via sample pre-treatment prior to GC–MS [17]. Instead, a comprehensive profile of natural, artificial and synthetic organic pigments along with their ageing products can be achieved by the application of liquid chromatography with spectrophotometric or mass spectrometric detection [18–21], provided that the compounds of interest are soluble in organic solvents.

Exploiting the full range of possible analytical techniques available for the characterization of paint materials in micro-samples, we adopted a multi analytical approach, entailing both non-destructive (Raman spectroscopy) and micro-destructive techniques (high-performance liquid chromatography coupled with diode array detector and tandem mass spectrometry (HPLC–DAD–ESI–Q–ToF), gas chromatography–MS (GC–MS), and pyrolysis coupled with gas chromatography–MS (Py–GC–MS)). The multi-analytical approach was applied both on samples collected from the Wall Drawing #736 and the inks used for its production, provided us as archive materials. The results enabled us to determine a complex composition characterised by animal glue, shellac resin, and synthetic organic pigments, with differences depending on the investigated colour. Further investigations of the materials used by Marescalchi and Sansotta for Wall Drawing #736 were performed by Py–GC–MS and Raman spectroscopy.

Eight microsamples were collected from the wall drawing, representing the entire colour scheme of the mural in accordance with the archives of the Center for Contemporary Art Luigi Pecci (Prato). This strategy allowed us to assess the presence of a fixative on the Wall Drawing #736 and to identify the binder employed in the white preparation layer, reconstructing the artistic criteria used for the creation of the artwork.

The purpose of the research was to understand the nature of the materials constituting Wall Drawing #736 to support present and future conservative interventions on this artwork and on other paintings made with this technique. Indeed, Sol LeWitt *modus operandi* demands an in-depth knowledge of the artist's materials and methods to preserve this peculiar category of works and presents a unique case study in this regard. This study builds on the information collected during a 2011 interview with Marescalchi.

The idea of “remaking” the drawing infinite times, as foreseen by Sol LeWitt, can only be pursued if the original materials can be reproduced and made available accordingly to the authors' instructions, or opportunely substituted with idoneous new materials. Since the production of commercial inks is often discontinued by the manufacturers, the analysis of the available archive artists' materials, besides that of the actual work of art, is pivotal in this case study. The results of the multi-analytical approach entailing spectroscopic, chromatographic, and mass spectrometric techniques applied to artists' materials (inks) and micro-samples collected from Wall Drawing #736 were compared with information gathered interviewing Marescalchi in 2011.

## 2. Materials and Methods

### 2.1. Contemporary Inks from the Marescalchi Archive

Andrea Marescalchi (Rome, 1954–Florence, 2015), known as “Bobo”, was an Italian artist, collaborator of Sol LeWitt since the 1980s, and executor, usually together with

Sansotta, of many of his wall drawings in Italy. Since 2017, the “Associazione Culturale Archivio Andrea Marescalchi”, or Marescalchi archive, has been dealing with promoting the archival activity and the diffusion of the work of Andrea Marescalchi. Based on the information found in the archive, drawing inks (Pelikan D.I.) were used in Sol LeWitt’s mural drawings. Bottles of the original inks used to draw a series of paintings in Tuscany and in other parts of Italy in the decades 1980s–1990s are presently conserved in the Marescalchi archive. 1 mL of each ink was collected from their original bottles to perform preliminary analyses on their composition. Each ink was then cast onto a microscope glass slide, spreading it with a spatula to obtain a homogenous layer. The ink mock-ups were allowed to dry for two weeks before sample collection. The dried samples were then subjected to both non-destructive and micro-destructive analysis, as described in Section 2.4.

## 2.2. Technical Information from the 2011 Interview with Andrea Marescalchi

In 2011 we had the opportunity to interview Andrea Marescalchi, regarding the wall drawings of the Giuliano Gori collection in Celle, near Pistoia, made in the mid-1980s with the same materials used for the one in Prato. Marescalchi, on that occasion, provided us with highly valuable technical information. Here we summarise the guidelines followed in the production of the artwork as described in the interview [22].

After preparing the wall with semi-washable white acrylic paint and having obtained an orange peel-like surface similar to watercolour paper, the drawing was transferred with graphite from a diagram to the wall; then a mask was made for each section using paper rolls for calculators and adhesive tape. For Pecci’s work, to obtain precise boundary lines and prevent the ink from “smudging” between one section and the next, the tape was sealed with an acrylic emulsion applied by brush. In the section to be coloured, two more white layers were applied prior to the coloured paint. Once the tape was removed, the boundary line was extremely well defined. Following the artist’s scheme, each specific listed colour was applied, after dilution in water in precise proportions, in the exact sequence indicated (colours were superimposed and not mixed), so that the different sequences of primary colours created an extraordinary variety of tones. In contrast, the black ink was initially diluted in water (1:60, v/v) to obtain a grey ink that was added to the red, yellow, and blue ones before their application, as detailed in the guidelines reported in the Marescalchi archive (1987 formulations, Figure 1).

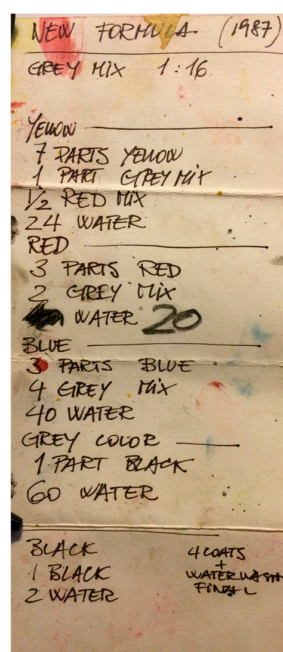


Figure 1. Guidelines reported in the Marescalchi archive (1987 formulations).



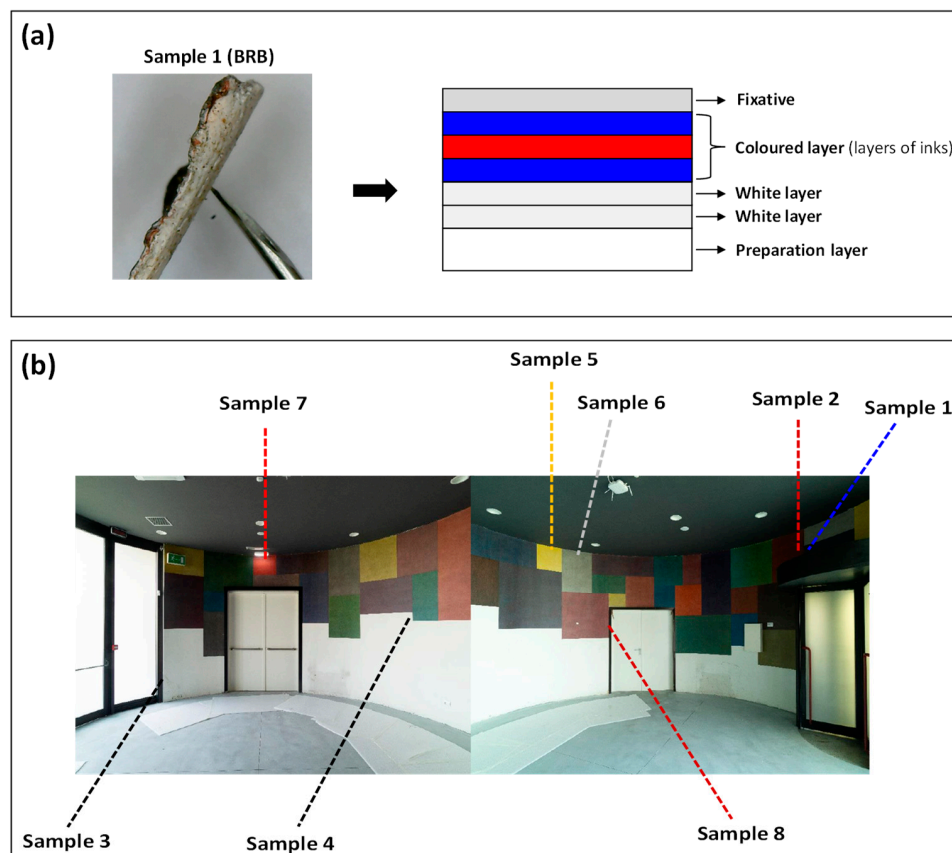
Each colour was applied in three overlapping coats, using pads made from seamless cotton jersey t-shirts to avoid any visible marks. The first layer was applied in three layers using circular movements with a technique that Marescalchi defines as “wiped”, the second also in three layers by dabbing, and the third once again by “wiping” as the first one. As the ink dried rapidly, it was necessary to work quickly.

Finally, a matte varnish produced by the company Lascaux, probably 575UV Matte [23], was applied as a fixative by airbrush.

### 2.3. Technical Information from the 2011 Interview with Andrea Marescalchi

The Wall Drawing # 736 (338 × 1908 cm) consists of a grid of coloured rectangles that covers the upper part of the walls of a circular room. The production technique involved the use of drawing inks, overlapped in different layers of colours, above a white preparation layer, as described in the previous section. The sequence of the colour layers was specified in the diagram written by LeWitt by acronyms (R = red, B = blue, Y = yellow, G = grey), where the sequence of letters indicates the expected order of application of the inks. Moreover, a preliminary examination with UV lamp have highlighted fluorescent regions, further investigated with a Dinolite microscope on the edges of the wall painting, which suggested the presence of a fixative finishing. Sansotta reported the use of a matte varnish by Lescaux, applied as a spray. Figure 2a shows a scheme of the stratigraphic section of Wall Drawing #736. To investigate the organic materials constituting the artwork, eight representative samples of Wall Drawing #736 were collected and analysed:







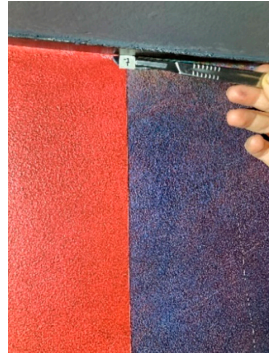

- Samples 1, 2, and 8 were fragments detached from the wall;
- Samples 3, 4, 5, 6, and 7 were selectively collected to fully characterise the materials used in the wall drawing.



**Figure 2.** Wall Drawing #736. (a) Stratigraphic section of sample n°1 (BRB). Image obtained with the optical microscope (left) and stratigraphic scheme (right). (b) Sampling points from Wall Drawing #736.

The sampling points are shown in Figure 2b, while a detailed description of each sample is provided in Table 1.

**Table 1.** Samples and description.

Label	Description	Sample Fragment	Label	Description	Sample Fragment
1	<b>BRB:</b> collected from the floor below one of the blue areas: fragment with layers of blue and red inks on a white base preparation.		2	<b>RYG:</b> collected from the floor below one of the red areas: fragment with layers of red, yellow, and grey inks on a white base preparation.	
Label	Description	Sampling spot	Label	Description	Sampling spot
3	White preparation layer without fixative.		4	White preparation layer with fixative.	
5	<b>YY:</b> selective surface sampling of yellow ink. Probable traces of black ink and fixative.		6	<b>GG:</b> selective surface sampling of grey ink (black ink diluted 1:60 in water). Probable traces of fixative.	
7	<b>RRR:</b> selective surface sampling of yellow ink. Probable traces of black ink and fixative.		8	<b>RRG:</b> fragment with layers of red and black inks on a white base preparation.	

## 2.4. Apparatus

### 2.4.1. Raman Spectroscopy

Raman analyses were carried out using a Renishaw RM 2000 instrument coupled to a Leica DLML optical microscope, equipped with a 50× NPLAN objective. The laser sources were a He–Ne and a diode laser with wavelengths of 633 nm and 785, respectively. The laser power output on the sample was adjusted between 1 and 5 mW. The spectrometer consists of a single grating monochromator (1000/1200 lines mm<sup>-1</sup>), coupled to a CCD. The spectral resolution was 0.5 cm<sup>-1</sup> @ 633 nm and 2 cm<sup>-1</sup> @ 785 nm; the spectral range analysed was between 100 and 3200 cm<sup>-1</sup>. The spectral calibration of the instrument was performed on the 520.5 cm<sup>-1</sup> band of a pure silicon crystal.

### 2.4.2. Gas Chromatography–Mass Spectrometry (GC–MS)

To determine binder and additives of the Marescalchi archive inks (black, blue, yellow, and red), they were investigated by gas chromatography–mass spectrometry (GC–MS) after hydrolysis, extraction, purification, and derivatisation steps for the identification of proteinaceous, lipid, polysaccharide, resin, and wax components [10]. A 6890 Gas Chromatograph coupled with a 5975 Single Quadrupole Mass Selective Mass Spectrometer (Agilent Technologies, Santa Clara, CA, USA) was used, and further details on analytical conditions are reported in [10].

### 2.4.3. Pyrolysis Coupled to Gas Chromatography–Mass Spectrometry (Py–GC–MS and Py(HMDS)–GC–MS)

Samples from the ink mock-ups and Wall Drawings #736 were also analysed by analytical pyrolysis combined with gas chromatography–mass spectrometry (Py–GC–MS). A multi-shot pyrolyser EGA/PY-3030D (Frontier Lab) coupled to an 8890 gas chromatograph, combined with a 5977B mass selective single quadrupole mass spectrometer detector (Agilent Technologies) was used. For the MS unit apparatus, the following parameters were applied: electron impact ionization (EI 70 eV) in positive mode; ion source temperature set at 230 °C; scan range of 35–600 *m/z*; interface temperature set at 280 °C. To characterise the different classes of materials, the following two different approaches were used: (a) for the identification of synthetic polymers and dyes, pyrolysis was carried out at 600 °C; (b) for evaluating the presence of shellac resin and/or gum Arabic or other natural organic binders and additives, pyrolysis was carried out at 550 °C with in situ silylation using 3 µL of hexamethyldisilazane (HMDS) as derivatizing agent. The pyrolysis products were separated by a HP-5MS capillary column (95% dimethyl-5% diphenyl-polysiloxane; 30 m × 0.25 mm, film thickness 0.25 µm; Agilent Technologies, USA). Helium (He, purity 99.9995%) was used as gas carrier, with a constant flow of 1.2 mL/min. The GC injector was operated in split mode at 280 °C and with a 20:1 ratio. The GC oven temperature programs were as follows: (a) for synthetic polymers and dyes analysis: 40 °C for 5 min, 10 °C/min up to 310 °C for 20 min; (b) for shellac resin and gum Arabic analysis: 35 °C for 10 min, 10 °C/min up to 310 °C for 20 min.

### 2.4.4. High-Performance Liquid Chromatography (HPLC–DAD–ESI–Q–ToF)

Prior to the liquid chromatography analysis, 1 mg of yellow and red ink was collected from the mock-up and solubilized in 300 µL of DMSO (99.8% purity; J.T. Baker, CA, USA). The DMSO sample pretreatment was performed in accordance with [24]. Injection volumes were 10 µL for HPLC–DAD and 2 µL for HPLC–ESI–Q–ToF experiments. The HPLC–DAD system consisted of a PU-2089 quaternary pump equipped with a degasser, an AS-950 autosampler and an MD-2010 spectrophotometric diode array detector (DAD) (Jasco International Co., Hachioji, Japan). The HPLC–ESI–Q–ToF system consisted of an HPLC 1200 Infinity, coupled to a Jet Stream ESI–Q–ToF 6530 Infinity detector and equipped with an Agilent Infinity autosampler (Agilent Technologies, Palo Alto, CA, USA). For both systems, the chromatographic separation was performed on a Poroshell 120 EC–C18 column (3.0 × 75 mm, particle size 2.7 µm, Agilent Technologies), equipped with a Zorbax





Table 3. Cont.

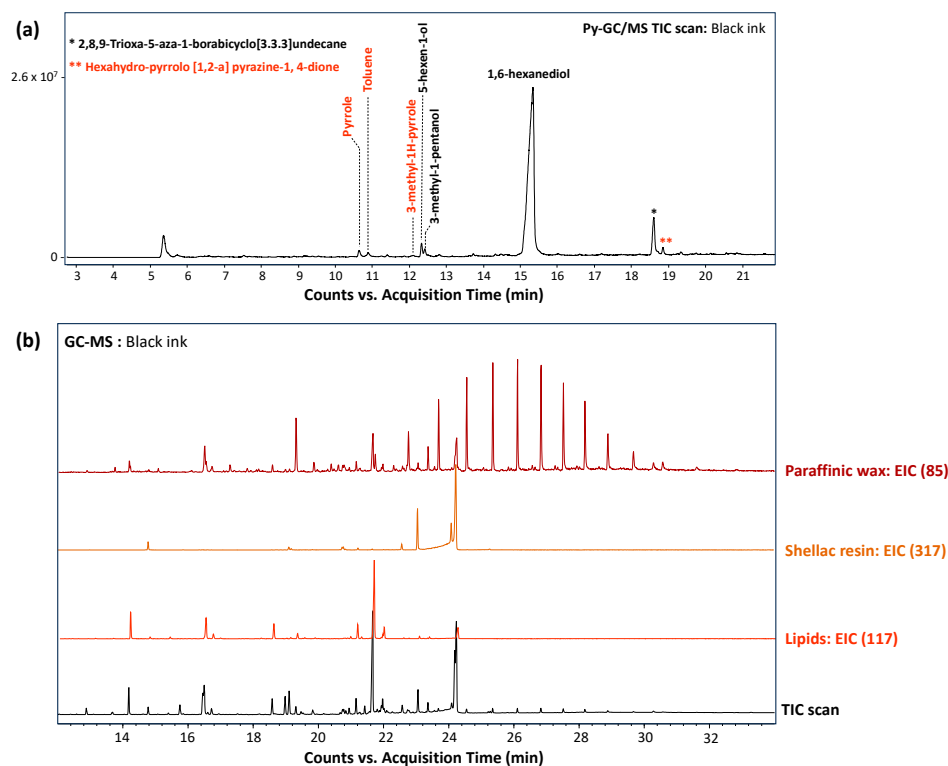
Material	Pyrolysis Products	$t_r$ (min)	$m/z$	Samples													
				G	B	Y	R	3	4	5	6	7	1	2	3	8	
PVAc (polyvinyl acetate)	Acetone	5.4	43, 58						x					x	x	x	x
	Acetic acid	7.2	43, 60						x					x	x	x	x
	Benzene	7.9	78, 51, 39						x					x	x	x	x
	Toluene	9.9	91, 65, 39, 51						x					x	x	x	x
	Ethylbenzene	11.4	91, 106, 51, 77						x					x	x	x	x
	Styrene	1.8	104, 78, 51, 63						x					x	x	x	x
	Indene	13.5	115, 89, 63, 58, 39						x					x	x	x	x
	1-methyl indene	14.4	130, 115, 51, 64, 77, 39, 102						x					x	x	x	x
	3-methyl indene	14.5	130, 115, 51, 64, 77, 39, 102						x					x	x	x	x
	Naphthalene	14.7	128, 102, 51, 39						x					x	x	x	x
	2-methyl naphthalene	15.5	142, 115, 63, 89						x					x	x	x	x
1-methyl naphthalene	15.6	142, 115, 63, 89						x					x	x	x	x	
Acenaphthene	15.9	154, 76, 115, 128, 51, 63, 102						x					x	x	x	x	
PBMA (poly (n-butyl methacry- late))	1-butene	4.9	41, 56						x	x	x	x	x	x	x		x
	Benzene	7.9	78, 63						x	x	x	x	x	x	x		x
	Methyl methacrylate	8.8	41, 69, 100, 85, 59						x	x	x	x	x	x	x		x
	Methacrylic acid	10.8	39, 86, 58						x	x	x	x	x	x	x		x
n-butyl methacrylate	12.7	69, 87, 41, 56, 29, 99, 113						x	x	x	x	x	x	x		x	
PEA (poly (ethyl acrylate))	Ethanol	5.2	31, 45						x								
	Ethyl acrylate	8.5	55, 45, 99, 73						x								
	Ethyl methacrylate	10.7	69, 41, 99, 84, 114						x								
	Diethyl glutarate	15.1	143, 115, 87, 55, 73, 101						x								
	Dimer	15.5	98, 154, 53, 81, 109						x								
	Trimer	18.2	134, 208, 255, 79, 181, 106, 152, 55, 125, 226						x								

### 3.1.1. Chemical Investigation of Binders and Additives

Py-GC-MS analysis enabled us to identify in the black ink pyrrole, hexahydro-pyrrole [1,2-a] pyrazine-1,4-dione, toluene, and 3-methyl-1H-pyrrole, characteristic pyrolytic markers of the collagen contained in animal glue (Figure 3a) [28]. The latter is historically recognised as the binder par excellence in *China* or *India ink* formulations [29,30], i.e., black inks obtained by mixing pine or oil lamp soot (carbon black) with pre-dissolved glue and additives to obtain sticks. In addition, 1,6-hexanediol was detected as an additive in the black ink. Moreover, our investigation enabled us to detect butolic acid-TMS (pyrolytic marker of shellac resin) by Py(HMDS)-GC-MS in the blue ink [31] and by HPLC-ESI-Q-ToF in red and yellow inks [26,32]. Shellac resin is a natural resin widely used over the centuries as adhesive and coating material but it was also exploited in inks for increasing their viscosity [26]. To confirm these results, and to further investigate the ink composition, a combined GC-MS analytical protocol was applied, allowing us to determine the proteinaceous material contained in the archive inks in terms of individual aminoacidic content. GC-MS analysis allowed us to detect hydroxyproline, the characteristic amino acid marker of animal glue [33,34], in all of the Marescalchi archive inks (black, blue, yellow, and red). Data elaboration on the complete aminoacidic profile (Table 4), compared to a set of reference materials [10], enabled us to confirm animal glue in the black, blue, and yellow inks, despite a relatively low glycine content compared to that reported in the literature for animal glue. For the red ink, a total aminoacidic content lower than the limit of quantitation was obtained; thus, it was not possible to quantitatively evaluate the aminoacidic profile. No polysaccharide markers were identified, proving the absence of plant gums in the archive inks. Instead, the examination of the lipid content allowed us to confirm the presence of shellac resin in all the formulations and encouraged us to further



investigate the presence of drying oils. In detail, shellac resin was confirmed by the GC–MS detection of butolic acid (18.7 min), laccishelloic acid (21.4 min), derivatives of aleuritic acid (23.0 and 24.1 min), and aleuritic acid (25.3 min). Jalaric and laccijalaric acid were not observed, suggesting that the resin had undergone ageing to a certain extent, or that it was pretreated in a specific way prior to its introduction in the ink formulation. Except for laccishelloic acid, no Cannizzaro-type disproportionation products related to the typical sesquiterpenoids of shellac resin were detected; however, this is expected because a soft saponification was performed, whereas stronger conditions are necessary to identify them by GC–MS [31].



**Figure 3.** Results obtained in the analysis of the binder/additives component of black archive ink. (a) Total ion chromatogram (TIC scan) obtained by Py–GC–MS. The peaks associated to animal glue and to additives are highlighted in orange and in black, respectively; (b) Total ion chromatogram (TIC scan) and Extract ion chromatograms (EICs) acquired by GC–MS. Total ion chromatogram (TIC scan, black chromatogram), EIC of  $m/z = 117$  (typical of carboxylic acids, markers for lipids, orange chromatogram), EIC of  $m/z = 317$  (typical fragmentation product of the molecular markers of shellac resin, yellow chromatogram), and EIC of  $m/z = 85$  (typical fragment ion of hydrocarbons, markers of paraffin wax, brown chromatogram). All chromatograms are reported in the same scale and are stacked for purpose of clarity.

**Table 4.** Semiquantitative results obtained for amino acids (AA) profile of the proteinaceous component of Marescalchi archive inks (black, blue, and yellow), compared with an average amino acid profile of reference protein materials. The results achieved for the red ink are not shown since values lower than the LOQ for proteinaceous materials were obtained.

Material	%Ala	%Gly	%Val	%Leu	%Ile	%Ser	%Pro	%Phe	%Asp	%Glu	%Hyp
Blue ink	3.9	3.0	5.9	6.6	9.7	12.7	4.8	11.4	9.7	11.8	20.5
Black ink	5.4	12.4	3.6	5.5	5.0	6.3	32.3	5.8	5.0	6.9	11.7
Yellow ink	16.0	8.8	4.9	5.1	7.7	11.1	3.9	8.7	7.7	9.7	16.5
Casein	5.0	3.0	7.6	11.9	6.6	5.8	11.5	5.9	8.5	22.2	0.0
Egg	7.7	4.8	7.7	11.0	6.7	10.3	5.7	6.4	12.6	15.0	0.0
Animal glue	12.3	29.4	3.9	4.7	2.5	3.8	12.4	2.8	6.6	9.9	7.7

As for the investigation of drying oils, different ratios between representative free fatty acids were evaluated and compared with the literature data and in-house databases to obtain information on the composition of the medium in the inks [35]. The details are as follows:

- A/P (azelaic acid/palmitic acid) is commonly evaluated to investigate the occurrence of drying oils ( $A/P > 1$ ), since the formation of dicarboxylic acids (peaking with azelaic acid) production occurs during the curing and ageing of drying oil. As for the black and blue inks,  $A/P < 1$  values were observed. The lipids observed in their chromatograms cannot be associated with a siccative oil, and their presence can thus be associated to free acids of shellac resin, given that Py–GC–MS analysis already excluded the presence of egg, another common source of lipids in binding media. Conversely,  $A/P > 1$  was observed in the red and yellow inks, consistent with a molecular profile typical of drying oils;
- P/S (palmitic acid/stearic acid) is a chemical parameter commonly used to differentiate drying oils based on the different relative abundance of the two main saturated monocarboxylic acids. The quantitative analysis performed for the red and yellow inks provided us with a P/S ratio values of 1.6 and 1.1, respectively, compatible with linseed oil, whose presence cannot be fully ascertained since mixtures cannot be excluded [35];
- %  $\Sigma D$  percentage (dicarboxylic acids sum/total free acids) and O/S (oleic acid/stearic acid) are chemical parameters useful to evaluate the degree of ageing/curing, since oleic acid is highly reactive towards oxidation, and as stated above dicarboxylic acids are auto-oxidation products. The values achieved ( $O/S = 0.7$ , for both red and yellow inks) suggest a partial oxidation of the lipid binder, consistent with the fact that the archive inks are quite contemporary (80s–90s) and were in liquid form when cast on the glass slides as mock-ups, which were further sampled and analysed just after few weeks; notably, we determined a higher ageing degree for the red ink (%  $\Sigma D = 50$ ) than for the yellow one (%  $\Sigma D = 36$ ).

In summary, the molecular profile of fatty acids and dicarboxylic acids observed in the red and yellow inks provided us with the identification of partially oxidised siccative oil. Concerning the additives, GC–MS analysis (Figure 3b) highlights the presence of paraffin wax in the black ink.

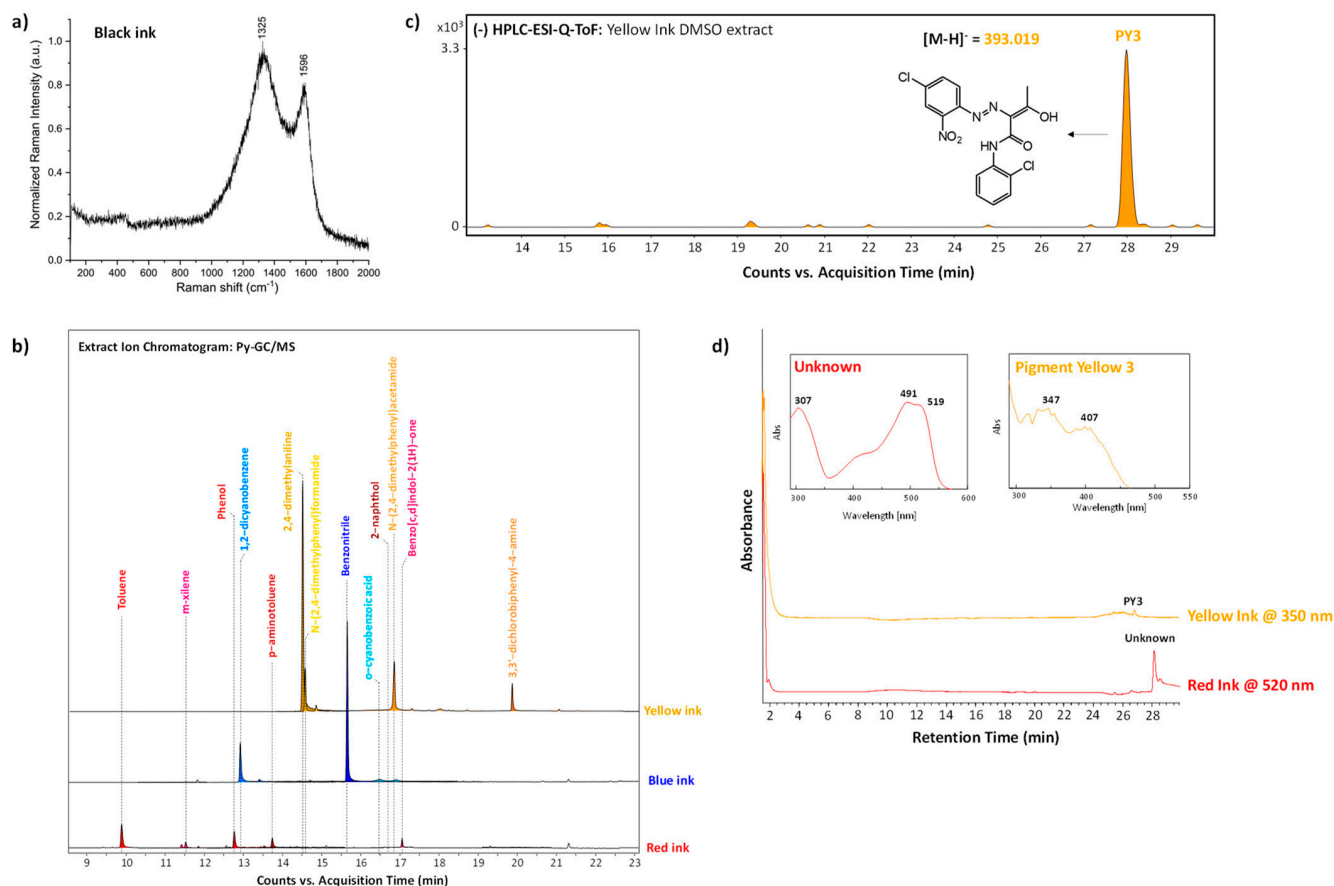
### 3.1.2. Investigation of Dyes and Pigments

The detection in the Raman spectrum (Figure 4a) of the G ( $1596\text{ cm}^{-1}$ ) and D ( $1325\text{ cm}^{-1}$ ) bands, typical of carbonaceous materials [36], enabled us to characterise the black archive ink as a carbon black-based. By combining the identification of carbon black and animal glue (3.1.1), we confirm the use of *China ink*, validating the information found in the Marescalchi archive. Neither Py–GC–MS nor HPLC–DAD–ESI–Q–ToF provided us with further information on the pigments, as carbon black is not detectable by either of them.

As for the blue ink, Raman spectroscopy provided us with the identification of Phthalo Blue 15:3 (PB 15:3), a phthalocyanine pigment widely exploited by several 20<sup>th</sup> century artists [37]. Consistently, the pyrolytic markers of phthalo pigments were detected by Py–GC–MS. However, the discrimination between different possible blue phthalocyanine pigments by analytical pyrolysis is quite challenging, since their pyrograms all present 1,2-dicyanobenzene and o-cyanobenzoic acid as main pyrolytic products [11,38,39]. Nevertheless, the detection of secondary markers as benzonitrile (Figure 4b) allows us to narrow the field down to PB 15 and PB 15:3, which only differ in their crystal structure. Phthalocyanine-based pigments are insoluble in almost all organic solvents, making them undetectable by techniques based on liquid chromatography.

The adopted multi-analytical approach applied to the yellow ink allowed us to highlight a mixture of synthetic organic pigments, comprising Pigment Yellow 3 (PY3), and Pigment Yellow 13 (PY13). PY3, a monoazo pigment firstly synthesised in 1910, was identified by HPLC–DAD–ESI–Q–ToF analysis (Figure 4c:  $t_R = 27.9\text{ min}$ ,  $\lambda_{\max} = 347, 407\text{ nm}$ ,

$[M-H]^- = 393.016 \text{ m/z}$  [40], while PY13 was identified by Py-GC-MS (Figure 4b) and Raman spectroscopy only (SOPRANO database of Raman spectra obtained on synthetic organic pigments [41] and the related publication [42]). According to pyrolysis fragmentation pathways proposed for diarylide pigments by Russel et al. [38], PY13 can be identified based on the detection of several dimethylaniline and dimethylphenyl compounds (Table 3). In this case, Py-GC-MS proved suitable for the specific identification of diarylide pigments which differ in the substituents on the terminal benzenes.



**Figure 4.** (a) Raman spectrum of the black archive ink; (b) Py-GC-MS extract ion chromatograms of the pyrolytic markers of SOPs identified in red, blue, and yellow ink. For the red ink, the markers of PR149 are highlighted in fuchsia, while the ones of the unknown naphthol AS pigment are reported in red. All pyrograms are reported at the same scale and are stacked for the purpose of clarity; (c) HPLC-ESI-Q-ToF Extract ion chromatogram (EIC) of the molecular ion of PY3 in the DMSO extract of the yellow ink; (d) HPLC-DAD chromatograms of the DMSO extract of red (extracted at 520 nm) and yellow (extracted at 350 nm) inks, and UV-Vis spectra of the two peaks detected. All chromatograms are reported in the same scale and are stacked for purpose of clarity.

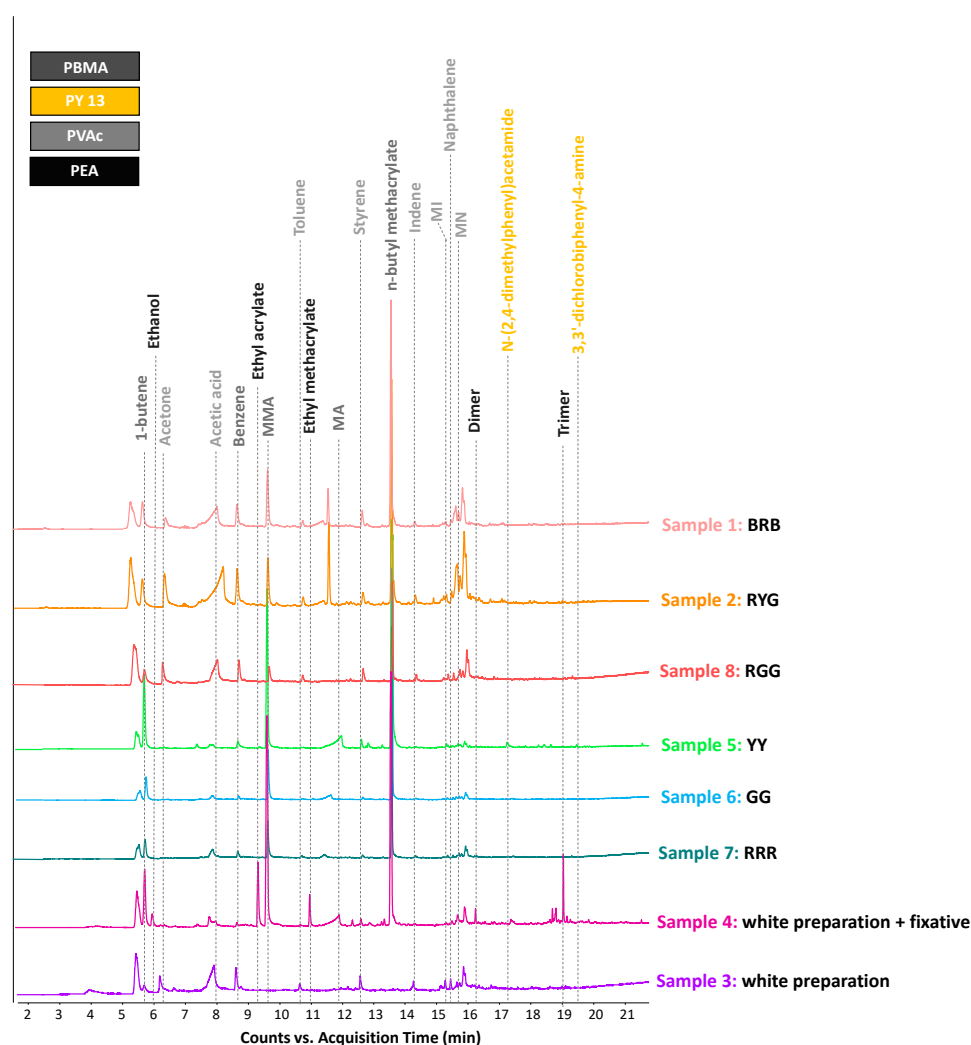
Finally, in the red ink, a perylene pigment (PR149) [43] and an unknown naphthol AS pigment were determined (Figure 4b). According to Russel et al. [38], the presence of PR149 could be ascertained by the detection of 1,3-dimethyl benzene by Py-GC-MS. However, also benzo[cd]indol-2(1H)-one was detected, and a fragmentation pathway analogous to naphthalimide formation reported by Gherardi et al. [11] can be hypothesised, further supporting the identification of a perylene pigment. In addition, the pyrogram acquired for the red ink allowed us to determine 2-naphthol, which may have originated by the pyrolysis of a naphthol AS pigment [39]. Both Raman and HPLC-DAD results confirm this hypothesis: the first by detecting Pigment Red 11, and the second by allowing us to identify the characteristic UV-Vis spectrum acquired by PDA of a compound belonging to this class (Figure 4d). Unfortunately, HPLC-MS analysis did not allow us to confirm the presence of

PR11 and identify the unknown naphthol AS pigment determined by HPLC–DAD, given the complexity of the chromatogram.

### 3.2. Samples from Wall Drawing #736

The organic materials present in the samples collected from the Wall Drawing #736 were investigated by Py–GC–MS and Raman spectroscopy. Py–GC–MS analysis (Figure 5) allowed us to highlight the presence of polyvinyl acetate (PVAc) in the white preparation (sample 3) and of poly (n-butyl methacrylate) (PBMA) and poly (ethyl acrylate) (PEA) in the white preparation containing the fixative (Sample 4). Moreover, the Py–GC–MS results achieved for the coloured samples (1, 2, 5, 6, 7, and 8) enabled us to determine the following information:

- PBMA in all the samples collected selectively from the surface (samples 5, 6, and 7);
- PBMA + PVAc in the samples obtained as fragments (degradation of the wall drawing), thus composed by both the coloured ink's layers and the white preparation (Samples 1, 2, and 8).



**Figure 5.** Total ion chromatogram (TIC scan) obtained by Py–GC–MS. White preparation (sample 3, violet pyrogram), white preparation + fixative (sample 4, fuchsia pyrogram), RRR (sample 7, dark green pyrogram), GG (sample 6, light blue pyrogram), YY (sample 5, light green pyrogram), RGG (sample 8, red pyrogram), RYG (sample 2, orange pyrogram), and BRB (sample 1, pink pyrogram). The peaks associated with poly (n-butyl methacrylate) (PBMA), pigment yellow 13 (PY13), polyvinyl acetate (PVAc) and poly (ethyl acrylate) (PEA) are highlighted in grey, yellow, light grey, and black, respectively. All pyrograms are presented in the same scale and are stacked for purpose of clarity.

Therefore, except for the white preparation (Sample 3), all the samples analyzed contained an acrylic binder (PBMA). This suggests that a PBMA-based fixative was applied in Wall Drawing #736, in accordance with the reports by Sansotta that a fixative was used. Moreover, it is possible to hypothesise that the preparative white layer contained PVAc as a binder, in accordance with the results obtained for most samples (1, 2, 3, and 8). Instead, the identification of PEA in sample 4 only, collected outside the painting area, is difficult to rationalise, and could be associated with a repainting of the wall with a different white colour, carried out in that specific area. Except for Sample 5 (YY), which featured the pyrolytic markers of the same yellow pigment (PY13) highlighted in the archive ink, neither signals related to the pyrolysis products of synthetic organic pigments nor of organic binders were observed in any of the other samples collected from the wall. This could be due both to the dilution to which the inks were subjected before their application and to the reduced quantity of pigments and binders compared to the inorganic content of the samples. However, the application of Raman spectroscopy enabled us to enhance our understanding regarding the pigment composition of Wall Drawing #736. Indeed, in sample 1 (BRB) the presence of PB 15:3 was revealed, while the investigation of samples 2 (RYG) and 8 (RGG) also enabled the detection of PR11. Thus, the results achieved with Raman spectroscopy allowed us to outline a matching dye/pigment composition with the Marescalchi archive inks. Moreover, rutile was identified in samples 1, 2, 3, 4, and 8, and calcite in sample 3. The detection of rutile could be linked to the white pigments in the preparation layer, while calcite could have been used as a filler.

#### 4. Conclusions

Our research led to a deep understanding of this special ink-on-wall technique developed by LeWitt and his collaborators. Four inks conserved in the Marescalchi archive were fully characterised by a multi-analytical approach. Animal glue and shellac resin were determined as binder and additives, suggesting a molecular profile similar to the so-called China inks. In addition, a siccativ oil (possibly linseed oil) was identified in the red and yellow archive inks, while paraffin wax was determined in the black ink only. Concerning the pigment component, the black ink turned out to be carbon black-based; in the blue ink, Phthalo blue 15:3 (PB15:3) was determined, and complex mixtures of SOPs were detected both in the yellow (PY3, and PY13) and red (PR11, PR149, unknown naphthol AS pigment) inks. The materials used for painting the wall were also accessed: polyvinyl acetate (PVAc) and poly (ethyl acrylate) (PEA) were identified as the binder of the white preparative layer before and after a restoration campaign at the Center for Contemporary Art Luigi Pecci, while poly (n-butyl methacrylate) (PBMA) was determined as the fixative in the entire Wall Drawing #736. Despite the high dilution of the inks in the final wall painting and the presence of a finishing varnish, the composition of the samples matched that of the archive materials for the dyes and/or pigment components. Finally, rutile and calcite were identified in the preparation layer of the wall drawing investigated, suggesting their presence as white pigment and filler, respectively.

By comparing archive inks with samples from Wall Drawing #736, we did not identify specific degradation products related to dyes or pigments, and the pyrolytic profiles of binders and fixative components did not highlight features related to ageing. This finding is consistent with the conservation conditions of the artwork, as the room housing the wall drawing is sheltered from direct sunlight, and a relatively short time has passed since the creation of the artwork.

The in-depth study of the ink's composition conducted in this work is a first step towards improving our understanding of the continuous technological improvements in the production of paints and inks and how this has influenced Sol LeWitt's choice of artistic materials. Indeed, while the composition highlighted for Wall Drawing #736 matches that of the materials used in street art murals during the second half of the 20th century [15], that of the original inks proved to be an interesting combination of historical binders (animal glue and shellac resin) with synthetic dyes and pigments. Most importantly, the



acquired knowledge on the paint technique and palette of the artist is highly relevant for supporting conservators in restoration and consolidation interventions; gathering detailed physical–chemical information on the unique technique used by Sol LeWitt will permit the implementation of the relationship between project and realization, as envisioned by the artist.

**Author Contributions:** Conceptualization, A.F., I.D., and F.M.; methodology, A.F., I.D., J.L.N., B.C., S.L., and F.M.; formal analysis, A.F., M.F., B.C., S.P., R.P., and C.T.; data curation, A.F.; writing—original draft preparation, A.F., I.D., C.T., and F.M.; writing—review and editing, S.L., C.T., and F.M.; visualization, A.F.; supervision, I.D., C.T., and F.M.; project administration, F.M.; funding acquisition, F.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the PRIN2020 project “SUPERSTAR -Sustainable Preservation Strategies for Street Art” (2022–2025), an Italian network project, <https://prin2020superstar.dcci.unipi.it/> (accessed on 10 July 2024), funded by the Italian Ministry of University.

**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author, I.D., upon reasonable request.

**Acknowledgments:** The authors acknowledge Serena Bencini and Zita Marescalchi for their collaboration in the study of the Marescalchi archive and for allowing the sample collection from the archive materials. With regard to the Center for Contemporary Art Luigi Pecci, the authors acknowledge the support to the project aimed at the study, restoration, and conservation of the Wall Drawing #736, granted by the former and present Directors, Cristiana Perrella and Stefano Collicelli Cagol, respectively; the Head of Collection and Archives, Stefano Pezzato; and the Installation, Collections, and Photo Archives Coordinator, Raffaele Di Vaia. This research was supported by Fondazione per le Arti Contemporanee in Toscana.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. LeWitt, S. Wall Drawings. *Arts Mag.* **1970**, *44*, 45.
2. Sol Lewitt, interview by Claes Soederquist, Hanno Fuchs and Andi Loor reported in *Vanishing Point*, catalogue Moderna 510 Museet, Stockholm, Sweden. 1984.
3. Aveilhè, L. *Long Live the Ephemeral: Cataloguing Sol LeWitt's Wall Drawings*; LeWitt, L., Areford, D.S., Eds.; Yale University Press: New Haven, CT, USA, 2021; pp. 203–230.
4. Areford, D.S. (Ed.) *Locating Sol LeWitt*; Yale University Press: New Haven, CT, USA, 2021.
5. Armando, L. (Ed.) *Le installazioni. Conservazione, Movimentazione e Riallestimento, Kermes*; Nardini: Firenze, Italy, 2020; Volume 117.
6. Pugliese, M.; Feriani, B. *Monumenti Effimeri. Storia e Conservazione Delle Installazioni*; Electa: Stockholm, Sweden, 2009.
7. Hogan, J.; Snow, C. Sol Lewitt's Wall Drawings: Conservation of an ephemeral art practice. In *Proceedings of the Objects Specialty Group Postprints, Volume Twenty-Two*, Miami, FL, USA, 13–16 May 2015; Hamilton, E.E., Dodson, K., Barack, S., Moomaw, K., Eds.; The American Institute for Conservation of Historic & Artistic Works: Washington, DC, USA, 2015; pp. 37–46.
8. Rousaki, A.; Vandenabeele, P. Raman Analysis of Inorganic and Organic Pigments. In *Analytical Chemistry for the Study of Paintings and the Detection of Forgeries*; Colombini, M.P., Degano, I., Eds.; De Gruyter: Berlin, Germany, 2022; pp. 289–315.
9. Tamburini, D.; Sabatini, F.; Berbers, S.; van Bommel, M.R.; Degano, I. An Introduction and Recent Advances in the Analytical Study of Early Synthetic Dyes and Organic Pigments in Cultural Heritage. *Heritage* **2024**, *7*, 1969–2010. [[CrossRef](#)]
10. Andreotti, A.; Bonaduce, I.; Colombini, M.P.; Gautier, G.; Modugno, F.; Ribechini, E. Combined GC/MS Analytical Procedure for the Characterization of Glycerolipid, Waxy, Resinous, and Proteinaceous Materials in a Unique Paint Microsample. *Anal. Chem.* **2006**, *78*, 4490–4500. [[CrossRef](#)] [[PubMed](#)]
11. Ghelardi, E.; Degano, I.; Colombini, M.P.; Mazurek, J.; Schilling, M.; Learner, T. Py-GC/MS applied to the analysis of synthetic organic pigments: Characterization and identification in paint samples. *Anal. Bioanal. Chem.* **2015**, *407*, 1415–1431. [[CrossRef](#)] [[PubMed](#)]
12. Moretti, P.; Germinario, G.; Doherty, B.; van der Werf, I.D.; Sabbatini, L.; Mirabile, A.; Sgamellotti, A.; Miliani, C. Disclosing the composition of historical commercial felt-tip pens used in art by integrated vibrational spectroscopy and pyrolysis-gas chromatography/mass spectrometry. *J. Cult. Herit.* **2019**, *35*, 242–253. [[CrossRef](#)]
13. Degano, I.; Modugno, F.; Bonaduce, I.; Ribechini, E.; Colombini, M.P. Recent Advances in Analytical Pyrolysis to Investigate Organic Materials in Heritage Science. *Angew. Chem. Int. Ed.* **2018**, *57*, 7313–7323. [[CrossRef](#)] [[PubMed](#)]
14. Germinario, G.; van der Werf, I.D.; Sabbatini, L. Chemical characterisation of spray paints by a multi-analytical (Py/GC–MS, FTIR,  $\mu$ -Raman) approach. *Microchem. J.* **2016**, *124*, 929–939. [[CrossRef](#)]

15. La Nasa, J.; Campanella, B.; Sabatini, F.; Rava, A.; Shank, W.; Lucero-Gomez, P.; De Luca, D.; Legnaioli, S.; Palleschi, V.; Colombini, M.P.; et al. 60 years of street art: A comparative study of the artists' materials through spectroscopic and mass spectrometric approaches. *J. Cult. Herit.* **2021**, *48*, 129–140. [[CrossRef](#)]
16. La Nasa, J.; Orsini, S.; Degano, I.; Rava, A.; Modugno, F.; Colombini, M.P. A chemical study of organic materials in three murals by Keith Haring: A comparison of painting techniques. *Microchem. J.* **2016**, *124*, 940–948. [[CrossRef](#)]
17. Colombini, M.P.; Andreotti, A.; Bonaduce, I.; Modugno, F.; Ribechini, E. Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry. *Acc. Chem. Res.* **2010**, *43*, 715–727. [[CrossRef](#)]
18. Degano, I.; La Nasa, J. Trends in High Performance Liquid Chromatography for Cultural Heritage. *Top. Curr. Chem.* **2016**, *374*, 20. [[CrossRef](#)] [[PubMed](#)]
19. Ferretti, A.; Sabatini, F.; Degano, I. Linking historical recipes and ageing mechanisms: The issue of 19th century iron gall inks. *J. Cult. Herit.* **2024**, *67*, 111–120. [[CrossRef](#)]
20. Ferretti, A.; Hunt, E.; Degano, I. Exploring the optimal HPLC-DAD-HRMS parameters for acid dye-based artistic materials: An analytical challenge. *Microchem. J.* **2024**, *204*, 111111. [[CrossRef](#)]
21. Tamburini, D. On the reliability of historic books as sources of reference samples of early synthetic dyes—The case of “The Coal Tar Colours of the Farbwerke vorm. Meister, Lucius & Brüning, Höchst on the Main, Germany—A General Part” (1896). *Dye. Pigment.* **2024**, *221*, 111796.
22. Cadetti, S.; Casarano, A.; Felici, C.; Fornari, C.; Marchese, L.; Musa, C.; Todaro, C. Sol LeWitt, Wall Drawing 445; Wall Drawing 494. Intervista ad Andrea Marescalchi. In *Il Futuro del Contemporaneo*; Montalbano, L., Patti, M., Eds.; Edifir: Firenze, Italy, 2013; pp. 145–150.
23. Sansotta, A.; Singer, S. Notes. In *Sol Lewitt, Wall Drawings 1984–1992*; Singer, S., Ed.; Kunsthalle Bern: Bern, Switzerland, 1992; p. 216.
24. Sabatini, F.; Degano, I. Investigating the fragmentation pathways of  $\beta$ -naphthol pigments using liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry. *Rapid Commun. Mass Spectrom.* **2020**, *34*, e8789. [[CrossRef](#)] [[PubMed](#)]
25. Sabatini, F.; Giugliano, R.; Degano, I. Photo-oxidation processes of Rhodamine B: A chromatographic and mass spectrometric approach. *Microchem. J.* **2018**, *140*, 114–122. [[CrossRef](#)]
26. Ferretti, A.; Degano, I.; Legnaioli, S.; Campanella, B.; Sainati, A.; Colombini, M.P. Shedding light on the composition and degradation mechanism of dyes in historical ink's collection (19th–20th century). *Dye. Pigment.* **2023**, *220*, 111672. [[CrossRef](#)]
27. La Nasa, J.; Nodari, L.; Nardella, F.; Sabatini, F.; Degano, I.; Modugno, F.; Legnaioli, S.; Campanella, B.; Tufano, M.K.; Zuena, M.; et al. Chemistry of modern paint media: The strained and collapsed painting by Alexis Harding. *Microchem. J.* **2020**, *155*, 104659. [[CrossRef](#)]
28. Wei, S.; Fang, X.; Cao, X.; Schreiner, M. Characterization of the materials used in Chinese ink sticks by pyrolysis-gas chromatography-mass spectrometry. *J. Anal. Appl. Pyrolysis* **2011**, *91*, 147–153. [[CrossRef](#)]
29. Wei, S.; Fang, X.; Yang, J.; Cao, X.; Pintus, V.; Schreiner, M.; Song, G. Identification of the materials used in an Eastern Jin Chinese ink stick. *J. Cult. Herit.* **2012**, *13*, 448–452. [[CrossRef](#)]
30. Centeno, S.A.; Lladò Buisan, V.; Ropret, P. Raman study of synthetic organic pigments and dyes in early lithographic inks (1890–1920). *J. Raman Spectrosc.* **2006**, *37*, 1111–1118. [[CrossRef](#)]
31. Colombini, M.P.; Bonaduce, I.; Gautier, G. Molecular pattern recognition of fresh and aged shellac. *Chromatographia* **2003**, *58*, 357–364. [[CrossRef](#)]
32. Tamburini, D.; Dyer, J.; Bonaduce, I. The characterisation of shellac resin by flow injection and liquid chromatography coupled with electrospray ionisation and mass spectrometry. *Sci. Rep.* **2017**, *7*, 14784. [[CrossRef](#)] [[PubMed](#)]
33. Dallongeville, S.; Koperska, M.; Garnier, N.; Reille-Taillefert, G.; Rolando, C.; Tokarski, C. Identification of animal glue species in artworks using proteomics: Application to a 18th century gilt sample. *Anal. Chem.* **2011**, *83*, 9431–9437. [[CrossRef](#)] [[PubMed](#)]
34. Mazurek, J.; Svoboda, M.; Maish, J.; Kawahara, K.; Fukakusa, S.; Nakazawa, T.; Taniguchi, Y. Characterization of binding media in Egyptian Romano portraits using enzyme-linked immunosorbent assay and mass spectrometry. *e-Preserv. Sci.* **2014**, *11*, 76–83.
35. Colombini, M.P.; Modugno, F. *Organic Mass Spectrometry in Art and Archaeology*; Wiley: Hoboken, NJ, USA, 2009; ISBN 9780470517031.
36. Coccato, A.; Jehlicka, J.; Moens, L.; Vandenabeele, P. Raman spectroscopy for the investigation of carbon-based black pigments. *J. Raman Spectrosc.* **2015**, *46*, 1003–1015. [[CrossRef](#)]
37. Lomax, S.Q. Phthalocyanine and quinacridone pigments: Their history, properties and use. *Stud. Conserv.* **2005**, *50*, 19–29. [[CrossRef](#)]
38. Russell, J.; Singer, B.W.; Perry, J.J.; Bacon, A. The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography-mass spectrometry. *Anal. Bioanal. Chem.* **2011**, *400*, 1473–1491. [[CrossRef](#)] [[PubMed](#)]
39. Sonoda, N. Characterization of organic azo-pigments by pyrolysis-gas chromatography. *Stud. Conserv.* **1999**, *44*, 195–208.
40. La Nasa, J.; Biale, G.; Sabatini, F.; Degano, I.; Colombini, M.P.; Modugno, F. Synthetic materials in art: A new comprehensive approach for the characterization of multi-material artworks by analytical pyrolysis. *Herit. Sci.* **2019**, *7*, 8. [[CrossRef](#)]
41. SOPRANO (SOP Spectral Library). Available online: <https://soprano.kikirpa.be/index.php?lib=sop> (accessed on 29 November 2023).

42. Fremout, W.; Saverwyns, S. Identification of synthetic organic pigments: The role of a comprehensive digital Raman spectral library. *J. Raman Spectrosc.* **2012**, *43*, 1536–1544. [[CrossRef](#)]
43. Scherrer, N.C.; Stefan, Z.; Françoise, D.; Annette, F.; Renate, K. Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2009**, *73*, 505–524. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.