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Comprehensive characterization of modern industrial Argentinian paints for improved chronological painting attribution

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ABSTRACT

Throughout the twentieth century, the paint industry developed a multitude of new binding media, pigments and additives that improved the appearance, ease of application, and performance of modern industrial paints. Depending on when and where they were first manufactured, and when they were introduced into paint formulations, some of these new paint components could conceivably be chronological markers useful in assigning attribution to specific artists or in the study of forgeries. The aim of this study was to develop a systematic methodology for characterizing organic and inorganic materials in modern paints, and search for potential chronological markers. Colored reference paints manufactured by local companies in Argentina from the 1940s and 1950s were studied with a multi-analytical approach that included Fourier-transform infrared spectroscopy, gas chromatography coupled with mass spectrometry, Raman spectroscopy, X-ray diffraction, X-ray fluorescence and scanning electron microscopy with energy dispersive X-ray analysis. A wide range of compounds was identified due to the complementarity use of the analytical techniques. Historical references, patents, books, and scientific publications about the materials used in that time period provided invaluable information in establishing tentative timelines for modern paint components. This investigation was part of a broader interdisciplinary investigation of Concrete Art, an international art movement of the beginning of the twentieth century, which took place in Argentina and other nearby countries during the 1940s and 1950s. To prove the concept, a micro-sample from *"Obra N° 171"* by Raúl Lozza was analyzed. Organic and inorganic fractions were studied and the information collected was correlated with developed timelines to support the authentication process. Ultimately, the information from this study may also have a direct impact on the key areas of material characterization, aging behavior, and conservation of works of art made from these products.

1. Introduction

Modern paint formulations reflect the wide range of materials produced by industrial and technological processes developed during the twentieth century. They are composed of a variety of natural and synthetic oleoresinous binding media, organic and inorganic additives, organic and inorganic pigments, and inorganic extenders. Compared to more traditional paints, modern paint formulations afforded improvements in drying rate, formation of self-leveling films, rheological properties, lightfast colors, and intensity in hue and shade variations [1–3].

The breadth of modern paint formulations poses an analytical challenge for cultural heritage researchers seeking to distinguish different types of binding media, learn about manufacturing processes and subsequent artists' modifications, and deepen the knowledge of the material markets in the twentieth century. Characterizing of these organic and inorganic fractions is complicated

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by the limited samples sizes available for analysis from artworks. Analytical research contributes to technical art history studies of artists' techniques and aids conservators in their efforts to prevent material deterioration [1,4–6]. One particularly desirable outcome would be the discovery of materials that could serve as chronological markers relating to production date, which would aid in studies of attribution and in the identification of forgeries.

For natural oleoresinous binding media, drying oils combined with pine resin defined the "common enamels" as they were called at the local paint industry [7]. On the contrary, synthetic enamel paints were composed of alkyd resins combined with organic additives as metal stearates (which are also present in "common enamels"), raw or modified fatty acids and reaction controllers [7,8]. The types and proportions of polyols and polybasic acids, which constitute the polyester resin alkyd backbone, all vary according to the manufacturing period [8].

Regarding modern pigments, the pigment legacy of the latter part of the 19th century was greatly augmented by the thriving industrial output of the 20th century to expand the palettes of ambitious artists and the commercial marketplace who sought after new hues and shades without compromising their color stability. This led to the advent of new synthetic inorganic and organic pigments with reduced toxicity that exhibited subtle variations of hues and lightfast brilliant colors and also lowered manufacturing costs [2,3,5]. In particular, organic pigments have a broad range of chemical compositions, so they are studied under diverse classification systems. Their chemical variability was altered by manufacturers to achieve improved stability, solubility, and hue. The breadth of composition together with small particle sizes and low concentration in paint formulations make their identification in modern paints challenging [9,10]. The analytical situation is further complicated from the early 1930s to the late 1950s by the introduction of additives [1–3]. They were added to binding media in order to reduce drying times, prevent pigment decantation and improve rheological properties, among others [11]. Concerning pigment additives, it was important for domestic and commercial paint industries to improve lightfastness and color intensity but also to control the cost. To this end, development of coatings on pigment grains, the addition of salts, and crystalline structure modifications became common practices. Surface treatment of the grain in some inorganic pigments or metal replacement in the salt crystal structure, together with possible manufacturing by-products, broaden the range of elements that can be detected in paint samples [12–14].

Several studies on the characterization of modern painting materials carried out throughout the last decades have enriched our understanding of modern paint formulations [4,5,15–18]. Some of the analytical techniques applied for this purpose are Fourier-transform infrared spectroscopy (FTIR) [5,12,19,20], Raman spectroscopy [5,12,20,21], pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS) [6,20], GC/MS using various derivatization reagents [8,16,18,22], X-ray fluorescence spectrometry (XRF) [12,23], X-ray diffraction (XRD) [24], and scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX) [12,18,24]. Due to the highly complex modern paint matrixes, these studies illustrate the challenges of obtaining detailed and exhaustive characterization from heterogeneous small samples. To this purpose, some aspects have been thoroughly studied: the industrial modifications of paint components, the analytical tools to unravel these subtle component variations and the optimization of multianalytical protocols for studying microsamples from paintings. In this regard, analysis of reference material collections has been essential for keeping track of manufacturing processes and development of in-depth material databases.

The aim of this study is to contribute to the characterization of modern paint components as well as the search of potential chronological markers which will improve painting attribution studies. Further, this research is part of the interdisciplinary investigation of Concrete Art, an international art movement of the beginning of the twentieth century, specifically the 1940s and 1950s, which took place in Argentina and Brazil [25,26]. That group of artists pursued sleek and pure geometrical forms in trying to reach the objective predominance of materials themselves without leaving any personal footprint [25]. It offers an interesting potential link between the aesthetics and the selection of materials. However, the scarce history of the local paint industry does not provide sufficient information to fill the knowledge gaps. The study of modern paints using a multi-analytical approach, in combination with archival research, helps to provide the necessary information [26]. In this study, a reference paint collection from circa 1950s and the artwork "*Obra N° 171*" by the concret artist Raúl Lozza have been studied using a multi-analytical protocol with emphasis on the colored paints, complementing and expanding upon published research on the white paints in the palette [18]. However, new challenges had to be overcome when facing the colored palettes of twentieth century, in which complex combination of pigments, dyes and extenders can be found for color design purposes [1,3]. Blue, green and red paints of local brands from the reference collection were analyzed. The inorganic fraction, which is mainly pigments and extenders, was studied using X-ray diffraction, micro-Raman spectroscopy, X-ray fluorescence, and scanning electron microscopy with energy-dispersive X-ray analysis. The organic fraction composed of binding media, organic additives, and organic pigments was characterized by gas chromatography-mass spectrometry. Additionally, Raman spectroscopy and FTIR were also employed for compound and crystalline structure identification. Additionally, to prove the concept, a micro-sample from *Obra N° 171*" authored by Raúl Lozza was studied. The chemical information collected was correlated with developed timelines to give a time framework for the painting materials involved in the artwork.

2. Research aim

This study aims to comprehensively characterize modern paintings by applying a multi-analytical approach, which includes X-ray diffraction, scanning electron microscopy, gas chromatography coupled to mass spectrometry, Raman spectroscopy, Fourier-transform infrared spectroscopy, and X-ray fluorescence. Additionally, the obtained results were cross-referenced with historical references, patents, books, and scientific publications. The final goal is to detect specific compounds that can serve as time markers, ultimately contributing to resolving painting attribution issues.

3. Materials and methods

3.1. Reference samples

Brand, color, and description of the reference paints studied in this paper are shown in Table 1.

All the products, originally acquired before 1958, were donated by a local hardware store. The content was certainly not adulterated since the cans were never opened until the moment of analysis. Paints were deposited onto glass slides and dried at room temperature for 30 days. Depending on the analytical technique, samples were taken with a scalpel if needed or directly analyzed.

3.2. Artwork sample

"*Obra N° 171*" (1948), in the collections of the *Museo de Arte Moderno de Buenos Aires* (MAMBA), is part of the Argentine Concrete Art corpus and has no previous restorations. It is a three-dimensional object with six geometrical shapes arranged on the

Table 1
List of reference paints, indicating color, brand and code.

	Color name	Brand	Code
	Green (*Verde ilusión*)	Alba	VIA
	Green	Mi Luz	VML
	Blue	Mi Luz	AML
	Light-blue (*Cielo*)	Mi Luz	CML
	Light green (*Menta*)	Colorín	MC
	Vermillion	Bull Dog	BBD

background. A red microsample of paint (less than 1mm^2) was removed from the front edge of one of the geometrical shapes (Fig. 1) using a scalpel, under the supervision of the museum conservator, in keeping with the concept of minimal invasiveness of a work of art. Sampling proved to be challenging task due to the sleek and smooth surface. The sample was divided into two pieces for separate analyses and stored in a 2 mL Eppendorf tube.

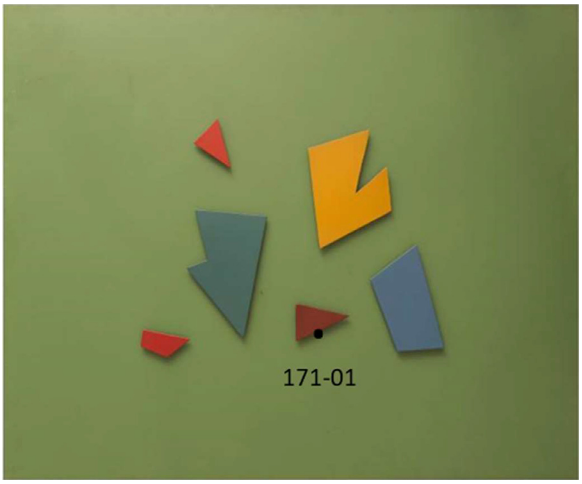


Fig. 1. Artwork "Obra N° 171" by Raúl Lozza. Sample 171–01 was taken from the corner of the bordeaux geometrical shape.

3.3. Cross section and optical microscopy

In order to visualize the layering structure of the paint, a cross section of sample 171–01 from "*Obra N° 171*" was embedded in a single-component light-curing acrylic resin (Technovit LC2000) and polished by hand using abrasive cloths of different grits (1500 to 12,000). Optical microscopy was performed using a Leica DM4000. Micrographs were taken with a Flex Camera (Diagnostic instrument) under visible polarized light.

3.4. Gas chromatography-mass spectrometry (GC/MS)

Reference samples were analyzed using a GC–MS Agilent 7890A GC/5975C inert MSD equipped with a Thermal Separation Probe (TSP). For qualitative analysis, a small sample of paint ($\leq$0.5mm^2) was added to a TSP vial, mixed with 1.6 µl of 2.5% tetramethylammonium hydroxide (TMAH) in methanol (Sigma Aldrich), then the vial was placed in the TSP probe. After inserting the probe into the multimode GC inlet, the inlet was heated ballistically to 450 °C and held at that temperature for 30 s. Injection was performed in splitless mode with a solvent delay of 4.5 min. A J&W DB-5MS-UI capillary column (30 $m \times$ 0.25 mm $\times$ 0.25 µm) was used for separation, with helium carrier gas at 1.2 mL min^{-1}. The oven temperature program was: 35 °C for 3.5 min, 60 °C min^{-1} to 100 °C, 8 °C min^{-1} to 240 °C, 3 °C min^{-1} to 250 °C, 20 °C min^{-1} to 310 °C, and isothermal for 11.5 min. The mass spectrometer was operated in full scan mode between 12 and 600, with the electron multiplier set to the autotune value.

Data interpretation was carried out using ESCAPE (Expert System for Characterization using AMDIS Plus Excel) for synthetic modern materials, which was developed by the Getty Conservation Institute (GCI) working with experts from other institutions [27,28]. Compounds were identified by mass spectra and retention index (RI) matching. Kovats RIs were calculated from the analysis of an n-alkane ladder.

Sample 171–01 was analyzed using an Agilent 6890 N/5973 inert GC/MS system (Agilent) with a fused silica capillary column Zebron ZB-5HT Inferno (Phenomenex, US) stationary phase 5% phenyl–95% dimethylpolysiloxane, 30 m length, 0.25 mm i.d., and 0.25 µm film thickness. The separation and quantification methods were based on our previous work [18].

3.5. Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)

SEM-EDX analyses of reference samples were performed using a SEM-EDX FEI QUANTA 250 (FEI, Oregon, USA). The accelerating voltage and current employed were 10 kV and 1.1 nA, respectively. The working distance was 10 mm. Sample 171–01 was analyzed using a FEI-Philips XL30 ESEM-FEG with 20 kV accelerating voltage, 0.9 Torr pressure, and 10.5 mm working distance.

3.6. X-ray diffraction analysis (XRD)

X-ray powder diffraction analysis were carried out using a PANalytical X'Pert Powder diffractometer. Cu Kα radiation between 5° and 70° (2θ), path length 0.02° and 315′ of counting time were used.

3.7. Raman spectroscopy analysis

Raman spectra acquisition was accomplished employing a Lab RAM HR Raman system (Horiba Jobin Yvon), coupled to an imaging microscope with a magnification of 10X, 50X, and 100X. The spectrometer is equipped with two monochromator gratings and a charge coupled device detector. The spectral resolution achieved was 1.5 cm^{-1} with a grating of 1800 g/mm and hole of 100 µm. The excitation source was a He-Ne laser line at 632.8 nm. In order to avoid sample overheating, the laser fluence was filtered with a power density around 1.4 W/mm^2.

3.8. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis were carried out using a 15X magnification Schwarzschild objective on a Hyperion 3000 FT-IR microscope (Bruker Optics Inc.). The instrument has a liquid nitrogen-cooled mid-band MCT detector purged with dry air. Samples were positioned on a diamond window and a metal roller was employed to flatten them. The spectra were the sum of 64 scans with 4 cm^{-1} resolution within the range between 600 cm^{-1} and 4000 cm^{-1}.

3.9. X-ray fluorescence (XRF)

Samples were analyzed employing a portable micro-XRF model Elio (Bruker) with energy dispersive detection. Spectra were acquired using an unfiltered Rh X-ray radiation at a potential of 40 kV and a current of 40 µA for 120 s.

4. Results and discussion

For the sake of clarity, results will be structured in *reference samples* and *artwork sample* sections. Likewise, each section will be divided into four sub-sections: *binding media, pigments, additives, and integration of results*. Notably, the sub-section *additives* comprises organic and inorganic compounds whose presence was intended to enhance color intensity, light fastness, drying properties, and desired surface finishing of paints. Finally, the sub-section *integration of results* collates all the information experimentally obtained with the chronological evidence found in literature for the purpose of generating a timeline based on paint technology.

4.1. Reference samples

4.1.1. Binding media

Alkyd resins are modified polyesters formed by the combination of polyhydric alcohols and polybasic acids. The final properties are tuned by the addition of fatty acids or fatty oils. The FTIR technique enabled the identification of oil-modified alkyd resin in most of the paints (VIA, VML, AML, CML, and MC), and drying oil for BBD. The alkyd resin nature characterized by a high content of oil and fatty acids gives similar C–H and carbonyl stretching absorption bands (circa 2930, 2860, and 1730 cm^{-1}) to drying oils. At circa 1270 cm^{-1} a distinctive peak is found for alkyd resins together with two sharp bands at 1130 and 1070 cm^{-1}. In addition, alkyd resins spectra present peaks at 1450 and 1583 cm^{-1} due to aromatic skeletal ring [29]. In Table S1 are listed the results obtained from FTIR. The obtained spectra are presented on the Supplementary Material (Figures S1-S6). The classification of the type of binding media can be done based on the presence or absence of polybasic acids distinguished on Table 2 (phthalic acid, and terephthalic acid). The paints VIA, VML, AML, CML, and MC can be classified as alkyd resins due to the presence of these polybasic acids [8]. This result is consistent with these paints being classified as *synthetic enamel*. As described by local documentation from early 50 s, this classification corresponds to alkyd resins in combination with processed drying oils [7]. The sample BBD corresponds to an oleoresinous paint due to the absence of polybasic acids. The GC/MS results are reported on Table 2 and their chromatograms are presented in the supplementary information (Figures S7- S12).

Although phthalic acid was the major polybasic acid identified, other components with similar functional groups were also iden-

Table 2
Reference samples GC/MS analysis results. Component ratios are expressed in terms of GC–MS peak areas. Experimental details are summarized in *Section 2.3*.

	Components	VIA	VML	AML	CML	MC	BBD
Polyol	Glycerol	X	X	X	X	X	X
	Pentaerythritol		X	X	X	X	
Polybasic acids	Phthalic acid	X	X	X	X	X	
	Terephthalic acid			X			
	Benzoic acid	X	X	X	X	X	
Fatty acids	Short chain fatty acid (<10C)	X	X	X	X	X	X
	Lauric acid	X		X		X	X
	Myristic acid	X	X	X	X	X	X
	Palmitic acid	X	X	X	X	X	X
	Margaric acid	X	X	X			X
	Oleic acid	X	X	X	X	X	X
	9,12-Octadecadienoic acid (Z,Z)	X					
	8,11-Octadecadienoic acid		X			X	
	Stearic acid	X	X	X	X	X	X
	Arachidic acid	X	X	X	X	X	X
	Behenic acid	X	X	X	X	X	X
	Lignoceric acid	X	X	X	X	X	X
	Pimelic acid	X	X				X
	Suberic acid	X	X	X	X	X	X
	Azelaic acid	X	X	X	X	X	X
	Sebacic acid	X	X	X	X	X	X
	Undecanedioic acid						X
	Dodecanedioic acid						X
Additives	Pine resin	X					X
	Decamethylcyclopentasiloxane			X			
	All FAs/Glycerol	3.16	4.43	5.88	8.33	18.24	16.10
	All FAs/Polyols	3.16	3.48	5.62	6.27	3.04	16.10
	Benzoic acid/PA	0.27	0.04	0.03	0.03	0.05	–
	A/P	0.6	0.5	0.5	0.3	0.6	0.5
	Dicarboxylic/P	0.21	0.14	0.20	0.14	0.18	0.59
	A/Sub	5.65	6.37	5.02	5.22	5.22	1.90

tified: terephthalic acid and benzoic acid Although the latter is a monobasic acid, it was included in Table 2 along with polybasic acids since it also serves as a marker for the presence of an alkyd resin. It is reported in patents related to this type of paint manufactured since the 1930s, and apparently its use continued during the 50′s. It was added to prevent gelation in “short-oil” alkyds (those with a low proportion of fatty acids) with pentaerythritol as the main polyol, [30] or as a reaction controller [19,30–33]. Benzoic acid was also added to affect certain polymer properties, such as increasing the glass transition temperature (T_g) [8]. To somewhat complicate matters, benzoic acid may form as degradation product of phthalic acid by the loss of an acidic moiety [17]. Looking at the material chronology, phthalic anhydride was manufactured locally in 1953 [34]. Prior to that, the local paint industry imported it from other suppliers. This fact, together with the scarcity of raw materials during WWII, should be considered as an impulse for diversifying resources. In this sense, the use of alternative acids such as benzoic acid could be a natural option. Among the reported ratios, *benzoic acid/phthalic acid* (which considers the sum of the dicarboxylic benzene isomers), only the paint VIA has a high value (0.27) which seems to indicate an intentional use of benzoic acid.

Regarding polyols, BBD and VIA contain glycerol, whereas the other paints contain glycerol and pentaerythritol. During the late 1940s pentaerythritol has gained popularity in alkyd resins as its four hydroxyl functional groups allowed higher oil content in the resulting alkyd formulations giving economic benefits compared to glycerol [3]. In addition, it also improved physical properties such as flexibility, water resistance, gloss and gloss retention [8,11]. The low value reported for the ratio *All FAMEs/polyols* in paints CML and MC in comparison with *All FAMEs/glycerol* suggest a higher content of pentaerythritol.

Regarding dicarboxylic acids, the reported ratios *azelaic acid/palmitic acid* (A/P), dicarboxylic acids/palmitic acid (dicarboxylic/P) and *suberic acid/azelaic acid* (Sub/A) are relatively similar so no further conclusions can be drawn. However, in the case of BBD, the Sub/A ratio could suggest the use of heat-bodied oil supported also by the high proportion of dicarboxylic acid and palmitic acid [35].

4.1.2. Pigments

Table S1 also shows the pigments which could be detected by FT-IR. Sample BBD (Figure S6) shows absorption lines that could be matched with bibliography and identified as B-naphthol lake (PR 49) [36]. Notably, the complexing metal will determine the color shade variation. According to IRUG [37] database, the BBD sample FT-IR spectrum seems to be from sodium salts that correspond to PR 49. The other variations, PR 49:1, PR 49:2 and PR 49:3, are complexed with Ba, Ca and Sr, respectively. The FT-IR absorption lines helps narrow down the possibilities although the combination with an elemental technique contributes to a more detailed characterization.

Sample VML shows an intense and distinctive absorption line at 2094 cm^{-1}, which is assigned to Prussian blue. For samples VIA and VML, the absorption region between 810 and 940 cm^{-1}, could be attributed to the Cr-O stretching [29]. This could be related to chrome oxide content pigment associated to those with chromate anion ($CrO_4{}^{-2}$) combined with metals such as Pb, Ba, Sr and Zn giving yellow and red pigments. Additionally, other chrome oxides corresponding to green pigments as $Cr_2O_3 \cdot 2H_2O$ and Cr_2O_3 can be also achieved. Although some distinctive bands are suggested for correct pigment characterization by FT-IR [38], strong lines from the binding medium overlap the region 1079–1168 cm^{-1} for pigment differentiation. Therefore, Raman spectroscopy has been applied to aid in the identification of chromium-based pigments. Raman spectra (Figure S13 and S14 from supplementary information) confirms the presence of chrome yellow, showing the characteristic bands at 844 and 350 cm^{-1} attributed to crocoite ($PbCrO_4$) for VIA and VML [39]. For VML sample, the Raman bands at 2153, 2091, 2074 cm^{-1} also give a clear identification of Prussian blue. However, the green shade of the paint could be associated to the one described in the technical manual edited in 1947 in Buenos Aires “*El pintor decorador*” (the decorator painter), where several paint mixtures are detailed [40]. For the “*verde hoja*” (green leaf) mix, 2 parts of chrome yellow, 2 parts of Prussian blue and 1 part of emerald green were needed [40]. The latter pigment does not represent a precise name and several chemical compositions could be attributed [41]. A possible association could be copper acetate arsenite ($Cu_4(AsO_2)_6(CH_3CO_2)_2$ which use is reported for interior design and easel paintings from the 19th century. Its last use was reported in 1925 although these types of pigments were banned at late 19th century due to their toxicity [42]. CAMEO database mention the lack of standardization to the term “*emerald green*” which could also be associated to chrome oxide or synthetic pigments [43]. The Pigment compendium goes further in the explanation about of the misunderstanding of this term and says that the French term *vert émeraude* refers to a transparent chromium oxide, the English viridian. However, it suffered an incorrect translation as emerald green (and possibly *verde esmeralda* in Spanish as well) leading to the confusion with the copper and arsenic-based pigment [41]. Raman spectrum of VML sample (Figure S14 from supplementary information) shows a band at approximately 530 cm^{-1} which could be attributed to viridian green but [42] it is not conclusive although this result would be consistent with the information reported above.

Raman spectrum of sample BBD (Figure S15 from supplementary material) shows the presence of the following bands: 1617, 1602, 1558, 1482, 1464, 1449, 1424, 1413, 1350, 1256, 1231, 1216, 1199, 1135, 1096, 991, 719, 643, 604, 527, 479, 469, 410, 342, 299, 154 cm^{-1} which could be consistent with presence of B-Naphthol red (PR 49) [9,44,45]. The rest of the paints, namely VIA, AML, CML and, MC, (Figures S13, S16-S18) are consistent with the organic pigment phthalocyanine [9,46]. This pigment is generally present at low concentration in paints due to its high tinting strength [47]. In this line, phthalocyanine characterization with Raman spectroscopy is convenient since it is practically undetectable by other techniques such as FTIR. Phthalocyanines were commercially available in 1935 [21] and different blue and green shades were obtained according to the presence or absence of halogenated substituents [48,49]. Although the characteristic Raman spectra of these different phthalocyanines are very similar, the spectral region between 1350 and 1550 cm^{-1} is a fingerprint [50]. This spectral region describes the cavity size of the organic structure to host different metal ions [46]. These characteristic bands are reported in bold in Table S2. According to literature, the reported values correspond to either copper, iron or cobalt phthalocyanine. In particular, the line at circa 1530 cm^{-1} is highly influenced by the metal that is complexed [46]. Thus, elemental analysis results are a vital complement to these studies. The work developed by Scherrer [9] presents a flowchart where different organic pigments with very similar spectra can be distinguished. The measured Raman lines lead us to PB 15:3 which corresponds to the unstabilised B-copper phthalocyanine. In connection to Raman identification of phthalocyanine, attention must be paid to possible misinterpretation of results. For instance, CML and MC Raman spectra (Figure S17 and S18 from Supplementary Information) could be mistaken for a green earth pigment spectrum. This pigment is generally composed by K, Al, Fe and Mg silicate [51]. Nevertheless, its composition and crystalline structure can be subjected to modifications according to the origin of the ore [52]. Although it is confirmed the use of this pigment in modern palettes, it is reported to have a low tinting strength, leading to its use in high concentrations in paints [53,54]. Consequently, this would lead to higher

Table 3
XRD, Raman and XRF results. The elements presented in bold correspond to those which confirm the components detected through XRD and spectroscopy technique. Experimental details summarized in *section 2.5.* (XRD), *section 2.6.* (Raman) and *section 2.8* (XRF).

Code	XRD	Raman	XRF
VIA	Rutile (TiO_2) Crocoite (PbCrO4)-(Monoclinic and orthorhombic)	Crocoite ($PbCrO_4$) PB15:3 (B-copper phthalocyanine), Iron phthalocyanine or cobalt phthalocyanine.	**Ti, Pb, Cr, Fe, Cu, Co**, S, Sb, Zn, Ni, Cl
VML	Barite plumbian ((Ba,Pb)SO4) Crocoite ($PbCrO_4$) Prussian blue $Fe_4(Fe(CN)_6)_3(H_2O)_{14}$ Litharge (PbO)	Prussian blue ($Fe_4[Fe(CN)_6]_3$) Crocoite ($PbCrO_4$) Viridian $Cr_2O_3{\cdot}2H_2O$	**Pb, Cr, Fe,** Cl, Ca, Zn, Mn, Zr, Ti
AML	Rutile (TiO_2)	PB15:3 (B-copper phthalocyanine) or Iron phthalocyanine	**Ti, Fe, Cu**, Ca, S, Zn, Pb
CML	Rutile (TiO_2)	Iron phthalocyanine or Cobalt phthalocyanine Rutile (TiO_2)	**Ti, Fe, Co,** Ca, Zn, Pb, Sr, Ni
MC	Rutile (TiO_2)	Iron phthalocyanine, Cobalt phthalocyanine or copper phthalocyanine	**Ti, Fe, Co, Cu,** Ca, Zn, Pb, Sr, S, Cr, Cl
BBD	–	B-naphthol lake, PR 49	**Ca, Ba,** Cl, Pb, Fe, Co, Mn, Zn, Zr, Sr

paint manufacturing costs which is not congruent with a post-war local paint industry looking for alternative raw materials. In addition, it was difficult to obtain high-quality green earth from 1913, especially out of Europe, which lead to the common practice of pigment adulteration [53]. In connection to this, in Figure S19 the database Raman spectrum of phthalocyanine is presented together with the database spectrum of green earth. It can be seen by the coincidence of several bands beside their different composition that the reference material employed may have been green earth adulterated with phthalocyanine. In Table S2, results from Raman spectroscopy are reported.

The results from XRD, Raman and XRF for the different studied samples are summarized in Table 3. The presence of TiO_2 in the rutile form in VIA, AML, CML and MC, would indicate the manufacture of these paints after late 1930s/early 1940s as their first synthetic manufacture dates from 1937. Before that, only titanium white in the anatase form was used in paints [55]. In samples VIA and VML the presence of chrome yellow is confirmed. However, it is not clear if the crystalline structure of crocoite ($PbCrO_4$) is either monoclinic or orthorhombic, and if it was co-precipitated with lead sulfate ($PbSO_4$). Although chrome yellow appeared on artists' palettes in the late 19th century, its well-known color degradation led the industry to develop improvements during the 20th century to increase color intensity and achieve lightfastness without compromising production costs [13,39,41,56]. The possible presence of barium sulfate in VML could be related to the addition of this salt, as well as Sr and Ca sulphates, to improve color intensity, [57] although these elements were not detected through XRF.

Elemental analysis using XRF allowed to confirm the components detected through XRD and vibrational spectroscopic techniques. In Table 3, these elements are shown in bold together with those found which are possibly complexed to organic pigments, such as phthalocyanine and naphthol red. In sample VIA (Figure S20 from Supplementary Information), Ti, Pb, Cr, Fe, Cu and Co were identified. The elements Ti, Pb and Cr confirm the presence of rutile and crocoite respectively. The elements Fe, Cu and Co are in agreement with the analysis performed by Raman spectroscopy related to the presence of phthalocyanine. In sample VML (Figure S21 from Supplementary Information), the elements Pb, Cr and Fe were identified. They confirmed the presence of crocoite, litharge, viridian and Prussian blue detected with XRD and Raman. The Barite plumbean identified through XRD is coherent with the presence of Pb but neither Ba nor S were detected. In samples AML, CML and MC (Figures S22-S24) can be seen the presence of Ti in correspondence with the rutile identified through XRD. Regarding possible metals complexed with phthalocyanine, the possibilities are: i- Fe and Cu for AML, ii- Fe and Co for CML and iii- Fe, Cu and Co for MC. Finally, in sample BBD (Figure S25), Ca and Ba were found. This could be attributed to metals complexed with B-naphthol red which can be related to the presence of PR 49:1 (Ca) and PR 49:2 (Ba) [58]. However, the high wavenumber absorption bands at 3560 and 3496 cm^{-1} from the FTIR spectrum have a better match with PR 49 which corresponds to the sodium salt [37]. This information cannot be corroborated by XRF since light elements ($Z \leq$ Na) cannot be detected because of the absorption of low-energy X-rays through air path. However, low Z elements could be confirmed with SEM-EDX. On the contrary, the maximum accelerating voltage employed with this technique is restricted by the possible sample charge. This fact limits the detection of high Z elements; thus, if necessary, it is convenient to complement the analysis with a more sensitive technique such as XRF. At the same time, SEM-EDX detection limit is approximately 1000 µg/g while XRF detection limit is about 10–50 µg/g. Table 4 reports the comparative results obtained with both elemental techniques.

4.1.3. Additives

The XRF and SEM-EDX results enable the detection of elements that form components not detected by other techniques, either because of their lack of crystallinity or low proportion. Most of the time, these compounds could represent potential chronological markers. As described in the Introduction, these components correspond to additives employed by industry to improve the properties of binding media or pigments. The determination of these additives through elemental analysis results mostly inconclusive but, in combination with molecular techniques, it might shed light over a great number of cases. In this line, it is worth mentioning that an element can be present in different types of additives so the consideration of the chronological evolution of the paint industry could also work as a complement.

As it was described in *section 3.1.2*, Table 4 detailed the elements detected through XRF and SEM-EDX techniques (Figure S26-S31 from Supplementary Information, SEM-EDX results). To focus on the possible additives content, the elements described will be those not detected through molecular techniques. In general, most of the metals could be present forming metal soaps [59–61]. All samples contain Zn and Al, possibly assigned to metal stearates mentioned in 1920 [59]. Their intention was to modify rheological properties, increasing body and suspension properties. Locally, in a publication in 1942 about stearates, mainly based on Al, but also from different metals including Mg, Ca, Ba, Pb, Ti and Zn, is reported its use as flatting and suspension agents [61]. It is not precisely detailed when they were included by local paint manufacturers, but they seem to gain popularity during the decades of interest. Some of these metals are present among the samples. Sample VML contains Ca and Ti; samples AML contain Ca and Pb while CML and MC, only contain Ca. For BBD, Pb was detected. However, these and other metals could be also from different types of driers whose properties were also part of the manufacturing strategy. In a

Table 4
Comparative results of XRF and SEM-EDX. The elements in bold green color are the ones coinciding. For SEM-EDX column those elements between brackets are those detected under quantification limit.

Code	XRF	SEM-EDX
VIA	**Ti, Pb, Cr, Fe, Cu, Ni,** Co, Zn, S, Sb, Cl	**Ti, Pb**, Al, (**Cr**, Si, **Fe, Ni, Cu,** Mn)
VML	**Pb, Fe**, Ca, Cr, Zn, Mn, Zr, Ti, Cl	**Pb**, (Al, **Fe**, Na, Si, Cu, Co, S)
AML	**Ti, Fe, Cu,** Ca, Zn, Pb, S	(**Ti**, Al, Pb, **Fe**, Si, S, Ca, **Cu**)
CML	**Ti, Pb,** Fe, Co, Ca, Zn, Sr, Ni	(Al, **Ti, Pb,** Na, Si)
MC	**Ti, Fe,** Cu, Co, Ca, Zn, Pb, Sr, S, Cr, Cl	(Al, **Ti**, Pb, **Fe**, Ca, Ni, Si)
BBD	**Ca, Ba,** Zn, Pb, Fe, Co, Mn, Zr, Sr, Cl	Al, (Na, S, Pb, Fe, **Ba**, Si, **Ca**)

patent from 1952 [60] three types of driers are described: primary driers, secondary or bottom driers and auxiliary driers. The formers were supposed to speed up the process of producing a tack-free surface in a short time. The most popular of them was Co soaps which did not have the staining disadvantage of Mn and V soaps. Secondary driers, used in combination with primary driers, promoted the drying through the paint film. The most popular were Ca and Pb soaps. The auxiliary driers did not have adequate drying properties but, used in combination with the primary and secondary ones, they contributed to enhanced drying processes and the final surface appearance. The most popular of the latter were Zn, Al, Li and alkaline earth metal soaps. This same patent reports the new incorporation of a “booster drier” which consists in the use of Zr. It had the advantage of replacing a high proportion of primary driers, diminishing staining issues, giving more hardness and surface adhesion. According to this information, only VML and BBD could have primary driers due to their content of Mn and Co. However, the co-presence of Ca and Pb in samples AML, CML and MC as possible secondary driers is not congruent with the absence of potential primary driers. Only sample VML is consistent with the presence of Mn and Co as a primary drier and Ca and Pb as a secondary drier. In sample VML, Zr was detected through XRF analysis, possibly as a “booster drier”.

For those samples containing chrome yellow, VIA and VML, metals could be present also forming salts as pigment additives to improve lightfastness and color intensity. In a patent from 1937, [62] it is suggested the use of Zr and Ti salts to stabilize the chrome-based pigment. In VML these two metals are present. In a patent of 1943, [63] the use of trivalent Sb salts (usually chlorine salts) is proposed for improving weather and light stability. As can be seen in Table 4, sample VIA contains Sb and Cl, while Zr was not detected. As stated in references [2,64], the presence of Al and Si along with rutile, could be due to alumina and silicate pigment coatings which diminish the chalking effect. Nevertheless, chronological information concerning these coatings is not clear. Some part of the literature point out that this technology was implemented between 1935 and 1940 [64] while other part mentions these coatings were developed at the late 1950s and early 1960s [2].

In addition, some organic components could have been also added as flow promoters and non-ionic surfactants. In sample AML, decamethylcyclopentasiloxane is reported in Table 2. This component represents a cyclic siloxane which according to the literature were incorporated during the 1950s [65].

4.1.4. Integration of results

This section intends to integrate the lines of evidence collected from different analytical techniques as well as different paint functionality (i.e., binding, pigment or additives). To this end, Fig. 2 summarizes the results obtained from chemical studies along with historical documents describing paint technology advances from different moments in history.

In this example (Fig. 1), the sample VIA seems to be a paint from late 50′s since it has antimonium salts and rutile white titanium coating of silica and alumina. Furthermore, Figures S32-S36 from Supplementary Information illustrate the results obtained for the rest of the reference samples.

Regarding samples AML, MC and CML are attributed to late 40 s since they have pentaerythritol as polyol. Sample VML and BBD could be from early 1950s due the presence of zirconium salts as a drier.

4.2. Artwork sample

4.2.1. Binding medium

GC/MS analysis of paint sample 171–01 from *“Obra N° 171”* showed a large proportion of phthalic acid together with fatty acids and polyols, which is consistent with alkyd resin. During an interview in 1999 with Raúl Lozza, he mentioned using drying oils mixed with synthetic varnishes to reduce drying times. This practice contributed to the increased durability of the paints, and made it possible to sand his works between paint layers to obtain smooth surfaces [66]. As described by local documentation from 1944, synthetic varnishes were composed of alkyd resins [67]. Although these test results are consistent with a mixture of drying oil and alkyd resin, it is not possible with this analytical method to differentiate drying oil/phthalate alkyds from mixtures of drying oils with phthalate alkyds.

Regarding polyols, glycerol and pentaerythritol were reported. The latter is consistent with the late 40 s or early 50 s date estimated for the artwork, when pentaerythritol gained in popularity [3]. The fatty acid profile is constituted by saturated fatty acids (palmitic, stearic, behenic, arachidic and myristic), and dicarboxylic fatty acids (suberic, azelaic, pimelic, and sebacic). In addition, oleic acid was identified in spite of the processes of autoxidation and polymerization, which occur during natural aging, that cause a decrease in unsaturated fatty acid content [68]. This phenomena is often observed in paints that contain pigments such as zinc white that decrease drying rate [69]. Previous research of Concrete Art artworks carried out by this group also showed zinc white paints associated with high levels of oleic acid [18]. Furthermore, high levels of dicarboxylic fatty acids (52%) were indicative of autoxidation and cleavage of unsaturated fatty acid chains caused by aging. Table 5 summarizes the results obtained by GC/MS, and the chromatogram is shown in figure S37.

4.2.2. Pigments and additives

Fig. 3 shows polarized light and backscattered electron images for the cross section of sample 171-01. Four violet layers were identified on the lower part of the sample, and three red layers on the upper part. SEM-EDX analysis were performed for each layer. The spectra appear in the supplementary material (Figure S38) with elemental mapping of the cross section (Figure S39).

Figure S39 shows layer 1 is rich in Zn, which is associated with zinc white and high levels of oleic acid. Zinc in combination with Ba and S could be related to lithopone (ZnS + $BaSO_4$), a pigment patented in 1874 [70] and locally produced starting in 1943 [71]. Although its crystalline structure cannot be specified, the content of Ti suggested the employment of titanium white in layers 2, 3, 4

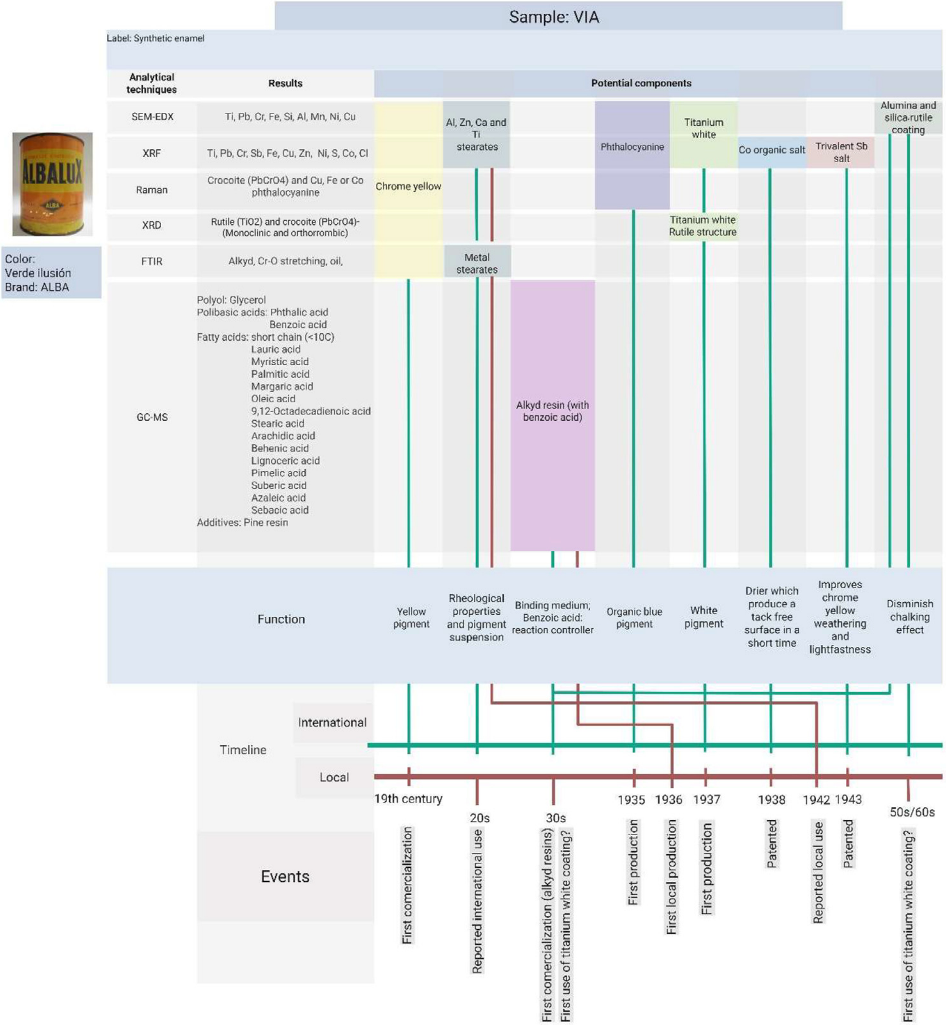


Fig. 2. Integration results of sample VIA. First column indicates the analytical techniques applied; second column gives the results obtained. Each block displayed on the center of the figure represents the components attributed. All of them are connected with green and red arrows to their function and the timeline at the bottom. Green arrows represent international events while red ones indicate local events. Finally, the last row explicits each event connected to dates.

Table 5
Sample 171-01 GC/MS results. Dicarboxylic percentage is expressed in terms of GC–MS peak areas.

		171-01
Polyol	Glycerol	X
	Pentaerythritol	X
Polybasic acid	Phthalic acid	X
Fatty acids	Myristic acid	X
	Palmitic acid	X
	Oleic acid	X
	Stearic acid	X
	Arachidic acid	X
	Behenic acid	X
	Pimelic acid	X
	Suberic acid	X
	Azelaic acid	X
	Sebacic acid	X
Aditivos	Pine resin	X
	%D	52%

and 5. Ba and S show a similar distribution along the cross-section, which is consistent with barite as an extenderas the presence of Ca and Mg together suggest calcium and magnesium carbonate extenders. Additionally, the presence of P and W may be related to PTA pigment, which refers to phosphotungstic acid used for preparing pigments by precipitation with basic colorants [72,73]. PTA was patented in 1917, but its usage reduced due to the scarcity of certain materials due to WWI [74]. In a local documentation from 1944, it is described the employment of this type of pigments [67].

Regarding red colorants in the paint sample, GC/MS analysis identified marker compounds associated with PR3, an organic pigment that emerged in 1904 [75]. Previous research carried out by the Getty Conservation Institute on Concrete Art also reported this pigment as part of their palettes [26].

The presence of Sb could be associated with antimony oxide. As it is described in a manual of 1966, [76] this pigment was employed a few years before in combination with anatase titanium white in order to control chalking, leveling and ease of application.

The presence of Si and Al is consistent with colloidal silica and aluminum stearates coatings on the titanium white pigment that decreased chalking [59,77]. Fig. 4 summarizes the results obtained by SEM-EDX considering in a layer-by-layer approach and GC/MS data for the whole sample.

4.2.3. Integration of results

This section presents the integration of results for sample 171-01 (Fig. 5). Titanium white may be present in either rutile or

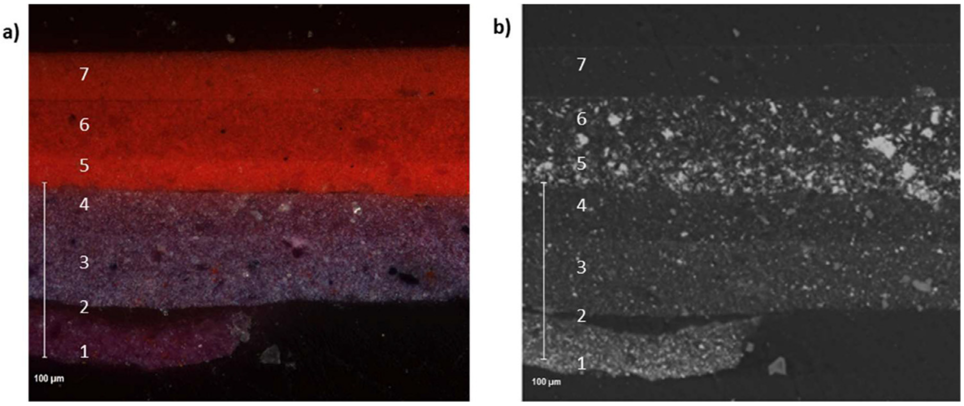
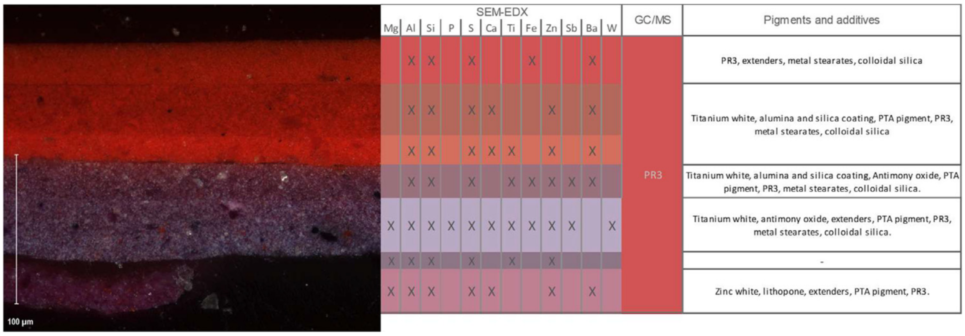


Fig. 3. a) Cross section 171-01 image under polarized light. b) Sample 171-01 backscattered electron image.



SEM-EDX Mg	Al	Si	P	S	Ca	Ti	Fe	Zn	Sb	Ba	W	GC/MS	Pigments and additives
	X	X		X			X			X		PR3	PR3, extenders, metal stearates, colloidal silica
	X	X		X	X			X		X			Titanium white, alumina and silica coating, PTA pigment, PR3, metal stearates, colloidal silica
	X	X		X	X	X		X		X			
	X	X		X		X	X	X	X	X			Titanium white, alumina and silica coating, Antimony oxide, PTA pigment, PR3, metal stearates, colloidal silica.
X	X	X	X	X	X	X	X	X	X		X		Titanium white, antimony oxide, extenders, PTA pigment, PR3, metal stearates, colloidal silica.
X	X	X		X		X		X					-
X	X	X		X	X			X		X			Zinc white, lithopone, extenders, PTA pigment, PR3.

Fig. 4. SEM-EDX and GC/MS results of sample 171-01. The last column summarizes the pigments and additives identified.

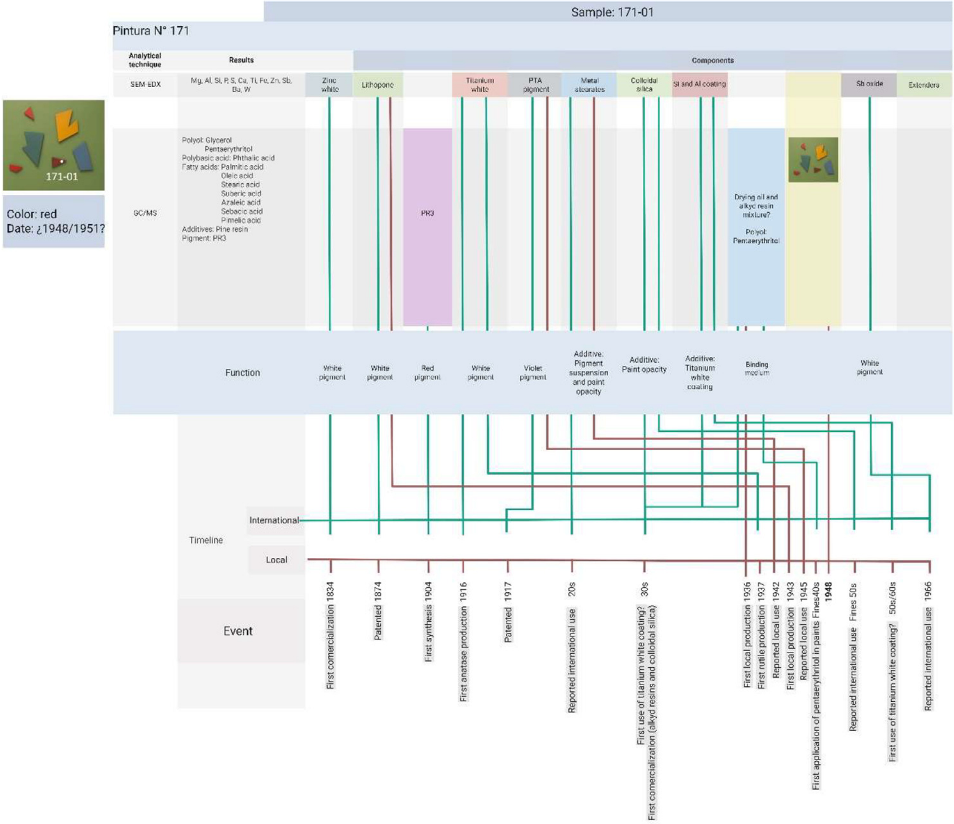


Fig. 5. Integration of results of sample 171-01.

anatase crystalline structures. However, the presence of antimony oxide would suggest the anatase form that was manufactured in 1916, a few decades before the date assigned for *"Obra N° 171"*[78]. At the same time, the presence of titanium dioxide coating is consistent with some part of the literature which points out that this technology was implemented between 1935 and 1940 [64]. Zinc white, lithopone, PR3 and PTA pigments were in production well before *"Obra N° 171"* was made. In addition, it is worth mentioning that PTA pigment was reported in local documentation from 1945 [67], which strongly suggests its presence. Ultimately, the presence of pentaerythritol in the paint binding media indicates the artwork was painted after the late 1940s.

5. Conclusions

This work presents a new multi-analytical protocol to reveal the organic and inorganic fractions in the complex formulation of colored modern paints. The combination of analytical techniques provided a comprehensive methodology for obtaining systematic results. The paint industry from the mid-twentieth century searched for ways of improving the quality of painting materials while at the same time decreasing production costs. This led to a vast and diverse range of compounds used in paint formulations throughout the years. The comprehensive characterization was focused not only on describing the binding media and pigments, but also on elucidating the presence of organic and inorganic additives. In addition, the detection of possible chronological markers in connection to technological improvements implemented since 1930s was pursued. For these purposes, red, blue and green paints presumably from before 1960 were analyzed through GC/MS, FT-IR, XRD, SEM-EDX and XRF techniques.

GC–MS allowed characterizing the content of fatty acids, as well as different organic markers, such as short-chain dicarboxylic acids, polyols and polybasic acids. Furthermore, this technique was able to differentiate between alkyd and drying oils. FT-IR contributed to the attribution of the type of binding medium at the same time it helped detecting organic pigments and organic additives.

For the inorganic fraction, the characterization through vibrational techniques as Raman spectroscopy enabled the identification of inorganic and organic pigments. It was possible to deepen the information associated to pigments and also to complement the compounds detected by Raman spectroscopy in combination with crystalline structure elucidation using XRD. A detailed characterization of pigments as well as of organic and inorganic additives was performed using SEM-EDX and XRF. The determination of elements that are not part of the crystalline structure or are present in low quantities helped to elucidate the role of metal complexes in organic pigments and those forming organic salts as part of organic additives. Their identification also contributed to ascertain the presence and composition of some inorganic pigment coatings, a common practice in the synthetic pigments during mid-twentieth century. Since these detailed characterizations also allow the determination of chronological markers, associating the results to a specific date of the paint manufacturing record, this work includes references (patents, books and scientific publications) of the materials used in the period studied. To prove the concept, a microsample from the artwork "*Obra N° 171*" by Raúl Lozza, part of the corpus of Argentine Concrete Art, was studied. The identification of different chronological markers taken from the timeline allowed us to precise the artwork was painted after late 1940s. In this case, the most relevant marker was pentaerythritol, implemented after WWII. This data demonstrates that comprehensive data interpretation could be a useful tool for attribution issues of modern artworks and for technical art history studies.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2024.03.001.

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