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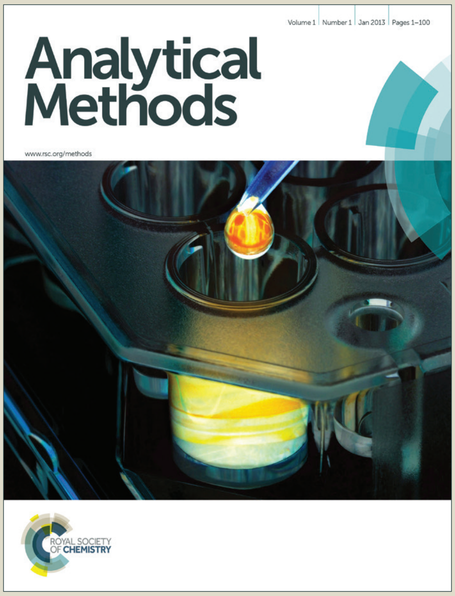

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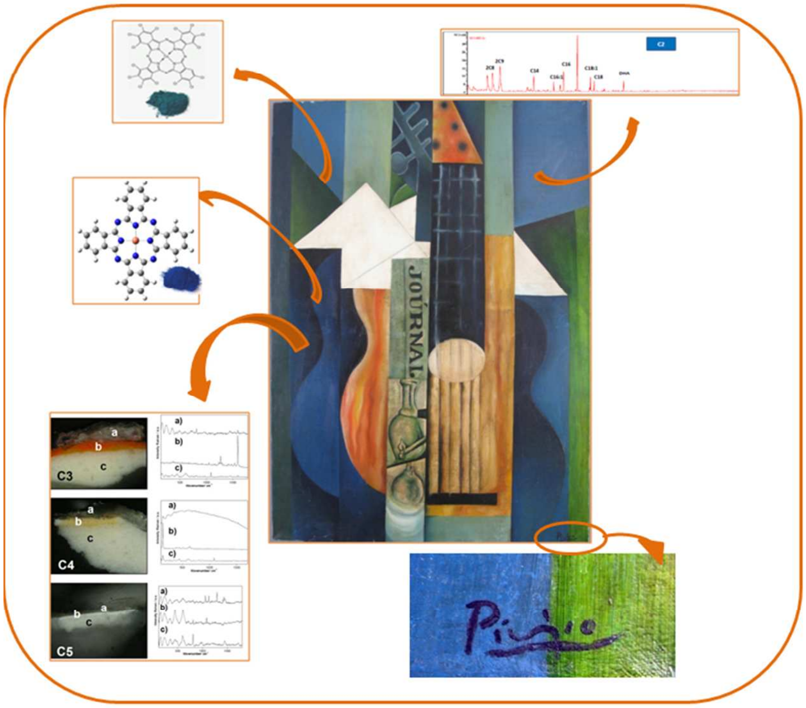

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Study of modern artistic materials using combined spectroscopic and chromatographic techniques. Case study: painting with the signature "Picasso"

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ABSTRACT

A painting bearing the signature “Picasso” was investigated and its components – pigments and binders – characterised using micro-Raman spectroscopy (mRS) combined with other analytical techniques such as Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM/EDX), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS). We identified the pigments in order to assess chronological inconsistency (anachronistic pigments) with the work of the Spanish artist Pablo Picasso (1881-1973) by means of *in-situ* and cross section analyses by mRS. Using mRS we identified the pigments ‘phthalocyanine blue’, ‘phthalocyanine green’, ‘pyrazolone orange’, ‘anatase’ and ‘rutile’ (titanium dioxide). These results were corroborated by SEM/EDX elemental analysis, which detected Ba, S and Zn among others, so prompting discussion about the use of ready-mixed house paints (Ripolin®). The ground layer was also investigated by mRS, which confirmed the use of rutile (titanium dioxide), calcite and phyllosilicates (Al, Fe). mRS on the white area identified the binding media as beeswax, the most important wax used in art. ATR-FTIR and GC-MS analysis support the presence of a wax and an oil-resin mixture as the binder, described in previous research as being used by Picasso. All the artist materials identified were widely used in art at the beginning of the twentieth century according to the available bibliography and are therefore consistent with the Picasso era. To the best of our knowledge this is the first attempt to investigate a painting related with Picasso using the combination of analytical techniques proposed here.

Keywords: Micro-Raman Spectroscopy; Scanning Electron Microscopy-Energy Dispersive X-ray analysis; Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy; Gas Chromatography-Mass Spectrometry; Picasso

1. Introduction

Art production has propitiated a speculation in art prices and illegal art trade. This has promoted a growing interest in the scientific analysis of paintings to help authenticate authorship, to detect forgery and to date and determine the provenance of the materials used in artworks [1-3]. The goal of scientists is to establish whether the materials in the artwork are consistent with those used in the times of the attributed artist. The confirmation or rejection of authorship of paintings in some cases of controversial or doubtful attribution is a difficult challenging task, which in the case of many precious works of art remains incomplete. Progress is however being made with the continuous development of analytical approaches based on the use of new and traditional instrument systems.

Pigment analysis is well established as one of the most appropriate strategy for solving forgery debates regarding paintings. Scientists look for chronological inconsistency (pigments anachronism), in other words pigments that were not available at the time the painting was created. For these purposes it is essential to know when the pigment was first used or at least became commercially available. This information is usually well documented in the case of synthetic colorants and pigments used in 19-20th centuries [4-6].

Nowadays micro-Raman Spectroscopy (mRS) is widely applied in the analysis of different artworks. This technique is sensitive, reliable and suitable to be used *in situ* in non-destructive analyses [7-9]. Thanks to the high lateral resolution, it is possible to record Raman spectra from pigment grains with a diameter down to 1 μm, and inorganic and modern synthetic organic pigments can be examined by recording their Raman spectra [10,11]. Other materials apart from pigments, such as binding media and varnish, can also be identified in a non-destructive way [12,13]. Raman spectroscopy (RS) and particularly mRS is therefore a very important technique for a complete study of the materials used in artworks.

Its potential for pigment identification also makes it a useful technique for detecting forgeries. Several works have been published in which mRS was applied to achieve fast reliable identification of the pigments in the artist's palette and to look for anachronisms in the materials. These studies include the detection of forgeries in Egyptian papyri [14], the Vinland Map inks [15], paper and cancel marks on postage stamps [16], Arabic illuminated manuscript [17], and paintings by artists from the Russian avant-garde (approximately 1900 to 1935) such as Malevich, Kandinsky, Rodchenko and Popova [2,18].

Raman study has also been performed successfully on a number of paintings by Picasso (1881-1973), such as the oil on canvas "Cubist Figure" (1909), "Still Life" (1914), "Weeping Woman" (1932) and "Nude Woman in a Red Armchair" (1937) [19,20]. It was also used in the identification of cobalt-based synthetic pigments in a Picasso painting entitled "The Red Armchair" [3].

Despite the usefulness of RS for characterizing the components of artistic materials, more reliable results can be achieved by combining it with other analytical techniques. Some pigments do not give an identifiable Raman spectrum either because they are poor Raman scatterers or because of the fluorescence of the binding medium. In these situations it is necessary to complement the micro-Raman technique with other analytical techniques in order to thoroughly characterise the palette used. Such techniques include micro-X-ray fluorescence spectroscopy (μ-XRF), X-ray diffraction (XRD), SEM-EDX, FTIR and GC-MS [17,20-21]. There is sparse information in the literature about the alkyd paints used by artists with conclusions and conflicting findings. Arslanoglu [22] indicated the possible use of non-traditional artist's paints in some Picasso’s paintings from the museum's Metropolitan Museum of Art but not necessarily house, alkyd, or enamel paints. On the other hand, THM-GCMS (Thermally assisted hydrolysis and methylation-gas chromatography–mass spectrometry) and FTIR proved crucial in identifying industrial alkyd paints in various artworks by Jackson Pollock and Pablo Picasso [20]. Scientific investigation of an important corpus of Picasso paintings from the Picasso Museum in Antibes (France) has recently been published [23]. The effective combination of non-invasive (XRF, MIR, NIR, UV-Vis-NIR FORS, UV-Vis Fluo) and micro-invasive techniques (FTIR, mRS, SEM-EDX, PLM) enabled fine discriminations between various types of white enamel paint used by Picasso in addition to important new information on surface coatings and the presence of metal soaps.

The study presented in this paper is part of a wider research contract devoted to the study of the materials used in two canvas paintings both clearly exibiting the signature "Picasso", which was previously authenticated by a handwrite expert in Picasso’s signature. In this paper we will be examining a painting named “Guitar” which in terms of genre would normally be classified as a work of Synthetic Cubism since the original model is fragmented into different types of geometric figures. The goal of our research was to identify the pigments (organic and inorganic) and the binders used by the artist by mRS applied *in-situ* and to cross sections in order to establish a possible time window within which the painting was done. We then confirmed the mRS results using various complementary analytical techniques such as Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM/EDX), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS). With this combined approach, we identified various modern artists’ materials and suggested others that may have been used by the painter.

It is important to make clear that the ultimate aim of this kind of scientific technical analysis is not to authenticate the work or attribute it to one specific artist. Technical study has many aims, among them, the discovery of anachronistic materials that can provide useful clues for identifying possible fakes.

2. Experimental

2.1. Description of the painting

The painting is titled “Guitar” (95.0x64.2cm) (Fig. 1) and is composed of irregular, angular surfaces representing geometric elements that are in clear contradiction with the guitar, which is characterized by its own elements, such as the sinuous silhouette of the rim, sound hole, strings, fingerboard, headstock and tuning pegs; essential attributes that identify this instrument beyond doubt. The signature “Picasso” is clearly visible in the bottom right-hand side of the painting. The exterior shape of the guitar is represented by a clearly recognizable sinuous stylization, in which the shape is perfectly separated and projected on several planes embodied in a double curve evoking the side of the guitar. The painting also contains a degree of realism in the imitation of the grain of the wood in the body by means of undulating parallel lines of reddish color. There is also a narrow vertical strip with a possible subliminal purpose, containing the word "Joúrnal", in newspaper format, two bottles and a lit match, used as iconographic motifs. An overall view of the painting shows that the predominant colour is blue of which there are several different shades distributed throughout. Other colours such as green, white, yellow, orange, brown, black and violet can also be observed albeit in much smaller proportions.

Figure 1. Positions from which samples of the "Guitar" painting were taken. Samples are labelled from S1 to S9 corresponding to the *in situ* Raman spectra positions.

2.2. Preparation of the cross-section samples

Six samples (C1-C6) were removed from the main colours observed in the painting (blue, green, white and orange) with the help of a scalpel. They were embedded with a particular orientation in Technovit resin. They were then sectioned with a microtome and metallographic polishing machine Struer, model Tegrapol-15 (Struer, Bradford, UK) perpendicular to the paint layer. The cross-sections containing the different paint layers and ground were placed in the optical and scanning microscope where the structure of the paint layer and the grains of the pigments were observed.

2.3. Optical microscopy (OM)

The cross-sections of the samples were primarily observed by an optical microscope Jenapol (Carl Zeiss, Jena, Germany) with a magnification varying from 50 to 500, and were recorded with a digital camera (Olympus, model Camedia C-5060- Wide Zoom, Tokyo, Japan) adapted to the microscope. The optical images presented in this article were collected with a magnification of 100x and were used to study the layered structure of the painting.

2.4. Scanning electron microscopy-energy dispersive X-ray detector (SEM-EDX)

After graphite sputter-coating, the polished thin sections were investigated by backscattered electron (BSE) image using a Scanning Electron Microscope

(SEM; Leo 1430VP, Carl Zeiss NTS), equipped with an energy dispersive X-Ray Spectrometer (EDX; INCA 350 Oxford, UK). SEM-EDX was used for qualitative analysis of the chemical elements in the pigments and fillers.

2.5. Micro-Raman Spectroscopy (mRS)

Raman spectra were recorded in a Renishaw Invia micro-Raman spectrometer. Wire 2.0 from Renishaw has been used for spectral data manipulation. It is well known that some compounds respond differently depending on the excitation line. In our research we therefore decided to analyse each sample using a high power Renishaw NIR diode laser emitting at 785 nm, which can reduce sample fluorescence from most organic molecules. This excitation wavelength was considered the most appropriate for the coloured pigments involved in the painting. The microscope was equipped with a 50x objective (numerical aperture of 0.75). To avoid overheating during the measurement of Raman spectra and the possible thermal decomposition of the sample, neutral density filters with an optical throughput of 1% and 5% were used and the laser power aimed at the sample was between 1 and 5 mW. The resolution was set at 2 cm^{-1} and the geometry of micro-Raman measurements was 180°. The *in situ* micro-Raman measurements were performed by placing the painting below the lens at the corresponding focus distance. Before each measurement, the instrument was calibrated with a standard silicon sample (520 cm^{-1}). The Raman intensities have not been corrected for the spectral response of the instrument. A very slight smoothing process was performed to reduce noise and in some cases a baseline correction was necessary.

The pigments were identified by comparing the Raman spectra we recorded with those in the reference data base [10,11] and the IRUG database [24].

2.6. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopic (ATR-FTIR)

No special preparation was required for diamond micro-ATR analyses, which were easily performed by positioning the sample powder onto the FTIR microscope. ATR spectra were registered from 600cm^{-1} to 4000cm^{-1} with a resolution of 2 cm^{-1} and 200 scan with a JASCO 6200 (Easton, Maryland, USA) spectrometer controled by the Spectra Manager^{TM} v2 software package.

2.7. Gas Chromatography-Mass Spectrometry (GC-MS)

A Varian CP 3800 GC equipped with a CTC Analytics CombiPAL autosampler and automatic injector and split/splitless injection was used. The chromatographic separations were done on a VF-5 MS Highly inert Varian capillary column, interfaced to a MassDetector Varian Saturn 2200 (Lake Forest, CA, USA). The GC inlet temperature was set at 240 ◦C and the MS interface at 280 ◦C. The oven was programmed from 120 ◦C, with a 2 min hold, and then increased at a rate of 5 ◦C/min to 230 ◦C; the total run time was 24 min. Electron ionisation energy was

70 eV, with a maximum ionisation time of 25,000 μs. The m-(trifluoromethyl)phenyl trimethylammonium hydroxide (TFTMAH) was chosen as the reagent for methylation [25].

3. Results and discussion

3.1. In situ mRS pigment identification

Areas of various colors were analyzed *in situ* by mRS (Fig. 1, S1 to S9). Previously the painting was carefully studied by several imaging techniques [26], including UV-light to investigate whether the paintwork had been touched up. This information is crucial in that analysis of touched-up areas could lead to erroneous interpretation of the results. The photographs taken under ultraviolet lighting revealed that the painting had not been touched up, which meant that in theory we could locate the *in situ* Raman spectra anywhere in the painting. In practice however the painting was too big (95.0x64.2 cm) to enable us to position the centre under the laser, and we were only able to analyse a strip measuring approximately 10-15 cm from the edge of the frame. Despite this problem, the analysed areas were representative of the main colours observed in the whole painting and the cross-section samples complemented the colour range study. The results obtained from the Raman spectra are reported and discussed below according to the different colours under examination.

3.1.1. Blue pigments

The painting is dominated by different shades of blue. The analysis of the Raman spectra in these blue areas has shown a very similar spectrum that has been identified as phthalocyanine blue (PB) or copper phthalocyanine ($CuC_{32}H_{16}N_8$, PB). This is an organic pigment that has been commercially available since 1935 [27], which was adopted by many famous 20th century artists, including R. Lichtenstein, P. Delvaux, W. Kandinsky, Y. Klein, S. Francis, E. Kelly and B. Newman [27].

Figure 2 (a) shows the 150-1650 cm^{-1} region of the *in situ* Raman spectra of PB in positions S1, S5 and S7. In all cases the Raman spectra of PB is easily recognised because it has a very good signal-noise ratio. The main Raman bands of PB are recorded at 681 (m), 747 (s), 1143 (w), 1342 (m), 1452 (w) and 1530 (s) cm^{-1} in line with the results of previously published papers describing Raman studies of this pigment [3,10,11].

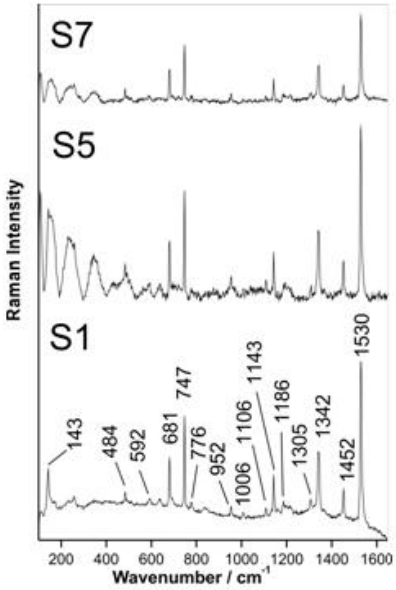


Figure 2. *In situ* Raman spectra (S1, S5, S7) of the sampling positions on the "Guitar" painting shown in Fig. 1.

As regards the vibrational assignment, it is well known that phthalocyanine compounds are an important group of blue and green pigments that reveal very characteristic signals due to the macrocycle. Table 1 shows the main experimental Raman wavenumbers (cm^{-1}) of PB and the proposed assignment based on published research [4,28].

Table 1. Raman assignments for the vibrational bands in the 100-1800 cm^{-1} region of phthalocyanine blue.

Raman wavenumber (cm^{-1})	
ν_{exp}	**Assignment***
1530 s	ν(C=N)
1452 w	$\nu_{isoindol}$, δ(CH)
1342 m	$\nu_{isoindol}$
1305 vw	$\nu(C{=}C)_{pyrrole}$
1186 vw	δ(CH)
1143 w	Pyrrole breathing mode
1106 vw	δ(CH)
1006 vw	δ(CH)
952 w	δ(C-N=C), δ_{ring}
776 vw	$\delta_{isoindol}$
747 s	$\delta_{macrocycle}$
681 m	Macrocycle breathing mode
592 vw	Macrocycle breathing mode
484 vw	$\tau_{macrocycle}$

*ν, stretching; δ, in-plane bending; τ, torsion

In Figure 2 (S1) the main Raman bands have been labelled and a very strong band can be seen dominating the spectrum at 1530 cm^{-1} attributed to the C=N azo stretching. The medium bands at 1342 and 681 cm^{-1} are assigned to isoindole groups stretching vibration and the breathing vibration of the macrocycle, respectively. Other weaker bands at 1452, 1143 and 747cm^{-1} are assigned to isoindole groups stretching, pyrrole breathing mode and the deformation vibration of the macrocycle, respectively. These are the most characteristic bands of the Raman spectrum of PB. Other weaker bands have however been assigned in Table 1.

3.1.2. White pigments

In this painting, the results indicate that phthalocyanine pigment was used in pure form to obtain the blue colours (i.e. Fig. 2, S5 and S7) and mixed with a white pigment to obtain lighter tones and different shades of blue (i.e. Fig. 2, S1 and Fig. 3). In the case of lighter tones, as seen in Figure 3, a very strong Raman band was recorded at 143 cm^{-1} and a medium one at 639 cm^{-1}. In this case, we believe that the pigment used to obtain the lighter tones was the white pigment, titanium dioxide (TiO_2) in anatase form (Table 2). The term titanium dioxide is used for both the anatase and rutile crystallographic forms of the pigment; however, these two different polymorphs can be easily distinguished by Raman spectroscopy. Previous research shows that anatase pigment is part of the formulation of ready-mixed house paints that were widely used in the first half of the twentieth century by artists such as Pablo Picasso [29].

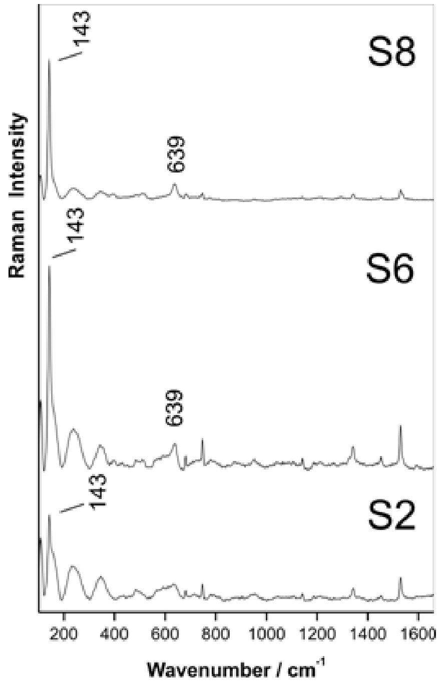


Figure 3. *In situ* Raman spectra (S2, S6, S8) of the sampling positions on the "Guitar" painting shown in Fig. 1.

Table 2. Composition of pigments and binding media identified by Raman spectroscopy and characteristic Raman bands (cm^{-1}).

Colour	**Pigment**	**Composition**	**Raman bands (cm^{-1})***	**Figure**
Blue	Phthalocyanine blue	$Cu(C_{32}H_{16}N_8)$	681m, 747s, 952vw, 1143 w, 1342m, 1452w, 1530s	Fig.2 (S1) Fig.5 (C1, C6)
Green	Phthalocyanine green	$Cu(C_{32}Cl_{16}N_8)$	684m,740m, 776w, 817vw, 1086vw,1212vw, 1280w, 1338w, 1538s	Fig. 4 (S9) Fig. 5 (C2)
White	Anatase	TiO_2	143vs, 396vw, 516vw, 639 w	Fig. 3 (S8) Fig. 5 (C2,C5)
	Rutile	TiO_2	146w, 232w, 447m, 609m	Fig.5 (C4)
	Calcite	$CaCO_3$	1086s	Fig. 5 (C1-C6)
Orange	Pyrazoloneorange	$C_{32}H_{24}Cl_2N_8O_2$	369vw, 1049vw, 1238vw, 1273m, 1049vw, 1538vw, 1597vs	Fig. 5 (C3)
Binding media	Beeswax	Mainly myricylpalmitate ester, $C_{15}H_{31}CO_2C_{30}H_{61}$	1062m, 1129m, 1295s, 1418w, 1440w, 1460w	Fig. 5 (C4)

*Relative intensity: vs: very strong; s:strong; m:medium; w: weak; vw: very weak

3.1.3. Other pigments

The *in situ* mRS study was performed on three other colour areas (not blue) located at positions S3, S4 and S9 in Fig. 1. The Raman spectra for these *colours,* black (S3), orange (S4) and green (S9), are shown in Figure 4. The black pigment did not exhibit any Raman signal at the 785 nm excitation line and we were unable to identify it. The orange pigment (Fig. 4, S4) has a Raman spectrum with a very low signal-noise ratio at this excitation wavelength, although we managed to detect some Raman bands. The band at 1595 cm^{-1} is specific to the aromatic ring vibration and could be due to disazopyrazolone pigments that were developed as early as 1910 [30]. More information about this pigment will be obtained from the cross-section samples. The observation in Figure 4 (S4) of other Raman bands at 1530 and 1342 cm^{-1} suggests the presence of phthalocyanine blue in the mixture.

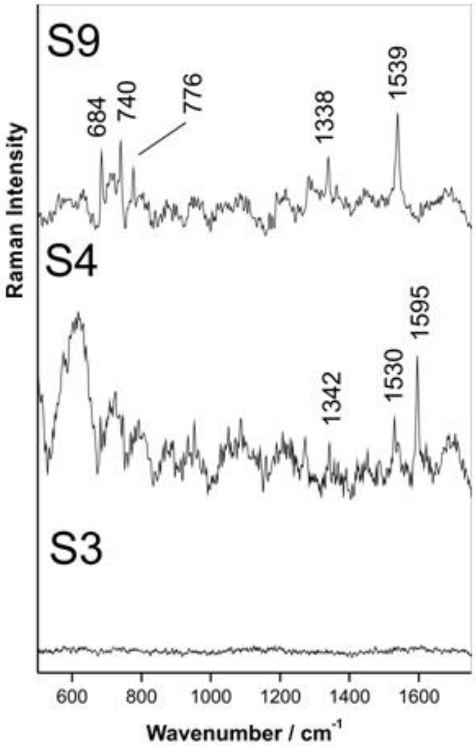


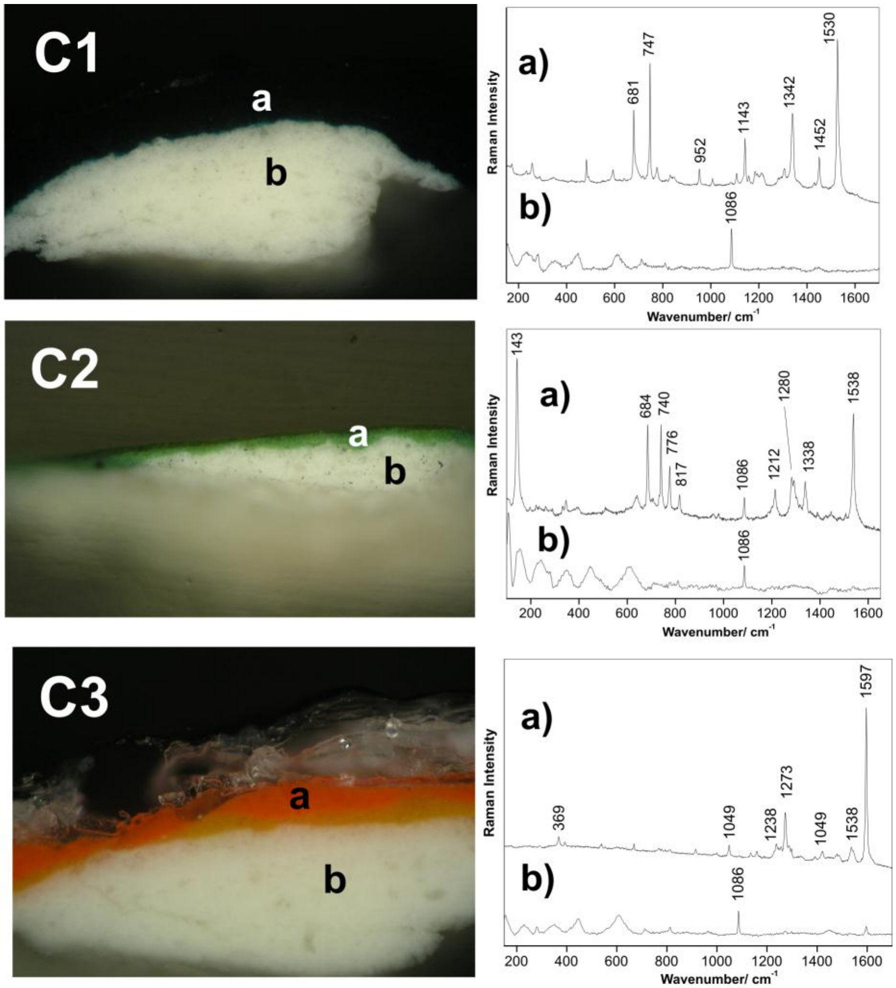
Figure 4. *In situ* Raman spectra (S3, S4, S9) of the sampling positions on the "Guitar" painting shown in Fig. 1.

Finally, the Raman spectrum obtained from the green area shown in Figure 4 (S9) exhibits bands at 684, 740, 1085, 1338 and 1539 cm-1. These bands are characteristic of the presence of phthalocyanine green, a synthetic green pigment from the group of phthalocyanine dyes, a complex of copper(II) with chlorination of the aromatic hydrogen that has also been prepared since 1936 [10]. The changes in position and intensity of the Raman bands of the green pigment with respect to phthalocyanine blue are due to the chlorine substitutes altering the symmetry of the molecule and the Raman activity of the vibrational modes [31].

3.2. Cross-section pigments identification

3.2.1. Optical Microscopy

Figure 5 shows the optical micrographs of cross-sections extracted from the painting “Guitar” with locations as indicated in Figure 1 (C1,C2,C3,C4,C5,C6). The samples were examined under the microscope and show a single layer of paint in orange, white, blue or green extended over a ground layer. In some colors a second layer of paint is observed with a darker tone to enhance the effects of light and shade in the picture. A very thin outer layer of varnish could be identified in a few areas of the painting. Most of the paintings analysed from the Picasso Museum in Antibes (France) have either no surface varnish or only a very thin external layer [23].


C1
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Raman Intensity
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Wavenumber/ cm-1
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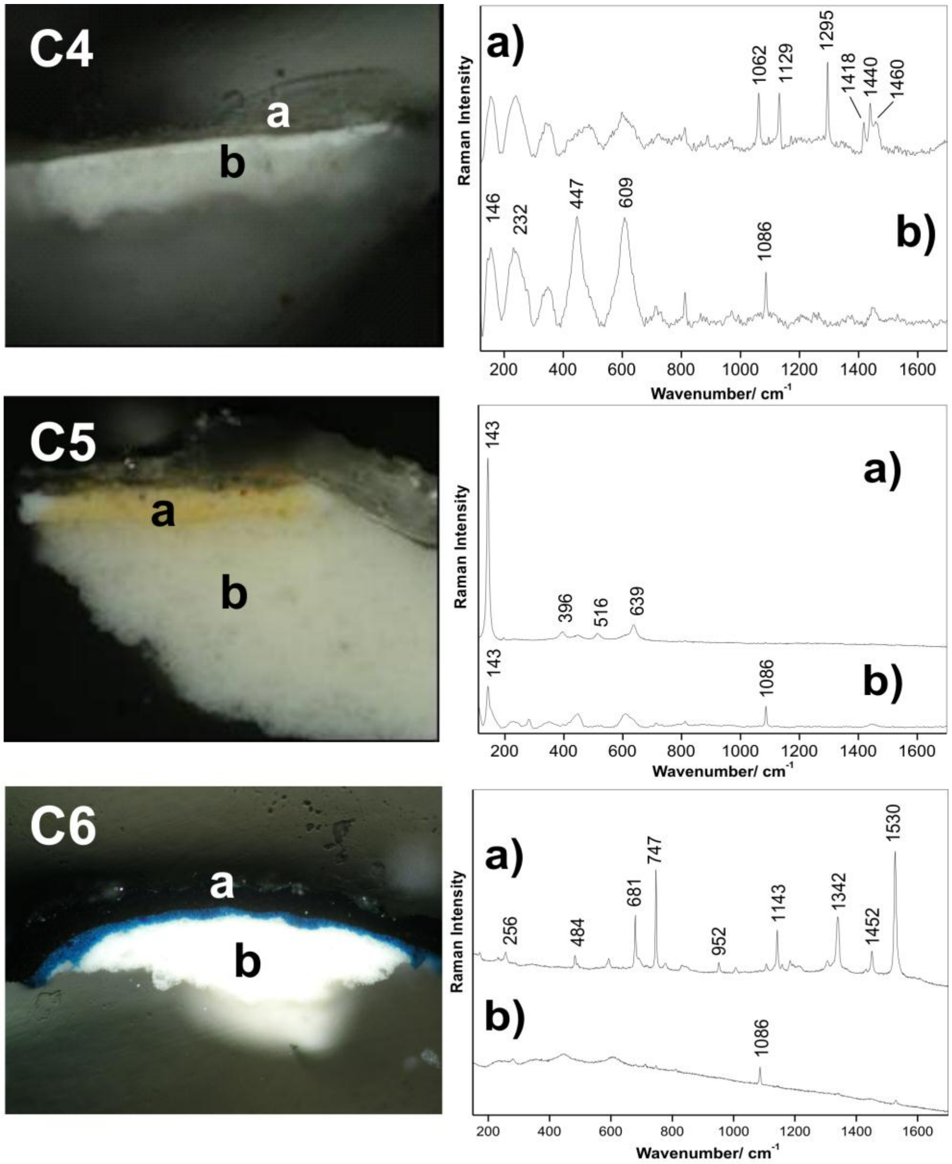

Figure 5. Cross-section micrographs of several samples (C1 to C6) extracted from the positions shown in Fig. 1. Raman spectra of different layers are depicted next to each micrograph.

3.2.2. Micro-Raman Spectrometry

The Raman spectra over the cross section corresponding to each layer were performed and then represented in Figures 5(a, and b). A summary of all the pigments identified is shown in Table 2. Bands at ca. 232vw, 447w and 609w cm^{-1} were observed in the white ground layer indicating the presence of TiO_2 in its rutile form [10] and a band at ca. 1086m cm^{-1} due to calcite, $CaCO_3$, a material widely used as a filler in “imprimatura” layers. The “imprimatura” may consist of binding media, but is often combined with white pigments to add depth and tone to the upper paint layers.

The analysis of cross-sections C1 and C6 confirms the presence of phthalocyanine blue in the paint layer as was identified previously in the *in situ* study. Their Raman spectra are shown in Figures 5(a, and b) (C1.a and C6.a). These samples were extracted from dark blue areas (see Fig. 1) and no mixtures with white pigment were detected.

The Raman bands of the spectrum in Figure 5(a) (C2.a) are recorded at 684m, 740m, 776w, 817vw, 1212w, 1280w, 1338w, 1538s cm-1. These Raman bands are representative of phthalocyanine green, as found in previous research [30] and confirm the very weak signal-noise Raman spectrum obtained in situ. In this sense, the main advantage of the cross-section samples is the high quality of the Raman spectra, which enables a more accurate assignment of the Raman bands. The cross-section C2 is extracted from a light green area with a mixture of phthalocyanine green and TiO2 white in anatase form.

The cross-section sample C3 is orange in colour and is taken from the trapezoidal shape in the top part of the painting. The Raman spectrum of the pigment layer of C3 shows two main bands at 1273m and 1597vs cm^{-1} which are characteristic of a group of disazopyrazolone pigments [35]. The Raman spectra for this group of pigments are slightly different depending on the molecular structure, but after consulting the literature we identified our orange pigment as pyrazolone orange PO34 [31]. The disazopyrazolones are similar in structure to diarylide pigments, but they incorporate a pyrazolone ring. Like monoazo yellow and diarylide yellow pigments, the first disazopyrazolone pigments were developed as early as 1910 but commercial application was delayed by some 20 years [32].

White pigment has been analyzed in cross-section C4 obtaining a Raman band at 1086 cm^{-1} (Fig. 5(b), C4.b) assigned to calcite. This material is typically used in the ground layers of the canvas and in the white areas of this painting, where it has been mixed as a filler with TiO_2 in rutile form for which Raman bands have been recorded at 146, 232, 447 and 609 cm^{-1}.The analysis of the upper layer of this cross-section (Fig. 5(b) C4.a) led to the identification of an organic binding media containing natural beeswax, the most important wax used in art, of which the main component is myricyl palmitate ester. The main Raman bands of this binding layer were recorded at 1062m, 1129m, 1295s, 1418w, 1440w and 1460w cm^{-1}, so confirming the findings of previous authors [13]. This result was further investigated by GC-MS.

Cross-section C5 (Fig. 5(b)) was taken from a yellowish area on the strings of the guitar. We were able to distinguish two different layers, a ground layer made of calcite and an upper layer identified as TiO2 in anatase form. The latter exhibited a very intense Raman spectrum characteristic of this white pigment. Contrary to what we thought at first, no yellow pigment has been detected in this. Finally, no binding media were detected in this area by mRS.

3.2.3. Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis

Cross sections were further analysed using SEM-EDX to identify inorganic pigments and fillers. In this paper, we used a combination of elemental, spectroscopic (ATR-FTIR) and chromatographic (GC-MS) methods to confirm the findings by mRS.

A Scanning Electron Microscope (SEM) micrograph of cross-section sample C6 shows two clearly differentiated ground layers (Fig. 6). Qualitative EDX microanalysis detected C, O, Si, Al, K, Ca, Mg, Fe and Ti suggesting the presence of $CaCO_3$, $CaMg(CO_3)_2$, TiO_2 and phyllosilicates (Al,Si). A similar elemental composition was found in both strata. Calcite and dolomite have been used as fillers in alkyd media, a binder used in contemporary art by a number of famous artists, including Pablo Picasso [33].

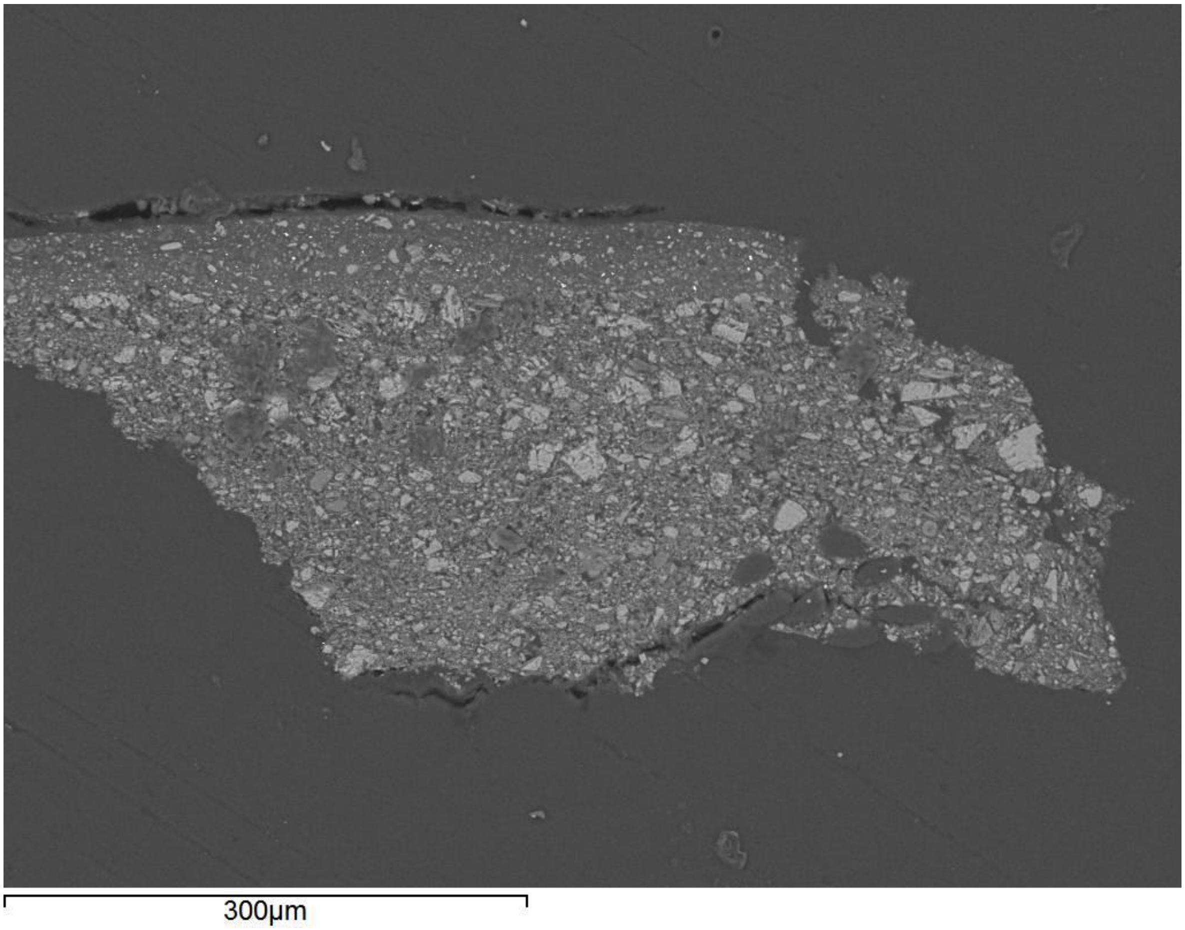

Figure 6. Backscattered electron (BSE-SEM) image of the cross-section from sample C6 (optical image in Fig 5).

EDX measurement of the paint layer from sample C1 shows that Ti and Cu were some of the main elements in the blue area. The spectrum suggests that an organic copper pigment was mixed with titanium dioxide to lighten the intensity of the blue. Although organic pigments are difficult to identify by SEM-EDX elemental analysis, the presence of copper is consistent with Phthalocyanine blue, a pigment identified by mRS. Likewise in sample C2, the chlorine detected by SEM-EDX supports Phthalocyanine green. All these results are compatible with and corroborate those from the previous mRS analysis. The predominant presence of aluminum in the C3 sample suggests a red lacquer in the paint layer; while the elements S, Ba and Zn imply barium sulphate and zinc sulphide in the same sample, probably due to the use of white pigments such as Lithopone, barite ($BaSO_4$) or zinc oxide (ZnO). The predominant presence of aluminum in the C3 sample suggests a red lacquer in the paint layer; while the elements S, Ba and Zn imply barium sulphate and zinc sulphide in the same sample, probably due to the use of white pigments such as Lithopone, barite (BaSO4) or zinc oxide (ZnO). In a general context, it is accepted that lacquers are difficult to identify. The results here obtained suggest that an Al-based red lacquer was mixed with white pigments in the orange area of the picture because no other elements were detected by SEM-EDX. Previous authors report that various twentieth century artists, including Picasso, used Ripolin®, an enamel paint made by a French manufacturer [29]. Although the scientific identification of Ripolin® is controversial due to the chemical similarities between Ripolin and tube paints used by contemporary artists, and the lack of knowledge of Ripolin paint formulations [29], its use has been confirmed in many artworks by Picasso such as “Figure”, a sculpture from the collection of the Art Institute of Chicago, and “The Red Armchair” painting [19,20] among others. In various written documents Picasso himself stated that he used this paint [34]. In the painting we are analysing, it is interesting to note the absence of basic lead carbonate, a pigment commonly found in tube paints and enamel paints, but not in Ripolin® brand paints. It is well known that at the middle of the 19th century (1845) zinc white started to replace lead white in house paints because of its toxicity [35,36]. On the other hand, research on another Picasso painting “Still Life” found that it did not contain Ripolin®, but did contain vermilion and lead white, which were not used in Ripolin® house paints [19]. According to the elemental analysis, we cannot rule out the possibility that Ripolin was used in this painting.

3.3. ATR-FTIR

We continued with this study of the possible use of the house paint Ripolin® by investigating the spectroscopic bands of metal soaps. ATR-FTIR analysis shows metal soaps from Ripolin® as a result of the interaction of the oily medium with the zinc white paints and other metals in the pigments and driers [29]. Among the spectroscopic signatures of these metal soaps reported in the bibliography (1583br, 1455 and 1418 cm^{-1}), only the single carboxylate band *v*s(COO^-) around 1410-1420 cm^{-1} was observed in all the samples studied from the painting “Guitar”. Hence the ATR-FTIR spectra of samples C1 to C4 do not match a likely Ripolin spectrum. In the same way, the characteristic bands of alkyd paints, sometimes used by Picasso, were absent [33], as occurred with the Picasso paintings from the Picasso Museum in Antibes (France) [23].

Nevertheless, bands around 2967, 2917, 2851cm^{-1} (stretching vibrations of CH groups) and 1740 cm^{-1} (stretching vibrations of the carbonyls of esters and aged oil) were consistent with wax and drying oil [37]. Wax coating and oil-resin binders were detected in some areas of the Antibes paintings [23].

3.4. GC-MS

For a better understanding of the painting technique, we focused particularly on the binders used by the artist. The main objetive here was to determine if the medium was oil-resin, alkyd or a single drying oil. To this end, the organic binding media of samples C1 to C6 were analyzed using a GC–MS method that was previously developed focusing on the characterization of drying oil by means of the palmitic–stearic acid ratio [25]. In this way we obtained the C_{16}/C_{18} and $2C_9/C_{18}$ ratio for all the analysed samples. Figure 7 shows two of these chromatograms, particularly those from samples C2 and C4. The C_{16}/C_{18} experimental ratios we obtained all fell within the interval 0.7–2.1, characteristic of linseed oil according to the consulted bibligraphy [25]. Nevertheless the low values of the azelaic/palmitic ratios $2C_9/C_{16}$ suggest the simultaneous occurrence of two different lipidic materials. It is therefore impossible to make a reliable identification of the particular oil used in the paint since these two ratios indicate a mixture of lipids. Nevertheless, these results clearly indicate the use of a drying oil as the binding medium.

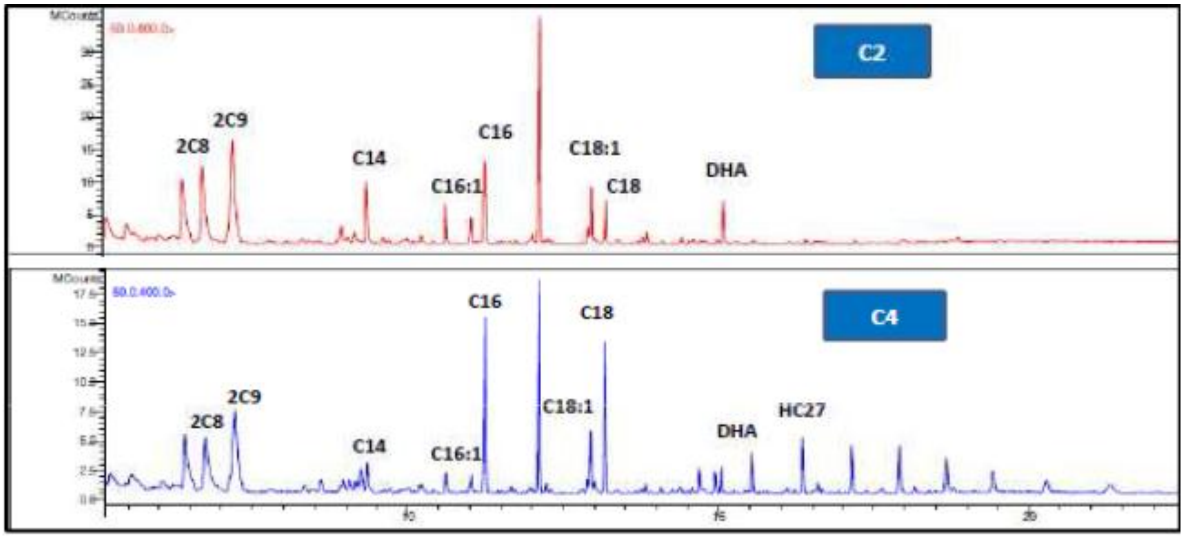

Figure 7. Chromatograms from samples C2 and C4.

In addition, the identification of hydrocarbons of odd chain carbon, of which the most intense is C_{27}, together with the high content of myricyl palmitate ester, which justifies the low value of $2C_9/C_{16}$, all point to the presence of beeswax in the samples, as was already suggested by mRS.

The characteristic chromatographic peak of dehydroabietic acid (DHA) was detected in several chromatograms. This acid is formed when the abietic acid in diterpenic resins from the Pinaceae family degrades over time. This compound is consistent with the oil-resin binder that was probably mixed with zinc white (ZnO) in combination with other whites and fillers.

The use of a mixture of these organic components as a binder was also found in the results of the analysis of the paintings from the Picasso Museum in Antibes [23].

4. Conclusions

This work contributes to demonstrate that mRS is a well suited technique to investigate the materials composition used in modern paintings, particularly when combined with the right set of analytical techniques. This combination can ensure a reliable identification of both pigments and binders, despite their complex composition.

In this case, mRS was successfully applied to the analysis *in situ* of a painting entitled “Guitar” with the signature “Picasso”. The information obtained using this non-destructive technique allowed us to identify three of the main pigments used: phthalocyanine blue and phthalocyanine green and anatase. mRS cross-section analyses confirmed the pigments found in the *in situ* Raman study and provided information about the other pigments used in this painting, such as pyrazolone orange. SEM-EDX microanalysis confirmed all these findings and also detected the presence of Ba and Zn in the white area, which could result from the use of white ready-mixed paint that contains zinc oxide pigment mixed with the barium sulphate-extended form of anatase. Picasso is reported to have used house paint (particularly Ripolin®) in some of his works in the first half of the twentieth century. In the present work, from the results obtained in this study of the “Guitar” painting, the use of house paint was not clearly confirmed by the ATR-IRTF study but it cannot be ruled out.

The composition of the ground was assessed by mRS of the cross-section. This study revealed $CaCO_3$ and TiO_2 in rutile form. The use of beeswax on the white areas was confirmed by the GC-MS analysis performed, as previously suggested by mRS. This study by GC-MS also indicated the use of an oleoresinous binder.

As regards the timeframe in which the pigments so far identified in the study of the painting “Guitar” were used by artists, it is interesting to note that they were first synthesized in the first third of the twentieth century. Thus, titanium oxide pigment dates back to the beginning of 20th century as shown by analyses carried out on Picasso’s early paintings.The use of anatase in the “Guitar” painting is compatible with the Cubist period of Picasso. Rutile was used in artists' paints after 1932 althought it has been proposed to be present in paints from 1908 [38]. Copper phthalocyanine was patented in 1929 by the Scottish Dye Works, and has been commercially available since 1935. PO34 (belongs to the disazopyrazolones) was discovered as early as 1910, although commercial application was delayed by some 20 years.

In conclusion, the materials used are chronologically compatible with the period in which Picasso painted. "La primera comunión" is considered one of his first paintings dated to 1895 while he continued to paint until 1972. However, any definitive authentication assessment must rely on an artistic and historical study of the painting and a detailed investigation of its provenance. Thus, the identification of the polymorphic modification provides chronological precisions, which will be used in upcoming research to clarify anachronisms.

A final obstacle is that although it seems likely that Picasso, like many artists, had clear ideas about the use of pigments, these often remained a trade secret of which there is little or no documentary evidence.

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