Multidisciplinary study of the origin of the painting from the early 20th century leads to Picasso

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Abstract: This study applied multiple scientific approaches to establish the significance of an old work of art, *Red Guitar*, by examining its historical origin and the color materials used in its creation. Furthermore, the study provides thus far unknown pieces of Olga Picasso's family history to be added to her biography. Scientific approaches included digital X-ray radiography, X-ray fluorescence spectroscopy, infrared Fourier transform spectroscopy, Raman spectroscopy, and elemental thermal conductivity analysis. This combination of techniques provided broad confirmation about the time when the painting was created. The work includes colors (white, black, blue, yellow, green, red, and brown/red) and prevalent use of lead-and iron-based historic pigments Chrome Yellow, Yellow Ochre and Red Ochre. It also documents the use of unconventional materials, the colorant Pigment red 4 and nitrocellulose. This investigation led to the conclusion that the art, *Red Guitar,* is genuine and in accord with Picasso's work during the first two decades of the 20th century.

Keywords: historic pigments, colorants, nitrocellulose, X-ray radiography, X-ray fluorescence spectroscopy, infrared Fourier transform spectroscopy, Raman spectroscopy

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1. Introduction

Complementary investigative approaches combine historic documentation with scientific analyses of the pigments and other materials to collect information required to establish the art work's provenance and separate original arts from forgeries. The information about pigments and synthetic colorants from the late 19th to early 20th century is well documented, and a growing number of databases is a testimony to the increased significance of the scientific methods in art history, conservation, and trade. An extensive analysis of Picasso's work was of value for the current investigation. The periods that were particularly considered include the artist's early years, works from the Blue and Rose periods, and synthetic cubism. The studies of painting materials of six portraits from 1895-1900 [1], *Blue room*-1902 [2], *Acrobat family*-1906 [3], and four 1917 cubist paintings [4] were of the most relevance for understanding the artist's palette and color techniques. During that period, Picasso also started experimenting with non-conventional materials and media supports that were of additional benefit for this study [5], [6], [7], [8].

This study applies multidisciplinary approaches to establish the origin and significance of a painting attributed to Picasso through the examination of historical and chronological records and materials used. Furthermore, the study provides new insights about Olga Picasso's family history to be added to her biography. It documents the use of pigments and non-artists materials in agreement with Picasso's work during the first decades of the 20th century.

1.1. *Art historical context*

The artwork, *Red Guitar,* is connected to Nikolaj Kokhlov, the brother of Olga Picasso. The current owner attests that Picasso gifted the work to the Yugoslav Army Chief of Staff Stevan Hazdic as appreciation for giving employment to Nikolaj Kokhlov. This statement was the start point for collecting additional evidence about this art. The evidence enlightens on the topic of familial connections, particularly during the period when Nikolay Kokhlov was in direct contact with Picasso and Olga. Of prominence in this is the information from a relative of Nikolaj Kokhlov, who offered letters, cards, and photos that demonstrate strong family connections between Nikolaj, Olga, and Pablo Picasso. Figures. 1a to 1d. show Nikolay Kokhlov in the Yugoslav

Army uniform, his wedding photo, and his wedding certificate from 1928. Also shown is a postcard from Picasso written to Nikolaj in 1923, signed in the Cyrillic alphabet. The archival documents show that there was a Picasso exhibition in Belgrade in October 1926, organized by Paul Rosenberg and Paul Epstein. Of note is that this exhibition was right before Nikolay's wedding and perhaps an opportunity for interactions between the family members. (Suppl. Fig. 1S).

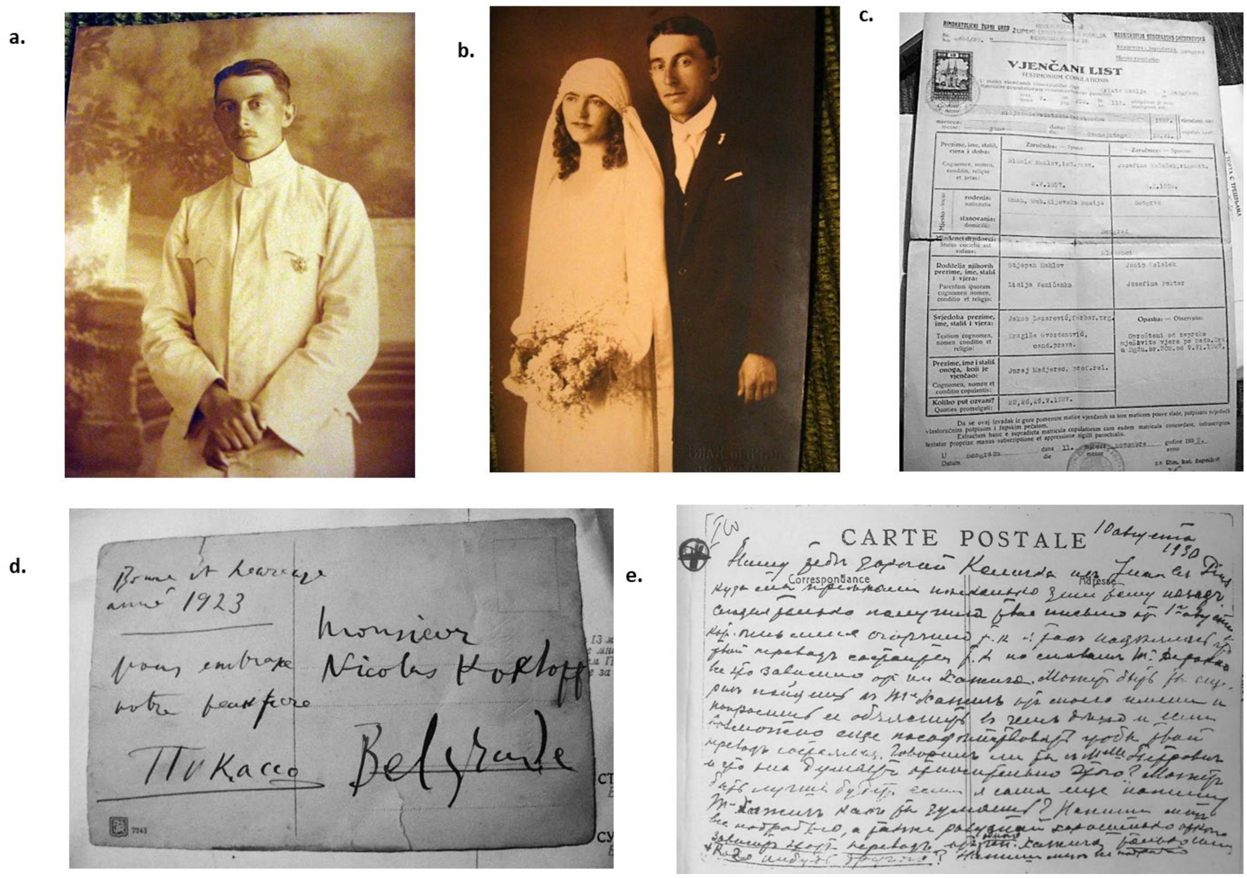

Figure 1. From Khokhlov Private Collection: **a.)** Nikolay Khokhlov, brother of Olga Picasso in Yugoslav Army uniform; **b.)** Nikolay's wedding photo and **c.)** the wedding certificate date Belgrade-12 July 1928. The certificate states: Nikolay Khokhlow (East orthodox, born 2nd May 1897 in Uman, Kiev) married Jozefina Kolacek (catholic, born 9th of October 1902 in Belgrade). The names of parents, witnesses and the priest are given. Dates when they visited this (catholic) church previously were 22, 26 and 29 May 1927. There is a comment that they were forgiven and free to marry even though they are from different religions. At the bottom are the signature and the date when this copy of the certificate was produced, 11/11/1939. The purpose of this copy of Nikolaj's wedding certificate is not known. **d.)** A postcard from 1923 written by Picasso to Nikolay Khokhlov-and signed 'Picasso' in Cyrillic. **e.)** A postcard of Olga to her brother Nikolaj dated 10 August 1930 (see the main text).

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Of importance is a letter from Olga to her brother from 1930 in which she offered to help him to get a job in the Yugoslav army (Fig. 1e). Olga wrote: *"I have received your letter however I was saddened by the news that your job transfer has been blocked. According to Derocco everything depends on Hadzic* (original art owner, Suppl. Fig. 2S). *Maybe you can talk to Madam Hadzic in my name and ask her to explain what happened and how they can help with your job transfer. Did you talk to brother and sister Petrovic and what they think about this? Maybe it will be better if I additionally write to Madam Hadzic. What do you think? Write to me in detail and figure out precisely on whom your job transfer may depend on in addition to general Hadzic. Maybe someone else. Write to me more details."*

In her letter, Olga references "Derocco," who is Aleksandar (Sacha) Deroko (1894-1988), a Serbian architect who made the acquaintance of Picasso's while on study scholarship in Paris in the mid-to-late 1920. Mentioning Derocco is significant because of the fact that Derocco in his autobiographic book describes how NIkolaj obtained the job. In his book "When the plane was flying above Belgrade" (Suppl. Fig. 4S), Derocco describes his relationship with Olga and Pablo Picasso. Derocco and Rasko (artist and diplomat) and his sister Nadežda (artist) Petrović, were a direct contact between Olga and Nikolaj, and they visited Picasso on several occasions. Derocco describes his role in helping Nikolaj through his close friendship with Hadzic's daughter. More importantly, the book references a painting changing hands from Picasso to Hadzic family. He described an instance when Picasso sent art gifts to Hadzic's wife, asking Derocco and Rastko Petrović to deliver them, but there is no mention that *Red Guitar* waspart of this particular event. He further commented that at the time Picasso worked for Rosenberg and was not allowed to give away his art to anybody. Thus, when leaving Rue de la Boete, Picasso asked them not to show drawings to the porter. See more in Fig. 3S.

One of the gifts Derocco received from Picasso is a variation on the theme of the guitar on the table. Picasso inscribed this work in French: "To Sacha Derocco for our friendship, Picasso," with the additional inscription on the side that reads: "Paris – December 1927" (Fig. 4S). This lithograph given to Derocco in 1927, is based on Picasso's painting "La table devant la fenêtre", dated 1919. It shows that it was not uncommon for Picasso to keep and give away older artworks as gifts, and that he was still in possession of some of his earlier works in the late 1920s.

It is not surprising that written statements from Hadzic or his heirs, the art exhibition history, etc., could not be found and this is for several reasons. The art was a gift and because of close connections with the King and the Monarchy, the Hadzic family was living a quiet post Second World War life in the communist Yugoslavia, when it was not popular to sell or export art privately nor it was very trendy to collect it. This political atmosphere explains why the art was inherited quietly, losing its authenticity in the process, when new owners did not even believe that the art was in fact an original Picasso. Taken together, the art back is officially stamped by the Serbia Ministry of Art and Culture and casts no doubt that the current owner of *Red Guitar* is legitimate. The documentation showed the history behind the narrative present in the official statement prior to the owner's acquisition of the art in 1997. The art is undoubtedly a gift directly linked to particular parties (Olga Picasso, her brother Nikolaj, Alexander Deroko, and Stevan Hadzic), mentioned in the letter from Olga to her brother Nikolaj, and in the autobiography book of Aleksandar Derocco.

1.2.Description of the painting

The subject painting is cubistic and belongs to synthetic cubism. This art named *Red Guitar* is 35.7 cm x 25.9 cm oil on cardboard painting (Fig.2a). It depicts a series of clearly delineated planes of color rendered in a bright palette that radiates uniformly across the composition. Emerging from these planes is a table surface set against a mottled red background. Upon this table rests a man's head, guitar, and bottle, among other abstract forms. The contours of each facet are clearly delineated with bold strokes of black paint, and each facet conjures a sense of compositional flatness.

a.

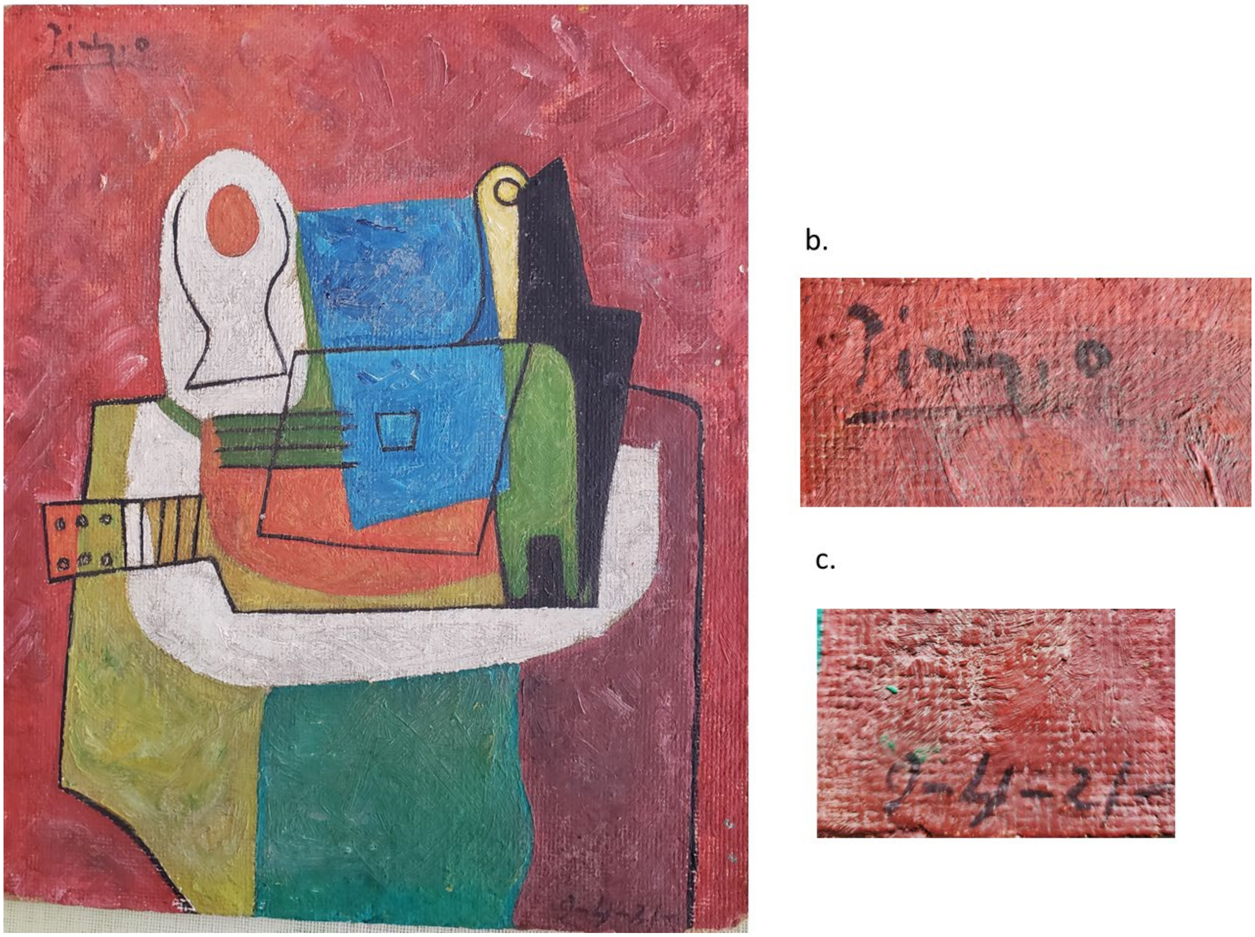

Figure 2. a.) *Red Guitar* painting investigated in this work. b.) The enlarged artist's signature and c.) date.

A signature reading "Picasso" appears in the art's upper right (viewer's left) with the date reading "9-4-21" at art's lower left (viewer's right). The enlarged images of the date and signature are shown in Fig. 2.b and c. Color smeared over the signature suggests that the signature was executed before the painting was finished. The date at the bottom is on the other hand placed on a dry, thick oil layer after the art was completed. The writing of numbers 4 and 2 was affected by uneven paint surface, and the number 9 has stains from a neighboring green paint. The *Red Guitar* signature and date are not notably different from Picasso's signatures and dates from the same period, and they are deemed authentic by the National Museum of Art (Belgrade, 20/4/2011, del.br 37.14).

The geometry and color palette in *Red Guitar* relate to Picasso's cubic paintings from the same period. The following information was obtained from 'Online Picasso Project" (https://picasso.shsu.edu/). The watercolor *Composition 1* (September 10/1920) has identical arrangements of the red-blue-yellow-green colors with the central red area reminiscent of *Red Guitar*. Gouache paintings from 1920 (*Femme à la guitare*, fall 1920, *Piano I*, Fall/1920, and *Le Piano,* 26-September/1920) also share the central positions of red and the color combination of *Red Guitar*. *Red Guitar* also has colors and elements from an earlier painting, *Fillette au cerceau* (Winter/1918~1919). The extensive use of white paint in the red backdrop of the *Red Guitar* is like the white use in *Compotier et bouteille sur un guéridon* (January/1920; OPP.20:141). Finally, works with the greatest similarity to *Red Guitar* are the two variations, both dated only a day later, namely *Guitare et compotier* (10 April 1921; OPP.21:014; Z.VI:1426) and *The Table* (10 April 1921 OPP.21:257**;** Z.IV:260), a watercolor/oil on canvas and a crayon on cardboard respectively, with a high level of similarity between *Red Guitar* and *Guitare et compotie*r (*'Blue*').

The immediate question was why such a close duplicate of the documented painting exists. During the 1920s Picasso had a habit of reproducing paintings in his various styles: The most obvious example is the cubistic painting *Verre et paquet de tabac*-Fall/1921, which exists in two identical versions and one modestly modified version **(**OPP.21:109, OPP.21:268 and OPP.21:077; from the Online Picasso Project: https://picasso.shsu.edu/). The next example is *The Portrait d'Olga,* cardboard,-Spring 1921 (OPP: 21:050). The ink on the paper version of this art has been found recently (OPP.20:492). Picasso kept this 1920 version in his collection until the 1970s, however, it was taken from his house by Pierre Le Guennec who was also in possession of never seen before Picasso' works from 1900 to 1932. These two examples indicate that the existence of multiple versions of Guitars resonates closely with the artist's tendencies in the early 1920s. Additional examples of duplicate works include *Pierrot et arlequin* Summer 1920 (OPP.20:010 and OPP.20:272), *Autoportrait de profil* March/1921 (OPP.21:082 and OPP.21:209), *Chien-loup*. 7-March/1921 (OPP.21:074 and OPP.21:266); *Femme assise* [Spring] Summer/1921 (OPP.21:230

and OPP.21:231), *Trois femmes à la fontaine* Summer/1921, OPP.21:224 and OPP.21:225 are very similar, while OPP.21:187 and OPP.21:227 are modestly different from the rest.

2. Materials and Methods

2.1. Digital X ray radiography

To allow the best sharpness and geometric detail, the X radiography scans were performed using a portable digital X-ray detector (Siemens Mobilett) with a wide dynamic range. This technique has an advantage over the use of traditional X-ray radiographic films that have limited range and, thus, reduced image contrast. The digital X-ray images are formed on the principle that a low density area experience higher radiation exposure and, therefore, produce darker shades, while more dense areas are less exposed and produce lighter shades on the images. After an optimal exposure of 200S (SPPED of the receptor) raw images were processed for display and storage using Digital Image Management System (DIMS) with image characteristics optimized without losing the initial quality.

2.2. Furrier-transform infrared spectroscopy

The analyses were performed on Thermo Scientific Nicolet 6700 FTIR spectrometer. FTIR spectra were measured in two ranges: 4000–225 $cm^{-}$with DLaTGS detector and CIS beam splitter. The spectra resolution was 4 cm^{-1} and the number of scans was 256. Thermo Electron's OMNIC software was used to collect and process the data.

2.3. Organic elemental analysis

Organic elemental analysis was conducted with Thermo Fisher Flash 2000 analyzer. Technique simultaneously detects C, H, N, and S in organic materials by pyrolysis, separation by gas chromatography and detection with a thermal conductivity detector (TCD). The samples were calibrated against thermal standard Acetanilide (C:71.09, H:6.71, N:10.36 and O:11.84%).

2.4. X-ray fluorescence

A portable Bruker Tracer III SD X-ray fluorescence spectrometer (XRF, S/N: T3S2416, Mfg date: 12/19/2012, Bruker USA) was used to investigate the elemental composition of the pigments. The spectrometer is equipped with a micro x ray tube with a Rhodium anode, and Silicon Diode Detector(SSD). The beam spot size was 10 mm in diameter and the distance of the spectrometer to the painting was 1 mm. The instrument was used in a stationary mode on a tripod. It was operated at 45 keV and 30 µA using a red filter (Ti, Al, Cu) without vacuum, with 120 s exposure time to maximize the signal to nose ratio.

2.5. Raman spectroscopy

Raman spectra were recorded with LabRAM HR 800 Raman spectrometer equipped with an integrated Macrochamber and Confocal Microscope for high spatial resolution imaging and a benchtop spectrometer that has a 633 nm He:Ne 20 mW laser besides externally mounted lasers at 785 nm (NIR) and 532nm Nd:Yagr. Measurements were performed using the 785 nm laser and depending on the sample, the maximum power was adjusted using neutral density filters (0.01% to 100%). The minimum wavenumber for 785 nm laser was 100 cm^{-1} and the maximum wavenumber was 3300 cm^{-1} with a spectral resolution 4 cm^{-1}. The recorder spectra had varying acquisitions parameters with time and power determined on a sample-by-sample basis. Spectra were corrected for instrument response, and when a strong luminescent background was present, the spectra were not taken into consideration.

3. Results and Discussion

3.1. Visual and X-ray analysis of the Red Guitar painting

The initial indication that the *Red Guitar* is not a copy of *Guitare et compotie*r (‘*Blue’*) was obtained by visual comparison of the two paintings (Fig. 3a,b). There was a difference in the way the contour of the bottle is conveyed in the two versions. In the *Red Guitar* composition, the edge of the vessel is not defined. Rather a shoulder-like top of the green vessel was rounded and narrowed, and a thick layer of black color indicated this change (Fig. 3a.b). In the ‘*Blue’* composition (see *Guitare et compotie*r OPP.21:014 in ‘Online Picasso Project’: https://picasso.shsu.edu/), the right-hand edge of the vessel is defined despite the fact that it falls over the stylized, jagged area of the bottle behind it. In addition, two vessel-like drawings clearly visible in the *Red Guitar* (inside the white rectangle in Fig. 3a) were overpainted into a jagged black shadow.

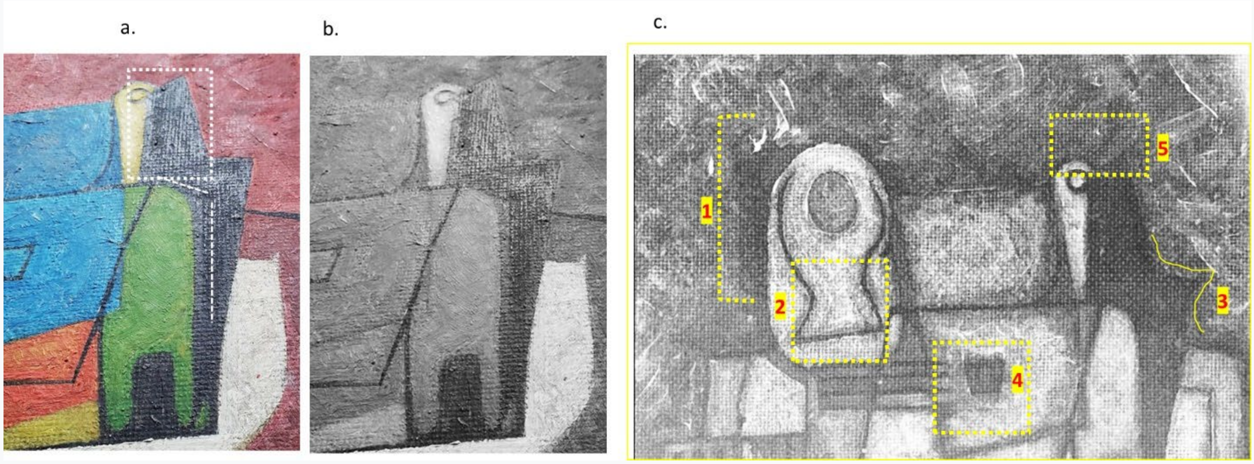

Figure 3. a.) The white dashed lines and the white rectangle point to the main visible changes in *Red Guitare.* b.) the same adjustments in black & white. c.) The X-ray image of the top area: yellow lines surround drawings elements absent or modified in the final composition.

Further evidence about artistic changes arose from the X-ray image analysis of the *Red Guitar* (Suppl. Fig. 5S and Fig. 3c). The bottom area of the X-ray image is white and not very informative (Suppl. Fig. 5S). The top area (Fig. 3c) revealed drawings that are not visible or modified in the final composition: 1) a big rectangle right and above the head, 2) the area inside the head redrawn several times, 3) the black jagged shadow was initially curved, 4) the small blue rectangle was initially a circle with extra lines around and 5) additional less defined drawings below the signature and above the bottle that were hidden in the final work. Those artistic changes demonstrate that *Red Guitar* is an original artwork not a copy of the '*Blue*' painting. To strengthen this conclusion, and provide further evidence, a detailed pigment analysis of *Red Guitare* was performed and compared to the pigments used by Picasso in other artworks .

Pigment analysis was obtained by non-invasive X-ray fluorescence (XRF) spectroscopy, and microanalysis of color samples using infrared and Raman spectroscopy. The results of pigments analysis, along with their elemental compositions and chemical compounds, is summarized in Table 1.

3.2. White paint

A strong XRF signal of Zn in the main composition and all other areas identified zinc oxide (Zinc white) as the primary white pigment (Fig. 4a). The other white pigments are based on Ca and Pb, in the form of calcium carbonate (Calcite) and lead carbonate (Lead white). This composition suggested the use of artistic tube paint, not the enamel type of paint (Ripolin), which is a high-quality zinc white that does not contain Ca and Pb components [9]. Traces of Co and Fe/Mn were also present, and they are known as impurities of Zinc whites. Sr is a known impurity of calcium carbonate [10]. Traces of Ti could be from the cardboard support, but also natural impurity of white pigments as proposed for Picasso's cubist painting *Man with a Fruit Bowl* (1917) [4] .

The ground layer pigments were analyzed from the leaked paint using FTIR and Raman spectroscopy (Fig. 4.b, c): Calcium carbonate was identified from the infrared signals at 1379, 872 and 712 cm^{-1} and the Raman signals at 1088, 714, 284 and 158 cm^{-1}. Traces of iron oxide (Burnt sienna) were identified at 116 cm^{-1} using the refence spectra from Pigments Cheker1 [10]. Other pigments were not detected in the leaked white paint.

Although the FTIR spectrum of the leaked white paint was overwhelmed with calcium carbonate (Fig. 4c) it additionally showed signals of an oleo resinous binder, with sharp peaks at 2850 cm^{-1} and 2919 cm^{-1}, and a shoulder at 2954 cm^{-1}. These signals were completely identical to a resinous binder from *Acrobat family (1906*) [3] .The binder signals included the oil carbonyl group at 1730 cm^{-1} and carboxylate bands at 1578 , 1584, and 1535 cm^{-1} from metal soaps formed from the reaction of zinc white and oil components.

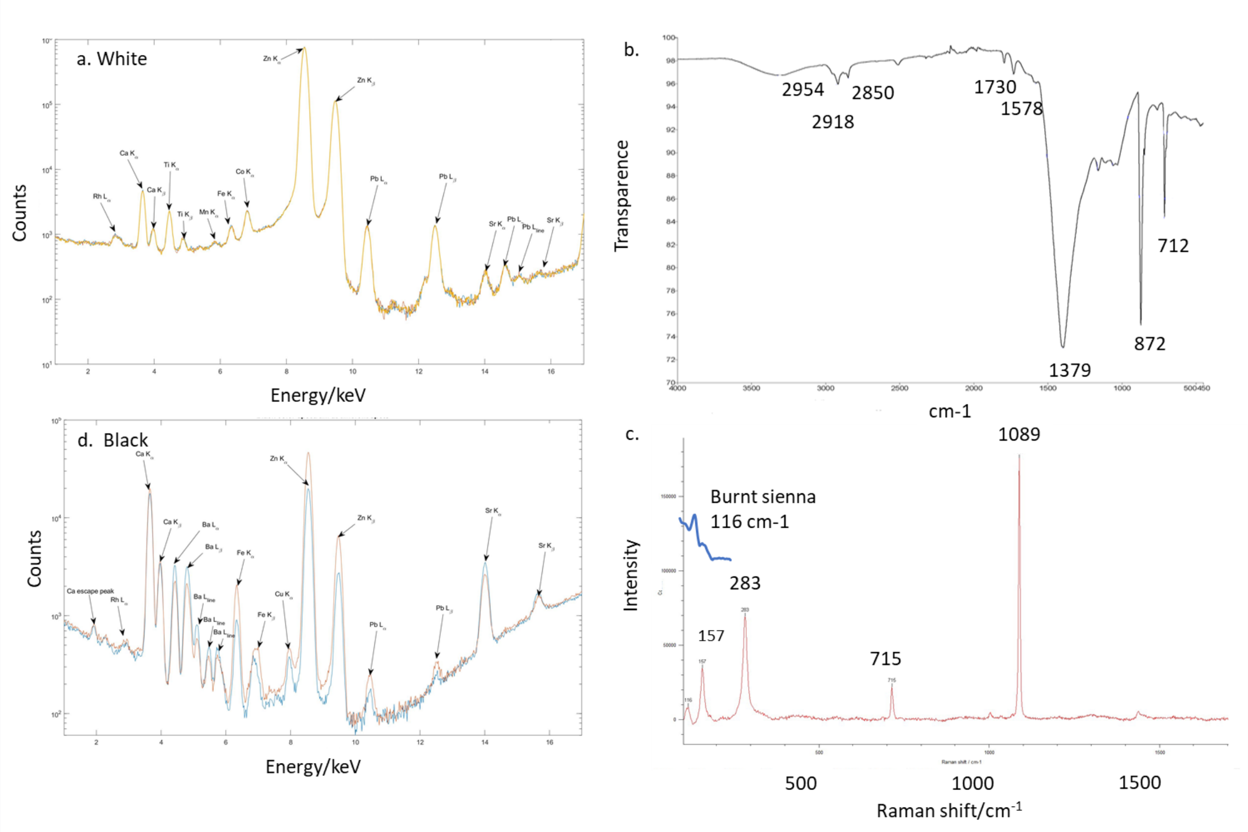

Figure 4. The elemental analysis of the main (a.) white and (d.) black areas. b.) FTIR and c.) Raman spectra identify calcium carbonate, with traces of an oleo resinous binder (FTIR) and iron oxide (Burnt sienna) (Raman), in the leaked white paint.

3.3. Black paint

Elementary analysis of the main black composition revealed the presence of Zn, Ca, Ba, Fe (Mn) and Sr (Fig. 4d). The signals for Ca and Sr were stronger in this black paint than in the white paint or any other paint. A very strong signal for Ca in the black pigment is usually attributed to Bone (Ivory) Black. The strong appearance of Sr is another evidence for Bone Black, as Sr is a common component of this type of pigment [10]. The strong signal for Fe could be from additional black pigment, black iron oxide (magnetite) but also from "Prussian Blue" (a cyanide iron complex that was a widespread pigment at that time). The mix of Bone black and Prussian blue was detected also in *Acrobat family* (1906) and in Picasso's early paintings [1] [2] [3]. Traces of Cu in the black paint could be from adjacent blue paint or from the support.

The strong presence of Ba is specific to this paint. Barium was not detected in any other color, and perhaps was used as a filler in this black pigment. The lines, signature, date, and dark areas in other colors did not contain Ba and, consequently, were executed with different black paint. The analysis in Fig. 3 documented that the jagged black composition does not completely match the initial drawing. Use of only one type of black pigment in this area means that the compositional changes were made during the process of art creation. If something had been subsequently changed, the XRF analysis would show differences in paint composition in altered and original areas [10].

3.4. Blue paint

Elementary analysis identified three blue pigments, based on Co, Cu and Fe in a mixture with large amounts of Ca and Zn whites, and traces of Ti, Pb and Sr from the white paint (Fig 5a). The blue area appears fragmented and discolored, however, a uniform blue color under UV light (Suppl Fig.6S) indicated that a fluorescent blue pigment was in the mixture. The pigments of Fe (Prussian Blue) and Cu (copper carbonate) do not absorb and appear black under the UV light [11]. Cobalt pigments are dark blue under the UV light, but the amount of Co seems insufficient to be the sole absorbent.

The only remaining pigment that is blue under the UV light is Ultramarine [11]. The faded blue appearance may suggest the "ultramarine disease", a catalytic process of degradation of oil binder when ultramarine acts as a catalyst of degradation [12]. Ultramarine was clearly detected in dark yellow paint by its specific Raman absorption at 550 cm-1 (Fig. 6a). In *Acrobat family (1906)* Picasso mixed Prussian Blue and Ultramarine to produce different blue shades and similar patches of faded blue paints were identified [3]. Additional analyzes of the blue, as well as black, orange-red, and light green paints, were not performed as sampling would be destructive to the painting.

3.5. Yellow paints

There are two different shades of yellow, bright yellow and dark yellow. They are both dominated

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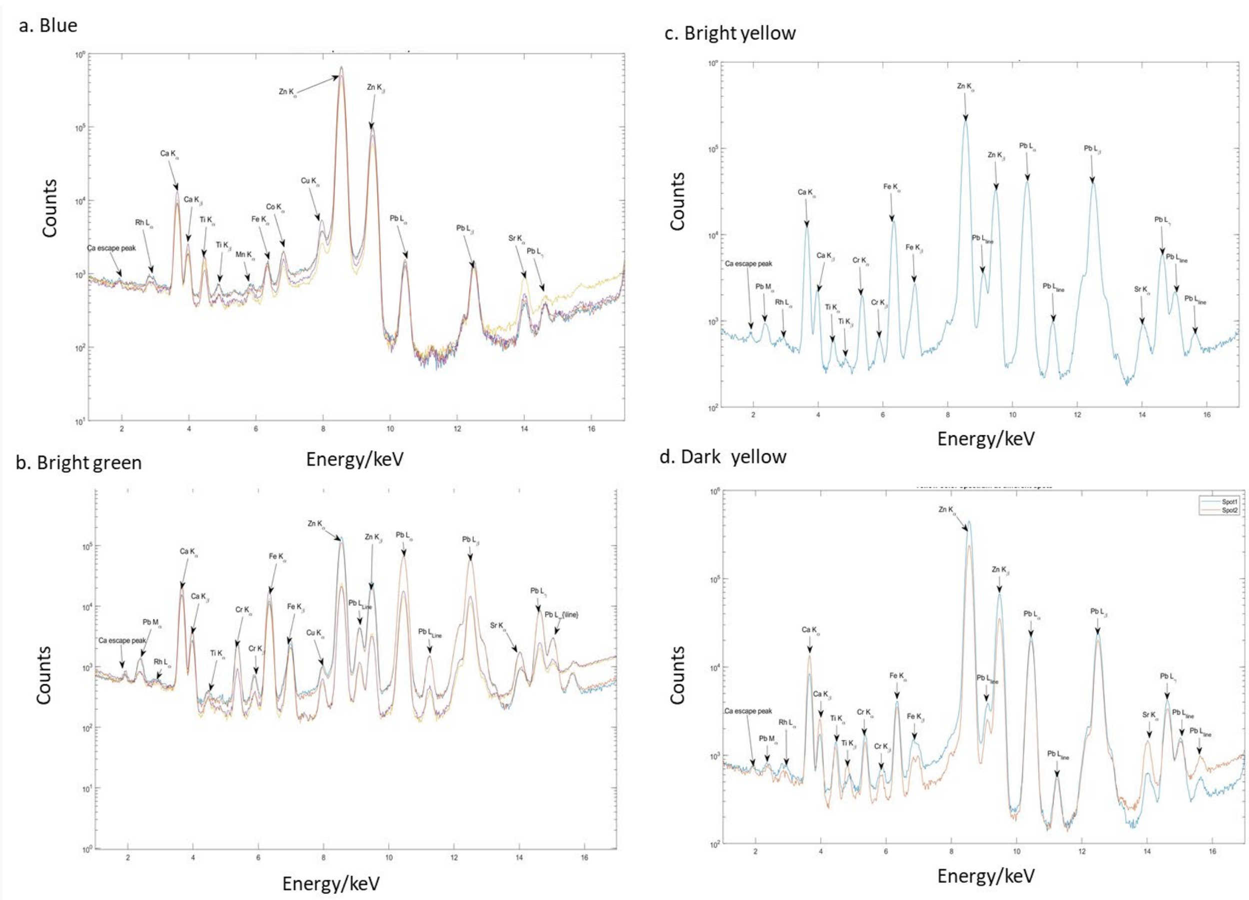

Figure 5. a.) The elemental analysis of the main blue , b.) bright green, c.) bright yellow and d.) dark yellow colors. The spectra were shown as semi-log plots of counts vs. energy. Various spots were represented in different colors.

by pigments based on Fe and Pb and Cr. Dominant Ca and Zn whites and their accompanying trace elements were present in both shades (Fig.5c,d). The presence of Pb and Cr is from lead chromate (PbCrO4, Chrome Yellow), frequently used in earlier works by Picasso but also by van Gogh and other 19th and early 20thcentury artists. Fig. 6 a,b shows images and Raman spectra taken from the leaked paint.

The pigment of Fe is iron oxide-hydroxide (FeOOH, Yellow Ochre), with characteristic Raman bands at 246, 301, 390, 480 and 550 cm^{-1} (Fig.6a). Yellow Ochre, however, has a weak signal at 550 cm^{-1}, therefore, the observed strong signal at 550 cm^{-1} is attributed to the presence of Ultramarine. This suggested that the green shades at the dark-yellow surface were probably created by a combination of Yellow Ochre and Ultramarine. Chrome yellow (lead chromate, $PbCrO_4$) was identified with characteristic CrO_4 signals at 844 cm^{-1} and additional signals at 389, 362, 337 and 325 cm^{-1} (Fig. 6b). The leaked paint also showed presence of calcium carbonate and the green pigment from the neighboring dark-green paint, described in Fig. 7.

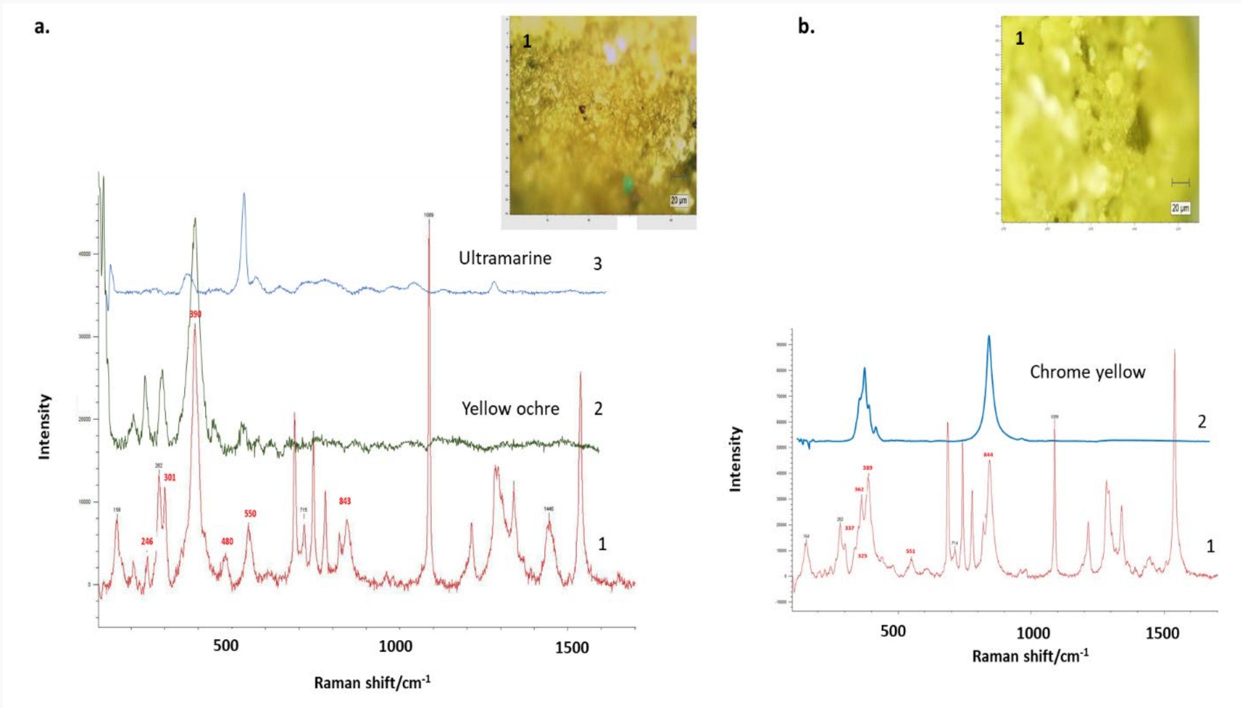

Figure 6. Images and Raman spectra taken from the leaked dark yellow paint. a.) Characteristic peak position shown in red numbers are from Yellow ochre, Ultramarine and Chrome yellow; b.) Characteristic peak position in red are for Chrome yellow.

3.6. Green paint

There are two different green colors in *Red Guitar*. The analysis of the centrally located light green identified Fe, Pb and Cr, indicating that the light green color was created by mixing Prussian blue and Chrome yellow (Fig. 5b). This combination of blue and yellow pigments to obtain green shades was common procedure of that time and it was used in Picasso's early works [1]. A combination of Prussian blue with a yellow pigment was used also in one of the *Acrobat family* (1906) green colors [3].

The bottom dark green elements are the same as those in the light green, and include Fe, Pb and Cr pigments (Fig. 7a). However, the overall look of the paint suggested that the area was repainted. The green stains were also evident in the adjacent colors, and especially noticeable in the neighboring dark red area and on the arts' date (Fig. 2c), demonstrating that this intervention was performed after the painting was completed.

The green pigment identified in the leaked green paint is copper phthalocyanine (PG7, phthalo green). This pigment was discovered in blue version (phthalo blue) in 1935, and the green version was available from 1938.

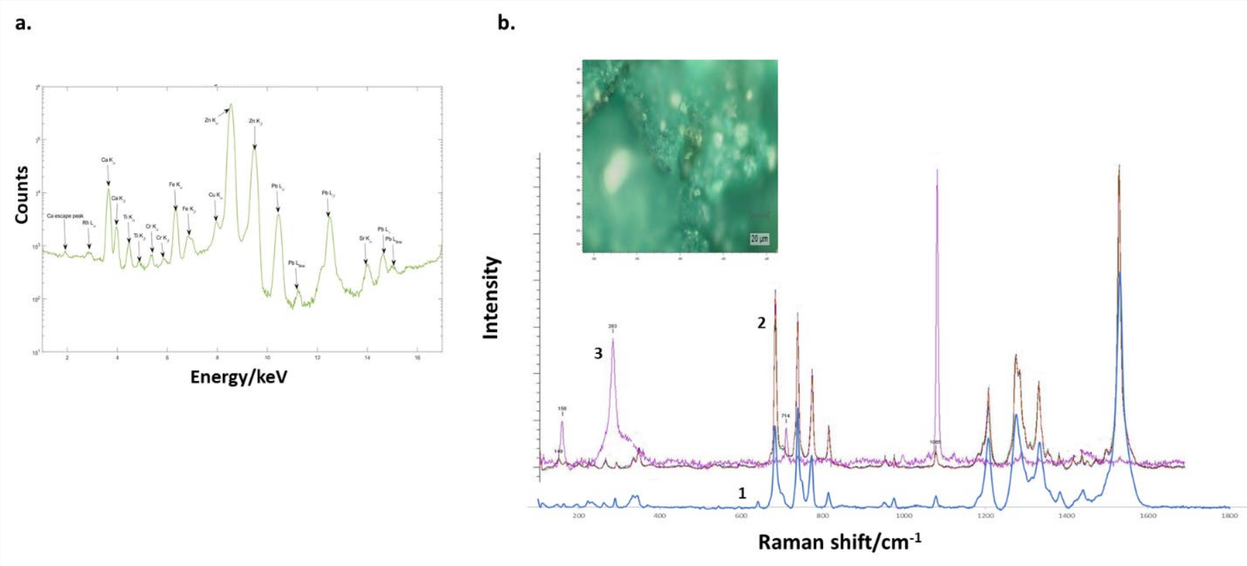

Figure 7. a) The elemental analysis of the main dark green area. b) Raman spectra of the leaked green paint identify copper phthalocyanine green (2) and calcite (3) peaks. The peak labeled as (1) is the reference spectra of copper phthalocyanine.

This is the only pigment that deviated from the date the painting was made. The appearance of the green stains over the date strongly attests that this was a later intervention. It is not known, however, who performed this intervention. Interestingly, the green color issues were present in Picasso's work. In a collage from 1913-14 a green area was multiple times retouched most likely by the artist himself [13] and the preparation of the second green color in *Acrobat family* was suspected to include a yellow die, but this was not confirmed [3]. Phthalo blue was used in the restoration of *La famille Soler* (1912) [14] and one green pigment used in the Antibes collection was not identified, but presumably it was not phthalo green [15].

3.7. Red paints

Three red colors were characterized: bright red, orange red and brown red. In addition to Zn and Ca white pigments, the bright red has Fe, Pb and traces of Cr (Fig. 8a). As with other samples taken from the liked paint, FTIR and Raman spectroscopy identified only calcium carbonate as a white pigment. Raman spectroscopy (Fig. 8b) identified Pigment Red 4 (PR4), an early synthetic mono-azo colorant also called Chlorinated Para Red, among other names. The reference spectrum (C.I 12085) of PR4 from the SOP spectral library (not shown) is completely identical to the paint spectrum 1. The red paint samples 2 and 3 (Fig. 8 b, d) show additional signals for iron oxide (Red ochre), with specific bands at 226, 291 and 410 cm^{-1} that were clearly separated from the PR4 signals. Thus, it can be concluded that PR4 and Red ochre were the main pigments used in the preparation of the bright red color.

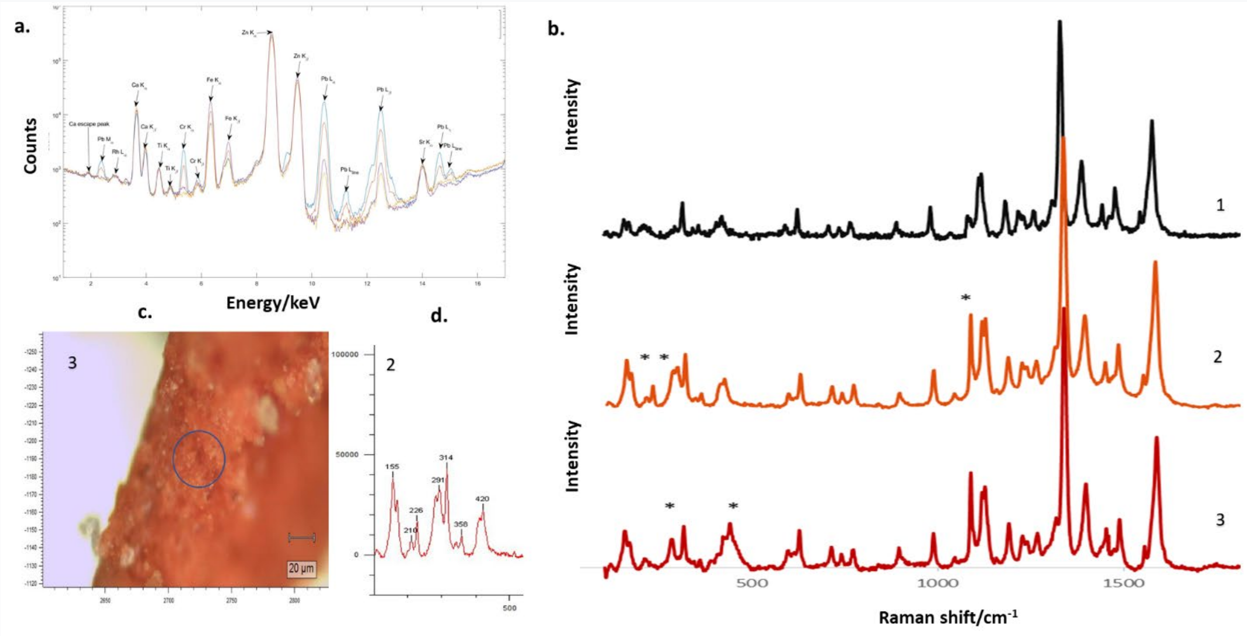

Figure 8. a.) The elemental analysis of the bright red area. b.) Raman spectra of the leaked red paints identify Pigment red 4 in three separate samples. The spectrum of the sample 1 is identical (https://soprano.kikirpa.be/index.php?lib=sop&id=PR4_B_785_kikirpa) to the reference spectrum of PR4. The paint samples 2 and 3 show additional signals labeled with (*); c.) the representative confocal image of the sample 3; d.) the focused area of the spectrum 2 showing Red ochre signals at 226, 291 and 410 cm^{-1}.

The centrally located orange red differed from other red colors by the dominance of Pb, with some amounts of Cr and Fe-based pigments. (Figure 9a). The amounts of Zn and Ca white pigments was the lowest in this color. Due to the dominant presence of Pb, the main pigment in this color is probably Red (Orange) Lead (Pb3O4, Minium). A significant amount of Cr however also indicated the presence of Chrome Yellow. An orange pigment, which is a combination of lead carbonate, lead chromate and lead oxide (Pb $(OH)_2$ $PbCrO_4$ + $PbO.PbCrO_4$) that has been used in France since the middle 19th century [16] cannot be excluded. The Fe based pigment could not be assigned and it could be Red Ochre or Yellow Ochre, identified in other areas of the painting.

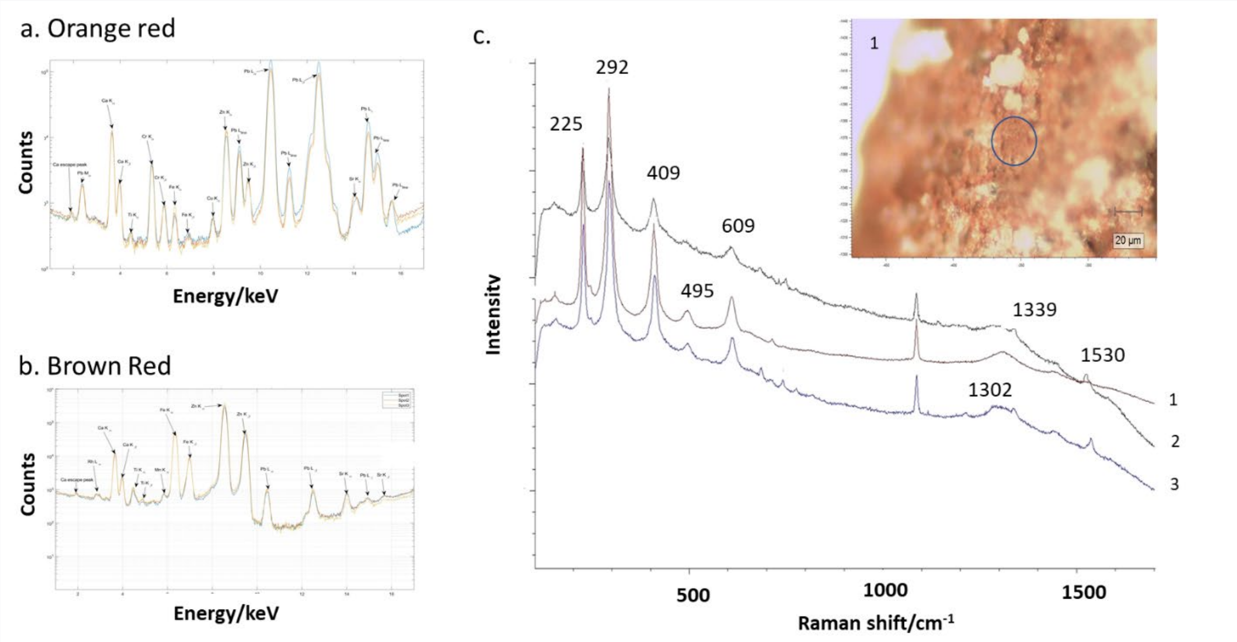

Figure 9. The elemental analysis of a.) orange red and b.) brown red paints. c.) Raman spectra (samples 1, 2 and 3) of the leaked paint from the brown red area identify Hematite (225, 292, 409, 495, 609 and 1302 cm^{-1}); Inset confocal image is for Raman sample #1.

The brown red color in the lower part of the painting was the least complex. This color contained Ca and Zn based white pigments, and the red pigment was exclusively Fe-based. Detection of traces of Mn showed that the Fe pigment is a natural earth pigment (Fig. 9b). Raman analysis identified ferric oxide in the form of Hematite, with signals at 225, 292, 409, 495, 609 and 1302 cm^{-1} (Fig.9c). Additional two signals in 1300-1600 cm^{-1} range suggested the presence of a black pigment. The presence of the Bone black pigment was excluded due to the absence of the signal for the phosphate group at 960 cm^{-1}.

3.8. Cardboard analysis

Infrared spectra detected hemicellulose and lignin that remain after cellulose production from wood pulp [17]. As shown in Fig. 10a, the art support was made of a highly lignified cellulose with characteristic signals for hemicellulose at 1726 and 1594 cm^{-1}, and lignin at 1506 cm^{-1} and 1252 cm^{-1}. Similar signals of hemicellulose and lignin are present in the spectra of French paper cellulose, but not in the German paper cellulose produced in the late 19th - early 20th century (Fig. 10b,c.) [18]. German paper was produced from more bleached cellulose, a technological process that removes hemicellulose and lignin [18]. In the cellulose spectrum of the *Acrobat family (*1906) cardboard the hemicellulose signal was masked by fillers, but the signal for lignin is strong (Fig.10c) and agrees with other analyses [3]. On the other hand, the cellulose spectra of early 20thcentury cardboard from Italy (Fig.3b) did not have a significant amount of lignin showing a different product process [19].

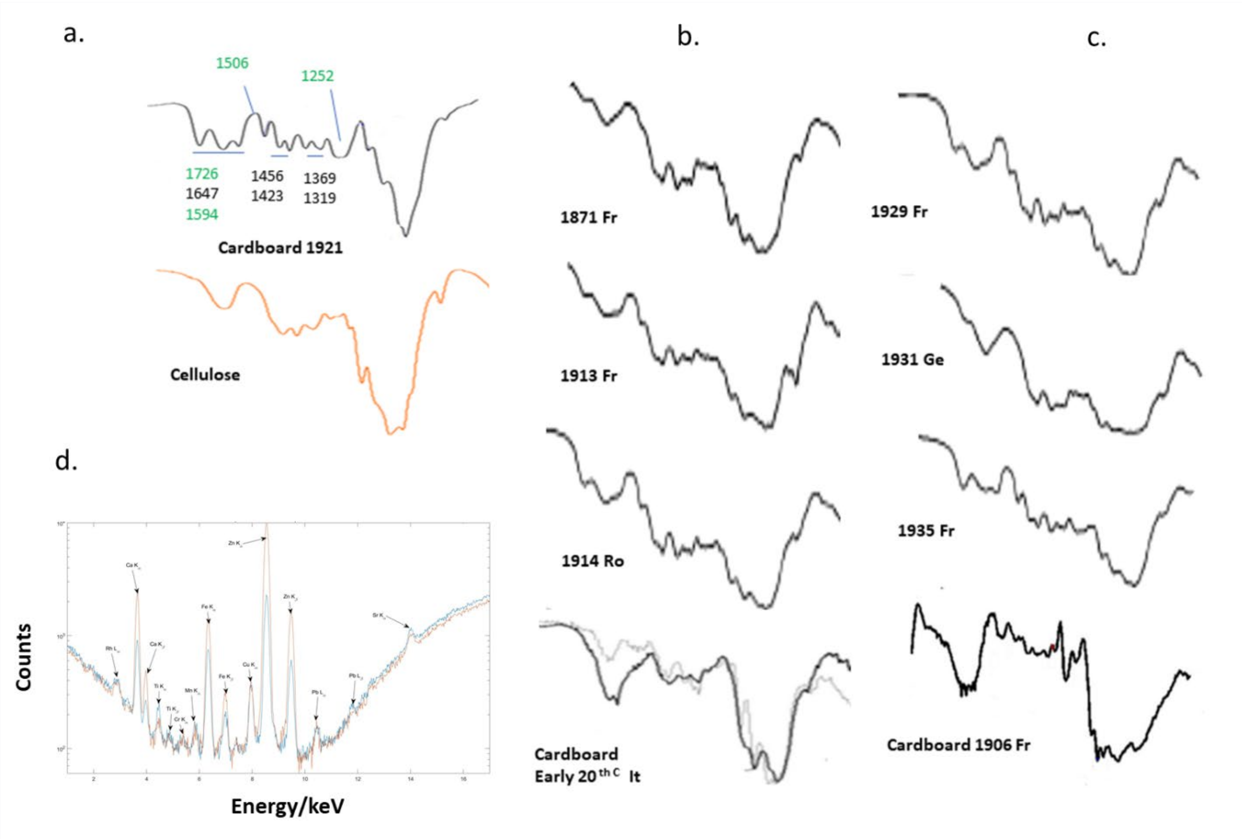

Figure 10. a.) The infrared 'foot-print' region of the painting cardboard cellulose and pure cellulose; The cardboard hemicellulose (1726 and 15524 cm^{-1}) and lignin (1506 and 1252 cm^{-1}) are not part of pure cellulose; b.) and c.) the infrared 'foot-print' regions of the old paper and cardboard cellulose according to references 3, 18 and 19 ; d.) the elemental analysis of the painting cardboard of *Red Guitar*.

The main inorganic components in the *Red Guitar* cardboard include Zn, Fe (Mn), Cu and Ca, with traces of Sr, Pb and Cr (Fig. 10d). Unexpectedly high amounts of Zn with traces of Pb and Cr were attributed to pigment migration into the cardboard. The European papers from the late 19th and early 20th centuries similarly have Ca, Fe (Mn) and Cu-based materials, with Zn and Ti varying depending on the country of origin and date of manufacturing [18]. The *Acrobat family* cardboard also contains Zn, Ca and Fe (Mn) as the main elements, while Cu and Sr are present as trace elements [3]. Thus, the old European papers and cardboards shared industrial ingredients, but highly lignified cellulose was common for the old French papers, Picasso's *Acrobat family* cardboard as well as the cardboard from which the *Red Guitar* support was built.

3.9.Composition of the back area

The smooth and shiny surface of an ivory color without visible traces of paintbrush of the art back area is reminiscent of the industrial house paint Ripolin (Fig. 11a). This type of house paint was popular among artists because of its good quality and lower price compared to artists' paints. They were used by Picasso, Kandinsky, and Picabia and this is widely documented. Contrary to visual expectations, the infrared spectra identified nitrocellulose as the major component in the varnish and paint layers.

3.9.1 Varnish Layer

Nitrocellulose is identified by characteristic infrared signals for-NO_2 group at 1641 cm^{-1} and 1275 cm^{-1}, CO group at 1062 cm^{-1}, and O-NO_2 group at 834 cm^{-1} (Fig. 11b). The spectrum has additional signals for the carbonyl group at 1720 cm^{-1}, aliphatic deformations at 1455 and 1372 cm^{-1}, and sharp bands for CH_2 at 2920 cm^{-1} and CH at 2851cm^{-1}, which together completely corresponded to the natural resin Copal [11]. The results cannot show whether nitrocellulose was mixed with the resin at the time of application or has already been applied. However, there is evidence that Picasso used Copal, most likely *Siccatif de Harlem*, and mixed it with oil paints as evident in *Still life* (1922) [2].

Nitrocellulose degradation is an autocatalytic process caused by aging. In nitrocellulose artifacts from 19th and early 20th century France and England, the percentage of nitrogen in degraded artifacts is 3-6%, and in undegraded artifacts 6.7-9.5%, with 11% maximum corresponding to the presence of two nitrate groups in nitrocellulose [20]. Nitrocellulose from the back varnish layer of *Red Guitar* contained 3.24% of nitrogen, showing that it was seriously degraded.

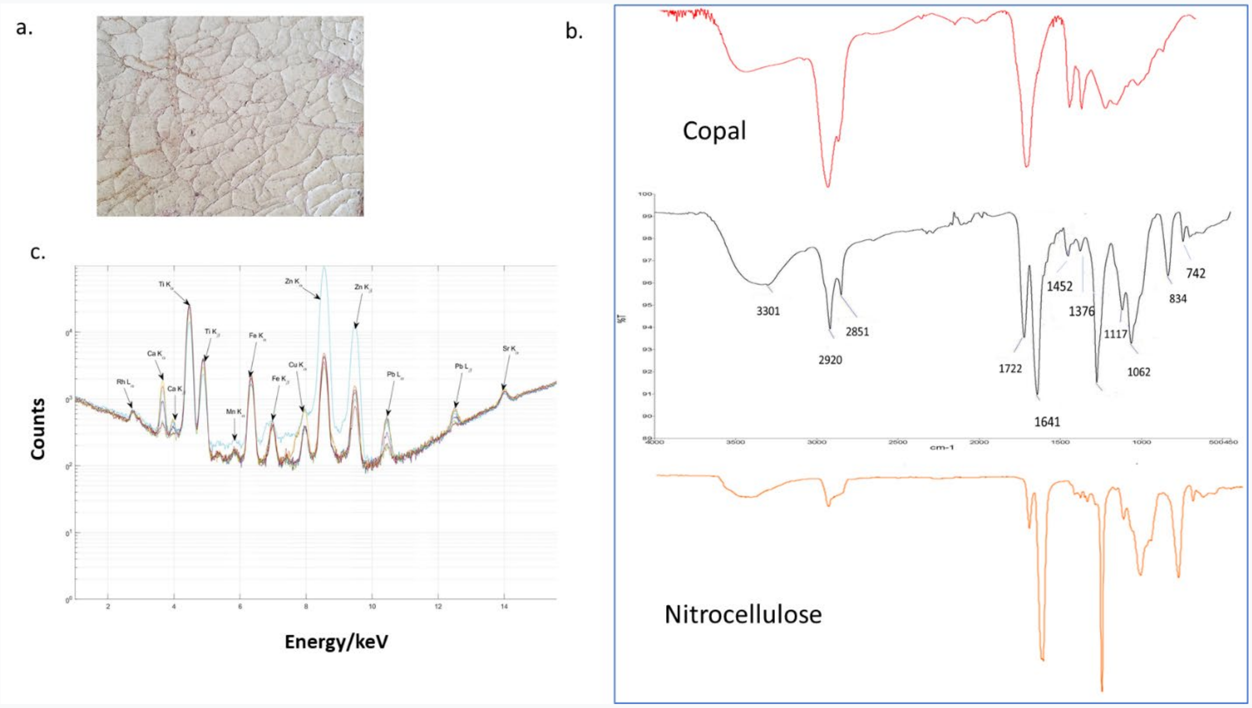

Figure 11. Characterization of the art back paint. a.) visual image; b.) the Infrared spectrum of the upper layer (black) identifies nitrocellulose and copal; the copal and nitrocellulose reference spectra are red [11]; c.) the elemental analysis of the back paint was obtained in several different areas; a high level of Zn at one spot is from a white stain at the surface.

Raman spectra of the varnish layer (Fig. 12a) identified the nitrocellulose plasticizer camphor with characteristic bands at 1728 cm^{-1}, 1451 cm^{-1}, and 852 cm^{-1} and diethyl phthalate with bands at 1600 cm^{-1}, 1581 cm^{-1}, 1167 cm^{-1} and 1042 cm^{-1}. Importantly, this chemical composition fully corresponded to a type of nitrocellulose known as "French ivory" that was widely used at the end of 19th and early 20th century [16].

3.9.2 Back Paint Layer

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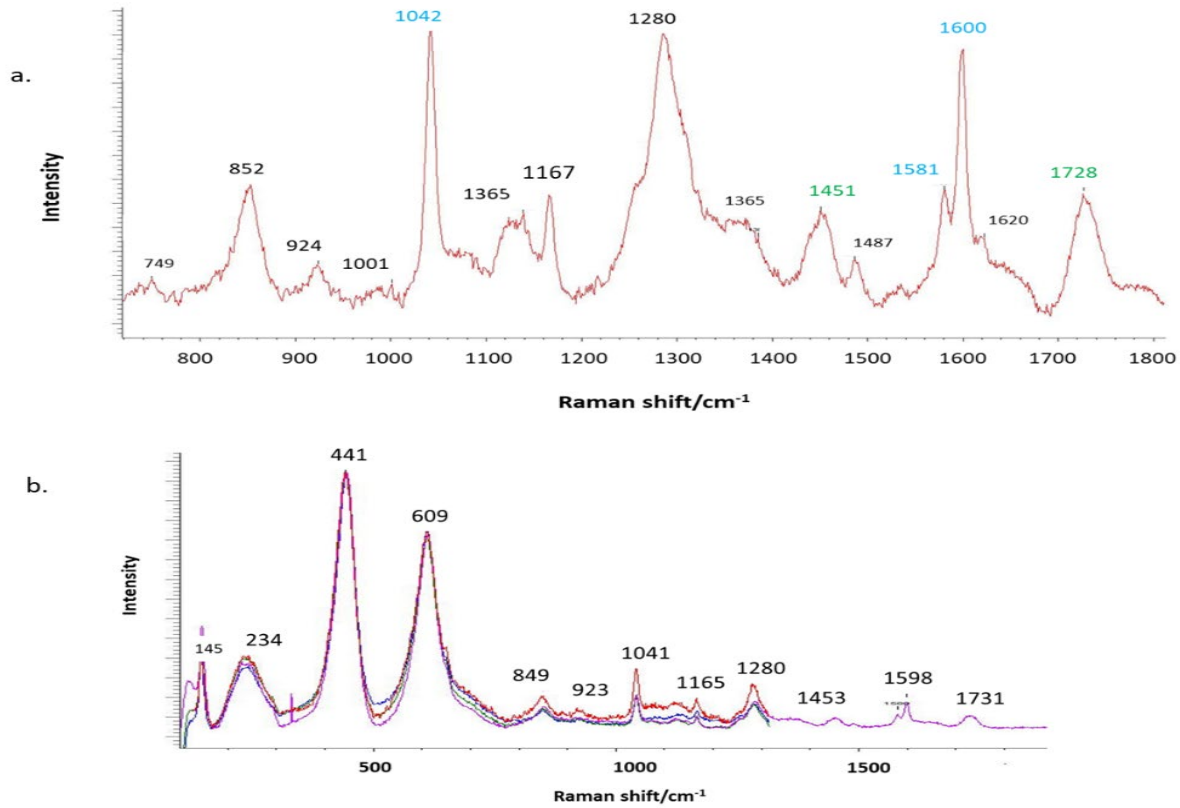

Figure 12. Raman spectra of the back area paint: a.) varnish layer contained nitrocellulose (black), camphor (green) and diethyl phthalate (blue). b.) Lower paint layer contains titanium dioxide mixture of anatase and rutile, with traces of the varnish components identified in spectra shown in a.).

The elemental analysis of the back paint established Ti, Zn, and Fe as major elements, with minor contributions of Ca and Pb white pigments, and traces of Mn, Cu and Sr. While Ti, Fe (Mn) and Cu did not vary, Zn, Pb, Ca, and Sr varied in different areas of the painting (Fig. 11c). This could suggest that Pb, Ca and Sr were part of zinc white paint that was applied separately from titanium white (with Fe/Mn and Cu impurities).

Raman analysis of the lower layer identified titanium dioxide in two crystalline forms, as anatase with characteristic band at 145 cm-1 and rutile with bands at 234, 441 and 609 cm-1 (Fig. 12 b). The spectra also detected traces of nitrocellulose (1280, 923, and 849cm-1), camphor (1731 and 1453 cm-1) and diethyl phthalate (1598, 1580, 1166, and 1041cm-1) in the paint particles. Lead white and calcium carbonate were not detected, which indicated that their amount was low, or they were mainly in the upper layer. The main Raman signal for Zinc white at 436 cm^{-1} overlaps

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with Rutile and it cannot be identified. Therefore, it could not be determined if Zinc white is present in the lower layer, varnish, or in both layers.

4. Significance and Conclusions

It was not anticipated that this work would become a historical journey into Olga Picasso's past. The autobiography of Aleksandar Derocco led to the information about Olga's brother, who lived in Belgrade in the 1920s. When Nikolaj's relative was found in Belgrade, the circumstances related to this work and why the painting was in Serbia became more obvious. The historical materials from the Nikolay Kokhlov collection, correspondence with Olga and their broader family, are of additional importance for future research on Olga Picasso. Her biography lacks information about her brother Nikolaj that could be now amended.

Without the information from Dr. Mullen's 'Online Picasso Project', it would be impossible to systematically study the artwork produced during the first two decades of the 20th century. This database was central for the identification of paintings that were by style not only from the same period, but also showing other duplicate works and two versions of *Red Guitar*. The visual and X-ray analysis exposed the process of creation of *Red Guitar* strongly suggesting that *Red Guitar* is an original artwork and not a copy of *Guitare et compotier*.

4.1. Use of Picasso's palette of historic pigments

The palette of white, black, blue, yellow, green, red, red-brown is the same color palette that Picasso used in his early work and maintained throughout his career. *Red Guitar* dominates by zinc, lead, and iron-based pigments. Chrome Yellow, Yellow Ochre, Red Ochre, Hematite, Ultramarine and the colorant Pigment red 4 were identified by Raman spectroscopy. Zinc white, Lead white, Carbon black, Prussian blue and Red lead were strongly implicated from the elemental analysis. According to this color palette the painting could be dated to the beginning of the 20th century.

Zinc white is the primary white pigment in *Red Guitar,* and in addition to the presence in the ground layer, it has been applied alone or in a mixture with calcium carbonate in the surface layer where provided a 'milky' effect around the main composition. Zinc white appears to be the primary white pigment in several paintings from the Picasso's Blue period: *Blue room* (1901),

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Poenies (1901), *The Child with a Dove* (1901) [2] and it was used in the ground layer of *Man with a Fruit Bowl (1917)* [4]. Another application was mixing a high amount of zinc white with other colors that was highly visible in blue and yellow areas, again, consistent with the color preparation documented for the *Blue room* [2] where zinc white was the basis for the preparation of blue and other colors. The surface application of zinc white appears in some early Picasso's portraits and Sessa and colleagues concluded that same trend was also recognized for Van Gogh paintings [1].

Red guitar has at least one black pigment identified as Bone (Ivory) black. Bone black was more frequently used in earlier Picasso paintings, including early portraits [1], *Blue room* [2] and *Science and charity* [21].

Chrome yellow was popular in the 19th century, but because it darkens upon light exposure, it has been replaced with cadmium yellow. While Picasso predominantly used cadmium yellow in his later works [22],[23],[24], the exclusive use of chrome yellow was documented in his earlier paintings [1] [2] [21]. Iron-containing earth pigments, red, yellow, and brown iron oxides, are used since antiquity and they were constantly present in Picasso's palette.

4.2 Use of industrial, non-artist materials

Picasso was innovative in working with different supports, binders, and paints during his career. [4] [5] [6] [7] [8]. This work clearly identified the same tendencies in the use of industrial products, the red colorant PR 4 and nitrocellulose. Natural and industrial organic dyes (printing colors, textile colors) are known to be used in the early 20th century paintings, but they are not well-characterized, even in Picasso's work. They are difficult to analyze and most of the time they could only be implicated by the presence of metals, like barium, used to precipitate those compounds into more durable 'lakes'. It was also not uncommon for the synthetic dyes to be added to artistic pigments, to change their color hue, or because they were much cheaper alternatives. In the early 20th century "Windsor and Newton" for example, used Pigment Red 3 (PR3) in artists' paints that was not officially acknowledged [25]. The earliest record of the use of PR3 in paintings is by German authors, Kirschner (1909) and in the paintings on glass by C. Menze (1913) [26]. The painting investigated here is the first known case in which PR 4 was identified in an artistic work, which is a significant discovery important for future classification of the historic use of PR4. PR4 was synthesized in 1906 [26] by coupling beta-naphthol with 2-chloro-4-nitroaniline. PR4 had major applications as industrial paint, but its use in artists colors, pencils and wax crayons are also known [27].

Nitrocellulose is the oldest semi-plastic material that became very popular in the early 20th century. The oldest product was Collodion, found in 1848, which was used for dressing wounds and preparing photographic plates. Wider applications of nitrocellulose began with the use of camphor as a plasticizer and the invention of Celluloid in 1872. Celluloid found very wide applications in household products, coatings, varnishes, and in the production of the first celluloid tapes for the film industry. The ivory-like French fans from the late 19th and early 20th centuries were made from Celluloid, with camphor as a plasticizer and diethyl phthalate as an additive to increase the strength of the material [16]. This type of celluloid widely known as "French ivory" because of specific type of celluloid production developed in France, was applied as a cheap substitute for real ivory in home and decorative products [16]. Zinc oxide was the main pigment used to produce that ivory look of the nitrocellulose products [28]. This historical description and the identification of identical nitrocellulose components, camphor and diethyl phthalate, was quite remarkable and demonstrated that the *Red Guitar* nitrocellulose resembles the “French Ivory” Celluloid.

Titanium dioxide was manufactured in the form of anatase until the 1940s, when pure Rutile was introduced [29]. Ilmenite ore, which is an ore of iron and titanium (Fe, Mg, Mn, Ti) O_3, was used to produce anatase. Before 1920, anatase was impure and of an ivory color since contained a large percentage of Rutile and iron due to inadequate industrial processing [11]. In 1920, France implemented a new procedure known as "the Blumenfeld process" for the manufacturing of pure anatase, but the purity remained problematic [11]. The very high presence of Rutile and Fe/Mn in a mixture with zinc white in the back paint of *Red Guitar* implicated an early product, dated between 1908 and 1920, when many attempts were made to produce purer anatase [11]. In the 1920s and 1940s, most Titanium white products were composites of 15-30% titanium dioxide with 85-70% barium sulphate or calcium sulphate/phosphate [29]. Sulphates and phosphates were not detected in *Red Guitar* showing that the used titanium white was not a composite. The ratio between Zn and Ti in the *Red Guitar* back paint is close to an early product that was on the market before 1920, known as Kronox Extra A, which had 30% zinc white and 70% Kronox Extra X. Kronox Extra X had low mounts of CaPO4 (25%) and $BaSO_4$ (10%) [29] that could have escaped detection.

Based on the paint leaks, the *Red Guitar* was completed after the back paint was probed. Perhaps the idea to combine nitrocellulose with copal varnish and titanium dioxide/Zinc white was an artistic experiment to test the properties of nitrocellulose or maybe it was an attempt to produce an ivory glossy paint that would mimic Ripolin. There is plenty of evidence that Picasso was experimenting with various materials, and in combining traditional oil paints with copal to make them look like Ripolin [23], [24], [30]. This work documents the earliest known use of nitrocellulose in art, famously used by David A. Siqueiros in the early 1930s [31] and Sidney Nolan in the late 1940s [32].

To conclude, the provenance of the artwork contains convincing, circumstantial, evidence to show how the artwork was gifted in an appreciation for help to Olga Picasso's brother to Hadzic family and how it found its home in Serbia. The artistic analysis offered strong support for the use of a color palette in accord with Picasso's artistic preferences. The scientific analyses of the paints and support materials provided validation of the use of historic pigments and materials in accord with the late 19th and early 20th centuries, and France as a place where the art had been produced. Therefore, the multidisciplinary approach to the analysis of *Red Guitar* gathered sufficient evidence and arguments to prove that this painting is Picasso's original.

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Table 1. *Red Guitar*: Colors along with th elements and components identified in the painting.

Color	Elements [a]	Painting materials [b]
White	**Zn, Ca,** *Fe(Mn), Co, Ti, Pb, Sr*	Zinc white, Calcite
Black	**Zn, Ca, Ba, Fe, Sr**, *Cu, Pb*	Bone (Ivory) black, Fe-pigments, Barium sulfate filler
Blue	**Zn, Ca, Co, Cu**, Fe(*Mn), Pb, Ti, Sr*	Zinc white, Calcite, Co and Cu blue pigments
Yellow:		
Yellow I (bright)	**Pb, Cr, Fe, Zn, Ca** *,Ti, Sr*	Chrome yellow; Yellow ochre, Zinc white, Calcite
Yellow II (dark)	**Pb, Cr, Fe, Zn, Ca,** *Ti, Sr*	Chrome yellow *;Yellow Ochre,* Zinc white, Calcite*, Ultramarine*
Green:		
Green I (bright)	**Fe, Pb, Cr, Zn, Ca,** *Cu, Ti, Sr*	Prussian blue, Chrome yellow, Zinc white, Calcite
Green II (dark)	**Fe, Pb, Cr, Zn, Ca,** *Cu, Ti, Sr*	Chrome yellow, Yellow ochre, Zinc white, Calcite#*, Drying oil# *Phtalocyanine green (retouch)**
Red:		
Red I (bright)	**Fe, Pb, Cr, Zn, Ca,** *Ti*	Red Iron*, Chrome Yellow, Zinc white*, Calcite*, Drying oil# , Pigment red 4 (PR4*)
Red II(orange)	**Pb, Cr, Zn, Ca**, *Fe, Cu, Ti, Sr*	Red Lead, Chrome yellow, Lead white Zinc white, Chalk, Yellow ochre (traces)
Red III (brown-red)	**Fe** (Mn)**, Zn, Ca,** *Pb, Ti, Sr*	Iron oxide (hematite)*, Zinc white, Calcite#* , Drying oil#
Preparation layer:		Calcite #*, Drying oil#
Back:	**Ti, Zn, Fe** (Mn), *Ca, , Pb, Cu Sr*	Titanium white , Zinc white, Iron oxide
Varnish		Nitrocellulose#*, Copal # Camphor*, Diethyl phthalate*
Ivory white		Titanium dioxide (anatase and rutile) * Nitrocellulose #*
Support:	**Zn, Ca,** *Fe(Mn), Cu, Cr ,Ti , Sr, Pb*	Cellulose # *(hemicellulose, lignin)#*

a) XRF: the main elements (**Bold);** the minor elements (*Italics)*

b) FTIR spectroscopy (#) and Raman spectroscopy (*)