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RAPID COMMUNICATION

Identification by Raman microscopy of anachronistic pigments on a purported Chagall nude: conservation consequences

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Abstract A painting purported to be by the artist Marc Chagall has been examined using Raman microscopy to check on its proposed execution date of 1910. The analysis shows that, due the presence of phthalocyanine pigments, the painting cannot have been created prior to c.1938. Transport of the painting to the Chagall Committee in France for inspection has led to their declaration that the painting is a forgery. Under French law the painting is required to be destroyed rather than retained for other forensic examination; the consequences for preservation of such items is of paramount importance, as is the need for auction houses to carry out analyses prior to auction.

1 Introduction

Marc Zakharovich Chagall was a Russian-born artist (1887–1985) who spent much of his life in Paris, France, eventually settling there permanently from 1947 until his death in 1985. Considered to be one of the important early modernist artists, Chagall was associated with many artistic styles, and in addition to his paintings, he created book illustrations, murals and stained glass works [1–3]. Recent sales of Chagall's paintings have included that of *Bestiaire et Musique* in 2010 in Hong Kong for US$4.18 million. It set a new record as the most expensive contemporary painting by a Western artist ever sold at auction in Asia. Other paintings by Chagall, such as *Le Cirque* (1956; sold in 2007 for US$12.3 million) and *L'Anniversaire* (1915; sold in New York for $14.8 million in 1990), have achieved significantly higher prices.

The current painting, entitled *Nude Woman Reclining* and apparently signed as being by Chagall, has a reported execution date of 1910 (Fig. 1). It was purchased in 1991 for £100,000 and has been in private ownership since then up to the time of the scientific investigation. The date 1910 is of particular significance as this was when Chagall left St Petersburg and relocated in Paris. The pastel painting, which measures c. 29 cm × 19.5 cm, depicts a female nude in a reclining pose and is executed in a range of colours, with no apparent evidence for restoration. In order to establish whether this date is correct and whether the work is by Chagall himself, non-destructive pigment analysis has been carried out directly on the surface of the painting using Raman microscopy.[1] The spectra obtained are compared with Raman data published previously on works of art [4–12], and the palette so determined is compared with those already established for works by other Russian artists [13–16].

2 Experimental method

Raman spectra of the pigments were collected using a Renishaw RM1000 Raman microscope system equipped with an 1800 lines/mm grating, a holographic notch filter, a thermoelectrically cooled charge coupled device (CCD) detector, and a Leica DM microscope. A He/Ne laser provided exciting radiation at 632.8 nm, with a laser power

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[1] This study formed the subject for the hour-long BBC TV "Fake or Fortune" programme broadcast in the UK on 2 February 2014.

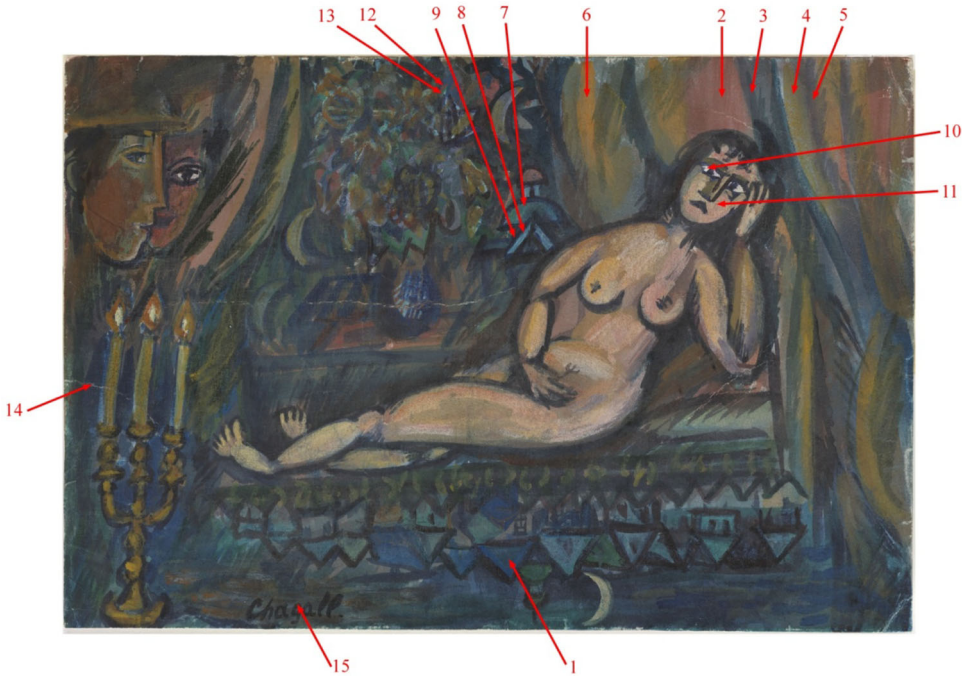


Fig. 1 Digital image of *Nude Woman Reclining,* with analysis sites indicated

at the painting's surface of about 0.4–0.8 mW. Spectra were recorded in the range 2500–100 cm^{-1} by collecting 10–30 accumulations each with a duration of 10 s and an estimated spectral resolution of 1 cm^{-1}; spectra were calibrated using the 520.5 cm^{-1} band of a silicon wafer, and background correction was necessary.

3 Results

3.1 Analytical findings

The compositions of the main pigments present at the surface of the painting were investigated at 15 sites (Table 1; Fig. 1). The pigments identified are: zinc white (ZnO), ultramarine blue, phthalocyanine blue ($CuC_{32}H_{16}N_8$), phthalocyanine green ($CuC_{32}H_{15}ClN_8$), and red and yellow iron oxides (FeO[OH] and Fe_2O_3; Fig. 2). These pigments have been used as very fine-grained intimate mixtures in each area of colour examined.

The identification of phthalocyanine blue and green pigments on the painting is of particular significance. Phthalocyanine blue, used in all blue areas of the painting examined (*Sites 1, 3, 8, 9* and *14*; Table 1; Figs. 1, 2), is a modern synthetic pigment, first manufactured for use as an artist's material c.1935/6 [17]; it is therefore anachronistic on a painting supposedly dating to 1910. Several different types of phthalocyanine blue pigments have been (and continue to be) manufactured, each with a slightly different chemical composition, structure, and colouration; the pigment used on the current painting is a variant of *Pigment Blue 15* (CI 74160 [8]; Fig. 2). In the majority of the blue areas analysed, the phthalocyanine blue component was found to be intimately mixed with *phthalocyanine green* (Fig. 2; except at *Site 14*, where phthalocyanine blue was found on its own). *Phthalocyanine green* is also a modern synthetic copper-based pigment, closely related chemically and structurally to phthalocyanine blue. It was developed after the blue form, becoming commercially available from c.1938 onwards [17]. The phthalocyanine green found on the painting has been identified as *Pigment Green 7*, which is widely used in all types of modern paints (Colour Index number CI 74260 [8]). This pigment was also identified as the main component in the green areas of the painting examined (*Sites 7* and *13*); in these areas, phthalocyanine blue was also present. A minor amount of zinc oxide (*zinc white*) is present in the pigment mixtures at many of the analysis sites (Fig. 2). Zinc white has been produced commercially since the 1780s although it was not widely used as an artists' material until the 1830s; it continued to be one of the three major white pigments in use until the mid/late-twentieth century, particularly in aqueous-based paints when it was displaced by titanium dioxide [18, 19].

Analysis of the selected red areas of the painting (*Sites 2* and *12*) shows that the main colourant is red *iron oxide* (Fe_2O_3); this has been used extensively in art in the form of natural ochres since prehistoric times and in its entirely synthetic form since the late eighteenth century. Yellow iron oxide is also thought to be present as a component in

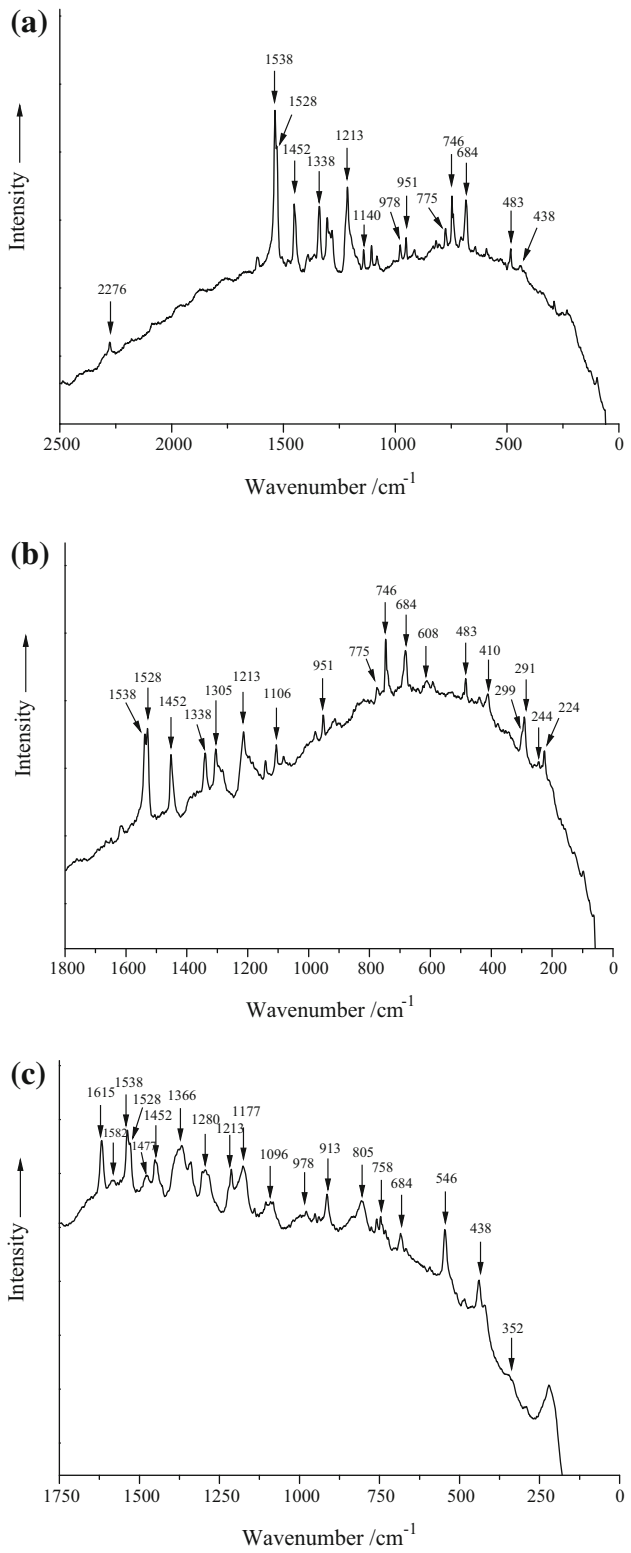
Table 1 Pigments identified on *Nude Woman Reclining* at each analysis site

Site #	Colour	Pigment(s) identified
1	Blue	Phthalocyanine blue and green
		Zinc white
2	Red	Red iron oxide (Fe_2O_3)
		Phthalocyanine blue and green
		Zinc white
3	Blue	Phthalocyanine blue and green
		Zinc white
4	Yellow	Red and yellow iron oxides (FeO[OH] and Fe_2O_3)
		Phthalocyanine blue and green
		Zinc white
5	Purple	Phthalocyanine blue and green
		Zinc white
		Ultramarine blue
		Monoazo red
6	Yellow	Phthalocyanine blue and green
		Red and yellow iron oxides (Fe_2O_3 and FeO[OH])
7	Green	Phthalocyanine green and blue
		Zinc white
8	Pale blue	Phthalocyanine blue and green
		Zinc white
9	Dark blue/black	Phthalocyanine blue and green
		Zinc white
10	White	Zinc white
		Phthalocyanine blue
11	Flesh-tone	Phthalocyanine blue
12	Red	Phthalocyanine blue and green
		Red iron oxide (Fe_2O_3)
		Zinc white
13	Bright green	Phthalocyanine green and blue
		Zinc white
14	Blue	Phthalocyanine blue
15	*Signature*	Phthalocyanine green

the yellow paints (*Sites 4* and *6* [20]). The oxides were found on the painting as fine-grained materials mixed with phthalocyanine green and/or blue in each case (Fig. 2).

The purple paint used in the background of the painting (*Site 5*) was found to contain *ultramarine blue* in addition to both phthalocyanine blue and green (Fig. 2); ultramarine blue has been widely available as a synthetic product since c.1828 [21, 22] and would therefore be appropriate on a painting dated as 1910. However, its admixture with the phthalocyanine components suggests that it is a later twentieth century commercially mixed product.

A minor amount of a *monoazo red* pigment was also detected in the purple paint. Azo pigments were first developed in the latter part of the nineteenth century, with many chemically distinct types introduced during the twentieth century. Azo dyes and pigments form a large class of modern (late nineteenth and twentieth century) synthetic compounds which range in colour from yellow to orange, brown and red. The class is subdivided according to chemistry into different sub-groups (such as monoazo, disazo, naphthol AS, β-naphthol, benzimidazolone and isoindolinone pigments). The first azo dye, chrysoidine (red), was synthesized in 1875, with the first water-insoluble pigments to be commercialized (the red β-naphthols) introduced from 1885 onwards; many new azo dyes and pigments have been since introduced post-c.1910 [17]. The complex Raman spectrum obtained from this overall purple pigment mixture means that it is difficult to establish precisely which azo pigment is present. Analysis of the white paint indicates that it contains *zinc white* (Fig. 2), found as a component in many other areas of the painting examined; no evidence for the presence of titanium dioxide white



◀**Fig. 2** Raman spectra obtained from the surface of *Nude Woman Reclining* showing the spectrum for pigment mixtures of **a** phthalocyanine blue (Pigment Blue 15—with characteristic bands at 1528, 1452, 1338, 1305, 1220, 1140, 1106, 951, 746, 679, 591, 483 and 288 cm^{-1}) and phthalocyanine green (Pigment Green 7—the bands at 1538, 1446, 1389, 1338, 1305, 1283, 1213, 1082, 978, 817, 775, 739, 684 and 642 cm^{-1}) obtained from the blue areas of the painting; the band at 438 cm^{-1} may indicate the presence of *zinc white*, **b** red iron[III] oxide, haematite (bands at 608, 410, 291 and 224 cm^{-1}), yellow iron oxide, goethite (bands at 244 and 299 cm^{-1}) and phthalocyanine blue and phthalocyanine green (bands at 1538, 1528, 1452, 1338, 1305, 1213, 1106, 951, 775, 746, 684 and 483 cm^{-1}) as found in the red areas of the painting examined, and **c** ultramarine blue (bands at 1096, 805, 546 and 352 cm^{-1}), monoazo red (bands at 1615, 1582, 1477, 1366 and 1177 cm^{-1}), phthalocyanine blue and green (bands at 1538, 1528, 1452, 1280, 1213, 978, 913, 758 and 684 cm^{-1}) and zinc white (the band at 438 cm^{-1}) as found in an area of purple paint (*Site 5*)

pigments, manufactured during the twentieth century (post-c.1920), was found. The white paint was also observed to contain microscopic blue particles of *phthalocyanine blue*, further indicating that it was applied after c.1935/6.

The paint used for the letter 'g' in 'the signature "Chagall", located towards the lower left corner, was also examined. This paint was established to contain a high proportion of phthalocyanine blue and green pigments (cf. Fig. 2).

3.2 Comparison with other works by Chagall

Analysis of selected known works by Chagall (including *The Lovers* [1929, oil on canvas], *The Wailing Wall* [1932, oil on canvas], *Jew with Red Beard* [1919, oil on paper], and *Solitude* [1933, oil on canvas]) showed that the artist regularly used pigments such as lead white, carbon-based black, Prussian blue, cerulean blue, ultramarine blue, cobalt blue, red iron oxide, and lead and zinc chromate yellows; pigments such as barium white, chalk, green earth, madder, and vermilion were also identified on these works.[2] These pigments were all available by the latter part of the nineteenth century (and many of them prior to this); however, no phthalocyanine pigments were found on these genuinely early Chagall paintings. The pigments used on a later painting by Chagall—*Commedia dell'Arte* (1959, oil on canvas)—reportedly included lead and zinc whites, Prussian blue, cobalt blue, ultramarine blue, vermilion, red and yellow ochres, Naples yellow, cadmium yellow, viridian and emerald green, but no phthalocyanine compounds [23].

4 Conclusions

Raman microscopic analysis of *Nude Woman Reclining* dated as 1910 and purportedly signed as having been painted by the artist Marc Chagall shows that the pigments

[2] Paint samples were taken from the listed Chagall works belonging to the Tel Aviv Museum of Art (Tel Aviv, Israel) and analysed by Dr. Tracey Chaplin as part of the conservation of the paintings, which was supported and sponsored by the Bank of America Merrill Lynch.

used for the painting include phthalocyanine blue, phthalocyanine green, monoazo red, red and yellow iron oxides, ultramarine blue and zinc white. The pigments are present as intimate mixtures, with the spectrum for phthalocyanine pigments dominant at every site analysed. Although synthetic ultramarine blue, zinc white and iron oxides have been in use as artists' materials since the late eighteenth/early nineteenth centuries, it is the presence of phthalocyanine pigments which provide a real indication of the painting's date. Phthalocyanine blue was first introduced in the twentieth century, c.1935/6, with phthalocyanine green introduced slightly later in c.1938. Such pigments, found extensively all over the painting, including in the signature, reveal that the painting could not have been executed prior to c.1938. The date of 1910 previously given to the painting is therefore considered to be incorrect.

Following the completion of the Raman research, the painting was sent by its owners to the Paris-based Chagall Committee for examination in the hope that they might provide more information regarding the painting's history. The Chagall committee stated that they would only offer their expertise if the owner submitted the work to them according to their standard terms and conditions (which made no explicit mention of the threat of destruction). However, the Committee agreed with us that the painting is a forgery and invoked French law which allows the seizure of items considered to be counterfeit and their destruction before a magistrate. The painting was part of a legal challenge but the destruction of the artwork is still due to go ahead. This calls up questions regarding the preservation of such items and the destruction of a body of forensic evidence which collectively may help stop the counterfeiting process.

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