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Painting on the margins: investigating the pigments, media, and techniques of Séraphine Louis

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Abstract

The richly decorative and imaginative works by French artist Séraphine Louis (1864–1942) have long elicited fascination, and her working methods have often eluded art historians and conservators alike. Working in secret and outside established art circles, Séraphine employed materials such as natural resin varnishes and was said to have used household paints in addition to traditional artists' oil paints. In this study of six works in the collections of the Musée d'Art et d'Archéologie, Senlis (MAA), The Museum of Modern Art, New York (MoMA), and The Metropolitan Museum of Art, New York (MMA), attention was given to Séraphine's choice of colors and paints, in addition to identifying possible additions to or manipulations of painting media by the artist. Technical imaging was carried out using UVF to visualize the extent of Séraphine's use of natural resins. Analysis of the palette relied on XRF techniques and limited sampling for analysis by Raman and μ -FTIR spectroscopies. Overall, the following pigments were identified: lead white, zinc white, carbon-based black, red and brown ochres, umber, vermilion, alizarin lake, rhodamine B lake, Prussian blue, cobalt blue, ultramarine blue, chrome green, emerald green, viridian, cadmium yellow, and lead chromates, including chrome yellow deep and light, zinc yellow, and chrome orange. THM-Py-GCMS analysis of selected samples supported the documentary evidence of Séraphine's use of household oil paints; a single instance of a cellulose nitrate enamel paint was additionally determined by μ -FTIR. The chromatographic analysis also indicated a natural plant resin in her varnishes, probably dammar in combination with pine resin. Overall, this material investigation, accompanied by the art historical record, better reveals the techniques of an experimental painter whose works have come to epitomize French outsider artists of the early twentieth century.

Keywords Séraphine Louis, XRF, Raman, SERS, μ -FTIR, UVF, THM-Py-GCMS, Household paints

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Introduction

Art historical context

Séraphine Louis, also known as Séraphine de Senlis or just Séraphine, was born in Arsy, France, in 1864. At eighteen, she began working as a housekeeper at the convent Clermont-sur-Oise, where she stayed for about twenty years. Séraphine drew from an early age and started painting when she moved to Senlis in 1906, where she worked cleaning houses. In conversations with Henry Gallot (b. 1903), a close neighbor in Senlis, Séraphine claimed that the divine spirit inspired her and that painting was a purpose bestowed upon her by the Virgin Mary [1]. After her first watercolor paintings on paper, Séraphine would paint on small pieces of wood, cardboard, or even small cream pots [1]. A handful of these cream pots remain in the Musée d'Art et d'Archéologie collection in Senlis.

Séraphine and her paintings were serendipitously discovered in 1912 when well-established German art collector Wilhelm Uhde (1874–1947) happened to take residence in the home where Séraphine worked as a housekeeper. Enchanted with her work, Uhde took Séraphine on as a patron and supported her career. Uhde was notable for being one of the first collectors of a new guard of painters, including Georges Braque, Raoul Dufy, Juan Gris, Auguste Herbin, Marie Laurencin, Fernand Léger, Jean Metzinger, Pablo Picasso, Jean Puy, and Henri Rousseau [2]. He championed the work of Naïve, or Outsider, artists, typically those without formal training [3].

In 1914, as the war broke out between France and Germany, Uhde fled France, leaving Séraphine behind in Senlis. In 1927, several of her works were accepted for an exhibition by *La Société des Amis des Arts de Senlis*, which Uhde attended with Séraphine on his mind [1, 3]. He reunited with Séraphine and again became her benefactor, supplying the artist with large canvases, painting materials, and a stipend. Possibly inspired by her religious beliefs and likely by her surroundings in nature, Séraphine painted psychedelic tableaux of fruit, flowers, and foliage against solid or two-toned backgrounds, often composed by applying one color to the top two-thirds of the painting and another color to the bottom third. In others, she would illustrate fields or rivers but almost always painted brightly colored and glossy, jewel-like plant life that buds from central, bushy tree trunks or decorative vases.

In 1928, Uhde organized an exhibition featuring a group of painters he named *Les Peintures du Coeur Sacré* after the title of the exhibition [4]. The artists included Henri Rousseau, André Bauchant, Camille Bombois, Louis Vivin, and Séraphine. Under Uhde's patronage, Séraphine became reasonably successful as an artist. However, around the financial crisis in the 1930s,

Uhde was forced to stop supporting Séraphine, even as her lifestyle had grown more lavish [3]. As a result, she felt abandoned, and her mental health deteriorated rapidly, growing depressed and despondent. Séraphine was subsequently institutionalized in Clermont de l'Oise in 1932. Even so, Uhde continued to champion her work. Most notably at the time, her paintings were included in *Les maîtres populaires de la réalité*, organized by the Musée de Grenoble in 1937, which traveled from Paris to Zurich and London [5]. Alfred Barr adapted the exhibition for *Masters of Popular Painting: Modern Primitives of Europe and America* (1938) at The Museum of Modern Art (MoMA) in New York [6]. After her institutionalization, Séraphine never painted again and passed away in 1942 due to ill-treatment and starvation, like many of the patients interned during the German Occupation.

Understanding Séraphine's working practice: scientific analysis

The resurgence in Séraphine's popularity, similar to other overlooked women artists working radically and experimentally along the margins of established art worlds, demands a more realized understanding of her working methods. As Körner and Wilkens state, "It is indeed not necessary to mystify her pictorial techniques to be fascinated by the work of this mystical painter" [1]. Moreover, they leave their readers with this plea at the end of their publication: "A scientific examination of the pictorial technique would put things in perspective."

To date, Séraphine's painting techniques were all defined by what those around her heard and saw; as a result, hearsay and guesswork have become attached to her known practice. Séraphine kept her techniques secret; in her lifetime, she locked her apartment while working and hid her materials when she had visitors [3]. Even under the patronage of established art figures, Séraphine was steadfast in using her own materials. Early on, Artist Charles-Jean Hallo (1882–1969), who lived in Senlis then, gifted Séraphine with painting supplies and offered her technical advice on painting [1]. Uhde recounts that "she found her own [pigments], and mixed them with a lacquer according to a formula of her own. She mixed them in secret and painted in secret" [3]. Pierre Guénégan writes in his catalog raisonné that Séraphine modified her paints with natural ingredients she found in her surroundings, such as flowers, branches, lichen, earth, feathers, blood, and lamp oil from the local church [7], although no evidence for these more unusual materials was found in the current study. Furthermore, Körner and Wilkins write, "Even if she conceived her artistic work as a spiritual exercise, Séraphine Louis did not abandon herself but worked thoughtfully, aware of

her means and her weaknesses, in this case at the technical level" [1].

In addition to elucidating her color choices, the integration of industrial paints into her working practice is also of interest; artist supplies were difficult to come by in Senlis and would have been expensive, especially for a housekeeper. Anecdotal evidence suggested that Séraphine used commercial paints commonly known as household or enamel paints, particularly Ripolin brand enamel paints, which were first created in 1897 [1]. These paints were undoubtedly available to Séraphine at the local drugstore of Monsieur Duval on Place de la Halle [1]. Pablo Picasso [8–11] and Francis Picabia [10, 12, 13] were noted to have exploited Ripolin in their works as well—Picasso as early as 1912 [8]. Other artists working later in the mid-twentieth century, like Vassily Kandinsky [14] and Sydney Nolan [15], also exploited the qualities of this household paint.

To further work out her techniques and use of household paints, this survey of Séraphine's mature works focused on six paintings from three institutions, all of which were examined scientifically. The paintings were executed between 1927 and 1930 when the artist had a firm command of her materials and exhibited her work publicly. The paints display features associated with household enamel paints: bright colors and the tendency to form flat, glossy surfaces that do not retain distinct texture except for small drying wrinkles on the surface, found throughout Séraphine's paintings. However, typical artists' practices, such as adding extra media, driers, and varnishes to artists' tube paints, could produce similar surface qualities to enamel paints and mislead visual assessment of their presence [16]. Additionally, traditional artists' and oleoresinous house paints from the early twentieth century often contain similar components and are thus not easily distinguished, even using advanced analytical techniques.

Of the works studied (Fig. 1), three paintings are in the collection of the Musée d'Art et d'Archéologie (MAA) in Senlis, two are in the collection of MoMA, and one is in the collection of The Metropolitan Museum of Art (MMA). These works, in chronological order according to Körner and Wilkens [1], are *Tree of Paradise* (c. 1928; MoMA), *Grapes* (c. 1928; MMA), *Grappes Bleues Avec Feuilles Roses* (1929; MAA), *L'Arbre du Paradis* (1929–30; Centre Pompidou/MAA), *Les Grandes Marguerites* (1929–30; MAA), and *Fruits* (1929–30; MoMA). The three works in the collection of the MAA were investigated previously as part of an international research project to integrate scientific research with art historical records for a better understanding of the use of household paints by modern artists, particularly Ripolin. The results discussed here for the MAA paintings were

summarized from internal reports at The Art Institute of Chicago (AIC) and after reexamination of the data [17].

The six paintings were analyzed without sampling by X-ray fluorescence (XRF) techniques; those in Senlis were studied with portable XRF (p-XRF) and those at MoMA and the MMA with XRF scanning. XRF results, in some cases, for MoMA and MMA works, were supported by the analysis of a small number of samples by micro-Fourier transform infrared spectroscopy (μ -FTIR), Raman, or surface-enhanced Raman (SERS) spectroscopies. Samples were obtained by gently scraping the paint surface with a scalpel without mechanically separating the paint layers in each sample. Organic media was further investigated with pyrolysis gas chromatography–mass spectrometry with thermally-assisted hydrolysis and methylation (THM–Py–GCMS). Technical imaging with UV-induced visible fluorescence (UVF) was further added to some pigment and organic media identification, especially Séraphine's use of natural resin varnishes. This scientific research, the first of its kind on Séraphine, complements the art historical record, and the results shed light on the techniques of an experimental artist whose fervent working practice is central to understanding her oeuvre.

Materials and methods

At MoMA, UV-induced visible fluorescence photographs (UVF) were taken using two Spectra Series CYC 100 LED Blacklights, 100–240 V (Altman Lighting, Yonkers, NY) as an excitation source. Capture was made with an unmodified Hasselblad H6D-400MS in pixel-shift mode to create a 230ppi image at the original scale (approximately a 325-megapixel image). A 2E filter supplemented the camera sensor's built-in filtration to minimize reflected UV and IR. Six exposures at 25 s each were required. At the MMA, UV photography was conducted using a Canon 5DS camera with Kodak 2E and Kodak CC40R filters. Illumination was provided by two 4-foot 40 W GE F40BLB lamps (UV-A glass mercury vapor lights with a peak at 365 nm).

At MoMA, large area X-ray fluorescence (XRF) scanning was conducted using a Bruker M6 Jetstream with a Rh target and 30 mm SSD at 50 kV and 600 μ A, with a 550 μ m spot size, 550 μ m pixel size, and dwell time of 10 ms/pixel under ambient conditions; small, detail maps were acquired with a 100 μ m spot size, 100 μ m pixel size, and 10 ms/pixel dwell time. At MMA, XRF scanning analysis of an area of the painting was done with a similar Bruker M6 Jetstream system under identical voltage and current settings with a 580 μ m spot size, 700 μ m pixel size, and 80 ms/pixel dwell time under ambient conditions. The spectral maps were processed using a combination of PyMca and Datamuncher software as

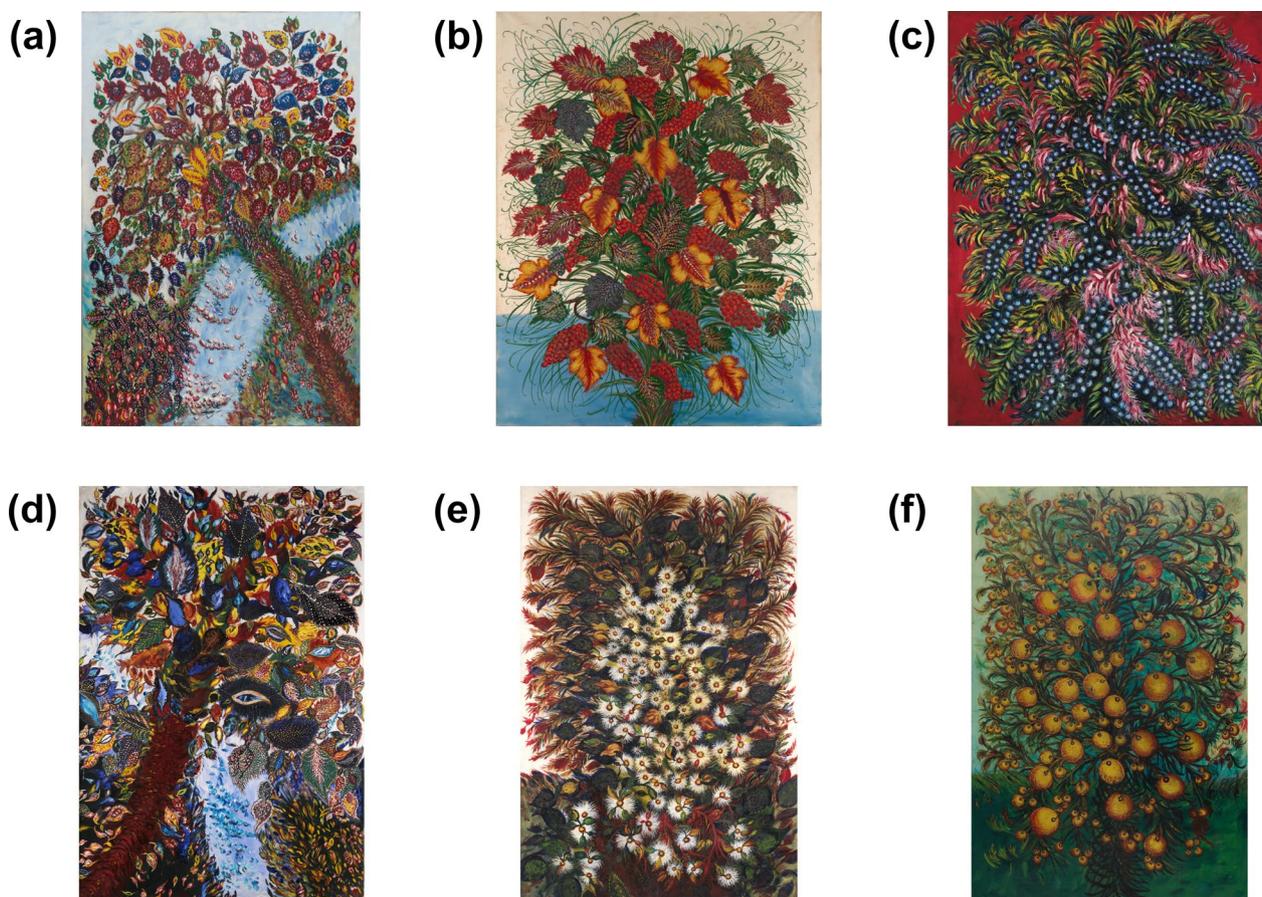


Fig. 1 Works by Séraphine Louis investigated in this study include: **a** *Tree of Paradise*, c.1928 (194.9×130.5 cm). Purchase. The Museum of Modern Art (MoMA) Accession number: 37.1971; **b** *Grapes*, c. 1928 (146.1×113.7 cm). Bequest of Miss Adelaide Milton de Groot (1876–1967), 1967. The Metropolitan Museum of Art (MMA) Accession number: 67.187.101; **c** *Grappes bleues avec feuilles roses*, c. 1929 (116×89.5 cm). Propriété de la commune, Senlis. Musée d'Art et d'Archéologie (MAA) Accession number: A.00.6.190; **d** *L'Arbre du Paradis*, 1929–30 (195×130 cm) Musée National d'Art Moderne – Centre Pompidou. Dépôt: MAA. Accession number: AM 2817 P; **e** *Les Grandes Marguerites*, 1929–1930 (195×130 cm). Propriété de la commune, Senlis. MAA. Accession number: A.00.6.176.; **f** *Fruits*, 1929–1930 (194×129 cm). Bequest of Richard S. Zeisler. MoMA. Accession number: 1449.2007. Image rights: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

described in [18] and the Bruker M6 Jetstream software. In Senlis at MAA, p-XRF was conducted using a portable Bruker/Keymaster TRACeR III-VTM energy dispersive XRF analyzer, with Peltier cooled advanced high-resolution Silver-free SiPIN detector and a 13 μm beryllium (Be) window. The system is equipped with a rhodium (Rh) transmission target; the size of the analyzer spot is approximately 6–8 mm in diameter. Spectra from each area were acquired using two sets of acquisition parameters for 180 s: 45 kV and 1.9 μA , using a Ti/Al filter in the beam path; and 20 kV and 4 μA , with no filter. Spectra were reexamined at MoMA with Bruker SP1XRF 3.8.20 software.

At MoMA, $\mu\text{-FTIR}$ spectroscopy was conducted in transmission mode using a Nicolet iS50- $\mu\text{-FTIR}$ coupled with a Thermo Nicolet Continuum infrared microscope equipped with an MCT-A detector. Spectra were

collected in the 4000–600 cm^{-1} range with a 4 cm^{-1} resolution and 128 scans using the Thermo Scientific OMNIC 9.0 software package. Sample scrapings were obtained with a scalpel and flattened between the windows of a diamond micro-compression cell. Spectra were examined using the Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software and compared with published libraries [19]. At AIC, samples from MAA works were flattened between the windows of a diamond micro-compression cell and analyzed in transmission mode using a Bruker Tensor 27 spectrometer, with mid-IR glowbar source, coupled to a Hyperion 2000 Automated FTIR microscope with and MCT D315 detector, collecting in the range of 4000–400 cm^{-1} . The spectra collected are the sum of 128 scans at a resolution of 4 cm^{-1} Spectra were

reexamined at MoMA using the Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software and compared with published libraries [19].

At MoMA, Raman spectroscopy was conducted using a Renishaw In-via Raman system equipped with a 785 nm diode laser operated between 0.3 to 3 mW, a 1200 lines/mm grating, and a Leica confocal microscope with a 50×LWD or 100×objective. Sample scrapings were obtained with a scalpel and placed in well slides, and the granules within each sample were analyzed. At the MMA, Raman spectroscopy measurements were done on sample scrapings using a Renishaw System 1000 coupled to a Leica DM LM microscope. All the spectra were acquired using a 785 nm laser excitation focused on the samples using a 50×objective lens, with integration times between 10 and 120 s. A 1200 lines/mm grating and a thermoelectrically cooled CCD detector were used. Powers at the sample were set between 0.5 and 5 mW using neutral density filters. Spectra were examined using the Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software and, in all cases, were compared to published libraries [20, 21].

Silver nanoparticles (AgNPs) for surface enhanced Raman spectroscopy (SERS) were prepared according to a method developed by Lux et al. [22]. A solution of 12.5 mL of 0.5 mM silver sulfate (Ag_2SO_4) ($\geq 99.99\%$), 0.5 mL of 1% sodium citrate dihydrate ($\text{C}_6\text{H}_9\text{Na}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) ($\geq 99\%$), and 1 mL of 1% D-glucose ($\geq 99.5\%$) were mixed in a Hydrothermal Synthesis Autoclave Reactor PTFE Tank (Baoshishan, China) previously cleaned with nitric acid at 30%. Once closed, the vessel was positioned in the center of a Panasonic model NN-SD372S inverter microwave and heated at 810 W for 2 min. 1.5 mL aliquots of this stock solution of citrate-capped AgNPs were centrifuged at 12,000 rpm for 15 min. The supernatant containing the citrate solution in excess was removed and replaced by distilled water to avoid sodium citrate interference in the SERS spectra. The sample was pretreated with HNO_3 to hydrolyze any lakes into the colloidal solutions by breaking the bonds with the base onto which the dye was precipitated. All chemicals were purchased from Millipore-Sigma, USA.

SERS was conducted using the same Renishaw In-via Raman system at MoMA, employing a 532 nm diode laser operated at 0.25 mW with an 1800 lines/mm grating. Spectra were evaluated using Spectral Search and Multicomponent Search tools available in the Thermo Scientific OMNIC Spectra 2.0 software and compared to the literature.

At AIC, samples for THM-Py-GCMS (a few tens of μg) were placed in Agilent micro vials (part #5190–3187), 1.5

μL of a 2.5% solution of tetramethylammonium hydroxide (TMAH) in methanol was added, and the vial placed in an Agilent Thermal Separation Probe (TSP) for analysis. The TSP was inserted into the Multimode Inlet of an Agilent 7890B GC, equipped with an Agilent HP-5 ms Ultra Inert column (30 m, 0.25 mm i.d., 0.25 μm film), and interfaced to a 5977B MS. The inlet, operated in splitless mode, was ramped from 50 to 450 °C at 900 °C/min to perform the pyrolysis. The final temperature was held constant for 3 min and then decreased to 250 °C at 25 °C/min. The GC oven was programmed from 40 to 200 °C at 10 °C/min, then to 310 °C at 6 °C/min, and held isothermally for 20 min for a total run time of 54.33 min. Some samples were run with a shorter program, with a maximum of 300 °C and no isothermal hold time for a total run time of 32.67 min. Helium was the carrier gas, with a constant flow of 1.2 mL/min. The MS transfer line temperature was 280 °C. The MS was run in scan mode (m/z 35–550 from 5–25 min, and m/z 50–700 from 25 min) with the ion source at 300 °C and the quadrupole at 150 °C.

Results and discussion

Ground preparation and the palette

Analyses of the paintings were undertaken using XRF techniques; the full elemental distribution maps resulting from XRF scanning are illustrated in Additional file 1: Figs. S1–S3. The identification of some pigments made up of elements below the detection limit of the XRF techniques and paint fillers inferred from the elemental analysis was supported by μ -FTIR and/or Raman spectroscopy (Additional file 1: Table S1) In particular, the use of XRF scanning on the MMA and MoMA paintings best uncovered Séraphine's technique. Many of the lushly packed compositional elements were built up with multiple, overlaying brushstrokes, like the branches of a tree and, at times, she worked over complete forms, such as painting a leaf over a bundle of grapes in *Grapes*. Curiously, microscopic glittering speckles were found in the lower center of *Fruits* and investigated with XRF scanning (Fig. 2). These flecks were found to be predominantly made of copper by XRF scanning and, therefore, could be a metallic powder [23] that Séraphine could have either applied to the surface of the picture or mixed into her paint, although it was unclear if the use of this powder was intentional or accidental. The following is a summation of the pigments firmly identified among the six works (Table 1): lead white, zinc white, carbon-based black, umber, vermilion, alizarin lake, rhodamine B lake, Prussian blue, cobalt blue, ultramarine, chrome green, emerald green, viridian, cadmium yellow, and lead

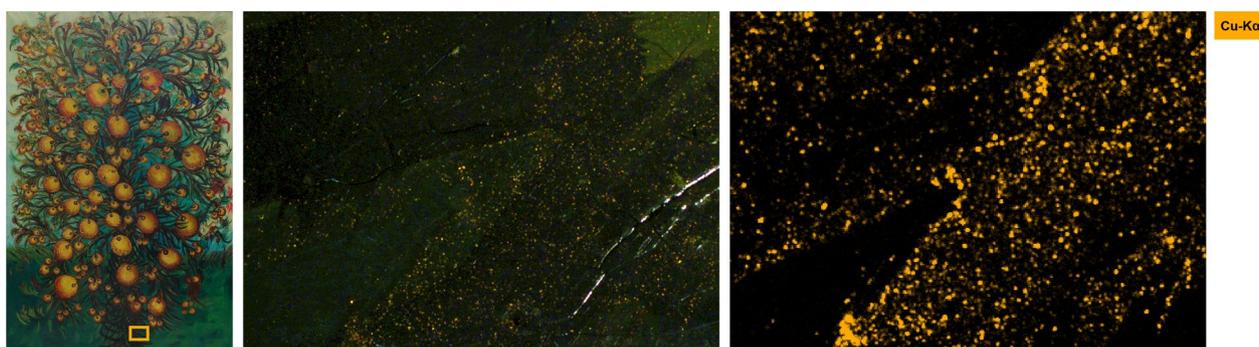


Fig. 2 (Left) *Fruits* with a yellow rectangle indicating the (center) detail area where (right) the elemental distribution map for copper (Cu-K α) was acquired by XRF scanning. The distribution map for Cu illustrates the presence of a metal powder. Image rights for *Fruits*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

Table 1 List of pigments identified in the six Séraphine paintings analyzed for this study

Title	Tree of Paradise	Grapes	Grappes Bleues avec feuilles roses	L'Arbre du Paradis	Les Grandes Marguerites	Fruits
Collection	MoMA	MMA	MAA	MAA	MAA	MoMA
Date	c. 1928	c. 1928	c. 1929	1929–30	1929–30	1929–30
<i>Pigment</i>						
Zinc white	X	X	X	X	S	X
Lead white	X	X	X	?	?	X
Carbon-based black	S					
Yellow ochre	X	X	?			X
Umber	X					X
Vermillion	S	X				
Alizarin lake	S	?	S	S	S	S
Rhodamine B lake						S
Chrome orange	S		?		?	
Chrome yellow deep		S [†]	X	S	S	
Chrome yellow light	S		S	S		S
Cadmium yellow	X	X				
Zinc yellow	X	X			S	
Emerald green	S					
Chromium-oxide based green	X	X	X			X
Prussian blue	S	S	S	S	S	S
Cobalt blue	X		X			X
Ultramarine blue	S	S		S	S	S

X indicates pigments inferred by XRF; S indicates pigments confirmed by Raman, SERS, and/or μ -FTIR spectroscopy; ? indicates the need for further analysis

[†]The type of chrome yellow pigment was not distinguished in this instance

chromates, including chrome yellow deep and light, zinc yellow, and chrome orange.

Ground preparation

In all of the works, the ground was visible on the tacking edges of the stretcher, which likely points to a commercial preparation. A p-XRF spectrum taken of the canvas in *L'Arbre du Paradis* showed significant amounts of lead

and indicated the presence of a lead white-containing ground. An elemental distribution map for lead acquired by XRF scanning on a small detail from *Fruits* illustrated the evenly spaced weave of a canvas primed with lead white (Fig. 3). Additional analysis by μ -FTIR of samples taken from the MoMA and two MAA works further confirmed the presence of basic lead carbonate in the ground (Fig. 4a); all spectra showed characteristic peaks

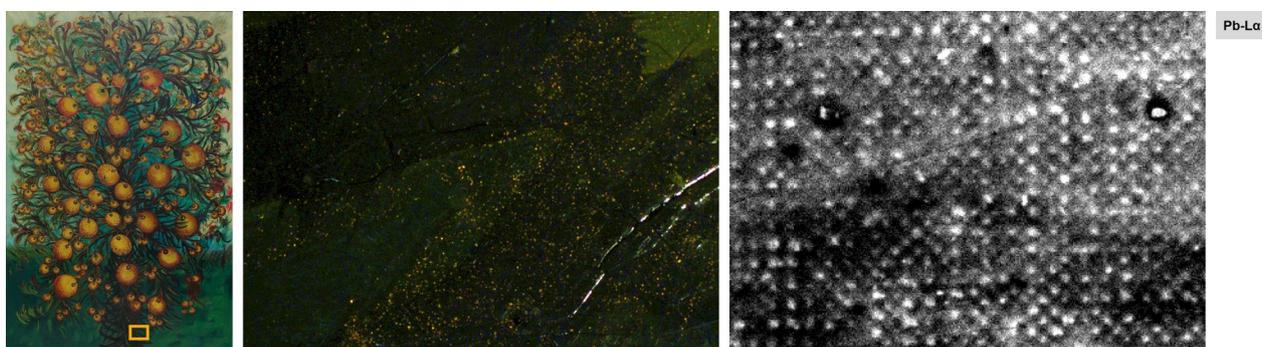


Fig. 3 (Left) *Fruits* with a yellow rectangle indicating the (center) detail area where (right) the elemental distribution map for lead (Pb-L α) was acquired by XRF scanning. The distribution map for Pb makes apparent the canvas weave of *Fruits*, which was prepared with a lead white ground. Image rights for *Fruits*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

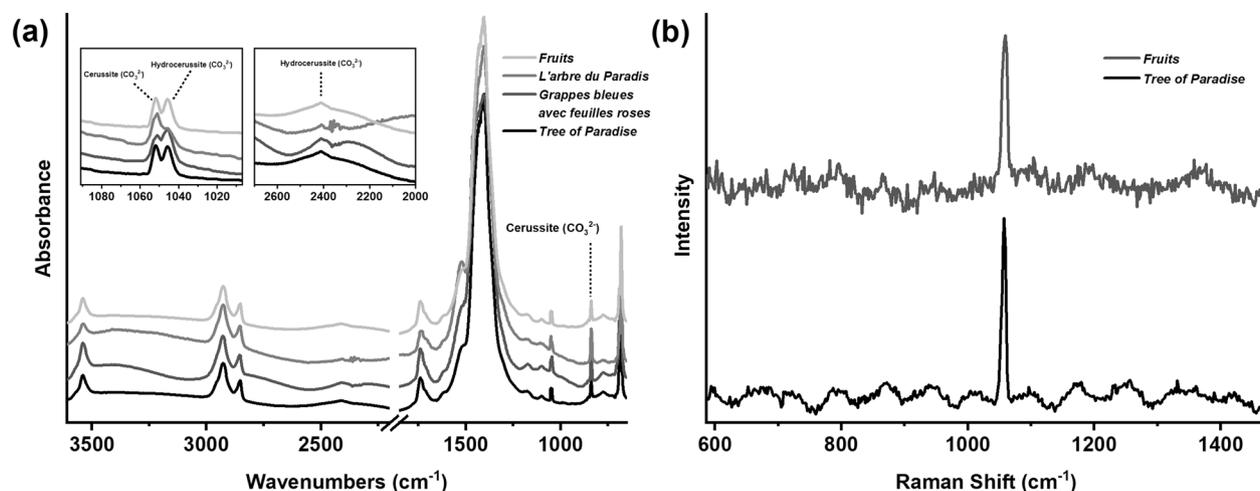


Fig. 4 **a** μ -FTIR spectra of samples representative of the ground preparation from four works studied here and **b** Raman spectra for the ground preparations of the two MoMA paintings

for hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) with O–H stretching mode at 3535 cm^{-1} , $\nu_3(\text{C}=\text{O})$ asymmetric stretching mode at 1400 cm^{-1} , $\nu_1(\text{C}=\text{O})$ symmetric stretching mode at 1045 cm^{-1} , $\nu_2(\text{CO}_3^{2-})$, out-of-plane bending mode at 851 cm^{-1} , $\nu_4(\text{CO}_3^{2-})$ in-plane bending modes of at 681 cm^{-1} , and a shoulder at 691 cm^{-1} that could be due to Fermi resonance with a crystal lattice mode [24]; a $\nu_1 + \nu_3$ combination band at 2410 cm^{-1} is also indicative of hydrocerussite [25, 26]. The presence of the anhydrate cerussite (PbCO_3), most likely an impurity [27], was further deduced by the presence of a $\nu_2(\text{CO}_3^{2-})$, out-of-plane bending mode at 838 cm^{-1} in addition to a weak peak at 1052 cm^{-1} for the symmetric C–O stretching mode of (CO_3^{2-}) [27–29]. Raman spectroscopy on samples from the MoMA works (Fig. 4b) confirmed the presence of a lead carbonate with a $\nu_1(\text{CO}_3^{2-})$ stretching mode at 1050 cm^{-1} [20], although differentiation between

the hydrate and anhydrate species was not possible based on a single mode common to both [28].

Although all works studied here vary in their dimensions, the relative uniformity in the compositions of the ground preparations based on XRF analysis and the detection of both cerussite and hydrocerussite by μ -FTIR in the MAA and MoMA works may speak to the origin of these grounds. The canvas dimensions of the works align with the standard canvas sizes or *toiles* available to artists at that time [30]. Portrait-style canvas sizes were referred to as *Figure* and numbered from sizes 0 to 120: *Tree of Paradise*, *L'Arbre du Paradis*, *Les Grandes Marguerites*, and *Fruits* were all painted on monumental *Figure 120* portrait-style canvas ($195 \times 130\text{ cm}$), *Grapes* on *Figure 80* ($146 \times 114\text{ cm}$), and *Grappes bleues* on *Figure 50* ($116 \times 89\text{ cm}$). The discovery of similar grounds across all these works and their standard sizes indicated a commercial canvas preparation and, in turn, validated the art

historical record of Uhde's patronage of Séraphine, which included the purchase of painting materials and supplies for the artist, specifically large canvases bought in Paris [3].

Whites, blacks, and browns

In these works, Séraphine utilized two whites, zinc white (ZnO) and lead white. Zinc white was best distinguished with XRF techniques by the signal for zinc in white passages or lighter colors (Additional file 1: Figs. S1–S3). Séraphine used zinc white liberally to highlight her depictions of fruit and leaves in thick daubs, splashes, or strokes applied in rapid succession. She also applied zinc white in broad strokes to evoke waves in her rendering of water in *Tree of Paradise* and *L'Arbre du Paradis*.

The use of lead white outside of the ground preparation was also noted. This pigment was initially identified by XRF, both portable and scanning, by the signals for lead and confirmed by μ -FTIR and Raman in some instances. The μ -FTIR spectra obtained from *Grappes bleues* only indicate the presence of hydrocerussite with the diagnostic peaks at 1052 and 2410 cm^{-1} [28] absent from the spectra, distinguishing this lead white from that used for the ground preparation. Sometimes, Séraphine applied lead white in thick circular blots, seen most clearly in *Grappes bleues*. In *Fruits*, these round daubs serve as an umbilical connection between fruit and stem, and they were further accented with red paint. This detail was a signature of Séraphine's style, seen in works such as *Les Grenades* (1925; Musée d'Art et d'Archéologie, Senlis), *Les Fruits* (c. 1928; Musée de Grenoble), *Feuilles, fleurs, fruits, bouquet* (c. 1929), and *Pommes aux feuilles* (1928–30; Collection Dina Vierny) [7]. In *Tree of Paradise*, the use of lead white was diverse, whereas, in the water, it was either alone in distinct blots or mixed into other colors directly on the painting to produce muted shades of gray, green, and blue in particular.

Only one instance of black was observed in a sample from *Tree of Paradise* analyzed by Raman spectroscopy, which showed carbonaceous D and G modes ca. 1330 and 1601 cm^{-1} [31] (Fig. 5), respectively. The μ -FTIR spectra taken of the same black sample did not display the characteristically strong ν_3 (PO_4^{3-}) peak associated with hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3$) [32], nor were calcium or phosphorus readily observed together by XRF scanning, which excluded the presence of a bone black. In *Tree of Paradise*, Séraphine contrasted with the black paint some of the branches amongst the colorful and densely packed flora. This pigment was also found in a gray paint made from a combination of emerald green and vermilion.

An earth-based brown pigment was identified with certainty by XRF techniques in some of the paintings

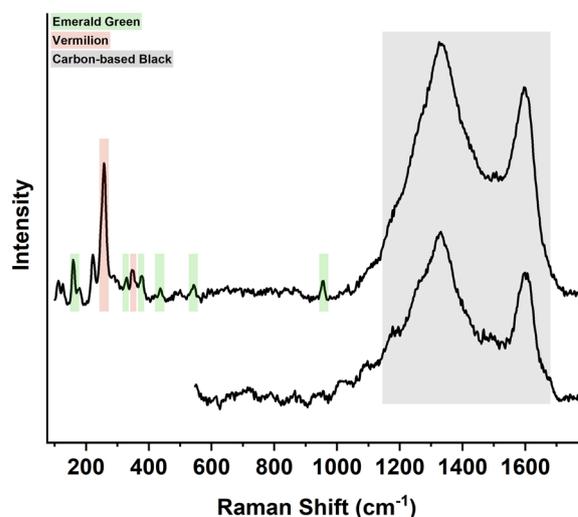


Fig. 5 Raman spectra of black (bottom) and gray (top) samples from *Tree of Paradise* illustrate the use of carbon-based black

studied. XRF scanning was beneficial for confirming umber in *Fruits* and *Tree of Paradise*. The co-localization of significant amounts of manganese with iron in dark strokes representing branches in *Fruits* (Fig. 6) and needle-like leaves in *Tree of Paradise* was connected to manganese oxides and hydroxides found in umber deposits [33]. Manganese and iron were also observed by p-XRF in some dark red passages of *Grappes Bleues*. Other light brown paints that showed iron, but not manganese, by p-XRF and XRF scanning could be composed of other iron-based pigments by co-localization with potassium in brown and ochre passages; however, further analysis would be needed to firmly identify these pigments.

Reds and oranges

While several red pigments were identified across the six works studied, Séraphine used synthetic alizarin lake the most. The organic pigment was confirmed spectroscopically in samples from MoMA and MAA paintings. Alizarin was identified in the MoMA works by Raman [21] and μ -FTIR (Fig. 7) [34], whereas in MAA works, this colorant was identified by μ -FTIR. Séraphine favored its deep, red hue and applied it freely to depict leaves, stems, flowers, and fruit. Some red passages with no inorganic pigments in *Grappes* suggested the presence of alizarin, although sampling would be needed for confirmation.

Séraphine also mixed alizarin-based paint with other colors to obtain a variety of shades. She mixed alizarin with zinc white to formulate a light pink color to fill in the curved, wild leaves in *Grappes Bleues*; this pink appeared streaky in a few passages and suggested that Séraphine blended colors directly on the canvas in some



Fig. 6 (Left) *Fruits* with a red rectangle indicating (center) the detail area where (right) the elemental distribution maps for iron (Fe-K α) and manganese (Mn-K α) were acquired by XRF scanning. The distribution maps for Fe and Mn illustrate the use of umber, where the co-localization of the two elements appears red with color subtraction. Image rights to *Fruits*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

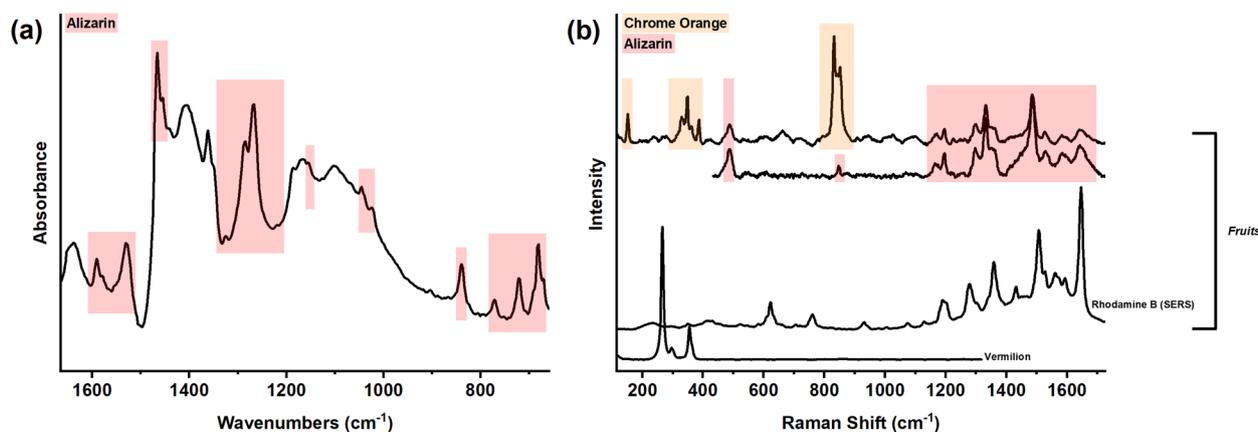


Fig. 7 **a** μ -FTIR spectrum of a red sample from *Tree of Paradise*. In **b**, Raman spectra of red and orange samples from MoMA works are illustrated: the three spectra on top are from *Fruits*, and the bottom spectrum, showing vermilion, is from *Tree of Paradise*

instances. Séraphine mixed alizarin with chrome yellow for an electric, bright orange color she used in *Fruits* to emphasize the spherical fruit; this hue was visible in the gaps among the cracks of alizarin-containing red paint. Another mixture discriminated by Raman spectroscopy in *Tree of Paradise* was found to contain alizarin and chrome orange (PbO·PbCrO₄) [35] (Fig. 7b). Séraphine used this lighter, more orange-hued red to paint several leaves in this vibrant tree.

The synthetic organic pigment rhodamine B lake (C₂₈H₃₁ClN₂O₃) was identified in a pink-hued red paint only used in *Fruits*. A synthetic xanthene-based paint in *Fruits* was first suspected when the picture was examined with UVF (Fig. 8d), where passages containing rhodamine B lake fluoresced bright orange-red. This lake pigment was identified conclusively with SERS (Fig. 7b) [36].

The characterization of this pigment was valuable as it is considered fugitive, equivalent to Blue Wool Scale (BWS) 2–3 even with UV-radiation filtered out, similar

to museum environments, with visible change predicted within 7 to 20 years of light exposure [37, 38]. This finding was also interesting for the latest works studied here and could suggest Séraphine's interest in new vibrant shades available to artists in the interwar years [39].

Finally, a deep red shade analyzed with XRF scanning in *Tree of Life* and *Grapes* was found to contain of vermilion (HgS) based on the elemental distribution map for mercury; the pigment was further confirmed by Raman spectroscopy [40] in *Tree of Paradise* (Fig. 7b). XRF scanning helped illustrate the distribution of other mixtures with vermilion in this picture: it was added to a chrome-yellow paint to produce a bright orange hue used to outline some leaves and to fill in others and was mixed with a carbon-based black and emerald green to produce a murky gray color used in the depiction of ripples in the stream. XRF scanning of *Grapes* shows that Séraphine used vermilion to paint the clusters of fruit dangling from lush vines.

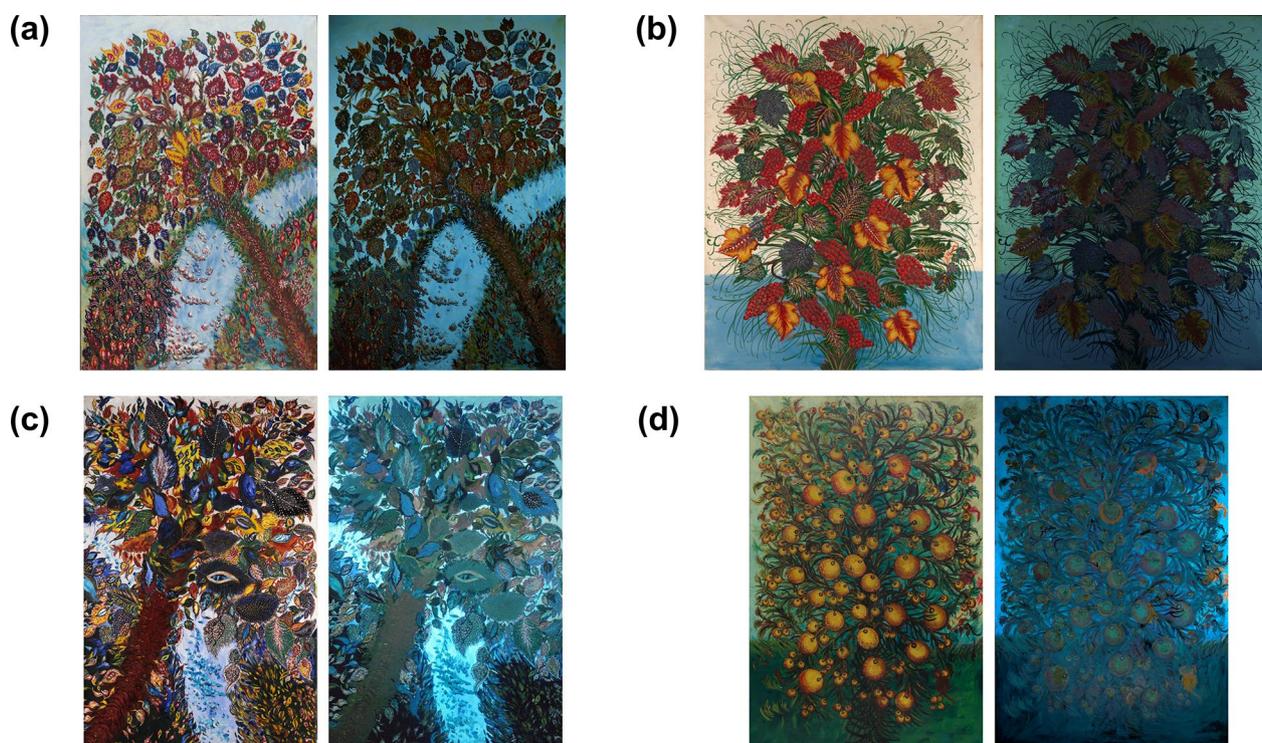


Fig. 8 UVF photographs of **a** *Tree of Paradise* (© The David Booth Conservation Center, MoMA), **b** *Grapes* (© Department of Paintings Conservation, MMA), **c** *L'Arbre du Paradis* (© C2RMF/G erard de Puniet), and **d** *Fruits* (© The David Booth Conservation Center, MoMA), all of which illustrate the use of a natural resin varnish by the hazy, green fluorescence observed under UV illumination. In **d** *Fruits*, bright orange fluorescence also indicated the presence of rhodamine B lake. Visible light image rights:   2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

Yellows

S eraphine predominantly favored using chrome yellow paint to describe flowers and leaves, among other features in her dense compositions across all six works, where it was identified with XRF techniques by the colocalization of lead and chromium in yellow passages. Chrome yellows are available as pure lead chromate (PbCrO_4) or as solid solutions of PbCrO_4 and lead sulfate ($\text{PbCr}_{1-x}\text{S}_x\text{O}_4$), in shades that range from yellow to orange ($x < 0.1$) to lemon-yellow ($0.2 \leq x \leq 0.4$) and pale yellow ($x > 0.5$) with increasing sulfate concentration [41]. Partial chromate replacement allows for the production of different shades of yellows. The color change is attributed to crystallographic compression from monoclinic for pure PbCrO_4 to orthorhombic with increasing exchange of chromate ions for smaller sulfate ions [41]. Differentiation between forms of chrome yellow pigments was accomplished with μ -FTIR of samples from four works, *L'Arbre du Paradis*, *Les Grande Marguerites*, *Tree of Paradise*, and *Fruits*; Raman spectroscopy was conducted on distinctly yellow samples from the two MoMA works. In these works, S eraphine appears to have employed two varieties of chrome yellow, a light and a

deep one. Distinguishing between these forms is also essential for preservation, as $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ pigments rich in (SO_4^{2-}) have been observed to darken more dramatically than those made primarily of lead chromates [42].

In *L'Arbre du Paradis*, S eraphine chose a darker yellow paint that was made with a relatively pure, monoclinic lead chromate (chrome yellow deep) as observed by μ -FTIR (Fig. 9a), with $\nu_3(\text{CrO}_4^{2-})$ asymmetric stretching modes at 853 and 830 cm^{-1} [41]. S eraphine also used a lighter yellow paint containing $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ (chrome yellow light) in *L'Arbre du Paradis* and *Tree of Paradise* and *Fruits*. The μ -FTIR spectra of this paint were characterized by $\nu_3(\text{CrO}_4^{2-})$ asymmetric stretching modes at 883, 859, 838, and 830 cm^{-1} in addition to $\nu_4(\text{SO}_4^{2-})$ asymmetric stretching modes at 1165, 1102, and 1058 cm^{-1} and an IR-forbidden $\nu_1(\text{SO}_4^{2-})$ symmetric stretching mode 966 cm^{-1} (Fig. 9a). Two $\nu_4(\text{SO}_4^{2-})$ asymmetric bending modes, 627 and 610 cm^{-1} , were observed in the spectra of the MAA work. Higher amounts of lead sulfates also lead to a gradual increase in the relative intensity of the mode at 610 cm^{-1} to the point of inversion; the positions and relative intensities of these peaks pointed to a 1:1 molar ratio of PbCrO_4 to PbSO_4 [41]. Raman

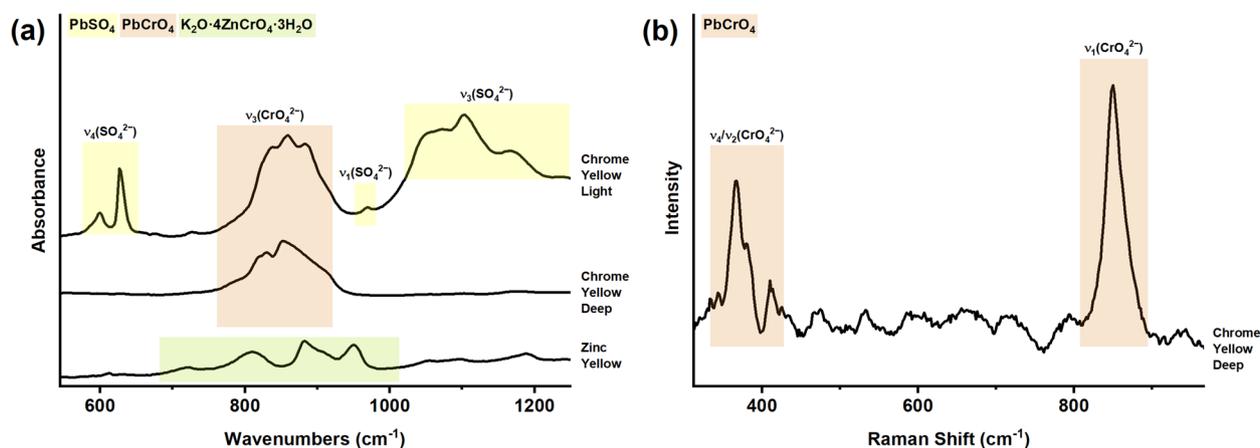


Fig. 9 **a** μ -FTIR spectra of yellow samples from *L'Arbre du Paradis* (chrome yellows light and deep, respectively) and *Les Grandes Marguerites* (zinc yellow). In **b**, a Raman spectrum of a yellow sample from *Tree of Paradise* further illustrates chrome yellow deep

spectra of samples taken from *Tree of Paradise* and *Fruits* also confirmed the presence of $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$, with the shifting of the $\nu_1(\text{CrO}_4^{2-})$ symmetric stretching mode and $\nu_4/\nu_2(\text{CrO}_4^{2-})$ bending multiplet to higher wavenumbers as a result of cell compression; the $\nu_1(\text{CrO}_4^{2-})$ symmetric stretching mode was observed at 847 cm^{-1} and the $\nu_4/\nu_2(\text{CrO}_4^{2-})$ bending multiplet at $278, 366, 379, 408\text{ cm}^{-1}$ (Fig. 9b) [43].

In addition to the chrome yellows, Séraphine used a cadmium-based yellow pigment for leaf highlights in *Grapes* (Fig. 10) and *Tree of Paradise* (Additional file 1: Fig. S1). Séraphine used either a pure cadmium sulfide (CdS) or a cadmium sulfide-zinc sulfide solid solution

($\text{Cd}_{1-x}\text{Zn}_x\text{S}$), where similar to chrome yellows, the introduction of ZnS into the lattice yields lighter shades [44]. Identification of this yellow was accomplished by XRF scanning, and differentiation between different cadmium yellow forms was not possible due to Séraphine's abundant use of zinc white. Séraphine also mixed a cadmium yellow paint with a chromium-based green to produce a range of deep greens and muted yellows in *Trees of Paradise* and *Grapes*, with evident strokes of yellow in some passages.

Finally, a zinc yellow ($\text{K}_2\text{O}\cdot 4\text{ZnCrO}_4\cdot 3\text{H}_2\text{O}$) was also identified in *Les Grandes Marguerites* by μ -FTIR [45] (Fig. 9a) and by the co-localization of chromium and



Fig. 10 (Left) *Grapes* with a yellow rectangle indicating the (center) detail area where (right) the elemental distribution map for cadmium (Cd-K α) was acquired by XRF scanning. The map of Cd illustrates the use of cadmium yellow. Image rights for *Grapes*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License



Fig. 11 (Left) *Grapes* with a green rectangle indicating the (center) detail area where (right) the elemental distribution maps for chromium (Cr-K α) and potassium (K-K α) were acquired by XRF scanning. The combined map illustrates the use of zinc yellow, where the co-localization of Cr and K appears near-white. The zinc (Zn) map is not shown here for clarity and can be found in Additional file 1: Fig. S2. Image rights for *Grapes*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

potassium in yellow brushstrokes in *Grapes* (Fig. 11) and *Tree of Paradise* (Additional file 1: Fig. S1). In the former, Séraphine highlighted the folds of the grape leaves and sprawling tendrils with this paint, while in the latter, she brushed it along the tree trunk, among other flourishes. This finding was of importance to future conservation and display as zinc yellow is susceptible to darkening over time due to the reduction of Cr(IV) to Cr(III) with exposure to light and humidity [46].

Blues

Séraphine used three distinct blues in her compositions: synthetic ultramarine, cobalt blue, and Prussian blue. Of the three, ultramarine blue ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$)

cannot be identified by XRF because it is composed of light elements well below the detection limit of portable or scanning techniques. Ultramarine blue was identified by μ -FTIR (Fig. 12a) and Raman spectroscopy (Fig. 12b) [47]. Séraphine used this blue abundantly across some of these works alone, resulting in a deep jewel tone or mixed with zinc white for a pale blue color. The latter was detected in her depictions of the water and sky of *Tree of Paradise* and *L'Arbre du Paradis*.

The use of a paint that contained Prussian blue alone ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3^-$) was conclusively identified in *Grapes* and *Fruits*. A sample taken from the leaves above Séraphine's signature in *Fruits* showed the presence of the pigment when analyzed with μ -FTIR [48]

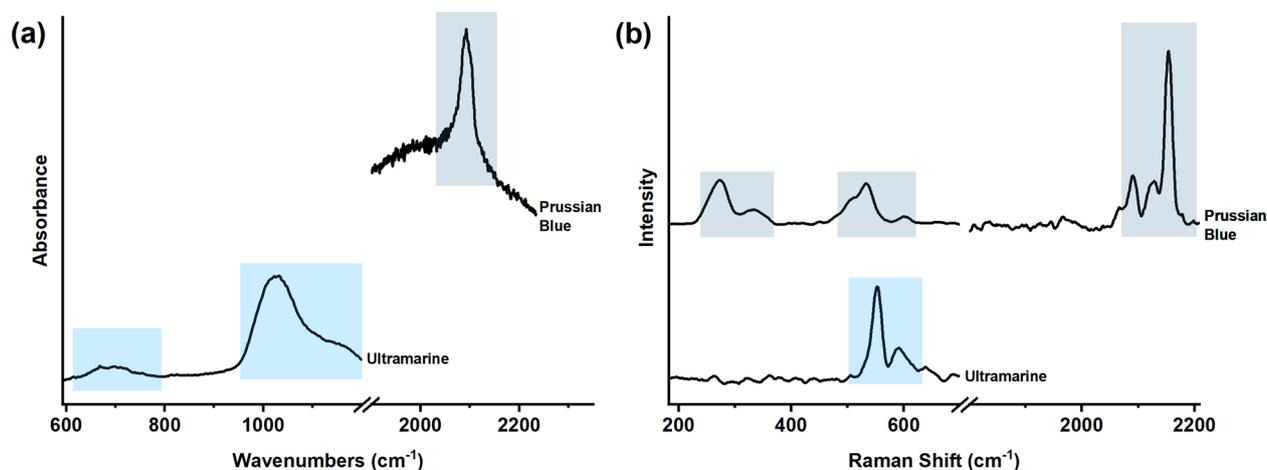


Fig. 12 a μ -FTIR and b Raman spectra of blue samples from *Fruits* illustrating the use of ultramarine blue and Prussian blue

(Fig. 12a) and Raman spectroscopy (Fig. 12b) [49]. A relatively large amount of iron was observed by p-XRF in a similarly colored brushstroke in *Les Grandes Marguerites*, suggesting the use of this pigment. The unvarnished, light blue background in *Fruits* was painted with a mixture of Prussian blue and zinc white, which could explain the heightened solubility issues encountered when cleaning the picture with a mixture of 0.5% w/v of citric acid in deionized water buffered to pH of 6. Citrates are potent chelators of iron ions and have been observed to lift the pigment from unvarnished or underbound oil paints [50, 51]; the background blue of *Fruits* was unvarnished, as observed by UVF (Fig. 8d).

Cobalt blue (CoAl_2O_4) was inferred with XRF by the relatively strong signal for cobalt in the absence of other detectable elements linked to other Co-based pigments in the spectra acquired of blue passages. The use of this blue color varied across the works studied. In *Grappes Bleues*, Séraphine colored the clusters of fruit that dominate the composition with cobalt blue. In *Tree of Paradise* (Additional file 1: Fig. S1), this deep color was used for many of the leaves to deepen the bushy tree trunk and emphasize the stream's ripples. In *Grappes* (Additional file 1: Fig. S2), she used it alone or mixed with zinc white to emphasize and highlight leaves and vines and interestingly mixed it with vermilion to produce a dark shade of red that dots the stretching vines. In *Fruits* (Additional file 1: Fig. S3), it was present alone in a singular and starkly blue leaf but also in a rather dark, near-black color achieved by mixing a cobalt blue paint with chrome green to create depth around those lead white daubs from which the stems grow; it also appeared mixed with umber in some branches.

Séraphine also outlined some of the alizarin red fruit in the picture with cobalt blue, like the technique she used in *Grappes*.

Greens

Séraphine employed chrome green, a commercial mixture of Prussian blue and lead chromate yellow, in all six works investigated. For example, Séraphine painted with this color entire leaves and highlights for others, as well as accents for the trunks of the trees in *Tree of Paradise* and *L'Arbre du Paradis*. This verdant shade was initially inferred from XRF techniques by the co-localization of iron and chromium in green passages and subsequently confirmed spectroscopically by μ -FTIR (MoMA and MAA) and Raman (MoMA and MMA) spectroscopies.

In the μ -FTIR spectra taken of green samples from the MoMA and MAA works, Prussian blue was discerned by a $(\text{C}\equiv\text{N})$ stretching 2093 cm^{-1} [48], along with the $\delta(\text{Fe}-\text{CN}-\text{Fe})$ bending mode at 501 cm^{-1} in the MAA samples (Fig. 13a) [52]. A $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ pigment was also identified primarily by a broadened $\nu_3(\text{CrO}_4^{2-})$ asymmetric stretching mode centered at ca. 873 cm^{-1} , in addition to $\nu_4(\text{SO}_4^{2-})$ asymmetric stretching modes at 1052 and 1090 cm^{-1} , $\nu_4(\text{SO}_4^{2-})$ asymmetric stretching modes $\nu_4(\text{SO}_4^{2-})$ asymmetric bending modes 627 and 610 cm^{-1} [41], and an IR-forbidden $\nu_1(\text{SO}_4^{2-})$ symmetric stretching mode 966 cm^{-1} (Fig. 13a) [43]. This pigment is possibly similar to the chrome yellow light seen above, where higher amounts of sulfates were deduced from the increase in relative intensity of the mode at 610 cm^{-1} compared to that at 627 cm^{-1} [41]. With Raman spectroscopy (Fig. 13b), Prussian blue was identified [48, 52] in addition to chrome yellow [43].

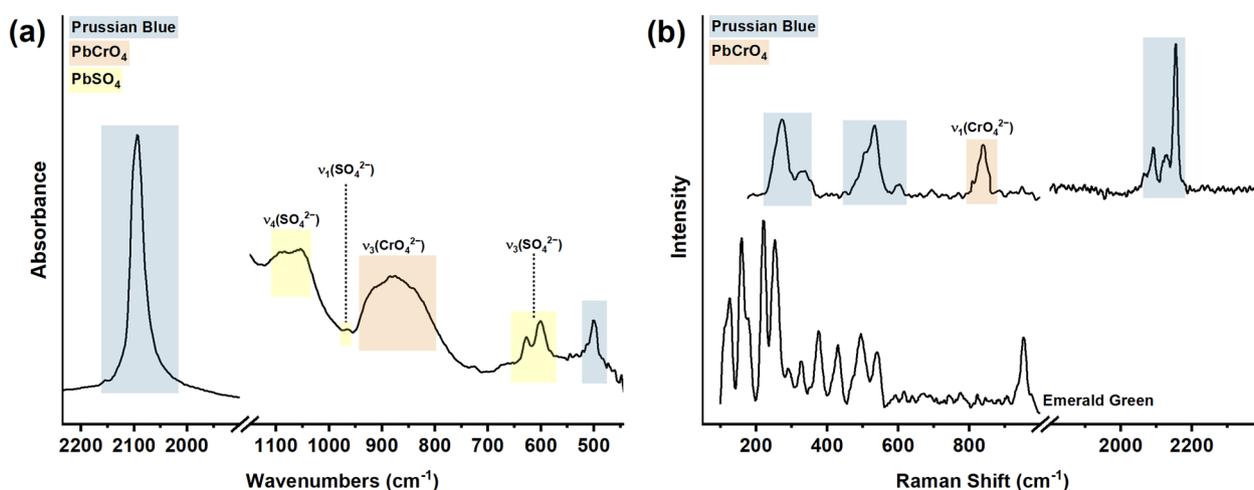


Fig. 13 **a** μ -FTIR and **b** Raman (top) spectra of green samples from *Fruits* illustrating the use of chrome green. In **(b)**, a spectrum (bottom) taken of a green sample from *Tree of Paradise* illustrates the use of emerald green

A second green paint in *Tree of Paradise*, *Grapes*, *Grappes Bleues*, and *L'Arbre du Paradis* appeared to contain a chromium-oxide green, possibly the hydrated viridian ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) inferred from its distinctive green shade. This pigment was only pinpointed by elemental analysis through p-XRF in the MAA works, and XRF scanning proved advantageous for identifying chromium alone in green passages without iron and lead indicative of chrome green (Additional file 1: Figs. S1-S2). No samples were found to contain viridian by spectroscopic techniques. This paint was applied to leaves and other bushy brushstrokes, but perhaps it was most interestingly applied by Séraphine in *Grapes* as a base color for the fruit to distinctly contrast the red grapes from the background and heighten the dimensionality of the clusters.

Finally, Séraphine painted with a copper and arsenic-based green in both *Tree of Paradise* and *Grapes*, which was identified as emerald green, or copper acetoarsenite ($(\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$), in a sample from *Tree of Paradise* by Raman spectroscopy [53] (Fig. 13b). In *Grapes*, this green pigment was deduced from the copper and arsenic elemental distribution maps in the flourishes of the grape vines, stubby brushstrokes along the edges of leaves, and underneath some of the fruit (Additional file 1: Fig. S2). In *Tree of Paradise*, emerald green was used alone but also in a mixture with vermilion, where the mercury distribution map shows the latter (Fig. 14). Additionally, Séraphine developed emerald green, vermilion, and carbon-based black mixtures to produce varying shades from a muddy brown-green to an outright gray with the addition of zinc white and a carbon-based

black. This color combination was used extensively, seen in copper and arsenic-rich dark gray ripples in the blue stream and the mercury-rich brown strokes in the bushy banks of the streams. This combination of emerald green and vermilion, with the addition of a carbon-based black, was confirmed by Raman spectroscopy (Fig. 5).

Fillers

The presence of barium sulfate (BaSO_4) and calcium (Ca)-based fillers was inferred from the p-XRF spectra but better visualized with XRF scanning. In some blue samples taken from *Fruits* and *Tree of Paradise*, BaSO_4 was confirmed by μ -FTIR [54] and Raman spectroscopy [20]. Hydrated calcium sulfate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was detected by μ -FTIR [55] in a zinc white paint from *Les Grandes Marguerites* and by Raman spectroscopy [56] in samples of blue and gray paint from *Tree of Paradise*.

Surface coatings and organic paint binders

Séraphine's varnishing technique to produce variably glossy and matte passages could be visualized by UVF imaging (Fig. 8), through which natural tree resins were characterized by intense greenish-white fluorescence. The resulting difference between glossy flora and matte backgrounds imparted further depth and texture to the scene. Séraphine not only applied varnish to enhance the gloss of particular areas but also exploited the properties of natural resin to describe features with transparency, like some leaves in *Fruits*, perhaps harkening to the stained-glass windows of the Cathédrale Notre-Dame de Senlis. Analysis was undertaken using μ -FTIR of the natural resin varnish Séraphine selectively applied to her

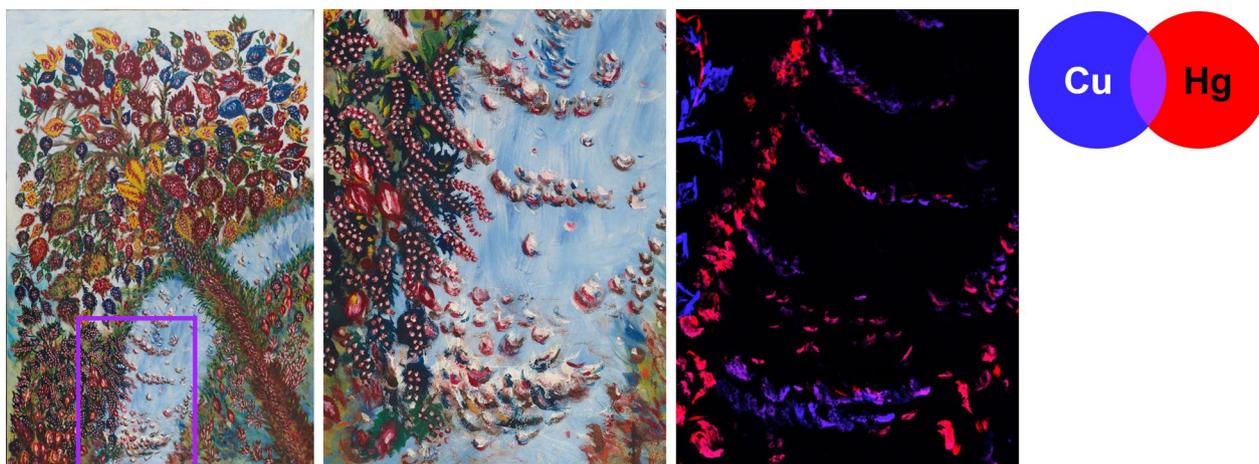


Fig. 14 (Left) *Tree of Paradise* with a purple rectangle indicating the (center) detail area where (right) the elemental distribution maps for copper (Cu-K α) and mercury (Hg-L α) were acquired by XRF. The maps for Cu and Hg illustrate the use of emerald green and vermilion. Different shades were deduced by the co-localization of the two elements, which appear purple of various intensities by color addition. Image rights to *Tree of Paradise*: © 2023 Artists Rights Society (ARS), New York. All reproductions of the work(s) are excluded from the CC-BY License

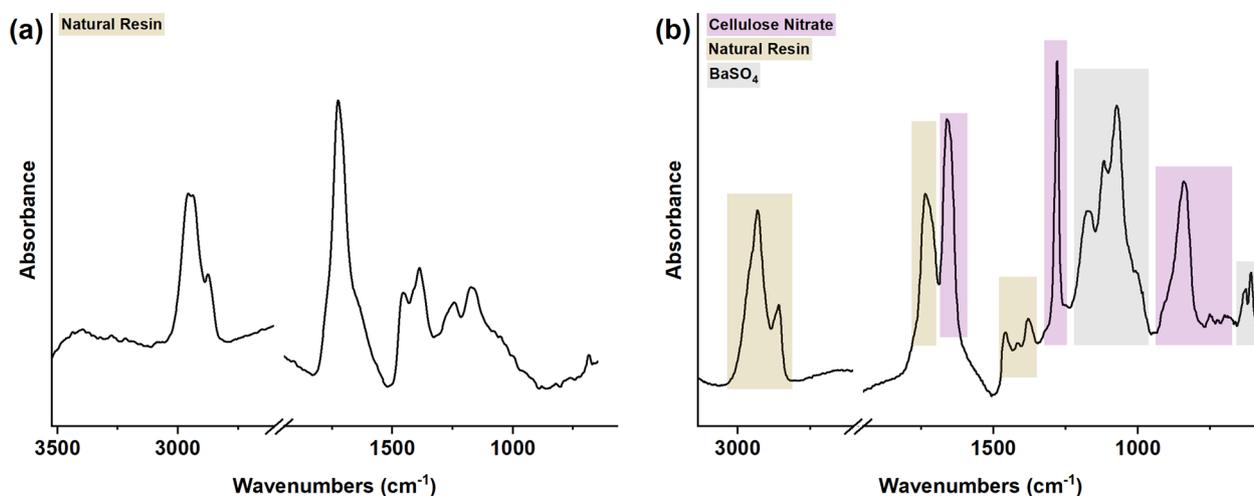


Fig. 15 μ -FTIR spectra illustrating **a** the presence of a natural resin in a sample from *Fruits* and **b** the presence of a cellulose nitrate enamel paint in a sample from *Les Grandes Marguerites*

compositions, and peaks were observed at 2956, 2875, 1726, 1454, 1388, 1243, 1172, and 686 cm^{-1} (Fig. 15a) [19]. Samples of varnish from *Tree of Paradise* and *Grapes* were further identified as a triterpene resin, probably dammar, in combination with a diterpene resin such as pine resin, by THM-Py-GCMS, based on the identification of a series of (unidentified) oleanane and ursane compounds, along with hexakisnor-dammaran-3,20-dione, in the triterpene region of the chromatogram, and oxidized abietane compounds (including dehydroabietic acid and 7-oxo-dehydroabietic acid) in the diterpene region of the chromatogram [57, 58].

Paint samples from MoMA and MAA works were analyzed with μ -FTIR, and an oil-based medium was inferred by peaks at 2926, 2855, 1735, 1163, 1096, and 725 cm^{-1} [59]. However, the presence of natural resins impeded conclusive spectroscopic characterization. Eight paint samples, five from *Tree of Paradise* and three from *Fruits*, were therefore further analyzed by THM-Py-GCMS. The samples were selected for analysis based on their glossy appearance and pigment composition, including zinc white, ultramarine blue, chrome yellow light, alizarin lake, Prussian blue, and chrome green, pigments that are known to have been added to Ripolin paints, as elucidated in previous research by Gautier et al. [60]. Additionally, some samples were taken from areas that exhibited the distinctive wrinkling associated with the drying of thickly applied household paints [10].

Fatty and dicarboxylic acids were detected in all samples in proportions characteristic of drying oil; a representative chromatogram of a blue sample from *Tree of*

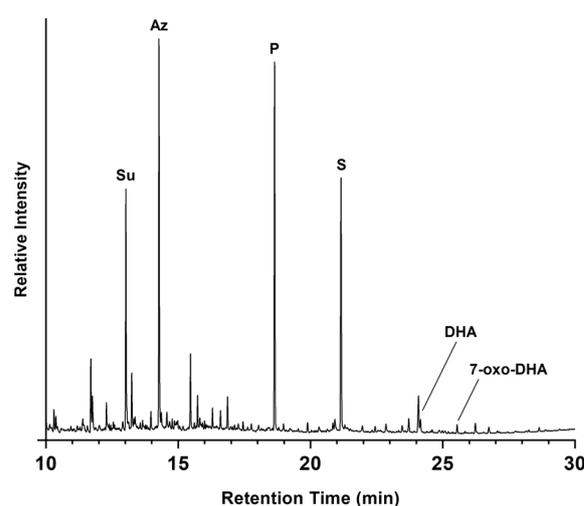


Fig. 16 THM-Py-GCMS data (total ion chromatogram) for a blue paint sample from *Tree of Paradise* showing the presence of fatty and dicarboxylic acids characteristic of a drying oil and oxidized diterpenes characteristic of Pinaceae resin. Su suberic, Az azelaic, P palmitic, S stearic, DHA dehydroabietic, 7-oxo-DHA 7-oxo-dehydroabietic acids; all compounds detected as methylated derivatives

Paradise is shown in Fig. 16. The ratios of palmitic to stearic acids were between 1.3 and 2.0, typical for linseed oil [61]. The ratios of the dicarboxylic acids suberic to azelaic were between 0.29 and 0.65, with all but one above 0.4, which indicated heat bodying of the oil and were consistent with the range of values observed in studies of historic household paints produced by Ripolin and other brands [62]. Heating up drying oils without

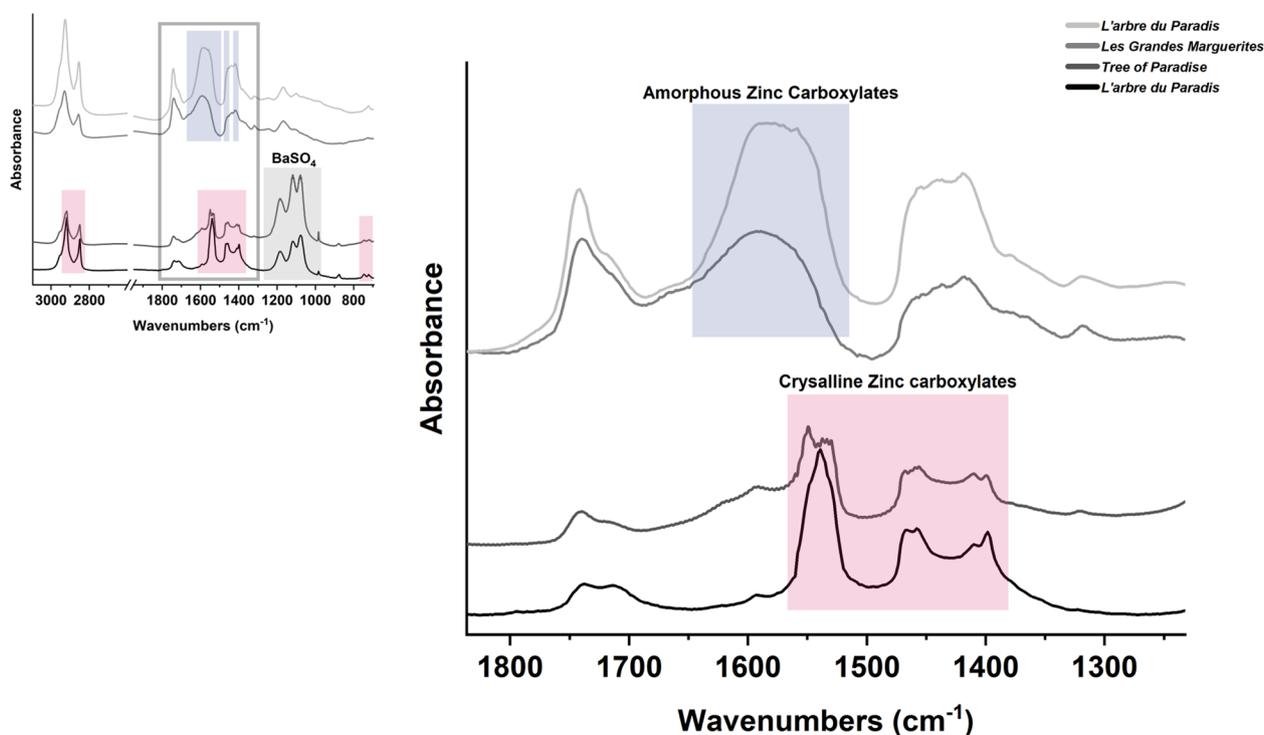


Fig. 17 μ -FTIR spectra of zinc white paints taken from three works by S eraphine illustrate the presence of amorphous (highlighted in purple) and crystalline (highlighted in pink) zinc soaps in samples of zinc white paint taken from three different works by S eraphine. Bands for barium sulfate (BaSO_4) are highlighted in gray

oxygen during manufacture increased their viscosity and weather resistance after drying, which was crucial for house paints, and adding natural resins improved paint gloss and leveling [8].

Research into the composition of Ripolin has also revealed that it was made with pine resin [62]. In the S eraphine samples, small and variable amounts of oxidized abietane diterpenes were detected in all cases, suggesting a pine resin. While an effort was made to separate the paint and varnish components of the sample before analysis, these compounds could not be confidently attributed to the paint formulation because of the possibility of contamination from the overlying varnish layer. Even so, the amount of diterpenes observed in the paint samples was lower than those typically detected in reference Ripolin paints, except for some of the lighter shades [62].

So, while the fatty acid ratios observed in the paint samples strongly suggest S eraphine's use of industrial or household heat-treated oil paints, the minor amounts of diterpenes were not consistent with previous studies of Ripolin brand paint specifically, except perhaps

for the lighter/white colored paints. It bears mentioning that while Ripolin is the trade name for a famous brand in France, other brands such as Valentine, Triton, and Zinolac would have also been available to S eraphine [8], and more work is needed to assess the composition of those paints for comparison.

In addition to the oil-based household paints, a yellow household enamel paint based on the semi-synthetic resin cellulose nitrate was characterized with μ -FTIR in *Les Grandes Marguerites* (Fig. 15b), with peaks at 1635, 1280, 842, 751, and 698 cm^{-1} [59]. This finding indicates S eraphine's resourcefulness in using other early household paint, many of which were based on semi-synthetic resins [63]. This paint likely contains a lead chromate pigment based on XRF analysis and barite based on μ -FTIR. [41]. And in another sample from a dark blue paint from *Fruits* made with Prussian blue pigment, a small amount of beeswax was indicated by characteristic hydroxyacids, long-chain fatty acids, and hydrocarbons [64]. This finding was consistent with the translucence and waxy texture of this passage of paint and may indicate a deliberate

modification of the paint by the artist or her use of a commercial paint formulation with a wax component.

In some of the μ -FTIR spectra of samples from *Tree of Paradise*, *Les Grandes Marguerites*, and *L'Arbre du Paradis*, evidence for the formation of zinc carboxylates, also known as zinc soaps, could be inferred in oil-based paints made or mixed with zinc-based pigments. Zinc carboxylates were observed in the whites, light ultramarine blues, and light greens of *Tree of Paradise* and *L'Arbre du Paradis*, the grays in *Tree of Paradise*, and the zinc yellow in *Les Grandes Marguerites*. In the μ -FTIR spectrum from *Tree of Paradise*, this was deduced by the presence of a sharp $\nu(-\text{COO}^-)$ asymmetric stretching modes ca. 1549 and 1530 (in addition to peaks at 1594, 1465, 1457, 1415, and 1319 cm^{-1}) characteristic of crystalline zinc soaps of fatty acids, particularly zinc oleate (zinc 9-octadecenoic acid, $\text{C}_{36}\text{H}_{66}\text{O}_4\text{Zn}$) (Fig. 17) [15, 65]. The single sharp $\nu(-\text{COO}^-)$ asymmetric stretching mode observed ca. 1539 in the spectrum from *L'Arbre du Paradis* could be indicative of a zinc palmitate (zinc hexadecanoate) or stearate (zinc octadecanoate) [65]. However, in other spectra, a broad, rounded $\nu(-\text{COO}^-)$ peak centered ca. 1580–1590 cm^{-1} was observed, which pointed to an oil matrix with amorphous zinc carboxylate species (Fig. 17) [66]. The broadening observed for $\nu(-\text{COO}^-)$ could indicate ongoing soap formation that manifested in the upper layers of a paint matrix and from where samples are usually taken; deposits of crystalline zinc soaps could remain concentrated deeper within paint layers [66].

S raphine's selection and manipulation of her paints likely contributed to the dramatic drying cracks that appear throughout her paintings, which have become a hallmark of her work (Fig. 6, center). Within the works studied here, this effect was most pronounced in the red, yellow, green, and blue leaves of *Les Grandes Marguerites* and the spherical bounty of *Fruits*. These webs of cracks are often attributed to improper painting techniques in which the artist does not adhere to the "fat-over-lean" rule, implying that paints with a lower oil content should be laid first before oil-rich, slow-drying paints prone to shrinking [67]. Layering these paints in the wrong order could thus provide one explanation for the occurrence of drying cracks in S raphine's paintings. S raphine may have created this effect by painting in layers the faster and slower-drying household enamel and artist oil paints, respectively. It is possible that she applied her paints deliberately to achieve these effects, or she accidentally produced these features, liked them after they appeared, and continued to produce them. Given that S raphine's varnish application was evident in these cracks, they

must have manifested either during her creation process or soon after. K rner and Wilkens proposed that S raphine's interaction with these cracks implies that she was thoughtful and not impulsive in her paint application and would exploit this phenomenon when it appeared, even if she did not necessarily understand why or how the cracks came about [1].

Conclusion

S raphine's paintings are enchanting and mystical with their jewel-like tones, layers of multicolored paint strokes, and textural surface qualities. Her fanciful portrayals of natural flora and fauna breathed life and movement into a two-dimensional painted surface. She used a diverse palette that included lead white, zinc white, carbon black, red and brown ochres, umber, vermilion, alizarin lake, rhodamine B lake, Prussian blue, cobalt blue, ultramarine blue, chrome green, emerald green, viridian, cadmium yellow, and lead chromates, including chrome yellow deep and light, zinc yellow, and chrome orange, and mixed them freely to produce numerous colors identified across several works. The identification of pigments could prove useful in the long-term preservation strategies for these works. For example, light-sensitive rhodamine B lake and zinc chromate yellow paints call for moderate illumination when on display. Additionally, the identification of Prussian blue across all works, either alone or in combination with chrome yellow, underscores the sensitivity of these surfaces to buffered or chelated water solvents used in wet cleaning. The use of zinc white also portends the formation of zinc carboxylates that may induce structural damage to the composition over time.

S raphine created a signature style by often contrasting matte backgrounds with discretely glossy passages enhanced with natural varnish throughout, perhaps to mimic the look of stained glass. The findings presented here indicate that S raphine used household paints made with heat-treated oils and, in at least one case, an early semi-synthetic household paint based on cellulose nitrate. The identification of Ripolin brand paint, per anecdotal accounts of S raphine's practice, could not be substantiated in this study, although several other brands would have been accessible to the artist. The use of wax-containing paint produced satin-like surfaces in contrast with areas of glossy paint. The deep drying cracks were found throughout her paintings, which she appears to have accepted or even intentionally enhanced to imbue texture to the surfaces.

Indeed, the scientific analysis presented here reveals that S raphine was an experimental and resourceful

artist with a command over her materials. Séraphine may not have been technically trained as an artist, but despite this, she developed her style to produce singular artworks that fascinated collectors, critics, and the public alike during her lifetime and now.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-024-01190-9>.

Additional file 1: Figure S1. XRF elemental distribution maps for *Tree of Paradise*. **Figure S2.** XRF elemental distribution maps for *Grapes*. **Figure S3.** XRF elemental distribution maps for *Fruits*. **Figure S4.** Annotated images illustrating the locations from where samples were acquired. **Table S1.** Main XRF, Raman, and μ -FTIR signatures for pigments identified in this study.

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Author contributions

AH carried out all XRF scanning, μ -FTIR, Raman, and SERS data acquisition and interpretation for the *Tree of Paradise* and *Fruits*. KS carried out THM-Py-GCMS analysis and data interpretation. SAC carried out XRF scanning and Raman data acquisition and interpretation for *Grapes*. GK carried out p-XRF and μ -FTIR for *Grappes bleues avec feuilles roses*, *L'Arbre du Paradis*, and *Les Grandes Marguerites* as part of the 2009 Senlis campaign. CH carried out UVF on *Fruits* and DHD on *Tree of Paradise*. AH prepared the main text, and KS contributed to the section on organic materials. All authors reviewed the main text and agreed to the submitted version of the manuscript.

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Availability of data and materials

The data is available upon reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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